PROCEEDINGS

OF THE

17th ANNUAL MEETING

FERTILIZER INDUSTRY ROUND TABLE

1967

.

Executive Committee

Vincent Sauchelli, Chairman

Housden L. Marshall, Sec'ty-Treasurer

Joseph E. Reynolds, Jr.

Albert Spillman

Bill E. Adams

Robert R. Heck

Editors

Executive Committee

Price $8.00

Copies may be purchased from

Housden L. Marshall, 1604 Walterswood Rd.

Baltimore, Maryland 21212

Please make checks payable to

Fertilizer Industry Round Table

Table of Contents

3

Wednesday Morning Session, Nov. 15, 1967

The 17th Annual Meeting of The Fertilizer Industry Round Table convened
at nine-forty o'clock a.m. in the Grand Ballroom of the Hotel Mayflower,
Washington, D. C., Dr. Vincent Sauchelli, Chairman, presiding

CHAIRMAN SAUCHELLI: Let's come to order, gentlemen.

It gives me much pleasure to welcome you to this 1967 Meeting of the Fertilizer Industry Round Table.

This is our 17th Annual Meeting. At every Round Table we seem to establish new records for the number of persons attending, the number of companies represented and for the number of guests from foreign countries.

Your Executive Committee is proud of the record and regards it as a vote of confidence in its efforts to organize a worthwhile program.

We feel certain it also reflects on the splendid cooperation of the membership in making this program worthwhile in every way. Without your helpful suggestions and willingness to participate in the program when called upon, there would be no Round Table.

We have prepared a very good program, if I am able to judge by the many favorable comments that have been made to us. It includes a variety of technical papers which represent many aspects of our new technology in the industry and some basic research concerning fertilizer production problems.

As I have pointed out at previous meetings, the main thrust of our planning is to provide a forum for the operational personnel of our industry.

With this large attendance, the excellent papers and, I hope, the lively discussions from the floor, and I emphasize that, lively discussions from the floor—I hope we can achieve that—we are going to have a stimulating and successful meeting.

Now to get to the program. I call your attention to a change in it. Owing to a misunderstanding on my part, for which I apologize, the last speaker printed on your program should be the initial speaker. The last shall be first.

I refer, of course, to Mr. Charles T. Harding, one of our outstanding personalities of the industry. He has spent a lifetime in the fertilizer business starting at the bottom and working his way up to the very top.

He retired from his old firm about a year ago but, like many of today's retired persons, he made another connection with a progressive company, Wellman-Lord, who profit from his broad experience and knowledge.

Mr. Harding has a perceptive observation of events and an acute sense of history. He chose as his subject Fertilizer Plant Operation Yesterday, Today and Tomorrow. Who, better than he, could survey the past and glimpse the future of our dynamic industry?

Let's give Charlie a warm welcome.

MR. CHARLES T. HARDING: Thank you, Vince.

Gentlemen, this is a real pleasure for me to be with this group: Many of you I have known for many years and I have met many interesting people since we arrived last night.

You don't know how happy I was when Vince asked me to appear on this program and talk about something that has been my love for all of my adult life. I have been a regular attendant of these meetings and when I look about, or look back at how the Round Table has grown, not only in numbers but in caliber, I feel that Dr. Sauchelli and his staff can be justly proud and that the industry will always be indebted to them.

So at the beginning of this 17th Meeting I would like to suggest that we give Dr. Sauchelli and his staff a rising vote of thanks.

CHAIRMAN SAUCHELLI: Thank you, Charlie, and everybody.

"Fertilizer Plant Operations Yesterday, Today, and Tomorrow"

Charles T. Harding

My subject is one that a group of old timers like Vince, Bill Price, Al Spillman could spend hours discussing and really enjoy it, however in the limited time I can only touch the high spots which I hope all of you will find interesting.

Lets break the last 50 years in this industry into periods:

Period One—1917-1933
  Pre-Depression

Period Two—1934-1948
  Post Depression

Period Three—1949-1958
  Yesterday

Period Four—1959-1966 Today

Period Five—1967-1980
  Tomorrow

5

For each of the first four periods, lets look at three things:

1. What we had to do.
2. What we had to do it with.
3. How we got it done.

Period 1—1917-1933
Pre-Depression

Lets use complete plants so as to cover the field—wet mix or dry mix operations have their individual places in this over-all presentation, but we will discuss them separately. First, we had to manufacture Sulphuric Acid, then normal Superphosphate or a low ammonia, high APA, wet base and finally a complete P.A.K. grade — today this is N.P.K.

Sulphuric plants were all Chamber Process type; most of them had changed to burning sulphur as their raw material by 1917, however there were still, here and there along the Atlantic Coast, plants burning pyrites. Sulphur burning plants were relatively simple to operate and maintain. The operating staffs consisted of four men — a combination acid maker and lead burner with one helper and one chamber man with a helper on each shift. Chamber Plants of all sizes were being operated from 20 to 200 tons per day basis of 60° Be.

The production of normal super or ammoniated wet base was required for sale as such to small mixers and for preparation of complete goods. These units generally were either 100 or 200 tons per day. Manpower requirements here consisted of 5 or 6 men—1 Rockmill, 1 mixer, 2 Den Men and a overhead car operator, with ammonia base, 1 ammoniation man added.

These products were mixed in a cast iron mixer and dumped into box type dens and excavated by hand. Where ammoniated wet bases were made, wool waste or leather scrap with small amounts of cyanamid, sulphuric acid 55° Be. and ground rock were used. The finished analysis of the base usually ran from 1 to 3% ammonia and 15 to 16% A.P.A., and normal super analysed about 17½ to 18%. During this period our phosphate rock ran about 70 to 72% BPL—remember this was before the days of flotation in the phosphate fields.

Superphosphate and ammoniated bases were usually allowed to cure 4 to 6 weeks before being worked into finished goods. The final production in the plant was the mixing of superphosphate or wet ammonia base with ammonium sulphate, cyanamid, tankage and manure salts (20% K_2O). All materials were dry and the popular field crop grades were 8-2-2 and 8-3-3 in the South, 12-2-2 and 12-2-6 in the Midwest. Considerable 16% or 18% superphosphate was also used in both areas. In the East and Northeast where potatoes and vegetable crops were grown, grades like 7-5-5 and 8-6-6 were popular. Most all analyses carried 40% W.I. Organic except the truck crop grades and they ran up to 60% W.I. Tobacco grades were formulated with at least half of the ammonia from cotton seed meal and/ or tankage. All finished fertilizers were shipped in burlap bags; in the South and East 200# size was used; in the Midwest 125# was the popular burlap size; and in the Northeast 167# with some 125# burlap were popular sizes.

Most all our orders were in car loads—10 to 30 tons occassionally a 40 ton car which was the load limit on the largest cars. In most cases they were received several days in advance of the shipping date. This allowed the plant people to schedule their work, number cars needed, labor for each day, printing of bags and tags where necessary. Wagon orders, as they were called in those days, represented a very small percentage of a plant's shipments, usually 2 to 3 tons per wagon or truck. Many of the plants located on the coast or rivers had some boat shipments. The boats were fairly well scheduled and presented no particular problem. These boat orders varied from 25 to 100 tons of bagged goods, no bulk.

During the last several years of this period, labor was plentiful; we had no unions for ordinary labor. Labor saving machines had not found their way into our industry to any extent. World War I ended during this period, some labor rates had increased from 20¢ to as high as 60¢ per hour in the middle of the busy shipping seasons of '17 & '18. The shipping seasons usually ran 4 to 5 months and a few plants worked more than the regular hour day, 7:00 A.M. to 5:30 P.M. with 5 hours on Saturday during the heavy part of the season. Wages gradually went back to the 20¢ level by the end of the period in a number of areas with 40¢ as a high in the Northwest and Midwest. Standard bases were made during the slack or summer months and then blended at time of shipment.

A summer crew of 15 to 20 men was kept to produce these standard grades and unloading of raw materials such as rock, potash ammonia, sulphur, etc. By January 15, we would normally have our buildings full and shipment would begin for early crops in the South by February 1st.

A shipping crew usually consisted of about 30 men to batch bag and load the finished goods. These 30 men could load 200 tons in a normal 10 hour day.

Period 2—1934-1948
Post Depression

Many changes took place during the next 15 years. Sulphuric Acid Contact Process Plants were being built, some as large as 100 tons per day at fertilizer plants and up to 300 tons per day at combination chemical and fertilizer plants. Most of the old chamber plants were still in operation. About the only changes in these plants were mechanical handling of sulphur and ammonia oxidation replaced the old Niter pot system.

Normal superphosphate production was mechanized in many plants. Better weighing and measuring systems were being installed. The Broadfield and Sturtevant type dens for mechanical excavation replaced the hand labor and improved mechanical condition of the product.

The wet ammoniated base, 15 1-0 types were abandoned. Phosphate rock grades rose to 75-77 BPL through a new flotation system in Florida and normal super phosphate with a 20% APA could be produced. The finished goods production was also mechanized with the installation of drum mixers, weigh hoppers and tractors replaced carts and wheel

barrows. Liquid ammonia in the form of B. liquor was replaced, some of the solid types of nitrogen and W.I. organic guarantees were lowered in most grades. Analyses were changed to the present N.P.K. system; higher analyses began to replace the lower grades, the old 8-3-3 in the South became 4-10-6, 5-10-5, etc., in the Midwest 3-12-6, 3-12-12 were the popular grades. Double strength analyses were being offered and used primarily in the Northeast, Grades like 10-16-14 or a double 5-8-7 in Maine for potatoes came on strong. Muriate of Potash 60% was fast replacing 20% Manure Salts. The Carlsbad mines came in during this period. During the middle 30's Allied and DuPont came in with ammonia-NIT, Urea-ammonia solutions and anhydrous ammonia. Concentrated phosphate 45-47% P_2O_5 was being produced in Florida in fairly large quantities and with these higher analysis raw materials the analysis of finished goods rose considerably in the Midwest and Northeast.

Granular — A relatively new type of finished goods came into production and several companies installed their first granular plants. Trucks were fast replacing car load shipments and our shipping seasons were shortened to 6 to 8 weeks. Labor unions and contracts for our plant personnel were with us for the first time. The 8 hour day and overtime came with these contracts. The plant superintendent's job, due to these changes, became more and more complicated. The office work at the plant was increased considerably. Formulation prior to this period was relatively simple, however with the rise in analyses, liquid nitrogen and a multiplicity of new grades, this task became rather complicated for the average plant superintendent.

World War II was responsible for many of the changes that were made in this period. The minimum wage law went into effect also during this period. This law set a minimum of $1.00 per hour on all industry doing business in Interstate Commerce. Practically all finished goods were made to grade in the summer months and very little batching was done at time of shipment. Railroad car capacities were now up to 50 tons and very few car loads were under 30 tons. The tractor or front end loader as we know them today, had been improved and with concrete replacing the wooden or dirt floors, the movement of materials for basing or shipping became relatively simple. With automatic scales and sewing machines our shipping crews reduced to about 10-12 men and we could still ship 200 tons in 8 hours with less than half the manpower.

This brings us up to more or less recent times in the Industry. For simplicity, I have divided them into three period. The first of these is:

Period 3—1949-1958—Yesterday

During this period there were very few changes in sulphuric acid production. Larger plants were being built however, and 500-600 and even 900 ton plants were built. All of these new plants were of the contact type. Some chamber plants were enlarged. Normal superphosphate production methods and equipment changed very little. Here again larger plants were built, one with a capacity of 100 tons per hour, and many plants that had operated only one or two shifts per day were operated around the clock for more production. Phosphate rock was being ground finer, stronger acid and granulation equipment for this material was installed in a number of plants.

This period saw probably the greatest growth in granulation facilities throughout the entire Midwest, Southwest, and Northeast with some installations in the South.

By the end of this period, concentrated phosphate production had grown to approximately 1,800,000 tons per year and normal superphosphate was beginning to decline. Ammonium phosphates had come in and in 1958 approximately 300,000 tons equivalent P_2O_5 was produced in a wide variation of grades, including 16-48-0 18-46-0 and 16-20-0. The above changes further promoted the growth of high analysis fertilizer. 5-20-20 — 12-12-12 became the big sellers in the Midwest, however grades like 8-32-16 — 7-28-14 were being manufactured. Producing these high analyses grades and keeping them on grade analysis-wise was and still is somewhat of a problem. Material analysis is so high that slight deviations in weight, particle size, or segregation can throw a sample out of tolerance.

Mechanical equipment such as tractors, bag packers, automatic weighing machines, etc. were greatly improved during this period. Many different types of conveying equipment from bagging machine to truck and/or railroad cars was installed. Practically all car loads now were 50 ton due to a better rate on this size loading and trucks with trailers were hauling as high as 30 tons per load.

Fork lift trucks and pallets were being tested with warehouse facilities at the plants to increase daily shipping capacity and better truck service. The length of the shipping season continued to shorten and by 1958 about 4 weeks full shipping in an area was all you could hope for. Sure you had maybe a gradual build-up for a week at the beginning, but this added still further pressure on the plant personnel and facilities. Shipping around the clock was common practice. Car load shipments had almost disappeared; some plants in highly concentrated farm areas were shipping 100% by truck. Paper bags replaced cotton and burlap; in most areas 80 and 100# sizes were popular ones. This also added to the plant shipping problems of more bags to handle per ton.

Bulk spreading of lime and some fertilizers, now that granulated was available, began to catch on and some plants began to equip themselves for this type loading. Many operators felt that this would not grow too fast and were slow to install proper facilities for this new type of business.

During this period granulation and mechanical conditioners had become such a factor in the industry that all grades were prebased for curing and analysis; granulated tonage per plant had increased and many plants had added additional finished goods storage as well as additional bagging machines to have the goods ready and get them bagged and shipped in the shorter seasons we were faced with. Multiple hopper systems, batching scales, overhead conveyors, and ad-

ditional elevating equipment further reduced the manpower requirements to prepare the stocks and get them bagged and loaded. Ratios were being recommended by most all state agriculture colleges and agencies — this added to the multiplicity of grades. As an example a 1-2-2 ratio was very popular. This gave us such grades as 4-8-8 — 5-10-10 — 6-12-12 and etc. Another was 1-1-1 ratio, 8-8-8, 10-10-10, 12-12-12, and so on. Trucks were taking the goods direct to the farm and it was not uncommon for a truck to have 2 or 3 different seizes and kinds of bags and 3 or 4 analyses in an 8—12 ton load. While we were able to reduce again the size crew to 6 or 7 men per bagging machine, the changes from grade to grade reduced our tons per hour; 160 tons per 8 hour day per machine average was about par for a plant. In some plants where the number of grades was limited, much larger tonnage per hour was produced.

Boat shipment had all but disappeared; there were still a few in the Baltimore area to Warehouses on the Eastern Shore of Virginia and Maryland. Common labor rate reached a high of $1.52 per hour in some places and a low of $1.25 in others.

Period 4—1959-1966—Today

During this period we have seen sulphuric acid plants being built up to 2000-tons per day. 600-ton to 900-tons per day were the most popular size. No large normal superphosphate units were built. 1500-ton per day Ammonia Plants and 1000-ton per day single train phosphoric acid plants. Even though more P_2O_5 was being consumed, the percentage of normal super continued to decline in favor of triple, DAP, and phos acid.

From 1958 to 1966 normal super declined about 2% from 1,300,-000 tons to 1,100,000 tons. Concentrated phosphate increased from 830,000 tons to 1,465,000 tons or approximately 80%. Ammonium phosphate increased from 290,000 tons to 1,253,000 tons or approximately 432%. All these increases and decreases are in terms of tons of P_2O_5.

These changes as such had little effect on sulphuric acid and normal super in regular mixed fertilizer plants. However, the tremendous plant food growth per ton of fertilizer in the high analyses grades has had its effect in the operations of these plants today.

The mixed fertilizer tonnage in the U.S. has grown from 16,000,-000 tons in 1959 to 19,658,000 tons in 1966. Here again this tremendous growth in tons does not give the whole picture. The increased units of plant food per ton and the tremendous growth of blend plants, small liquid operations and farm service centers have changed the production man's responsibility and added many new and complex problems.

The latest figures I have seen show blend plants have grown from approximately 700 in 1962 to over 2500 in 1965. Quite a number of these are individually owned but most of them are small distribution points for major producers. By far the largest number of these plants is located in the Midwestern states of Iowa, Illinois, Missouri, and Nebraska, with Indiana, Michigan and Ohio following. There were 2200 of the 2500 reporting operating in these seven states. Practically all mixed goods shipped from these plants is in bulk, except some so-called starter fertilizer in some areas that is in bags.

A major change in many plants has been the demand for fertilizers in bulk from normal bagging plants. This bulk in a way simplifies the plant operator's problems in that a bulk truck usually takes a full load of one grade and no bagging is necessary. This is nice buiness once you are prepared to handle it. Many plants today have installed drive-on-truck scales and in a number of cases, the truck can be loaded right on the scales.

The production of granular fertilizers has become more and more complex as the analyses increased. In 1966 the total nutrient of plant food per ton reached an average in the Midwest of 42.8 units per ton and in the South 27.75. These numbers however, include straight N.P.K. materials This is a far cry from 8-2-2 and 12-2-2 that carried 12 and 16 units of plant food.

Better weighing and measuring devices, larger granulators, and better spargers, better drying and cooling, better scrubbers along with more years of experience behind us has eliminated many of our problems.

Possibly one of the most troublesome areas of plant operations today is keeping the goods on analysis. Over-formulation is extremely expensive and under-runs are also expensive in both penalties and reputation.

I believe our good friends the control officials and I do mean our good friends, will in the near future get the uniform fertilizer laws enacted and this should help this problem considerably.

The short, highly concentrated shipping season is still with us and no doubt will remain. The 50 lb. bag in both paper and plastic have added considerably to the cost of bagging and handling.

The labor situation in most places is a real problem today. Round the clock operation in production and shipping during the busy season is a must and to find competent supervisors, and the necessary manpower, is in my opinion our greatest problem. Wage rates in many areas for common labor reached the $2.00 per hour mark. Higher skilled operators reached the $3.30 per hour.

Let's compare 12/31/1917 figures for U.S.A. with June 30 1966.

Nitrogen consumed for 1917	—	213,000 tons
Nitrogen consumed for 1966	—	5,313,700 tons (25)
P_2O_5 consumed for 1917	—	596,000 tons
P_2O_5 consumed for 1966	—	3,846,500 tons (6½)
K_2O consumed for 1917	—	33,000 tons
K_2O consumed for 1966	—	3,158,300 tons (96)

The above are U.S.D.A. figures.

Period 5—1966-1980 — Tomorrow

When we read of the new discoveries of potash and phosphate ores along with the known deposits and our ability to recover nitrogen from the air at most any point where it is needed, we can see a plentiful supply of these materials

8

is possible. The suphur supply could be a temporary problem, however since we have the know-how around it through the nitric acid or elemental phosphorus routes to produce available P_2O_5, if this becomes necessary. For example, our company Wellman-Lord has the new Norsk Hydro process for nitrophosphate fertilizers that will produce a product with 80 to 85% water-soluble P_2O_5. We expect elemental phosphorus to play an important role in phosphoric acid production in the future. Low cost atomic power with the known deposits of low grade phosphate rock are now making this source more attractive.

With the know-how we have today to build and operate plants of a size that only a few years ago was not believed possible, the problem of producing the necessary plant food for the world's needs is not beyond our capability. The big problems are, financing, marketing and distribution of this plant food and also the proper distribution of the food and fiber produced with these products. The education of farmers, operating personnel, engineers, etc. is also a tremendous task.

Most of you are familiar with what has been projected for consumption for the world in 1980, but let us look at these projections for a minute. The figures I will quote here on 1965 consumption and the projection for 1980 were taken from a World Fertilizer Forecast 1965-1980 that was prepared by the Research Department of Wellman-Lord, to provide additional service to our clients and to assist in our own planning.

For North America, U.S.A., Canada & Mexico: —
Nitrogen consumption in 1965 was 4.5 million metric tons; in 1980 it is projected to be 16.9 million. P_2O_5 consumption in 1965 was 3.6 million metric tons; projected for 1980 is 8.0 million tons. K_2O consumption in 1965 was 2.9 million metric tons; projected for 1980 is 7.0 million tons.

The *world* consumption and projections are as follows:
1965 — Nitrogen consumption 16.1 million metric tons. 1980 projected consumption 70.1 million metric tons P_2O_5 1965 consumption 13

million metric tons, 1980 projection is 33.0 million metric tons. K_2O 1965 consumption 11.1 million metric tons. 1980 projected 28.7 million metric tons.

The question naturally arises, where will it be produced and how will it be distributed. Certainly we know most of the North America's tonnage will be produced on this Continent but how much will we be called on to produce for export? In 1963 AID spent $45 million on its Fertilizer Assistance Program; 1967 is expected to reach about $300 million and the AID fund is projected to level off at abou $450 million by 1970. AID could be a source of considerable export tonnage in the next few years.

Let's make a few predictions for the future or tomorrow as we term it:

1. The demand for higher analysis will certainly continue.
2. Larger percentages of the tonnage will be moved in bulk or liquid forms.
3. Larger producing units for the basic materials will be built for more economical production.
4. Blend plants with liquid facilities as well as Farm Service Centers and distributing warehouses will be the avenues of distribution.
5. Even though the bagged fertilizers will decrease in percentage of total shipments, we may still need all our conventional plants to be used for mixing, storage and shipping of bulk and bagged goods. The blend and liquids will take care of the increased consumption.
6. If the sulphur shortage results in increased use of nitric acid processes or other forms of A.P.A. production, we may see some rather large mother plants built in high consuming areas.
7. We have seen some remarkable progress in farm production and fertilizer consumption in areas where irrigation is being practiced. Many acres that one time were not considered tillable are now in production on a profitable basis. This is a so-called new source of land and will consume considerable plant food.

In closing, let us again refer

to the Wellman-Lord World Fertilizer Forecast 1965-1980. Our findings indicate that the *world* fertilizer industry will grow at an accelerated rate in the decades ahead. We believe that the progress being made by this industry will greatly mitigate the problem of hunger, which, even today is prevalent throughout many parts of the world.

CHAIRMAN SAUCHELLI: Thank you, Charlie.

I regard that as a very valuable historical document. Only a person with the broad background that Charlie has could look backwards and then forward and measure the intensity of our dynamic industry. It certainly is a remarkable story.

Does anybody have any questions to ask Charlie?

DR. SAMUEL STRELZOFF (Chemical Construction Corporation): I have only one question. You mentioned 85 per cent P_2O_5, I suppose water soluble. Was that on the basis of Florida phosphate or any other type of phosphate that you had in mind?

MR. HARDING: Primarily Florida phosphate, which is the primary phosphate used in this country.

DR. STRELZOFF: Was that proved?

MR. HARDING: They'll guarantee it.

DR. STRELZOFF: Thank you.

CHAIRMAN SAUCHELLI: Any other comments or questions?

MR. DAHLGREEN (Chemical Producers, Dallas, Texas): I have one question. In looking at his projections, and I am sure all of us have made projections, I am wondering, and I am not trying to be humorous about what effect the pill is going to have on this. I think most of the fertilizer production is going to have to be keyed to population growth and it has entered my head that in the last ten years some of the population increases that were originally forecast are being revised downward and I am just wondering what Mr. Harding would predict or feel— what impact he would feel this would have on his projections?

MR. HARDING: These projec-

tions, of course, are ones that have been made by Wellman-Lord, TVA and IMC.

But you have raised a point about this pill thing. I have a son-in-law in Atlanta who is an obstetrician and his business has fallen off. There is no question about it.

MR. DAHLGREEN: The same is true at our house.

MR. HARDING: Further projections are going to have to be made about the effects of the pill, I think.

A MEMBER: You mentioned a 2,000-a-day fertilizer plant —

MR. HARDING: No, sulphuric acid plant.

MEMBER: Oh, I'm sorry.

CHAIRMAN SAUCHELLI: Any further questions?

Once more, Charlie, thanks very much for your very interesting presentation.

The next two papers deal with a very lively subject. Originally Bob Heck was to introduce the two speakers. Bob Heck, I am proud to say, has been added to our Executive Committee. Bob is not able to be here today for business reasons but he has Jim Zoellner of the IMC to represent him. Jim is going to introduce the next two speakers.

Introduction of Speakers on Air Pollution. James H. Zoellner.

One of the major problems facing the fertilizer industry today is that of air pollution control. In the United States we have seen this problem publicized through TV, radio, newspapers and the trade magazines.

Most of the states in this country, as well as the Federal Government, have appointed air pollution control boards, technical advisory committees and committees within legislative bodies to investigate the effect of air pollution on the community and to make recommendations concerning its control.

The fertilizer industry is responding to this problem and recognizes that it has a responsibility to the community and to itself to bring this problem under conrol as quickly and economically as possible.

This morning we have two speakers who will discuss methods of measuring, analyzing and controlling air pollution.

The first speaker is James Hammett, who is Special Projects Supervisor at IMC's laboratory in East Point, Georgia.

Jim has had broad experience in measuring effluent emissions, in establishing laboratory procedures for analyzing effluents and evaluating methods of controlling emissions.

He will speak to us on the composition of effluents from granular fertilizer plants.

rotary dryers and coolers were required to properly condition the granular materails and give them the desired physical properties; vibrating screeens were used to separate the desirable particles from the undesirable larger particles and excessively small particles; and crushing equipment was required to pulverize oversize particles. Almost every step in this process produced an effluent of some kind.

In order to learn to measure and control the effluents from granular fertilizer plants, IMC conducted dust and fume surveys at various plants throughout the U.S.

The plants in which these tests were conducted are described as TVA type plants and usually consisted of the following equipment: (1) a rotary drum ammoniator-granulator in which solid raw materials, nitrogen solutions and/or ammonia, acid, steam, water, etc. are introduced; (2) A rotary drum dryer; (3) a rotary drum cooler, and (4) dust and fume collecting equipment.

The effluents from this process consist of fumes and some particulate matter from the ammoniator, water vapor and particulate matter from the dryer, particulate matter from the cooler, and particulate matter (dust) from screens, elevators, conveyors, and crushing equipment.

Most of the plants in which tests were run removed ammoniator fumes by a natural draft or forced draft stack, but very few attempted to scrub the ammoniator fumes. Particulate matter from dryers, coolers, etc. was collected in single or multiple cyclones and 60% of the plants used a wet scrubber as a secondary collector.

The instruments and methods used to make the dust and fume surveys were of the type commonly used by many laboratories and also recommended by the National Air Pollution Control Center.

Basically the air flow information was obtained by use of measuring tape, wet and dry bulb thermometer, 1.0"-3.0" Manometer, U-Tube, and Pitot Tube. The particulate matter samples were collected in Alundum Thimbles and the fumes impinged into solutions of

Composition of Effluents From Granular Fertilizer Plants

J. A. Hammett

EFFLUENT control in the fertilizer industry is a relatively new concept. Prior to the mid 1930's almost all of the mixed fertilizer manfactured in the U. S. was made in batch mixing processes in which dry, relatively inert fertilizer materials were blended together. During the late 1930's, ammonia was introduced as a nitrogen raw material and was used to neutralize the acid in superphosphate. The chemical reaction resulting from this mixture was a rather mild reaction that produced no effluent —not even water vapor. During the

period from 1938-1950, the amount of ammonia per ton of fertilizer was increased from about 60 pounds to 100 pounds, but effluent emission was still practically non-existent.

In the early 1950's the fertilizer industry accepted a new technology which converted their process from simple mechanical mixing operations to rather complex chemcal operations.

This new process was defined as a granulation process and required the use of new and highly reactive fertilizer raw materials;

water, 1 N NaOH and 1 N H$_2$SO$_4$. The samples were drawn from the source by use of a vacuum pump and the air volume measured by use of a dry meter.

The techniques involved in the use of these instruments will be discussed in detail by a representative of resources research later in the program.

The following data is necessary for air volume calculated of the various ducts/stack.

	Unit
Stack Size	Inches I. D.
Velocity	Ft/Min.
Air Flow (actual)	C. F. M.
Air Flow (S.T.P.)	C. F. M.
Temperature	°F
Relative Humidity	%
Static Pressure	Inches Water
Vapor Pressure	Inches Mercury

The stack size, velocity, wet and dry bulb termperature, and static pressure were actually measured. The other data was calculated from these measurements.

These tests are necessary to determine the type and quantity of particulate matter and fume commonly discharged from granular fertilizer plants.

Tests	Unit
Particulate Matter	Lbs/Hr
Particle Size	Tyler Mesh & Micron
Free Ammonia (NH$_3$)	Lbs/Hr
Ammonium Chloride (NH$_4$Cl)	Lbs/Hr
Fluorides (H$_2$SiF$_6$)	Lbs/Hr
Total Nitrogen (N)	Lbs/Hr
Total Phosphate (P$_2$O$_5$)	Lbs/Hr
Total Potash (K$_2$O)	Lbs/Hr

We were primarily concerned with particulate matter, free ammonia, ammonium chloride, and fluorides. There are other fumes discharged from granular plants such as SO$_2$, SO$_3$, NO$_2$ etc., but the usual emission of these fumes was found to be less than 1 lb/hr.

The particle size of the particulate matter was determined and then analyzed for nitrogen, phosphate, and potash in order to determine the product loss as well as the composition of the effluent. The impinged fumes were analyzed for ammoniacal nitrogen, chlorides, and fluorides.

In determining the emission into the atmosphere from various sources in the plant, we are not only interested in the quantity and composition of the effluent, but we are also interested in methods or techniques to reduce the amount of effluent.

Generally the quantity of effluent is determined by many factors such as:
(1) Grade
(2) Formula
(3) Production Rate
(4) Recycle Ratio
(5) Air Flow
(6) Type Primary Collector
(7) Type Secondary Collector
(8) Condition of Collectors
(9) Inlet Load To Collectors
(10) Particle Size of Dust
(11) Velocity of Air
(12) Dryer Temperature
(13) Type Crusher
(14) Screen Size

The effect that the inlet load to cyclones and particle size of the particulate matter may have on material loss can be illustrated by

	Plant #1	Plant #2
Grade	6-24-24	6-24-24
Production Rate	12 T/Hr.	10 T/Hr.
Velocity Through Dryer	577 Ft/Min.	371 Ft/Min.
Recycle Ratio	Very High	Very Low
Particle Size Of Dust To Cyclone (-43 Micron)	4.0%	13.5%
Inlet Dust Load—Cyclone	4290 Lbs/Hr.	78 Lbs/Hr.
Exit Dust Load—Cyclone	133 Lbs/Hr.	19 Lbs/Hr.
Efficiency Of Cyclone	96.9%	75.5%

	Inlet Cyclone (lbs./hr.)	Exit Cyclone (lbs./hr.)
Particulate Matter	14-4289	4-133
Av. Particle Size	60-325 mesh	400-5000 mesh
Free Ammonia (NH$_3$)	14-171	14-171
Ammonium Chloride (NH$_4$Cl)	0.1-3.6	0.1-3.6
Fluorides (H$_2$SiF$_6$)	4.1-43.0*	4.1-43.0*
Total Nitrogen (N)	36-579	23-150
Total Phosphate (P$_2$O$_5$)	5-503	0.9-18
Total Potash (K$_2$O)	3-518	0.5-22

*When granulating 0-29-0

an actual condition that existed in the dryer system of two plants.

Both plants were manufacturing the same grade with very little difference in the production rate. Plant #1 had a much higher exit dust load, or material loss, than plant #2. This was due to the higher inlet load. From this data we could assume that the high inlet load was due to a higher recycle ratio and also a higher velocity through the dryer. Plant #2 did not have a high exit dust load, or material loss, even though the cyclone efficiency was poor. From this data it can be seen that the poor cyclone efficiency was due to a low inlet dust load of particles that were very small in size. In evaluating the data, the actual pounds of dust exiting the cyclone is a better criterion than the calculated efficiency of the cyclone.

The next table shows a range of particulates matter and fume that was discharged from various dryer systems.

The inlet load of particulate matter to the dryer cyclone varied widely with average particle sizes of 60 to 325 mesh. The particulate matter exit the cyclone, which was usually material loss, had a particle size of 400 to 5000 mesh.

The largest material loss from a dryer is usually free ammonia or dust. The average free ammonia is about 53 lbs./hr. The average dust loss is about 38 lbs/hr. Considerable amounts of fluorides were emitted when granulating 0-20-0. The nitrogen, phosphate and potash figures shown were obtained by analyzing the dust and fume samples. These figures are a sum of the dust and fume analysis.

The cooler system is evaluated in almost the same manner as the dryer system. A balance is also needed on the air flow through the cooler so as to sufficiently cool the product and remove the fine dust (-35 mesh) without creating too high a velocity through the cooler. At the high production rates used these days it is usually difficult to cool the product sufficiently without removing too many large particles. A velocity of above 500 ft./min. will remove a large amount of fines with the dust.

The following is a range of particulate matter and fumes discharged from various cooler systems.

	Inlet Cyclone (lbs./hr.)	Exit Cyclone (lbs./hr.)
Particle Matter	78-3552	16-135
Av. Particle Size	60-325 mesh	400-5000 mesh
Free Ammonia (NH_3)	1-38	1-38
Ammonium Chloride (NH_4Cl)	0.1-1.0	0.1-1.0
Fluorides (H_2SiF_6)	0-12*	0-12*
Total Nitrogen (N)	11-298	4-16
Total Phosphate (P_2O_5)	12-426	1-30
Total Potash (K_2O)	3-843	1-19

*When granulating 0-20-0

The inlet load to the various cooler cyclones varied widely as did the dryer. The average particle size was also 60 to 325 mesh. The particle size of the particulate matter discharged from the cyclone was 400 to 5000 mesh, which is about 2 to 37 micron. The free ammonia loss from the cooler was usually very low. (average 8 lbs./hr.) The largest loss was usually particulate matter. (average 50 lbs./hr.)

The fumes and dust not removed by the dryer and cooler cyclones were passed through a wet scrubber by 60% of the plants surveyed.

The next table shows a range of particulate matter and fume discharged from various dryer-cooler wet scrubbers:

	Inlet Scrubber (lbs./hr.)	Exit Scrubber (lbs./hr.)
Particle Matter	25-235	1-11
Av. Particle Size	2-40 Micron	-
Free Ammonia (NH_3)	15-208	5-175
Ammonium Chloride (NH_4Cl)	0.2-4.6	0.5-3.0
Fluorides (H_2SiF_6)	0.1-29.0*	0-2*
Total Nitrogen (N)	25-160	11-144
Total Phosphate (P_2O_5)	1-30	0.2-4.0
Total Potash (K_2O)	1-25	0.5-2.0

*When granulating 0-20-0

The heaviest load to the scrubber was particulate matter and free ammonia. More free ammonia is discharged from the scrubber than any other material.

It was interesting to have observed what can happen to a wet scrubbing system when granulating 0-20-0. The plume from the stack was light and dissipated rapidly. As the pH of the scrubber water became too acid it was neutralized with anhydrous ammonia. As the pH approaches 7, care must be taken so as not to exceed the rapidly approaching neutral end point. If this is exceeded a very heavy white fume of NH_4F will cover the surrounding area. During this particular observation the neutral point of the scrubber water was exceeded and a heavy concentration of white fume resulted.

Fumes from the ammoniator can be removed by a natural draft and/or a forced draft stack.

This table shows a range of particular matter and fume discharged from various ammoniators.

Here again we see that more free ammonia is discharged than any other material. (average 54 lbs./hr.)

	lbs./hr.
Particulate Matter	3-52
Free Ammonia (NH_3)	4-182
Ammonium Chloride (NH_2Cl)	0.1-16.0
Fluorides (H_2SiF_6)	0-1
Total Nitrogen (N)	12-179
Total Phosphate (P_2O_5)	0.1-2.0
Total Potash	0.1-8.0

Although the concentration of ammonium chloride discharged from the ammoniator is not very high in lbs./hr., it appears as a very heavy, white fume. This fume, or mist, is approximately 1 Micron in diameter and is very difficult to remove by scrubbing.

It was determined by pilot plant test that a concentration of .001 grains of Ammonium Chloride/FT^3 was invisible to the eye in most atmospheric conditions. In order to find the equipment suitable for reducing ammonium chloride to this concentration various systems were tested. The types tested were—

(1) Venturi type — short throat — low differential pressure

(2) Venturi type — long throat — high differential pressure

12

(3) Venturi type plus steam ejector
(4) Packed beds
(5) Bouncing ping-pong balls
(6) Impingement

The Venturi type—long throat—high differential pressure was selected as the most suitable for our particular use. This was a modified Heil scrubber.

The next table shows the performance of the Heil Scrubber installed on the ammoniator at one of the I.M.C.'s granular fertilizer plants.

Efficiency	
% Ammonium Chloride removed	91.0
% Free Ammonia removed	64.8
Differential Pressure	
Inches water	54
Gas Volume Through Scrubber	
C. F. M. (actual)	4600
Inlet Gas	
Grains Ammonium Chloride/FT^3	.0330
Grains Free Ammonia/FT^3	.6087
Exit Gas	
Grains Ammonium Chloride/FT^3	.0030
Grains Free Ammonia/FT^3	.2142

You will notice that a high differential pressure of 54 inches of water used in this system. The gas volume through the scrubber was 4600 C.F.M. Although the efficiency of the ammonium chloride removal was only 91.0%, this scrubber did a satisfactory job of removing ammonium chloride down to .003 grain/ft^3. The removal of free ammonia is not efficient, but this can be corrected, if necessary, by maintaining the pH of the scrubber water at less than 7.0.

This was the first scrubber installation of this type used by I.M.C. The total cost, including installation and associated changes, was about $40,000. This added a cost of about $.15 to each ton of fertilizer produced. Since the liberation of ammonium chloride is directly proportioned to the amount of sulphuric acid and/or muriate of potash used it may be more economical in some locations to change the formula so as to use phosphoric acid and/or triple super instead of sulphuric acid to absorb ammonia and aid granulation. The sparger arrangement and other mechanical adjustmens may also reduce the amount of ammonium chloride liberated.

The average emission of particulate matter into the atmosphere by granular plants without a secondary collector was 97 lbs./hr.

The average particulate matter discharged into the atmosphere by granulation plants with a wet scrubbing system was 7 lbs./hr. The wet scrubber in most cases will reduce the particulate matter discharged to meet most emission standards.

Another problem associated with scrubbing is the disposition of the scrubber water. Also, the plume from the wet scrubber may appear monstrous in cool weather, even though it is mostly water vapor. Dry collection systems do not arouse the neighbors in most cases because they can't see the plume as easily. High efficiency cyclones may be the answer for the reduction of particulate matter and also the recovery of materials.

The following example shows the $ value of N-P-K lost to the atmosphere and streams of six different plants.

Plant	Grade	Rate	N	Material Loss (Lbs./Hr.)			$ Value N-P-K
				P2O5	K2O		
1	5-10-15	32	145	36	42		$8.72
2	6-12-12	25	56	25	17		3.63
3	10-20-10	20	190	3	1		9.49
4	10-10-10	15	59	7	22		3.41
5	8-32-16	15	229	42	9		10.66
6	6-24-24	12	104	53	16		8.01

The dollar value lost varied from $3.41 to $10.66 per hour. In many plants we find losses as high as $20,000 to $30,000 per year. These losses present severe problems for the fertilizer industry and one of the challenges that faces each of us today is to find more economical and efficient methods of controlling fertilizer plant effluents.

MR. ZOELLNER: Thank you, Jim.

The second speaker is John S. Lagarias, who is President of Research Resources, Incorporated, Reston, Virginia.

Resources Research provides consulting and testing services and conducts special studies in all phases of air and water pollution control.

Mr. Lagarias is First Vice-President of the Air Pollution Control Association which is the foremost national organization concerned with air pollution control. Jack is well qualified to present the methods of measuring and evaluating effluents from granular fertilizer plants.

Method of Measuring and Evaluating Effluent From Granular Fertilizer Plants

Robert N. Allen, John S. Lagarias and David P. Barnes

FOLLOWING a paper on the nature of effluents from granular fertilizer plants, it will not be necessary to dwell on a review of basic granulation process differences. We do want to emphasize some of the production factors which directly influence the emissions and thereby the sampling procedures. Raw materials necessary for a particular formulation of fer-

tilizer obviously determine, to a large extent, what materials *can* and probably will be emitted.

"Granular fertilizer" may have different shades of meaning to each individual. To the person concerned with measuring and evaluating the emissions from any plant they are important. Many operations are trying to granulate, nodulize or pelletize all sorts of materials without changing them chemically. This can also include iron ore and phosphate rock. (Both of these processes, incidentally could quite conceivably emit hydrogen fluoride fumes.) More often, in the fertilizer business you are going to be producing physically changed granules simultaneously with the chemical reactions which are producing the product — and the unwanted emissions.

In granulation of fertilizers, it appears that water and heat in combination is one of the best ways to form a granular material, along with the rolling, segregation type of action that is produced in a rotating drum or some other variety of mixer. By adding the acids and other basic raw materials to this operation, it is possible to use the chemical heat of reaction and the moisture contained in the raw materials.

The above discussion applies first to a simple phosphatic material such as granular triple super phosphate. With only slight modification, the same process can be used for ammonium phosphates. Ultimately, the entire formulation can be produced in a similar manner. On the other hand, it is possible to add fully reacted, or cured, products as the raw materials to the granulation process. In many areas, it is not uncommon to make up the finished product by simple bulk blending.

Whether we ordinarily consider it or not, ammonium nitrate heated to the point of melting, then sprayed or dropped from the top of the prilling tower is going to give us a granulated fertilizer and it is going to give us problems quite unlike those processes previously mentioned. The Nissan spray tower process for granular fertilizer is going to be similar to other spray products such as detergents—with the tendency to form

dust, lots of air from which the product must be separated, etc. Generally speaking, each different type of process will give some sort of differences in the emissions to be expected. Certainly a fully cured material adding only moisture and minor amounts of heat is going to emit considerably less gaseous fluoride than in the process ending up with the same material but carrying out the complete chemical reaction right in the reactor-granulator bed.

Inherent Problems

There are overall influent and emission problems which stem directly from the nature of the products. The chemical properties are self-evident. Physical properties of nearly all of the fertilizers are those of sticky hygroscopic material which makes a pretty darn good cement when it dries. Likewise, when it gets a little bit wet and moist again, it makes a pretty good ice slide. Handling these materials, therefore, in moving equipment can create pollution problems. Material builds up and pushes belts off the rollers, builds up on the bottom of the belt, travels along the underside, then comes falling down in the most inopportune spots. This is going to put an unpleasant material, from the point of view of contaminants, in all the wrong places. Generally speaking, it is the difficult physical properties themselves which lead to the necessity of having covers removed from various pieces of equipment. Sledge hammer blows, etc., which warp, twist, cause leaks and generally imperfect construction, make complete enclosure and control of fumes and dust throughout a fertilizer granulation plant quite difficult. In addition to the physical properties of the fertilizer itself, the fact that a granular product is being produced requires a certain amount of air flow for drying and for cooling. These are usually separate because the cool air that picks up heat and would be very advantageously used in the intake air for the dryer is too contaminated to be used at that point. The dryer burner would gum up. Then there is the screening procedure to get the final size. Dust has the obvious properties of blowing all over the place if there are any leaks at all.

The oversize has to go to a grinding circuit which has the same problems of stickiness, hardening, etc., which cause openings and leaks.

Source Measurement

Liquid effluent flows are relatively easy to measure. The following discussion will concern those contaminants which leave the plant area as gases and airborne particulates or aerosols.

The task of measuring emissions from the fertilizer plant start rightly as source emissions, or stack sampling. We have been emphasizing, however, that more often than not the emissions are *not* neatly contained in a nice stack but waft gently out the doors, windows, holes, roof monitors and ventilators; from around the transfer points, loading docks, trucks, etc.

Although there may be a far cry in actuality between sources, materials, and problems, we believe there is a basic principle of source measurement that is a lot easier to state than to perform. All that's necessary is to put a big balloon over the stack for a short period of time and close it off. Physically, we have never been able to find a large enough balloon for the whole operation. It has been necessary to modify the principle, first down to a measurement of the total gas flow emitted or passing the fertilizer plant (operation). Secondly, we must take a representative sample from this mass of material (or gas stream) leaving the plant and analyze it for the desired constituents. If these two things can be done, it's a matter of simple calculation to determine the total amount of contaminants leaving the plant. This representative portion, however, can become pretty entangled — for instance, where there is a source of dust from some feeder up near the roof with the wind gently blowing it across an area with no boundaries and little access. We are not going to get too deeply involved in the theory of dividing up a stack area in the nice uniform rectangles or concentric circles and in the taking of umpteen individual samples. This is not only highly desirable — it is our normal procedure. We have (read) papers and descriptions

which tell you how to get a perfect sample from the stack, but they usually neglect to tell you how many people and how many days are required to do this. Meanwhile, we have found, in our experience, that the process has either shut down five times, changed twenty times, the shift is ended, or you are making a different grade of fertilizer. It is our opinion that in most work certain shortcuts must be taken in sampling procedures to compensate for the process variables (subject to discussion with the management to determine just what it is that is most necessary at that particular moment). Too often we hear all sorts of statements that stack sampling is inaccurate. Papers will describe the errors ascribed to a non-isokinetic sample, errors due to slight changes in barometric pressure, temperature, carbon dioxide or moisture content in the gases, ad infinitum. True, these things do create errors. On paper, by formula, they can be calculated. Some of them, in wind tunnels, could be demonstrated. But you know from experience that the average fertilizer plant does not sit still that long. We have come to the conclusion that stack or source testing of most stacks can be a good deal more accurate than the processes themselves. There is little point in making a twenty-four hour perfection type sample, making the umpteen traverses, etc., when nothing at all is learned about variability of the process. In a large number of cases, it is quite sufficient to use average velocity point sampling, with isokinetic flow just as a matter of safety and good practice, but taking several (usually three) short consecutive samples.

The average sampling train will consist of a nozzle, probe, collecting medium, method of measuring volume of sample, and source of vacuum. The various materials of construction can range from glass to plastic or metal. Although there are many areas in which there are differences of opinion, we find that type 316 stainless steel is quite satisfactory for the typical fertilizer plant. Nozzles made of this material are relatively free from easy damage, will sustain high temperatures, and have not shown any particular tendency to influence the results. The probe likewise may be made of ordinary quarter-inch, schedule forty, stainless steel pipe. This material provides a great deal of flexibility in size and fabrication. At the same time, it will provide a resistance to breakage and high temperatures often encountered in source testing work.

The collecting medium, on the other hand, may require a variety of materials and arrangements. Commonly used would be traps of some sort, a filtration assembly, and ordinary impingers or bubblers. The materials to be used will obviously depend upon the contaminants to be trapped. That is, their size, shape, corrosion, solubility, etc. The contaminants normally emitted from granular fertilizer plants can be handled in simple Greenburg-Smith impingers. The Greenburg-Smith impingers have been designed to be efficient in the collection of particulate matter down to one micron in size and also are efficient as bubblers. The ordinary duct or stack sample will normally have concentrations of contaminants such that special bubblers are not necessary. Because the ordinary Greenburg-Smith impingers are made of glass, they must be highly protected to sustain the wear and tear of climbing stacks several hundred feet in height along with the constant rehandling.

Several years ago we instituted the practice of using the internal portion of the impinger as provided in glass but inserting this into a polypropylene granulated cylinder with a neoprene stopper. Breakage has been greatly reduced and yet the advantages are largely retained. The only real disadvantage has been that when testing extremely hot stacks of flue gases containing large percentages of steam, the reduced heat transfer of a plastic cylinder makes cooling of the impingers more difficult. The sample train may be connected with ordinary rubber tubing, with tygon or special plastics, or ultimately with glass ball-joints. For fertilizer plant work, ordinary latex tubing has been found quite sufficient.

A dry test meter has been found best for measuring the sample volume. Other methods such as the use of flowmeters or orifice plates would be satisfactory, but the meter will measure the total flow without the necessity for careful timing. A stop watch or second hand enables the calculation of isokinetic flow, but an interruption in the process or the sampling procedure does not disrupt the sample measurement. Any source of vacuum is perfectly satisfactory, but experience has shown that the ordinary 110 volt vacuum pump has had the greatest adaptability. There are relatively few sources of steam or compressed air available in the field, and the use of battery driven pumps necessitates a great deal of work. However, there are some sources or sample points at which no source of power is available, and the battery driven pumps are the only solution. This would normally be true of the ambient air or leakage type sources rather than the ordinary stack exhaust sample.

Most of the fertilizer plants' emission are conveniently caught in distilled water; although in collecting ammonia losses it is best to use a dilute acidic solution and, of course, the sulfuric acid exhausts will require sodium hydroxide or hydrogen peroxide solutions.

A typical problem occurs in measuring the amount of fluoride being lost during the production of any fertilizer from the *building* in which it is produced—from the conveyor belts, from the transfer points and eventually from the storage building. Basically, we try to use the same principles in each case.

Although there may be no physical stacks, a cross sectional area is laid out — sometimes right in space, sometimes in doorways, windows, louvers, etc. An air flow is measured at the given area in the best way possible using anything from the ordinary pitot tube to velometer, thermal anemometers, and upon occasion by throwing dust into the air and measuring its rate of velocity with a stop watch. Samples of the contaminants are obtained from these cross sectional areas with either the standard equipment or with bubblers, or whatever is suitable to the occasion. It has been found that an absorber using glass beads for good contact and absorption can be built into

some of the new plastic bottles. This, along with a battery and a small pump, can be carried by one person to any point where access is available. The problems that can be encountered in a project such as this are limited only by the number of installations which are in existence. Nevertheless, you might be surprised at some of the duplication that has been achieved under different circumstances, by different personnel, and by different groups. When testing the same installation, one would hardly expect *close* duplication, but we have been able to keep within the same order of magnitude without apparent difficulty, as long as the operation was essentially the same. It might be pointed out that the greatest single matter of importance will be the wind velocity and direction. Excellent results can be obtained when the wind is relatively constant in velocity and is blowing at right angles to most of the openings.

The analytical problems are generally minimum in a source measurement program. It is simply necessary to collect the contaminants in the proper solutions and in sufficient concentrations for analysis by the method selected. For example, the West-Gaeke method of analysis for sulfur dioxide in ambient air is excellent, but it scarcely applies to the emissions from the sulfuric acid stacks. The Brink sampler, however, will enable the separation of the sulfur trioxide acid mist from the gaseous sulfur dioxide and at the same time give some indication of the particle size being encountered. The sulfur dioxide is then caught in impingers filled with five percent NaOH.

The analysis for total particulate matter emissions is usually subject to the limitation of the analytical balance, whereas the analysis for fluoride may be conducted down into the microgram range. Under these circumstances, the particulate matter may be correlated with the fluoride content or it may be necessary to take longer samples in order to achieve better accuracy.

Effect of Pollutants

Volumes have been written about the effects of typical fertilizer plant pollutants upon living matter. Everyone that has been close to a tube of smelling salts has some idea of the effect of ammonia upon the human nose. Some of the areas near metal smelters, with the production of sulfur dioxide, have had an almost complete devastation of vegetation. Standing too close to a match as it is lit will sometimes catch at your lungs with the sulfur fumes.

Of particular danger to livestock are fluorides which may be ingested with the large quantities of forage which they consume. In excess, this vital element will attack and alter the normal bone and tooth structure of both livestock and humans. Extensive studies have indicated that forage containing about 40 or 50 parts per million fluoride, depending upon the type of cattle, their age, and many other conditions, will begin to produce noticeable effects. Studies are currently in progress to determine some sort of similar guidelines concerning the effect of fluoride upon citrus. Gladiolus are particularly sensitive. Here the damage appears as tip-burn at the end of the leaves where the fluorides are concentrated.

To varying degrees in each case, the ordinary working man can put up with far greater concentrations of these contaminants than the surrounding vegetation. For instance, it takes relatively few parts per *billion* of gaseous fluorides to be absorbed by vegetation, but this will accumulate as *many* parts per *million* in the plant itself.

Ambient Measurements

No one is ever really concerned with the emissions they produce unless there is some effect that can be shown to be harmful or unpleasant to the neighbors. Fertilizer emissions can be harmful in sufficient quantity. Therefore, regardless of the source measurements, we are ultimately concerned with the concentration of these pollutants in the outside air and atmosphere. Ambient air measurements fall into a generally different category simply because of the low concentrations involved. These will usually be not only parts per million but parts per billion. Ordinary impingers, or bubblers, have been shown

to be satisfactory in the collection of sulfur oxides, fluorides, etc., but large long-term air samples are usually necessary to obtain the concentration of contaminant in solution so that it can be satisfactorily analyzed. Relatively automatic equipment has been produced for the measurement of sulfur oxide in the low parts per *million* range where it is of concern. Fluorides, on the other hand, are of interest in the parts per *billion* range and as yet no truly satisfactory automatic instruments have been devised for this purpose. We have been conducting tests on such an instrument, but the extreme sensitivity that is required produces a multitude of problems in the automatic control and operation of such a device. We, and several others in this field, have devised automatic samplers to take a series of bubbler samples over a period of a week or more; but these are limited in the period of time which can be adequately sampled. Each sample requires a considerable number of cubic feet in order to collect sufficient fluoride for analysis. Even if it were possible to collect a sample every ten minutes on some sort of caustic coated filter paper, the analytical problems being ground out from such a program are phenomenal.

The final receptors themselves, such as grass, leaves, and other plants are often able to be used as the test meaurement devices. Grass is easily obtained, and analyzed. The leaves from the citrus trees may be visually examined and chemically analyzed. The sensitive gladiolus leaf is especially appropriate for visual analysis. Not only do these receptors provide a method of test analysis but are directly the source of ultimate concern.

Artificial test devices, however, such as chemicals, filters fallout jars and the like can usually be placed in every location especially when vegetation is not growing at a convenient spot. The familiar lead candle is excellent for the long-term determination of relative sulfur oxide concentrations in an area, as are calcium oxide coated filter papers for fluoride concentrations. The oft discussed fallout jars are not only valuable for the determination of particulate matter but for

those materials which are soluble as well.

The ambient measurements are eventually decided on the basis of what contaminant is the problem, how much can be afforded for the survey at the time, and what sort of test device is most appropriate for the survey in question.

Material Balance

In the fertilizer industry, we have occasionally been approached on the possibility of providing a complete fluoride balance. Those who have been involved in making a balance of P_2O_5 values are aware of some of the problems. Whether or not the mechanics of fluoride balance for fertilizer is any more difficult than for P_2O_5 is not known. The answer being sought from a fluoride balance is to check the losses and emissions to the atmosphere or from unknown sources. When a good size plant production unit multiplies 3 or 4 percent fluoride content times the tons of rock being used, a lot of fluoride may be seen entering the plant. Likewise, when the remaining fluoride content in the final product is multiplied by those tons, some of the fluoride leaves the plant in this manner. The amount of fluoride going to the scrubbing water is often quite appreciable, but this too is very difficult to measure because the incoming scrubber water from a pond often contains nearly as much fluoride as the water leaving the scrubber. One is concerned with the analytical accuracy in determining fluoride in phosphate rock or product. This slight error does not seem like much until it is multiplied by the tons of materials in question, then it can become quite considerable. However, probably the most difficult point of all is in the *sampling* of both incoming rock and especially outgoing product. Taking a representative sample under some physical conditions can be quite difficult. Normal production involves quite a few variables from time to time; therefore, some sort of automatic representative sampling would be necessary. The ordinary equipment designed for this use is not usually conducive to a sticky or hydroscopic material without considerable attention.

Ultimately, the material balance will end up with a few large quantities of fluoride with a small inherent error in their accuracy. Unfortunately, the limit of this error is about the same as the total daily emissions that are expected. Therefore, if we want to know the emissions from a granular fertilizer plant, we must revert to a source testing program to determine what leaves in the air and upon ambient measurements to determine the effect upon the neighborhood.

MR. ZOELLNER: Jack, you have given the members of the Round Table a very good insight into the complexities of sampling stack emissions.

We have a short time now where we can entertain discussion on either of the papers.

Are there any questions?

Either the problem is so complex that it is over our heads or most of the plants are now getting it under control.

The scripts will be published and this will include all of the charts for further study.

CHAIRMAN SAUCHELLI: Thank you, Jim.

You have heard a subject discussed that is going to be more and more in the forefront of the fertilizer industry in the coming years. The chemical process industry is really facing some very difficult problems in this pollution and pollution is not going to rest now the Federal Government has taken such an active part in controlling or preventing it.

Before we proceed with the program, let me suggest that the speakers who have papers please give them to Miss Withers, here, upon delivery of the speech.

I want to recognize a couple of distinguished guests.

The first is Paul Truitt, president of the National Plant Food Institute. Mr. Truitt rose.

We hear so much these days of the potash developments in Saskatchewan that somehow the mining activities at Carlsbad in New Mexico are somewhat overshadowed but the Carlsbad deposits still play an important role in the potash industry and will continue to do so for some time yet.

The next speaker, Mr. J. M. McManus, is Assistant Mill Superintendent at the Southwest Potash Company works at Carlsbad. He will talk to us about air classification of potash.

Product Sizing at Southwest Potash Corporation—
Air Classification

J. M. McManus

FIVE years ago a decision was made to increase the production rate of muriate of potash from 750,000 tons per year to 1,000,000 TPY. Expansion and modification of the product screening plant constituted a large part of the overall program. The existing facility was already strained; the building was too small and much of the equipment was worn out, also the product screening plant had to include equipment to produce a new 35/150 mesh product to be called Uniscreen.

After a careful study of all the variables and available equipment, it was decided that the heart of the process would be a recently developed air classifier manufactured by the Buell Engineering Company. The equipment would fit into the flowsheet as shown on the slide.
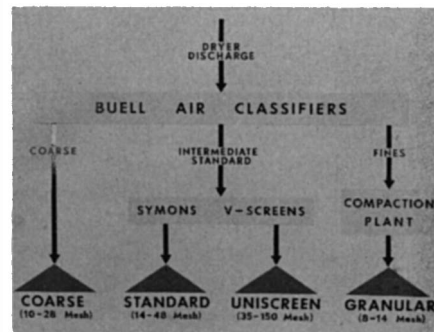

Figure 1
Flow Sheet Particle Classifications

The Air Classifiers are shown to take the hot feed from the dryers, and split it into three streams. One of these streams is a

finished product at 8/20 mesh and is marketed as SWP Coarse. The others are Intermediate Standard which is subsequently mechanically screened into Standard and Uniscreen, and the Fines which are routed into the closed circuit compaction plant.

The air classification installation came on stream in July of 1964. The system was unique at that time and as we had expected there were many problems of process development yet to be solved. However, the manufacturer had made certain performance guarantees, prior to sale of the equipment, and we at SWP enjoyed the full cooperation throughout the trying period of adjustment to the new plant, while running slightly in excess of design capacity.

The basic operating principle of the Buell gravitational classifier is described in the following diagrams.
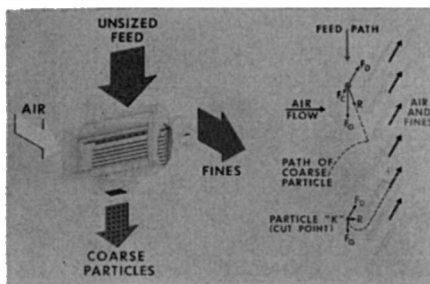

Figure 2
Unsized Feed Going Into Classifier

(a) A continuous curtain of feed enters the classifier at the top, through a choke feed gate which assures a uniform distribution across the width of the classifier. The gate will normally be open about one-half inch. An air stream at predetermined velocity enters at the inlet, and is made to flow through the feed curtain. The feed falls in front of the air outlet, which consists of a series of evenly spaced louvers. The air stream enters the feed curtain perpendicularly, but is changed to an upward direction as it passes through the vanes. Classification takes place as shown in diagram (b). Particles entering the classifier are acted upon by a number of predictable and closely controlled forces. The cut point is largely controlled by the air velocity through the vanes, determining the magnitude of the drag force (Fd). Air velocity is regulated by

the size and speed of the fans; and an air by-pass downstream of the classifier provides a fine control on the amount of air entering the classifier.

The system consists of three units in parallel, each having a seven foot long primary and secondary classifier, and each unit capable of accurately sizing 40 TPH of hot potassium chloride crystals. The next slide shows diagrammatically one of these units in operation.
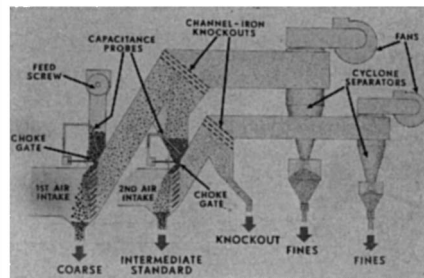

Figure 3
Feed Screw—Choke Gates Cyclone Separators

Hot feed, at 350°F, enters the system along the screw conveyor, choke feeding units 1 & 2, the excess falling into the feed hopper of unit #3 as shown here. The choke feed gates to the primary classifiers are controlled by a single capacitance probe in unit #3 feed bin. Any change in feed rate, or surging from the mill, is instantaneously compensated for by appropriate repositioning of the primary feed gates. Similarly the whole plant is started up - or shut down without operator attention. The capacitance probes consist simply of energized stainless steel rods protruding into the feed bins. A change in the material level in the bin produces a corresponding change in the electrical capacity of the probe, which unbalances the capacitance bridge in the instrument. The rebalance plates are connected to a bellows and a flapper valve which converts the signal to a proportional pneumatic impulse. This activates the Hagan air cylinder power positioner connected to the choke gates. The gates are designed in such a manner as to permit an even curtain of feed to fall down into the classifier as shown in the slide. This is a critical factor in the separation. A "ragged" or uneven curtain results in poor screening efficiency.

In the primary classifier, the air stream—moving at right angles to the falling potash—and at a controlled velocity, allows the plus 28 mesh particles to drop out to become coarse product, and sweeps the finer, minus 28 mesh—particles thru the louvers and up into a settling chamber.

The top discharge from the chamber is blocked by a labyrinth of sloping channel-iron baffles, which filter the remaining coarse particles from the air stream. The solids discharge at the bottom of the chamber is the feed bin for the secondary classification step. This bin also contains a capacitance probe, which actuates the choke feed gate maintaining a precise bin level depth, and providing a curtain of material over the second set of airsweep louvers. The coarser particles fall past the louvers to become the intermediate standard fraction. The fines from this second, lower velocity air sweep are pulled thru the louvers and up into a secondary knock-out chamber similar to, although smaller, than the first. The material settling out here is in the minus -35/plus 150 mesh range and can be used as a separate product. (Uniscreen) or as compaction plant feed. The air-streams containing material that did not settle out in the knock-out chambers go on to the cyclone separators. These cyclones extract the remaining dust very efficiently; only a light haze is visible at the six exhaust stacks from the product screening building. The potash dust and fines reclaimed by the cyclones goes on to make up the feed for the compaction plant, where it is compressed into hard board and then broken up and screened to minus 8, plus 14 mesh size.

The intermediate standard fraction is conveyed to a set of four Nordberg Symons V-screens. These cylindrical 3' x 12' centrifugal screens are equipped with 35 mesh screen cloth and make a very clean cut, the oversize being standard product at 92%/+35 mesh, and the undersize being Uniscreen at 5.0% plus 35 mesh, and 98.0% plus 150 mesh.

The first months of operation in 1961 were the most difficult. Due to increasing the mill feed rate from 380 to 480 TPH the particle

size distribution of the product became considerably finer than had been expected. Air velocity in the primary classifiers was too low to make the required split. The original equipment, 30 HP motors, were speeded up as far as possible, and finally changed out for 40 HP motors. With the new greatly increased air sweep, a marketable coarse product was achieved — but the velocity thru the settling chamber was also increased to a point that it resembled a cyclone. Only a fraction of the material settled out and the balance was pulled on through--to make unwanted quantities of compaction feed. A number of baffle systems had to be tried before arriving at the channel — iron labyrinth currently in use. In addition, the updraft duct had to be extended to break up the turbulence in the knock-out chamber, and leave a dead air space. All of which tended to increase the total dynamic head in the system, and the coarse product was again in jeapordy. To counteract this new development a set of feed deflectors — or crowd plates was installed. These plates fit into the air intake chambers and can be made to contact the falling muriate, altering the trajectory of the material and pitching it inward slightly toward the louvers. This introduces another force into the separation area which results in a coarser fraction being drawn into the K-O chamber and a cleaner coarse product. Small ducts were installed to remove any material which tended to fall back to the coarse product from the settling chambers.

This was the final modification made to the circuit. The end result is a versatile system capable of making a wide variety of product sizes. Many of the problems encountered with the system were concerned with instrumentation. However, such simple expedients as water jacketing the instruments, shielding the probes from falling potash, keeping the co-axial cable connections out of hot zones, and supplying clean dry air to the instruments proved to be effective. Instrument reliability is vital, and back-up devices have been built in to take over in the event of instrument failure.

(Some of the operating details of the air classifiers are as follows:)

The primary classifier fans are Norblo straight blade exhaust fans powered by 40 HP motors. Air is drawn thru the classifier at 14,000 CFM. The secondary fans are also Norblo exhaust fans and are powered by 10 HP motors, each pulling 6,000 CFM thru the system. The air velocity and hence separation cut point can be changed by adjustment of the by-pass air vents situated above the knock-out chambers. Opening the air vents allows air to be drawn into the system behind the feed curtain instead of passing thru it. The subsequent decrease in air sweep velocity brings about a corresponding decrease in the size of particle effected by the air stream. However, although these adjustments are available, they are seldom used. Consistency of quality in the finished product is more important than the ability to change quality at a moment's notice, as the 200,000 T warehousing capacity is limited to four products.

Power requirements are relatively high compared to a mechanical screening operation, particularly where the separation is being made in the coarse range, as at SWP. The volume of air to feed ratio is about 500 CFM of air per ton/hour of feed, and 1.25 horse power per ton per hour of feed. This includes both classification steps in which the feed is split into three or four separate products.

The screening efficiency of the air separators is good by any of the accepted efficiency formula. For example, the next slide shows a typical particle size distribution of feed and products from the system.

Particle size ranges are shown as percent cumulative retained on the Tyler screens shown in the first column.

Critical size range in the coarse product is 20 mesh; and in the intermediate standard the 48 mesh is critical in order to ensure quality of both Standard and Uniscreen after the screening step.

This product distribution, and classification efficiency is not necessarily the sharpest obtainable. It does represent the optimum sizing for this particular operation. All of the finished products must lie on a particle size distribution slope compatible with that of the other chemical fertilizer materials with which it may be blended. This is important in agglomeration and granulation, as well as to minimize segregation in dry mixing processes. The small proportion of coarse material present in the compaction plant feed is the minimum required for a high compaction efficiency.

Tonnage fluctuations through the air classifiers are a common occurrence, particularly on days when various parts of the mill are by-passed for maintenance. The classifiers have proven to be relatively insensitive to these changes in feed rate, and the particle size distribution of the products has remained essentially unchanged through ranges from 75 TPH to 180 TPH and units can be shut down or by-passed if the production rate drops lower--which is very seldom.

Maintenance in the system has

Figure 4.
Tyler Mesh Particle Size Ranges

Tyler Mesh	Feed	Coarse Product	Intermediate Standard (Including New K-O)	Compaction Feed (Large & Small Cones + K-O)
8	1.3	3.4	0.1	
10	12.3	33.2	0.9	
14	28.7	69.9	7.7	0.2
20	47.3	93.8	27.5	2.0
28	61.9	99.2	51.9	6.4
35	75.1	99.8	75.8	14.5
48	82.1		86.9	22.2
65	91.4	99.9	97.7	51.5
100	96.1		99.6	76.2
150	98.1		99.9	87.8
200	99.2			94.8
-200	0.8			5.2
	100.0	100.0	100.0	100.0

been very light since start-up in 1964. Over 3-million tons of muriate of potash has been treated up to the present time, with little or no wear visible anywhere in the system. Bearing changes, annual V-belt changes, and some failures in the rotary dust valve mechanisms is the extent of maintenance parts and labor during the past three years. A maintenance cost study between mechanical screening and air separation over a four year period revealed air classification costs at less than ten percent of screening costs. This difference is offset somewhat by the running costs, in which air separation power requirements are considerably higher. The overall cost picture, however, still heavily favors air classification.

Crystal degradation of the soft potassium chloride crystal can also be a serious problem in an industry in which product tonnages are planned according to sales forecasts a full fertilizer year ahead. However, in all the material balances which have been made, no signs of crystal breakdown have been detected. This observation is borne out by the lack of wear in the air classifier system. The abnormally high maintenance costs in the old screening plant were due in large part to problems involved in screening material at 350°F. Hot product problems did not end there, however. We operate approximately 5,000 feet of conveyor belts downstream of the screening plant, and even special hot material belting is subject to attack by hot salt. The hot potash also had a bad tendency to fuse onto the rolls in the compaction plant. This 'Glazing' as it is known at SWP, can be detrimental to production rate, and quality of product. In severe cases it can cause damage to an expensive piece of equipment, in addition to the resultant down-time. The present method of air classification has virtually eliminated all of these problems. Product temperature is well within the operating range of our conveyer belts and 'Glazing' on the compaction rolls is a relatively infrequent occurrence. The Nordberg screens are still in operation, with greatly reduced maintenance costs, and higher on-stream efficiency. Slide 5. Overall plant view Carlsbad, New Mexico.

Figure 5
Overall Plant View

This presentation has been general and non-specific with regard to costs and screening efficiency breakdown. However, we are prepared to elucidate any point of particular interest. This concludes my presentation — thank you for your attention, gentlemen.

CHAIRMAN SAUCHELLI: Thank you very much Mr. McManus, for your very worthwhile presentation. It is very interesting.

I am going to suggest that we skip the questions for the time being because the next speaker has to make a plane and we will ask your indulgence that we continue the program and give him an opportunity to talk.

They said it couldn't be done but Kalium Chemicals didn't know that so they went ahead and did it. I refer to the method of potash mining adopted by Kalium to extract the salts by a Frasch type solution method.

The next speaker is Mr. G. J. Lambillotte, Plant Manager, at Kalium's Potash Plant near Belle Plaine, near Saskatoon.

Mr. Lambillotte is a chemical engineer with a wealth of experience at home and overseas. He saw service with the United States Army Corps of Engineers in the South Pacific and earned the rank of Major.: His provocative subject is Why Solution Mining?

MR. G. J. LAMBILLOTTE: Gentlemen, it is a pleasure to be here this morning. Actually, when you live and work in a climate that has a record minimum low of 50 degrees below zero, it is more than a pleasure, it is a rare privilege to be in Washington in the wintertime.

Why? Solution Mining.

G. J. Lambillotte

I hope this morning to satisfy, to some degree, an answer to "Why is our Company in Solution Mining?" This has always been the question most asked of us — why did we choose a different route, why didn't we elect the conventional mining procedure to get into the potash business.

We have to begin with geography. This is the picture of Saskatchewan, 252,000 square miles, almost the size of Texas, but with a population of only about one million people. Rich in wheat, abounding in good fishing and wild game and over-supplied with potash producers.

This is the potash area of Saskatchewan. It extends approximately 200 miles north and south and 400 miles east and west with the deposit lying at a depth of from 1500-3000 feet in the north and sloping downward to a depth of 5400 feet at Kalium, located here, and fur-

ther dropping to a depth of about 7,000 feet at the U.S. Border, a little over 100 miles away from our plant. The slope of the potash beds is 10 to 30 feet per mile. Below the line of the orange shading the entire deposit is too deep for conventional shaft mining. Only solution mining makes these vast potash reserves to the south recoverable. So, in the geography and the geology we come to the first three reasons "Why Solution Mining?".

First: There are tremendous volumes of potash available for only such a process.

Second: The deposit is relatively uniform over wide areas and is fairly flat—necessary for economical solution retrieval.

and Third: The deposit is relatively thick, varying from 50 to 100 feet total in one or more zones.

The next important factor that has to be considered is that of good industrial location. Shaft mining

demands a relatively shallow thickness of very high grade material to satisfy its basic economics. Solution mining naturally can accept variation of quality and thickness as long as the combination results in a satisfactory recovery volume.

Thus, in Saskatchewan, if solution mining is contemplated it is possible to place a greater emphasis on the physical location of the facilities because the entire deposit area can be considered. As we noted earlier, depth of the ore zone places restrictions on the location of shaft type operations.

Kalium's plant is located with this view in mind.

It is between Regina and Moose Jaw, the first and third largest cities in the province, offering the advantages of available labor, good shopping facilities, established schools and churches, a University, stable government and good recreational and cultural activities. There is no need to become involved with the problems of building a new town or being responsible for some of the costs and headaches associated with a captive residential community.

From a transportation viewpoint, we are located just 2 miles off the Trans-Canada Highway and connected by an all-weather road. Both of Canada's major railroads, the Canadian National and the Canadian Pacific, are within 2½ miles of the plant and both serve us with relatively short spur lines. The Regina Airport is one of the main airports in Western Canada, in direct line with the East-West fly route across the country.

Kalium is a heavy user of energy. This fact was also considered in the location of the plant. The Trans-Canada gas line crosses Kalium property and a regional gas header of the Provincial utility is just off company property. In addition, an oil transport line and Pacific Petroleum's Propane-Butane pipe line crosses over our land.

Water, although 13 miles away, is close enough for economical piping from a dependable lake source and a supply of drinking water from the Regina city water line is obtained from 4 miles away.

So another reason in favor of potash solution mining is the relatively free choice in the location of a plant.

Next, we must look at the background of the companies involved in the formation of Kalium. Armour & Co. and PPG Industries are the co-founders and neither has a history nor wide experience in conventional mining. They both, however, have a background in chemical processing.

The Chemical Division of PPG Industries first considered potash solution mining with a reservoir of experience in evaporation, crystallization, heat cycles and above all, 75 years experience in the solution mining of salt.

Coupled with this experience was the current knowledge of the problems, expense and limited success associated with the sinking of shafts through the pressured water zone above the Potash deposits in Saskatchewan. So the simple logic became:—if you have to gamble, get involved in a game you've played before. And so the next reason that sold solution mining was simply that of experience—of confidence in people to do a specific job which their background fitted them to do.

It is impossible to avoid the subject of economics. Frankly, I'm in no position to offer you a comparison of costs of the two methods of potash recovery. This has been done by several authors combining a great deal of research and effort. Undoubtedly their data on the costs of shaft mining have been fairly accurate because the number of companies involved in this type of operation coupled with the long history of the process makes it almost impossible to keep secret the true costs of manufacture. On the other hand, we have the only figures on solution mining that are real and our history is now long enough to offer us some security in our figures.

Naturally, for someone considering the potash venture, there are some facets of costs favoring solution mining and some favoring conventional mining. Briefly, those favoring shaft mining are:

a) Lower fuel costs.
b) Less investment above ground.
c) More readily available cost data.

d) Low water consumption.

and those favoring solution mining are:

a) Lower manpower requirements.
b) Less investment underground.
c) Faster implementation of capital — a solution plant can be built in about 18 months.
d) Low chemical consumption.
e) Wider market participation.

I can only make a few points directly related to the economics of the solution mining process.

First, the investment is high in the industry. Probably 50 million dollars is the lowest investment committed for any potash operation plant in Saskatchewan. No one is going into a business with this much capital committed and place himself, knowingly, in a position of disadvantage in either manufacturing costs or return on investment.

Kalium has just recently announced a sizeable expansion to their plant in Saskatchewan. It is true that the present market price of potash does not support enthusiasm for investment in new facilities. However, the efficiencies gained in a larger volume production effort plus the increasing market demand for high quality potash made expansion practical at this time.

So the next reason to consider solution mining is that it is competitive in the total cost picture.

I have saved until last what was unquestionably the single most influencing factor in the decision to become involved in solution mining once the economic question was settled. That is product quality. Solution mining does allow for the precise control of particle size and in addition produces a product with improved physical characteristics. To paraphrase George Orwell, we believe all potash is equal but that our's is more equal than other's.

It is doubtful that anyone would question the fact that price and quality are the two most important factors in the market place.

It was, and still is, recognized

that a high quality potash has distinct advantages. Soduim chloride is the most common contaminant in potassium chloride; it has no nutrient value and represents only an undesirable impurity. In addition, a pure product has real freight advantages—saving in transportation. Most producers in Canada are invovled in a present or future capacity in excess of one million tons per year. The differences between 60% K_2O and 62% K_2O represents about 3% KCl—or, in a million tons, 30,000 tons a year of impurities being shipped at freight rates up to $20.00 a ton — about half a million dollars of transportation differential per plant.

Also considered was the desirability of a soluble product, with a minimum of silica, iron, calcium and magnesium. In other words, a universal product that could be used in any application the farmer desires. The future of soluble fertilizer is sound, the future of high purity, soluble fertilizer is even more secure. There are advantages, too, to the smaller consumer to have one inventory — of a product that can be used either in liquid or dry application.

Further, if we consider quality alone then next to high quality comes the importance of dependability of quality — the assurance to a customer that a product will not deviate greatly from one shipment to another. The advantage of a chemical oriented rather than a mining oriented process permits greater control over purity. This is a record of shipments made over two different months recently and shows a very close adherence to a consistant level of purity.

So these are the reasons "Why Solution Mining?".
1. The Nature of the deposit
   a) Vast volumes of potash are available for only solution mining.
   b) The deposit is dependable.
   c) The deposit is relatively thick.
2. Free choice for an industrial location.
3. Experience or background.
4. Competitive economics.
5. Quality
   a) Higher K_2O.
   b) Quality dependability.
   c) Solubility of product.

Cost Factors

Favoring Shaft Mining:

   a) Lower fuel costs.
   b) Less investment above ground.
   c) More readily available cost data.
   d) Low water consumption.

Favoring Solution Mining:

   a) Lower manpower requirements.
   b) Less investment underground.

c) Faster implementation of capital — a solution plant can be built in about 18 months.
d) Low chemical consumption.
e) Wider market participation.

CHAIRMAN SAUCHELLI: Thank you, John. I hope you make your plane.

I am going to ask Mr. Vise Miller, one of the top executives of Kalium to stand up. He was very cooperative in getting this fine paper for us.

Mr. Hignett has come back and I want to call on him to take a bow.

Mr. Travis Hignett, will you stand up, please. I guess you all know Travis.

This man is internationally known for his effective research in advancing the fertilizer industry.

Remember, we always welcome our guests from foreign countries who are in our midst. Please help them if you can, if they need assistance, and let's give a warm welcome to our foreign friends always.

We are adjourned until two o'clock.

Chemical Analysis of Samples of Standard Grade Muriate of Potash
Values Shown as wt %

	Producer 1	Producer 2	Producer 3	Kalium
NaCl	2.18	1.89	3.45	0.87
Ca	0.067	0.026	0.047	0.013
Mg	0.034	0.099	0.004	0.007
SO_4	0.166	0.143	0.102	0.013
Br	0.066	0.064	0.013	0.031
Water Insolubles	0.435	0.304	0.661	0.017
KCl	96.86	97.14	95.60	98.94
K_2O Equivalent	61.18	61.37	60.39	62.50

Wednesday Afternoon Session, November 15, 1967

The Round Table Meeting reconvened at two-ten o'clock p.m.

J. E. Reynolds, Jr., and Albert Spillman, Moderators

MODERATOR REYNOLDS: The production of ammonium phosphate has spread from a few isolated producers over the last several years to where it is very common for plants, no matter where they are, to be producing ammonium phosphate in various forms.

The technology of ammonium phosphates was in the beginning primarily restricted to ammoniation ratios and solubilities and just the plain ability to be able to operate. Many of the operating conditions were established within permissible limits from an economical standpoint and the production requirement but now they are on a basis here that is very large and very widespread.

We are now in an era of refinement and greater recovery and greater efficiencies. The behavior of the ammonium phosphate in process is of vital interest to us.

Our speaker today represents a company which has been an early producer of ammonium phosphates and has been around for quite some time and his subject relates to Citrate Insoluble Phosphate in Ammonium Phosphate Production.

It gives me pleasure to introduce Mr. C. M. Davis of the J. R. Simplot Company who is our next speaker.

MR. C. M. DAVIS: While I have this chance, I would like to again say hello to Mr. Hignett. He was and is an old and trusted friend of mine. In fact, he probably ran me off his back porch more than any other kid in the village at TVA.

results with "educated guesses" as to the level of C.I. present in order to meet specifications. Naturally, an experienced operator will provide himself with an operating cushion to avoid underformulating his product.

Just how unavailable is the P_2O_5 values in the citrate insoluble fraction as determined by present means? We have gathered evidence that this material actually has nutrient value to the growing plant that the manufacturers cannot take credit for. First, we have found that extended contact with the citrate extraction solution significantly reduces the reportable C.I. fraction in a given sample.

Second, we have found that the material which shows up as C.I. in ammonium phosphates is not tricalcium phosphate, the material for which the citrate solubility criterion was developed.

Third, we have sponsored greenhouse experiments, which indicated that the C.I. material actually is a valuable fertilizer material.

It was felt that in order to better understand just what caused the C.I. values in ammonium phosphate production, we should attempt to isolate the C.I. material from our product. This was done in exactly the same manner as outlined in the A.O.A.C. manual for C.I. P_2O_5 in triple superphosphate, as this is the procedure that must be followed for all C.I. analyses. Considerably larger quantities were used, however, in order to obtain useful amounts of material in a relatively short time.

Using this procedure we were able to obtain about one and one-half pounds of the citrate insoluble material for our studies.

The chemical analysis of the residue is of interest. The material from which the extraction was made analyzed 1.91 percent C.I. The other constituents of the residue are as follows:

Citrate Insoluble Phosphate In Ammonium Phosphate Production

J. L. Smith, P. E. and C. M. Davis

Introduction

The term citrate insoluble phosphates, or C.I. as it is more commonly called, is a term familiar to producers both of superphosphates and ammonium phosphate fertilizers.

The presence of C.I. material in ammonium phosphate production results in an economic loss to the manufacturer, since his product analysis is based on the percent P_2O_5 available and not on the total P_2O_5 present in the final product.

To certain producers of ammonium phosphate products these losses can become quite substantial over an extended period of time. In the preparation of this paper, the authors surveyed a number of commercial ammonium phosphate products. All of the products surveyed exhibited some C.I. content, ranging from a low of 0.05 percent to a high of 1.84 percent. At times, in our own ammonium phosphate plants we have seen the C.I. analysis reach a level of slightly more than 3 percent. At other times the C.I. falls near zero. More frequently we see values of 1.5-2.0 percent.

Another problem associated with the presence of C.I. material in ammonium phosphate production is the controlability of the producing operation. Since we must control for marketing on the available P_2O_5 level, variations in C.I. values must be compensated for during plant operations. The C.I. determination as set forth by the A.O.A.C. is a lengthy determination and does not lend itself to use as a control analysis. Therefore, we must control on total P_2O_5

Slide 1.
Analysis of Insoluble Material Obtained From Ammonium Phosphate

Ammo-Phos Used to Obtain This Material Analyzed 1.91 % C.I.

Total P_2O_5 on C.I. extract residue	40.89%
C.I. on rerun of C.I. procedure residue	19.10%
Total Nitrogen	7.92%
Water soluble nitrogen	0.16%
Fe_2O_3	1.77%
Al_2O_3	12.78%
MgO	10.82%
F	7.64%
SiO_2	Nil
SO_4	Nil
CaO	Nil
Na_2O	Nil

A sample of the C.I. residue was sent to the U.S.D.A.'s Agricultural Research Division Service in Beltsville, Maryland. Their findings on the material were as follows:

Moisture (vacuum method)	0.06%
Moisture (105°C)	0.73%
Nitrogen (as received)	7.77%
P_2O_5 (as received)	40.60%
Aluminum (as received)	7.10%

These last figures correlate well with the findings of our R & D Laboratory. We report aluminum as the oxide and they report it as elemental aluminum. Making the conversion to the oxide, U.S.D.A.'s value would then be 13.42 percent Al_2O_3 as compared to our value of 12.78%

The solubilization of the C.I. residue by extended contact with the citrate solution is shown in the rerun of the C.I. procedure on the original residue. Note that the level dropped approximately 50% from the original value. No doubt this value could be lowered still further by reapplication of the C.I. procedure. In fact, this has been pointed out on previous occasions by other workers in the field. A paper presented at the 136th National Meeting of the American Chemical Society Division of Fertilizer and Soil Chemistry in Atlantic City in 1959 by research personnel of Cominco made mention of this fact. A more detailed work by Gehrke and Kramer of the University of Missouri was published in the *Journal of the A.O.A.C.* in 1964. This paper deals extensively with the extraction time on citrate-insoluble P_2O_5 content of fertilizers and also stated that it reduces the amount of residue.

Getting back to the large scale extraction techniques employed by our laboratory, we extracted a sufficiently large quantity of this material so that greenhouse studies could be made to determine the effect of this material as a fertilizer.

We worked with Montana State University at Bozeman, Montana on the greenhouse studies. Actual greenhouse experiments were carried out at the Agricultural Experiment Station in Bozeman under the direction of Professor H. A. Kittams. The results of the greenhouse studies are tabulated as follows:

Slide 2.
Biological Evaluation of a Citrate-Insoluble Phosphate Material
Effect of Various Phosphate Materials and Rates on Total Yield (2 cuttings) in lbs./acre Ladino Clover

P Rate, lb./Acre	P Material			
	MCP	DCP	CI	Mean
80	12,220	11,600	10,900	11,570
160	14,240	15,180	12,560	13,990
320	16,110	16,180	15,270	15,850
Mean	14,190	14,320	12,910	

Check yield: 10,510

The first portion of the slide illustrates the effect of various phosphate materials, i.e., monocalcium phosphate, dicalcium phosphate and the C.I. extract and rates on total yield (from 2 cuttings) in pounds per acre of Ladino Clover.

The second portion of the slide illustrates the effect of various phosphate materials and rates on *P recovered* in pounds per acre by two (2) cuttings of Ladino Clover.

The C.I. material yielded somewhat less than either monocalcium phosphate or dicalcium phosphate. We have made statistical comparison for the P recovery data, however, and the differences between materials are not significant. Hence, we can conclude that the C.I. material is about equal in value to either MCP or DCP as a phosphate source—at least for Ladino Clover grown under the conditions used in this test. The results should be fairly applicable to field conditions as the literature indicates that results from greenhouse cropping with Ladino Clover correlate very well with field results with alfalfa.

What exactly is responsible for the citrate insoluble phosphates in the production of ammonium phosphates? As was mentioned previously, the original intent of the C.I. analysis was to determine the amount of unreacted phosphate rock in the manufacture of single and triple superphosphates. Since there is no tricalcium phosphate present in the manufacture of ammonium phosphate, obviously some other molecular species or combinations must be contributing to the formation of a "citrate insoluble" compound. Possibly, the composition of the C.I. material varies with time in a given plant.

Effect of Various Phosphate Materials and Rates on P Recovery in lbs/acre by 2 cuttings of Ladino Clover

P Rate, lb./Acre	P Material			
	MCP	DCP	CI	Mean
80	8.82	8.35	8.63	8.60
160	14.86	15.58	11.85	14.00
320	20.56	22.51	22.25	21.77
Mean	14.74	15.48	14.24	

P Recovery for treatment = P uptake for treatment— P uptake for check

The very nature of wet process phosphoric acid makes the identification of the compound or compounds responsible for these C. I. values extremely difficult to say the least. In fact, the same specific compounds may not exist from one manufacturer to another. One manufacturer's C.I. problem may be quite different in nature from another producer. Regardless of the causative factors, however, any producer with a C.I. problem will be penalized in the same way and in proportion to the severity of his problem.

A paper published in the *Journal of Agricultural and Food Chemistry* in 1966 by T.V.A. research workers lists twenty-six (26) of the most common precipitates which occur when wet process phosphoric acid is ammoniated. Examples of some of these salts are: magnesium ammonium phosphate or struvite, and if aluminum is present, the hydrated double salt of magnesium and aluminum will precipitate during the ammoniation step. Similar compounds containing calcuim, iron, magnesium and zinc were identified. Perhaps the presence of any one, or a combination of these compounds could cause the citrate insoluble effect.

Another paper published in the aforementioned journal in 1961 strongly indicated iron as the leading cause of a citrate insoluble fraction in their ammonium phosphate product. However, the Simplot operations produce variable C.I. levels with a relatively constant input of iron to the process, and the concentration of iron in our C.I. residue is much lower than those of other metals.

Work carried out at the R&D Laboratories of the J. R. Simplot Company tend to show that magnesium is a heavy contributor to the presence of a citrate insoluble fraction in our ammonium phosphate grades. This has also been borne out in full-scale plant tests. Time and again when we have made efforts to control the amount of magnesium entering the acid plant for ultimate use in our ammo-phos plants, we have seen dramatic proof of the effect that magnesium plays in the formation of a C.I. fraction in our products. SLIDE #3 illustrates the suppres-

SUPPRESSION OF C.I. IN 16-48-0 BY USE OF LOW MgO ORE

PERCENT OF C.I. P₂O₅ IN 24-HOUR COMPOSITE SAMPLE

DATE SAMPLE TAKEN
SEPTEMBER
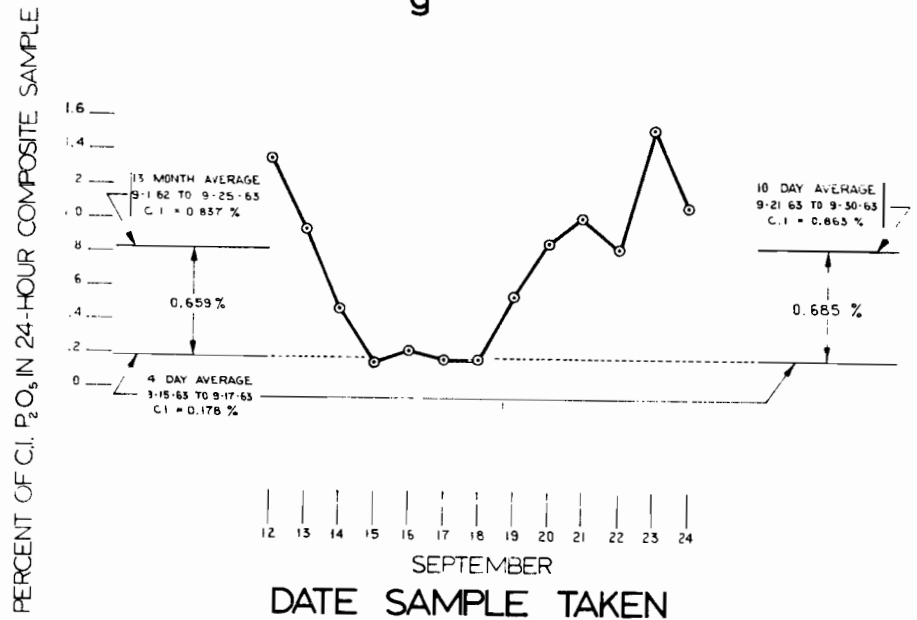
Slide 3.

sion of C.I. in 16-48-0 by use of an acid produced from an ore low in magnesium.

Prior to the start of the low magnesium ore run, the average C.I. content in our 16-48-0 was 0.48 percent. As the low magnesium acid begins to show up in the ammo-phos plant the percent C.I. begins a rapid decline until it reaches a point where the C.I. average is only about 0.18 percent. During the next four days the low magnesium acid has replaced the acid previously employed and we were able to maintain this low level. At the termination of the low magnesium acid run, the regular ammophos acid begins to phase out the cleaner acid and the C. I. level climbs back to a point near that which existed at the start of the low magnesium acid run.

Not once during any of our subsequent trials did the C.I. level fail to follow the magnesium concentration in the feed acid to the ammo-phos plants.

The following slides, representing data taken from full-scale plant operation, further illustrate the correlation between the magnesium and aluminum content of our ore and the amount of citrate insoluble phosphate in our plant products. (SLIDE #4) This pictures a statistical model in which we attempt to show in three dimension the re-
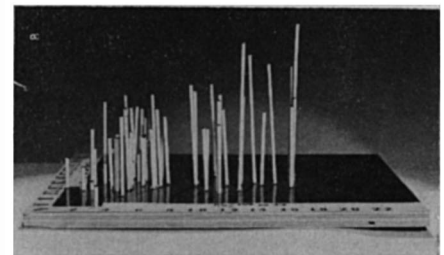
Slide 4.

lationship of citrate insoluble phosphates to the magnesium and aluminum concentration in our phosphate rock. Magnesium concentrations are given along the x axis while aluminum concentrations are shown along the y axis. The percent C.I. is then shown as the lengths or heights of the dowels along the z axis.

The maximum percent C.I. shown is slightly over three percent. Viewing the model perpendicularly to, and in the same plane of the axis on which are plotted the magnesium values we can see

Slide 5.
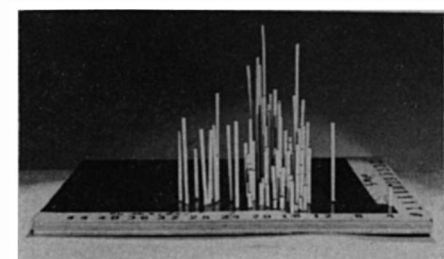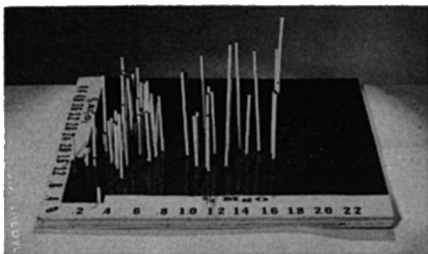
Slide 6.

that as the magnesium values increase the C.I. concentration also markedly increases. (SLIDE #5) If we view the model perpendicularly, and in the same plane along the axis on which are plotted the the aluminum values we can see a slight rise in C.I. concentrations; however, this correlation is not as definite as the magnesium—C. 1. correlation. (SLIDE #6) This view of the model is taken from above the x-y plane and is intended to show the pattern of the points which resulted from the plotting of the data.

It should be pointed out that the magnesium and aluminum values were obtained by colorimetric analysis of the feed acid to the ammonium phosphate plants. The values were then corrected back to the percent Al_2O_3 and MgO present in the phosphate rock. The C.I. values were obtained from the daily composites product samples submitted to our Analytical Laboratory.

Another instance that further showed the correlation of high magnesium acid to high C.I. ammophos products occurred last month. The results of this run possibly indicate that fluorine may also be involved in C.I. formation.

We were asked by our Sales Department to produce an experimental high analysis monoammonium phosphate grade. To produce this grade we needed to use a clean feed acid.

The way we chose to meet this requirement was to take 70% P_2O_5 superphosphoric acid from our 10-34-0 plant and dilute it back to approximately 45% P_2O_5 for use as a feed to the ammo-phos plant. The vacuum concentration step of raising the P_2O_5 value from 52% to 70% is also effective in reducing the fluorine (F) content of the final product to approximately 0.3%.

In the manufacture of 10-34-0 liquid fertilizer we make a concerted effort to prevent an acid of high magnesium content reaching the superacid evaporator. The post precipitation problems in 10-34-0 attributable to the presence of magnesium are well known to those skilled in the art.

This then, was the history of the acid used for the production of the high analysis monoammonium phosphate. It was an acid of low magnesium concentration and low fluorine concentration.

The production run was routine. The final analysis of the product was a surprise, but, in retrospect, should not have been. The N content was 11.29%. The P_2O_5 level was about 58%. Only *trace* amounts of citrate insoluble phosphates were present, and at trace levels the analytical procedure is not accurate.

Previously we mentioned the cost problem associated with the presence of a citrate insoluble phosphate fraction in the ammonium phosphate products. These costs arise primarily in that the ammophos plants must be run continuously in a condition of over-formulation, that is, more phosphoric acid and ammonia than are theoretically required to make a given grade are charged to the plant, the difference between theoretical and actual requirements being equal to the amounts of these materials which become citrate insoluble.

If a steady supply of low magnesium feed acid were made available to a Western ammo-phos plant, it is estimated that the following savings would be realized during a typical year of operation.

Say the plant produces 500 tpd 16-48-0 for a 330 day per year operation. Assume phosphoric acid production is 160,000 tons per year P_2O_5 with a cost of $65.00 per ton based on a rock cost of $5.00 per short ton and sulfur at $39.00 per long ton.

$$\text{Then:} \quad (160,000) \, (.00695) \overset{\triangle \text{ C.I.}}{=} 1,120 \times \$ \, 65. = \$72,280.$$

Bear in mind that this figure does not include the value of the nitrogen which is also lost in the citrate insoluble fraction.

Several alternatives suggest

themselves as solutions of the ammophos C.I. problem.

Selective mining and stockpiling of the phosphate ore is one alternative. One can readily see the monumental costs and waste of otherwise good ore reserves that would be incurred if this procedure were followed.

Perhaps control of the ammoniation step as outlined by researchers at Cominco and set forth in their paper mentioned earlier in this talk would serve to diminish the C.I. level. However, this would introduce more operating parameters with their added costs and difficulties of operation.

We feel the best solution would come about by taking a long hard look at the actual justification of the necessity of declaring a citrate insoluble fraction in these ammonium phosphate products. It may well be that for these products the total P_2O_5 content should be declared as available, or that a different availability method, more suited to the materials, should be used.

At this time we would like to thank those producers who supplied us with samples of their products for evaluation of the citrate insoluble phosphate content.

They are:
1. Agrico Chemical Company.
2. Occidental of Florida.
3. International Minerals and Chemicals Corp.
4. Gulf Oil Corporation.
5. Western Co-operative Fertilizers Limited.
6. Cominco Ltd.
7. Northwest Nitro-Chemicals.
  -and-
8. Stauffer Chemical Company

Finally, the authors would like to express their appreciation to the J. R. Simplot Company for the opportunity to present this paper at The Fertilizer Industry Roundtable.

Thank you.

MODERATOR REYNOLDS: Thank you very much.

I think we have a few minutes for some questions while it is fresh in your minds.

If you have a question, would you proceed to the microphone, please, and state your name.

DR. NIELSEN (Western Co-op Fertilizers): How do you feel the accuracy of your method of determining CI is? What is your standard deviation?

MR. DAVIS: The whole problem is that the method of determining CI was based on determining tricalcium phosphate and I think for that particular method the CI procedure works fine.

However, we are dealing with ammonium phosphate and we doubt that the procedure actually determines the amount of citrate soluble material present.

DR. NIELSEN: We have used the AOAC procedure and have obtained a standard deviation on the mean of an appreciable proportion of the high analysis that we can get.

MR. DAVIS: That's right.

DR. NIELSEN: And this causes some concern as to just how accurate you can be when you specify .8 per cent C.I. It might be .3 or 1.3.

MR. DAVIS: I think probably over a year's time that average may be a little bit closer than indicated. That was one full year's analysis and I think probably the analysis, if followed to the letter, is fairly accurate. However, if you leave the material in solution for, say, another hour, you drop the P_2O_5 level by 50 per cent. So you have to hold your parameters pretty stringently.

MODERATOR REYNOLDS: We had another question over here.

A MEMBER: Was the x-ray diffraction of any use?

MR. DAVIS: TVA did the work and they identified as I mentioned these 26. I think probably the author of that paper or one of the authors is here. We didn't use it, no, we didn't.

As a matter of fact, we are not sure what causes this CI problem, though we are pretty sure that magnesium is contributing somehow.

DR. STRELZOFF: Is there any correlation between pH in production and the rate at which you produce ammoniation and the temperature at which you are drying that to CI?

MR. DAVIS: I think the paper by Cominco did indicate pH values

that were significant. This was the controlling of the ammoniation step.

It has been so long since I read their paper. I know they did mention it and they were indicating iron pretty heavily and this is probably true but I think, as I mentioned, it may be different from one manufacturer to the other. It depends on the nature of your own ore. But they did mention iron and particularly ferrous iron.

MODERATOR REYNOLDS: Okay. Thank you very much.

The trend to high analysis mixed fertilizers is well recognized. This trend has been with us for some time and is continuing at an increasing and rapid rate.

The technology of producing these higher concentrations is being rapidly developed and expanded. Perhaps our product and quali-

ty standards in this country have largely been influenced and guided by the experiences of our friends across the Atlantic.

We have been extremely fortunate over the past several years to be able to bring speakers from Europe to us and in our forward thinking of the requirements and what we will be expected to do. They have been most helpful to us in achieving these accomplishments.

Our next speaker represents a company with a worldwide reputation for outstanding knowledge in the fertilizer industry.

The subject to be discussed is The Pechiney-Saint Gobain Compound Fertilizer Process for Production of 17-17-17.

The paper has been prepared by Mr. Yves Detuncq and will be presented by Mr. Pierre Boutan of Pechiney-Saint-Gobain.

Manufacture of High-Analysis Fertilizers 17-17-17

Yves Detuncq

History

At the beginning of the century, the main sources of fertilizers were: Superphosphate 14 per cent, Chilian sodium nitrate, ammonium sulfate and sylvite. A compound fertilizer made from these various raw materials would have had for formula 3-5-3 if manufactured at that period.

The introduction of ammonium nitrate, the enrichment of KCl up to 60 per cent K_2O, the discovery of richer phosphates or of processes leading to superphosphates containing 18 per cent P_2O_5 made possible the production of triple 10 and even of triple 11.

To obtain higher analyses the calcium must be separated from the phosphate. This is partially achieved in the nitric attack of phosphates by removal of the calcium nitrate and more completely in the manufacture of phosphoric acid by removal of the calcium sulfate.

The latter process leads to 17.17.17 with monoammonium phosphates and 18.18.18 with diammonium phosphate.

In these formulas ammonium nitrate reacts with potassium chloride to give potassium nitrate, a compound with excellent physical properties.

We omitted urea which leads to even higher grades because urea does not possess this added advantage as it does not react with potassium chloride.

Pechiney-Saint-Gobain Processes

The techniques of Pechiney-Saint-Gobain in the fertilizer field are very diversified and they are exploited in eleven of its plants and in over twenty plants throughout the world under license.

Let us mention among these techniques;
—The manufacture of pulverulent normal or concentrated superphosphates in rotary dens with capacities in excess of 30 metric tons/hour.
—The manufacture of granular fertilizers by sulfo—or phosphonitric attack of phosphate rocks, well known processes described in Mr. Sauchelli's books.
—The manufacture of 33.5% or
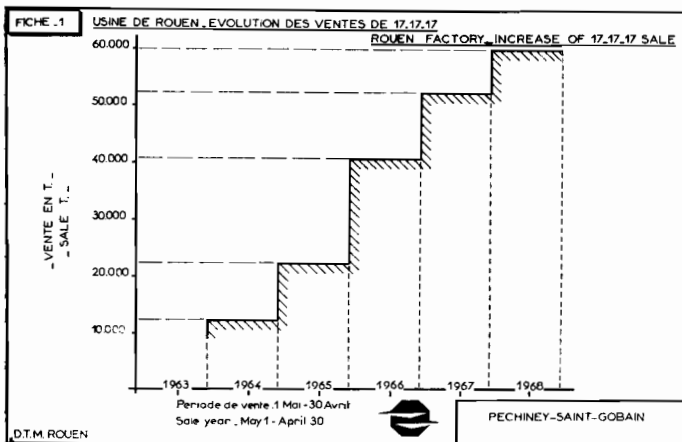
Slide 1

Slide 2

lower grades ammonium nitrate by granulation.

—The manufacture of several granular mixed fertilizers containing superphosphates, ammonium nitrate, ammonium phosphate and potassium chloride.

To avoid any confusion we shall confine our discussion to the manufacture of 17.17.17. This does not imply that the described process is limited to this grade of fertilizer. On the contrary, one of the main advantages of our process is its flexibility. It can be adapted to the manufacture of a great number of formulas by use of various raw materials and of different methods of operation.

General Comments on 17.17.17

The manufacture of 17.17.17 started in May 1963 in our plant of Rouen. Sale's growth is shown on slide I. The slight decrease of the growth curve is due to the development of formulas of the same type such as 18.22.12 or 15.12.24 Triple 17 is applied to fields of beet roots at the rate of 800 Kg per hectare and is used as top fertilizer for wheat at the rate of 300 Kg hectare.

The composition of this fertilizer as written on labels is:

17% total nitrogen constituted of 10.25% ammonia nitrogen derived from ammonium chloride, ammonium nitrate and ammonium phosphate and 6.75% nitrate nitrogen derived from ammonium nitrate and potassium nitrate.

17% phosphoric acid (P_2O_5) water and ammonium citrate soluble derived from ammonium

phosphate (about 16% water soluble.)

17% Potash (K_2O) water-soluble derived from potassium nitrate.

Raw Materials

The theoretical composition of 17.17.17 and the actual raw material requirements are shown on slide 2.

The acid used for the production of ammonium nitrate liquor is 58% nitric acid. Anhydrous ammonia is used either as a gas or as a liquid depending on its place of addition in the process.

The potassium chloride used contains 60% of K_2O and less than 1% of water. It is comprised of particles of 1 mm or less. According to the theoretical composition shown, phosphoric acid must contain a quantity of impurities equivalent to less than 13% of P_2O_5.

Practically, industrial experience in Rouen has shown that Triple 17 can be obtained with acids based on Morocco 75 or Togo without any settling. Florida Swift 73 B P L is also used in Rouen but a simple gypsum settling before the concentration is required. At this stage, slurries can be recycled into the phosphoric acid reaction tank without undue trouble in the filtration whereas the settling of concentrated acid would not permit such a recycling because of the presence of iron and aluminum phosphate in the slurries. 52 to 54% phosphoric acid is used, in order to improve the over all water balance of the fertilizer plant. During this concentration a certain amount of fluorine ranging from 4 to 5% of the P_2O_5 content is released. It lowers the impurities of phosphoric acid we employ. Fluorine is recovered as a fluosilicic acid, solutions

Slide 3

28
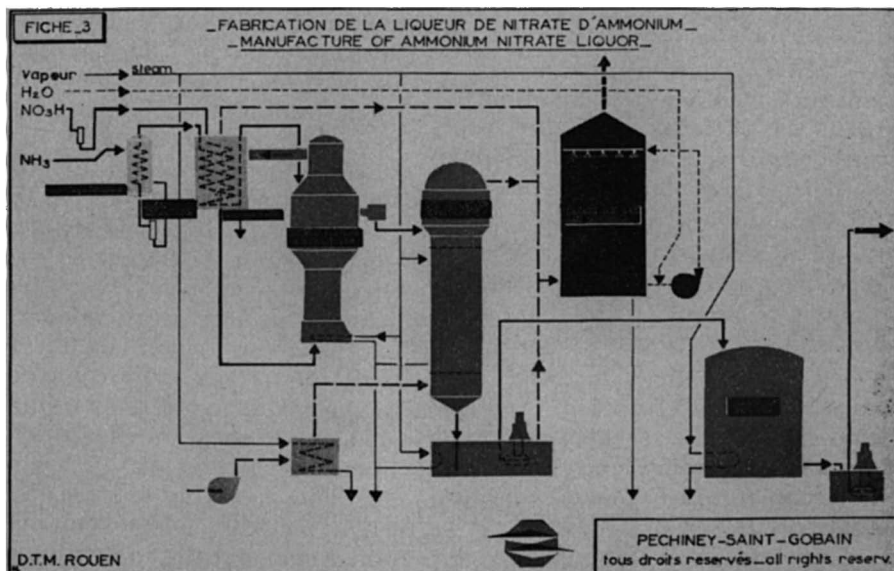
which are converted into sodium fluosilicate.

Manufacture of Ammonium Nitrate Liquor

The process is described in slide 3. Ammonia and nitric acid previously heated by reaction fumes are fed in a thermo-siphon neutralizer where the reaction takes place under atmospheric pressure. At this stage the concentration of the solution is 90-92% ammonium nitrate.

This solution is next concentrated to 97% in a falling film evaporator under atmospheric pressure. Heating is by steam on the outside of the pipes, and by hot air current inside. The temperature never exceeds 150°C and consequently does not give any operating hazards.

Manufacture of Ammonium Phosphate

Ammonium phosphate is prepared continuously in an agitated stainless-steel saturator (NSM 22 S of Ugine equivalent to 316 L) equipped with four ammonia nozzles (slide 4)

Ammonia can be used as a gas or as a liquid but we generally use it as a gas in order to evaporate as much water as possible in the tank especially since the evaporation of ammonia contributes to the conditioning of air in the fertilizer cooler.

The molecular ratio NH_3/H_3PO_4 is kept at 0.6 during the ammoniation and never exceeds 0.7 to maintain a high fluidity of the slurries; the make up of ammonia to the ratio 1.05 is made in the granulator.
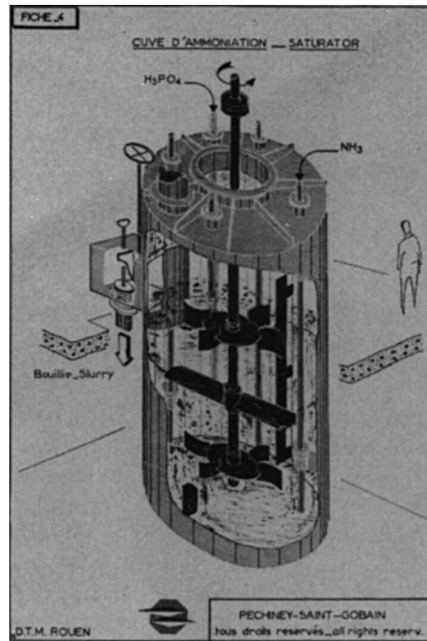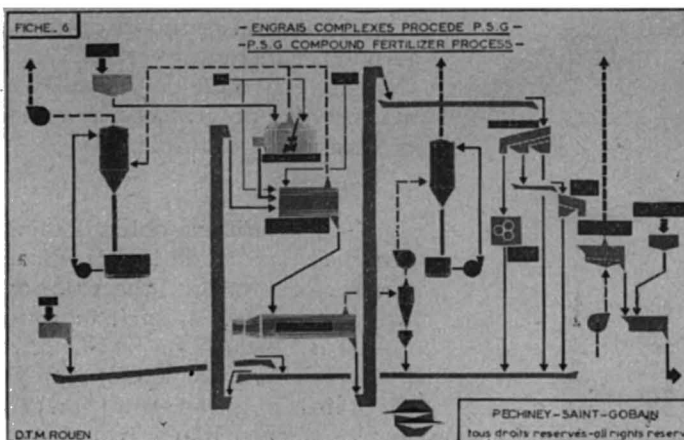
Slide 4

This principle is also used in the manufacture of diammonium phosphate (not the subject of this lecture) where we stop ammoniation at a ratio of 0.7 in the first tank and at a ratio of 1.4 in the second tank. The latter ratio corresponds to a maximum in the solubility after going through a minimum at the ratio of 1. (Slide 5).

The ammonium phosphate slurry flows by gravity into the granulator through an opening whose height is regulated by an adjustable dam holding back the foams.

Granulation Plant

The flow sheet reproduced in slide 6 is classical.

Note the recycle of the undersize which has neither cooling nor intermediates surge-bin. This reduces the loss of heat and the whole
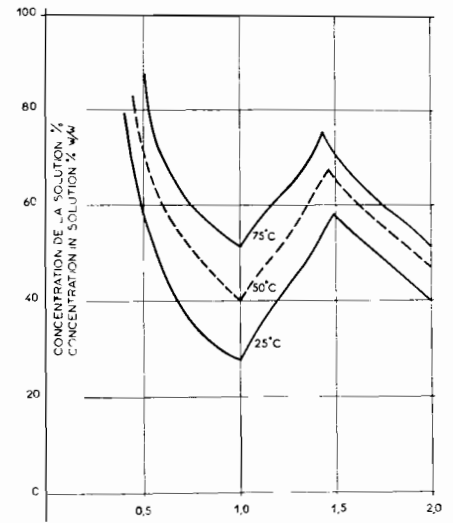
Slide 5

circuit can be kept between 80 and 100°C.

A) *Granulation*

The granulation is carried out in a rotary drum (slide 7) which receives:
1) The ammonium phosphate slurry fed through an open channel.
2) The ammonium nitrate liquor delivered by a perforated pipe. The liquor could be introduced if desired into the ammonium phosphate reactor.
3) The solid products: KCl and the recycled product through a feed pipe at the inlet of the granulator.
4) The liquid anhydrous ammonia through a row of nozzles immersed in the bed of the material during the granulation. These nozzles can be lifted if required to either be cleaned or if manufacturing formulas for which there is no need for ammonia during the granulation.

Slide 6

Slide 7
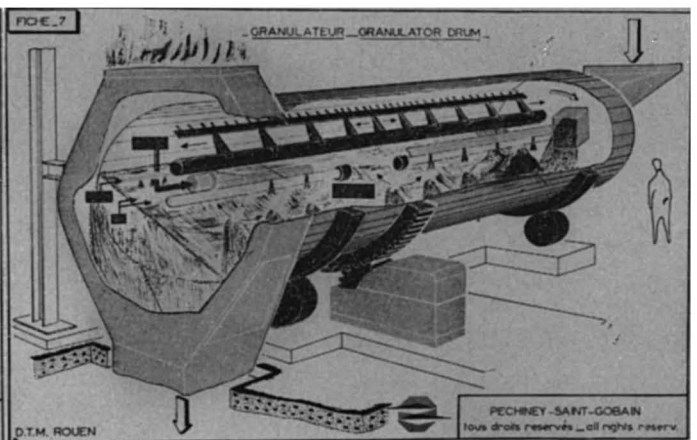
The introduction of liquid anhydrous ammonia reduces the ammonia loss to a minimum and increases greatly the quantity which can be fixed—up to 500 kilo/hour per nozzle—in some productions. Water or steam can also be introduced into the granulator for formulas other than 17.17.17, for example the granulation of 0.25.25 from superphosphate and KC1.

The granulator is kept clean by a scraper with teeth which can be replaced when worn out. The scraper is automatically propelled lengthwise by a hydraulic or a pneumatic jack at regular intervals. The edge of the tools and their distance to the walls have been studied carefully in order to keep on the walls a protective coating which facilitates the granulation.

The scraper is held in position by a powerful springs, which will give if required, for instance if it were to meet a rock. There is also a device to lift the scraper.

B *Drying*

Drying is made with concurrent flows in a rotary drum equipped with numerous flights (slides 8A and 8B). The inlet air temperature is kept for safety's sake under 200°C when drying formulas which contain ammonium nitrate. We do not notice in these any important ammonia losses as we do when drying formulas which contain di-ammonium phosphate.

An efficient drying is essential to obtain a fertilizer of this type which will store well. The present quality of our 17-17-17 is due to a great extent to the small amount of water — under 0.5% and often
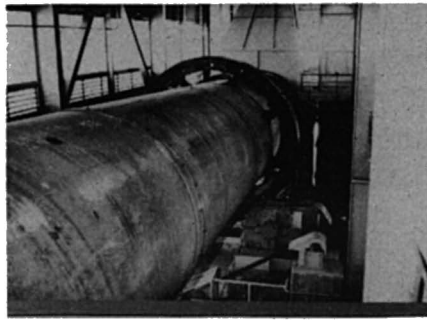
Slide 8B.

under 0.2% of water — present in the finished product.

As an example in a dryer 4 meters in diameter (12 feet) and 25 meters long (75 feet) it is possible by keeping a recycle ratio of 4 to 5 to produce 30 metric T/hour of product. The product which contains approximately 1% of free water when entering the dryer will come out with 0.25%.

Even though it is possible to reduce the quantity of product recycled, it is better to recycle 4 to 5 times the production as in the above example. The granulation becomes more regular because it takes place by successive coats and the drying is more gradual. Furthermore, when the difference in water content of the product at the inlet and at the outlet of the dryer is small, the granulates obtained are better looking, harder and store very well.

C) *Screening*

We use standard double deck screens (slide 8C). The size of the final product ranges from 2 to 4 mm. The average composition of Oversize (over 4 mm) = 25% the output is:

Slide 8A.

Slide 8C.

Onsize (2 to 4 mm) = 50%
Fines under 2 mm = 25%

If all the 2 to 4 mm product was sent to the storage the total output would be twice the production. To have a larger recycle ratio, a part of the 2 to 4 mm. fraction is recycled.

The increase of the quantity of recycled product has little effect upon the investment cost (only on the size of the elevators, the conveyor belts and the screens). Clogging of the screens is very slight with such a formula, which is thoroughly dried, even though the temperature of the product can reach up to 100°C. Other types of screens with electromagnetic vibration can most likely be used and might require smaller surfaces.

D) *Grinders*

Pechiney-Saint-Gobain developed almost 20 years ago a three rolls grinder trademarked the TRIO grinder. This grinder was developed for the grinding of sticky fertilizers particularly formulas based on superphosphate.

One of the rolls is mounted on a moving support and firmly held by powerful springs at a given distance from the two other rolls. The distance can be adjusted so as to obtain the required particle size (slides 9A and 9B).

We use this grinder for all our formulas including 17.17.17 although this could be ground with many types of grinders, hammers or chains, for example.

E) *Cooling*

The fertilizer cooler is of the fluid bed type (slide 10). It is made of a perforated metal sheet through which air either as such or conditioned is blown. The bed fertilizer 5 to 10 cm. thick flows over the sheet in a fluidized condition. Under some particularly bad climatic

Slide 9A

BROYEUR TRIO NM 66
Modèle   600 x 1000

SYSTÈME : PECHINEY - SAINT GOBAIN
CONSTRUCTEUR : S.^{té} Nouvelle A. MAGUIN
02 Charmes   France
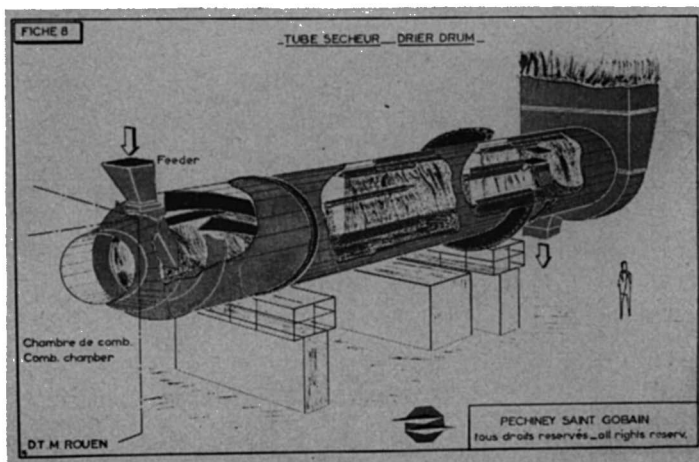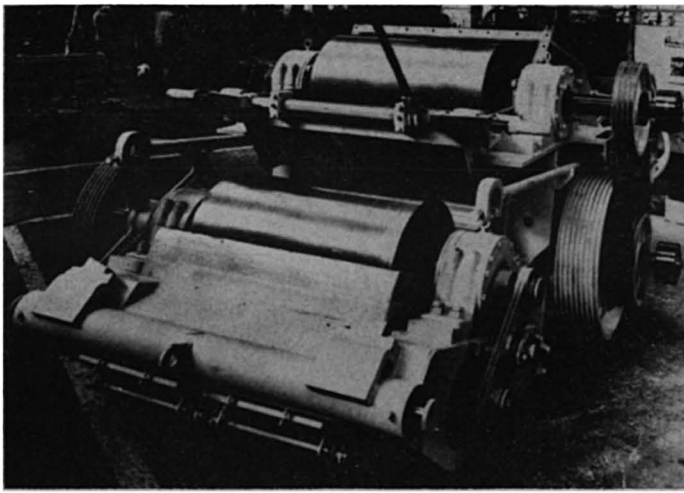
Slide 9B

conditions or for the cooling of very hygroscopic fertilizers (for example ammonitrates) several drying sections can be used. The air blown in at least the last section may be conditioned by vaporization of the ammonia used to prepare the ammonium nitrate liquor.

F) *Coating-Storage and Bagging*

The fertilizer is coated in a rotary drum with 1.5% of a kaolin which has been treated with amines. It is then stored in bulk in a non-conditioned storage where it can be taken up again when wanted and after a final screening shipped in bulk or in bags.

G) *Gaseous Effluents Treatment*

Besides cyclones used to collect dust from the dryer and other equipments, we generally advise the use of empty towers which are sprayed with water or TCA towers which contain a bed of floating balls or Venturi type scrubbers

(Air-Mix). Spraying with water, which is sufficient here since ammonia is not to be recovered, removes efficiently the fluorine. If phosphoric acid were used to scrub, more fluorine would be released because part of the fluorine present in the acid would be removed in the scrubber. A water scrubber would have to be added after the ammonia recovery.

Quality and Control of the Fertilizer

The quality of our fertilizer is very important not only for the sale of our own production but also for the sale of the process. We first guarantee the analysis of the product and then the particle size distribution. Over 95% must be between 2 and 4 mm and close to 80% should be from 2 to 3 mm. The latter size gives a sufficient dispersion of high analysis fertilizers while keeping a correct delivery when contrifugal spreaders are used.

Slide 10

FICHE .10

REFROIDISSEUR A LIT FLUIDISÉ ___ FLUID BED COOLER

Sortie Air - Exhaust

Tôle perforée
Distribution plate

Air de fluidisation
Fluidizing Air

D.T.M ROUEN

PECHINEY - SAINT - GOBAIN
tous droits réservés ...all rights reserv.
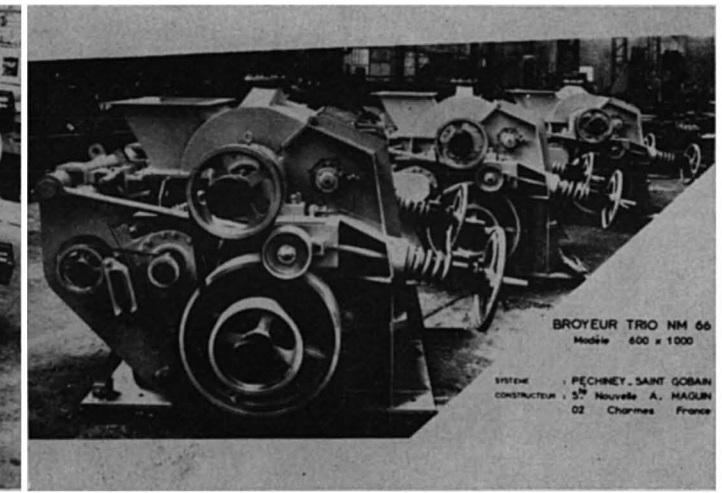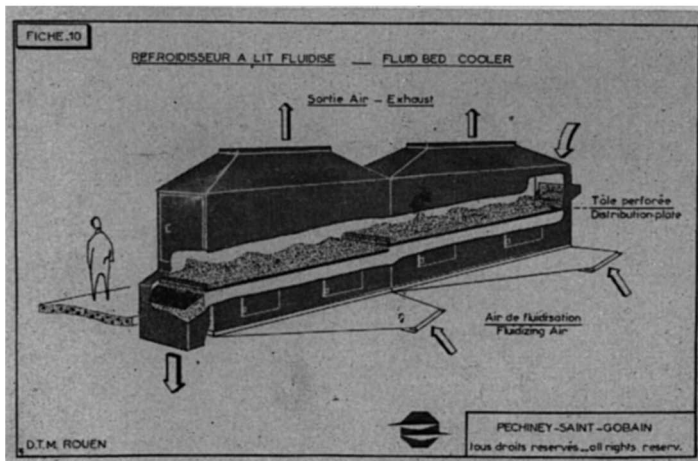
The other systematic controls carried out are:

—Moisture content: it must be as low as possible for this type of fertilizer because of the soluble salts such as NH_4NO_3, NH_4Cl etc. . . . contained.

—Sphericity: this is checked by rolling the granules on an inclined plane with a 12% slope.

—Crushing strength: it is measured by the force required to crush a granule of a given size. It is about 3 Kg for 2.5 mm granules of 17.17.17.

—Hygroscopicity: changes in weight and in the crushing strength of the granules in humid atmosphere are used to control it.

—Caking: this is measured by the force necessary to crush a fertilizer cake prepared under given conditions of pressure, temperature and time. It increases with the water content but decreases with the crushing strength.

We used two tests, one at 20°C for 12 days under 12 kilos and the second at 35°C for six days also under 12 kilos.

Size Of Units And Cost Price Figures

The biggest unit in our plant of Rouen has a daily output of 700 metric tons. Five men per shift operate this unit. The dryer measures diam. 4 m by 24 m. The raw materials requirements have already been given. 30 Kwh and 14 kg of fuel oil per metric ton are also necessary. Water consumption will vary according to the type of washing used.

Capital investment will be dic-

tated by local conditions. In our plants we figure it at 10,000 F. per metric ton per day for capacities ranging from 300 to 700 metric tons a day. Maintenance is of the order of 5 to 10 per cent of the investment and varies from plant to plant.

The two biggest units presently on the drawing board are for the USSR (Slide II). For each of
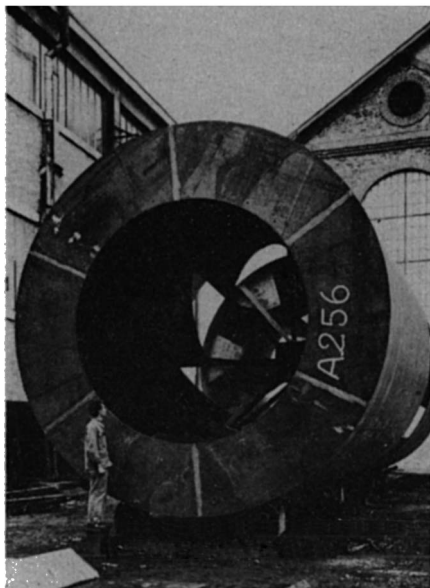
Slide 11

them, we guarantee a production of 900 metric tons/day, of 17.17.17 but it could produce much over 1000 metric tons/day in the operating conditions of Rouen. Moreover we have already submitted bids for units of over 1000 metric tons/day.

Decomposition Hazards

Under our operating conditions and when keeping the temperature at the inlet of the dryer under 200°C, we have never noticed any decomposition during the production of fertilizers based on ammonium nitrate, ammonium phosphate and potassium chloride.

The conference of N.J.F. Steen (Norway) at the ISMA meeting of September 1967 includes diagrams proving that: a triple 17 with a high content of water soluble P_2O_5 is outside the zone of self-sustaining decomposition (cigar burning test).

Conclusion

We did not attempt to discuss here all the techniques of Pechiney-

Saint-Gobain in fertilizers. These are in constant evolution and the object of studies in Rouen where two pilot plants each with a capacity of I metric T/H have been installed for this purpose.

We have described a process which though not revolutionary, is very reliable and leads to a product of excellent quality.

Aside from urea or diammonium phosphate which have several drawbacks — difficult granulation and poor storage properties for urea, the necessity of recovering ammonia when making diammonium phosphate — triple 17 is the highest analysis fertilizer in the ratio 1.1.1 which can be obtained with a P_2O_5 content over 90% soluble in water. Nitric acid attack of phosphate rocks cannot yield analysis as high and give only 50% of water soluble P_2O_5, the sulfate cycle excepted. Triple 17 though not in general use, is no longer new today. Several producers offer this formula often with diammonium phosphate rather than mono-ammonium phosphate.

We now have over 4 years of experience in its manufacture and I sincerely hope that this paper reflects them.

MODERATOR REYNOLDS: Thank you very much for that most interesting paper.

We have time for some questions and I am sure there will be some. Who would like to be first?

DR. STRELZOFF: First of all, I want to congratulate you on a really well presented and well illustrated paper.

I have a few questions. You mentioned $2,000 per metric ton per day. Does this include the cost of grinding material and manipulation and bagging and all this sort of thing needed in a fertilizer plant or strictly just the plant erected?

MR. PIERRE BOUTAN: $2,000 is cost in France by our people. It is battery limit also.

DR. STRELZOFF: Just for the information of you gentlemen, the answer was that the plant costing $2,000 per ton a day means the equipment erected but without crushing, without grinding and all of the material manipulation, no bagging.

Is that correct?

MR. BOUTAN: That is correct. However, grinding and manipulation described in our paper before storage are included.

DR. STRELZOFF: Thank you.

MR. BOUTAN: I think you know more about the cost of our process than we do.

A MEMBER: What kind of conditioner is used in selling this 17-17-17 fertilizer?

MR. BOUTAN: This was forgotten, I am sorry. We used a clay treated with an amine to coat the fertilizer. The quantity used is one per cent by weight.

A MEMBER: Is there a real difference in the granulating ability when you make a DAP grade as compared with MAP triple 17?

Also, is there a difference in the storage quality or the storability of the DAP as compared with the MAP grade?

MR. BOUTAN: We have no experience in making triple 17 mono-ammonium phosphate. That is the first part of your question.

DAP doesn't present to us the difficulty of storing and there are no coatings.

DR. STRELZOFF: May I ask one more small question?

The figure of 305 kilograms of nitric acid, does it mean 100 per cent HNO_3, or what is it?

MR. BOUTAN: 58 per cent nitric acid.

DR. STRELZOFF: And 305 kilograms?

MR. BOUTAN: It is the quantity of 100 per cent HNO_3.

MODERATOR REYNOLDS: We have time for another question.

A MEMBER: Is the nozzle used in the ammoniator or granulator for increasing the molecular ratio of ammonium phosphoric acid up to 1.05 located underneath the bed of the rolling material?

MR. BOUTAN: Yes, it is under the bed. It is injected into the material.

SAME MEMBER: Is it a single nozzle, one orifice, one hole?

MR. BOUTAN: It is a series of nozzles in a pipe which brings the ammonia into the granular.

SAME MEMBER: I see.

What particle size muriate is used in the process, what screen size?

MR. BOUTAN: About 1 millimeter size.

SAME MEMBER: Thank you.

ANOTHER MEMBER: What is the moisture content of the material leaving the granulator?

MR. BOUTAN: 1 per cent.

MR. FERRIS: (Foster-Wheeler): This is not so much a question but a comment.

There was a paper referred to I believe presented at ISMA when you mentioned that you were outside the cigar-burning range and I think that paper might be of interest to a great many people here because, with the advent of nitric attack, with varying amounts of calcium left in the fertilizer, this paper shows that the cigar-burning area is extended, the more calcium left in the fertilizer.

I think perhaps if you repeated the reference, so the members here might have it if they are interested.

MR. BOUTAN: It is a paper by N. J. F. Steen, in Norway. It was given at the ISMA Meeting of September, 1967.

A MEMBER: We are not sure if the $2,000 per metric ton there includes the neutralization or not. There is quite a neutralization sector there.

MR. BOUTAN: Of ammonia nitric acid?

SAME MEMBER: Yes.

MR. BOUTAN: In that figure it is included.

MODERATOR REYNOLDS: Any other questions?

If not, then we will conclude this paper and go on to the next one.

Thank you very much for a most interesting paper.

Two of the most popular fertilizer grade ratios in the United States that have evolved over the last several years are the 1-4-4 and the 1-4-2 ratio grades.

The plant food concentration for these grades has continued to increase from several years ago when we were talking of a 3-12-12 to a 4-16-16 to a 5-20-20 to a 6-24-24 and we now find ourselves ready for the need in the next step, namely going to the 7-28-28.

The economies of balance in the raw material costs, the operating costs, the handling costs, transportation, balance definitely in fav-

or of the higher concentrations of plant food.

Processing in these higher concentrations is of immediate interest to us and considerable investigative work is being conducted.

Our next speaker has previously appeared to us at our Round Table and he needs no introduction to many of us here but today he is coming to us to discuss some pilot plant work that was done on the production of 7-28-28.

Mr. John Surber of International Minerals and Chemical Corporation will give the paper.

Pilot Plant Manufacture of 7-28-28 Granular Fertilizer

John H. Surber

Early this year, a series of tests were conducted at IMC's pilot plant in Mulberry, Florida. The grade studied was a 7-28-28 granular fertilizer. The primary purpose of these tests was to gather the necessary data to evaluate granulation characteristics of different types of potash. Four types of potash were evaluated. Graph Number 1 illustrates the basic differences in size of the four types.

Type 1 potash is the coarsest with over 70% plus 35 mesh material, while the curves for Types 2 and 3 are quite similar with about 15% plus 35 mesh and slightly over 90% plus 150 mesh. Potash Type 2 is a white potash. Potash Type 4 contained 14% plus 35
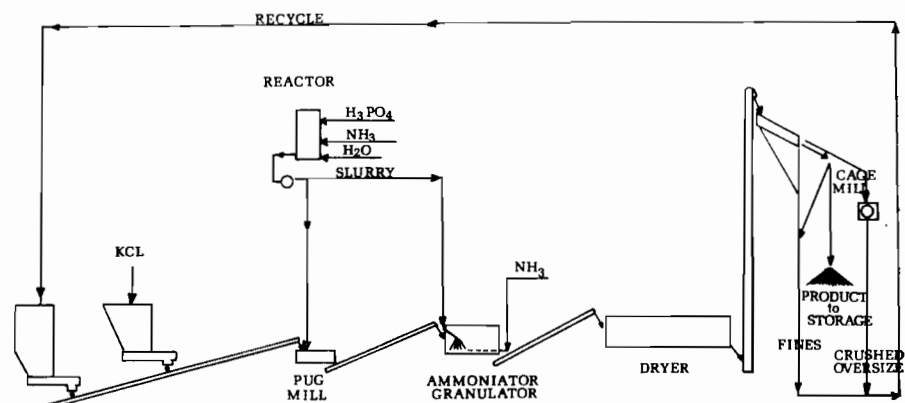
SCHEMATIC DIAGRAM – 7-28-28 PILOT PLANT

Graph 1

Graph 2
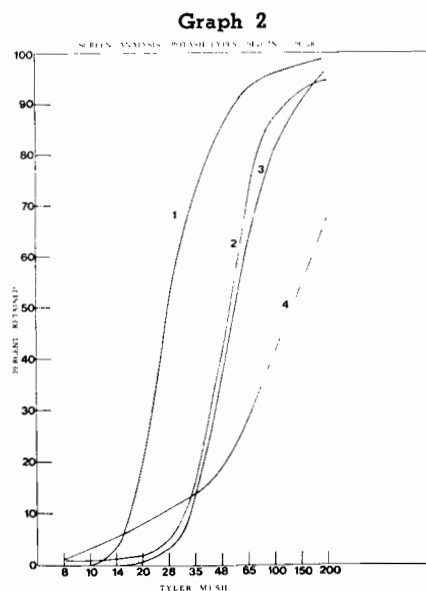
mesh material and over 30% minus 200 mesh.

Other variables evaluated were:
1) Operating conditions in the preneutralizer
2) Point of addition of slurry to the process (Pugmill or drum granulator)
3) Steam addition to drum granulator
4) Quality of phosphoric acid

To make these evaluations, the following data were collected:
1) Operating rates
2) Process temperatures
3) Recycle rates
4) Screen analyses (Product, dryer discharge and ammoniator discharge)

33

In addition, samples were analyzed as follows:

1) Potash—daily composite of each test run. (Screen analysis, K₂O. NaCl, Mg, Insol., H₂O)
2) H₃PO₄—daily composite (Total P₂O₅, H₂O, % solids, sp. gr., impurities)
3) Product-composite of each test run. (Sreen analysis, chemical analyses, chemical analysis of screened fractions, hardness) An enlarged photograph was made of each product.
4) Preneutralizer overflow — composite every two hours (N, P₂O₅, mol-ratio, pH, sp. gr., H₂O)
5) Dryer discharge — composite (Screen analysis, H₂O, chemical analyses)

Test Runs

The pilot plant tests were conducted using the granulation unit as illustrated. Potash was fed through a one ton hopper equipped with a variable speed screw conveyor. The hopper was filled by a front-end loader. Recycle was fed to the system through another variable speed screw under the recycle hopper. Both feeders discharged onto an inclined belt conveyor which discharged into a double shafted pugmill. The dimensions of the pugmill were 1'-6" by 6'-0" long and the shaft speed was 100 RPM. Material discharging from the pugmill was conveyed to a 5'-0" diameter x 10'-0" long, stainless steel lined, TVA type ammoniator-granulator. The ammoniation section was 6'-8" in length and separated from the granulation section by a 10" dam. The pre-neutralizer was 4'-0" in diameter and 10'-0" high, of stainless steel construction and provided a working capacity of 600 gallons. It was insulated and equipped with heating strips to maintain slurry temperature during down time. Anhydrous ammonia and wet process phosphoric acid were metered into the pre-neutralizer and the resulting slurry pumped to either the pugmill or ammoniator-granulator. The balance of the liquid anhydrous ammonia that was required to make grade was added in the ammoniator-granulator through a 5' long drilled pipe sparger.

Material discharging from the granulation section was conveyed to a 5'-6" diameter x 26' long cocurrent rotary dryer. Dryer discharge material was elevated to a 4' x 10' double deck Tyler-Hummer screen. The top deck was a square mesh with an opening of .035" providing a 7 mesh separation. The bottom deck was of Ty-rod construction providing an approximate separation of 14 mesh. The oversize from the screens was crushed in a cage mill and returned to the recycle hopper to prevent cracked oversize from appearing in the product. The fines and product needed as recycle were returned by belt conveyor to the recycle hopper. Finished product was diverted to the storage bin.

The formulation as illustrated in Table I was used throughout all of the tests, and provides one half of one percent overage in each nutrient. This was done to avoid reformulation for each run since the various potash types had not been previously analyzed. In addition, the chemical analyses of the phosphoric acid was subject to variation with shipments.

TABLE I
Formulations 7-28-28

Pounds	Material	Analysis	H₂O	N	APA	K₂O	H₂O
182	NH₃	82.2	—	150			—
1055	H₃PO₄	54.0	18		570		190
933	KCl	61.2	—			570	
2170	Sub Totals			150	570	570	190
-170	Evaporation Loss						-170
2000	Net Totals			150	570	570	20
	Theoretical Analysis			7.5	28.5	28.5	1.0

Mol-Ratio: 1.326 NH₃:H₃PO₄
Ammoniation Rate: 6.67 lbs. NH₃/unit P₂O₅

TABLE II
Screen Analysis of Esterhazy Potash Used in Pilot Plant Run

Run	Potash	8	10	14	20	28	35	48	65	100	150	200
1	1		0.3	4.7	25.3	58.0	79.4	89.0	94.7	96.7	97.7	98.7
2	1			3.7	22.2	51.0	74.0	85.9	93.3	96.3	97.4	98.1
3	1			2.9	17.1	44.3	67.1	81.4	91.4	95.7	97.1	98.6
4	4	1.6	3.1	5.5	7.8	9.8	11.7	16.4	26.6	40.6	53.9	67.2
5	4	1.3	3.3	6.7	9.3	12.0	15.3	20.0	30.0	44.0	56.0	70.0
6	2	1.0	1.4	1.9	2.4	4.8	16.7	40.0	74.0	89.5	93.3	95.7
7	2	1.3	1.7	2.2	2.6	5.2	15.7	36.5	68.7	85.2	89.6	93.9
8	3				.6	2.9	14.7	35.9	61.2	80.6	90.0	96.5
9	1			2.3	16.8	44.5	68.6	82.7	91.8	96.4	97.7	98.6

TABLE III
Chemical Analysis of Esterhazy Potash Used in Pilot Plant Run

Run	Potash	Slurry	K₂O	NaCl	Mg	Insol	H₂O
1	1	Pugmill	59.97	2.50	0.13	0.15	0.57
2	1	Gran	59.91	2.28	0.13	0.16	0.26
3	1	Gran	60.31	2.50	0.12	0.09	0.86
4	4	Pugmill	57.91	4.41	0.28	0.21	0.87
5	4	Gran	57.52	4.53	0.31	0.22	0.97
6	2	Gran	62.30	0.50	0.05	0.01	0.09
7	2	Pugmill	62.15	0.60	0.08	0.02	0.46
8	3	Gran	60.40	3.40	0.06	0.10	0.34
9	1	Gran	60.69	2.65	0.06	0.05	0.23

TABLE IV
Ammoniator-Granulator Discharge

Slurry to	Comp. Sample Run No. 1 Pugmill	Comp. Sample Run No. 2 Ammoniator
Potash	Std.	Std.
Recycle Ratio	3.8:1	3.8:1
Disch. Temp.-°F	140	138
Recycle Temp.	160	149
Dryer Temp.	220	198
Product Temp.	—	148
+ 6	15.7	23.5
-6 + 8	11.4	19.6
-8 + 10	14.7	15.8
-10 + 12	14.6	10.7
-12 + 14	11.9	7.8
-14 + 16	13.2	9.1
-16 + 20	8.3	5.7
-20	10.2	7.8
TOTAL	100.0	100.0

TABLE V
Phosphoric Acid Composite Analysis

Sample	1	2	3	4	5
Run	1	2	3	4,5,6	7,8,9
Total P_2O_5	54.00	53.60	53.40	52.20	53.80
% H_2O	23.45	23.90	20.97	16.03	15.11
CaO	0.35	0.30	0.20	0.30	0.30
SO_3	2.69	3.05	3.77	3.38	3.04
F	1.27	1.28	0.90	1.42	1.30
Fe_2O_3	1.42	1.44	1.33	1.57	1.62
Al_2O_3	2.17	2.11	2.10	1.99	1.97
MgO	0.63	0.67	0.66	0.63	0.65
Na_2O	0.087	0.076	0.069	0.120	0.130
K_2O	0.089	0.097	0.075	0.073	0.085
Solids	4.92	4.89	3.51	7.35	4.39
Sp. Gr.	1.685	1.696	1.698	1.712	1.720
P_2O_5 Dry Basis	70.5	70.4	67.5	62.3	63.4

A synthetic 7-28-28 recycle was prepared by blending 13-52-0 with granular potash. A short run was made to balance the recycle and check out the system. Observation indicated that an open pipe was not adequate to distribute the slurry evenly enough on the tumbling bed of material in the ammoniator to obtain uniform granulation. Large granules that contained an insufficient amount of potash were formed. A spray nozzle for slurry distribution in the drum granulator also caused difficulties due to plugging, but distribution of the slurry was good and uniformity in granulation could be obtained. The problem of plugging of the spray nozzle was nearly eliminated by steam tracing the slurry line from the pre-neutralizer and by bleeding steam into the slurry line.

Nine runs were made using the potash types shown in Table III. This table also indicates the point of slurry addition as well as the chemical analyses of the potash composited during the particular run.

The first run was made using potash Type 1. During this run the slurry was added to the pugmill. The production rate was 2 tons per hour. Granulation was achieved quite easily and the resulting product appeared uniform. Granulation was controlled by the addition of water to the pugmill and by changing the recycle rate.

The second run was basically the same as the first except that the slurry was added to the ammoniator-granulator. As with the first run, granulation was controlled easily, with a large portion of the granulator discharge on-size. Table IV shows that slurry addition in the ammoniator-granulator tended to form a greater amount of oversize than slurry addition to the pugmill under similar operation conditions.

The third run also utilized potash Type 1. During this run the slurry was added to the ammoniator-granulator at a production rate of 2.5 tons per hour. The run was cut short due to equipment problems with the pre-neutralizer and the cage mill. At this time, it was discovered that nitrogen analyses had been low and the anhydrous ammonia meters were recalibrated. The recalibration revealed that the meter to the ammoniator-granulator was incorrect and that insufficient ammonia was being added to the ammoniator. In order to make quick checks, equipment required to run nitrogen analyses was installed in the pilot plant laboratory.

The fourth and seventh runs were made with the slurry being added to the pugmill. The fourth run utilized potash Type 4 and the seventh run utilized potash Type 3. The fifth, sixth, eighth, and ninth runs were made with the slurry being added to the ammoniator-granulator. During these latter runs all four types of potash were utilized. The production rate for these six runs was two tons per hour and in all of the tests the necessary data were recorded and samples taken for analyses.

The nitrogen analyses came up to acceptable levels as soon as the proper amount of ammonia was added to the ammoniator-granulator. The variable speed screw conveyor for feeding recycle into the process caused the major problem in these test runs because of rapid

build-up on the screw and in the trough. This cut down on the amount of recycle being fed to the system. Low recycle caused over-granulation to occur and affected chemical analyses, because at times, the slurry rate had to be reduced in order to dry up the ammoniator bed. The lower slurry rate caused the product to be high in K_2O and low in P_2O_5. Meeting chemical analyses would not have been a problem if proper control of flows and recycle rates could have been maintained consistently.

At this time, it should be pointed out that the pilot plant was borrowed from IMC's Florida Development Group and used without major modifications to adapt it to this test program. The prime objective was not making grade, since this is a function of acid clarity, but rather to determine physical properties of a 7-28-28 produced utilizing various types of muriate of potash.

Discussion of Results

The slurry in the pre-neutralizer was controlled at a mol-ratio of 0.80 and a specific gravity of 1.52 to 1.53, with the temperature of the slurry being about 230°F. This slurry was reasonably fluid and caused troubles only during periods of shutdown, because the slurry would set up rapidly in the pipes if they were not flushed properly. The mol-ratio was held at 0.80 by pH control at 2.3. Changes in the amount of free sulfuric acid contained in the phosphoric acid caused small changes in the mol-ratio at a constant pH. The water content of the slurry was between 20 and 24 percent.

Steam addition to the ammoniator-granulator had little effect on granulation control. With cold recycle in the system, additional heat from steam was useful and could be used as a fine control to make small changes in granulation; however, changing recycle rate was the best means of controlling granulation.

The degree of granulation when comparing the addition of slurry to the pugmill or ammoniator-granulator appeared to be about the same. No consistent difference could be found by comparing the screen analysis of the product or

TABLE VI
Slurry Composite Analysis

Run	Sample	N	Total P_2O_5	W.S. P_2O_5	H_2O	Mol Ratio	pH	Sp. Gr.	°F
1	6-Comp	6.40	42.40	—	—	0.766	2.3	1.539	232
1	6-Comp	7.62	43.80	—	—	0.882	2.4	1.526	232
1	7-Comp	7.26	45.40	—	22.43	0.812	2.3	1.526	232
1	5-Comp	5.31	42.60	—	—	0.632	2.3	1.524	233
1	6-Comp	7.48	45.20	40.80	24.37	0.839	2.3	1.525	233
2	7-Comp	6.84	44.00	—	26.71	0.787	2.3	1.528	228
2	7-Comp	6.99	45.20	40.80	25.72	0.783	2.3	1.528	231
3	GRAB	7.21	45.80	—	—	0.798	2.3	1.528	230
3	GRAB	7.71	44.80	—	—	0.870	—	—	—
4	4-Comp	6.62	43.80	—	23.66	0.766	2.2	1.529	232
5	4-Comp	6.76	44.00	—	25.84	0.779	2.3	1.529	232
6	4-Comp	7.17	44.60	—	21.15	0.814	2.3	1.525	229
7	4-Comp	6.71	42.80	—	31.48	0.795	2.3	1.522	227
8-9	4-Comp	6.67	43.67	—	29.08	0.776	2.3	1.523	233

TABLE VII
Production Data

Run	to	Slurry Potash	Recycle Ratio	Am-Gr Temp.	Recycle Temp.	Dryer Temp.	Product Temp.
1	Pugmill	1	3.8:1	140	160	220	—
2	Am-Gran	1	3.8:1	138	149	198	148
3	Am-Gran	1	3.7:1	142	145	203	149
4	Pugmill	4	4.2:1	167	160	213	169
5	Am-Gran	4	4.0:1	166	159	211	170
6	Am-Gran	2	3.4:1	156	148	205	162
7	Pugmill	2	3.6:1	157	142	210	150
8	Am-Gran	3	3.9:1	162	160	223	179
9	Am-Gran	1	3.5:1	164	152	230	176

TABLE VIII
Dryer Discharge Screen Analysis

Run Sample	1 Comp	2 Comp	3 Comp	4 Comp	5 Comp	6 Comp	7 Grab	8 Comp	9 Grab
+6	32.3	8.0	18.6	5.5	19.7	29.4	31.5	36.7	21.1
—6 + 8	14.4	23.6	12.7	26.1	28.9	19.9	27.4	24.6	39.2
—8 +10	12.2	25.4	10.9	31.2	28.7	21.1	19.9	20.1	24.6
—10+12	10.3	16.5	12.7	16.7	12.2	12.5	13.9	10.1	7.6
—12+14	8.3	8.2	12.2	8.3	5.3	6.2	5.4	4.0	2.8
—14+16	9.4	8.1	13.4	6.5	2.7	5.9	0.6	2.2	2.2
—16+20	5.8	4.4	8.2	3.1	1.2	2.1	0.4	0.8	1.3
—20	7.4	5.8	11.3	2.6	1.3	2.9	0.9	1.5	1.2
+6	32.3	8.0	18.6	5.5	19.7	29.4	31.5	36.7	21.1
+8	46.7	31.6	31.3	31.6	48.6	49.3	58.9	61.3	60.3
+10	58.9	57.0	42.2	62.8	77.3	70.4	78.8	81.4	84.9
+12	69.2	73.5	54.9	75.5	89.5	82.9	92.7	91.5	92.5
+14	77.5	81.7	67.1	87.8	94.8	89.1	98.1	95.5	95.3
+16	86.9	89.8	80.5	94.3	97.5	95.0	98.7	97.7	97.5
+20	92.7	94.2	88.7	97.4	98.7	97.1	99.1	98.5	98.8

36

TABLE IX
Product Screen Analysis

Run Sample	2 3 Hr. Comp.	2 3 Hr. Comp.	3 3 Hr. Comp.	4 3 Hr. Comp.	5 3 Hr. Comp.	6 3 Hr. Comp.	7 Grab	8 3 Hr. Comp.	9 Grab
+ 6	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
—6 + 8	23.2	12.0	9.5	5.3	11.4	4.5	5.4	10.5	10.3
—8 +10	44.2	34.4	51.3	50.4	56.9	44.8	53.8	59.2	55.5
—10+12	21.6	30.2	27.7	31.3	21.2	30.2	26.8	21.8	21.9
—12+14	7.6	17.9	8.9	10.2	7.4	12.5	9.0	6.3	8.3
—14+16	2.7	4.7	2.1	2.4	2.5	6.3	2.0	1.5	3.2
—16+20	0.4	0.4	0.2	0.2	0.3	1.2	2.6	0.4	0.5
—20	0.3	0.3	0.3	0.2	0.3	0.5	0.4	0.3	0.3
+6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
+8	23.2	12.1	9.5	5.3	11.4	4.5	5.4	10.5	10.3
+10	67.4	46.5	60.8	55.7	68.3	49.3	59.2	69.7	65.8
+12	89.0	76.7	88.5	87.0	89.5	79.5	86.0	91.5	87.7
+14	96.6	94.6	97.4	97.2	96.9	92.0	95.0	97.8	96.0
+16	99.3	99.3	99.5	99.6	99.4	98.3	97.0	99.3	99.2
+20	99.7	99.7	99.7	99.8	99.7	99.5	99.6	99.7	99.7

TABLE X
Variation in Chemical Analysis of Different Screened Fractions

		+8	—8 +10	—10 +12	—12 +14	—14
Run 1	N	5.9	5.6	5.6	4.8	4.4
	APA	28.16	28.12	26.54	24.96	21.66
	K_2O	28.5	28.9	30.9	32.7	34.7
Run 2	N	5.9	5.9	5.8	5.7	5.2
	APA	28.04	28.24	27.78	26.18	24.68
	K_2O	28.6	28.1	28.9	30.9	32.4
Run 3	N	6.1	5.9	5.7	5.8	4.9
	APA	27.12	26.86	25.86	25.96	22.74
	K_2O	28.2	29.1	29.8	29.5	34.6
Run 4	N	7.5	7.3	7.2	7.4	7.1
	APA	25.72	25.08	25.17	25.24	24.54
	K_2O	28.8	28.9	28.7	29.1	30.1
Run 5	N	7.0	7.1	7.3	7.5	7.3
	APA	25.66	25.66	25.50	25.68	25.06
	K_2O	29.0	28.3	28.5	28.1	29.1
Run 6	N	7.3	7.3	7.3	7.5	7.3
	APA	25.70	25.74	25.52	26.12	24.88
	K_2O	30.7	30.7	30.5	30.8	31.77
Run 7	N	7.2	7.5	7.6	8.2	7.6
	APA	24.32	25.08	25.28	26.66	24.90
	K_2O	31.8	31.1	30.8	29.5	31.70
Run 8	N	7.4	7.2	7.1	7.2	6.6
	APA	25.38	24.96	24.56	25.20	23.26
	K_2O	30.9	31.5	31.7	31.6	31.7
Run 9	N	7.6	7.5	7.4	6.9	5.8
	APA	25.30	24.88	24.12	22.80	19.68
	K_2O	30.3	31.0	31.7	32.5	37.0

the dryer discharge other than a slightly larger amount of oversize when introducing slurry into the ammoniator-granulator.

The enlarged photographs of the products show that slurry addition in the pugmill yielded a more attractive product physically due to smoother surface granules. Slurry addition in the ammoniator-granulator yielded product containing some granules of irregular shape due to agglomeration of several smaller granules. When using the pugmill for slurry addition, there was a slightly longer time lag between the time that a change was made in the granulation control variables and the time that the results of those changes could be visibly seen in the ammoniator-granulator discharge, but this caused no problem in control.

With the addition of slurry into the ammoniator-granulator, agglomeration was easily controlled by minor changes in water addition or recycle rate. The chemical analyses of the screened fractions showed little differences, but the product made with the slurry addition in the pugmill was slightly more uniform.

Variations in the phosphoric acid within the range of impurity levels received from the acid plant did not change the granulation characteristics or the physical properties of the slurry.

The recycle temperature was between 150°-160°F., and the material in the ammoniator-granulator was between 155°-165°F. during periods of optimum granulation. The free moisture content of the dryer feed was from 3 to 4 percent.

In attempting to evaluate the effect of screen size of the various potash types upon the degree of granulation efficiency, little difference could be found between Type 1, the coarsest, and Type 4, the finest. All granulated quite well. The finer material required a slightly higher recycle rate to prevent overgranulation, which was contrary to what had been expected. Chemical analyses of the screened fractions show that the coarser potash did not form quite as uniform a product in the minus 14 mesh ranges as did the finer types.

In all cases, the minus 14 mesh material was high in K_2O, but this fact is insignificant because the percentage of minus 14 mesh material in the product was small. The enlarged photographs of the products made with different types of potash indicated that potash Types 3 and 4 produced a more attractive product than when made with Types 1

TABLE XI
Adjusted Analysis—Back to 7-28-28

Run	1	2	3	4	5	6	7	8	9
Potash Type	1	1	1	4	4	2	2	3	1
% K_2O	60.0	60.0	60.3	57.9	57.5	62.3	62.2	60.4	60.7
N	7.07	7.09	7.17	6.97	7.07	7.38	7.25	7.22	7.17
APA	27.81	27.99	28.19	27.41	27.79	29.00	28.53	28.39	28.19
K_2O	27.81	27.99	28.19	27.41	27.79	29.00	28.53	28.39	28.19
H_2O	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Dry P_2O_5	63.7	64.1	64.9	63.3	66.2	66.8	64.2	65.7	64.4

TABLE XII
Product Hardness

Sample	Run No.	Potash Type	Slurry	Hardness[1]	H_2O
Z-20	4	4	Pugmill	6.0	1.50
Z-56	5	4	Gran	7.5	2.25
Z-64	6	2	Gran	4.7	1.50
Z-57	7	2	Pugmiil	5.0	1.50
Z-93	8	3	Gran	6.3	1.50
Z-101	9	1	Gran	7.1	1.25

[1]Pounds of force to crush granule

and 2. Product made with potash Type 2 contained granules that were an agglomeration of smaller particles, so that the product was not smooth. This was true to some extent in all cases, but was especially noticed in the product made with white potash with the slurry added to the ammoniator-granulator. All of the product made in the pilot plant looked as good as, or better than, other granular fertilizers of the same ratio from a random sampling of the industry.

The dryer discharge screen analyses showed no significant differences in the comparison of variables. They did show that a large amount of the material is product-sized so that a close screen specification should be easily met. Thirty to forty percent of the dryer discharge material was in the range of minus 8, plus 14 mesh. Therefore a close screen specification can be met since a 4 to 1 recycle rate is required. This recycle rate is required to prevent over-granulation and still give some room for fine control with water or steam addition.

Hardness tests run by IMC's East Point laboratory on product samples compared favorably with other granular fertilizers. The products made with white potash were not as hard as those made with other forms of potash. Product made with potash Type 1 had a hardness of about 7, while that which was made with white potash was about 5. These readings are the pounds required to crush the granule. A product having a hardness of 5 or greater is considered acceptable by the U.S. industry.

Based upon the data that were gathered at the pilot plant, there should be no problem using potash similar to the types used in this test to produce a 7-28-28 fertilizer. A very satisfactory product can be made from Type 1 potash, both chemically and physically. There is very little advantage gained by using a finer form of potash such as Type 4 or by introducing the slurry to a pugmill prior to the drum granulator. Phosphoric acid with 64.9 percent P_2O_5, on a bone-dry basis, is required to make a 7.3-28.2-28.2 fertilizer with 60.5 percent (K_2O) potash. This is equivalent to 54 percent P_2O_5 phosphoric acid, with 17 percent water. The quality of wet process phosphoric acid is not critical regarding granulation efficiency.

Acknowledgment

MODERATOR REYNOLDS: Thank you, John, for a very fine, a very detailed paper.

I think we have time for a couple of questions:

MR. ALBERT E. GIBSON (Red Barn Chemicals, Inc.): Is there any significance in the data that showed that the hardest granule contained the highest percentage of moisture? 7.5% Hardness Versus 2.5% Moisture.

MR. SURBER: There may have been some significance in that one. However, there were some others that had low hardness figures that had lower moistures and so I would say that it would be pretty difficult. I would say certainly that the test was not conclusive but these were figures that we had and so we presented them.

MR. GIBSON: May I ask one other question?

Were the hardness tests conducted on a standard size granule or any size granule?

MR. SURBER: I would say it was on a standard size granule because there was very little variation, as I think you could see from the photograph. All the granules were very nearly the same size but I think probably Jimmy Archer is here and he could probably tell you exactly.

MR. ARCHER: It was on a ten mesh screen.

ANOTHER MEMBER: You quoted a pH value of 2.3. Was this the pH of the material leaving the ammoniator-granulator and, if so, did you find this had any effect on your screening and, let's say, the crushing equipment?

MR. SURBER: The pH value that I gave was the pH of the slurry from the preneutralizer.

SAME MEMBER: What was the value of the pH leaving the ammoniator-granulator then?

MR. SURBER: Did we run one?

MR. ARCHER: No, we did not.

MR. SURBER: We didn't have any ammonia there then.

MR. SURBER: I beg your pardon?

SAME MEMBER: There was ammonia out of the ammoniator-granulator, wasn't there?

MR. SURBER: Yes.

MR: JOHN B. VAN SANT (Southwest Potash Corporation): Regarding the quality of the recycle on the night runs, was the

average size particle of the recycle approximately the same, was it observed at all?

MR. SURBER: I believe that in general it was. Obviously, there probably were occasions when there were more fines. I am sure that we don't include that in the data.

MR. VAN SANT: What was the approximate recycle ratio?

MR. SURBER: The recycle rate, did you say?

MR. VAN SANT: Ratio, recycle to product ratio?

MR. SURBER: Four to one.

MR. VAN SANT: Four to one.

MR. SURBER: Well, it was very close to four to one. I think we got as low as three-and-a-half to one in some runs. This again is completely laid out in the data.

MR. VAN SANT: Was there any significant difference between the size of the muriate type one to type four, versus the quality or the size of the recycle and would you expect that the finer recycle was the lower recycle you would get and the more significant the quality of the potash would be?

MR. SURBER: I don't think that we found that although we expected that we would. I think you perhaps have reference to the fact that I mentioned that with the finer the potash we had a higher recycle rate. I think that when you see the data and look it all over you might want to slightly deviate from that; but, we did, observe, with the white, or with one of the finer ones—I believe it was the white—required a slightly higher recycle rate than any of the rest and we could find no basic difference in screen sizes of the recycle. Perhaps you might want to draw some conclusions that this had something to do with the solubility of that particular type of potash.

MR. VAN SANT: Thank you, John.

MODERATOR REYNOLDS: Okay, John. Thank you very much.

At this time I am going to turn the program over to my colleague, Al Spillman, who will introduce the next speaker. Thank you very much.

MODERATOR SPILLMAN:

At several previous Round Table Meetings we had thorough discussions on ammoniation and granulation in various type batch and continuous mixers. Our next paper by Dave W. Leyshon and Q. D. Bowers of Door-Oliver, will give you an up-to-date review on the concepts of ammoniation and granulation in the blunger.

Mr. Leyshon will present this discussion.

Concepts of Ammoniation and Granulation in the Blunger

D. W. Leyshon and Q. D. Bowers

Introduction

In the early 1930's, as a result of development work done in Berlin, Germany, the Dorr Company pioneered two important fertilizer processes. One process resulted in the Dorr strong phosphoric acid process. The other became the Dorr granular fertilizer process. The first commercial installation was at Trail, British Columbia. The device used in this plant as a granulator has evolved into today's Dorr-Oliver blunger.

In this paper we'd like to review some of the characteristics of the blunger as a granulation and ammoniating device. We'd like to discuss the particular field of application and present some performance data.

Blungers, over 50 of them, are used in over 30 plants throughout the world to manufacture 5 million tons of fertilizer each year. At the present time there are under construction 9 fertilizer plants in places like England, India, Japan, and Louisiana employing 21 Dorr-Oliver blungers, with a total capacity in excess of 2.5 million tons per year of fertilizers. We'd like to examine blunger granulation and ammoniation in detail here to determine the basis for this continued patronage.

The early Dorr blunger installations were in slurry process triple superphosphate and mono-ammonium phosphate-ammonium sulfate fertilizer plants. In 1955 di-ammonium phosphate was first produced in the Missouri Farmers Association plant at Joplin, Missouri using a blunger, but with all the ammoniation taking place in slurry tanks. Since 1955 a number of mechanical improvements have been made to the blunger, and more is understood of its capabilities. About 1962 W. R. Grace made what was probably the first installation of an ammonia sparger in the Dorr blunger. Since that time, ammonia spargers have become a standard part of the blunger and many existing installations have been converted to blunger ammoniation.

Description

The Dorr-Oliver blunger may be described as a reactor for producing a fluidized bed, wherein recycled fines, solid raw materials, wet slurry, and ammonia are thoroughly mixed and reacted. The fluidization is mechanically produced by blades fixed to two outboard turning shafts. The action of the paddles which are set helically on the shaft is to simultaneously mix and propel the ingredients through the reaction zone. The bed actually bounces violently and resembles a boiling liquid, the paddles being completely submerged. Bed depth in the ammoniating zone is about 30 to 36 inches. This action is not the kneading type of mixing that is provided by pug mill superphosphate mixers which somewhat resemble a blunger. A characteristic of the Dorr-Oliver blunger is the fluidizing action and tremendous conveying capacity which are not characteristic of superphosphate type pug mills. Particles are subject to a shearing action rather than a rolling action. Growth is by layering of the slurry on bouncing seed particles, and to a lesser extent by agglomeration of fine particles.

Figure 1 is a shot of two blungers which have recently been installed at a plant in Louisiana.

These particular blungers are 5 feet wide by 12 feet long. Each unit is powered by a 100 horsepower motor. Dorr-Oliver also manufactures a 5 foot by 8 foot blunger for situations where little or no
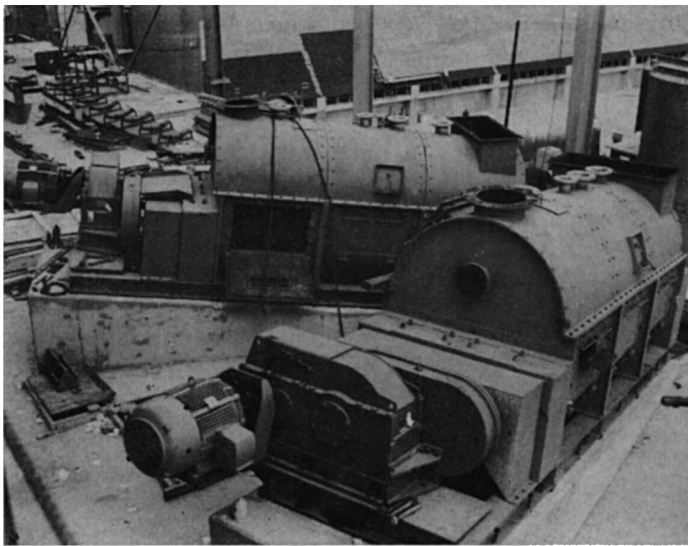
Figure 1
View of blungers being installed at the Gulf Faustina, La. Plant.

ammonia is to be used in the blunger. The drive has a twin output Falk reducer.

Paddles are replaceable and are made of nihard or cast steel, and can be stellited. Blades could be made of stainless, but in most situations corrosion and erosion is not severe enough to warrant this. Shafts are very massive, and corrosion or failure of the shafts has not occurred to our knowledge.

The domed cover contains the openings for recycle and various liquid streams. Slurry can be distributed by a sawtooth weir arrangement, easily accessible from the top, or by a spray header. The tank is mild steel varying in thickness from $1/4''$ to $5/8''$. The reaction zone is easily accessible so that adding the raw ingredients in a particular order is easliy done.

Not shown in Figure 1 are the ammonia and steam connections for the sparger. A 5 foot by 12 foot blunger has space for about 6 feet of sparger length. This length can be divided off into as many as 4 separately valved sections. This means a total of 8 sections in 12 feet of sparger length on each fertilizer line. This provides quite precise distribution for the ammonia, something rather difficult to achieve in a drum, since carrying individual pipes into the drum would make a very cumbersome arrangement. Slurry is individually metered to each blunger.

Blunger Applications

Slurry Process TSP

Probably the most notable blunger application is in direct slurry process triple superphosphate, 0-46-0. To our knowledge this is the only granulator which has been consistently successful for the manufacture of once through triple superphosphate. The process, which is not new, is described in an article in Industrial and Engineering Chemistry, October 1955, by Inskeep, Fort, and Weber. Continued process improvements have more than doubled capacity capabilities mentioned in this article. There has been a recent revival of slurry process triple because of market demand for direct application and bulk blending, and because of lower costs of production. Also, it is possible to build a plant which will produce both TSP and DAP without the denning and curing operation. Blungers have been installed in at least 12 plants using

the slurry TSP process, the most recent Dorr-Oliver installation being at Farmland Industries in Greenbay, Florida.

In the Dorr slurry process for TSP a predominant feature is the tendency to overgranulate. The system tends to be sticky and will run to oversize quite easily. This is a condition with which the blunger is most able to cope because of its positive mixing and conveying action. The blunger will handle granulator contents which would mud up, slide, or ball up in drum granulators.

High Nitrogen Grades

The complete roll call of grades made in blunger plants is too long to list here. However, there is much interest presently in high urea and high ammonium nitrate grades. Table 1 gives a list of some of these grades which are being handled in blungers. All the plants listed are Dorr-Oliver designed except the I.C.I. plant which is a revamp of a Dorr plant, and was extensively described at last year's Round Table.

These grades, because of the high solubility of ammonium nitrate and urea, tend to overgranulate, to produce lumps and balls at any place where mixing is not positive. Wet lumps containing ammonium nitrate or urea are virtually impossible to dry in the time available in a commercial fertilizer plant. If too much agglomeration occurs, sufficient moisture is not released in the dryer and moisture is then evolved in the screening station and in the fines return conveyor where it is particularly deadly, and in the pulverizers, resulting in blinding and scaling of equipment, lost time, and lower capacity. Blunger granu-

Table 1
High N Grades Produced In Blungers

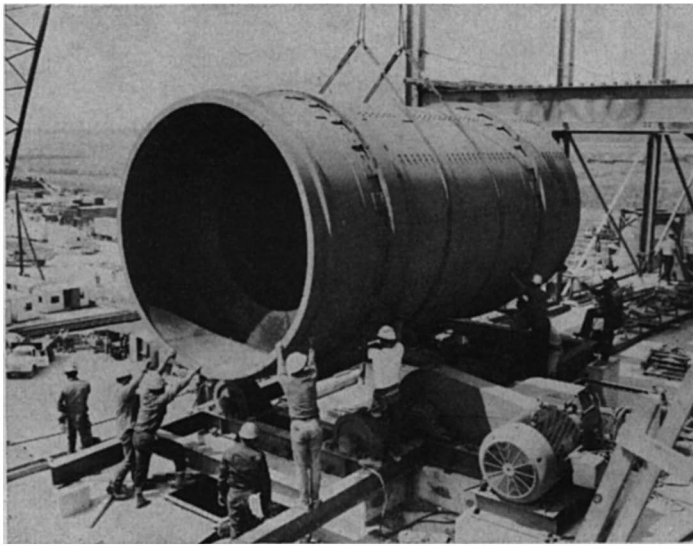| Plant	Grade	Formulated With
C.I.C. (Rumania)	23-23-0	50% AN
C.I.C. (Rumania)	13-26-13	20% AN
CARBOCHIMIQUE (Belgium)	17-17-17	40% AN
I.C.I. (England)	22-11-11	55% AN
SHERRITT-GORDON (Canada)	23-23-0	25% UREA
NITTO (Japan)	20-10-20	33% UREA
NITTO (Japan)	17-17-17	20% UREA

Figure 2
View of 12 ft. diameter by 24 ft. long TVA Ammoniator Granulator
being installed in Dorr-Oliver designed plant.

lation is one of several devices and techniques employed to reduce dryer detention requirements and increase capacity on these grades. The application of blunger granulation to high nitrogen grades may not be quite as clear-cut as the application for slurry process TSP, but in our opinion it is a proven route to making these grades.

Granulating Drum Applications

We don't believe any discussion of blunger granulation could be complete without covering some of the characteristics of rotary drum granulation which make it unique from blunger granulation. Dorr-Oliver has been thought of mainly in terms of blunger granulation, but we'd like to say that we have had considerable experience in drum granulation as well. Pictured in Figure 2 is the latest Dorr-Oliver installation of a 12 ft. by 24 ft. TVA ammoniator granulator actually being lowered into position at a Louisiana plant. The bolts holding the rubber lining are easily visible. Figure 3 shows a section of the control board at the Forenade Superfosfatfabriker NPK plant at Landskrona, Sweden, a plant which was engineered by Dorr-Oliver, N.V., of Amsterdam. The operators can observe granulating conditions at the discharge of the 12 ft. by 28 ft. TVA granulating drum on a television screen in the control room.

Granulation of Superphosphate Based Products

The largest single application of the TVA ammoniator-granulator has been a wide variety of superphosphate based products often incorporating ammonium sulfate, potash, ammonium nitrate, and other materials. The rolling action of the drum is ideally suited for solid raw materials, and granulation takes place under relatively dry conditions. A similar application is granulation of run of pile triple superphosphate using steam, water, and small amounts of phosphate rock. In a Dorr-Oliver installation in Florida, a granulating drum similar in size to the ones we have just shown produces about 60 TPH to 65 TPH of granulated triple.

Diammonium Phosphate

Most people in the industry are quite familiar with the successful application of the TVA ammoniator to DAP. With good slurry and ammonia distribution it is possible to apply and ammoniate several layers of slurry in a large part of the drying.

According to the 1966 proceedings of the Fertilizer Round Table there were over 150 TVA ammoniator-granulators in existence. TVA has published a great deal of information describing formulas, operating conditions, and so forth. We could not hope to cover all the applications. However, the granulation of superphosphate based products and DAP are perhaps the most widely practiced areas of drum granulation, and there are relatively few blunger applications, particularly in superphosphate granulation.

Blunger Performance

We have mentioned the two most successful applications of the blunger, slurry process triple superphosphate and the processing of grades containing high quantities of ammonium nitrate or urea. However, on DAP excellent performance has also been achieved.

Figure 3
Part of control panel at Forenade (Sweden) NPK plant showing television view of
granulator discharge.

Figure 4
Aerial view of the Occidental Plant, White Springs, Florida. The 750 TPD Phosphoric Acid Plant is shown on the upper right. At the upper part of the picture is a two line 2000 TPD Titlestad Sulfuric Acid Plant. The two train Fertilizer Plant is located between the TSP storage building and the DAP storage building in the foreground.
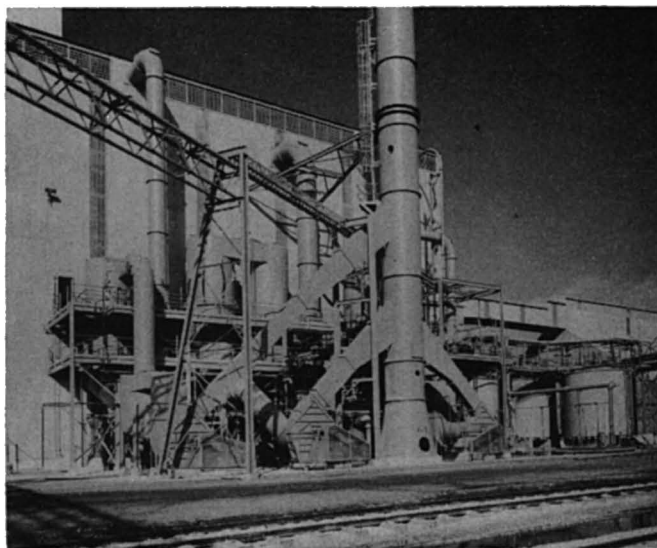

Figure 5
View of the Occidental Fertilizer Plant, White Springs, Florida showing Airetron scrubbing system for one of the two fertilizer lines.

Occidental Plant,
White Springs, Florida

In September 1966, Occidental Agricultural Chemicals Corporation started operation of a two line fertilizer plant at White Springs, Florida.

Each line was capable of producing either diammonium phosphate or slurry process triple superphosphate. An aerial view of the complex is shown in Figure 4.

A close-up view of the fertilizer plant and scrubber system for one line is shown in Figure 5. This scrubber system supplied by Airetron handles either DAP or TSP.

The operation at Occidental for making DAP, 18-46-0 is similar to the conventional TVA process. Most of the phosphoric acid is introduced into the scrubbing system at 35% to 37% P_2O_5. 54% P_2O_5 acid sludge at 10% to 11% solids and 48% P_2O_5 is added directly to the preneutralizer. A 1.45 mol ratio slurry is pumped to the blungers. Liquid ammonia is used in both the preneutralizer and blunger. The dryer discharge elevator has a capacity for 35 TPH. Each of these fertilizer lines is operating at maximum rates in excess of 50 TPH of 18-46. Typical product made at this rate contains 1.0% to 1.2% moisture, has a pH of 7.6 at 20:1 dilution, and has a particle size of 9.6% + 8 mesh, 86.1% + 10 mesh,

and 99.9% + 14 mesh. Bulk density is 61.5 pounds per cubic foot.

The operating staffs at Occidental believe the plant is capable of substantially higher tonnages if feeding bottlenecks were eliminated. They base this prediction on the fact that at present only the upstream three foot section of the ammonia sparger is in use. The granules are already dry at this point in the blunger and the introduction of ammonia further downstream results in excessive ammonia loss. Occidental's operating staff believe that an improved slurry distribution device or spraying the slurry would increase ammoniation capacity.

The blungers in the Occidental plant are essentially the same as those shown previously in Figure 1; each blunger has a 100 HP motor. A view of the discharge end of the Occidental blungers while operating on DAP is shown in Figure 6.

Maximum operating rates on slurry process triple superphosphate, 0-46-0, are in excess of 40 TPH. The particle size of the product is virtually the same as DAP, 10% + 8 mesh, 86% + 10 mesh, and 99.9% + 14 mesh. The bulk density is 76 pounds per cubic foot. The dryer discharge elevator has a capacity of 440 TPH for TSP operation.

Occidental has also made 13-52-0 and 17-22 in this plant at similar rates to those for DAP and TSP production. They have in addition made 13-52-0 and 18-46-0 with part of the P_2O_5 derived from superphosphoric acid. The 18-46 made this way contained 3 to 3.5 units of nonortho P_2O_5, and the 13-52, 5 to 6 units of nonortho P_2O_5. Virtually all of the nonortho P_2O_5 in the superphosphoric acid was contained in the finished products. Bulk density of 18-46 containing 3 units of polyphosphate was 64.5 pounds per cubic foot.

Figure 6
Discharge end of blunger installation at Occidental DAP - TSP Plant, White Springs, Florida.
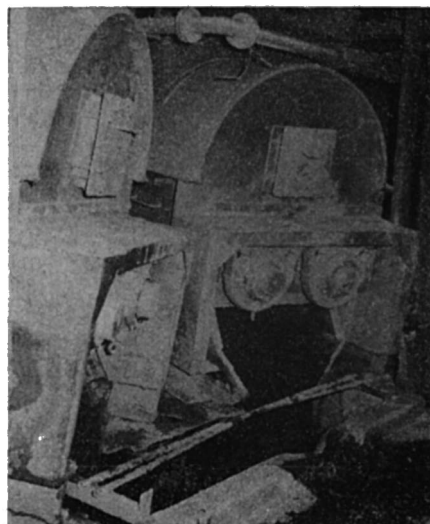
We believe that for the granulation of many products it is less difficult for the operators to learn the technique of granulation in the blunger. There is a tolerance for a wider range of liquid phase in the blunger than there is in a drum granulator bed, which means that control of moisture levels in the blunger is less critical. The Occidental staff considers the startup of both lines to have been particularly smooth. A 10 day performance run on DAP was completed 23 days after the initial feeding of ammonia and phosphoric acid to the plant.

Occidental replaces 12 or 14 cast steel blades every 3 weeks when operating on TSP. These are only the blades in about two feet of wetted length of the blunger. On DAP the replacement of blades is necessary only after several months. Frequency of blunger cleaning depends on operator control. Sustained periods of wet operation, too high an acidulation ratio on TSP, and too much iron and aluminum in TSP will result in more frequent cleaning. One European company that has been operating a blunger for several years on high nitrate grades reports going 10 or 12 months without cleaning the unit. A realistic period for TSP blunger cleaning is perhaps once per week. For DAP, once in two weeks or longer. We believe the problems of scaling and cleaning are less difficult in a blunger because it has a built-in scraping action and overlapping blades which make the unit partially self-cleaning. It can be reported that the percentage of on-stream time has been very high in many blunger plants.

Some General Features Of Blunger Granulation

One aspect of blunger granulation which we'd like to cover is its ability to make either a coarse or a relatively fine product. Table 2 shows a coarse product as produced in a European blunger plant, and also a pinhead product which was made for a time in Europe. These analyses give something of the size range capabilities of the blunger. Listed also on Table 2 are two "normal" size ranges which can be produced in blunger plants. These size specifications are prob-

Table 2
Blunger Product Size Analyses

Type of Product	% Within Size Range	Tyler Mesh	MM.
NORMAL	95%	— 8+12	—2.5+1.5
NORMAL	99%	— 7+14	—3.0+1.2
COARSE	95%	— 5+ 8	—4.0+2.5
PINHEAD	95%	—10+48	—1.5+0.3

ably tighter than can be produced economically by prilling or spraying techniques on most grades.

Blungers have been used successfully for many years to make high potash ammonium phosphate grades such as 12-12-18, 6-24-24, and 14-28-14. Some producers, including Forenade in Sweden, however, have told us that they believe high potash grades are more easily granulated in a drum, and that the pellets are harder. On granulation of potash grades, slurry mol ratio and viscosity, potash particle size, slurry distribution, and potash wetting are important. We believe it would be difficult to completely evaluate all these factors. Certainly both the blunger and granulating drum have been used successfully on potash grades.

It has been frequently stated that blungers require a higher quantity of recycle than a granulating drum. This statement needs some discussion. In general it is not true. If one compares a DAP process with ammoniation in the drum with a DAP process using no ammonia in the blunger, then more recycle is required by the blunger. But if it is conceded that a blunger can be operated with a wetter discharge than a drum granulator because of the former's positive mixing action, then at least in some situations the blunger will actually require less recycle.

We believe that so much emphasis has been placed on the false economics of low recycle rates that very many DAP plants and many NPK plants now in operation are producing well below their capacity capabilities because of limitations in the quantity of recycle. The added cost for adequately sizing recycle conveying equipment in the initial design of the plant is really rather nominal, and a very inexpensive way of getting maxi-

mum capacity out of a given plant.

One word about costs. Two blungers are considerably less expensive than an 11 x 25 foot or similar sized granulator, particularly if it is rubber lined or has an oscillating scraper. On an installed basis, two blungers are at least no more expensive than a granulating drum, and the chances of having both blungers out of service at one time is almost nil.

Summary

In summary, blungers have been demonstrated to be very effective for the granulation of grades which are sticky and tend to produce excessive quantities of oversize. Slurry process triple superphosphate and high nitrogen grades using urea or ammonium nitrate are particularly suited to blunger granulation. In addition, it has been demonstrated in several recent installations that high degrees of ammoniation can be very effectively carried out in the blunger because of the deep, violently agitated bed which makes it possible to use the heat of reaction to evaporate large quantities of water. It is therefore possible to produce DAP and DAP based NPK grades at high rates using the blunger.

The concept of ammoniation during granule formation is an important one. The result is a hard granule containing low moisture. We believe the blunger is well suited for this task.

. . . . .

MODERATOR SPILLMAN: Thank you,, Mr. Leyshon, for that very fine paper.

Do we have any questions, please, and would you come to the mike, please.

A MEMBER: You have shown a few grades made in the blunger with ammonium nitrate and urea.

MR. LEYSHON: Yes.

SAME MEMBER: Can you tell us in what form and concentration were urea and ammonium nitrate added to the blunger?

MR. LEYHORN: The first two in the Rumanian installation, it was 84 per cent ammonium nitrate solution. At Carbochimique it is about 93, I think, and I don't know what the ICI unit used. It's in last year's Round Table paper, I think.

A VOICE: 97.

MR. LEYSHON: Yes.

Sherritt Gordon uses solid urea and I believe MICO also uses solid urea.

Is that right, Dick?

A VOICE: That's right.

MR. LEYSHON: Dr. Hignett.

DR. TRAVIS HIGNETT: In making 23-23-0 using urea, I wonder what else is added to get that low a grade?

MR. LEYSHON: That was in Sherritt Gordon in Canada. They have used ammonium sulphate.

MODERATOR SPILLMAN: We have time for about one or two more questions.

A MEMBER: Have there been any fires or explosions when blungers and ammonium nitrate were used together, to your knowledge?

MR. LEYSHON: No. In Dorr-Oliver experience with blungers and ammonium nitrate, we have stayed pretty much with a temperature in the 85 to 95 degree Centigrade range.

Now, in some granulation drum operations where they have sulfuric acid present also, you can get temperatures much higher than this and we used to regularly have a slightly orange color out of a granulator that I worked in in the Middle West.

But in the blunger we don't normally add sulfuric acid at this point. Usually the sulfuric acid if it is present in the formula would be added to the preneutralizer.

MODERATOR SPILLMAN: Thank you, Mr. Leyshon.

I will now turn the meeting back to Vince.

CHAIRMAN SAUCHELLI: Thank you, Al.

Let's have a one-minute stretch and, please, one-minute only.

At the recent TVA conference at Knoxville, H. S. Ten Eyck, well known in our industry as an authority on phosphates and superphosphoric acids, predicted that the present shortage of sulphur would continue for the next three to five years. Within this period a large enough supply would emerge. He declared the evidence was clear that enough elemental sulphur will become available in countries outside the United States to provide an adequate supply.

In addition, an anticipated production of pyrites will supplement the supply of brimstone sulphur at reasonable costs and the combination will alleviate the shortage.

Sulphur is of fundamental importance in the manufacture of fertilizers. About one-half the total consumption is used by the fertilizer industry.

We are fortunate to have on our program three eminent representatives of the sulphur industry who will discuss different phases of the sulphur situation.

The first of this trio for this afternoon is Dr. Serge Levitsky, Manager of Market Research of the Texas Gulf Sulphur Company. The title of his paper is: Sulphur: Quo Vadis?

We are all anxious to know the answer.

Sulphur: Quo Vadis?

Serge L. Levitsky

Recently sulphur producers have announced new increases in the price of sulphur, and allocation of the quantities supplied. Why were they necessary when voices, here and abroad, continue to be heard, heralding a new abundance of this vital mineral?

Looking at the vast empty spaces where, only a few years ago, sulphur vats rose like familiar landmarks, Figures IV & V, the producers' most immediate concern was not about 1975 or 1980, but about this year and the next. It was to halt the seemingly irresistible downward slide in the level of inventories which has continued since 1962. Where Free World inventories of elemental sul-

Figure IV

Figure V

phur represented 83.7% of total sales at year-end 1962, or 43½ weeks of supply, and appeared sufficient to provide for any national emergencies for years to come, the following year—the first year of our current shortage—they decreased to less than 70% of sales, or 36 weeks of supply. In 1964, inventories fell to 51.8% of sales, or less than 27 weeks of supply. In 1965, they dropped to 38% of annual sales, or less than 20 weeks of supply. And last year, they represented a mere 30.6% of sales, that is, less than 16 weeks of supply. (Figure III & Table II).

Since the time the sulphur shortage began, in mid-1963, Free World producers have withdrawn
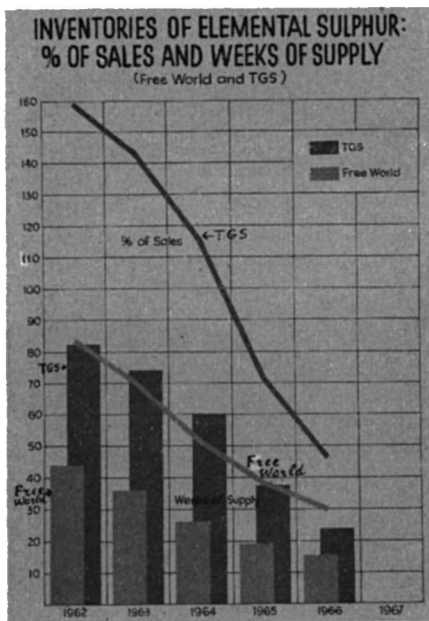
INVENTORIES OF ELEMENTAL SULPHUR: % OF SALES AND WEEKS OF SUPPLY
(Free World and TGS)

Figure III

a total of some 3½ million tons of sulphur from their inventories. As the first half of 1967 came to a close, inventories had shrunk further, to barely 14 weeks of supply. And although producers had generally endeavored to reduce their volume of sales, it became evident that no further withdrawals from stocks would be possible without bringing even the reduced shipping program to a grinding halt. At mid-year 1967, all hopes that might have been entertained for an early end to the current world-wide sulphur shortage had to be abandoned. Clearly, the sulphur industry was heading for its fifth straight year of shortage in supplies, and sulphur producers were forced to take drastic steps to stabilize their levels of inventories, by further allocating their sales.

What has caused this shortage?

It came almost unheralded at a time when producers were still smarting under the economic effects of oversupply. Only four years ago, the Research Council of Alberta published a study of the sulphur industry in which the statement was made that "the likelihood of world sulphur demand and supply coming into balance by the end of the decade would appear to be remote".

In 1963, when this and many similar statements were made, the Free World had just gone through eleven years of continuous oversupply of sulphur. In 1962 alone, the excess of production over consumption amounted to more than one million tons. Stockpiles were accumulating in the United States. Canada and elsewhere, and a French sulphur official was quoted as predicting in the summer of 1963 that the mounting stockpiles of sulphur would create a deterrent to further active exploration for natural gas in Western Canada. And yet, when the year 1963 came to an end, and the figures became available, it was soon apparent that the Free World had actually experienced that year a modest sulphur *deficit*. The following year, this deficit grew to over 950,000 tons, and we have had similar deficits in 1965 and 1966. (Table I &

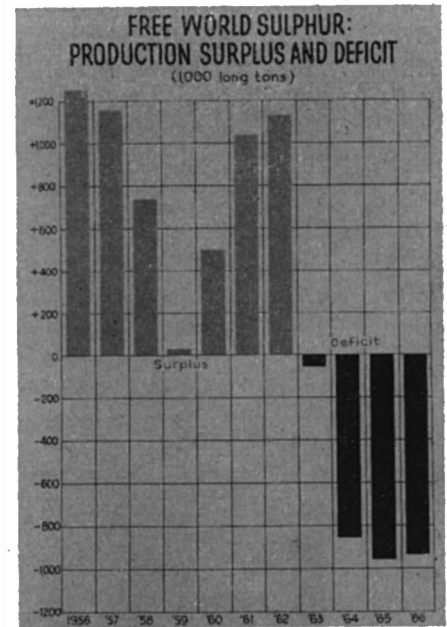FREE WORLD SULPHUR: PRODUCTION SURPLUS AND DEFICIT
(1000 long tons)

Figure II

Figure II). And today, several sour natural gas properties in Western Canada are actually being developed for their sulphur value alone.

The circumstances which had conspired to make the oversupply of 1952-1962 inevitable, are not likely to be duplicated in the foreseeable future: We have had a period of slow growth, and even stagnation, in consumption when, almost simultaneously, three major new sources of supply emerged in world markets. Production of sulphur from two of these sources, because of its by-product nature, responded more readily to the economics of natural gas than to the vicissitudes of the supply-demand balance of sulphur. The timing of this new recovered sulphur production may have been unfortunate from the point of view of the economics of sulphur. Had this production been foreseen a decade earlier, some of the new Frasch capacity might never have come on stream. A decade later, it would have been easily absorbed by the greatly increased demand. But this timing became inevitable because of the demand for sweet natural

Table II
Free World Inventories* of Elemental Sulphur
(1,000 long tons)

Year	Free World Elemental Inventories	Free World Inventories as % of Sales Total Free World	TGS**	Weeks of Supply Free World	TGS**
1956	5,044	65.0	79.1	33.8	41.1
1957	5,610	73.2	109.6	38.1	57.0
1958	5,865	77.1	142.7	40.1	74.1
1959	5,578	67.7	120.5	35.2	62.7
1960	5,571	60.9	125.1	31.7	65.0
1961	6,831	74.3	152.5	38.6	79.3
1962	7,970	83.7	158.7	43.5	82.5
1963	7,764	69.9	143.1	36.3	74.4
1964	6,763	51.8	115.6	26.9	60.1
1965	5,508	38.1	72.0	19.8	37.5
1966	4,662	30.6	46.1	15.9	24.0

*Year-end At-mines and Away-from-mines Inventory.
**Includes TGS inventory in Mexico.

Table I
Free World Production and Consumption of Sulphur in All Forms
(1,000 Long Tons)

Year	Production Elemental	Production Non-Elemental	Total	Consumption Elemental	Consumption Non-Elemental	Total	Production Surplus or Deficit
1956	8,684	8,872	17,556	7,824	8,475	16,299	1,257
1957	8,227	9,016	17,243	7,606	8,480	16,086	1,157
1958	7,718	8,886	16,604	7,469	8,398	15,867	737
1959	8,211	8,662	16,873	8,573	8,275	16,848	25
1960	9,229	8,975	18,204	9,217	8,491	17,708	496
1961	10,104	8,850	18,954	9,162	8,754	17,916	1,038
1962	10,577	8,851	19,428	9,688	8,611	18,299	1,129
1963	10,913	8,424	19,337	11,050	8,440	19,490	— 53
1964	11,931	8,891	20,822	12,833	8,943	21,776	— 954
1965	13,076	9,265	22,341	14,339	8,976	23,315	— 974
1966	14,284	9,800	24,084	15,116	9,900	25,016	— 932

Annual % Growth

| Year	Elemental	Non-Elemental	Total	Elemental	Non-Elemental	Total
1965	14.3	10.4	12.3	6.1	5.4	5.7
1957	— 5.3	1.6	— 1.8	— 2.2	0.1	— 1.3
1958	— 6.2	— 1.5	— 3.7	— 1.8	— 0.1	— 1.4
1959	6.4	— 2.6	1.6	14.8	— 1.6	6.2
1960	12.4	3.6	7.9	7.5	2.6	5.1
1961	9.5	— 1.4	4.1	— 0.6	3.1	1.2
1962	4.7	0.01	2.5	5.7	— 1.6	2.1
1963	3.2	— 4.8	— 0.5	14.1	— 2.1	6.5
1964	12.8	5.5	8.0	16.1	6.0	11.7
1965	9.6	4.2	7.3	11.7	0.4	7.1
1966	9.2	5.8	7.8	5.4	10.3	7.3

gas, spurred on by the advances in long-distance transportation and the grant of export permits, and the demand for desulphurized refinery products requiring the removal of the hydrogen sulphide component.

In 1963 alone, these three new sources of production, Mexico, France and Canada, have added a combined total of over 4 million tons of incremental sulphur to the production from traditional sources.

But when industrial activity again began to pick up, the prospect of an almost unlimited supply of the economically-attractive elemental sulphur, at a time when greater availability of fertilizer came to be generally regarded as one of the means to solve the looming world food crisis, provided a powerful impetus to capital investment in new sulphur-using plants. Consumption of sulphur, which historically grew at about 4% a year, soared, world-wide, to an increase of 6.5% in 1963, 11.7% in 1964.

Figure I

FREE WORLD PRODUCTION AND CONSUMPTION OF SULPHUR IN ALL FORMS
(Millions of long tons)
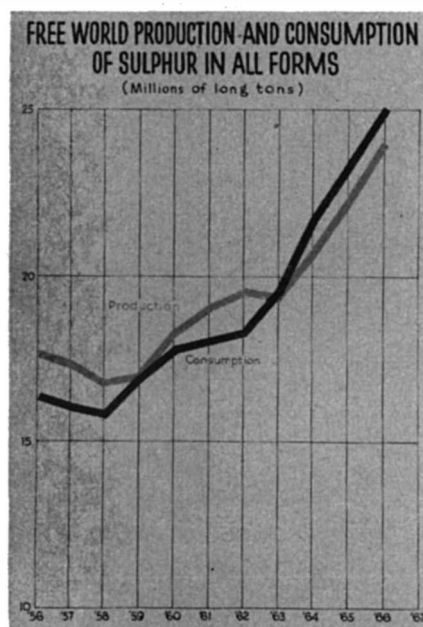
7.1 in 1965 and 7.3 in 1966. (Figure I). Most of these increases were attributable to higher use of sulphur in the production of phosphatic fertilizers. The sharply increased consumption rates coincided with the emergence of new markets for sulphur and a diminished rate of increase in the availability of sulphur, particularly from the three foreign sources which had previously contributed to the oversupply.

How long is the current sulphur shortage going to last? The huge inventories are virtually gone now and cannot be counted upon to help fill any gaps between supply and demand. Current production rates are clearly inadequate to sustain the world-wide growth in sulphur consumption. On the other hand, even if the historical growth rate in consumption of 4% a year is increased by only half-a-per-cent, this will still mean that in 1970 the Free World will need an additional 5.7 million tons of sulphur over and above the 24 million produced in 1966.

Sulphur producers knew that their duty to customers was not limited to providing for their needs this year and the next; that although depletion of inventories, coupled with a drastic allocation program, would have the effect of depressing actual consumption levels of sulphur in the Free World, plans for the future would now have to be based on demand rather than on consumption. Because a significant portion of the demand would not be filled.

And as the producers cast their eyes upon the future, 5, 10 and 15 years from now, they could discern no signs of weakening in the current high rates of *demand*. When the trends prevailing in the Free World during the past five years were projected into the future, total demand for sulphur in 1970 was conservatively estimated in the neighborhood of 32 million tons. Significantly, this level of demand, based on a mathematical projection of current trends was confirmed by analyses based on per capita growth in consumption, and on anticipated fertilizer use in the Free World. (Figure X).
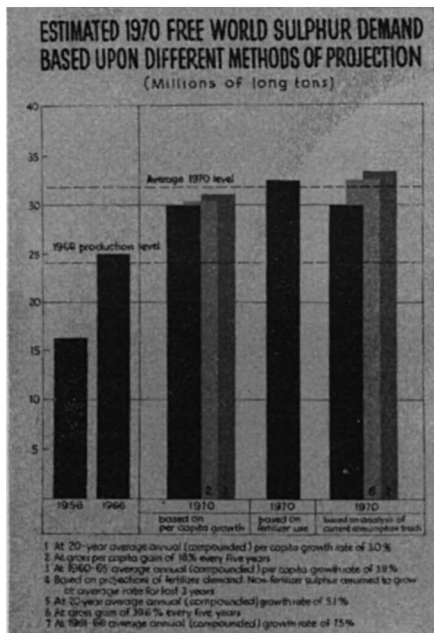
ESTIMATED 1970 FREE WORLD SULPHUR DEMAND BASED UPON DIFFERENT METHODS OF PROJECTION
(Millions of long tons)

Figure X

Producers knew that the spectacular rise in the annual consumption rates of sulphur in the Free World during recent years was largely attributable to higher use of sulphur in the production of phosphatic fertilizers. In 1966, almost 80% of the increase in consumption was due to the rapid growth in demand for phosphatic fertilizers and to the trend toward higher-analysis materials, using greater quantities of sulphur.

The percentage share of fertilizers in total demand for sulphur has been steadily increasing over the past ten years. In the United States, it went up from 35% to 45% and, on a world-wide basis, it increased from 40% to 50%. In 1970, some 52% of all sulphur markets could very likely be represented by the fertilizer industry. And, although industrial uses still account for half of the entire consumption of sulphur in the Free World, it is the sulphur used in the manufacture of fertilizers which, during the next five years, will continue to set the trend in total sulphur demand. *Phosphate* fertilizer materials, which take up perhaps as much as two-thirds of all the sulphur used in fertilizers, must be especially watched. Ammonium sulphates account for much of the remaining third.

Predictably, the long-range annual growth rate in the Free World consumption of P_2O_5 in plant nu-

trients was revised upwards by phosphate industry forecasters. The exceptionally high percentage increases in demand for phosphatic fertilizers during the past few years seemed to herald a new trend, borne out by the contemplated expansions in plant capacities. The Tennessee Valley Authority, which in 1965 conducted a survey for the United States Agency for International Development to determine total world capacity for the manufacture of phosphatic fertilizers, estimated that this capacity would increase by more than 60%, between 1965 and 1970, from 12.2 million tons of P_2O_5 to at least 19.4 million tons of P_2O_5. Currently, the anticipated capacity for 1970 is even higher: over 23 million metric tons of P_2O_5.

If the phosphate industry were to operate at 75% of the capacity indicated by TVA for 1970, Free World demand for P_2O_5 would be growing, between now and 1970, at an annual compounded rate of 6% to produce some 14.7 million tons of P_2O_5. This is a more conservative annual rate than the phosphate industry is currently experiencing. The amount of *sulphur* required to produce the 14.7 million tons of P_2O_5 would be in the neighborhood of 10 million tons. If we add to this figure the sulphur required for the manufacture of ammonium sulphates and of other fertilizer materials, and assume that non-fertilizer uses of sulphur will continue to grow at the current modest annual rates, total demand for sulphur in the Free World in 1970 would reach almost 32 million tons.

A similar level of 32 million tons of sulphur is obtained if our projections are based on anticipated *use*, in 1970, of the three essential plant nutrients, N, P, and K in the Free World. (Figure VII).

The various projections of fertilizer use, of course, are based on the premise that the Free World will have sufficient quantities of sulphur available *to produce* these fertilizers. There is no fear about future availability of nitrogen, of phosphates, and of potash; sulphur, alone, remains a question mark.

Projected use of fertilizer materials is an important, but by no means the only yardstick by which we can measure future demand for
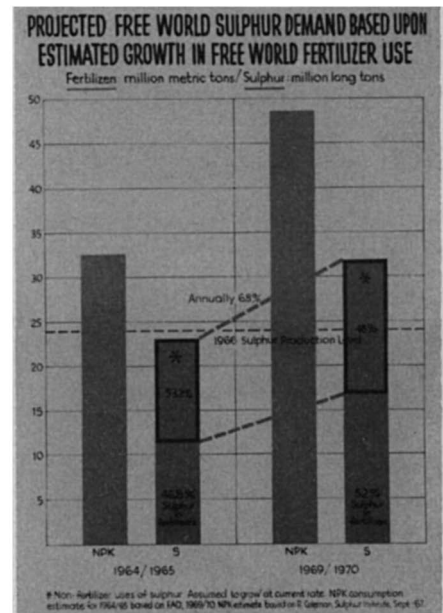

PROJECTED FREE WORLD SULPHUR DEMAND BASED UPON ESTIMATED GROWTH IN FREE WORLD FERTILIZER USE
Fertilizer: million metric tons/Sulphur: million long tons

Figure VII

sulphur. Projections based on *per capita* consumption of sulphur give us additional clues. Significantly, and luckily for the forecaster, they lead to similar results. Because sulphur is used in the production or processing of nearly every product associated with our daily lives, a country with a high per capita consumption of sulphur is also a country with high living standards. In the United States, per capita consumption of sulphur grew, from 33.8 pounds in 1920, to 106.3 pounds in 1966. Over the past twenty years, the average annual growth in the per capita rate of sulphur consumption followed very closely that of per capita GNP, expressed in 1958 constant dollars. The increase was 1.6% for each, but was exceeded by the growth in population of 1.8% a year. During the last six years, however, sulphur consumption per capita has shown a definite tendency toward a much faster growth, and is now increasing at an average of 7.0% a year, compared with 3.7% for per capita GNP, and only 1.4% for population. (Figure VIII).

In the Free World as a whole, the average per capita consumption of sulphur is, understandably, much lower than in the United States; it amounted to 23.5 pounds in 1965. However, a similar trend toward faster growth was noticeable during the last five years; namely 3.8% annually, compared with an average 3.0% a year over the past
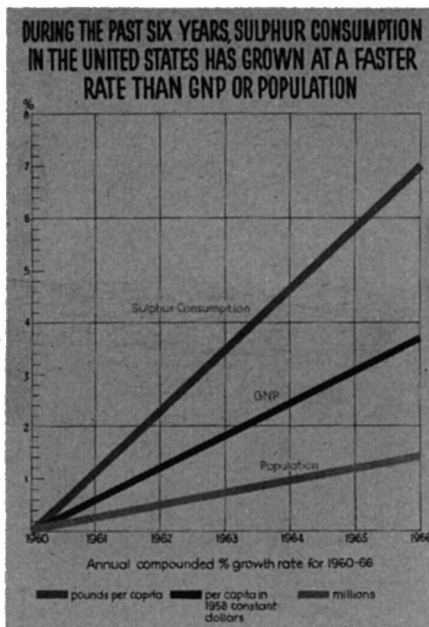
Figure VIII

twenty years. The gross gain for the past five years was 18%.

If the recent growth trends in per capita consumption of sulphur, are projected into the future and converted into long tons of sulphur, a total demand for sulphur of over 31 million tons may be anticipated in 1970, which is seven million tons more than was produced in the Free World in 1966. (Figure IX.)

PROJECTED FREE WORLD SULPHUR DEMAND BASED UPON CURRENT GROWTH RATES IN PER CAPITA CONSUMPTION
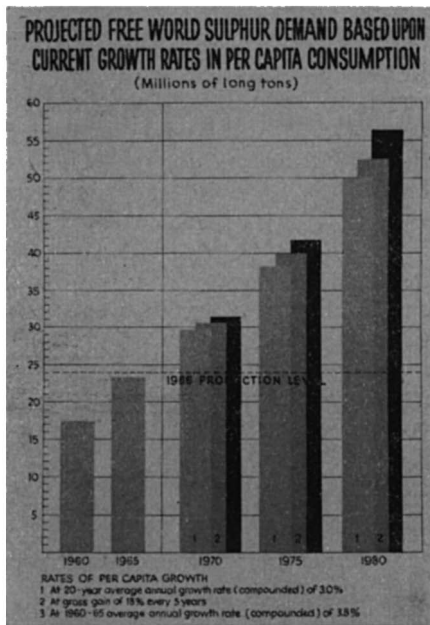(Millions of long tons)

Figure IX

The analysis of growth trends in per capita consumption of sulphur in the Free World thus seems to confirm and strengthen the con-

clusions reached through projection of the sulphur requirements based on anticipated fertilizer use.

But the sharp increase in Free World sulphur consumption, alone, cannot explain the current sulphur shortage. True, the rapid growth in sulphur used did help absorb the production excesses of the past years. But we also witnessed the emergence of new, hitherto unavailable markets; and, most important of all, growing demand was coincidental with a diminished rate of increase in the availability of sulphur, particularly from the three major sources which had previously contributed to the oversupply: France, Mexico and Western Canada.

In France, production from the sour gas fields at Lacq reached its designed capacity several years ago. The 1966 output of 1.5 million tons was virtually identical to that of 1965, and of 1964. In Western Canada, the rate of growth in production has been slower in the past few years than was originally anticipated, and the 1966 output of 1.7 million tons represented an increase of only 137,000 tons over 1965. And in Mexico, the level of Frasch sulphur production in 1966 was actually 15,000 tons lower than in 1964.

During the period of oversupply (1956-1962), the average annual increase in the output of "recovered" sulphur at Lacq was 114.6% compared with only 3.1% during the shortage of 1962-66. In Western Canada, "recovered" sulphur production grew at an average 80.4% a year during 1956-62, compared with 12.9% during 1962-66. The annual growth in Mexican Frasch sulphur production diminished, from 7.2% during 1956-62, to 3.7% during 1962-66. There has also been a noticeable decrease in the average rate of growth of U.S. "recovered" sulphur, from 17.2% a year during 1956-62, to 8.6% during 1962-66. In contrast, the output of U. S. Frasch sulphur, which had been decreasing by an average of 2.9% a year during the over supply of 1956-62, grew at an average 10.0% a year during the shortage of 1962-66. (Figure XI).

Clearly then, U.S. Frasch sulphur has carried the main burden in the race toward narrowing the
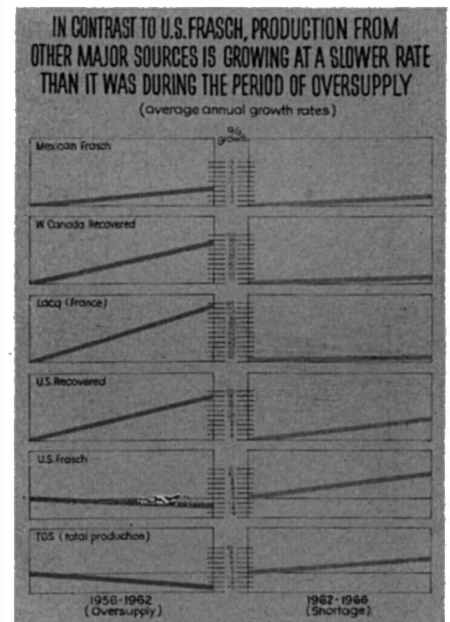
Figure XI

gap between production and demand. (Table III). In 1966 alone, production increased by 14.3% over the previous year. It is improbable, however, that this rate of growth can be sustained in the future. For example, to maintain its present share in Free World sulphur markets, at a 6% annual growth in consumption, U. S. Frasch output would have to increase by 590,000 tons every year. During the first nine months of 1967, on the other hand, U.S. Frasch sulphur registered a gain of only 54,000 tons over the analogous period of 1966.

Total Frasch sulphur production in the Free World (i.e., United States and Mexico), has increased by 250,000 tons during the first nine months of 1967 in comparison with the first three quarters of 1966, whereas an average annual increase of 700,000 tons would be necessary to maintain the present market share at 6% annual growth in consumption.

United States Frasch sulphur mines have already yielded a cumulative total of 119.5 million tons of sulphur in Texas, and over 60 million tons in Louisiana, since they came into production. They are not inexhaustible. A portion of the new Frasch capacity which is now being installed, or planned, on the Gulf Coast will almost certainly be called upon to replace some of the existing capacity. Future production levels in Mexico, on the other

Table III
Free World Frasch Sulphur Inventories
(U.S. and Mexico)
1,000 long tons

Year	United States				Mexico				Combined Total			
	at mines*	ex-mines	Total	% Growth	at mines*	ex-mines	% Total	Growth	at mines*	ex-mines	Total	% Growth
1956	3,544	391	3,935	+ 23.7	572	—	572	+ 63.9	4,116	391	4,507	+ 27.7
1957	3,989	434	4,423	+ 12.4	741	—	741	+ 29.5	4,730	434	5,164	+ 14.6
1958	4,007	435	4,442	+ 0.4	970	—	970	+ 30.9	4,977	435	5,412	+ 4.8
1959	3,375	434	3,809	— 14.3	973	6	979	+ 0.9	4,348	440	4,788	— 11.5
1960	3,309	352	3,661	— 3.9	947	35	982	+ 0.3	4,256	387	4,643	— 3.0
1961	4,084	610	4,694	+ 28.2	946	38	984	+ 0.2	5,030	648	5,678	+ 22.3
1962	4,130	707	4,837	+ 3.0	902	58	960	— 2.4	5,032	765	5,797	+ 2.1
1963	4,108	584	4,692	— 3.0	829	39	868	— 9.6	4,937	623	5,560	— 4.1
1964	3,303	840	4,143	— 11.7	478	46	524	— 39.6	3,781	886	4,667	— 16.1
1965	2,160	1,173	3,333	— 19.6	355	51	406	— 22.5	2,515	1,224	3,739	— 19.9
1966	1,811	844	2,655	— 19.3	368	52	420	+ 3.4	2,179	896	3,075	— 17.8
1962-1966 Cumulative Decreases			— 2,182	— 45.1%			— 540	— 56.2%			— 2,722	— 47.0%
1956-1962 Average Annual % Change				+ 2.1%				+ 7.1%				+ 2.9%
1962-1966 Average Annual % Change				— 16.1%				— 30.3%				— 17.9%

*includes bottoms

hand, are still a matter of conjecture.

The sulphur shortage, now in its fifth year, imposed a heavy strain on the productive capacities of sulphur producers. Existing mines have been pushed to the limit and no spectacular gains in output can be counted upon from these mines. I think that when the year 1967 comes to a close and final figures will become available, we might even see a departure from the trends noticed during the past few years. We could see an increase in the output of natural gas sulphur from Lacq in France, perhaps of the order of 8-9 per cent; a similar increase in Mexican Frasch; a significant increase in "recovered" sulphur in Western Canada, possibly in excess of 23 per cent; and virtually *no* increase in the output of U.S. Frasch sulphur.

Canadian sulphur will continue to grow in the next few years. But it will not end the imbalance between supply and demand in the Free World. Hopes for an early end to the current shortage will depend on the speed with which (1) new reserves are discovered; (2) presently known but still undeveloped reserves are brought into production; and (3) other, high-cost sources and forms of sulphur are tapped and developed.

(1) We have no assurances, and little hope, that despite costly exploration programs, commercial quantities of economically attractive sulphur will be found and developed in time to have an effect on the present imbalance between supply and demand. In December

Figure XII

In 1965, a number of companies have paid a total of $33.7 million in bonuses to the U.S. Government for the right to explore for sulphur on underwater lands off the coast of Texas:

Company	Tracts Successfully Bid	Acres	Total Bonus Paid
Atlantic Refining	5	7,200	$ 4,451,270
Continental Oil	1	1,440	57,600
Conoco-Atlantic-Cities Service	1	1,440	92,254
Shell Oil	3	4,320	123,784
Humble Oil	26	37,440	14,603,000
Freeport Sulphur	7	10,080	11,964,960
Texas Gulf Sulphur-Gulf Oil	7	10,080	2,447,440
TOTAL	50	72,000	$33,740,308

So far, no sulphur of commercial significance has been found, despite costly drilling programs.

1965, for example, a number of companies have paid a total of $33.7 million in bonuses alone, to the U.S. Government for the right to explore for sulphur on 72,000 acres of underwater lands off the coast of Texas. Costly drilling programs have not revealed any commercial deposits of sulphur. (Figure XII).

(2) There are no longer any known large undeveloped reserves of low-cost sulphur left. Continuing shortage and higher sulphur prices have led many companies to re-evaluate small and marginal properties for possible new production. On all continents, projects are being announced to produce sulphur from known, but hitherto uneconomical deposits. Some of these projects involve Frasch sulphur, others sour natural gas and petroleum refinery gas. But it should be remembered that (a) even if all of these projects do materialize as scheduled, the additional supply of sulphur which will be generated from these sources will not suffice to sustain the anticipated growth in sulphur consumption; (b) foreign governments are likely to impose burdensome conditions for the exploitation of reserves located on their territories; (c) many of these projects are temporary substitutes rather than reliable permanent sources of supply. They are not likely to survive the current sulphur shortage.

(3) There are, however, vast known reserves of higher cost sulphur available in many parts of the world such as pyrites and other forms of non-elemental sulphur, as well as certain types of elemental sulphur. The costs of extracting and transporting sulphur from these sources is very high, requiring heavy investment on the part of producer and consumer alike. In contrast, the size of the reserves makes these forms of sulphur eminently suited to become a permanent source of supply for decades to come.

Sulphur economists were convinced that only higher prices would bring out these additional sources of sulphur, so urgently needed in the world today. The price appeared clearly as the key— possibly the only key—to re-establishing a balance between supply and demand, and to generating a new abundance of this vital mineral: sulphur.

If it is axiomatic in our economy that the free interaction of supply and demand in the market place sets the price for the product, it is also true that, during a period of acute shortage such as we are experiencing today, a decision to artificially maintain prices at inadequate levels would tend to interfere with the built-in corrective mechanism available to industry. Higher sulphur prices *will,* we know from past experience, bring forth production from higher-cost sources, and stimulate search for new sources of supply. Sulphur is one of the most plentiful elements occurring in nature; but just as lower-cost Frasch sulphur spelled the doom of Sicilian native ore at the beginning of this century, so, inversely, must higher-cost and non-elemental sulphur remain unavailable in greater quantities until its production becomes more economical. Pressures to maintain sulphur prices at inadequate levels, in discouraging the search for new sources of production, could, in effect, prolong the sulphur shortage.

This, in essence, was the philosophy underlying the recent price increases. I think that the pricing policies of domestic sulphur producers during the past decade, 1956-1966, have faithfully reflected the economics of the sulphur industry. This was a period of continuous oversupply, ending in four years of a growing and eventually acute shortage. The oversupply was reflected in diminishing shares of world markets, fierce competition leading to all sorts of competitive allowances, dwindling revenues from sharply depressed prices, gradual displacement of higher-cost sources of production, and no incentives to explore for new sources.

The years of oversupply profoundly affected the earnings picture of the Frasch producers at a time when costs, wages, and the price of all goods and services continued to climb. But when oversupply gave way to the current period of shortage (1963-   ), recovery was very slow: (Figure XV).

(1) Despite a series of price increases, the posted prices for domestic Frasch sulphur, f.o.b. Gulf Ports, *have actually declined* by 2.5%, during the decade of 1956-1966 which included *four years of sulphur shortage.* During the same period, the Wholesale Price Index *rose* 10%, the cost of mining machinery and equipment increased by 34.7%, and the average hourly earnings in manufacturing industries went up by 42%. Prices of other commodities also registered sharp increases:
non-ferrous metals, by 3.6 per cent
iron and steel, by 11.7 per cent
inorganic chemicals, by 9.1 per cent
pulp and paper, by 5.6 per cent.
(Figure XIV).

(2) During the first half of 1967, the domestic price of sulphur was further increased, to $33.50 per long ton, bright, f.o.b. Gulf Ports. This price, however, was still signi-
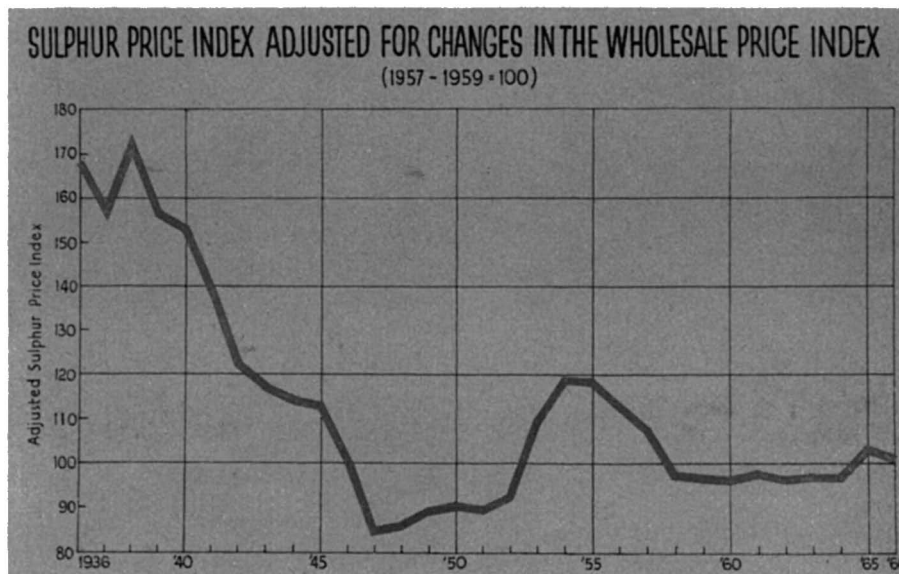
Figure XV

SULPHUR PRICE INDEX ADJUSTED FOR CHANGES IN THE WHOLESALE PRICE INDEX
(1957 - 1959 = 100)

RELATIVE PRICE AND WAGE CHANGES 1956-1966

% Change

Fert'l. Mater. 3.3; Non-Ferrous Metals 3.6; Pulp Paper & Allied Products 5.6; Non-Metallic Mineral Products 7.8; Inorg. Chem. 9.1; WPI 10.0; Iron & Steel 11.7; Finished Steel 17.9; Agric. Mach. & Equip. 28.8; Mining Mach. & Equip. 34.7; Mfg. Wages 42.0; Sulphur -2.5

U.S. Bureau of Labor Statistics   Sulphur: Bright, F.O.B. Gulf Ports, Oil, Paint and Drug Reporter

Figure XIV

Federal Reserve Board's Index of Industrial Production, (Figure VI) and the per capita use of sulphur is a good indicator of the living standards of the population of a given country. Sulphur is also important in defense industries, but half of all the sulphur is consumed in the production of fertilizers which are so essential in modern man's quest for more food, in view of the anticipated growth in world population. A severe or prolonged shortage of sulphur, such as we are experiencing today, may endanger corporate investments of the sulphur-using industries, affect the economic growth of a country, imperil defense requirements, and jeopardize the entire world food production program.

The users of sulphur are asking themselves whether they will have to abandon their plans for expansion, curtail production, close down their plants, convert to more costly raw materials, or experiment with new processes. The world's fertilizer industry needs assurance of an adequate supply of sulphur before it can commit itself to the $6-billion world-wide expansion program contemplated for the next five years. Producers' inventories are down to essential working levels and production is increasing at a slow rate. A significant portion of the demand for sulphur may be destined to remain unsatisfied. Eventually, the shortage of sulphur could result in shortages of the products of which sulphur is a major raw material.

ficantly lower than the export price of $39.00/LT, and it was considerably lower than the prices then charged by foreign producers, notably the Mexican.

But the inadequacy of the domestic sulphur prices in the early part of 1967, Figure XIII was

Figure XIII
Current Price of Sulphur
Compared To That Of Other Products

Product	Cents per pound
Tin	151.000 ¢
Nickel	85.250 ¢
Copper	37.950 ¢
Aluminum	25.000 ¢
Lead	14.000 ¢
Zinc	13.500 ¢
Sulphur	1.496 ¢
Salt	1.090 ¢
Potash	0.920 ¢
Iron Ore	0.470 ¢
Sand	0.180 ¢
Sugar	7.34 ¢
Steel	6.73 ¢
Chlorine	3.25 ¢
Wheat	2.53 ¢

not due to their being lower than those charged, or realized, by other producers. The economic function of a price increase in sulphur, during the period of a critical shortage in supplies, lies in its ability to generate new sources of production. Since the United States is the largest producer and consumer of sulphur in the world, U.S. sulphur prices carry

a great weight when investments in new projects are being considered. Higher sulphur prices would, we felt, steer foreign countries toward greater self-sufficiency in sulphur, making, in turn, available greater quantities of sulphur to U.S. consumers from their natural suppliers, the U.S. sulphur producers. It was then that the decision was made to increase the sulphur prices to their current levels.

Quo Vadis, Sulphur?

The effects of our recent sulphur history are at best still uncertain:

(1) Sulphur is a vital mineral used in the production or processing of very nearly every product of our daily lives. Consumption of sulphur follows very closely the

Figure VI

CORRELATION: FRB INDEX OF INDUSTRIAL PRODUCTION AND U.S. SULPHUR CONSUMPTION
(1957-59 = 100)

W.W.II

FRB Index of Industrial Production
Index of Sulphur Consumption

Table IV

MAJOR INDUSTRIES AND PRODUCTS USING SULPHUR

Acetate	Dyes	Lubricants	Road Surfacing
Acids	Ebonite	Magnesium	Materials
Alcohols	Electroplating	Matches	Rubber Goods
Alum	Explosives	Medicine	Soap
Bleaching Agent	Fertilizers	Metallurgy	Soda
Carbon Dioxide	Fire Extinguishers	Oil Refining	Solvents
Carbon Tetrachloride	Fire Proofing Agents	Paints and Pigments	Steel Pickling and
Casein	Fireworks	Paper Pulp	Galvanizing
Caustic Soda	Food Preservatives	Pesticides	Storage Batteries
Cellophane	Fumigant	Petroleum Products	Sugar
Celluloid	Fungicide	Pharmaceuticals	Sulphonated Oils
Cellulose Esters	Glue	Phenol	Synthetic Fibres
Cement	Glycerin	Photography	Synthetic Rubber
Chlorine	Impregnant	Plastics	Textiles
Coke	Inorganic or Organic Acids	Plate Glass	Tires, Rubber
Copper	Insecticide	Rayon	Uranium
Dehydrating Agent	Leather	Refrigerants	Viscose
Detergents	Livestock Food	Resins	Water Purification

SELECTED CHEMICALS USING SULPHUR

Aluminum Sulphate	Chrome Tan Leather	Hydrofluoric Acid	Phosphorus Sesquisulphide
Ammonium Sulphate	Chromic Acid	Hydrogen Cyanide	Potassium Sulphate
Aniline	Citric Acid	Indanthrene	Salicylic Acid
Anthraquinone	Copper (from Oxide Ores)	Iodine	Sodium Dichromate
Beta-naphthol	Copper Sulphate	Lactic Acid	Sodium Tetrasulphide
Boric Acid	Cresols	Lithium Carbonate from	Sodium Thiosulphate
Bromine from Sea Water	DDT	Spodumene	Sulphite Pulp
Carbon Disulphide	Diammonium Phosphate	Nitrobenzene	Sulphur Dichloride
Cellulose Nitrate	Dicalcium Phosphate	Normal Superphosphate	Sulphur Monochloride
Chloral	Ferrous Sulphate	Oxalic Acid	Sulphuric Acid
Chlorine Dioxide	Flavanthrene	Phosphoric Acid	Titanium Dioxide
Chloroform	Formic Acid	Phosphorus Pentasulphide	Triple Superphosphate
Chlorosulphonic Acid	Hydrochloric Acid		Viscose Rayon

(2) Sulphur producers have instituted allocation programs designed to ensure a judicious distribution of the existing supplies, and halt the drain on inventories. The most recent figures seem to indicate that inventory levels are gradually being stabilized. At the end of September, preliminary estimates put Free World sulphur stocks at 18.8 weeks of supply, compared with 14 weeks at the end of June. But the allocation program will have, in my opinion, drastic effects upon Free World consumption levels this year and the next. Total 1967 consumption of sulphur in all forms in the Free World could very likely register an increase of only some 3.0 per cent; i.e., below the historical growth rate, and well below actual demand, as the production deficit is being artificially reduced.

(3) The shortage of sulphur may also have a paradoxical effect on the phosphate industry which could actually begin to experience a shortage in P_2O_5 production while remaining in a position of overcapacity. It may yet *need* the large inventories which it has, of late, accumulated.

(4) The allocation program initiated by the sulphur producers went hand in hand with price increases designed to stimulate new production. (Figure XVI). Today, even gypsum is being investigated as a possible source of economical sulphur. But the search for new sources of sulphur goes hand in

Figure XVI

SULPHUR COST REPRESENTS A SMALL PART OF THE PRICE OF MOST END-PRODUCTS
A $5.00 INCREASE IN THE PRICE OF SULPHUR REPRESENTS A SMALL ADDITION TO ITS COST IN END-PRODUCTS

hand with a search for economical substitutes for sulphur. Dave Bixby and Dr. Burns will devote, tomorrow, a paper to a discusion of the merits of some of these new processes.

CHAIRMAN SAUCHELLI: Thank you, Dr. Levitsky. Dr. Levitsky has quite a reputation among market research people.

His very thoughtful and comprehensive paper given here this afternoon gives us some idea of why he has earned that reputation.

Because of the hour, we are going to skip questions.

Dr. Levitsky has given us some idea of Quo Vadis with sulphur and I am going to suggest to you folks: Quo Vadis now will be the State Room on the other side of the hall for refreshments, thanks to the generosity of Tom Athey and his associates in the paper industry.

We will meet tomorrow morning and start promptly at nine. We have a wonderful program for you for tomorrow and I hope that most of you at least will be here.

We stand adjourned.

Thursday Morning Session, Nov. 16, 1967

Dr. Vincent Sauchelli and Albert Spillman Moderators

The Round Table Meeting reconvened at nine-ten o'clock a.m.

CHAIRMAN SAUCHELLI: Good morning. It certainly makes a fellow feel fine to see such a good group at this early hour of the morning.

We have an interesting program for today and we also have provided for a coffee break this morning thanks to the generosity of the N.P.F.I.

Now we will proceed with our program.

The fertilizer phosphate industry, based on sulphur as a raw material in the acidulation of phosphate rock, is feeling the effects of rising prices of sulphur, short supply, strong demand, the inevitable result. It is therefore natural for the phosphate industry to explore the claims of alternate methods of preparing available P_2O_5 from phosphate rock.

One of the more popular successful alternates is to acidulate the rock by nitric acid. The method has been successfully employed in many European countries.

The next item on our program deals with the alternate method. Two competent representatives of The Sulphur Institute will evaluate the sulphuric or nitric acid-based phosphates from both the economic and agronomic viewpoints.

Dr. G. R. Burns will discuss the agronomic phase. David Bixby, staff chemical engineer, remembered by most of us for his contribution to The Sulphur Institute Bulletin on Phosphate Fertilizers, will discuss the economic phase.

I am sure we are in for a profitable round of discussion of this subject.

Mr. Bixby will be the first speaker.

tions just mentioned and by others.

A wide-spectrum direct economic comparison of fertilizers made by processes based on nitric acid and sulphuric acid is not possible because of the dissimilarity of the end products. It would be meaningless for example, to make such a comparison between an Odda type nitric phosphate plant and a DAP plant. The Odda plant is constrained to produce much more nitrogen than phosphate, whereas for the straight DAP plant the opposite is true. Similar considerations, varying in degree, apply to the other types of plants to be discussed.

One might consider trying to separate the costs of making N and P_2O_5 in order to compare them directly. However, because of the fact that nitric acid supplies nitrogen and at the same time acts as an acidulant for phosphate rock, the costs of N and P_2O_5 are inseparable.

One approach has been to fix the costs of either N or P_2O_5 in the processes selected for comparison. The differences in the final costs of the other constituent can then be observed. While interesting, such comparisons are not entirely valid, because the cost of N and/or P_2O_5 for various processes will differ. Phosphoric acid from a small plant, for example, will cost more than from a large one. N as nitric acid will cost more than N as ammonia.

Another way of attempting an economic comparison of the relevant processes is to assume equal outputs of N and P_2O_5. This involves taking the most restricted nitric acid process, the Odda process, and adapting the other processes to it by increasing their nitrogen output. This is the approach we have chosen to use, although we realize

Sulphuric or Nitric-Based Phosphates—an Economic and Agronomic Evaluation

D. W. Bixby and G. R. Burns*

D. W. BIXBY: One of The Sulphur Institute's principal functions is to continually study the value of phosphates produced from sulphuric acid and its competitors. Much of the information obtained is reported in our Technical Bulletin No. 8 which has been widely distributed in the fertilizer industry. This paper will report on the value of phosphates produced from sulphuric versus nitric acid. In this study a comparison has been made to determine (1) the relative costs of manufacturing and distributing

the products and (2) the relative plant food value of the phosphatic fertilizers. I will report on the economic portion and my colleague, Dr. Burns, will present the agronomic considerations.

The literature prior to 1966 contains isolated cost estimates for particular products and situations, but none that we knew about which directly compared the more popular nitric phosphates with sulphuric acid-based methods.

I shall not go into the chemistry or technology of any of the processes to be discussed. This has already been done in the publica-

*Assistants to the Directors of Agricultural Research, The Sulphur Institute, Washington, D. C.

that this tends to give an economic advantage to the Odda process by using it as a standard and adapting the conventional processes to the relatively inflexible N/P_2O_5 ratio inherent in the overall Odda process.

The Odda process commonly makes a 20-20-0 product and a co-product, calcium nitrate, calcium-ammonium nitrate, or ammonium nitrate. The co-product contains up to 0.7 tons of nitrogen per ton of nitrogen in the product. Thus, all other processes used for comparison have also been adapted to make the maximum 1-1-0 ratio which can be achieved and to make a co-product containing .7 tons of nitrogen per ton of nitrogen in the product.

For the supplemental co-production of nitrogen with the conventional processes, we have assumed that the nitrogen would be made available in this as urea or ammonium nitrate. When time permits, we hope to make an additional comparison, wherein the additional nitrogen is supplied as ammonia. This comparison would be particularly valid for the increasing number of regions where large amounts of N are applied as anhydrous ammonia. Undoubtedly, such a comparison would show DAP and triple in a very favorable light.

In any economic comparison of processes, the relatively greater flexibility of the sulphuric-phosphoric acid-based processes is of considerable importance. Unlike the nitric phosphates, a product with a high content of P_2O_5 (DAP, triple, phosphoric acid) can be made on a site where low cost phosphate rock is available. This product can then be shipped economically to wherever it is to be used. At the point of use, nitrogen and potash containing products made at, or convenient to, that site may be added to it or added to the soil independently of it, as is the case with anhydrous ammonia.

The location of an Odda type nitric phosphate plant, on the other hand, is limited to the most economical site of nitrogen production. This is because it produces substantially more nitrogen than P_2O_5, and nitrogen is therefore the dominant economic consideration. Nitrogen is everywhere, but the cost plays an important part in de-termining the cost of the necessary hydrogen will vary with location. Because the product and co-product, taken together, are not of sufficiently high analysis to justify shipping great distances, the plant must be near the site of product use and the phosphate rock must be shipped to that point.

The P.E.C. process is less dependent on the site of nitrogen production than is the Odda process. Nevertheless, nitrogen cost of P_2O_5 in the product, whereas for the conventional sulphuric acid-based processes, P_2O_5 is independent of nitrogen cost.

It was intended that the evaluations to be made should be applicable to any location. Thus a direct comparison can be made between fully integrated plants making equal amounts of N and P_2O_5. Those costs, which differ as a result of location will differ in about the same degree for all processes. In Europe, or other places where rock must be imported, the comparison seems fully valid. In the United States and other areas in which it is possible to establish a plant near a source of low cost phosphate rock, the comparisons are still valid. However, they must be viewed in the light of the restricted conditions imposed. If the fertilizer requirements of a locality dictate a lower N/P_2O_5 ratio than is possible with nitric phosphates, then there is no adequate basis for direct comparison. In such a locality, the high N/P_2O_5 production ratio of a nitric phosphate plant would obviously present a serious marketing problem as well.

Six conventional processes were selected for comparison with five nitric phosphate processes. The characteristics of the materials obtained from these processes are summarized in Figure I.

The conventional products used were the current dominant sources of solid N and P_2O_5, normal, triple, DAP, urea and AN. The last two also serve as the nitrogen containing co-product required to make direct comparison with Odda and the other nitric phosphates which have been adjusted to conform with it. All, of course, use ammonia as the primary nitrogen source.

It was considered including potash containing 1-1-1 grades in the formulations, but it was decided to omit them as serving no purpose in these particular comparisons. A possible exception, although we did not deal with it, relates to the fact that many nitric phosphates need to use an expensive grade of high purity potassium sulphate instead of potassium chloride, in order to minimize combustion hazards associated with the products.

In the last column, WSP is the

Selected 1:1:0 Grades from Various Materials

Conventional Products

Made from DAP, Triple Superphosphate (Triple), Normal Superphosphate (Normal), Urea, Ammonium Nitrate (AN)

Formula	Materials	Grade (Maximum)	Co-product	WSP
Normal-1	Normal-Urea	13.9-13.9-0	Urea	98.5
Normal-2	Normal-AN	12.5-12.5-0	AN	98.5
Triple-1	Triple-Urea	23-23-0	Urea	87
Triple-2	Triple-AN	19.3-19.3-0	AN	87
DAP-1	DAP-Urea	28.5-28.5-0	Urea	100
DAP-2	DAP-AN	25.1-25.1-0	AN	100

Nitric Phosphates

Formula	Process	Grade	Co-product	WSP
Odda-1	Odda	20-20-0	CN	30
PEC-1	Carbonitric	16.5-14-0	AN	0
PEC-2	Sulphonitric	14-14-0	AN	30
PEC-3	Phosphonitric	20-20-0	AN	30

percentage of total P_2O_5 in the water soluble form. For the nitrophosphates, the WSP content relates to the specific processes used in this comparison and may be considered typical for these processes now operating. We will have additional comments on this later.

We are aware that a modified Odda process exists, in which the removed calcium nitrate may be treated with ammonia and carbon dioxide to give ammonium nitrate and calcium carbonate as co-products. Or, the extra ammonium nitrate may be incorporated in the NP product. We have not been able to obtain detailed costs on this conversion step, and so do not include it in our comparisons. It would, of course, benefit economically from a higher nutrient concentration in the product and/or co-product, as well as a higher proportion of cheaper N from ammonia. On the other hand, the conversion step must be assigned a cost, and overall, the ratio of N to P_2O_5 output is even greater than the conventional Odda process.

On the next series of slides are shown the relative production cost indices obtained when Odda-1 (Index number 100) is compared with some of the other processes at three sulphur cost levels and two delivered cost levels.

In the interest of simplification and time consumption, only a portion of the data are presented and the cost comparisons are shown as indices.

To prepare this table, the battery limits production costs of an equal amount of N and P_2O_5 in the maximum 1-1-0 grade possible by all of these processes was calculated for a fully integrated plant, then compared to the Odda process, which is set at 100. The cost index refers to the *total* plant production (products and co-products).

Here, for example, in plants making 250 tons each of N and P_2O_5 per day as a 1-1-0 product plus 170 tons of N per day in a co-product, and assuming sulphur at $42.-50/ton, the production cost index of only the triple-urea and normal-urea combinations are lower than the Odda products.

The battery limits production costs of the various nitrophosphates were based, whenever possible, on

Index of Plant Nutrient Costs of Various Processes (Odda- = 100)

Production Cost Indices

Plant capacity and sulphur cost	Process					
	Odda-1	PEC-2	PEC-3	DAP-1	Triple-1	Normal-1
"250" S @ $35.00/ton	100	106	115	106	99	90
"250" S @ $42.50/ton	100	107	117	108	101	92
"250" S @ $50.00/ton	100	108	119	111	104	94

Delivered Cost Indices
Handling & Shipping Charges @ $2.00 per ton of product

Plant capacity and sulphur cost	Process					
	Odda-1	PEC-2	PEC-3	DAP-1	Triple-1	Normal-1
"250" S @ $35.00/ton	100	104	112	100	95	90
"250" S @ $42.50/ton	100	105	114	103	97	91
"250" S @ $50.00/ton	100	107	116	106	100	93

Delivered Cost Indices
Handling & Shipping Charges @ $5.00 per ton of product

Plant capacity and sulphur cost	Process					
	Odda-1	PEC-2	PEC-3	DAP-1	Triple-1	Normal-1
"250" S @ $35.00/ton	100	104	109	94	91	90
"250" S @ $42.50/ton	100	104	110	96	93	92
"250" S @ $50.00/ton	100	105	112	99	96	94

data furnished by companies directly associated with the sale or use of these processes. Sulphuric or phosphoric acids have been charged in at their production costs which reflect the effects of variations in capital investment, operating labor, etc., on those costs. We hope to make comparisons of nitric phosphate processes other than those shown, such as the DSM sulphate precipitation and the TVA sulphate cycle processes when adequate data become available.

Footnotes have been omitted to make the slide more legible. They will, however, be in the proceedings. Tons are metric, for example. Co-products are prilled. Those raw materials which the processes have in common and which are not influenced by process size have been assigned the following costs: phosphate rock, $10.00 per ton; natural gas, $.40 per 1000 cu. ft.

These costs may or may not reflect actual conditions, but being invariable (i.e., the same in cost and quantity used) for all processes permit a direct comparison be-

tween them, and favor neither the sulphuric acid nor the nitric acid-based processes. Sulphur costs were varied. Some costs were calculated from material presented in The Sulphur Institute's Technical Bulletin #8 (revised). This can be inspected here, or a copy may be mailed free of charge from the Institute to those who are interested.

Production costs of Normal-1 were calculated for non-granular normal superphosphate. To obtain indexes for the same product using granular normal add 2 to the index given. Even so, normal super shows up very well indeed even at an appreciable distance from the plant.

The on-site production costs tell only a part of the story, of course. A more meaningful comparison is obtained when on-farm delivered costs are used.

This is the same as the previous slide, but with a $2 per ton product handling and shipping charge added. The more concentrated DAP urea combination has dropped from 106 to 100 (sulphur

at $35.00), and from 108 to 103 (sulphur at $42.50).

Here we have arbitrarily added a $5 per ton of product handling and shipping charge. Indices for the more concentrated materials are lowered. DAP-urea is now under Odda for all assumed sulphur costs, as are both triple-urea and normal urea.

Delivered Cost Indices

Handling & Shipping Charges @ $10.00 per ton of product

Plant capacity and sulphur cost	Process					
	Odda-1	PEC-2	PEC-3	DAP-1	Triple-1	Normal-1
"250" S @ $35.00/ton	100	100	99	81	83	89
"250" S @ $42.50/ton	100	102	103	82	84	90
"250" S @ $50.00/ton	100	102	105	87	88	94

A $10 handling charge. This could be 500 miles at 2¢/ton-mile, or a lesser distance with some other charges included. Significant changes in the relative position of the processes can be seen. When ammonium nitrate instead of urea is assumed to be the co-product, the DAP, triple and normal indices increase about 4-6 units.

Slide 6 shows the relationship of plant nutrient content to freight costs. Of course, this chart illustrates a point well understood by all of you, namely the beneficial effects of higher analysis on shipping costs. It does serve as a convenient way of showing the relationship of the various processes we are talking about. Keep in mind that the plant nutrient contents are the average of the total plant production, i.e., product plus co-product.

Slide 7 is one of a group we made to show the effect of overall product analysis and the cost of sulphur on the relationship of these processes. On the vertical axis, the "cost per ton of plant nutrient" is the battery limits production cost per ton of N and P_2O_5 for both the product and co-product, plus a $5 per ton product (including co-product) handling and shipping charge (say 250 miles at $.02 per ton-mile). On the horizontal axis is shown the cost per metric ton of sulphur. The dotted lines are nitric phosphates, those which are horizontal use no sulphur. Given this handling and shipping charge, the DAP-urea costs less than the least

cost nitric phosphate process, the Odda, up to $50 sulphur, triple-urea and normal-urea up to $66 and $73 sulphur respectively. Note the good showing of normal-urea at this distance, in spite of a lower analysis. Also note the plant capacity. 250 tons P_2O_5 per day is a low capacity for DAP, but the restriction is necessary in order to make this *direct* comparison.

Water Soluble P_2O_5 Content

At this point, a few words about WSP content of these products, as it relates to manufacturing costs.

Sulphuric Acid Using Processes

Essentially, all of the P_2O_5 in the conventional formulations is water soluble. This is not known to be the case with any of the nitric phosphate processes compared here.

Nitric Phosphates

In generalizing about nitric phosphates, there is often a tendency to think of them as having little or no WSP content. This is true of the carbonitric variety. The sulfonitric, phosphonitric, and Odda processes can and do currently produce materials with 25-30% WSP contents. They can also be used to make fertilizers containing theoretically, up to 100% of the P_2O_5 in a water soluble form if so desired. However, increasing WSP results in progressively greater costs and/or reduced analysis of product.

The carbonitric product has essentially no WSP content. WSP can be obtained only from an external source such as DAP. Obviously, such a procedure would not be economically favored.

In the sulphonitric process, sulphuric acid is used, to increase the WSP content of the product. Typical, it is 14-14-0 with 25-30% WSP. Straight substitution of sulphuric acid for nitric acid would

increase the WSP percentage, but would lower the analysis of the final product as well as decrease the N to P_2O_5 ratio. Additional nitric acid and ammonia, in effect ammonium nitrate, would be needed to maintain the original N to P_2O_5 ratio. If the latter procedure is followed, it may be calculated that going from 30% WSP to 100% would cost about $9.00 per ton of P_2O_5, with sulphuric acid at $20.00 per ton (100% basis).

The phosphonitric process can be used to obtain any desired level of water solubility by simply adding enough phosphoric acid to convert all of the P_2O_5 into the monocalcium phosphate form. Of course, increasing the water solubility in this way decreases the N to P_2O_5 ratio (assuming no excess nitric acid and ammonia) to 1:4 or more at 100% WSP. The cost of achieving 100% WSP may be shown to be about $28.00 per ton of P_2O_5 if H_3PO_4 is valued at $60.00 per ton (100% basis.)

In contrast to the sulphonitric process, increasing the WSP of the P_2O_5 produced in the phosphonitric process increases the analysis of the product, resulting also in reduced costs for bagging and shipping per ton of plant nutrients. Even with these advantages, WSP via the phosphonitric process is several times more expensive than via the sulphonitric, largely because of the high cost of the phosphoric acid produced in a relatively small size plant.

In an Odda type process, the amount of calcium removed by crystallization as calcium nitrate determines the degree of WSP of the product. Cooling the slurry resulting from acidulation to about 63°F will precipitate about one-third of the calcium, but no P_2O_5 will be in the water soluble form at this point. By cooling another couple of degrees, sufficient calcium is removed to allow the product to contain 25-30% WSP, which has been typical. Cooling to 50°F yields 50% WSP. At 41°F, two-thirds of the calcium nitrate may be separated and the product P_2O_5 may theoretically be 100% water soluble. In actual practice, a temperature of about 20°F results in about 80-85% WSP. To achieve this degree of water solubility, it is also

necessary to acidulate with 60% acid, rather than the typical 58% nitric acid.

Artificial refrigeration is required to get beyond the 25-30% WSP level. However, vaporization of ammonia to make nitric acid can provide much of the cooling capacity needed, so the refrigeration energy requirement, as such, need not add greatly to production costs. Evaporation of about $1\frac{1}{2}$ additional tons of ammonia per hour will obtain an increase of about 10% in WSP content in a 40 tons per hour 20-20-0 plant.

Nevertheless, increasing WSP must have the effect of increasing production costs by virtue of necessary increase in equipment sizes (heat exchangers, filters, etc.) to maintain the same production rate, or by reduced efficiencies if the same equipment is used for products of varying WSP content.

Further, the additional calcium nitrate removed from the system must be dealt with, either by selling as such, conversion to calcium ammonium nitrate, or conversion to ammonium nitrate and calcium carbonate, all of which could entail added costs. In the latter case, extra processing cost is probably offset to some extent by virtue of a higher NH_3NO_3 ratio in the product.
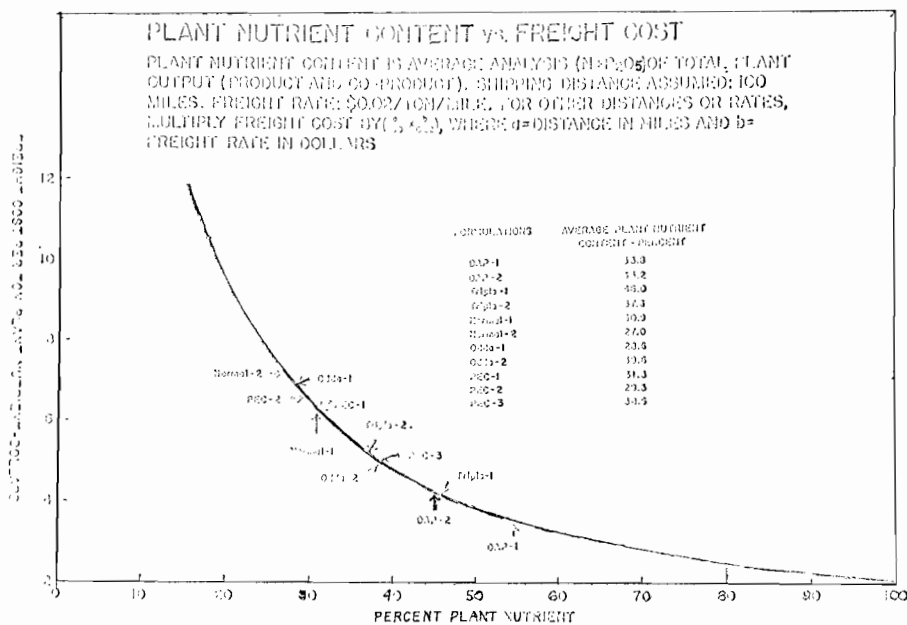
These brief comments on WSP merely serve to illustrate that while varying degrees of water soluble P_2O_5 may be obtained with nitric phosphates, one should not overlook cost considerations associated with obtaining the added WSP.

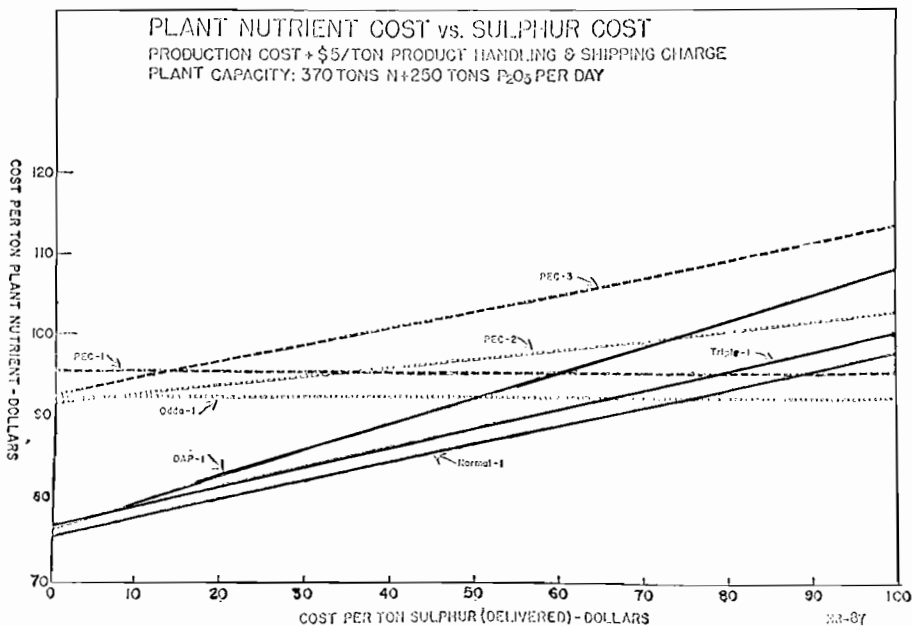(Dr. G. R. Burns then presented his prepared paper.)

Agronomic Evaluation

Dr. G. R. Burns

Evaluation of nitric acid and sulphuric acid-based phosphates from the farmer's point of view is extremely important. Fertilizer manufactures need to make this kind of evaluation in determing which route should be taken if the company plans to increase or initiate phosphate fertilizer production.

There are many farming situations in which the sulphuric acid based phosphates clearly fit the farmers needs better than nitric acid based phosphates. On the other hand, I know of no farming situation under which nitric phosphates are consistently better than the sulphur-based phosphates whenever the farmer follows recommended liming practices in his farm operation. If one is to engage in new phosphate fertilizer production, he should spend at least as much time and effort evaluating his alternatives from the farmers' point of view as from the production point of view.

During the next few minutes, we will consider the agronomically important properties of phosphatic fertilizers; then consider the soil, crop and environmental characteristics that affect responses to phosphate fertilizers; and finally examine these from the point of view of a corn farmer in Iowa.

All of these factors are closely interrelated; nevertheless, let's first consider the properties of the fertilizer itself. Some of the more important fertilizer properties are: water solubility of the phosphorus, particle size, $N:P_2O_5$-ratio, and form of contained nitrogen. Also

Slide 1

PLANT NUTRIENT CONTENT vs. FREIGHT COST

Slide 2

PLANT NUTRIENT COST vs. SULPHUR COST

important is the placement of phosphate fertilizers in the soil.

Regardless of whether the phosphate is water soluble or not, it must become water soluble when it is applied to the soil before plants can use it. Thus, phosphate that is already in a water-soluble form, or that is easily converted to a soluble form in soils, is most available to crops.

The phosphorus in sulphur-based phosphates is usually higher water-soluble. In ammonium phosphates, triple super, and non-ammoniated super-phosphate, it is essentially 95-100% soluble. In contrast, the phosphorus in nitric phosphates is usually less than 50% soluble in water, although more soluble nitric phosphates can be made, usually at a greater manufacturing cost. In the recent fertilizer and marketing conference in Knoxville sponsored by TVA, Mr. Slack said that a survey of major U.S. companies in the fertilizer industry indicated that the drawback to nitric phosphates mentioned most frequently is their limited water solubility. Inflexibility of the $N:P_2O_5$ ratio was also mentioned.

The particle size and placement of a phosphate fertilizer markedly affect the availability of the phosphate to plants. In this regard, it should be emphasized that there is a very strong interaction between particle-size and water solubility in terms of plant response. The availability of low water-soluble phosphates decreased markedly as the particle size increases. This point is emphasized with the present trend toward fertilizer granulation.

If one is thinking in terms of granular phosphates, he should look closely at the agronomic data. Conclusions in published reports are frequently based on the use of small particle sizes, but this is not always clear unless the article is studied thoroughly. For example, the following conclusion came from some of the early work done with nitric phosphates in this country. It is as follows:

"The phosphorus in the nitric phosphate is as available as concentrated superphosphate to corn, cotton, and small grain on acid soils in the Southeastern United States.

Also on these soils, the nitric phosphate products containing nitrogen, phosphate, and potash were fully as effective as commercial-type mixtures of similar NPK ratios for corn and cotton."

But this conclusion is based on experiments conducted with nitric phosphates of very small particle sizes. These same workers also drew the following conclusion concerning nitric phosphates:

"Particle size. The 12-to-50 mesh range in size of particles appears to be about optimum for these materials. There was definite indication that particles coarser than 12 mesh were less effective and some evidence that material finer than 40 mesh was inferior."

As you can see, the particle size of nitric phosphates, or any phosphate as far as that goes, may affect the results which are obtained.

The ratio of $N:P_2O_5$ and the form of the nitrogen in the phosphate fertilizer are very important. Nitric phosphates have relatively inflexible $N:P_2O_5$ ratios, the most common being 1:1, with at least one-half of the nitrogen in the final product being in the nitrate form. Because of their nitrogen content, nitric phosphates are generally not suitable for soybeans, alfalfa and certain other leguminous crops. Furthermore, because of the nitrate content of nitric phosphates, they are not recommended for fall fertilization. And as you all know, fall fertilization is increasing very rapidly, especially in the Mid-West. Many states recommend fall applications of potash, phosphates and ammonium forms of nitrogen, but I know of no state that is recommending fall application of nitrate nitrogen for crops that are to be planted the following Spring.

Because of the inflexible $N:P_2O_5$ ratio, nitric phosphates do not fit recommendations for certain other crops. For example, Iowa State University recommends a 1:4 $N:P_2O_5$ ratio for row fertilization of corn.

Soil, crop and environmental conditions influence crop response to nitric phosphates and to the sulphur-based phosphates. I should like to read a statement to you that

was written by Dr. Robert S. Whitney, Past President of the American Society of Agronomy, concerning pH and Ca content:

"Probably no other practice affects soils as a plant growth medium as much as liming acid soils. Every aspect of the plant's growth and life is touched in some way as acid soils are neutralized by liming. . . . Of particular significance in this regard is the interaction and availability of plant nutrients."

This point is strongly emphasized because recommended rates of liming have been increasing, especially during the last 4 or 5 years. In the future, farmers will lime their soils to near pH of 7.0. This emphasis on liming is extremely important for it is in acid soils that nitric phosphates best compete with the more water-soluble phosphate fertilizers. Even in acid soils, granulation of phosphates of low water solubility generally reduces the phosphorus availability, but in well limed and naturally calcareous soils, the undesirable effects of granulating these phosphates becomes much greater.

Earlier I indicated that nitric phosphates are not suitable for alfalfa, soybeans and certain other legumes because of their high nitrogen content. In addition, because of their high nitrate nitrogen content, they are not best suited for paddy rice. Under waterlogged conditions, much of the nitrate nitrogen may be reduced and lost as a gas.

Environmental conditions are important. In areas with cool climates and short growing seasons, and in areas where winter crops are grown, nitric phosphates of medium to low water solubility may be less efficient than more soluble phosphates, especially on crops with limited root systems, such as potatoes.

Time does not permit a complete summary of research done on "Crop Response to Various Phosphates," but copies of this bulletin on this subject are available on the table here. I would like to read one paragraph from this bulletin to you.

"In general, it may be concluded that when the degree of

water solubility of the contained phosphorus in fertilizers and the granule size are comparable, there is likely to be little if any difference in the effectiveness of materials based on sulphuric, phosphoric, or nitric acid acidulation. However, highly water-soluble phosphates such as ammonium phosphates and the superphosphates will give satisfactory results under all circumstances where crop response to an applied phosphate is possible. While water-insoluble phosphates and those of low water solubility may give equally good results under some circumstances, they are not as universally suitable as are the water-soluble materials."

I would like to expand and alter the last sentence a bit and say, "Because of the high water-solubility of the contained phosphorus and flexibility in N:P_2O_5 ratio of sulphur-based phosphates, these phosphate materials meet a wider range of farmer requirements than do nitric phosphates." If the nitric phosphate is granular, say 6-14 mesh, and contains less than 50% of its phosphorus in a water soluble form, then there are few farmers that can fit it into their total farming program without a decrease in profit.

To illustrate, take a corn farmer in Iowa. He grows corn and soybeans and has a few acres of alfalfa and permanent pasture. Nitric phosphates would not be suitable for his alfalfa and soybeans because of their high nitrogen content. He wants to topdress his permanent pasture with N, P, K, but granular nitric phosphates of water solubility of 50% or less are likely to be much less effective on the pasture than highly soluble phosphates, especially so when they are surface applied.

For his corn he wants to apply a large part of the N, P, and K in the fall of the year, but chances of nitrogen loss are much greater with nitric phosphates than with fertilizers containing nitrogen only in the ammonium form. Because he plans to plant his corn as early as possible in the Spring and in narrow rows, he should use a little starter fertilizer in the row. But nitric phosphates will not fit in this particular case because Iowa State University recommends an N:P_2O_5 ratio of 1:4 in starter fertilizer for corn. Too much nitrogen in the row may adversely affect germination and stand of the corn.

In winding up, I would like to show you a graph illustrating the importance of water solubility of phosphorus under certain conditions. This graph was drawn using field data of Dr. John Webb of Iowa State University.

"Value of corn yield increases per ton of P_2O_5 of varying degrees of water solubility. One ton of P_2O_5 applied in the hill to 66.7 acres of corn at the rate of 30 pounds per acre."

Plotted on the vertical axis on the left is the value of the increased corn yield due to the fertilizer—expressed in dollars per ton of P_2O_5, and on the horizontal axis the per cent water solubility of the phosphate fertilizer. On the vertical axis on the right is plotted the value of water solubility — expressed in dollars per ton of P_2O_5.

The increase in the water-solubility of one ton of P_2O_5 from 0 to 50 per cent resulted in an increased yield of corn worth approximately $560. Or one can say that the value of the water-soluble phosphorus in one ton of the 50% soluble P_2O_5 was $560. The value of 80% water solubility was $685 per ton of P_2O_5 or was $125 more than the P_2O_5 in 50% water-soluble material. This difference in value would

Slide 3

essentially cover the cost of the entire ton of P_2O_5. The increase in value above 80 per cent water solubility is relatively small.

In conclusion, it is extremely important to determine how well a new phosphate fertilizer will meet the agronomic needs of the farmers in the market area before the fertilizer plant is built.

CHAIRMAN SAUCHELLI: I am sure The Sulphur Institute will be glad to mail copies to anyone who is interested.

It is remarkable that in the few years that The Sulphur Institute has been in existence it has prepared and released such fine bulletins. I really have been impressed by the literature issued by the Sulphur Institute.

We have a few minutes for questions on these papers.

MR. BENNETT (Humphreys & Glasco, International, Limited): I would like to start by declaring my interest too. Humphreys & Glasco are licensees of the Norsk Hydro Nitro phosphate process which we believe to be the most advanced technology in this area and I would like to start by making some factual observations on the paper.

CHAIRMAN SAUCHELLI: Which paper are you referring to now?

MR. BENNETT: The paper that has just been delivered.

CHAIRMAN SAUCHELLI: The agronomic phase or the —

MR. BENNETT: Oh, well, they apply to both, really.

In one of Mr. Bixby's tables he showed the grade of material from the Odda type process as 20-20-0. I would just like people to know that you can in fact get up to 23-23-0 with the Norsk Hydro process and a product with as low an N:P ratio as 20-30-0 is also possible. This is achieved by removing the calcium, as described by Mr. Bixby at the end of his paper, by deepfreezing. There is no addition of phosphoric or sulfuric acid required.

The calcium is removed as calcium nitrate and this, in fact, achieves a product containing about 80 per cent (or rather more) of the P_2O_5 in the water soluble form.

This, gentlemen, is a reality. There is a 1650-tons-per-day plant in operation in Norway which uses this process.
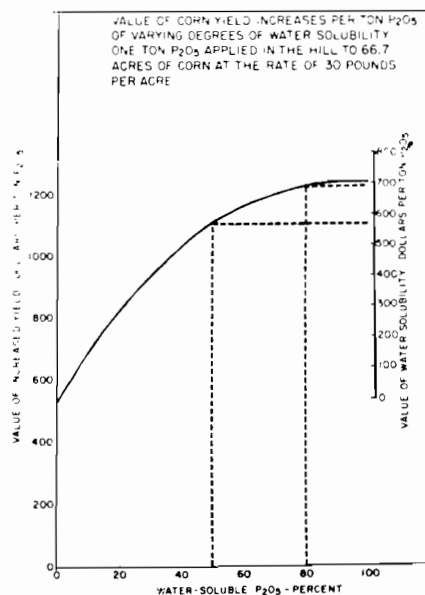
Now I would just like to make some general observations on the economic aspects which Mr. Bixby referred to.

CHAIRMAN SAUCHELLI: Did you have a question that you wanted to ask the speaker?

Or did you want to make a statement?

MR. BENNETT (Michael J. Bennett, Director, H. S. Operations, Humphreys and Glaskow International Limited, London, England): I'm making a statement, really. Is that all right?

CHAIRMAN SAUCHELLI: Go ahead.

Firstly, I entirely indorse his remarks regarding the marketing situation and to consider nitrophosphate you must be in a situation where you can sell roughly twice as much nitrogen as P_2O_5. However, as I understand it, this is the situation in the U.S.A. There are about two tons of N put on the ground for every ton of P_2O_5. Individual companies may well be in different situations, of course, but the overall picture is not unfavorable to nitrophosphates and in such a situation our studies have shown by making comparisons of the sulfuric-phosphoric route as compared to the nitrophosphate route that in fact there is an operating cost saving for the nitrophosphate route in all cases, which corresponds approximately to the amount of sulphur which you save.

If you are making a compound high in P_2O_5 you save rather more per ton of product than one which is low in P_2O_5 but you still save an amount of money in dollars approximately equivalent to the cost of sulphur which would otherwise be required and in this situation the capital cost of the two routes is comparable and it is certainly not more expensive in capital to go the nitrophos route.

I would also just like to make a few observations on the agronomic aspects of the paper to say that these products now, with the bulk of the calcium removed, are in fact closely comparable to products made by the DAP type process and the water solubility is in the 80 per cent region which Mr. Burns showed gave the kind of response that, really, it was hard to better. His last slide showed that.

I would also like to comment on his point regarding the nitrate content of the materials. Now, in the 20-30-0 that I referred to only approximately 25 per cent of the nitrogen is in the nitrate form. Granted you have a byproduct in this case which is ammonium nitrate but you can use that for other crops. So I wouldn't like people to be judging nitrophosphates entirely on the basis that all of the nitrate nitrogen which has to be produced must go along with the P_2O_5. This is not the case.

CHAIRMAN SAUCHELLI: I hate to interrupt you but you are taking too much time.

MR. BENETT: I am just about finished now.

I would just like to say I will be happy to talk to anybody who wants to get some up-to-day information on nitrophosphates.

CHAIRMAN SAUCHELLI: Just one question.

DR. STRELZOFF: Our friend from England covered so much of the ground that I cannot use most of my remarks but I would like to start by a question.

Why is The Sulphur Institute running scared? After all, the three papers that were heard gave a somewhat prejudiced picture. In their presentation it looks as if there is no room whatsoever in the United States for nitrophosphate.

When I joined Chemical Construction in 1941, the Vice President of the Agriculture Chemicals Division of Cyanamid, we were a subsidiary of American Cyanamid Co., also told me there was no room for fertilizers in the United States.

When I offered him the suggestion that we were using ammonium nitrate in Belgium since 1927, he told me that this was an explosive material. So I believe that you gentlemen in 1941 and 1967 seem to be on the same level.

Nitrophosphate will have to be introduced in the United States. In Europe they are using ten millions of tons already of various types and I don't understand at all when an agronomist tells me about soybeans, alfalfa and paddy rice as being the major crops of the United States and Canada. After all, we have something else growing here too.

And there have been comparisons made with natural gas which is certainly not fair because no matter what you say about the ammonia business in the United States, most of the ammonia is possible in the area where natural gas costs 20 cents or maybe 25 cents and I could go on and on. I have quite a list of comments that I would like to make here but I asked Dr. Sauchelli to reserve some time tomorrow after all the papers on nitrophosphates have been presented here to allow me to make some kind of conclusive remarks.

I have only spent 42 years in this kind of business and I have waited for this kind of a situation and when I heard yesterday the Polish lyrics about the rain from the train and so on. I would like to say something about Russian lyrics too.

I will sincerely conclude my maybe too many remarks. But as far as the ratio of P_2O_5 to nitrogen, regardless of what the processes, we know about some processes which can make P_2O_5 to nitrogen or water soluble P_2O_5, 100 per cent, and the ratio is between 1.5 to 2.

I am not offering today any commercial proposal for that kind of process but I would like to refer you to the patent of 1954 and to Mr. Hignett's paper in 1965 when the comparisons between sulphur base and nitric acid base were made in more, let's say, neutral ways than was done by The Sulphur Institute.

Thank you.

CHAIRMAN SAUCHELLI: I said at the beginning that this is a lively subject.

DR. G. R. BURNS (The Sulphur Institute): I would like to say just one or two words.

I wouldn't have come to this microphone — I would have gone to that one but he was bigger. But he sat down, so I don't mind using this one.

But you said that The Sulphur Institute was running scared. I don't know about the running but I know I was certainly standing scared up there.

With regard to the agronomic section that was given, in my case, my paycheck won't be coming from the Sulphur Institute soon and the thing I would like to emphasize to

this group of people here, and very strongly, is that we really need to look at this thing from the point of view of the farmer. Examine the agronomic data. That is what I am saying. Look at it, study it, and just see which fertilizer is best for him.

As the situation presently prevails in this country, I don't think that any farmer that uses nitric phosphates that are presently available in his total farming program will do so at a decrease in profit. I have studied this for a long time and this is my opinion and not based on The Sulphur Institute.

I would like to emphasize that you people need to look at the farmer point of view of this thing. TVA has done a tremendous job because they have looked at it closely from the farmer point of view and I would hope that you gentlemen, you have done it in the past and I would hope that you would do it more in the future. Examine it from the farmer point of view because I believe you will sell more fertilizer that way.

CHAIRMAN SAUCHELLI: Thank you, Dr. Burns.

I feel strongly that those products should be evaluated from the farmer's point of view, the agronomic point of view. After all, you produce for that one purpose and I was glad to include the agronomic angle on the program because I think it is important.

I see that they have started on this coffee break before we really intended them to. So I wonder if I dare call for a 15-minute break now and expect you to return to your seats right after that.

CHAIRMAN SAUCHELLI: You know one of the advantages and one of the purposes of our organization is to encourage discussion, questions from the floor and so on and we want to continue on that basis, however, we have a program to carry through and we will start with our program now.

In the production of superphosphates operators have experienced at times differences in the reactivity of rock from different suppliers.

I know of several instances in which the superintendent was unable to find a satisfactory reason for this difference. Like so many persons, he assumed that phosphate rock is a chemical compound, that it had a definite molecular composition such as ammonium sulphate might have.

Apatite, which is the principal mineral in phosphate ores, varies widely in chemical reactivity and thermal stability, as is experienced by the differences in how they behave in acidulation processes.

The next speaker has devoted a great deal of time and effort in trying to find out the why of such behavior.

On one of my visits to the TVA Fertilizer Research Center I was greatly impressed with the results of their study to correlate the mineralogical compositions of apatites with their reactivity. The study involved at least 55 samples of apatites from 47 domestic and foreign commercial deposits but let us have the story from the man who was responsible for the work.

It is a pleasure to call on James R. Lehr of the Division of Chemical Development, Tennessee Valley Authority. His subject is: Variations in Compositions of Phosphate Ores and Related Reactivity.

Variations In Composition of Phosphate Ores and Related Reactivity

James R. Lehr

The principal phosphate mineral in commercial phosphate ores is usually considered to be apatite, which refers to a group of structurally related minerals that vary widely in physical, chemical, and crystallographic properties. For examples, the apatites in igneous and metamorphic deposits (Kola Peninsula, Canada, Sweden, South Africa, Missouri) have compositions close to that of fluorapatite, $Ca_{10}(PO_4)_6F_2$, but the microcrystalline sedimentary apatites show wide departures from this composition because of extensive substitutions for calcium and phosphorus.

The mineralogy and structural properties of many apatite minerals have been investigated extensively (2, 9, 15, 17, 20) as have the gross chemical compositions of phosphorus rocks (15, 16, 19), but no systematic survey by modern analytical methods of the apatites in commercial phosphate ores has been reported. There is a critical need for this information, however, if we are to develop a rational basis for correlating the physical and chemical properties of commercial ores with their thermal stability and chemical reactivity.

This report on TVA's characterization studies describes the results of examinations of apatite concentrates from 145 phosphate rocks that represent almost all the commercial deposits in the world. The methods of investigation included x-ray powder diffraction, petrography, infrared spectroscopy, electron microscopy, and chemical analysis. Correlations that have been established between chemical data and results of instrumental examinations now make it possible to estimate rapidly the type of apatite in a particular ore or concentrate. Details of the laboratory preparation of phosphate rock samples, analytical methods, and instrumental procedures have been described elsewhere (15, 17, 20).

Our samples of 145 phosphate rocks were representative high-grade commercial apatite concentrates that had not been calcined or otherwise altered. In preliminary studies of four selected phosphate rock concentrates, the homogeneity of the apatite component was established by characterizations of subfractions separated according to particle size and morphological form. No significant variations were found. Elimination of this possible source of variability permitted the examination of commercial concentrates without further treatment. On the other hand, ores from a particular geographical area differ enough with respect to their apatite component to require characterization to guide further processing.

Chemical Characteristics

Although commercial phosphate concentrates consist mainly of apatite and have very similar gross chemical compositions (19), they differ markedly in the manner in which the chemical constituents are combined, particularly with regard to the apatite mineral. Over 25 elements have been reported to occur in apatites. Igneous and metamorphic apatites (Kola, Canada, South Africa, Missouri) contain the largest number of substituting elements, but the amounts of each are usually significant. On the other hand, the substitutions in sedimentary phosphorites are fewer in number, but they have considerable analytical significance.

The important elemental substitutions in sedimentary apatite are illustrated in Table I. The sub-

Figure 1

Relation Between Sodium and Magnesium Contents of Apatites and Degree of Carbonate Substitution.

SUBSTITUTIONS IN FLUORAPATITE

$$Ca_{10}(PO_4)_6F_2$$

CONSTITUENT ION	SUBSTITUTING ION
Ca^{+2}	Na^{+1}, Sr^{+2}, Mn^{+2}, K^{+1}, U^{+4}
	Mg^{+2}, R.E.$^{+2,3}$ (Y, Yt, Ce)
P^{+5}	C^{+4}, S^{+6}, Si^{+4}, As^{+5}, V^{+5}, Cr^{+6}
F^{-1}	OH^{-1}, Cl^{-1}
O^{-2}	F^{-1}, OH^{-1}

$$(Ca, Na, Mg)_{10}(PO_4)_{6-x}(CO_3)_x F_y F_2$$

Table I

stitutions of CO_3 for PO_4, F for O, and Na, Mg, K, and rare earths for Ca are almost universal. However, the amounts of K and rare earths are usually so small that they can be ignored in the general empirical formula that represents the apatite compositions. The four major constituents, Ca, P, CO_2, and F, provide a satisfactory basis for correlating the mineralogical properties of the apatites.

Since the substitutions are interrelated, the apatite compositions change systematically (17). Electrostatic imbalance resulting from substitution of CO_3^{-2} for tetrahedral PO_4^{-3} is only partially compensated by F in vacant oxygen sites, so that a coupled monovalent cation substitution for calcium is necessary. These relationships are shown in Figure 1, which includes results for about 100 apatites whose

complete compositions have been determined.

The sodium content of natural apatites ranges from 0.05 to 1.70% Na_2O and the magnesium content from 0.05 to 0.65% MgO, in direct proportion to the degree of carbonate apatites substitution. In the most highly substituted carbonate about 7% of the calcium and 25% of the phosphorus has been replaced in the fluorapatite structure.

At least two important conclusions with regard to commercial concentrates can be drawn from these chemical characterizations. It is now established that the apatite mineral is a significant source of sodium and magnesium, as well as fluorine, in wet-process phosphoric acid. The apatites represented by open circles in Figure 1 contain nearly all the sodium and magnesium in their repective concentrates, and this sodium and magnesium obviously cannot be removed by beneficiation. Exceptions are denoted by the solid circles that represent concentrates in which the sodium and magnesium are distributed between the apatite mineral and occluded accessory minerals such as chlorites, sodium bentonite, volcanic glass, and glauconite.

Another important consideration is the effect of these substitutions in the apatite on the grade of the commercial concentrate that can be obtained. Comparison of typical apatite compositions from four domestic ore deposits (Table II) shows a range in P_2O_5 content

from 33.4 to 39.2%, as compared to 41.6% for stoichiometric fluorapatite. In Figure 2, the theoretical
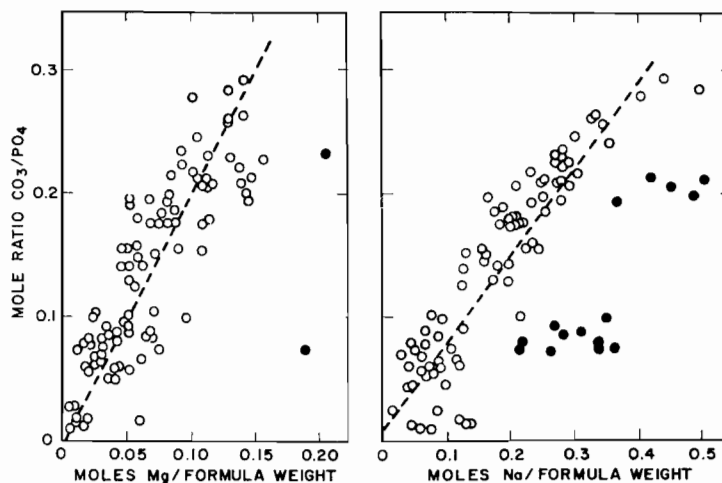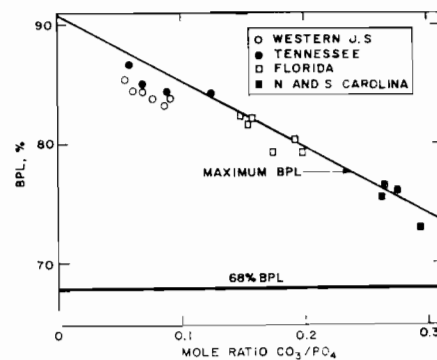

Figure 2

Limits of Benefication of Different Phosphate Rocks.

grades of the apatites are compared with an arbitrary level of concentration (68% BPL). An efficiency of 90 to 95% must be obtained in the beneficiation of the most highly substituted apatites to obtain the indicated P_2O_5 grade, whereas only 75 to 80% efficiency is required to obtain the same grade when the apatite has a low degree of substitution. It is apparent that concentrates with the same P_2O_5 grade may differ considerably in the amounts of associated gangue minerals they contain.

Crystallographic Characterization

Variations in the chemical constituents of the apatite structure are reflected in differences in crystallographic unit-cell dimensions, optical properties, and infrared adsorption spectra.

TABLE II
Compositions of Apatites in Domestic Phosphate Rocks[a]

Source	Empirical formula $Ca_aNa_bMg_c(PO_4)_x(CO_3)_yF_z$						Mole ratio		a-axis of unit cell, A.	Composition, %	
	a	b	c	x	y	z	$(CO_3+F)/10CaO$	CO_3/PO_4		P_2O_5	BPL
Western U. S.	9.96	0.08	0.05	5.59	0.31	2.08	2.40	0.055	9.359	39.23	85.5
	9.65	0.29	0.24	5.48	0.34	2.19	2.62	0.061	9.365	38.72	84.4
	9.85	0.26	0.03	5.47	0.38	2.23	2.65	0.069	9.360	38.66	84.3
	9.77	0.34	0.04	5.43	0.42	2.10	2.58	0.078	9.360	38.42	83.8
	9.79	0.30	0.05	5.39	0.47	2.09	2.61	0.088	9.354	38.13	83.1
	9.77	0.27	0.05	5.42	0.49	2.21	2.76	0.091	9.362	38.45	83.8
Tennessee	9.90	0.12	0.03	5.62	0.34	2.22	2.58	0.060	9.356	39.71	86.6
	9.96	0.11	0.03	5.53	0.37	2.23	2.61	0.066	9.358	38.95	84.9
	9.88	0.13	0.05	5.46	0.48	2.18	2.70	0.089	9.351	38.64	84.2
	9.86	0.14	0.05	5.43	0.68	2.24	2.96	0.126	9.348	38.54	84.0
Florida	9.74	0.16	0.05	5.27	0.78	2.21	3.07	0.147	9.339	37.73	82.3
	9.66	0.25	0.05	5.23	0.82	2.34	3.27	0.156	9.337	37.66	82.1
	9.70	0.23	0.05	5.22	0.81	2.32	3.22	0.154	9.338	37.52	81.8
	9.63	0.23	0.08	5.08	0.98	2.47	3.58	0.193	9.334	36.92	80.5
	9.62	0.25	0.08	5.05	0.99	2.31	3.43	0.197	9.330	36.42	79.4
	9.75	0.21	0.08	5.08	0.89	2.23	3.20	0.174	9.327	36.32	79.2
North and South Carolina	9.45	0.33	0.13	4.82	1.27	2.38	3.86	0.264	9.324	35.08	76.5
	9.42	0.40	0.10	4.77	1.30	2.52	4.05	0.273	9.322	34.98	76.3
	9.50	0.33	0.13	4.78	1.26	2.11	3.55	0.262	9.322	34.68	75.6
	9.47	0.44	0.14	4.61	1.35	2.39	3.95	0.292	9.326	33.40	72.8

[a]From data in references 15 and 17.

X-Ray Examinations. — Precise measurements of the unit-cell parameters of apatites in phosphate rocks have been obtained from high resolution x-ray powder diffraction patterns; the instrumental conditions and computation methods are described elsewhere (17, 20). The unit-cell dimensions change regularly as the chemical composition changes. The correlation shows a regular change with increasing degree of substitution of CO_3 for PO_4, and also shows an additive effect of CO_3 and F as PO_4 is replaced. The apatites described in Table II and illustrated in Figure 3 show these relationships. The statistical correlation shown in Figure 3 is highly significant; there is a progressive change in unit-cell dimensions *a* and *c* as $(CO_3 + F)$ replaces PO_4 in the apatite structure. It is possible, therefore, to estimate an apatite's composition from its unit-cell data on the basis of the chemical correlations that have been established.

Crystallite sizes of the apatites, which are determined from the broadening of selected diffraction peaks in the x-ray powder patterns, show a general decrease with increasing substitution of carbonate,
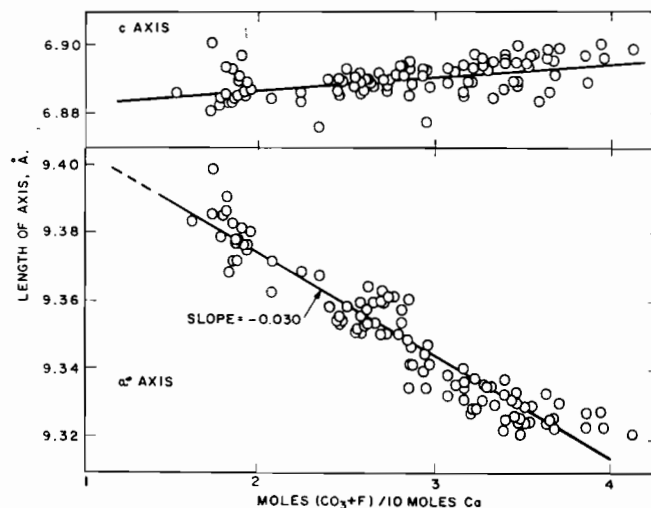

Figure 3

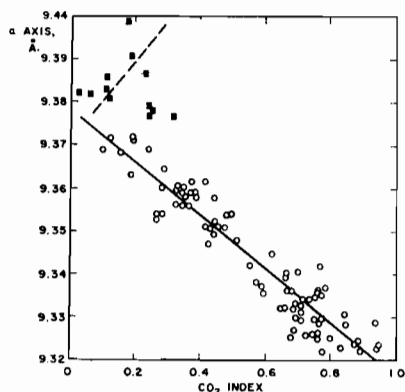**Relationship Between Degree of Substitution and Unit-Cell Dimensions of Apatite.**

sodium, and magnesium. Sizes range from microscoptically coarse crystals for igneous and metamorphic apatites to submicroscopic crystallites only a few hundred Angstrom units in the most highly substituted sedimentary apatites. This size trend has been verified by electron microscope examinations now being made. A similar dependence of crystallite size on concentrations of Na, Mg, and CO_3 has been reported for syn-

thetic and biological apatites (14). Thus an indirect relationship between the chemical reactivity and the chemical composition of apatites is implied by these marked differences in average crystallite size.

Infrared Examinations. — The infrared absorption spectra of the apatites reflect changes in the nature and relative amounts of the chemical constituents. Fluorapatite and its carbonate-substituted varie-

ties, francolite, which commonly occur in commercial ores, differ mainly in the relative intensities of C-O and P-O absorption bands in their spectra (15). The ratio of intensities of selected C-O and P-O bands, defined here as the "CO$_2$ index," is directly proportional to the weight ratio CO$_3$:PO$_4$ in the apatite, and is independent of concentration effects.

Thus, the "CO$_2$ index" can be correlated with chemical composition or with crystallographic properties; the correlation between the unit-cell dimensions a and the CO$_2$ index is illustrated in Figure 4.

Figure 5

Correlation of Refractive Index with CO$_2$ Content of Apatite.

Figure 4

Correlation of CO$_2$ Index with a-Axis Dimension of Apatite.

This is a useful method for rapid preliminary estimation of the form of an apatite.

Petrographic Examination. — Although microscopic examinations provide much useful information on the accessory minerals and their mode of aggregation with an apatite, the colloidal form of most apatites precludes a detailed optical study. Refractive index is the most useful property, but impurities occluded in the apatite aggregates, especially free carbonate minerals, are a source of error in the measurements.

Although apatite may exist in several textural forms in a concentrate, it is homogeneous in composition and has a uniform refractive index. This established correlation between chemical composition and refractive index also can be used for rapid estimation of apatite composition, as illustrated in Figure 5.
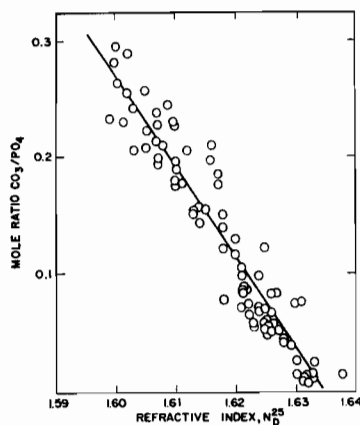
Thermal Stability

When phosphate rock is upgraded by calcination, adsorbed moisture is driven off and organic matter is destroyed. More importantly, however, carbonate and some fluorine are expelled from the carbonate apatite structure. This alteration of the original apatite affects its chemical reactivity because of changes in its physical and chemical properties (10, 15). Since the thermal stability of carbonate apatites decreases with increasing degree of substitution, phosphate rocks do not show uniform behavior on calcination.

The results of recent calcination studies (15) illustrate the na-

ture of these thermally induced alterations. The 17 phosphate rocks described in Table III were selected to provide a wide range of compositions representative of important geographical deposits. In these studies, the changes in composition, crystallite size, and unit-cell dimensions of the apatites were determined at different stages of calcination.
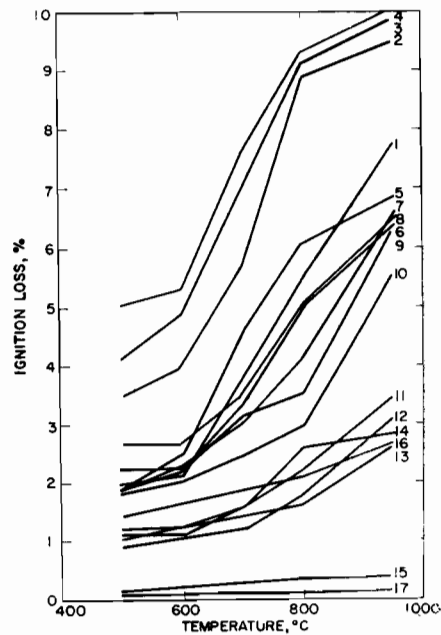
As shown in Figure 6, one-

Figure 6

Weight Losses of Apatites on Calcination.

TABLE III

Apatite Concentrates Used in Calcination Study

Sample No.	Source	Length of a axis, A.	Mole ratio	
			$(CO_3+F)/10Ca$	CO_3/PO_4
1	South Carolina	9.322	4.05	0.273
2	Gafsa	9.324	3.95	0.285
3	North Carolina	9.324	3.86	0.264
4	North Carolina	9.326	3.65	0.259
5	South Carolina	9.326	3.48	0.211
6	Florida	9.330	3.43	0.197
7	Florida	9.331	3.50	0.209
8	Florida	9.334	3.58	0.193
9	Morocco	9.336	3.41	0.185
10	Florida	9.338	3.26	0.156
11	Morocco	9.347	2.92	0.098
12	Togo	9.351	2.80	0.075
13	Tennessee	9.356	2.63	0.060
14	Wyoming	9.365	2.62	0.061
15	Australia	9.369	2.23	0.012
16	Ocean Island	9.377	1.91	0.044
17	Quebec, Canada	9.381	1.95	0.008

third to one-half of the total weight loss, representing organic matter and adsorbed water, occurs below 500°C., without change in properties of the apatite. Above 500°C., however, the additional weight loss corresponds closely to the combined amounts of CO_2 and F expelled from the carbonate apatite. The total weight loss for each phosphate rock thus is directly proportional to the amount of $(CO_3 + F)$ initially substituted for PO_4.

The decrease in thermal stability of the apatite with increasing degree of substitution is illustrated also by these weight-loss curves and by changes in CO_2 content of the selected samples shown in Figure 7. Highly substituted apa-
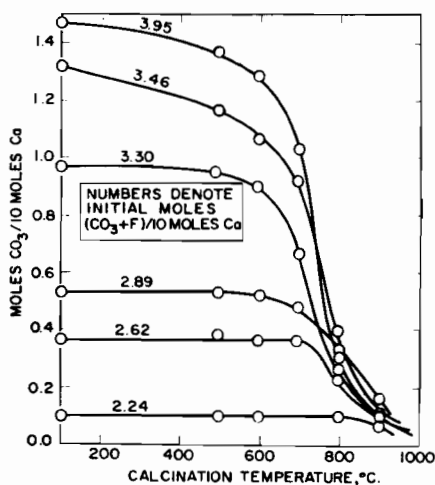
Figure 7

Relationship Between Thermal Stability and CO₂ Content of Apatites.

tites begin to alter between 500°C and 600°C., whereas those with the least substitution are stable to temperatures between 700° and 800°C.

The unit-cell dimensions and compositions of the 17 carbonate apatites changed regularly during calcination, and those of the final products closely approached those of fluorapatite. All 17 samples showed the same relationship, which is illustrated in the composite plot in Figure 8. The change in unit-cell dimensions with decreasing $(CO_3 + F)$ substitution is the same linear relationship that was found for the natural apatites. Calcination, therefore, causes a gradual structural alteration of the carbonate apatite, rather than an abrupt decomposition and formation of fluorapatite.
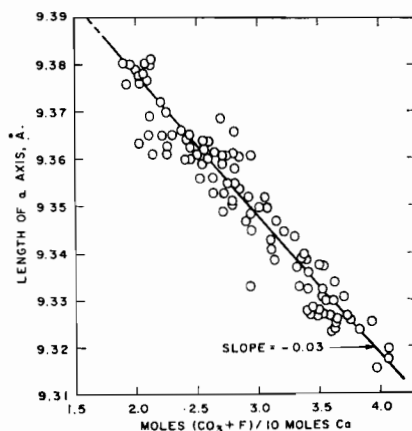
Figure 8

Relationship Between Changes in Composition on Calcination of Apatite and Length of a-Axis.

There is a marked increase in crystallite size during the final stage of calcination when the apatite approaches the composition of fluorapatite. As shown in Figure 9,
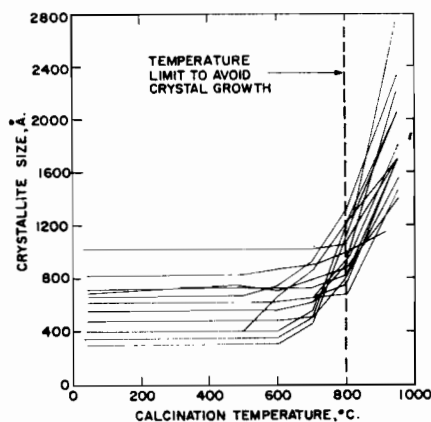
Figure 9

Recrystallization of Apatite on Calcination.

this recrystallization occurs just above 800°C., after most of the CO_2 and excess fluorine has been evolved. During this recrystallization of fluorapatite from the defect apatite, the excess calcium crystallizes as CaO, and some dendritic CaF_2 forms also by reaction of the CaO with the liberated fluorine. Physical changes occur in the apatite aggregates that tend to decrease their chemical reactivity. Crystal growth of the apatite results in decreasing specific surface, loss of capillary structure, and a partial filling of the pores by the newly formed CaO and CaF_2 phases.

Because of the relationship be-

tween thermal stability and the mineralogical form of natural apatites, considerable care must be taken in selection of conditions of calcination. For example, advantage may be taken of the lag between the evolution of volatile constituents and the onset of recrystallization (Figure 9) to obtain a substantial increase in P_2O_5 content without permitting marked changes in physical texture.

Chemical Reactivity

Since commercial processes demand a very high efficiency of extraction of P_2O_5, the total dissolution process must be considered in defining chemical reactivity. The overall rate of reaction can best be represented as a summation of several recognized factors that influence the kinetics of the heterogeneous reaction. These factors can be grouped according to the initial properties of the phosphate rock and to the coating reactions that occur during acidulation.

Many investigators have related the initial physical and chemical properties of phosphate rock to their solubility behavior in mild solvents. These reactivity indexes, however, provide an indication of relative reactivity, but show only a rough correlation with the actual reactivity of phosphate rocks in mineral acids (8).
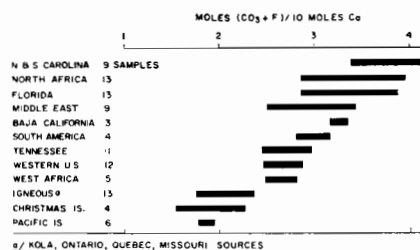
As illustrated in Figure 10, the

Figure 10

Degree of Substitution of Apatites from Different Geographical Sources.

geographical deposits, when arranged according to apatite composition, fall into the general order of reactivity that has been observed in commercial practice. The figure also shows that phosphate rocks from the same geographical source may differ considerably in composition.

Moreover, the physical prop-

erties of these apatites are related to their chemical composition. As the degree of carbonate substitution increases, there is a progressive decrease in crystallite size (2, 15), an increase in specific surface (3, 8, 12), and changes in pore volume that lead to a lowering of bulk density (4, 12). Many correlations of these physical parameters with the behavior of the phosphate rocks in neutral ammonium citrate solution and 2% citric acid have been reported (2, 3, 5, 8, 11, 12, 15, 16). An example of such a correlation is shown in Figure 11,

Figure 12

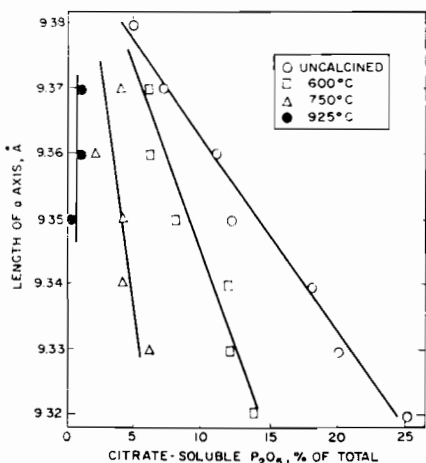Relationship Between Crystallite Size and Rate of Dissolution of Apatite in Acid.

Figure 11

Relationship Between Citrate Solubility and Composition of Raw and Calcined Apatites.

which also illustrates the change in solubility on calcination.

Thus, when limiting salt concentrations are avoided, the dissolution of apatitic phosphate rocks is diffusion controlled (6, 13) and the dissolution is dependent on the physical characteristics of the apatite. These differences in solubility become less significant in mineral acids, and fail to account for the variations found in commercial processes. For example, Figure 12 shows that the time required for total dissolution in 2% HNO_3 of 25 sedimentary apatites which represented a wide compositional range (15), ranged only from 0.5 to 10 minutes. These dissolution times do not account for the variations encountered in commercial processes. The additional factor that must be considered is the crystallization of insoluble reaction products at the reaction interface. Surface properties of the phosphate
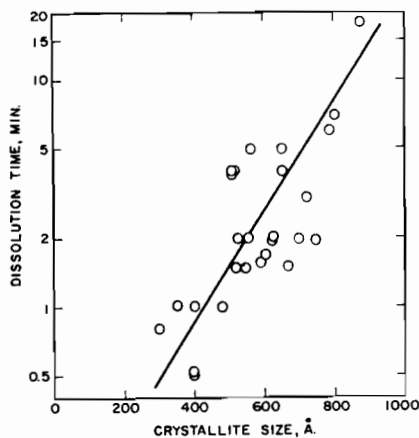
rock particles are altered by deposition of precipitates within pores and as surface coatings (1, 7, 8, 18). These precipitates impede the diffusion of both the acid and the dissolved products. In sulfuric acid processes, the interfering precipitates have been reported to be calcium sulfates (1, 7). With HNO_3, the formation of calcium fluoride coatings was found to be the controlling factor, and the precipitation of calcium fluoride was strongly influenced by the amount of dissolved aluminum.

The time required to reach a critical supersaturation level obviously depends upon factors that control the initial dissolution rate as well as upon process conditions, but may also be affected markedly by dissolution of accessory minerals. Supersaturation can be hastened by dissolution of accessory calcium-containing minerals, or delayed by complex formation, as
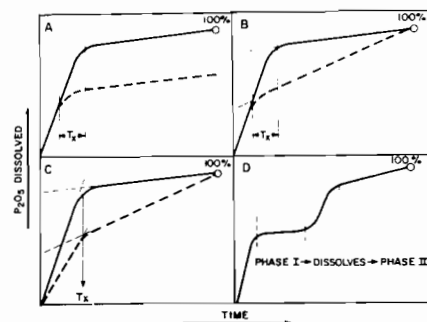

Figure 13

Models Illustrating Effects of Initial Dissolutions and Subsequent Coating Reactions on Total Dissolution of Phosphate Ores.

when aluminum dissolves and complexes fluoride. When the precipitation stage is reached, the formation of coatings slows down the rate of solution of the apatite.

The grouping of factors according to these two recognized stages of phosphate rock dissolution is shown diagrammatically in Figure 13. In example A, two phosphate rocks with the same apatite composition, initial rate of solution, and coating mechanism may differ considerably in total time required for dissolution due to a time differential, T_x, in the onset of the coating reactions. Example B is similar to A, but illustrates the effect of texture of the coating phase on the total dissolution time. Another example of compensating effects is shown in example C; initial differences in solubility of two phosphate rocks may be offset by dissimilarities in the coating structures. Example D is a more complex mechanism first described by Aalto et al. (1). Here, the total dissolution can be divided into two cycles. Formation of a metastable coating phase slows down dissolution in the usual manner, but during the time of phase transition the original dissolution rate is restored as surfaces of rock particles are temporarily re-exposed.

Our results indicate that inhomogeneity of the apatite mineral is not a contributing factor to difficulties in its dissolution. Chemical and crystallographic studies of phosphate rock residues after successive stages of dissolution in dilute (2%) nitric acid showed no changes that would indicate a selective dissolution process. Similarly, phosphate rock residues recovered from gypsum filter cakes had the same chemical and crystallographic properties as the initial rock, but the particle surfaces had become sealed off by calcium sulfate coatings.

Conclusions

When all the stages of the dissolution process are included in a definition of chemical reactivity, it is apparent that reactivity indexes based on the initial physical and chemical characteristics of a phosphate rock have only limited applications. They are useful for characterizing new phosphatic de-

posits and for detecting gross variations in concentrates, but they are unsatisfactory for predicting the behavior on dissolution in commercial acid reagents.

A meaningful method for evaluating the chemical reactivity of a phosphate rock must consider not only the dependence of its rate of dissolution on its mineralogical composition, but also the restrictions imposed by precipitation reactions. A successful laboratory procedure must employ standardized conditions that closely simulate the conditions of acid concentration, temperature, and solid-to-liquid ratios used in the proposed commercial process. These factors strongly influence the precipitation reactions, but their effects are minimized or avoided in conventional laboratory methods for measuring solubility rates.

In conclusion, it is unlikely that a standardized reactivity test, if available, could be broadly applied, since the chemical processes operating variables, and nature of concentrates fed to the processes vary so widely among manufacturers. The reliable procedures for forecasting chemical reactivity that are in use are those based on simulated process conditions rather than those that merely consider the properties of the phosphate rock.

Literature Cited

1. Aalto, E., and Vahervuori, T. K., *Proc. of I. S. M. A. Tech. Conf.*, Helsinki, Finland, September 1963. Paper No. 14.

2. Ando, J., Matsuno, S., and Watanabe, T., *Kogyo Kagaku Zasshi 67*, 2014-19 (1964).

3. Carbona, F., and Cuzin, J. L., *Proc. Natl. Acad. Sci., India 25A*, Pt. 6, 550-61 (1956).

4. Caro, J. H., and Freeman, H. P., *J. Agr. Food Chem. 9*, 182 (1961).

5. Caro, J. H., and Hill, W. L., *J. Agr. Food Chem. 4*, 684-87 (1956).

6. Chepelevetskii, M. L., *Trans. Sci. Inst. Fert. Insectofungicides (USSR) 137*, 10 (1937).

7. Dahlgren, S. E., *Proc. of I. S. M. A. Tech. Conf.*, Stockholm, September 1959.

8. Dee, T. P., Nunn, R. J., and Sharples, K., *Fertiliser Soc.,*
(*Engl.*), *Proc., No. 44*, January, 1967, London.

9. Deer, W. A., Howie, R. A., and Zussman, J., *Rock-Forming Minerals*, Vol. V, John Wiley & Sons, Inc., New York (1962).

10. Freeman, H. P., Caro, J. H., and Heinly, N., *J. Agr. Food Chem. 12*, 479-86 (1964).

11. Hampton, M. G., *Proc. of I.S.M.A. Tech. Conf.*, Edinburgh, Paper No. 7, September 1965.

12. Hill, W. L., Caro, J. H., and Wieczorek, G. A., *J. Agr. Food Chem. 2*, 1273 (1954).

13. Huffman, E. O., Cate, W. E., Deming, M. E., and Elmore, K. L., *J. Agr. Food Chem. 5*, 266 (1957).

14. LeGeros, R. Z., Trautz, O. R., LeGeros, J. P., and Klein, E., *Science 155*, 1409-11 (1967).

15. Lehr, J. R., McClellan, G. H., Smith, J. P., and Frazier, A. W., "Characterization of Apatites in Commercial Phosphate Rocks," *Proc. Intern. Colloquium on Solid Inorg. Phosphates*, May 1967, Toulouse, France.

16. Marshall, H. L., Radar, L. F., and Jacob, K. D., *Ind. Eng. Chem. 25*, 1253 (1933).

17. McClellan, G. H., and Lehr, J. R., "Crystal Chemical Investigation of Natural Apatites," presented at *Geol. Soc. Am.*, 1967 Annual Meeting, November 20-22, New Orleans, La.

18. Pozin, M. E., Grigorjeff, G. S. Kopylev, B. A., and Sokolova, A. D., *Zh. Prikl. Khim. 31*, 693 (1958).

19. Slack, A. V. (Editor), *Phosphoric Acid Monograph*, Vol. II, Chapt. III, Marcel Dekker, Inc., New York, 1967. In press.

20. Smith, J. P., and Lehr, J. R., *J. Agr. Food Chem. 14*, 342-49 (1966).

CHAIRMAN SAUCHELLI: Thank you, Jim.

I imagine many of you must feel the way I felt listening to Jim's talk. I was utterly fascinated by the research into the characteristics and behavior of these phosphate rocks.

Maybe the future superintendents in drawing up specifications will have to know a great deal more about the product that he purchases than is the case now with conventional methods.

I know Bill Waggaman said he was fascinated and also Kenneth Jacob because of their long association with phosphate and phosphate rocks.

Are there any questions.

Jim, I congratulate you on that splendid talk. We are, I think, very honored to have you present a paper like that to this group.

The next paper fits in well with the TVA study. This is work done in the W. R. Grace & Company Research Division laboratories concerning the Mineral Contaminants in Florida Phosphate Rocks.

The research was carried out by Frederick Swanson under the supervision of Cass C. Legal. Mr. Swanson will present the paper but I am going to ask Mr. Legal to stand up and be recognized.

Mineral Contaminants In Florida Phosphate Rock

V. F. Swanson and C. C. Legal

A petrographic study was made of the type and sources of mineral contamination occurring in phosphate rock products from Florida. Emphasis was placed on contaminants in the screened rock (+1 mm) since this portion of the product undergoes no physical benefication except for scrubbing to remove slimes. Since iron and aluminum content of the finished product affect the salability, special emphasis was placed on identifying types and sources of these contaminants and relating chemical composition to visual characteristics.

Wavellite derived from the overburden was the major aluminum contaminant, with some aluminum being included as secondary clayballs. Iron occurred as phosphates in the overburden, and as collodial oxides included in the phosphate pebbles. Chert and lime-

stone contamination were derived from the formation underlying the phosphate matrix.

Introduction

Iron and aluminum are common contaminants of Florida phosphate rock, and most rock consumers have stringent requirements about the maximum content of iron and aluminum in the rock they buy. Iron is undesirable in rock and as feed to electric furnaces because it combines with phosphorus to form "ferrophos", a furnace byproduct with little market value. Aluminum is undesirable in rock used to make wet-process phosphoric acid because it forms insoluble chemical complexes with phosphate which settle slowly and creates sludge problems. High iron and aluminum content also creates problems in manufacture of superphosphate, giving poor physical condition upon curing.

Therefore, the purpose of this study was to determine primarily how iron and aluminum contaminants occured in the phosphate rock product and to determine if these contaminants could be removed economically.

The Florida phosphate rock deposits are alluvial in character, formed about 20 million years ago. Draglines strip overburden lying on the "matrix", as phosphate ore is called, and then remove the matrix, which is slurred and pumped to a washer. Figure One illustrates

Fig. 1
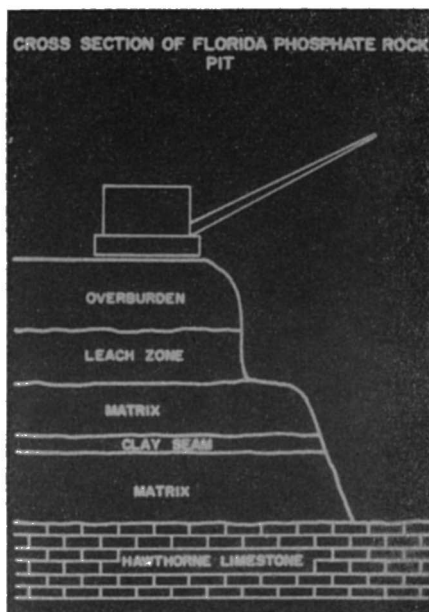
a typical cross section of a Florida phosphate rock pit. At the washer, the matrix is scrubbed and screened; the plus 1 mm fraction being considered a finished product. The minus 1 mm fraction from the washer is deslimed at 150 mesh in cyclones, the slimes are discarded. The deslimed sand is treated by Froth flotation and agglomerate tabling techniques to separate the phosphate rock from silica sand. The silica sand is discarded.

The only real control of product grade exercised by the Florida phosphate rock producers is through the selection of that part of the deposit to be mined.

Contamination by iron and aluminum is particularily a problem in the plus 1 mm product less so in the agglomerate tabing and flotation concentrates.

The first step of the study was to examine the mineralogical composition of phosphate rock product. Once the mineralogical characteristics of the contaminants were determined, field samples were taken from the pits in Florida to determine the source of the contaminants.

Mineral Identification

The procedure for mineral identification, while not a set routine, can be described roughly as follows:

1. Select a pebble of unknown composition.
2. Saw, or break the pebble into two halves.
3. Pulverize one half of the pebble to obtain material in the 100 to 140 mesh size range.
4. Examine portions of the sized fraction under the microscope with index oils. Positive identification of some constituents can be made at this point by determining the indices of refraction and some of the optical properties. Optical parameters should be obtained on all constituents at this point, if possible.
5. Constituents of unknown composition should be isolated at this point. Heavy liquid separation is often used to concentrate the unknown into a given density fraction. Handpicking from a microscope slide is quite often necessary.
6. The isolated sample of unknown is submitted for x-ray and emission spectroscopy. The data obtained from these two diagnostic techniques is usually sufficient to identify the unknown or at least reduce the number of possible species to a given few.
7. To determine the relationship between the constituents of a pebble and to discover other constituents possibly destroyed in the pulverized sample, a thin section is made from the remaining half of the pebble.

A thin section is a slice of rock with a thickness of 0.03 mm. This is the optimum thickness for determining optical properties of the constituents and for identifying the relationships between the constituents.

To make a thin section, the pebble is first ground flat on one side, using wet corundum paper. The pebble is ground until a surface is obtained which is suitable for study. The flat surface is polished to remove all scratches and grinding damage. Once polished, the flat surface is attached to a microscope slide with a thermoplastic mounting media which has a known index of refraction. The mounted pebble is then ground on the corundum papers until examination with the microscope indicates that it is approaching the proper thickness. The slice is then polished and the final thickness is achieved by grinding with the polishing compound. The softness of the phosphate pebbles dictated careful handling.

By using the identification techniques outlined above iron and aluminum contamination of the Florida phosphate rock product was found to be from several sources. Contaminants included imcompletely removed primary clays, undisintegrated secondary clayballs, sandrock (quartz grains cemented with aluminum phosphate), fine grained iron oxide inclusions, barbosalite (iron phosphate) pebbles, phosphate limestone nodules, and chert (SiO_2) inclusions.

Samples of the matrix, and overburden in contact with the matrix, were taken from the mining pits in Florida. These samples indicated that many of the con-

taminants, including sandrock, wavellite, and barbosalite, were derived from the overburden. Much of the chert, and phosphatic limestone came from the bottom rock (rock below the matrix). Occasionally, matrix contained an included stratum of hard clay. The aluminum bearing contaminants occurred predominantly in the overburden. The iron bearing contaminants were distributed between overburden and matrix. The iron phosphates occurred in the overburden while the iron oxides occurred in the matrix. The latter, being disseminated inclusions in the pebble, are not separable without size reduction.

A detailed description of the various contaminants and proposed methods of removal follows:

Aluminum Contamination

Aluminum contamination derives from several sources, each presenting a different problem in removal. Each source which has been identified to date is described below:

a. *Primary Clays* — These are the unconsolidated plastic clays that bind the matrix. The clay is a mixture of kaolinite, montmorillonite $(Mg,Ca).Al_2O_3.5SiO_2.nH_2O$, crandallite (pseudowavellite, $CaO.2Al_2O_3.P_2O_5.5H_2O$) and unconsolidated apatite slimes. This clay is removed for the most part in the washer plant, although incomplete removal of this material accounts for some aluminum contamination. This clay also causes operating difficulties in the flotation plant. No fixed analysis can be attached to this material, but it will range from 5 to 15 percent Al_2O_3.

Clay from the leach zone is much higher in Al_2O_3 than clays from the matrix and is probably enriched in crandallite and wavellite.

b. *Secondary Clay* — This is the name given to clayballs still relatively consolidated after treatment in the washer plant. These clayballs are from a clay stratum observed in the matrix. These clayballs contain no entrapped matrix and, indeed, have no coarse particles entrapped in them.

Two types of clayballs have been observed, yellow and white. The main difference between the two is in the iron and magnesium
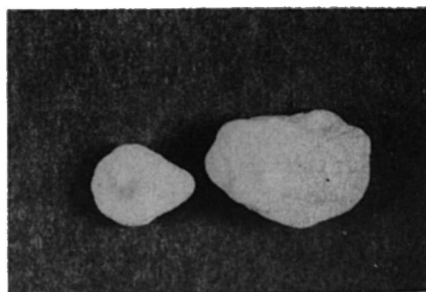

Fig. 2. White Secondary Clayballs

analyses. Figure 2 illustrates the appearance of these clayballs.

Emission spectroscopic analysis indicated no sodium or potassium or other alkaline earth metals. The X-ray spectrograph gave a distinct pattern similar to the mica minerals but not comparable to any of the clay minerals other than illite or attapulgite.

Analysis of Secondary Clayballs

Analyses		White	Yellow
	CaO	3.94	2.98
	P_2O_5	2.80	2.70
	Al_2O_3	5.78	6.76
	Fe_2O_3	4.34	11.52
	SiO_2	54.86	51.00
	MgO	7.12	4.09
	CO_2	1.92	2.54
	F	.54	.57
	H_2O	11.4	10.8
Totals		92.6	93.0

These clayballs break up slowly when violently scrubbed, and would be expensive to remove by scrubbing. They have a low apparent specific gravity of 2.00 and their plate-like form indicates that they could be removed by jigging or some similar gravity-type separation.

c. *Sandrock Pebbles* — These pebbles have the appearance of quartz sandstone. Petrographic analysis indicates that the sandrock consists of quartz (SiO_2) grains cemented together with wavellite, $Al_3(OH)_3(PO_4)_2.5H_2O$. Figure 3

Fig. 3. Sandrock — Quartz grains cemented together with wavellite.
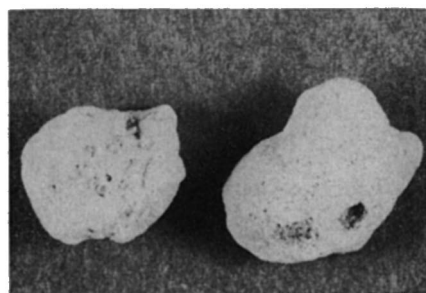
shows the pebbles of sandrock as they appear in the coarse rock product. These analysis of sandrock will vary, depending upon the ratio of quartz to wavellite; a typical analysis would be 44.6 percent BPL, 14.5 percent Al_2O_3, 1.32 percent Fe_2O_3 and 34.3 percent SiO_2. Emission spectroscopic analysis indicated a maximum CaO content of 1.4 percent; sodium and potassium were not detected.

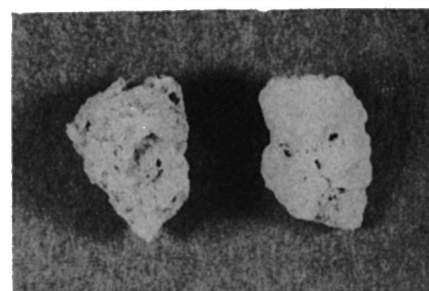d. *Wavellite Pebbles* — These pebbles are illustrated in Figure 4.

Fig. 4. Wavellite Pebbles

They are usually quite porous with many cavities and voids; however they are quite hard. They are usually bluish gray. Microscopic examination (Figure 5) indicates that the
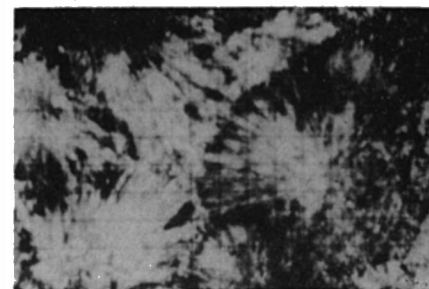
Fig 5. Photomicrograph (small squares equil .077 mm) showing stellated structure of wavellite

pebbles are usually relatively pure wavellite with some quartz inclusions. A typical analysis for this material would be 50.7 percent BPL, 28.1 percent Al_2O_3, 1.26 percent Fe_2O_3 and 16.9 percent SiO_2 with less than 1 percent CaO.

Removal of sandrock and wavellite from coarse and fine rock products can be accomplished by the use of heavy media sink-float separation whereby these alumina contaminants are floated off to leave a sink fraction with a reduced Al_2O_3 content and, an increased BPL content.

e. *Miscellaneous Aluminum*

Contamination — Aluminum contamination also occurs as granular inclusions of wavellite and crandallite in collophanite pebbles as well as thin crandallite coatings on pebbles. The degree of contamination is variable but increases in pebbles near the top of the matrix or in the lower part of the leach zone.

Iron Contamination

Iron contamination of the phosphate rock products, as for aluminum, is derived from many different sources. Samples of the primary clays mentioned above have contained up to 37.1 percent Fe_2O_3. Secondary clays mentioned above also contain iron, as can be seen by the analysis given earlier for the yellow clay balls.

a. *Iron Oxide Contamination* — The major part of the iron present in well-washed coarse and fine rock products occurs as minute inclusions of iron oxide in the pebbles, primarily the mineral goethite ($HFeO_2$, or $Fe_2O_3 . H_2O$) or other hydrated ferric oxides. The pebbles shown in Figure 6 are distinctively
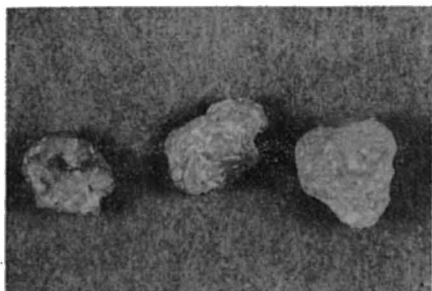

Fig. 6. Phosphate pebbles contaminated with iron oxide

red-brown in color, and typically analyze up to 4.5 percent Fe_2O_3. Figure 7 illustrates the appearance
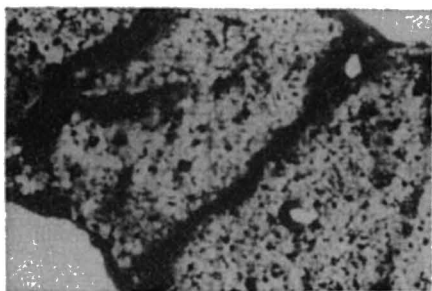

Fig. 7. (small square = .007 mm)

of a section of a red-brown pebble under microscope. The large grid in Figure 7 is slightly larger than a 45 mesh screen (U.S. Standard).

Obviously, complete liberation of this form of iron would be nearly impossible.

b. *Iron Phosphate Contamination* — Several black strata were noted at the east end of one mining pit. These strata were as thick as 18 inches at times and looked like veins of coal. A photo of a fragment of the sample is shown in Figure 8.
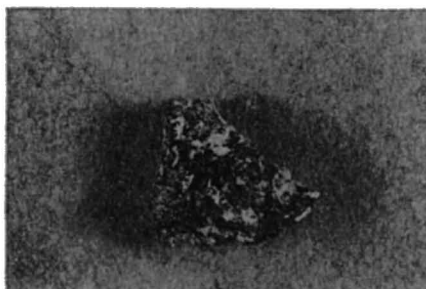

Fig. 8. Iron phosphate (Barbosalite) from overburden

Emission spectroscopic analysis indicated that the material contained considerable iron, and subsequent microscopic examination showed the main bulk of the black material to be Barbosalite, $Fe"Fe"'_2 (PO_4)_2 (OH)_2$, with some Rockbridgeite, $(Fe",Mn") Fe"'_4 (PO_4)_3 (OH)_5 . 2H_2O$. Dufrenite, $Fe"Fe"'_4 (PO_4)_3 (OH)_5 . 2H_2O$, is a greenish alteration product of Barbosalite. The greenish color develops on drying iron phosphate-rich pebbles found in the various washer products.

The iron phosphates are admixed with both wavellite and phosphorite. A typical analysis of several handpicked pebbles rich in iron phosphate (similar to those in Figure 7) is as follows: 65.1 percent BPL; 4.21 percent Al_2O_3; 13.1 percent Fe_2O_3 and 10.3 percent SiO_2. These iron phosphates can be avoided by careful stripping of the overburden.

c. *Turgite* — A very minor source of iron contamination has been observed only twice during the course of this study in coarse rock washer products. This a hydrous ferric oxide called Turgite, or bog iron. The two observed pebbles were deep red-brown, pulverant, and are nearly pure iron oxide. They were claylike and probably would have been broken up if submitted to severe attrition scrubbing. Their source is unknown.

d. *Vivianite* — Another minor, but mineralogically interesting source of iron contamination occurred in the form of Vivianite crystals ($Fe_3 (PO_4)_2 . 8H_2O$) up to a centimeter in length occuring in cavities or vugs in the wavellite pebbles. When these crystals were dried in an oven, they turned brown and became pulverant.

Miscellaneous Observations

a. *Phosphatic Limestone* — Pebbles similar to those shown in Figure 9 are frequently seen in

Fig. 9. Phosphatic limestone pebbles

washer plant products. These pebbles are usually flat, black on the two large surfaces and cream-colored on broken surfaces. Pebble inclusions are usually present on the top surface. The material constituting the bulk of the sample is a phosphatic limestone. It is extremely fine grained, with individual grains of $CaCO_3$ being approximately 1 micron in diameter. A typical analysis of the material is as follows: 33.0 percent BPL; 1.93 percent Al_2O_3; 1.44 percent Fe_2O_3; 40.6 percent CaO; 2.97 percent MgO; 13.0 percent SiO_2; 20.4 percent CO_2; 1.53% F; 0.84% H_2O. (Total=97.7 percent.)

b. *Siliceous Impurities* — The most common contamination of coarse and fine rock products comes from quartz grains included in the phosphorite pebbles. Besides the quartz grains entrapped in the sandrock, and free quartz grains in the minus 20-mesh fraction of the matrix, several other forms of silica have been observed.

A frequently observed source of silica is in the form of chert (hydrous silica) lumps. These are observed mostly as coming from under the matrix. The chert lumps can often be of large size; one such lump observed in a monitor sump

at the pit was approximately 2½ feet in diameter.

Chalcedony (cryptocrystalline SiO_2) has been frequently observed in washer rock products as fossil shell casts.

Large fragments of quartz have been observed, infrequently. One such fragment was one inch long. These fragments have all the appearance of vein quartz and may have been from imported gravels to the plant site, although they have been observed frequently enough to assume that they are from the mine site.

Impurity Prevention and Removal

Most of the aluminum contamination can be eliminated from the phosphate rock product by (1) practicing pit control, that is, using trained geologists to insure that the overburden is thoroughly stripped off the matrix before the dragline begins to dig the matrix. Most of the sandrock, wavellite, and iron phosphate will be removed by pit control; although some of these pebbles will still be found in the matrix as a result of natural intermixing before mining.

If an excessive amount of natural intermixing of sandrock and wavellite occurs in the matrix, these aluminum bearing pebbles can be removed by heavy media separation. If the matrix is interlayered with clay seams as illustrated in Figure 1 earlier, careful removal of the upper matrix, followed by careful stripping of the clay seam will eliminate most of that problem. However, thin clay seams cannot be removed in this manner. If clay seams must unavoidably be included in the matrix in the mining operation, simple jigging of the screened product could be used to remove the clay.

Thorough scrubbing and screening will remove the primary clay contamination.

Some iron will be removed by careful mining practices, but, as illustrated, most of the iron contamination consists of collodially dispersed goethite intimately mixed with good calcium phosphate. No simple beneficiation procedure will remove this form of iron contamination.

Phosphatic limestone contamination, undesirable because it consumes sulfuric acid when making phosphoric acid, can largely be eliminated by not digging too deep when mining matrix. The Hawthorne limestone is relatively hard, and cannot be broken up by the dragline bucket, but loose surface fragments break off and enter the matrix if the dragline operator tries too hard to get "the last drop" of matrix.

Good Phosphate Rock Pebbles

Since so much has been said about what the impurities look like in the phosphate rock product, it might be interesting to see what good pebbles look like. Good phosphate pebbles are usually hard and somewhat shiny with numerous voids and fossil casts. Their color when very pure is white, as illustrated on the left of Figure 10. A small amount of iron contamination will make the pebbles tan. Or-

Fig. 10. Good phosphate pebbles
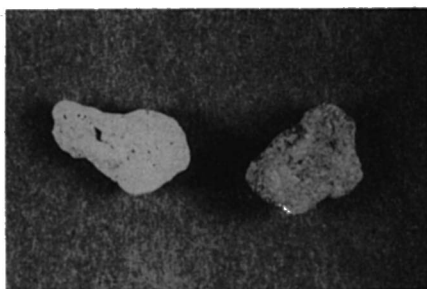
ganic inclusions make the pebbles black. These black pebbles are shiny and hard, which distinguishes them from the soft, dull iron phosphate pebbles.

CHAIRMAN SAUCHELLI: Thank you, Fred.

There is more to phosphate rock than meets the eye apparently. We are running short on our time so that we are making a change in the program.

We are going to have the next speaker, Henry Plate, Manager of Bulk Blend Plants, Agway Incorporated, and I will turn the meeting over to my associate Al Spillman.

MODERATOR SPILLMAN: We have had a good many requests from the membership to have a thorough discussion on bulk blend economics. It is a pleasure for me to introduce Henry Plate, formerly manager of "Bulk Blend Plants" for Agway, Inc., Syracuse, N. Y., now agronomist for Agway. Henry is a good friend of the Round Table and an associate of mine before I retired from Agway. He is well equipped to discuss "Bulk Blends." During the past year Henry has supervised 28 bulk blend plants throughout Agway territory.

Bulk Blend Economics

Henry Plate

My discussion today on the economics of blend plants is based directly upon our experience with 28 plants located in seven of 12 states we operate in. As such, I would like to give you some background of these before we start into the actual economics.

Table 1
Agway Blend Operation

Wholesale —
  33% Sales Responsibility
Sell to Retail
Plant Food Per Acre —Net Tons
50 Unit Tons
Corporate Administration
Blend is Satellite to Ammoniation
Ammoniated Grades in Planter
Spreader Service —
  Wholesale or Retail
Bulk Only—No Bagging

As table 1 indicates, in Agway the blending operation is actually a wholesale production operation. Although controlled by the wholesale division, about one-third of the manager's time at these blend plants is devoted to actual retail sales responsibility in coordination with our retail divisions. These plants sell all their materials as an internal transaction through a retail sales point. This may be either to wholly owned stores or a local farmer representative who handles the products.

Sales are in terms of plant food per acre, such as 120-64-96, and not in terms of actual tons or grade. The main advantage to this is production of the highest analysis possible, averaging a little over 50 units (we use ammonium nitrate, urea, diammonium phosphate, muriate of potash and triple in formula-

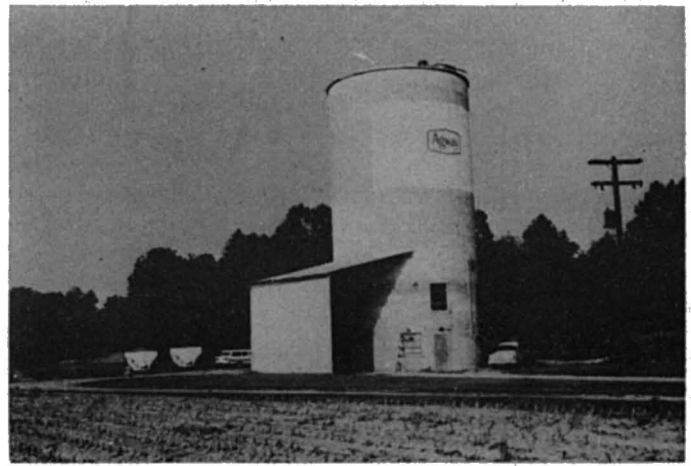| Illustration 1	Illustration 2
Horizontal blend plant, 7 bay, 700 tons total storage. Unloading leg and rail line in left rear. Load out leg and holding bins on right. Service equipment in foreground.	Vertical concrete silo blend plant 6 bins, 125 tons each bin. Weighing area at level of window over door. Rail track and elevator at rear of plant. Load out belt under shed in foreground.

tions.) This also gets the farmer thinking in terms of plant food, reduces the transportation, and simplifies the actual formulation of the fertilizer.

These plants are under corporate administration and the actual economics you will see do not include the cost of the corporate administration. Supplies are also ordered centrally. These 28 blend plants are set up on a semi-satellite basis to the 12 ammoniation plants, so that the blend plants fill in the holes at the greater distances from the ammoniation production units. Ammoniated grades are recommended for row application. The homogeneous granulated grades are well worth the small extra cost in terms of avoidance of any possible segregation of materials.

The blends, of course, can be taken in bulk by the farmers or Agway will spread them using truck spreaders. These trucks may be operated either by wholesale or retail. Bulk blends are not bagged — they are only available in bulk. Bagged ammoniated grades are available for those who require bagged products.

Let us review the requirements for a blend plant location. As shown in table 2, it must have a potential of 3,500 tons (50 unit tons.) This would be the equivalent of 7,000 tons of 5-10-10. Blend plants must have a rail siding to handle incoming materials, although outgoing materials go by truck. A 600 to 800 ton storage

Table 2
Requirements For A Blend Plant

1. 3,500 tons potential (50 unit tons)
2. Rail siding
3. 600-800 ton storage
4. Separate unloading and load-out
5. 60 t/hr. unload and loadout capacity
6. 20 t/hr. output
7. 2,000 tons and under - 1¼ men
8. 2,000-3,000 tons - 1½ men
9. over 3,000 tons - 2 men
10. Plus spreader operators
11. Uniform mixing without grinding

capacity is reasonable and necessary for this operation.

Separate unloading and load-out system is required so supplies can be replenished while shipping. The capacity of these unloading and loadout legs is 60 tons per hour in order to keep up a 20 ton per hour output of the plant.

Manpower requirement for a plant operating at 2,000 tons per year and under is about 1¼ men

per year. By this we mean we need a manager year around and a part time man for about three months of the year. For 2,000 to 3,000 tons about 1½ men, and for over 3,000 tons two men. Now this manpower requirement does not include the need for spreader truck drivers. These would be in addition to the manpower listed.

The last requirement is a uniform mixing of the ingredients without grinding of the particles.

Several of our plants are shown in the pictures. The horizontal plant is a one floor operation employing payloader. Note elevators, nitrogen solution tank, holding bins for finished materials (not put in new plants) and spreading equipment. Plant is 56 feet by 84 feet.

The vertical plant is a concrete silo consisting of six pie shaped bins—125 tons capacity per bin.

The picture of the inside shows the weighing operation beneath the overhead bins which feed into a cone mixer below floor. In future arrangements we would substitute a rotary mixer.

Table 3   Features Of

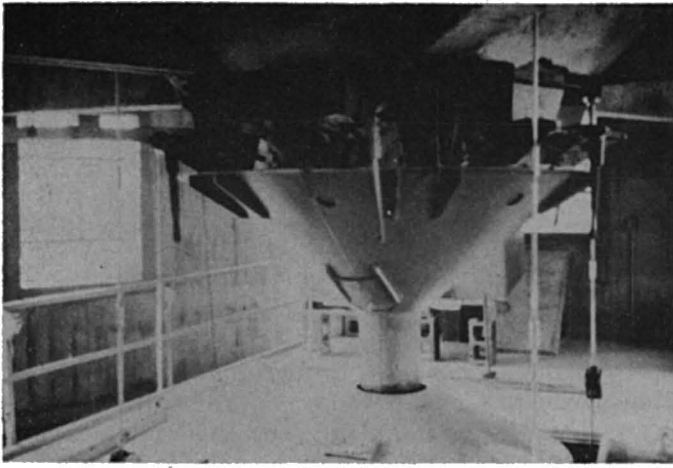| Horizontal	Vertical
Expandable	Non Expandable
AN—ok	AN—No.
Payloader	No Payloader
Higher Labor	Lower Labor
Lower Initial Cost	Higher Initial Cost
No Hang Up	May Hang Up
Slower (W/O Mat. Hoppers)	Faster

Illustration 3

Interior view of hopper gates at base of overhead bins in concrete silo. These feed into combination weigh hopper and cone mixer below floor level.

Illustration 4

Part of spreading equipment used at one horizontal plant. In the background beginning at left; six ton spreader trucks, six ton trailer tender, four ton trailer spreaders. In center four ton portable bins with small trailer spreaders in foreground.

Table 3 summarizes some of the features of each of these. The horizontal plant is expandable compared to the vertical plant which is nonexpandable. By this we mean it is expandable in two ways. First in a horizontal we can construct extra bins at one end of the plant for additional storage capacity and also room to install a second mixer if so required. Even more important is the fact that when incoming materials gang up on you in a rainy spring, it is possible to roll some of the material right across the alley way and get an additional 200 to 300 tons in the plant over and above designed storage capacity. With the vertical plant this is not possible, since once it is full, it is full and you can do nothing else but spill it off the top on to the ground or else let it sit in the car and draw demurrage.

Ammonium nitrate can be used in a horizontal plant. It should not be in the vertical plant due to the depth of storage and the pressure that is generated.

The horizontal plant requires the use of a payloader, increasing the expense. The horizontal, however, has a lower initial cost of construction. Materials may on occasion set up or hang up in the overhead bins in a vertical plant. When they do, it can be quite a problem to get them started down again and keep them feeding down. Materials can set up in a horizontal plant, but it is much easier to get at them and loosen them up.

Table 4   Blend Plant Costs

	Horizontal	Vertical
Land & Improvement	$ 6,000	$ 6,000
Building	25,000	)
		)
Equipment & Install	19,100	) - 63,000
		)
Electricity	3,400	)
Siding	12,500	12,500
Engineering	1,400	1,400
Misc.-Water, Legal	2,600	2,600
	$70,000	$85,500

Due to the need to use a payloader to feed the mixer mounted on a scale the horizontal plant is somewhat slower in its operation. However, we feel that the use of overhead material hoppers over the mixing unit could speed this up considerably and we are seriously considering it for one or more plants for this coming year.

Table 4 reviews the cost of building a horizontal versus a vertical blend plant. These are built according to specifications that we have been employing and construction costs would vary from area to area and design to design. These are meant to be typical of the actual figures that we have. They do not represent any one individual plant but rather a composite of the recently built plants and adjustments where necessary on all the plants for current costs. In both types, land and improvement to the land will average approximately $6,000. This is for a site of ap-

proximately 2 acres. For the horizontal plant the wooden building, 56 x 84 with office, of pole type construction, will run approximately $25,000. The equipment, which includes the unloading elevator leg, unloading auger under truck, cross conveyor screw on the roof, a rotary mixer, loadout elevator and other minor equipment, plus installation will approximate $19,100. Future plants would probably use a belt cross conveyor to reduce physical breakdown. Electrical installation will run $3,400 on the average. This has run any where between $2,600 and $4,300 for comparable construction depending upon union rates in the area.

For a vertical blend plant, the building, equipment and installation, and electrical — a turn key type of operation—using a concrete silo construction is estimated at an approximate current cost of $63,000.

The siding in both cases with

room for three to four cars on track will cost in the neighborhood of $12,500. $7,500 of this is normally tied into the installation of the switch and the balance in the extension of the side track for the necessary length. Engineering costs have averaged approximately $1,400 on these plants. Miscellaneous factors such as legal activity, water supply, etc., will run approximately $2,600. This gives us a total of $70,600 for the horizontal plant and $85,000 for the vertical plant.

Operating costs exclusive of spreading are shown on table 5. Operating costs are just settling down to a reliable pattern since the blend plant area is relatively new to the organization. Fourteen of the 28 plants were built in the spring of 1966, four in the spring of 1967 and six were acquired by the merger. While each plant should have a potential of 3,500 tons per year, initially many plants have run less, so comparison of two different sizes — 2,200 tons and 4,300 tons is shown. In addition on the 2,200 ton plant, costs are shown for both vertical and horizontal construction.

Salaries and payroll costs run about $7,800 for the 2,200 ton plant and $9,000 for the 4,300 ton. The managers, with more responsibility, are receiving higher pay. Salaries and payroll costs for part time men $800 for the vertical; $1,500 for the horizontal at the 2,200 ton level and $5,000 for a year around employee for the 4,300 ton plant. Travel runs higher for the larger plants. The fact that our larger plants spend more for travel may mean they are large because the managers get out and do more sales activity.

Maintenance is low on the vertical plants. At least this has been the experience to date. On the horizontal plants it will vary some according to the tonnage moving through the plant and the wear and tear on equipment. Improved maintenance procedures and different selection of equipment, may cut this maintenance cost. Electricity for fuel, light and power will vary according to the locality, but approximate the figures shown.

Demurrage is the real problem to meet at the plants. As mentioned in the features comparing the vertical versus the horizontal plants, it is extremely difficult to put in more into a vertical plant than it will actually hold. Experience this past spring, with the real wet season, showed that demurrage on the vertical plant averaged approximately $1,800. It doesn't take many cars at a $15 figure a day sitting on track to run this up. The better operators in the horizontal plants have kept demurrage quite low with a $90 figure being consistent for many of these plant. Keep in mind that 2,200 tons only needs a three time turn over of the material in the plant to get out the capacity and a portion of this moves in the summer and fall period. Contrast this with the 4,300 ton plant where material must turn over approximately six times. Shipments may be 500 tons a week, requiring almost two fillings enroute at certain periods of the spring season (two week shipping is normal from the supply points for many of the materials.) The $3,500 demurrage figures indicates what can happen in wet seasons, as experienced last spring. I am purposely not trying to pull any punches in this talk, but merely to show you actual problems that have been encountered.

Inventory adjustment is figured at approximately $\frac{1}{2}$ of 1% of the incoming cost of materials. Of course, there is the ever present telephone. Rent and insurance on the plant and the materials, runs higher on the vertical plants due to its higher initial cost than on the horizontal plants. This rent included depreciation, taxes, money use, insurance, etc. A payloader is not required for the vertical plant but is for the horizontal plant. Payloader costs do include depreciation, based on a 10 year depreciation schedule.

Total cost for the vertical plant $22,000; for the horizontal plant almost $21,000. The increased costs for the vertical plant are the higher demurrage and higher rent. These are partially compensated for by the higher salaries, maintenance and payloader in the horizontal plant. For the 4,300 plant the operating costs total $33,000. The final income of spreading is in table 6. Sales are figured at an approximate $75 a ton wholesale. Remember these are 50 unit tons. If we assume an 18% gross on sales, you will note the income from the various operations. With the operating expenses from table 5

Table 5   Operating Costs
(Exclusive of Spreading)

	2,200 T (Vert.)	2,200 T (Horiz.)	4,300 T (Horiz.)
Salaries & Cost-Mgr.	$ 7,800	$ 7,800	$ 9,000
Salaries & Cost-Part Time	800	1,500	5,000
Travel	600	600	1,000
Maintenance	510	950	2,600
Fuel, Light, Power	320	320	740
Demurrage	1,800	90	3,500
Inventory Adjustment	600	600	1,200
Telephone	420	420	860
Rent, Ins.	9,350	7,800	8,300
Payloader	—	850	900
TOTAL	$22,200	$20,930	$33,100

Table 6 Income Statement

	2,200 T (Vert.)	2,200 T (Horiz.)	4,300 T (Horiz.)
Sales ($75/T)	$165,000	$165,000	$322,500
18% Gross	29,700	29,700	58,050
Operating Exp	22,300	20,930	31,100
Net	$ 7,400	$ 8,770	$ 26,950

Table 7 Spreading Operations—Expenses

	2,200 T		4,300 T	
Trucks @ $3,500	$ 7,000	(2)	$17,500	(5)
Trailers @ $575	1,150	(2)	575	(1)
Drivers	2,700	(1-6 mos.)	5,200	(1-12 mos.)
	1,500	(1-3 mos.)	2,700	(1- 6 mos.)
			4,500	(3- 3 mos.)
TOTAL EXPENSES	$12,350		$30,475	

we have a net of approximately $7,400 for the 2,200 vertical plant; $8,700 for the horizontal plant and for the 4,300 plant $26,950. Once again, it is the volume that pays in these plants. Under our operating conditions these plants will break even with an 18% gross at approximately 1,700 tons. Remember however, this allows nothing for corporate administrations, order service, accounting functions, and many of the other factors centrally administered, which are covered by net margin.

Table 7 assembles some figures for the spreading operation required for 2,200 ton plant and a 4,300 ton plant. Our experience indicates that the only way that you are going to get the tonnage is by having the spreading services available. It doesn't matter whether this is retail, wholesale function or custom operation — it is needed and the expenses are still there. For purpose of this talk these figures are handled as if the spreading operation was handled by one particular phase of the company. Trucks for depreciation, insurance, licensing and operating cost and repairs will average $3,500 a year. Trailer spreaders for the same factors approximate $575 —this does not include delivery of the trailer to the farm. Drivers have been obtainable for approximately $5,200 per year. How long this continues is a good question. This is the real problem where drivers are needed for only part of the season. Where possible these drivers are shared with retail points, petroleum operation, etc. A man does not become a good spreader operator over night. All operators must attend a driver training school prior to actual driving a truck. Purpose of this school is to teach safety in the operation of the truck, both in terms of possible hazard to others, and for better maintenance

on truck and longevity of the life of the equipment.

Spreader truck bodies are of our own design. These are spinner type with separate power on the spinners and a belt, wheel driven in relation to ground speed. These six ton capacity trucks now cost approximately $8,600 to $8,700. On the average these trucks will spread 700 tons. It is a curious factor, but in smaller plants farmers will haul more of the fertilizer themselves than they will in the larger plants. I think this is due to the emphasis that is given on custom spreading and the fact that our larger plants have grown to that capacity due to the presence of good spreader equipment in the area.

Let's run down the 2,200 ton plant and see what spreading equipment is needed. Experience indicates the need for approximately two spreader trucks and two trailer spreaders. Spreader trucks can be used to deliver the trailers to the farmers if the farmer does not care to pull them himself. For pulling by the farmers these trailers must be equipped with electric brake that can be actuated from a portable unit in either the cab of the pick-up truck or on the seat of the tractor. One truck driver is needed for six months and one driver for three months of the year. This gives a total expense of $12,350.

For the 4,300 ton plant a higher percentage of the fertilizer will be custom spread. Five trucks will be required but only one trailer spreader. Trailer spreaders are less popular in the larger plants. The farmer wants more and more custom work. He has seen what can be done; that the job is accurate and that it is easier and more economical than he can do it. Here one truck driver is needed for 12 months, one for six months and three for a three month period during the spring rush. Those in the spring period, of course, earn considerable over time, so that their salaries are proportionately higher during this period than the average for a year. Total expenses are $30,475.

Actual income from the trucks is shown in table 8. A $9 per ton spreading charge is used for the truck. Actually this is based upon an acreage rate of a little over $1.75 per acre and spreading approximately 400 pounds per acre. For presentation these were converted to a ton basis. On trailer spreaders a charge of 75¢ per acre is made for the use of the spreader (or $3.00 per acre based on 500 lb. rate.) Delivery charges are additional and are not shown. Rate of application with the trailer spreader seems to be a little higher than it is with the truck, approximating 500 pounds per acre. Total income for a 2,200 ton plant is $13,500, leaving a net income of $1,150.

Similarly for the 4,300 ton plant we show a $1,475 net income. We do not plan to make money from the spreading operation but only to break even. It would be nice if these figures were always this good. In a wet season, when you are planning on 4,300 tons and only get 3,500 tons and yet have the trucks, drivers on hand can

Table 8 Spreading Operation—Income

	2,200 T		4,300 T	
700 T/Truck @ $9.00/T	$12,600	(2)	$31,500	(5)
150 T/Trailer @ $3.00/T	900	(2)	450	(1)
TOTAL INCOME	$13,500		$31,950	
TOTAL EXPENSES	12,350		30,475	
NET INCOME	+$ 1,150		+$ 1,475	

really knock you into a hole on the spreading operation.

In summary with the allocation of costs as indicated, and the type of a retail-wholesale integrated operation, blend plants can return a good net profit to the organization.- They must, however, be properly operated, well planned, located in the right position, and backed very adequately by a sales force. Remember a goodly part of this net income is needed for administrative expenses of the blend area. Like any other business, if these are poorly operated, poorly placed or lack sales activity, you can have real problems. The plants I have picked have been the average for the well operated ones in the area. We do have a few plants where, much as we hate to admit it, lack of sales activity, poor management or similar character-

istics have really been a problem.

I appreciate your time and attention to discuss with you the economics of operating blend plants as handled in our own organization.

MODERATOR SPILLMAN: Thank you, Henry, for this excellent and thorough report.

MR. SPILLMAN: Now, gentlemen, let's have some questions from the floor. We have had more requests to have this discussion than any other subject we are discussing at this meeting.

MODERATOR SPILLMAN: Do you have any figures on in-plant shrinkage costs?

MR. HENRY PLATE: Approximately half of one per cent on the basis of the cost of incoming materials.

A MEMBER: You gave a spread-

ing charge of $75 an acre. Was that 75 cents by any chance?

MR. PLATE: Excuse me. That should be 75 cents rental on the trailer spreaders. Thank you.

A MEMBER: Based on your experience with both vertical and horizontal plants, would you care to express a preference for future plants that you are going to build as to which type it will be?

MR. PLATE: I would say that in all probability it would be the horizontal plant. Total investment in the vertical plant is considerably more and this pushes your expenses up a little too much, I'm afraid.

MODERATOR SPILLMAN: Thank you, Henry.

We will now adjourn for lunch and we hope you can get back promptly at two o'clock because we have an excellent program for this afternoon.

Thursday Afternoon Session, November 16, 1967

The Round Table Meeting reconvened at two-ten o'clock p.m.

Mr. J. E. Reynolds, Jr., and Dr. Vincent Sauchelli, Moderators

MODERATOR REYNOLDS: Gentlemen the subject of Nitro-Phosphate Processes remains a very definite and extreme interest to us, as I guess was very evident this morning in some of the discussions or some of the fringes of the discussions.

The ability to produce these products remains a matter of record. The processes have been discussed in the past but we need to keep extremely aware of developments in the process and the changes that have developed since these were last presented.

The balance between the sulphur prices and the nitrogen prices appears to be the controlling factor in the phosphate rock attack system and this is something that we have to be aware of and to follow.

This afternoon we are very happy and very pleased to bring

you a speaker who, in fact, just arrived from Europe last night, Mr. Clem Giles, who has appeared before the group before. I think several years ago he was here. This time he is going to discuss the Re-

cent Applications of Nitric-Phosphate Processes. The paper was prepared by Enrico Pelitti, Clem Giles and Vincent J. Russo of C. & I. Girdler, Incorporated.

Clem Giles will give the paper.

Recent Applications of Nitric Phosphate Processes

Clem B. Giles, Enrico Pelitti and Vincent J. Russo

In 1960 a paper was presented at the Fertilizer Industry Round Table, describing what was then considered a novel process for the manufacture of nitric phosphates.. The process generated considerable interest on the part of the members of the Round Table, particularly in private sessions away from the conference room. But apart from the plants built by Chevron Chem-

cal (formerly California Chemical Company), with whom one of the authors was associated at that time, and a couple of smaller ones, no additional nitric phosphate plants were built in the U.S. since.

Through the years, the subject has been frequently and extensively discussed, and voluminous reports have been undoubtedly accumulating in the files of most fertili-

zer companies on the technical and economic advantages and disadvantages of nitric phosphates. Though little or no action appears to have been taken on any of these studies, the recent sulfur shortage has made nitric phosphates once again the hot topic of most fertilizer meetings. In view of this interest, it appears appropriate to review for you, at this time, some of the recent applications and developments in nitric phosphate processes with which C &I/Girdler has been associated, primarily outside of the United States.

No attempt will be made here to review the chemistry of nitric phosphates, which has been amply covered in the literature and in previous Round Table meetings. On the other hand, there are certain aspects of nitric phosphates, other than technical and economic, which do not appear to have been given adequate consideration.

What are the problems facing a fertilizer manufacturer who is considering a new facility for the production of NPK fertilizer, A very important one, in most cases, is what grades should the plant be designed to manufacture.

If it has been producing NPK fertilizers before, the fertilizer company knows what grades have sold well in the past. It has to take an educated guess as to what will sell well in the future, and at the same time attempt to forecast what is going to happen to the price and availability of sulfur, and what will be the mood in Congress concerning low-interest long-term loans to foreign countries for fertilizers. So, what should the plant be designed to make? The ideal plant is one that will make every possible combination of plant foods at high rates with high efficiency. As we all know, this particular type of plant is not available, but we feel that a basic nitric phosphate plant comes closer to this ideal than any other now known. It is a plant which can be built now, and easily modified or added to later in order to stay abreast of developing marketing conditions.

Figure 1 shows what we call the basic plant. It consists of 3 basic sections, or building blocks: Acidulation, Neutralization and Spherodizing. Phosphate rock can be acidulated with nitric acid, or mixed acids, followed by conversion of the excess calcium nitrate, and neutralization. With the addition of optional raw materials, fertilizers with a wide range of nutrient ratios can be made, with practically any degree of P_2O_5 water solubility, from 0 to over 90%. Product quality for any of the materials produced will essentially be the same, when the C & I/Girdler spherodizing process is used.
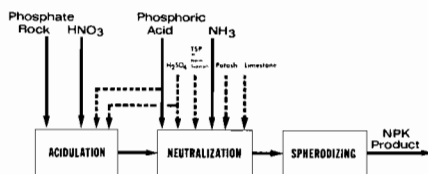

FIG. 1   BASIC NITRIC PHOSPHATE PLANT

The principle of the spherodizer was described at the 1960 and 1961 Round Table meetings. The basic feature of the spherodizing process is that the drying and granulation steps are performed simultaneously, resulting in a simplified operation and a product of superior physical qualities.

Figure 2 is a view of a recently completed spherodizer installation. The slurry piping in front of the spherodizer leads to a nozzle projecting into the rotating drum. In fact, the nozzle projects through the breaching through which the hot
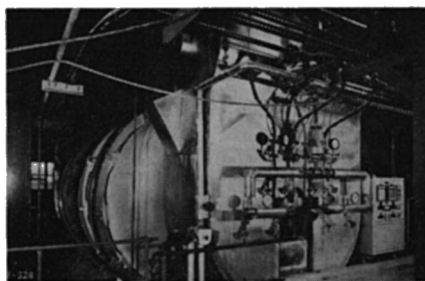

Figure 2 Spherodizer installation

air is drawn. The slurry is pumped under pressure through the nozzle onto a dense curtain of recycled fertilizer, which has been returned to the front of the spherodizer. As droplets of slurry hit the recycle granules, water is flashed off, forming a new onion skin layer around each of the solid particles every time they are cascaded as a curtain across the spraying section of the rotating drum. Exceptionally dense and well-rounded granules are the resulting product. The water content of the slurry varies with the type of fertilizer being produced. Our tests have shown that essentially all the water in the slurry is released at the moment of impact on the recycle particles, provided enough air is available. With good operation, the material leaving the spherodizer usually is 60 to 65% product size, 25 to 30% under-size and 5 to 10% over-size. After screening, the fines and the crushed over-size with about half of the product size fraction are returned as recycle.

Figure 3 shows the control panel and a pictorial flowsheet of one of the latest C & I/Girdler nitric phosphate plants. At left is the wet section, with the raw material
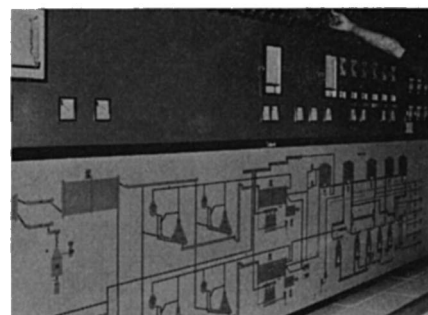
Figure 3 Control panel of nitric phosphate plant

bins and feeders on top, and the acidulation and neutralization reactors below. Two spherodizers with their related air handling facilities are at the center screening and milling equipment appears on the right. Under the panel is the electrical control console, from which substantially the whole plant can be operated.

Figure 4 is a picture of the slurry pumps and piping with one of the pumps removed to show the insulated pump suction line.
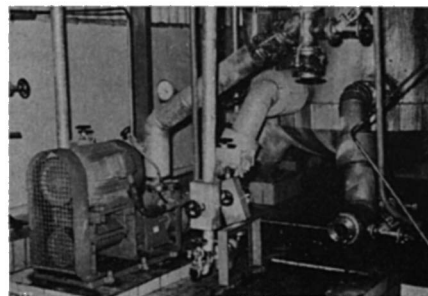
Figure 4 Slurry pumps and piping

Figure 5 shows the electric vi-
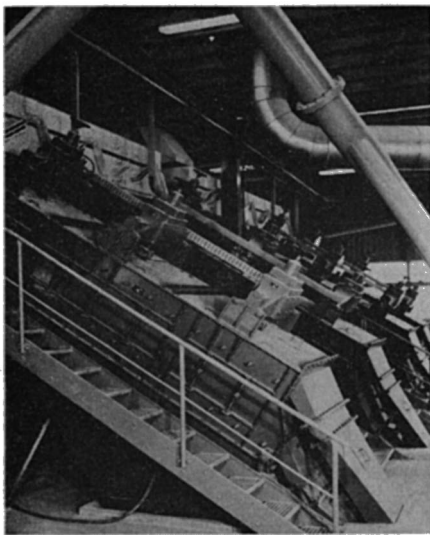
Figure 5 Vibrating screens

brating screens, with the dust collecting air ducts in the foreground. The cage mills for the over-size are shown in Figure 6.
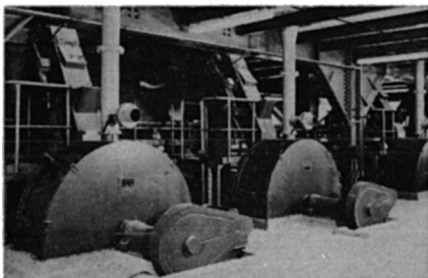
Figure 6 Cage mills for over-size

The most impressive feature of this basic nitric phosphate process is its flexibility. While at the time of the first Round Table presentation only 14-14-14 and 20-20-0 had been produced commercially at substantial rates, its ability to produce a wide variety of nutrient ratios and grades has since been amply demonstrated. Spherodizers have now been used in over 20 plants all over the world, and they have produced in commercial quantities all the grades shown in Figure 7.

While a large number of these plants employed the well-known PEC nitric phosphate process, other combinations have been equally successful. In the last three years C & I/Girdler has been associated with the construction of four large nitric phosphate plants in Europe, in which spherodizers have been found to be an excellent method to handle a variety of nitric phosphate products. Two of these plants use

Figure 7
Fertilizer Produced In Spherodizer Plants.

| Nutrient Ratio or Product Type		Grade
1 - 1 - 1	• • •	13 - 13 - 13
		14 - 14 - 14
		15 - 15 - 15
		16 - 16 - 16
1 - 1 - 0	• • •	20 - 20 - 0
		22 - 22 - 0
1 - 1 - X	• • •	12 - 12 - 24
		13 - 13 - 21
1 -1.5- X	• • •	10 - 15 - 15
1 - 2 - X	• • •	6 - 12 - 18
1 - -3 - X	• • •	12 - 36 - 12
		13 - 34 - 10
2 - 1 - X	• • •	14 - 7 - 10
		18 - 9 - 18
		19 - 9 - 0
		20 - 10 - 10
Ammonium Nitrate/Limestone		21 - 0 - 0
		26 - 0 - 0
Ammonium Nitrate/Sulfate		26 - 0 - 0
Ammonium Nitrate/Phosphate		27 - 12 - 0
Ammonium Phosphate/Sulfate		16 - 20 - 0
Ammonium Phosphates		11 - 48 - 0
		11 - 52 - 0
		16 - 48 - 0
		18 - 46 - 0

variations of the phospho-nitric process, representing simplifications and improvements of the basic technology. One plant uses a variation of the well-known Odda process, involving calcium nitrate separation. The fourth plant is equipped with two parallel nitric phosphate systems, one a conventional phospho-nitric, the other a modified Odda system.

The fertilizer grades shown in Figure 7 cover a wide range of chemical compounds. While all fertilizers containing ammonium nitrate are ideally suited for the spherodizer process, mono-ammonium and diammonium phosphates have also been produced in the same plants. The rate of production varies with the amount of moisture necessary to form a satisfactory slurry. It also depends on the decomposition temperature of the formulation. Fertilizers of lower nitrate content can stand a higher temperature than those with a higher percent of nitrate.

Product moisture is an important factor in the physical characteristics and storability of granular fertilizers. The actual moisture level at which different products store satisfactorily, however, varies with the nature of composition of the constituents. In this respect it appears that the spherodizer process has an inherent ability to dry products to the optimum level of moisture at which they will exhibit the hardness and stablity required for good storage characteristics.

Let us now examine how the basic nitric phosphate plant illustrated in Figure 1 can provide the flexibility required to meet changing market and raw material patterns. Let us assume that a fertilizer producer has built such a plant at a time when prices and availability of sulfur and/or phosphoric acid made it attractive. With sources of sulfur becoming more scarce and costs on an upward trend, an alternate method of eliminating the excess calcium nitrate produced in the nitric acidulation of phosphate rock has to be found. At this point it would be easy to add a calcium nitrate removal section, and a calcium nitrate conversion section, as shown in Figure 8. Using technology recently developed by C & I/Girdler, this would make it possible to obtain a product with a P_2O_5 water solubility of 60 to 80%, without using any phosphoric acid and, consequently, sulfur.

Basically, all the products shown in Figure 7 can still be manufactured in this plant, as long as the required raw materials are available; in addition, most of the NP and NPK grades could now be produced with a P_2O_5 water solubility of 60 to 80%, depending on the type and grade of the phosphate rock used, even when no phosphoric acid or sulfur are available from outside sources.

If fertilizers of still higher P_2O_5 water solubility are required, they can be produced by the simple addition of another section, or building block, as shown in Figure 9. In this case, a portion of the calcium nitrate which was left in the liquor after the removal step shown in Figure 8 is converted to gypsum by the addition of a small amount of sulfuric acid. By this method, any degree of P_2O_5 water
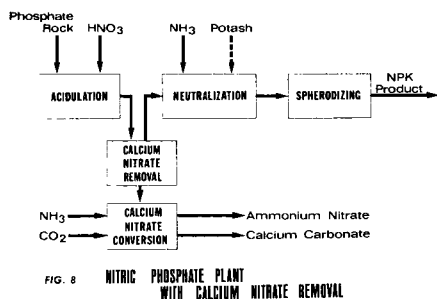
FIG. 8 NITRIC PHOSPHATE PLANT
WITH CALCIUM NITRATE REMOVAL

solubility can be obtained, though we know of no practical case where more than 90% would be required. The calcium precipitated as gypsum can be left in the product, if the formulation permits it, or removed by filtration.

By using the flexible approach described above, most situations and changes in market patterns can be met by additions to the existing plant, with a minimum of disruptions for the necessary tie-in connections.

For those fertilizer companies who believe recent predictions that elemental sulfur is soon to become a rare element, Figure 9 shows a
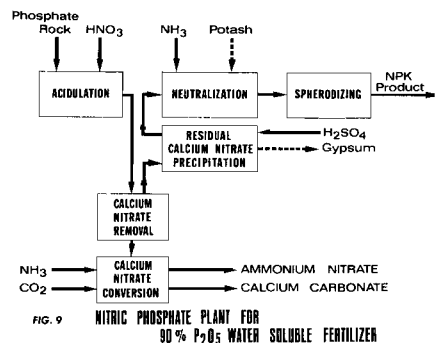

FIG. 9 NITRIC PHOSPHATE PLANT FOR
90% P_2O_5 WATER SOLUBLE FERTILIZER

program they can undertake immediately. If only 1-1-0, 1-1-1 and inverse grade products are of interest, the prilling route may be preferable for the final granulating section. C & I/Girdler is undertaking to build such a plant for producing 27-14-0 and 23-23-0 with 90% P_2O_5 water solubility, using only a small fraction of the sulfur required by the conventional sulfuric acid-phosphoric acid route.

A paper presented at the Fertilizer Production and Marketing Conference held by TVA at Knoxville, Tennessee, last month, reported the results of a questionnaire submitted to 19 major U.S. fertilizer companies, soliciting their views on nitric phosphates. Most of them did not feel they were justified in

entering the nitric phosphate field, for 5 basic reasons. In closing this presentation, we would like to review those reasons, in the light of our own experience in building over 20 nitric phosphate plants around the world, and of the updated technology referred to in this paper.

The drawback mentioned most frequently was limited water solubility. This point is well answered by the fact that we are now designing a plant based on nitric acid acidulation of phosphate rock, which will produce a fertilizer with 90% P_2O_5 water solubility.

The second drawback reported was grade flexibility. Most European companies who operate nitric phosphate plants make a very wide range of products. Granted, they frequently use some phosphoric acid, but whenever they use phosphate rock instead of phosphoric acid they are saving money.

Next was listed the problem of the over-all nitrogen to phosphate ratio. Until we can commercially convert calcium nitrate back to nitric acid, this point is bound to remain a problem for those companies which are not interested in becoming basic in nitrogen. On the other hand, the trend of nitrogen fertilizer producers to become basic in phosphates is bound to induce the phosphate producers, in turn, to become basic in nitrogen. And the fact that nitric acid is used twice when over-all nitrogen P_2O_5 balance permits it, is one of the major advantages of the nitric phosphate approach.

Storage properties were considered a problem. Certainly a nitric phosphate grade is more hygroscopic than DAP or triple super, but nitric phosphate producers have had very satisfactory experience in this country and abroad with bulk shipments of their products under a great variety of conditions. Moreover, most bulk blends today contain urea or ammonium nitrate, and are essentially similar in this respect to nitric phosphates.

Process complexity was cited as a disadvantage, because of the difficulty in switching grades in nitric phosphate units, as compared to superphosphate-based plants. The plants we have built have had no

difficulty in switching grades, and in many cases grade changes can be accomplished as fast or faster than in mixing plants.

In summary, we feel that none of the objections to the nitric phosphate route are sufficiently valid, even in relation to the U.S. market. There is no question that the processes and techniques to build these plants are available now. We anticipate that in the years to come more facilities of this type will be built than plants using the conventional route.

MODERATOR REYNOLDS: Thank you very much, Clem, for that very fine paper.

I think we have some questions in the audience, we will take a few minutes for them.

MR. WILLIAM WEBER: I think Mr. Giles has pointed out in the approach to the nitro-phosphate processes that there is a great deal of possibility there which was glossed over in the paper this morning by the Sulphur Institute.

The total mixed acid approach using the sulphate nitric or the phospho nitric process of course has been used because it is a relatively simple one. But the sulfuric acid savings are not dramatic if you want to produce a variety of grades and if you want to produce other than a rather high N-P ratio.

He has suggested a variation whereby he would remove some of the calcium as calcium sulphate. It is entirely possible as we know, from the work that TVA has done and work that we did many, many years ago. We built nitro-phosphate plants before anybody realized their significance. We built a complete sulphate recycle nitro-phosphate plant in 1930, but it was ahead of the times.

You can also remove the calcium with ammonium sulphate which you derive from outside sources as Stamicarbon is doing, or you can get it by the conversion of your gypsum to ammonium sulphate. This process is particularly attractive because it will produce a substantially completely water soluble product, except for the iron and aluminum phosphates.

I think this is the most attractive possibility, the combination of the Odda process with sulphate precipitation and recycle because

it has flexibility as to grade and extreme flexibility as to water solubility.

There is something I would like to point out in addition, which is the fact that we are now already using large tonnages of essentially nitro-phosphates in this country. A lot of these objections that are raised when you ammoniate superphosphate or triple-super-superphosphate, you have ammonium posphate and dicalcium phosphate and when you use nitrogen solution you have a combination of ammonium and ammonium nitrate. So you have a combination of ammonium phosphate, dicalcium phosphate and ammonium nitrate, which is nitro-phosphate, and these products are being extensively used in this country. Therefore I don't know why people think this is some radical step that is being proposed.

Furthermore, it is pointed out as to this question of water solubility, again, that when superphosphates and triple-superphosphates are used as a base, the formulation is usually dependent upon ammoniating the superphosphate and you are reducing the water solubility and most of the products that are produced that way in this country have relatively low water solubility and have been accepted.

MR. CLEM B. GILES: Of course, I agree with Mr. Weber.

One thing I was going to do when I started this paper, I considered opening up by saying, Let's get rid of this dirty word "nitro-phosphate." It has always had a bad connotation, as Bill so well described. We should just have a different word. Maybe we can concoct a word which will mean something new.

MODERATOR REYNOLDS: Are there questions concerning the paper?

MR. WILLIAM J. ROSENBLOOM (Mobil Chemical Company): There is no doubt about it, it is an extremely interesting talk and I am sure everybody appreciates this other side of the picture.

One thing that hasn't been mentioned and I am sure everybody will want to know is how the investment costs would compare with the old type process and with your new process incorporating the method of spherodizing.

MR. ENRICO PELITTI: Your question is how the method of spherodizing compares in investment with the conventional method of granulating?

MR. ROSENBLOOM: Actually, we are talking about two processes here: The generation of the mix and processing that to produce a solid, so that we should compare the cost of both, that is, one with the standard method and the other with prilling or producing solids in your way.

MR. PELITTI: Our experience in the building of nitro-phosphate facilities with spherodizers has shown that the investment cost can be definitely very competitive when the overall requirements are considered.

In other words, how many plants would be needed starting from the basic raw materials.

As to the new variations of the nitric phosphate approach, we are undoubtedly adding some sections that will increase the capital investment. We have not proceeded as yet far enough to present data on the final investment cost with the new approaches that were shown in the slides that you have seen.

Basically, however, I would like to point out that in the granulating step that we have shown we have some advantages as related to the conventional process, inasmuch as the spherodizer incorporates an internal recycle, you might call it, which replaces some of the external recycle required in other methods of granulating.

This reduces somewhat the size of the equipment, but the major advantage that everybody that has seen plants of these types has recognized is the simplication, and the fact that these plants can be so clean and can be kept so nice looking even after a few years of operation.

MODERATOR REYNOLDS: Do we have one more question? One short question.

DR. STRELZOFF: Well, I think this time I gave some other people the start.

I only want to ask you one question on the spherodizer itself. You mentioned that this is very successful in every plant, under every condition, climatic condition, like in Inda, was that successful too?

MR. PELITTI: The spherodizers have been successful whenever they have been constructed and operated and maintained properly. We have undoubtedly plants, like every company has had, where units have been eventually assembled by other contractors, where some problems have arisen that were reflected on the spherodizer itself because it was part of that particular project.

I don't think it has anything to do with the process nor with the basic approach refleced by the spherodizer.

MODERATOR REYNOLDS: Okay. I think this will conclude this part of the program. Thank you very much, Clem and Enrico.

I will turn the program back to Dr. Sauchelli.

CHAIRMAN SAUCHELLI: We will have opportunity tomorrow forenoon for a further discussion of nitro-phosphates. We know that it is a very timely subject and that we are almost at a turning point in the history of this technology of nitro-phosphates as against the conventional types and we are glad that the Round Table has been a forum for this purpose.

We have got to go on with our program. Sampling is unquesionably an important part of the chemical analysis function. The work of the analyst can be frustrated by bad sampling. In the modern fertilizer plant automation has necessarily replaced many manual operations which were common to the batch type plant. Sampling is one of them.

The next speaker, Mr. J. E. Carr, represents a company that has been a leader in the production of automatic sampling equipment, especially for the mining industry. I refer to the internationally known Denver Equipment Company. I am sure Mr. Carr will give us an interesting insight into new developments in automatic sampling.

New Developments In Automatic Sampling Within The Fertilizer Industry

J. E. Carr

Every plant manager is concerned with errors which affect a company's profits! Processing errors can, and do, occur. Large direct losses of profits can occur if material used in processing is represented by a biased sample. Today, costly blunders can be and are being eliminated by use of modern sampling technology. This report presents four new trends that supplement information given to this meeting ten years ago. This report will also reflect some of the important progress that operators are making in the field of eliminating errors by proper application of automatic sampling.

Since sampling is a long established practice in the fertilizer industry, much of what is "new" is actually a refinement of techniques. A great variety of problems are met and many interesting systems are observed. Some devices in use date back many years and show the early origin of many good sound ideas in current use. Also, one doesn't need to look very far before finding shocking examples of sampling practice that, like "Topsy" just growed. Many of these make-shift systems are worse than useless for they imply that a control technique is being used yet the results are booby-trapped with errors-

We have reviewed many fertilizer sampling projects since Mr. Cook (1) of Denver Equipment Company talked to the Round Table ten years tgo. We can see how the character of sampling has changed. One thing has not changed and that is the basic importance of sampling. Every plant which is concerned with quality, or anyone who sells a product based on a guaranteed analysis cannot overlook the importance of sampling, indeed, few do. In fact, most companies have elaborate facilities for analyzing samples. Unfortunately, and this has been observed in many, many cases, the elaborate and costly procedure for analysis often ignores the quality or reliability of the sample. The point here is "The Analysis of a Sample Can be no More Reliable Than the Sample on Which it is Based"!

Four identifiable areas show a trend in the fertilizer industry's continuing change.

1. Bigger sampler drive mechananisms are available for bigger tonnage plants and systems.
2. Better chute type samplers are being produced to improve sampling accuracy.
3. On-stream analysis is being applied to speed accumulation of quality data.
4. Experimental design methods are producing more standardized and realiable sampling systems.

I will touch briefly on the first three and discuss the fourth a little more since it has produced methods that promise substantial improvement in sampling practice.

One of the changes in equipment is the development of Big Mechanisms. They produce more than just the ability to sample bigger streams and bigger pieces. A versatile unit is shown in figure 1.

Figure 1

It carries a 1500 pound cutter at 150 feet per minute suspended direct from the mechanism. This cutter samples-4" material from a 500 TPH stream. In addition to the extra heavy duty applications, these big units handle large cantilevel loads; their speed can be changed easily in the field; bigger chutes can be sampled. These and other features make these mechanisms an important tool and permit more ambitious designs. Most important, they make it possible to apply the theoretical technique of sampling in a practical way to produce RELIABLE perfect samples.
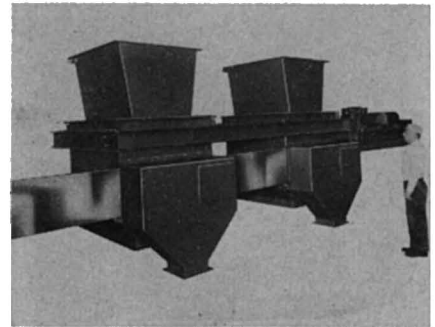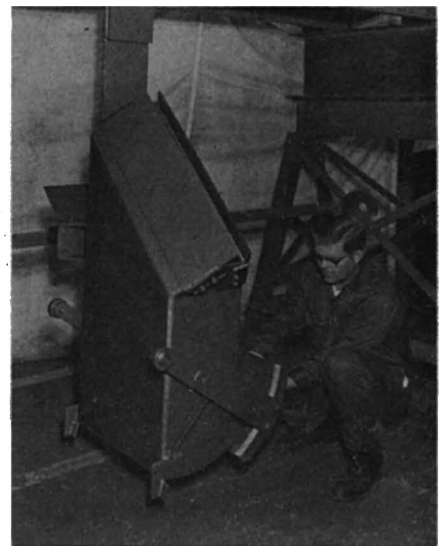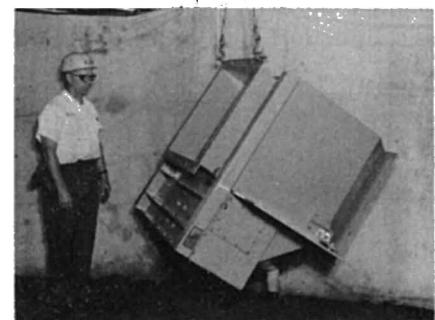

Figure 2

Figure 3

Chute Samples continue to improve. Note the integral mechanism and seal arrangement in figure 4.

Figure 4

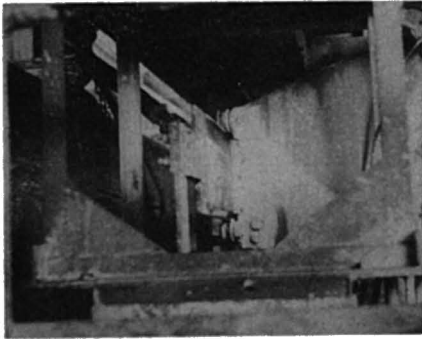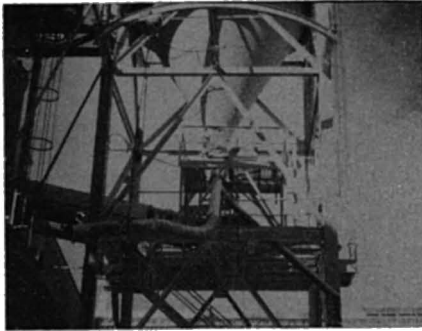Further installations are shown on figures 5, 6, and 7.
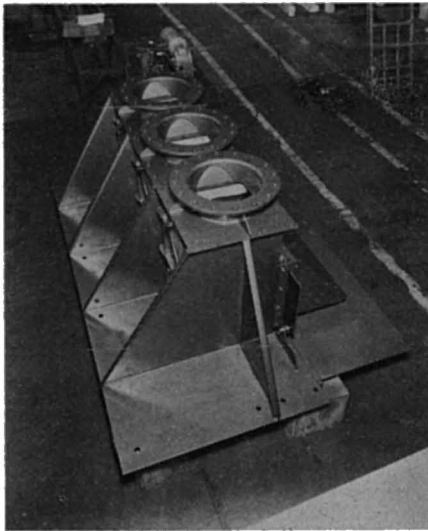

Figure 5

Figure 6

Figure 7

Not only are these units essential for reliably sampling dusty materials, they offer flange to flange engineering which can permit savings in design time and installation costs.

On-Stream Analysis has been discussed in recent papers) (2). As far as sampling equipment is concerned, several requirements are common to such projects. On-stream analysis equipment requires a uniform stream from the sampling system. Accuracy in sampling

must be consistent with the instrument systems accuracy. Where it is used to feed back information to control a process, the time the sampled material remains in both the sample preparation system and the material handling equipment must be limited. Time in process problems and sample contamination problems occur where the particle size of the sample must be reduced, to be accomodated by the on-stream analyzer. Fortunately, the large quantity of sample analyzed by on-stream methods often minimizes these time-lag and contamin.-tion errors.

Experimental Design Methods are being used to solve problems concerning the basic factors involved in sampling systems, such as cutter width, method of taking cut, amount of sample, etc. The data required in order to apply these standards to a specific problem is best obtained by direct experimentation (3). These experiments can be simplified quite a bit by working directly on the sampling problem so that less comprehensive, detailed data is adequate.

Factors that cause errors in sampling systems are (1) variations in the stream to be tested, (2) variation due to segregation, (3) random error at the mesh sizes involved, and (4) errors caused by contamination.

To illustrate how these concepts of error can be handled we will discuss the typical steps in a sampling problem. Five steps are used. They are studied in terms of the information needed to properly engineer the sampling system and they evaluate the errors that can be permitted in the final sampling system.

These five steps include the determination of:

1. Width of the sampler cutter opening.
2. The method of cutting the stream to be sampled.
3. Amount of sample necessary per cut.
4. Frequency of taking a sample.
5. Amount of total sample required.

If multi-stage sampling is necessary, Items 1 through 5 must be applied once again to subsequent stages of sampling.

In the phosphate industry, the *sample cutter opening* is specified as $3\frac{1}{2}$ times the largest particle diameter for the width. Other areas of the fertilizer industry use a rule of thumb as is illustrated by figure 8.
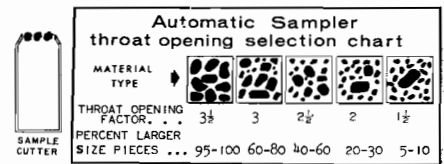
Figure 8

Trial and error have shown that this method is satisfactory.

Two factors dictate that the cutter opening be ample to accommodate all sizes of material in the feed stream. Too small a cutter width will fail to cut a sample in direct proportion to the flow. Either effect will consistently give a biased analysis. While the error probably will be small in both cases, it will usually produce errors in one direction consistantly.

The Method of Taking a Sample is dictated by the segregation which occurs in the solids. This segregation frequently occurs in phosphate rock since its analysis varies with mesh size. Plus 35-mesh phosphate rock may vary from 68 to 71% BPL while minus 35-mesh

Figure 9
Analysis Of Grab Sample Of Fertilizer Recycled For Blending

Retained on Screen	% of Sample	% CaO	% K₂O	Total % P₂O₅	% Fe₂O₃	% Al₂O₃	% H₂SO₄	Ratio SiO₂
No. 6	2.2	4.22	28.55	23.94	6.48	0.72	1.02	1058
No. 8	3.3	4.51	25.78	26.17	7.03	0.79	1.12	996
No. 10	5.8	4.31	24.45	27.34	7.34	0.81	1.20	948
No. 12	7.3	3.91	24.41	27.72	7.46	0.80	1.17	826
No. 14	28.0	3.84	24.95	27.37	7.36	0.79	1.19	857
No. 20	42.7	2.68	30.58	23.14	6.60	0.67	1.04	664
—20	10.7	1.51	40.87	14.94	5.03	0.51	0.87	542
	100.0							

sizes may vary from 55 to 62% for for the sample. Manufactured fertilizers will also vary similarly as figure 9 illustrates.

The methods of sampling applicable to these types of material is shown in figure 10. This figure is

Cuts Taken From Conveyor

Fig. 10
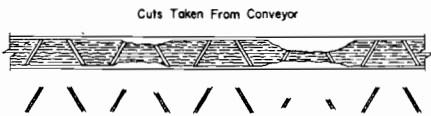
Figure 10

included to show a stream on a conveyor and the section cut out of it by a sampler.

This method consists of moving a cutter with parallel blades at uniform speed completely across the stream to be sampled. This is done when the material is in free fall. The sample cut by this method is in proportion to the volume of flow of material at the time the cut is taken so that subsequent cuts can be composited and will be represented by weight. As an example, assume that a sampling system yields 6 lbs. per cut from a 100 tph stream. The identical mechanism would yield 12 lbs. per cut from a 200 tph stream.

The concept of removing a sample in direct proportion to this total stream also applies to the individual cut as it traverses completely across the stream. The stream on a conveyor varies in weight and analysis from side to side and yet is automatically composited by weight to yield a representative sample by this method.
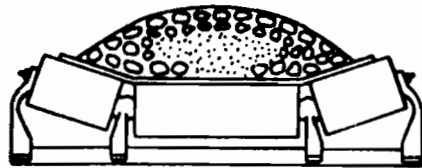
MATERIAL SEGREGATION IN BELT LOADING

Figure 11

A problem in the design of sampling systems has plagued not only the fertilizer industry but also most other industries. It is "How much of a sample is needed to be sure that the sample is representative of the entire lot?"

Guess-work has been eliminated and the trend now is to the application of statistical data to determine the amount of sample necessary. This data is applied to determine the *amount of sample per cut*. It can be applied again in a similar way to calculate the *total sample required* after the individual cuts have been accumulated.

The amount of sample per cut is in proportion to the sample cutter opening and the cutter speed. The amount of sample per cut must be large enough to minimize random errors. The total volume of the sample is determined by the number of cuts taken. This sample must again be large enough to minimize errors due to random accumulation of material in a single sample analysis, yet small enough for conventient handling in the analytical laboratory. Figure 9 shows how random accumulation could occur to give a 40% K_2O and 15% P_2O_5 in place of 29% and 24% actually present.

Random variations can be estimated by experimental work. For phosphate rock this test could consist of taking about 100 samples of 1/2 lb. each from the center, edge, bottom, and top of a well mixed control sample. After mesh analysis and BPL are run on the 100 1/2 lb. samples, the variance can be calculated for 1/2 lb., 1 lb., and up to 5 lb., samples by combining samples mathematically. A variance of less than 0.15 will probably be found for all samples above three pounds for typical full size phosphate rock. This 3 lb. figure is reduced by crushing to about 1/2 lb. for 1/4" material.

Variance will increase as the sample weight decreases below 3 pounds and can be estimated for practical purposes by direct proportions. These methods are outlined in ASTM bulletin D2234-65 (3). Figure 12 shows the method of calculation.

The variance gives us an approximation of variations which will occur due to particle size, number of cuts, and size of sample. It lets us solve some of the problems associated with these factors by direct proportions.

Variance is precisely defined in statistics. For this discussion it is easiest to think of variance as the square of the error you might expect from a sample.

Operating data to compare with experimental data is meager for full sized phosphate rock because the size of the primary sample is usually much bigger than the minimum weight for the primary cut. More information is available for secondary and tertiary samples, since they often take very small samples per cut see figure 13.

Variance figures are valuable here because the many cuts available with continuous secondary units often allow the use of small sample cuts.

The frequency of taking a sample at the primary sampler is usually controlled by the variation in the material to be sampled. The requirements here are dramatically

	BPL	BPL-69.07	$(BPL-67.07)^2$
	69.88	0.81	0.656
	68.76	−0.31	0.096
	68.89	−0.18	0.030
	68.50	−0.57	0.325
	68.52	−0.55	0.302
	69.44	0.37	0.137
	68.96	−0.11	0.012
	69.57	−0.05	0.250
	69.02	−0.05	0.003
	69.15	0.08	0.006
	690.69		1.817

Figure 12

$$\text{Mean} = \frac{690.69}{10} = 69.07 \qquad \text{Variance} = \frac{1.817}{(10\text{-}1)} = 0.202$$

$$\text{Standard Deviation} = \sqrt{0.202} = 0.45$$

PRIMARY FEED

PRIMARY SAMPLE CUTTER

PRIMARY SAMPLE

SIZE REDUCTION

SAMPLE REJECTS TO PLANT

SECONDARY SAMPLE

HOPPER FEEDER

FINAL SAMPLE

SAMPLE REJECTS

1. 48" DENVER BELT CONVEYOR
2. DENVER AUTOMATIC SAMPLER EXTRA HEAVY DUTY
3. 10" x 20" DENVER JAW CRUSHER
4. 14" DENVER BELT FEEDER WITH HOPPER
5. 28" DENVER VEZIN SAMPLER CONTINUOUS
6. 12" DENVER GYRATORY CRUSHER AND FEEDER
7. 20" DENVER VEZIN SAMPLER-CONTINUOUS
8. COVERED SAMPLE BUCKET
9. 8"x 5" DENVER BUCKET ELEVATOR-REJECT
10. 48" DENVER BELT CONVEYOR-REJECT

TYPICAL SAMPLING TOWER ARRANGEMENT INCORPORATES GRAVITY FLOW OF SAMPLE THROUGH VARIOUS STAGES OF SAMPLE CUTTING AND SIZE REDUCTION

DENVER SAMPLING TOWER
GENERAL ARRANGEMENT F-5915
7-6-64

Figure 13

affected by the blending equipment just ahead of the sampling point and the time interval over which variations occur. For instance samples collected while a 10,000 ton ship was loaded indicated that a minimum of five different types of phosphate rock were used to make up the shipment. These lots consisted of flotation concentrate averaging 72.69% BPL and phosphate rock as shown in figure 14.

As listed, calculations indicate that the maximum interval between sample cuts should be 42 seconds, 95 seconds, 3 minutes, 5 minutes,

and 47 seconds. This system handles more varied ores and smaller shipments so that it actually uses an interval of 30 seconds.

Procedures for these calculations are outlined in a number of references (6).

The new information developed here and an important advance, is that for practical purposes the ratio of the variance obtained for the system to the variance specified will equal the number of cuts needed.

Conclusion

At Denver Equipment Company, we accumulate data from coast to coast and correlate it with existing sampling systems. This permits the use of comparative data and the development of general data that is useful in new problems.

The four new developments, (1) bigger sampler mechanisms, (2) better chute samplers, (3) on-stream analysis, and (4) experimental design methods, are being applied to projects and many projects can now be handled logically that previously were handled intuitively. Methods are now available to determine the feasibility of complex sampling and control systems.

1) Economics of Automatic Sampling by Paul E. Cook
2) Automated Quality Control For P_2O_5 In Phosphate Rock by H. H. Roberts and A. N. Bauman
3) ASTM Specification D2234-65
4) Problems Sampling Bulk Blended Fertilizers Paper Given For 1964 Round Table By L. J. Pircon
5) Methods used and Adapted by the Association of Florida Phosphate Chemists 1960
6) Mechanical Measurements — Beckwith and Buck Addison Wesley.

CHAIRMAN SAUCHELLI: Thank you, Mr. Carr. I am sure automatic sampling is going to become a more and more important feature of all modern plants.

Are there any questions? We have a few minutes for the questions.

You have covered the subject well. There are no questions, Mr. Carr. Thank you again.

We will go right along with

Figure 14
Five Lots Making Up 10,000 Ton Shipment

% BPL	72.69	69.3	67.5	65.3	63.0
Weight (tons)	457	2369	4875	2347	886
Time For Tonnage To Pass Sampler (Minutes	21	110	224	108	40
Variance	0.15	0.22	0.35	0.21	1.53
Time Between Cuts, (Seconds)	42	95	180	300	47

Instrumental and Automated Analysis. Having heard the presentation on automatic sampling, we are ready to learn about automated analysis.

We asked Mr. J. R. Archer, Quality Control Manager of the IMC, to arrange a panel discussion on the subject. Mr. Archer is one of the forward-looking, progressive chemical analysts and a leader in our industry.

It is an honor to have him on our program and he will introduce the distinguished panel members he has selected for discussion.

Analytical And Quality Control Program

J. R. Archer, Panel Leader

The components of the industry are sales, production, technical service, research and quality control. Our production plants are complex manufacturing facilities presenting difficult quality control problems. Yet, we cannot accept operation deficiencies as inevitable.

The control man, of necessity, has under his direction technicians who perform the same routine job day in and day out. There is very little romance in their job. However, it has been said that "few things attract more favorable attention than a routine job done with exceptional intelligence."

"If the do-it-yourself craze continues; it might even extend to thinking." Gentlemen, the industry quality control people have been thinking—they have taken advantage of improvements offered in instrumental and automated analysis —adapting them to fit special needs and developed innovations of their own.

The panel speakers are Mr. Robert A. Hofstader, Esso Research and Engineering, Linden, New Jersey.

Mr. Ernest E. Barrett, Jr., Senior Chemist, IMC Monitor Control Lab, East Point, Georgia;

Dr. Elwyn D. Schall, Indiana State Chemist, Lafayette, Indiana; and

Dr. James F. Marten, Technicon Corporation, Ardsley, New York.

We are going to deviate a bit from the printed program and ask Jack Barrett to lead the discussion His presentation is entitled Analytical and Quality Control Programs.

I might state that each of the panelists will give his presentation and then after the entire panel has made its presentations, we will entertain questions from the audience.

Analytical and Quality Control Programs

E. E. Barrett, Jr.

Instrumental methods of analysis, whether completely or partially automated have contributed much to the overall quality control program of the fertilizer industry. Demands by producers and consumers for more rapid analysis has led many chemists to reconsider their laboratory organization in the light of recent advances in the field of automated analytical techniques.

The object of this presentation is two fold: (1) To demonstrate the laboratory organization supporting the product quality control program for International Minerals and Chemical Corporation, empha-sizing our plan for producing more accurate and reliable analytical results through the use of automated methodology and time-saving innovations. (2) To demonstrate the use of instrumental techniques in programs supporting our sales staff, such as soil and tissue analysis, and in production support liaison groups dealing with problems of water and air pollution and special analytical techniques for specific problems.

The Rainbow Division of International Minerals and Chemical Corporation operates plant food production plants and blending plants within an area roughly bounded by New York State and Florida from North to South, and Texas and South Carolina from west to east.

Rapid control analysis is needed at each plant in order that problems in mixing and formulation may be determined immediately. For this reason, we maintain a small laboratory in each plant. Equipment and personnel is provided for Nitrogen, total P_2O_5, and Potassium determinations.

To serve the vast needs of production and to provide analytical assistance to plant laboratories and customers, I.M.C. has, since its founding in 1909, maintained a central quality control laboratory. Located in East Point, Georgia, the facility employs some 29 persons and has an annual budget of approximately $300,000.00.

The laboratory is divided into four key sections: (1) the fertilizer analytical section with its supporting facilities including a sample preparaton area and central weighing district; (2) the physical and special testing sections; (3) the soil and tissue laboratory, including its supporting sub-sections — a preparation area and an instrument room which is used jointly with the fertilizer laboratory, and (4) the administrative and clerical area. This latter space consists of offices for the quality control manager, supervisor of facilities, and senior chemists in charge of the various departments.

Our fertilizer facility provides an excellent example of the effects of automation on improved out-put and accuracy. Samples are submitted to the East Point laboratory with a sample label showing such information as guarantee, plant locations, and tons represented. After being assigned a laboratory number the samples are prepared for analysis by personnel working in this area.

After preparation the samples are placed in the weighing area. Each individual analyst then determines which samples are to be analyzed for the day and a separate list is made for Phosphate, Nitrogen and Potassium evaluation.

The weighing room is the pivot-point for the Phosphate, Nitrogen, and Potassium sub-

sections. Each analyst is assigned a balance, and the balances are arranged concentrically about a revolving three-tiered table, upon which all prepared samples for the day are placed. Each analyst may place any given sample within his reach by simply rotating the tier. We believe that this innovation provides the maximum result with the least amount of movement.

After samples are weighed, they are taken into individual laboratories for digestion and dilution and subsequent analysis by either automated techniques or, in the case of Nitrogen, the Kjeldahl Volumetric method. One analyst can produce 96 Nitrogen determinations, from weighing to the final result, in an 8 hour day.

The Phosphate laboratory provides an excellent example of how automation has helped us to improve our out-put of samples with less personnel. Located to the right is the area in which insoluble phosphate is analyzed. To the left is the area in which total phosphate is evaluated. The volumetric method previously used in our laboratory is too time consuming. The instrument seen here is a Technicon Autoanalyzer, which is capable of determining the total phosphate content of the digested fertilizer at a rate of forty samples per hour with an accuracy of one-tenth of one percent relative. Innovations developed by the agricultural chemicals division of our company have made possible the reading of phosphate content directly in percent. A digital readout may be worked into the system to print the percentage directly on a moving tape. Comparison between the older volumetric method and the new automated method clearly shows that several steps can be entirely eliminated. There are 18 steps used in the volumetric method as opposed to 8 for the photometric. Previously two persons were required to produce 96 phosphate determinations daily. With the installation of the Technicon Autoanalyzer, we are now able to produce 110 determinations with one analyst.

Since 1954, potassium has been screened by flame photometry. Prior to the purchase of our autoanalyzer for the analysis of potassium, one analyst was producing 50 determinations per day with questionable accuracy. Since the installation of the automated system, our analyst can produce 75 determinations per day with accuracy comparable to that obtained by the widely accepted sodium tetraphenyl boron method. Samples are prepared in the potash laboratory and moved to the instrument room for final evaluation.

Upon completion of the analysis, each analyst records his result on the original sample label. The senior chemist in charge of the fertilizer section and the quality control manager decide which figures are to be reported back to the plant. If results are below established tolerances, they are rechecked again the next day. If they are significantly below the tolerance, the standard volumetric methods are used to confirm the automated result.

The sample labels originating at the plants are then duplicated and mailed to plant superintendents. The original sample label is kept in the laboratory files.

For mixed fertilizer, we follow the scale recommended by the tolerance committee of the A.A.F.C.O., except we set the same tolerances above guarantee as below guarantee.

Superphosphate control is related to the rock-acid balance and is expressed in pounds of acid per 1000 pounds of rock variance from the desired formula. The tons of fertilizer having N-P-K analyses within the range of the tolerance scale are considered "on specifications". The tons of fertilizer having either N, P, or K analyses outside the scale are considered "off specifications". The tons of fertilizer having either N, P, or K analyses below the scale and therefore subject to penalty are listed under "below specifications". In the example given, plant number 1 manufactured 3928 tons, 75% of which were "on specifications", 25% "off specifications", and 9.2% "below specifications".

The analyses are given a statistical treatment and the percent of guarantee and coefficient of variation are shown for each grade. Plant number 2 is having difficulty with percent of guarantee on nitrogen and the coefficient of variation indicates a wide spread. This plant is definitely having trouble with nitrogen. The data shown gives management a clue as to the approach which should be taken to bring the analysis in line.

Having covered the fertilizer section and its automation, we shall proceed with a discussion of the soil and tissue facilities and show what effect automation has had there.

Samples for analysis by both instrumental and manual methods are prepared here. The chemical constituents are extracted using the buffer recommended by the state from which the sample originates.

After preliminary preparation, the extracted solution is tested for many different constituents among which are: metals, nitrogen, sulfur, and phosphate. This laboratory is also capable of determining total digestible nutrients. The instrument room shown here is located adjacent to the soil section and samples are brought here for final testing.

This atomic absorption unit is used jointly by the soil and special testing departments for evaluating metals in small concentration. The soil section analyzes for copper, magnesium, manganese, iron and zinc in both soils and tissues: The special testing section evaluates metals in trace quantities in premium fertilzers and in connection with dust and fume surveys.

Sulfur in plant tissues is evaluated using this Leco Sulphur apparatus. Eighty samples of plant tissue can be analyzed in an eight hour day by one analyst. This smaller atomic absorption unit is used for the evaluation of potassium and calcium in soil and plant tissues.

The next slide shows the physical testing section of the laboratory, which is concerned with water and air pollution problems as well as acidulation, granulation, ammoniation and hardness techniques.

The chamber seen here is used for studies of relative humidity and hydroscopicity of materials and mixed fertilizer.

International Minerals and Chemical Corporation formulates pesticides into their fertilizers. Per-

sonnel in the pesticide laboratory shown here, perform the necessary extractions and determine the organic constituents by infra-red spectroscopy. The instrument shown is a Beckman IR 10 unit convering the infra-red spectra from 2 to 35 microns and using potassium bromide optics.

During the course of this discussion, we have tried to show how automation has significantly im-

proved our quality control program and made work easier for the analyst in addition to contributing to more accurate results. A company's most precious asset is its reputation and ability to distribute quality products . . . and that is our goal.

MODERATOR ARCHER: Thank you, Jack.

Our next speaker is Mr. Hofstader who will give a specific application of automated analysis.

Normal testing procedures in a well equipped control laboratory are limited at best to a 1-2 complete analyses per 8 hour shift for a fertilizer containing 4 components, namely; ammonical nitrogen, nitrate nitrogen, P_2O_5 and K_2O. Process control is generally only carried out when a serious problem exists. Analysis of raw materials can only be made on a very small sample which may not be representative of the entire batch material. Such limited data makes it difficult to assure homogeneity of product to customers or to make any changes in operating parameters during a process run. With sufficient data and lack of confidence in a single analysis up to 16 hours can pass before adjustments to correct formulation can be made. The possible over or under formulation during this time could lead to large

Rapid Control Methods For Analysis Of Complex Fertilizers As Applied At Fertica

Roul Oquendo, Edwardo Zumbado and Robert A. Hofstader

Fertica's fertilizer plant at Puntarenas, Costa Rica has a capacity of 185,000 metric tons of fertilizer/year, 2/3 of which is complex fertilizer and 1/3 ammonium nitrate.

At the Fertica fertilizer plant, a system of product and process analytical control was instituted. The basis of the analytical system is the basic components of the AutoAnalyzer manufactured by Technicon, New York. The use of this apparatus as applied to the formulation and product at the plant has permitted very close control of the product in process as well as in its final form.

General Plant Description

The complex fertilizer plant at Puntarenas utilizes a process of phosphate rock, ammonium phosphate, ammonia and potassium chloride reacted in a slurry form in a series of 16 reactors. The process is such that the reactions in the slurry form assure uniformity of product and after the product has been spherodized that each pellet is as uniform as the total product. Similar processes are used at BASF,

RUHR, HOECHST and others. A similar diagram of the process appears below:

Table 1
Classification Of Product According To Raw Material

Formulation	% Ammonia	% Ammophos	% Rock	% Nitric Acid	% KCl
14-14-14 13-13-20	6-7	13-26	6-24	22-33	23.40
12-24-12 10-30-10	3-5	36-51	13-19	14-20	17-22
20-20-0	10-11	24-25	21-25	40-43	—
18-10-15 EM 17-11-22 20- 7-12 EM 20-20-15	8-12	17-27	—	27-40	22-36
10-40-10	2	80-81			17-18

Table 1 classifies the products produced in the complex fertilizer plant along with the range of raw material used in the formulation.

The Analytical System

Analysis of raw materials, intermediate products, and of final product are essential to product and process control in any plant.

expenditures of money, for the following reasons,
- desire for assurance of homogeneity of product
- continued knowledge of the process to make a specification product
- a rapid technique of analysis

the Analytical Research Division of The Esso Research and Engineering Company developed the automatic rapid analysis applied at Fertica to carry out product and process control. Similar product quality analysis is being carried out at Imperial Chemical Industries in England.

When it was decided to evaluate rapid analytical control methods in fertilizers it was of primary importance that all the results obtained be statistically comparable
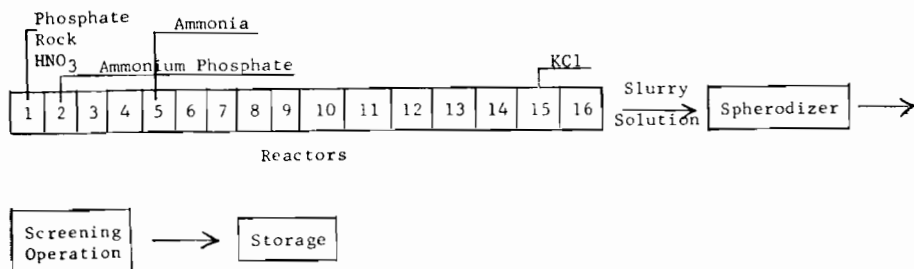

Figure 1

to those obtained by conventional methods, primarily of AOAC (American Association of Analytical Chemists).

The system which was developed and installed at Puntarenas consists of basic AutoAnalyzer components in series to accomplish simultaneout determinations of ammoniacal nitrogen, nitrate nitrogen, total P_2O_5 and K_2O, with an analytical capacity of 30 samples solutions/hour equivalent to 120 determinations per hour. With the present analytical capabilities at Puntarenas, it is possble during plant runs to monitor the product 24 hours/day. At present samples of products are taken at one hour intervals. To supplement product analysis, samples of slurry are removed from reactors 4 and 16 at various intervals. The information obtained from material at reactor 4, prior to ammoniation, is used to adjust nitrict acid, ammophos and rock based on the formulation. The data obtained from reactor 16, just prior to entering the spherodizer, is calculated on a "dry basis" and any nutrients can then be adjusted so that specification product will be obtained. The calculation of "% on dry basis" is based on the assumption that the water content in the final product is relatively constant. The calculation appears in the Appendix.

Such control makes it possible to make formulations adjustments in less than one hour.

The AutoAnalyzer

The AutoAnalyzer is a system of modules which automatically carries out wet chemical procedures and is shown schematically (Figure 2). The basic principle on which the system operates is to set up a state of dynamic equilibrium throughout the modules. For ex-
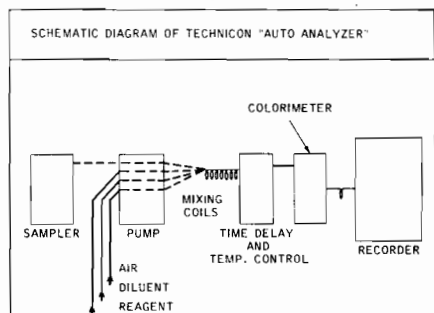
Figure 3
MANIFOLD FOR 14-14-14
P_2O_5-K_2O-NO_3-NH_4

Figure 2
SCHEMATIC DIAGRAM OF TECHNICON "AUTO ANALYZER"
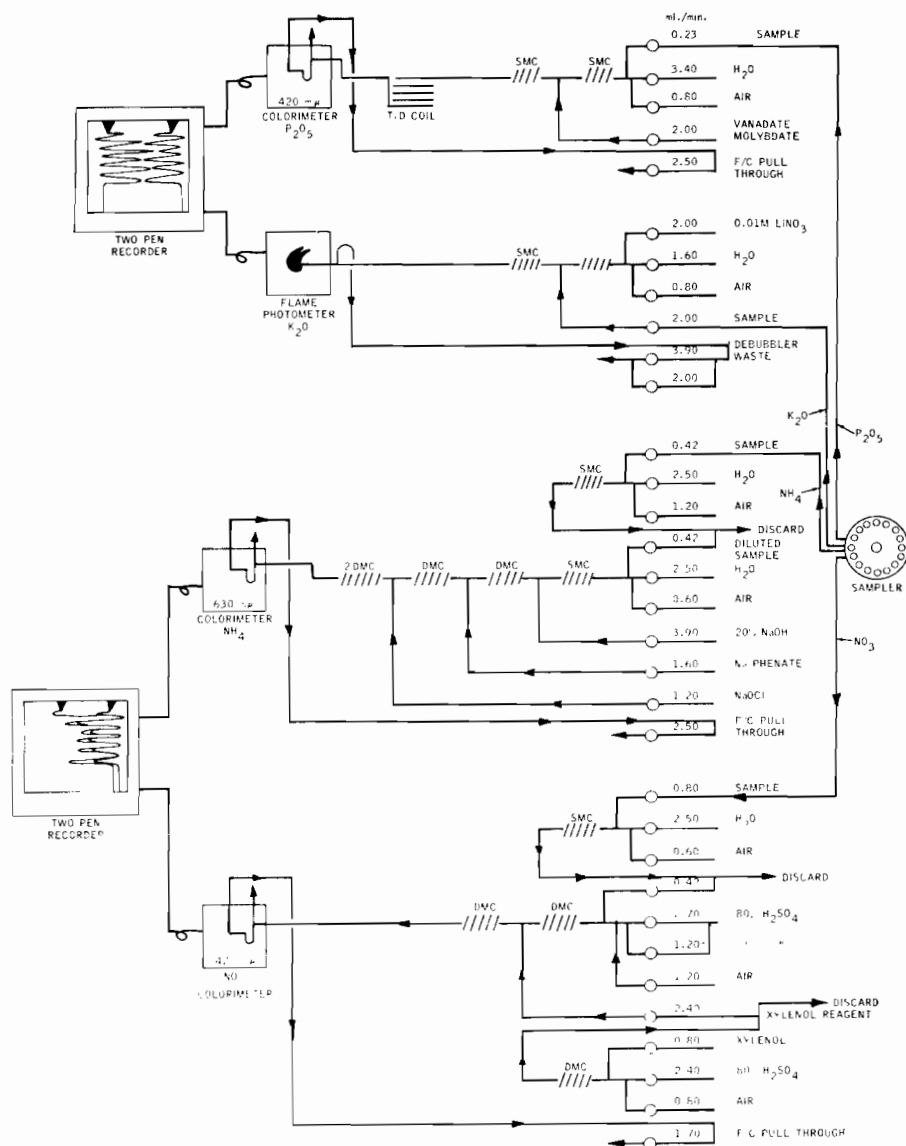
ample, in the spectrophotometric determination of ammoniacal nitrogen, nitrate nitrogen and P_2O_5 a metered flow of sample solution mixes with reagents passes through a photometer which has a continuous flow through cell. All the conditions are maintained constant, and as a result the intensity of the color developed is proportional to the concentration of the constituent being analyzed, and is recorded. In a similar way a flame photometer is used for the analysis of potassium. Calibration of the apparatus is achieved with standard solutions containing all the elements being determined.

The technique, since it is based on a dynamic equilibrium, is not influenced by small changes in am-

bient conditions, making the apparatus very suitable for plant operations. The equipment is rugged with very few parts capable of breakage with normal handling.

A more detailed description of each of the modules appears in the Appendix.

Application to Fertilizer Analysis

The chemistry involved in the analytical procedures which were applied to the Auto-Analyzer is as follows:

Phosphorus: The fertilizer solution containing phosphate is reacted with molybdovanadic acid to form yellow phosphomolybdic acid, the intensity of which is proportional to the phosphorus concentration.

Figure 4
MANIFOLD FOR 10-40-10
P_2O_5-K_2O-NH_4

TWO PEN RECORDER

COLORIMETER P_2O_5 — 420 mµ

T/D COIL

SMC ///// SMC /////

ml./min.	
0.23	SAMPLE
3.40	H_2O
0.80	AIR
2.00	VANADATE MOLYBDATE
2.50	F/C PULL THROUGH

FLAME PHOTOMETER K_2O

SMC ///// SMC /////

0.42	H_2O
2.00	0.01 M $LiNO_3$
0.80	AIR
3.40	SAMPLE
3.90	DEBUBBLER
2.00	WASTE

P_2O_5
K_2O
NH_4

TWO PEN RECORDER

COLORIMETER NH_4 — 630 mµ

2DMC ///// DMC ///// DMC ///// SMC /////

SMC /////

0.42	SAMPLE
3.40	H_2O
1.20	AIR
0.42	DILUTED SAMPLE → DISCARD
1.20	H_2O
0.80	AIR
3.90	20% NaOH
1.60	Na PHENATE
1.20	NaOCl
2.50	F/C PULL THROUGH

Figure 7
MANIFOLD FOR 10-7-12-3-1.2
P_2O_5-K_2O-NH_4-NO_3

TWO PEN RECORDER

COLORIMETER P_2O_5 — 420 mµ

T/D COIL

SMC ///// SMC /////

ml./min.	
0.30	SAMPLE
3.40	H_2O
0.80	AIR
2.00	VANADATE MOLYBDATE
2.50	F/C PULL THROUGH

FLAME PHOTOMETER K_2O

SMC ///// SMC /////

2.00	0.01M $LiNO_3$
1.60	H_2O
1.20	AIR
2.00	SAMPLE
3.70	DEBUBBLER WASTE
2.00	

K_2O
NH_4
P_2O_5
NO_3

SAMPLER II

COLORIMETER NH_4 — 630 µ

2DMC ///// DMC ///// DMC ///// SMC /////

SMC /////

0.42	SAMPLE
3.40	H_2O
1.20	AIR
0.42	DISCARD / DILUTED SAMPLE
1.60	H_2O
0.80	AIR
3.40	20% NaOH
1.60	Na PHENATE
1.20	NaOCl
2.50	

TWO PEN RECORDER

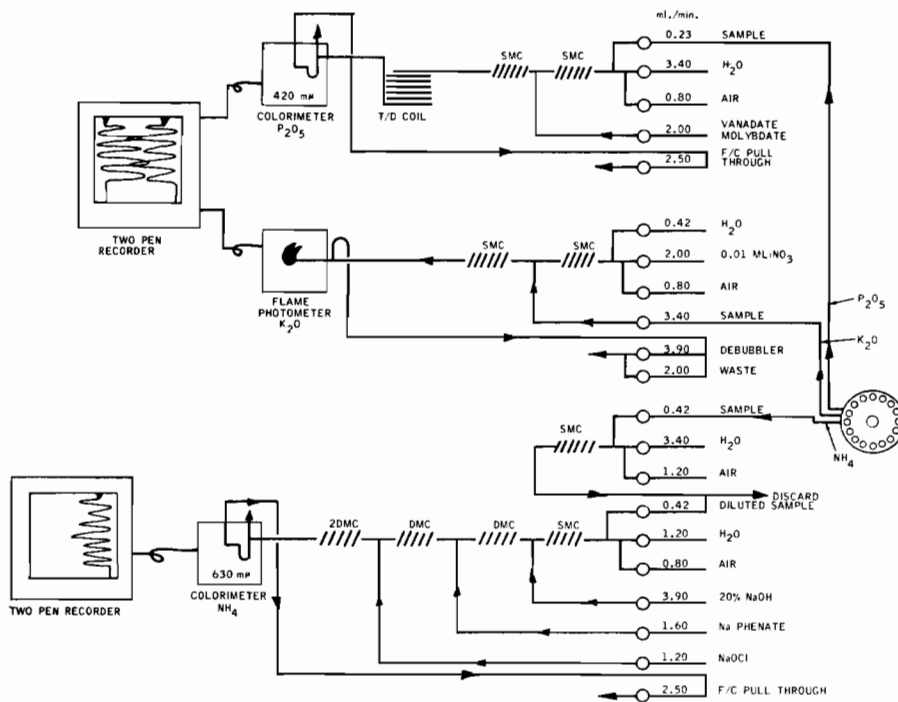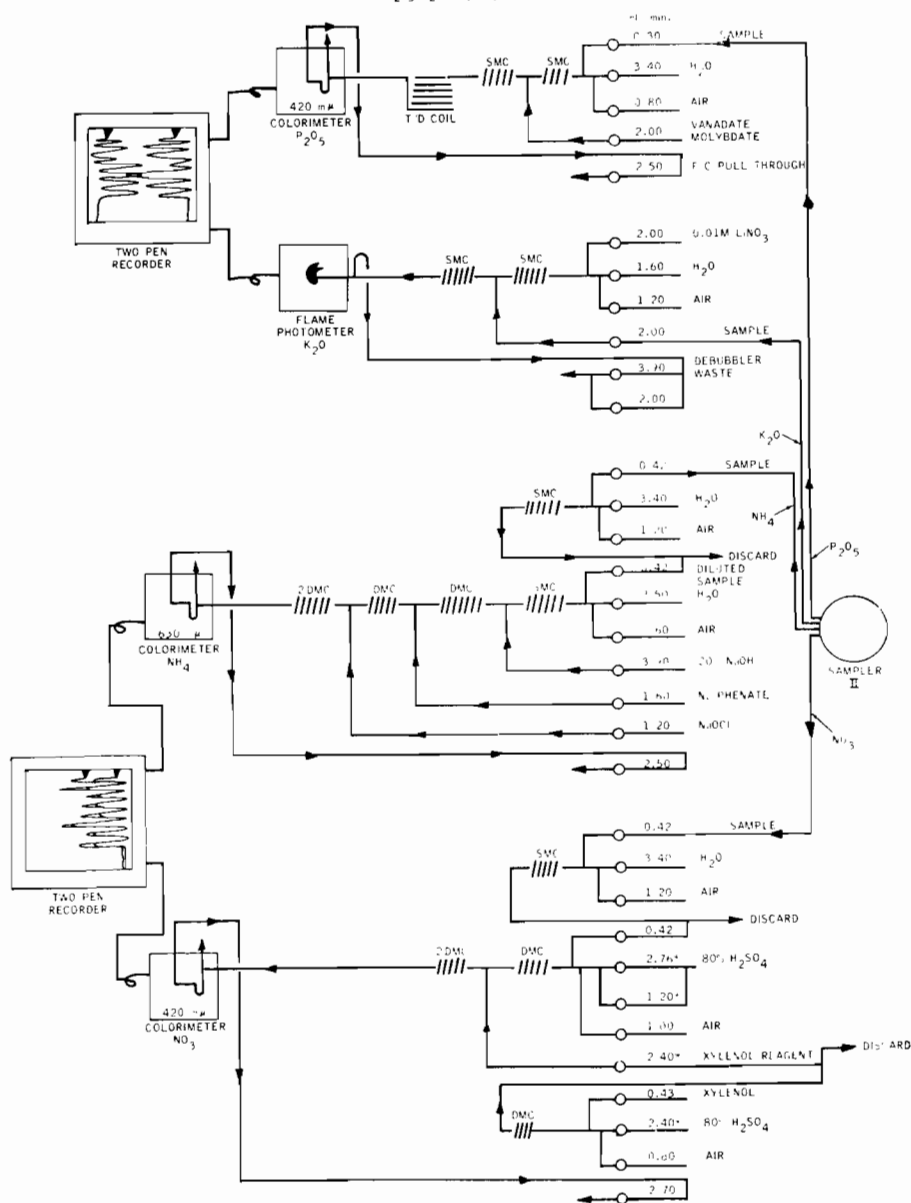COLORIMETER NO_3 — 420 µ

2DMC ///// DMC /////

SMC /////

DMC

0.42	SAMPLE
3.40	H_2O
1.20	AIR
0.42	DISCARD
2.76	80% H_2SO_4
1.20	
1.00	AIR
2.40	XYLENOL REAGENT → DISCARD
0.43	XYLENOL
2.40	80% H_2SO_4
0.80	AIR
2.70	

Nitrate-Nitrogen: Nitrate content is measured by the color formed by the reaction of 2:4 xylenol with nitrates to form a nitration product of the xylenol in the presence of 80% H_2SO_4.

Potassium: Potassium is measured in fertilizers by measurment of the emission intensity ratio between a lithium interval standard and a potassium containing solution when burned in a propane-oxygen flame.

Ammoniacal Nitrogen: Quantitation of ammonia is achieved with a phenol/hypochlorite reaction. The ammonia is converted to a blue colored compound of the indophenol type.

Details of the automation of various of these procedures were previously reported by Ferrari, (1) Docherty, (2) Gerke (3) and others.

To achieve the determination of 4 parameters on various formulations such that the determinations would be simultaneous, synchronized recordings obtained, and that all optical density and emission ratio be in the most accurate range of the curve, separate flow manifolds have been designed for the following formulations: 14-14-14, 10-40-10, 12-24-12, 10-30-10, 20-7-12-3-1.2, and 20-20-0. These different flow manifolds cause no inconvenience in plant analysis since it is always known in advace what product is being formulated. Figures 3 thru 8 show the various flow diagrams for the above mentioned formulations. To change from one manifold to another only requires changing 2 or 3 tubes delivering sample and/or diluent.

The simultaneous procedure involves taking 4 samples simultaneously from a single solution with a special adaptor on the sampler, each sample then follows in turn individual patterns on the manifold designated for a given analysis. Figure 9 is a recording for P_2O_5 and K_2O obtained on one recorder and Figure 10 is a recording of ammoniacal nitrogen and nitrate nitrogen on a second 2 channel recorder. Both of these recordings were obtained simultaneously on a sample of 20-7-12-3-1.2.

Experiments were carried out to determine the optimum operating rate for the AutoAnalyzer. Var-
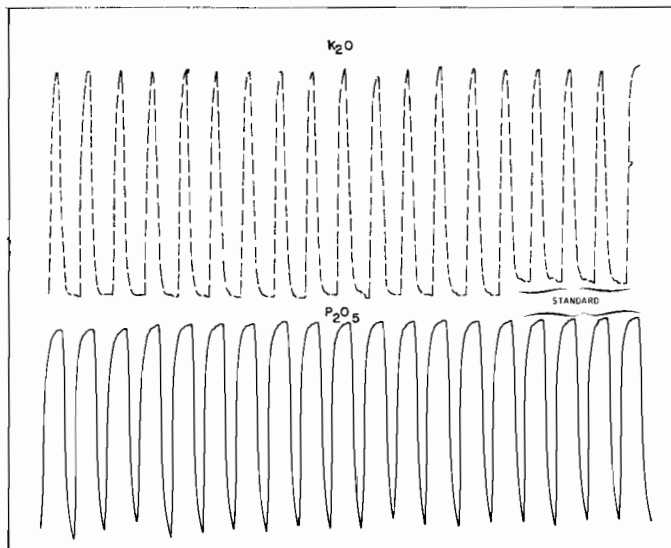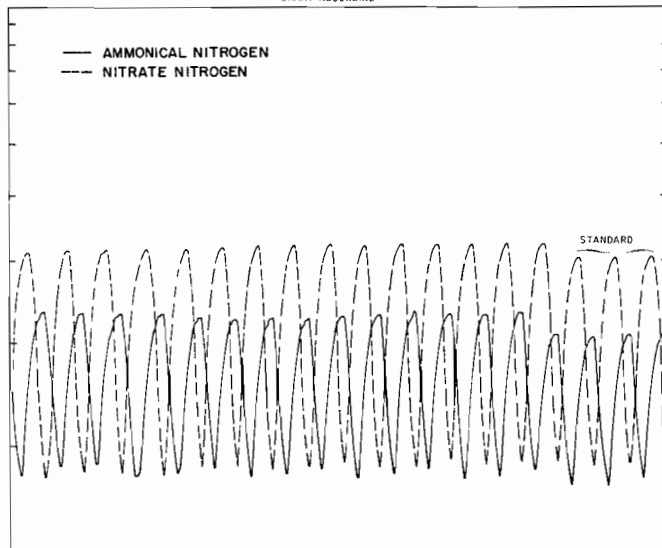
Figure 9
CHART RECORDING P_2O_5 + K_2O

Figure 10
CHART RECORDING

Figure 9
CHART RECORDING P_2O_5 + K_2O

Figure 10
CHART RECORDING

— AMMONICAL NITROGEN
--- NITRATE NITROGEN

ious rates with and without water washes were evaluated and the results indicated that 50 samples/hr with water washes and 30 samples/hr, without were both well defined and free from interference from previous samples.

Preparation of the Sample for Analysis

Since the formulations produced at Puntarenas are not all water soluble, prior digestion is necessary to make available all the nutrients for analysis. In an effort to study the methods available to obtain total nutrient values, several digestion (sample preparation) techniques were evaluated on the various formulations. Techniques included the following digestants 50% hydrochloric acid; 15% sulfuric acid, water at pH5; 25% acetic acid; 50% acetic acid; 25% formic acid; 50% formic acid; and 1:1 hydrochloric: nitric acid. The

data obtained which appear in Table 2 shows 15% sulfuric acid to be superior choice for all the formulations.

In the product analysis 1-2 grams of fertilizer are weighed and transferred to a flask containing 25 ml of 15% sulfuric acid and heated to boil for 5 minutes, the material is then diluted to one liter and analyzed as indicated on the flow diagram.

Slurry samples are removed manually with a suction device as shown in Figure 11. This device has

Figure 11

SUCTION METHOD FOR SAMPLING OF SLURRY

RUBBER STOPPER
GLASS TUBING 1/4" I.D.
WEIGHING BOTTLE
RUBBER TUBING
BULB
SLURRY SAMPLE
IMMERSION

been designed to dip into the overflow tank after the reactor to a depth of 12 inches and draws 7 gms of flowing sample to assure homogeneity. The device consists of a glass stoppered weighing bottle with a two hole rubber stopper, a rubber bulb and a "U" shaped glass tube. In practice, the weighing bottle is tared, and the rubber stopper with its tubes attached as indicated. The end of the long tube is inserted into the slurry, and the rubber bulb squeezed and released. The slurry thus brought to the tared weighing bottle. The rubber stopper is removed and the glass top replaced. The tared sample container is weighed and the net weight of the sample recorded. The weighed sample is then diluted for analysis and made available for the simultaneous determination of the nutrients.

Recently the solid sampler has been applied to the analysis of both final product and slurry. The
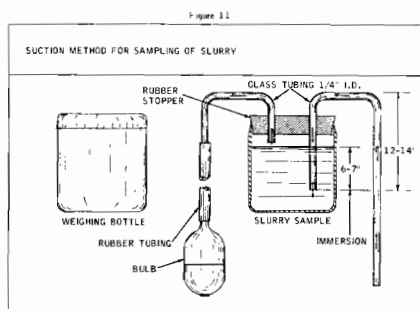
Table 2
Evaluation Of Digestants For Various Complex Fertilizer Formulations

Digsetions	Formulations														
	20-7-12			12-24-12			20-20-0			10-30-10			10-40-10		
	N	P_2O_5	K_2O	N	P_2O_5	K_2O	N	P_2O_5	K_2O	N	P_2O_5	K_2O	N	P_2O_5	K_2O
Std. AOAC	20.30	7.68	12.30	12.39	24.91	12.08	19.66	20.30	0	11.62	28.87	10.38	10.62	42.00	10.33
HCl 50%	20.30	7.68	12.30	12.39	24.91	12.08	19.66	20.30	0	11.62	28.87	10.38	10.62	42.00	10.33
H_2SO_4 15%	20.20	7.70	12.50	12.30	24.90	12.10	19.80	20.37	0	11.90	28.87	10.61	10.92	42.20	10.69
H_2O pH5	20.10	7.80	12.60	12.20	16.20	12.00	19.70	15.68	0	11.85	24.90	10.50	10.34	38.74	10.45
CH_3COOH 25%	20.44	7.18	12.03	12.03	22.98	12.05	21.61	18.53	0	12.63	26.27	10.56	10.77	39.42	10.33
CH_3COOH 50%	20.32	7.20	11.93	11.93	22.92	11.87	21.02	15.53	0	12.87	26.27	10.61	10.87	40.24	10.15
HCOOH 25%	20.87	7.44	12.30	12.75	24.46	12.08	21.44	19.69	0	13.22	27.91	10.70	10.92	40.37	10.21
HCOOH 50%	19.47	7.44	12.24	13.19	24.40	12.29	22.76	19.76	0	13.50	28.19	10.70	11.43	41.05	10.69
HCl + HNO_3							0	19.89	0	0	28.73	10.70	0	41.90	10.60

Figure 12
USE OF SOLID SAMPLER

tables are on a 12-24-12 formulation. Equally satisfactory results were obtained on samples of formula 20-7-12-3-1.2. Formula 12-24-12 contains a large amount of ammophos and moderate amounts of rock and acid, whereas formula 20-7-12-3-1.2 has a high content of ammonia and acid and a moderate amount of ammophos and no rock.

Table 4 includes data obtained on raw material analysis of KCl as it was received. K_2O values were obtained by standard laboratory procedures, and by AutoAnalyzer. The average value for the shipment is the same, by both techniques,

material is placed directly into the sampler and the analysis proceeds as indicated in Figure 12. To present, there has been only a limited amount of data obtained with this sampling system; however, it will be utilized in future analysis for all product and process control.

An automatic pump has been designed and will be used for slurry analysis at the reactor. In the near future the sample will be drawn at the reactor, directly and precisely into the solid sample container, placed on the AutoAnalyzer and analysis of four components measured simultaneously. The final product would still require weighing directly into sample apparatus. With the use of this "solid sampler" manpower utilization for a control laboratory will be cut to a minimum to oversee the operation, and an analysis of either slurry or product would be completed every few minutes.

The calculation for % nutrient after analysis and recording appears in the Appendix.

Experimental Data

It was most important when considering the use of the Auto-Analyzer for fertilizer control that the results obtained by this technique be comparable to those obtained by standard laboratory procedures. The standard procedures used at Fertica were those recommended by AOAC (American Association of Analytical Chemists). Comparative data was obtained and appears in Tables 3A and 3B, and has shown differences which do not exceed those obtained by the same method. The data in these

Table 3A
Comparative Data Between Standard Procedures And Autoanalyzer

Sample 12-24-12					
Standard Procedures (AOAC)			AutoAnalyzer		
N	P_2O_5	K_2O	N	P_2O_5	K_2O
12.4	24.8	13.6	12.5	24.8	13.6
12.0	24.8	13.6	12.0	24.9	13.6
13.3	26.2	12.0	12.5	26.2	11.9
12.2	25.7	11.7	12.2	25.8	11.9
11.8	24.6	13.9	12.0	24.9	14.0
11.9	25.4	12.6	12.3	25.3	12.4
11.9	25.0	12.4	12.2	25.2	12.1
13.2	26.5	11.4	13.5	26.8	11.7
12.5	24.6	12.3	13.1	24.8	12.5
12.4	24.8	13.6	12.6	25.0	13.4
12.5	24.8	12.1	12.4	24.9	12.1

Table 3B
Comparative Data Between Standard Procedures And Autoanalyzer

Standard Procedure			AutoAnalyzer		
Sample of 10-30-10					
Standard Procedure			AutoAnalyzer		
N	P_2O_5	K_2O	N	P_2O_5	K_2O
12.3	30.8	10.4	12.7	31.3	10.6
11.8	30.7	9.9	12.0	31.0	10.2
11.7	32.0	9.2	11.7	32.0	9.6
12.0	31.6	9.9	12.3	32.1	10.2
11.5	30.2	10.8	11.5	30.3	10.9
12.0	30.8	10.9	12.2	31.3	10.9
11.9	30.9	10.6	12.0	30.9	10.7
12.1	31.0	11.3	12.3	31.4	11.1
12.2	30.8	11.2	12.4	31.4	11.1
12.0	30.4	11.5	12.2	30.5	11.3
12.0	30.8	10.3	12.2	31.0	10.6
Sample of 14-14-14					
N	P_2O_5	K_2O	N	P_2O_5	K_2O
13.5	14.7	15.5	13.5	15.0	15.6
14.2	15.5	14.0	14.4	15.5	14.3
13.8	15.1	14.4	14.2	14.7	14.7
14.2	14.9	13.6	14.0	15.3	13.9
14.1	14.3	14.2	14.1	14.3	14.5
14.2	14.4	14.3	14.2	14.5	14.6
14.3	14.3	13.9	14.3	14.3	14.0
14.2	15.1	13.8	14.2	15.2	13.9
14.0	15.3	14.7	13.8	15.1	14.6

Table 4
Potassium Chloride—Individual Samples As Received

Date	Time	AOAC K$_2$O	Date	Time	AutoAnalyzer K$_2$O
4/14/66	8:15	61.3	4/14/66	10:45	61.1
"	8:35	61.4	"	8:30	61.0
"	8:15	61.0	"	17:05	61.3
"	9:15	61.5	"	19:15	61.4
"	9:35	60.5	"	23:50	61.2
"	9:55	60.8	4/15/66	8:30	61.3
"	10:15	61.0	"	5:10	60.9
"	10:25	60.8	"	11:45	60.7
4/15/66	19:45	60.6	"	11:45	61.0
"	20:00	61.5	"	17:10	61.2
"	20:15	61.3	"	19:30	60.5
"	20:30	60.3	"	22:50	60.9
"	20:45	60.1	4/16/66	2:00	61.0
"	21:00	60.0	"	6:25	60.2
"	21:15	60.1	"	9:45	60.4
"	21:30	61.4	"	5:20	60.4
4/17/66	23:20	60.0	"	15:45	60.8
"	23:35	60.9	"	23:35	60.7
"	23:50	60.3	4/17/66	9:45	60.6
4/18/66	0:05	61.0	"	23:10	60.3
"	0:20	60.6			
"	0:35	60.6			
"	0:50	60.8			
"	1:05	61.1			

Humidity: Range=0.29
   Average = 0.15
Potassium: Range=1.2
   Average = 60.8

Humidity: Range=0.41
   Average = 0.22
Potassium: Range=1.2
   Average = 60.8

however, the range for automatic analysis is lower than that for standard methods. Since this is raw material analysis and the samples were taken at various times, the range does not necessarily indicate precision.

The precision of the analytical procedures when 4 simultaneous analyses were being carried out, was evaluated when a previously standardized sample of formulation 20-7-12-3-1.5 was run 20 times for simultaneous analysis. The standard deviation for P$_2$O$_5$ is calculated to be + 0.13; K$_2$O, + 0.10; NH$_4$, + 0.092 and NO$_3$, + 0.16. All the standard deviations are expressed as 20 (95% confidence).

It is important to note that all data presented in this report were obtained at the plant without any adjustments of normal plant conditions.

Operational Cost of AutoAnalyzer

The operational cost of the AutoAnalyzer appears in Table 5. It includes the reagents used for each of the tests along with the cost of

operation for a 24 hour period. The total cost for continuous operation over a 24 hour period is $44.50. In continuous operation it is possible to monitor a plant for N, P and K and make adjustments in formulation within 5 minutes. A closed loop system, which is presently being considered would limit necessary manpower by eliminating the need for manual sampling and adjustment.

Future Considerations

As previously indicated, consideration is being given to the use of a closed loop system which would permit the continuous automatic monitoring of samples after the various points in the manufacuring process. Two schemes are under consideration, each having its own merit.

Scheme A (Figure 13) consists of a Moyno pump and a recirculating sampling loop which would remove a continuous supply of slurry from the reactor at a point some 14″ beneath the surface and return it back again to the reactor. From this primary recirculating sampling loop a smaller network of tubing will remove a small amount of sampling and deliver it to a homogenizing chamber so that a constant dilution may be achieved of the removed sample with the appropriate diluent and reagents.

A similar pump differing in its capacity and coupled to the same motor, will simultaneously proportion differing volumes of sample and diluent. In this fashion, regardless of the speed of the motor, the ratio of sampling to dilution will remain constant. The homogenizing chamber if equipped with an overflow waste tube will thus permit the volume to remain constant. At some point a sampling tube would be connected to the manifold and thus permitting the continuous measurement of the chemical constituency of the in-process slurry sample. The homogenizing chamber would be equipped with a motor and stirring blades which will revolve at speeds up to 10,000
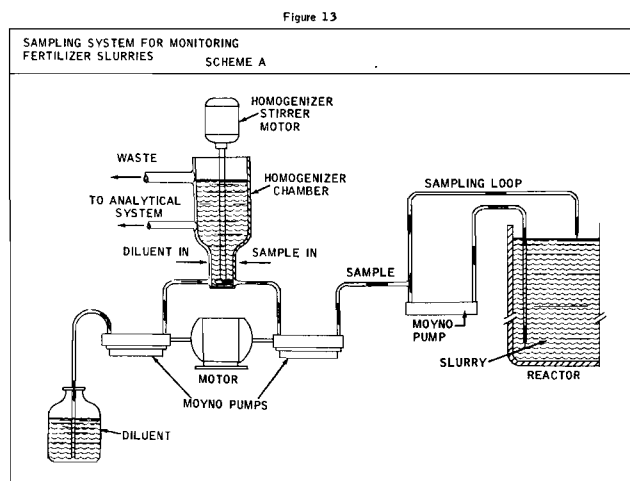

Figure 13

SAMPLING SYSTEM FOR MONITORING FERTILIZER SLURRIES   SCHEME A

Table 5
Operational Cost For Automatic Analysis

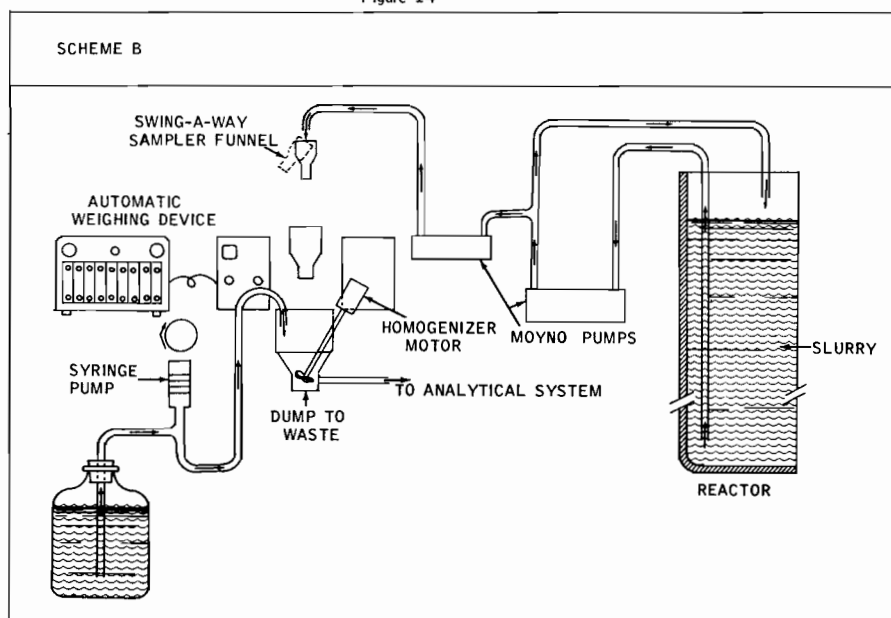| Test	Reagent	Quantity for 1 liter	ml/hr	ml/day	Reagent Consumption 1 hr	24 hrs	Price $ US	Operating Cost/24 hrs
NH$_4$	Sodium hydroxide	200 g	330	7.92	66 g	1584 g	1.28 lbs	4.50
	EDTA	30 g	234	5.62	7 g	172 g	8.70 lbs	3.50
	Liquid phenol 88%	2.76 ml	96	2.30	26.5 ml	636 ml	1.70 pt	2.30
	Sodium hypochlorite	1 lb	72	1.73	72.0 ml	1730 ml	0.75 bt	1.30
NO$_3$	2,4-xylenol	10 ml	25	0.60	0.25 ml	6 ml	5.75 oz	1.24
	Glacial acetic acid	800 ml	25	0.60	20 ml	480 ml	2.20 pt	2.20 (?)
	Sulfuric acid	800 ml	534	12.82	427.2 ml	10.3 l	.50 lb	9.50
P$_2$O$_5$	Ammonium molybdate	30 q	120	2.88	3.6 g	86.4 g	6.0 lbs	1.14
	Ammonium metavanadate	1 g	120	2.88	0.12 g	3 g	17.0 lbs	1.15
	Perchloric acid 70%	225 ml	120	2.88	27.0 ml	653 ml	2. 0lbs	5.10
K$_2$O	Lithium nitrate	0.7 g	120	2.88	0.1 g	2.7 g	5.25 lbs	0.05
Other Materials	Propane Gas	1 cylinder each 3 months (estimated					10.50 cyl	0.12
	Oxygen	1 cylinder each 13 to 14 hrs					1.70 cyl	12.40
Recorder Charts		20 inch per hour x 2						?
Pump Tubing		1 each 500 hours						?
							Total	44.50

rpm. On unweighed slurry this technique would facilitate ratio analyses.

On Scheme B (Figure 14); a sample is weighed intermittently rather than proportioned at a constant ratio with a diluent as in A. The recirculating sampling loop of tubing provides material to a small Moyno type pump which is controlled through the programmer of of a special weighing system. The pump on start-up will proportion material through the network of tubing until all previous contained materials have been cleared and fresh material provided. The material delivered by the pump will be diverted to waste by a swing away sampler funnel. The material will then be deposited into the weighing chamber of a Mettler automatic weighing device. Upon completion of the weighing operation, the proportioning pump providing the sample is automatically stopped, the swing away funnel moved so that no further sample is introduced into the device and the contents deposited into homogenizing chamber. On command

Figure 14

SCHEME B

SWING-A-WAY SAMPLER FUNNEL

AUTOMATIC WEIGHING DEVICE

SYRINGE PUMP

HOMOGENIZER MOTOR

MOYNO PUMPS

TO ANALYTICAL SYSTEM

DUMP TO WASTE

SLURRY

REACTOR

from the programmer then a diluent can be directed into the homogenizing chamber at a finite volume. The programmer then should activate the homogenizer motor, which in turn will operate for a fixed period of time to complete homogenization. On command then a sample is pumped into the analytical manifold and the contents of the homogenizing chamber dumped to waste. The interior of the homogenizing chamber is then rinsed and left on standby for the next sampling operation. In this type system, since the sample is weighed prior to analysis, a direct per cent of nutrients can be obtained from the recordings.

Summary

An automatic four channel analytical system has been described for the simultaneous determination of P_2O_5, K_2O, ammoniacal nitrogen and nitrate nitrogen in complex fertilizers. The accuracy and the precision of the analytical system has been shown to be comparable to standard techniques. Consideration for the use of such systems on a totally automatic basis where sample would be obtained, processed and analyzed, totally independent of human intervention has been discussed. The analytical data then could control the plants to regulate the various nutrients being fed into the process.

In conclusion it can be said that automatic chemical analyses of complex fertilizer samples in a fertilizer plant has been presented and the economics associated with these analyses and their advantages leave no doubt that for proper in process control of complex fertilizers, automatic analyses and frequent inspections are essential.

and presentation of samples to the sampling point (crook) is managed through the use of individual metal cams with corresponding cutouts which extend or shorten the sampling time. For experimental purposes, variable cams rather than fixed sample to wash ratios can be obtained. The sampling crook moves into the sample cup during the sampling period and back into the wash cup into which a wash fluid is flowing at all times. In this way, from the very onset, the sample line is rinsed after each sample has been aspirated. This eliminates contamination and provides a constant volume of flow through the analytical system at all times in order that the ratio not be upset.

A cover is provided for the sample tray in order to minimize evaporation of the fluid contained in the sample cups.

Solid Preparation.

The solid preparative system is available to handle solid samples and consists of a tray with capacity of 20 plastics cups. On command from the programmer, the tray rotates and at a predetermined point, each cup inverts its quantity into the funnel hopper of the homogenization chamber. Also on command from the programmer, the appropriate diluent is introduced through multi-jet openings which supply the necessary diluent and also serve to rinse the funnel down and, if necessary, the interior of the sample cups in order that no sample residue be left behind. The homogenization motor is turned on for a predetermined length of time on command from the programmer and rotates at 10,000 rpm, thus assuring complete disintegration, homogenization and dispersion of the solids.

On command from the programmer, the high speed cycle of the homogenizer is stopped and a slower speed instituted during which the programmer controls the opening of the valve to permit the sampling to take place. The sampling duration is controlled by the programmer and can be lengthened or shortened at will.

After sampling, the waste valve is opened on command from the programmer, and under vacuum,

Calculations

Calculation for Per Cent Nutrient on Product:

$$C_p \times \frac{P_p}{P_m} \times \frac{L_x}{L_p} = Component$$

$C_p =$ Concentration of Std x 100
$P_p =$ Weight of Std/liter $= 1$
$P_m =$ Weight of Sample/liter (1-2)

$L_x =$ Optical Density Sample
$L_p =$ Optical Density Standard

Calculation for Per Cent Nutrients from Slurry:

$\Sigma N_1 = \Sigma$ nutrients in standard fertilizer of same formulation

Assuming

H_2O content of final product $= 0.5\%$

Then total solids in product $100 - 0.5 = 99.5$

$$Factor = \frac{Total \ Solids}{\Sigma N_1}$$

H_2O in slurry $= 100 - (\Sigma N_s \times factor)$
$N_s =$ nutrients in slurry

Dry Basis:
$\Sigma N_s \times factor = \%$ Solids
$$\frac{\% N_s \times 100}{\% \ Solids} = \% \ N \ dry \ basis$$

Description Of The AutoAnalyzer Components For Use In The Analysis Of Fertilizers

Sampling System

Sampler II:

Sampler II is the standard liquid sampling device. A sample tray holder with a capacity of forty individual samples is so designed that sample cups of 1 ml up to 10 ml, can be supported conveniently. The smaller capacity sample cups resemble plastic thimbles and the larger cups (10 ml) are rectangular in shape.

Programming of the rotation

this removes the contents of the homogenizing chamber, rinses the interior of this chamber and prepares the system for the new sample preparation cycle.

All parts that come in contact with the fluids of the sample preparative system are made of stainless steel or of appropriate plastic materials.

The diluent volume is adjustable from 50 ml to 200 ml. Gears are available to permit sampling cycles of from 5 per hour to 60 per hour.

Proportioning Pump

The proportioning pump is a multi-channel device capable of pumping continuously up to 15 separate streams simultaneously while varying the individual output of each stream in any ratio up to 13:1. The pump consists of two parallel stainless steel roller chains with spaced roller thwarts that bear continuously against a spring loaded platen.

The diameters of the tubes comprising the manifold (pumping network) are chosen to deliver the correct ratio of sample and reagents. As the chain travels across the platen, the rollers advance the liquids in the system in the exact proportions required in the analytical method. All the liquids in the system are being impelled simultaneously, manifolded, segmented by air and subsequently mixed at a ratio dependent upon the diameter of the tubes. Regardless of the diameter of the pump tubes, the wall thickness is constant, thus, all tubes have the same cross-section when compressed.

Continuous Filter

In order to facilitate the removal of solids from the sample stream prior to analysis, the suitably prepared suspension of solids is proportioned on a device on which a ribbon of appropriately filtered material is continuously passing through. The material to be filtered is deposited in excess on the upper surface of the filtering material while it is being pulled across the Teflon platen provided with a center perforation. A portion of the aspirated filtrate is then sent on into the analytical network and constitutes an aliquot of the filtrate.

Flame Photometer

The determination of potassium is performed by burning a suitably diluted aliquot of the sample in the hot flame produced by the combustion of oxygen and propane.

In order to insure a constant reference source, the flame photometer is provided with a reference photo cell which visualizes the same portion of the flame as that visualized by the sample photo cell. By comparing the emission intensity of a known concentration of the lithium, a direct comparison and thus quantitation of the unknown potassium emission can be made.

In order to insure homogeneity of the emission signal visualized by the photo detectors, a mirrored surface surrounds the flame and gathers the total emission energy thus providing a well integrated flame image for the detectors. Irregularities thus found in any portion of the flame are integrated or smoothed out. Suitable neutral density filers for attenuation are available for the emitted signal as well as narrow half band interference filters for the respective wave lengths.

Colorimeter

For the colorimetric determination of the respective nutrients a double beam, narrow half band interference type colorimeter is employed. A single light source is viewed simultaneously by right angled light axis, one by the reference photo cell, the other by the sample photo cell. Front surface lenses gather and focus the light passing it through the corresponding interference filter where it then passes through a small tubular flow cell. The internal volume of this tubular flow cell is 0.1cm³.

The colorimeter forms part of the electronic network of the recorder thus forming a ratio recording system. In this type of network, differences in light intensity due to voltage fluctuations or a change in the emittance characteristics of the light bulb, are automatically ignored inasmuch as both photo cells see these changes simultaneously. The only factor that would change the output of the system is the reduction in the light intensity striking the sample measuring photo cell due to absorptive characteristics of the solutions flowing through the flow cell.

Literature References

1. Ferrari, A., "Nitrogen Determination by a Continuous Digestion and Analysis System, *Ann. N. Y. Acad. Sci.* 87, 792-800 (1960).
2. Docherty, A. C., "Standard Physical and Automatic Methods for the Analysis of Fertilizers"; paper presented at Technicon International Symposium, New York, 1964.
3. Gehrke, C., "Automation of the A O A C Flame Photometric Method for Potassium in Fertilizers," *"Journal of the AOAC,* 47, 3, 1964.

MODERATOR ARCHER: We are fortunate that our next speaker, Dr. Elwyn Schall, accepted the invitation to be on this program.

In addition to being State Chemist in Indiana, Dr. Schall is general AOAC referee on fertilizer. His laboratory at Lafayette is recognized as being a leader in investigating and evaluatng new analytical developments.

The industry is concerned with the position which AOAC will take on automated analysis. Dr. Schall will give us the present position of AOAC on automatic analysis and tell us about any new developments in instrumental analysis in the laboratory.

Automation In The Fertilizer Laboratory

E. D. Schall

Automation is one of the foremost topics in everyone's mind these days and certainly so with any of you who have the responsi-

bility of supervising a laboratory or in some other way have responsibility for the analytical work of your company. Everyone dreams of that magic machine setting in your laboratory waiting with anticipation for you to present it with a sample which it eagerly gobbles up and, a few seconds later, presents you with a print-out of the analysis of any number of components for which you may be interested. Unfortunately, I am not going to describe such a machine for you today. Progress is being made and some of the things you have heard today approach this ideal. For the most part, however, we have to be content at this time with partially automated apparatus.

Why all this pressure for automation? Certainly the labor market is a primary factor. With salaries ever creeping upward it is only natural that we turn to any labor-saving device. The report released by the American Chemical Society less than one month ago shows the average starting salary for inexperienced BS chemists averaged nearly $8,000 on a nation-wide basis during the past year. This makes even the higher priced instruments look attractive. But even if you are willing and able to pay these salaries, you still face recruitment difficulties if you are looking for a quality control or routine analyst. Today's graduate has a multitude of opportunities awaiting him. The graduate school explosion will provide the qualified members any number of opportunities for advanced degree work with rather sizable stipends. If he doesn't choose to do this, he will have many opportunities of joining research teams and most of your young people today find this more challenging and glamorous than routine analytical work. With personnel both expensive and difficult to obtain, we must automate any of our analyses which are adaptable.

For my part of the panel, I should like to discuss three areas. As indicated above, I do not have any magic monster to describe to you, but perhaps some views as General Referee for Fertilizers of the AOAC would be of interest. Here I shall include a look at the present situation in atomic absorption as a technique which is well-established. Secondly, we shall take a quick look at specific ion electrodes as a promising tool for the fertilizer laboratory. Thirdly, I should like to give you the AOAC viewpoint, as I understand it, toward automation and summarize current activity in the fertilizer area.

The impact of atomic absorption of fertilizer analysis, particularly in the micro-nutrient field, is well-known to all of you. At the AOAC meeting just concluded here in Washington last month, methods were adopted as Official, Final Action for six elements commonly encountered in fertilizers. These were calcium, magnesium, copper, iron, manganese, and zinc. The method is firmly establisned and I should like to describe a few of the advances in instrumentation currently of interest. And here again, I think we can divide it into three areas.

First of all, we have the development of the relatively simple instrument intended for routine laboratory operation. These do not have all the versatility of the more sophisticated instruments, but rather, are designed for ease of operation with as few controls as practicable. Examples of these are the Perkin-Elmer Model 290, the Jarrell-Ash Model 82-700, and the Techtron Model AR-200. These fall in the $3,000 area and represent about the minimum investment for atomic absorption. Other companies also have instruments available in this range, but the above examples are typical of those in this class.

Instruments with greater sophistication are available at somewhat increased costs. It is this group that you are probably most familiar with since a great deal of the published work has been conducted on them. These include the familiar Perkin-Elmer Model 303, the Techtron Model AA-4, the Jarrell-Ash Models 82-250 and 82-500, and the Beckman Model 979. Again, this is only a partial listing, is not meant to be all-inclusive, or to imply endorsement of any model.

The operation of all of the examples cited above is usually manual with a meter readout of the results. Each reading takes only a few seconds and the operation of the instrument is quite repetitive. Thus, it is a natural candidate for auomation, and this, in fact, has been done. If we were to distinguish between automated and semi-automated, the application to atomic absorption would probably be described best by the latter term.

A number of automatic sample changes are available on the market and getting these together with atomic absorption had all the earmarks of a natural union. This has been done and relieves the operator of the necessity of presenting each sample individually to the instruments. This can be illustrated by the Unicam SP90 which handles 32 samples at one loading. I believe that automatic sample changers are now available and adaptable to all instruments presently on the market.

Units are also available which provide automatic dilution and these have been coupled with the sample changers. This can be a real advantage in atomic absorption for dilution is required on nearly all samples, and it is a time-consuming step. Using this combination, a series of solutions prepared from the solid sample can be presented to the instrument and the unit will take over the dilution and introduction of the sample to the burner.

Of course, you don't save a great deal of time by automating the introduction of the sample unless you also automate the read-out. This can be done with recorders and various types of digital read-outs, including digital printers. This entire combination can be demonstrated by the Perkin-Elmer unit which provides sample handling capacity for 200 samples without dilution, or for 100 samples if dilution is to be included. The results are printed out in sequence with each sample being identified by its number. Thus, the operator can present the instrument with 100 or 200 samples , depending upon the situation and go about other duties while these are being analyzed.

All of the examples cited so far have the limitation of being able to handle only one element at a time. We quite often wish to de-

termine several elements by these methods in fertilizer analyses and to do this the runs must be repeated with lamp changes between each run. The ideal situation would be the preparation of one sample solution containing all elements and to determine these simultaneously. Such an instrument is available now in the Jarrell-Ash Model 82-600 Multi-Channel Unit which is capable of analyzing up to twelve elements simultaneously on a single sample by either absorption or flame emission. Other multi-channel units are also in various stages of development and will be appearing on the market in the months ahead.

Turning now to a different area, I believe the recent developments in specific ion electrodes should be of rather deep interest to the ferilizer chemist. Ten years ago we knew almost nothing about this subject and not much more as recently as five years ago. Many of these have become available, however, in the past year or two and have attracted a great deal of interest. The operation is similar to that of the glass electrodes for measuring pH and the same expanded scale pH meter can be used with them. Cation specific electrodes are currently available for calcium, magnesium, copper, sodium, silver, and potassium. Those specific for anions include fluoride, chloride, bromide, iodide, nitrate, perchlorate, cyanide, and sulfide. Although not yet available commercially, electrodes for phosphate and sulfate have shown promise and I am sure we will see further developments in these. I can see several very interesting applications for the phosphate electrode if this can be developed successfully. Although not an automated procedure, it would provide a very quick and simple way of determining phosphate concentration in a solution. There are some problems with selectivity with these electrodes, but these will be solved as we learn more about their operational characteristics.

Your Chairman asked that I comment on the position of the AOAC in regard to automation. This organization, of course, has established a world-wide reputation for the high quality of its official procedures. This has come about through the continuing use over the years of the collaborative study method of evaluating new procedures. This provides a test of the method under very widely varying condition, including laboratory and personnel variables, and any method which can survive these and still provide results that will pass a critical evaluation is bound to be good.

The advent of automation has posed some new problems for the AOAC. In the wet chemical proceures of the past, all details of the metnod were carefully spelled out and could be followed to the letter by the collaborator. Later, as colorimetric methods became quite common, the decision had to be made as to whether particular instruments were to be specified in methods. A colorimeter or spectrophotometer is a tool to measure one variable, just as a pipet or a balance each measure one variable. Even though the quality varied somewhat between various makes of instruments, the principles upon which they operated were all the same and the choice of which particular instruments to use has been left to the analyst.

We have a different situation in automated methods. We now find the instrument handling a succession of variables and various instruments may do this in an entirely different manner. Compare, for example, the determination of potassium by an automated atomic absorption procedure, and by the Technicon AutoAnalyzer. The approach is quite different in the twɔ procedures.

In late 1965, the AOAC appointed the Committee on Automated Methods to recommend a policy for handling these methods. The immediate problem facing the committee was whether the use of the Technicon AutoAnalyzer in the official spectrophotometric determination of total and available phosphorus in fertilizers would affect the standing of the method. After much consideraion and correspondence with other associations involved in methodology, this committee, chaired by W. M. Hoffman, recommended that any modification of an Official, Final Action method to include the use of an automated system or automated equipment be submitted to an appropriate collaborative study. The recommendation was adopted by the AOAC in October, 1966. This policy then sets the responsibility for the study of automated methods and the developments of effective collaborative tests with the Associate Referees and confines the committee to an advisory role.

This then, is the present policy. In effect, it states that any new automated instrument must be studied collaboratively. This poses no serious problem at the present time since the number of such instruments is somewhat limited. However, it appears to me we may be facing difficulty in the future as more and more companies develop their own versions of automated procedures for a given determination. If all of these are studied collaboratively as independent methods and successfully pass the study, we would have a great proliferation of official methods. If this were to happen, we might find our present one volume Methods of Analysis taking on the appearance of a twenty-four volume encyclopedia. Under this system there would also be pressure to conduct a new collaborative study each time an instrument manufacturer came out with a new model. Do I have any volunteers for Associate Refereeships in fertilizers?

I think we can handle the collaborative testing satisfactorily under the present policy in the present stage of development. As automation gains momentum, however, and there is no question that it will, we may be forced to take another look. I don't know at this time what the outcome will be but perhaps specifications could be written into a method outlining tests of precision and accuracy which any instrument must meet to be applicable to that method. I am sure the committee on auomation would welcome any comments any of you may have on this subject.

As for present activity in the AOAC with regard to automated fertilizer methods, I should like to report that Dr. Caudill of the University of Kentucky, who is the Associate Referee for Phosphorus, is

planning a collaborative study this year with the AutoAnalyzer. He had planned to get this done during the past year but some difficulties delayed the work.

The potash referee, Larry Hambleton of our laboratory, will be studying this instrument also, particularly from the standpoint of determining potassium simultaneously with phosphorus using the citrate extract. And, of course, developments are moving ahead in the Missouri laboratory where the nitrogen referee, Paul Rexroad, and Dr. Gehrke are adapting the AutoAnalyzer to the Kjeldahl nitrogen method. Thus, we are hopeful that at least some official automated methods will be available to the fertilizer chemist in a year or two and I can assure you the next ten years are going to be exciting.

MODERATOR ARCHER: Thank you, Dr. Schall.

Our next speaker is Dr. James Marten of Technicon. His company has made substantial contributions to the field of automated analysis. Their equipment is used widely throughout the world.

Dr. Marten will tell us some of the developments in overseas laboratories.

Applications Of Automatic Analysis In The Fertilizer Industry

James F. Marten, Ph.D.

The Fertilizer Industry has changed considerably in the last two years. New, larger production units have been built and the distribution of fertilizers in bulk and in liquid has captured a large part of the market.

The obvious objective of every manufacturer is plant construction at the lowest capital cost consistent with the highest rate of return on investment. This objective is known to be consistent with the construction of plants with very high rates of production. This high volume production makes imperative close control of the process for maximum yield while minimizing or virtually eliminating out-of-specification product. In other words, close production control and quality control are now mandatory and especially worthwhile since these aims can be realized without significant capital outlay.

Automatic control has been shown to be economical and practical by several workers (2, 5) in practically all facets of the fertilizer production cycle.

Let us take as an example, the control of the production of wet process phosphoric acid. Kronseder (1) and others have reported that in this process, with increasing rates of production there is a corresponding decrease in recovery. Table 1 which is reprinted from Kronseder's report clearly indicates this fact.
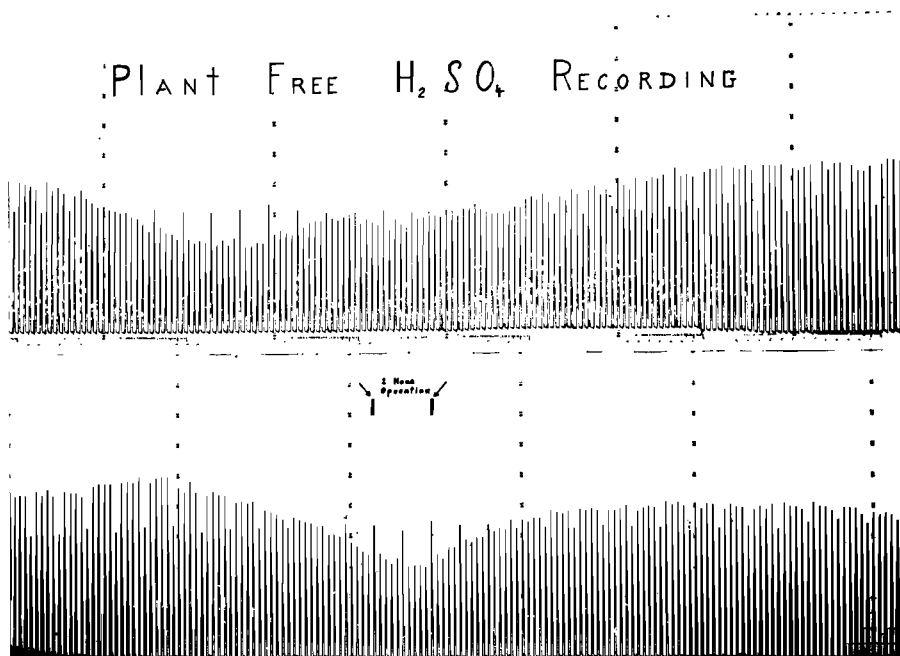
Table 1. Recovery Based on Measurable Losses

Rate Tons P_2O_5/Day	Recovery Overall	From Measurable Losses
400	94	96.9
500	93	95.5
600	92	95.0
750	91	94.1
900	89.5	92.5

It is further known that decreased digestion time is accompanied by increasing loss due to water-soluble P_2O_5 left in the filter cake (1) Two factors account for this increasing loss, one, the lack of control of the growth of gypsum crystals, the other, the rising load on the filter with operating rate.

Since small increases in productivity in high-volume plants bring about a considerable increase in profitability, these two chemical controls are vital in phosphoric acid manufacure:

Firstly, in order to control gypsum crystal growth, sulphuric acid concentration in the digestor must be closely controlled. Secondly, with the rapid rise in sulphuric acid costs and the indication of further rises to come, the optimum control of sulphuric acid in the digestor becomes urgent.

In summary, sulphuric acid level should be controlled for:

- Maximum extraction of P_2O_5
- Easily filterable and washable, gypsum.
- Maximum utilization of sulphuric acid.

The question arises, why then if there are such significant savings to be realized, continuous control has not been applied before.

Continuous sampling of the hot, acidic, corrosive, supersaturated slurry in the phosphate digestion tank has, up to now, posed a real problem. Today, however, both here and abroad, the problem is being overcome by using in-plant filter-samplers. Such a system is now available in a complete package as the Technicon Phosphoric Acid Production Monitor. The filter cloth of the Filter-Sampler, with weekly external cleaning, lasts more than five months before it is renewed. One company reports (2) that the first twelve months of operation have yielded an operating factor of over 90%.

The secret of the sampler's unique ability to successfully combat the hostile environment, is the rapid dilution of the filtrate by means of proportioning diluent directly into the sample head. This immediately relieves the super-saturated condition present in the slurry, and allows the sample to be handled like any other clear stream. Results obtained appear on a remote recorder in the control room and are readily available to the plant operator so that immediate corrective action can be taken (Fig. 1).

A computation of actual percent gains in efficiency is hard to prove in any plant, since many physical and operational variations are present in the total plant. It can be seen, however, that for the expenditure of $16,000 for the Phosphorus Acid Production Monitor, only minute increases in efficiency are necessary to recover the capital equipment expenditure in a matter of weeks.

For example, in one 500 tons-per-day P_2O_5 operation, the small increase in efficiency of 0.15% has saved $3,000 per month, by control in the manner described. This sav-

PlAnt Free H₂SO₄ Recording

Slide Figure 1 Remote Recorder in Control Room

ing has been realized month after month, for the past 18 months.

Also, loss of phosphate either by entrainment in the filter cake or loss in wash-water from phosphoric acid concentrators and slurry coolers, can significantly affect material balance of the phosphoric acid plant. In many cases it is difficult to pinpoint plant losses. However, continuous analysis of the common drain 'has been proved to quickly alert plant operatives to these losses. (3)

In a large production complex, including a phosphoric acid plant, two phosphoric acid concentrators, two ammonium phosphate plants and a compound granular fertilizer plant, automatic analysis was first applied to continuous phosphate analysis on the main works drain carrying effluent from all these plants, primarily as a measure of works efficiency and to assess where the most benefit would arise from monitoring individual plant drains. It became obvious that significant short term losses were occurring in the phosphoric acid plant.

The P_2O_5 efficiency of a phosphate acid plant in practice is not easy to measure. For a plant running at 90% efficiency a measuremen of efficiency to an accuracy of 1% involves product measurement to 1 in 90, whereas the same result can be obtained from effluent measurement to 1 in 10.

In the past it has been recommended that extraction and filtration efficiency should be measured from samples of gypsum taken immediately prior to discharge. Many producers have found it practically impossible to determine efficiency by this method.

Far better is the measurement of soluble phosphate loss from filtration and other productions by measurement from the drain itself. A Phosphate Drain Monitor costing in the region of $6,000 can be used for such an over-all plant efficiency estimation.

Under normal conditions, with no phosphate disposal except from the filter, this Technicon Monitor registers the efficiency of washing of the gypsum cake.

Losses from the filter, of course, can depend on many factors:
● Loading of gypsum on the filter.
● Porosity of the gypsum.
● Quantity of wash water and contact time.
● Strength of phosphoric acid.
● Rate of removal of wash water.

The relation of these factors to phosphate loss has been realized for many years, but adjustments of filter conditions have been difficult to assess rapidly since reliance has been placed on visual examination of the filter and on the slowly changing specific gravities in the receiving vessels.

While these assessments may be useful, they cannot tell the whole story. For instance, the operator can, with continuous phosphate analysis, more accurately control his primary wash-water feed to give a pre-determined efficiency; and alter his wash positions, to give a desired range of specific gravities in his receiving vessels, while knowing how his cake washing is beng affected.

In summary, automatic monitoring of the filter is used to:
● Accurately control the primary wash water feed.
● Eliminate high short-term losses.
● Indicate maximum loading after startup.
● Load filter to maximum capacity.
● Indicate deterioration of filter cloth.
● Indicate choking of wash system.

The solids-carrying effluent should be transferred with a glandless or diaphragm pump for reliability in the presence of abrasive materials. For best results, the inline filter is suspended in an overflowing basin in which turbulence is adequate to avoid build-up of solids on the filter face, and also to insure mixing of individual streams and even distribution of soluble phosphate from the suspended gypsum.

If the flow in the drain is variable, some indications of flow is necessary for daily losses. The output of the flow indicator can, in fact, be made a variable shunt to the AutoAnalyzer Recorder so that the trace provides a true record of drain loss.

Two evaporators, with a common hot well positioned where the condenser discharges are sent to drain, have also been monitored for spillage and carryover of acid mist. A Phosphate Monitor has also been applied to a submerged combustion evaporator. Considerable process control information has been obtained on the relationship of atomization and burning, to the extent of carry over of acid fume past the cyclonic separator.

It is temptingly easy to take wasteful short cuts in producing a liquid which can disappear down a drain without a trace. A con-

tinuous Phosphate Monitor therefore provides a warning against unexpected short duration loss.

As regards maintenance, figures are available through published case histories. (4)

In one case, a single worker looks after 14 continuous analyzers throughout the plant, which includes three phosphate digestors. Previously a total of 14 analysts had been required to do the manual analyses arising from the various sources. Preventative maintenance is carried out on a fixed schedule. For example, every seven days the system is washed out with dilute EDTA. Every month pump tubes, recorder charts, and colorimeter bulbs are replaced.

Running costs have also been computed for reagents, pump tubes, charts, bulbs and electricity at, $9.00 per week. Manufacturer's repairs average $3.00 per week.

A description of finished product control in an installation which manufactures 60% of all the fertilizer nitrogen consumed in the United Kingdom, some 500,000 tons per annum has been reported by Docherty & Singer (5). The completely automatic system for inline sampling and analysis of fertilizers which has been perfected yields individual NPK results, automatically, every six minutes; and the time delay from sampling to presentation of results is about 20 minutes. The stages for sample preparation and analysis can be summarized as:

Greco sampler
  160g-1600g
Tyler sample divider
  10g-100g
Mettler automatic dispensing balance
  10g
Technicon Solidprep dissolving unit
  50g/Liter
Technicon pump for dilution
  1g/Liter
Technicon AutoAnalyzer for fertilizer sample analysis

The sample is automatically taken by passing a funnel and connecting tube rapidly through the falling stream of fertilizer from the conveyor belt. This is automatically subdivided to 1/16th of its original size and a representative 10g portion of this is weighed on an automatic balance.

This sample is dissolved in a solid preparative unit and automatically analyzed for ammonium, nitrate, phosphate and potassium.

After nine samples have been analyzed, a standard sample of the fertilizer being manufactured at the time (and which already has been analyzed by official methods of analysis) is passed through the entire system for calibration purposes. All the operator need do is compare the target composition with sample. The peak heights themselves would clearly indicate whether or not the product was out of specification.

The results appear in the control room on recorder charts, and the intention is eventually to link these results to a computer controlling the entire process. Thus, by automatic analysis, results are available in 20 minutes, whereas previously they required 5-man hours.

Among other applications in the wide range available (Fig. 2) are such installations as:

1. Urea-ammonium — nitrate measurements in liquid nitrogen solution control minimizing the most common problem of nitrogen deficient product.
2. Control of the mole ratio of N:P in the preneutralizer during ammonium phosphate manufacture. This control is used to:
   a. Make subsequent granulation easier
   b. Reduce drying costs
   c. Eliminate over-ammoniation

This would be applicable to other processes, such as, ammonium nitrate production.

3. Phosphate quality control, where Continental Oil Company reports (6) analyses over the range $1 - 75\%$ P_2O_5 with 0.5% relative precision and accuracy. While another (7) measures P_2O_5 in the range $46 - 54\%$ with a precision of $\pm$ 0.5% and an accuracy of $\pm$ 0.10% on all of the 14,000 samples per month which are analyzed with this single instrument.

This review has sought to cover the applications of continuous chemical analysis throughout the fertilizer industry. It has discussed applications that have been proven in practice both as technically valid and economically sound.

References

1. John G. Kronseder, (Dorr Oliver Corp., Conn.) Chem. Eng. Prog., 1967, 63, 52, Phosphoric Acid Plant Design.
2. A. N. Baumann, (IMC, Florida) Proc. Technicon Inter. Symp. 1967, Automatic On-line Sulphate Ion Determination in Wet Process Acid Systems.
3. J. S. S. Reay, (SAI, Scotland) Private communications.
4. T. W. L. Atkinson, (Marchon, England) Phosphorus and Potassium, Feb. 1967, Continuous Determination of P_2O_5 in Wet Process Acid Plant Effluent.
5. A. C. Docherty, (ICI England), Proc. Technicon Inter. Symp. 1967, Automatic Stampling and

Slide Figure 2

PRIMARY MANUFACTURE OF FERTILIZERS
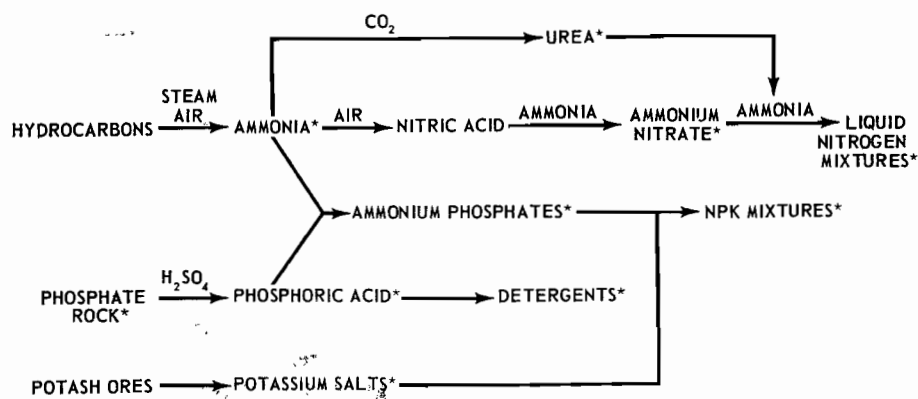
*AUTOANALYZER APPLICATION

Analysis of Compound Fertilizer.

. D. E. Jordan, (Continental Oil, Oklahoma) Proc. Technicon Inter. Symp. 1967, High Precision Determination of P_2O_5 in Concentrations from 0.1 to 7.5 mg P_2O_5 m/l.

. J. I. Longest, (Central Phosphates, Florida) Proc. Technicon Inter. Symp. 1967, Precision Determination of High Level P_2O_5 Contents.

MODERATOR ARCHER: We are running behind time. We have time for a question or two. Does anybody have a question for the panelists?

A MEMBER: Could you tell what would be the approximate price for the installation of ICI for the total control of NP and K?

DR. MARTEN: Yes, the analytical system cost is approximately $15,000, that is, for the four channels. Then, in addition to that, one must remember the Tyler sampler, the Geco sampler and the Mettler weighing balance and as a rough estimate I would say that would add another $10,000.

SAME MEMBER: Thank You.

ANOTHER MEMBER: Mr. Hofstader, Dr. Marten mentioned something about the technical competence of the technicians and how difficult it is to attract them to doing routine analyses.

What would you say would be the general technical background of the people who were running this complicated system that you showed?

MR. HOFSTADER: The competence of the people who have actually run this particular system that I showed here was laboratory technicians who were strictly trained in the laboratory. These people were not of American background, of course, because the lab was in Central America. They are people from the area itself and they have been able to work quite well.

Just a point on technicians and automation. I hope that it is not ever interpreted that automation eliminates technicians because this is, you know, not really the kind of thing you want to get across.

What we would like to do, of course, is to make the job of the technician that much more interesting, to take out some of the real routine drudgery of being a technician and this is a lot of the stamina that is involved with someone wanting to become a good technician and I think the more of this kind of thing we can get out of it the more of our development work we can get from our technician who really is the fellow who is on the bench and can do the job best for us in terms of knowing what is to go on.

SAME MEMBER: One more question for Mr. Hofstader. Do you have any figures or can you give us a rough estimate of the financial savings or the economic data on the system that is installed in your Furtica plant?

MR. HOFSTADER: I can tell you that over a six-months period in operation in 1966 we have been on target in terms of formulation almost 100 per cent. Our on target is really quite good. We have had very little over-formulation.

Previous to this time we did have considerable over-formulation because it is obviously much easier to overformulate than it is to underformulate and go back and add more to it.

So our control has put us on formulation in many cases.

MODERATOR ARCHER: One more question.

ANOTHER MEMBER: Mr. Barrett said that at IMC they had seen accuracies with auto-analyzers of two-tenths per cent. Is that a three sigma accuracy?

MR. BARRETT: Yes, only, when I say two-tenths of a per cent, actually, this varies according to the per cent of P_2O_5 that you are dealing with. As you go higher, of course, towards triple super phosphate, the accuracy is somewhat less—if you compare it with the AOAC method, say, volumetric methods, why, then the accuracy is plus or minus four-tenths of a per cent for triple superphosphate but I believe that this has been shown to be a bias in the volumetric method.

So when we say plus or minus two-tenths of a per cent, we are talking about P_2O_5 range anywhere from one to upwards of 20 per cent P_2O_5. Higher than that, of course, the deviation would be more.

MODERATOR ARCHER: Any other questions?

Vince, I am going to turn the program back to you. Thank you very much.

CHAIRMAN SAUCHELLI: Thank you, Jim, for arranging such a splendid panel discussion. I know that the analytical laboratory is a very vital part of production. As one man pointed out here a short time ago, you can't sell a pound of fertilizer without the approval of the analytical laboratory, and, with these new developments, in automation and so on, we are seeing marvelous things.

I predicted some time ago that in a few years you won't be able to find a chemist that is familiar with the wet chemical methods. It would be very difficult to find one because of the intrusion or the acceptance of the automatic analytical methods.

Before I forget it, let me announce that Dr. Charles Gehrke, Professor of Agricultural Chemistry at the University of Missouri, is holding a short course on automated analysis of fertilizers on December 11th, 12th and 13th at the Missouri Agricultural Experiment Station Chemical Laboratories.

If any here are interested, see me for details. This is a splendid opportunity for our industry men to become familiar with these new methods and with the equipment.

MODERATOR ARCHER: Vince, I just wanted to be sure I understood your statement. You didn't mean to say that there wouldn't be any chemists around, did you?

I am happy to say that we will always need chemists. They are a very essential part of our industry and of all chemical processing industries.

Another announcement. We are not going to have our business meeting this afternoon out of deference to our Treasurer, who wasn't feeling too well. We will have the business meeting the first thing tomorrow morning.

Now, we will continue with our program.

The next speaker is so well known to our members he needs no lengthy introduction.

Al Phillips is one of the highly respected members of the Chemical Engineering Staff of TVA, that research organization to which we are all indebted for its scientific contributions to the advancement

of the fertilizer industry at home and abroad.

We are honored to have Al on our program.

Mr. Phillips will give us some highlights of the new developments at TVA's National Fertilizer Development Center.

New Developments At TVA's National Fertilizer Development Center

A. B. Phillips

IT is a pleasure to appear on the Round Table program again—especially with a subject like this. Instead of going into detail I can just ramble. And that's what I intend to do—ramble on about what we are doing at TVA—then if anything strikes your individual interests you can get in touch with us later for any amount of detail that you may wish and that we have.

First, let me take a minute or so to explain what we do at TVA— for those of you who don't know us very well.

TVA is an independent Government agency created in 1933 to do several things—most of which involve the development of the Valley of the Tennessee River. However, it was charged with one national program—a fertilizer program that centered around the use of a war surplus nitrate plant at Muscle Shoals, Alabama. This program might be summed up in terms of the following objectives.

1. To develop new and improved fertilizers and processes for their manufacture in order to lower their cost to the farmer and to increase their effectiveness.
2. To demonstrate the value of the best methods of fertilizer use.

We try to meet these objectives with a program of research and education—research to develop new technology and education to get it put into use.

The research side includes fundamental and applied laboratory and greenhouse work on fertilizers and development through pilot plants and larger demonstration-scale plants.

The large plants provide new fertilizers for the educational side —through nationwide tests and demonstrations, both with the farmers and with fertilizer dealers.

When a new process or product is fully developed and introduced on the farms, hopefully the fertilizer industry will take it up. Then we can move on to something else.

Thus, our program is highly dependent on close contact and cooperation with industry. And we hope it benefits both the farmer *and* the industry, rather than just the farmer. You in the fertilizer industry—and those who serve the industry—are more than welcome to the information our program generates.

So much for the background—

We get our basic phosphorus production by the electric-furnace method—for several reasons, including national defense commitment built into the TVA Act. There is more and more interest these days in this process for commercial fertilizer production—what with higher sulfur prices and prospects for lower power costs.

The largest and most modern of our several phosphorus furnaces is the one we call our No. 7. It is really not very new—built in 1963— and not very large—17,000 tons' phosphorus per year—with a 25,000-kw. electrical rating compared to 50-75,000-kw. for the largest. But we have developed some new technology with this furnace and certainly extrapolation from it would be useful in considering the larger furnaces that might serve the fertilizer industry tomorrow.

Also, detailed design innovations such as dry seals for dust precipitators and telescoping electrode seals have been developed and tested in our phosphorus plant. These are available to anyone who would like them.

We have in process the installation of a new charge preparation (phosphate agglomerating and calcining) system for our furnaces. This will consist of a traveling grate kiln followed by a rotary kiln to heat treat compacted phosphate charge. Information on the performance of this system will be available for comparison with alternate ways of charge preparation. It is scheduled for operation late next spring.

Through the years almost all of the phosphorus going into our fertilizer programs has been first burned to form phosphoric acid. Consequently, by experience, we have built up a storehouse of information on this subject—covering both what to do and what not to do.

This experience has culminated in the design of two stainless steel acid plants. The first, our No. 6 unit, was built in 1962 to replace a portion of our capacity then supplied by several units constructed from graphite.

Profiting from the experience gained from this plant, we recently built our second stainless unit—in fact, we started operation only last month. It replaces the remainder of our old graphite facilities.

In this plant, phosphorus is burned in a water-jacketed, unlined stainless steel tower. The combination gases are scrubbed in a second tower with recycled weak acid forming a strong acid product—super acid up to 85 percent P_2O_5 if desired. Recirculating acid is water cooled. Tail gases are cleaned up in a venturi type scrubber followed by a demister.

The capacity of the unit appears to be about 7800 pounds of phosphorus per hour—or about 75,000 tons of P_2O_5 per year. It is a very efficient, effective design on which we have much detailed data —all available to industry, of course.

The only other new feature of our phosphate plant is some pollution abatement facilities, which I will mention later.

There is very little that is new about our *basic* nitrogen plant. In fact, our ammonia plant is probably one of the oldest in operation; we recently celebrated its 25th anniversary. It was originally designed to utilize water gas from coke

but revamped for natural gas reforming in 1951.

We do have a new atmospheric ammonia storage tank. It has a capacity of 6000 tons, about the minimum I understand that makes atmospheric storage attractive. The unit has served us well and has been trouble-free. If information about it would be helpful, you are welcome to it.

One innovation of recent years has been our new nitric acid plant. It is a modern unit built for us by C&I that has the capability of producing 65 percent nitric acid instead of the usual 58 to 60 percent. This is of considerable help in uses such as nitric phosphate where the water balance is critical or where scrubber effluent from pollution control have to be returned to the process. The higher strength is accomplished mainly as a result of the design of the column—the shape, the number of trays and the volume of liquid retained on the trays.

After some preliminary problems, the plant is now operating at the design rate of 165 tons of HNO_3 per day, with a tail gas concentration less than 1500 p.p.m. and a product concentration of 65 percent HNO_3. The plant has a refrigeration system which we have not yet activated which may permit concentration up to 68 percent.

We also have two smaller nitric acid units—55 tons per day each—which we have recently modified to improve efficiency. This modification involved several design changes—the addition of 24 trays to the column, a new bleacher and a heat exchanger. The modifications resulted in a 60 percent reduction in stack losses from the plant.

Incidentally, these design changes were calculated by use of a mathematical model set up in a computer program. A second program was set up to verify the model from data collected after the changes were made.

Those of you with older acid plants might be interested in more details of this project.

Next, I'd like to discuss progress in a *relatively* new facility we call our combination fertilizer plant—or "Jolly Green Giant." This was designed to demonstrate

three processes we had developed in our pilot-plant studies and to provide sufficient quantities of the products to use in our introduction programs.

They are:

- The pan-granulation process for high-nitrogen fertilizers,
- The mixed-acid nitric phosphate process, and
- Ammonium polyphosphate.

All are now operating well—after a somewhat agonizing period of development—and we are accumulating information on their production on this semiworks scale.

The pan-granulation process produces granular ammonium nitrate, ammonium phosphate nitrate (30-10-0 or 25-25-0) or ammonium nitrate sulfate (30-0-0, 5% S).

In this process, which I'm sure many of you know about, the appropriate acids—nitric, phosphoric, or sulfuric—are neutralized in two stages with a vacuum concentration step in between. The resulting solution, containing 5 percent water or less, is worked into granules by spraying in a pan granulator—the granules are then dried, cooled, and screened.

The nitric phosphate process we are demonstrating in this plant is the mixed-acid type—phosphoric acid is used along with the nitric to tie up calcium and increase water-soluble phosphate. We formulate the two grades we make—20-20-0 and 26-13-0—to have about 40 percent water solubility.

The process involves extracting phosphate rock with the mixed acids—preneutralizing the acidulate with ammonia and granulating with recycle in a rotary drum where neutralization is completed. The granules are dried, cooled, and screened in the usual manner.

Although we developed this process primarily to simplify the nitric phosphate approach, it may have particular merit because of the similarity of its flowsheet to the popular granular DAP process. Perhaps existing DAP plants could be modified to use this process if it becomes necessary to extend the short supply of sulfur—only a little over half of the P_2O_5 need come from phosphoric acid.

The third process used in this

plant is one for producing ammonium polyphosphate, 15-60-0, by neutralizing superphosphoric acid with NH_3 in a pressure neutralizer. The result of the neutralization is a sort of melt that is made into granules in a pugmill or blunger. The granules are cooled and screened—no drying is required.

So far, we have used only furnace super acid in this plant, but we are making arrangements for some testing of wet-process acid.

I mentioned earlier that we had been involved in an extensive pollution control effort recently. I won't get into all the details, but it has included both water and air, with a little more emphasis at first on water perhaps.

One of our earliest installations was a system to treat and recycle water that had been in contact with elemental phosphorus—"phossy water" we call it. This was important because phosphorus is quite toxic and we wanted to preclude any possibility of its getting into the river among the fishes.

The system we installed involves collecting the water, adding glue as a flocculant, and settling the phosphorus and impurities in a thickener. The overflow goes back to the process; the underflow is centrifuged to recover phosphorus from the dirt.

We have also made a large effort to reduce losses of plant nutrients—phosphates and nitrogen—to the river. The need to do this was brought to our attention by a profuse growth of water weeds in the river downstream from us three summers ago.

We were quite successful in this effort which was done largely by tightening up on many sources of leaks and spills, some new facilities, and the monitoring of key streams of cooling water effluent with conductivity cells so we could tell when a leak occurred and correct it.

Incidental to this work we conducted fairly extensive greenhouse studies of the nutrition of the type of water weeds that were plaguing us.

Our effort in air pollution abatement—which still has some ways to go—has been mainly the addition of dust and fume scrubbers on equipment such as the dryer

used for our phosphate feed material. Our combination fertilizer plant contains a complex collecting and scrubbing system with scrubber effluent streams returned to process.

I am sure many of you are working on similar problems in your plants.

I want to mention only very briefly some of our research and development work because most of it has been reported at other meetings and in other publications recently.

We have a new plant, just completed, in which we will study still another nitric phosphate process—one that requires no sulfuric or phosphoric acids and produces high-analysis fertilizers with high water solubility by employing a sulfate recycle step.

The phosphate rock will be extracted with nitric acid and the extract treated with an ammonium sulfate solution to precipitate gypsum. After filtration, the solution phase phosphoric acid and ammonium nitrate will be ammoniated and granulated to make ammonium phosphate nitrate fertilizer. The gypsum will be reacted with ammonium carbonate to regenerate ammonium sulfate solution for recycle. This principle has been known for some time and has been practiced in Europe to some extent.

In other pilot-plant work we are progressing well with the development of a process for making ammonium polyphosphate directly from 54 percent P_2O_5 phosphoric acid. Most of the problems encountered earlier are now being solved.

We're working on a pilot-plant scale for producing sulfur-coated urea—a slow-release nitrogen fertilizer—after some encouraging results from the laboratory and greenhouse work.

One of the most interesting things we have in our laboratory research now is studies of extra high analysis N-P compounds that hold promise as the fertilizers of tomorrow—some of these contain twice as much plant food as anything marketed today—but even pilot-plant work on these is some time off yet.

In our research and development activities we are getting quite involved in studies of the recovery of sulfur from the flue gases of coal-burning power plants. Since TVA operates such plants—and we also are involved with the greatest sulfur-consuming industry—it is natural that we would have this interest. Much of this work is in co-operation with the Public Health Service. Ultimately, we expect it to involve large pilot-scale studies on our steam plants to test processes already under consideration as well as research to find new and better approaches.

As we accumulate information in the course of this work, we will be glad to share it with those who are interested. This overall development of sulfur recovery could, of course, have a great impact on the fertilizer industry.

In closing, there are two other items I'd like to mention briefly because they may hold something of value to some of you.

For the past few years we have been asked by the Agency for International Development to help in their work in the developing countries. As a result, we have sent teams of engineers, agronomists, and economists to 13 countries to study and make recommendations on fertilizer production and use. The reports that resulted from some of these trips and some other special projects we have carried out for AID are available to those who have an interest in the developing countries.

Last, we're trying to build our technical library at Muscle Shoals into one of the leading storehouses of fertilizer-oriented information. We have enlarged it, added a modern information retrieval system, and have arranged to acquire pertinent information from many of the leading institutions in the United States and in Europe. Anyone with an interest and need is most welcome to use the facilities of our library.

One of the interesting services that our library will offer at the start of the year is the publication of an abstract booklet. It will be issued monthly and offered to anyone interested on a subscription basis. It will contain abstracts of current articles that we think will be of interest to all who are concerned with fertilizers. Actually, this is an extension of an internal abstract service we have had for years for our own technical people. The booklet will also contain a list of all new publications of our own work that were issued during the month.

This has been a rather sketchy summary of some of the current activities at our National Fertilizer Development Center at Muscle Shoals. It has been designed to stimulate your interest in what we are doing because you—the fertilizer industry—are a vital link in the chain of events needed for us to get our job done. So let me assure you again that we welcome your request for more details of any of the activities I have described, and we will be glad to see you at Muscle Shoals at any time.

CHAIRMAN SAUCHELLI: Thank you, Al.

One spirit that seems to prevail in TVA is this one of wanting to share the information that they collect with the industry both here in the United States and in foreign countries.

Tomorrow we have a very fine program. You all are interested in this nitro-phosphate business. We have two excellent papers from overseas, from Germany. I know you will all want to hear them and we will provide some time for lively discussion.

Nitro-phosphate is coming rapidly to the front. I appreciated the remarks made by Bill Weber regarding the chemical changes in the conventional process that were not apparently fully understood and in connections with comparisons with nitro-phosphate. We will probably have more of those comments to discuss tomorrow.

So let's have a fine meeting tomorrow. Also, there is going to be a paper by Christopher Pratt in connection with the nitro-phosphate.

Is John Osguthorpe here? Stand up please, John.

John Osguthorpe is with the AID organization and he is a very big factor in this fertilizer sales business.

John, we are glad you can visit with us.

We stand adjourned until tomorrow morning at nine o'clock, sure, sharp.

Friday Morning Session, Nov. 17, 1967

The Round Table Reconvened at 9.15 A.M.

Dr. Vincent Sauchelli, Moderator, Presiding

CHAIRMAN SAUCHELLI: Good morning. I am pleased to see such fine attendance this morning.

We are going to continue with the program as printed, with this exception that the Business Meeting scheduled for yesterday afternoon will be held now and then we will follow with the regular program.

Before we start the meeting I want to announce that we are getting international all right, as Bill Weber said yesterday. We have 19 visitors from overseas, four from West Germany, five from England, three from Mexico, two from Ireland, one from France, one from Spain, one from Australia, one from Denmark, one from Japan, and, of course, we have always a fine delegation from our neighbors across the northern border. We don't include them with the foreign overseas guests. We are always glad to have the delegation from Canada.

As I mentioned in my first remarks, we welcome guests from other countries and we hope that our membership will take good care of our foreign guests and make them feel at home.

We have a registration of about 500.

Now I am going to call on our Secretary-Treasurer for his Report.

Secretary - Treasurer Report, HOUSDEN L. MARSHALL: Mr. Chairman, members of the Round Table: Your Secretary is wearing the Secretary's hat right now, and I would like to state that your Secretary's Office has been rather busy this year. We made three circulations to the membership and I would like to hear some response about that idea that we put out first, a general subject outline of the program we had in mind and

then, when it was finalized, we sent you the printed program.

If you fellows like that, we will continue it. Otherwise, we will revert to the one circulation. You have got to bear in mind that these mail circulations run around $300 to $400.

That is part of the organization's work. The rest is keeping up with getting the speeches and the papers, editing the proceedings and getting them mailed out. We have done well at that. Of course we take care of the back orders.

I do want to emphasize that after this year, if you expect first-class mail delivery, you must give us your zip code; otherwise, the Post Office Department will have the privilege of putting it into third-class mail.

Now, relative to the back issues of up to 100 for 1963 1963 through 1966. I can furnish these complete.

1958, 1959 and 1960, 1961 and 1962 are very scarce and what I have been doing when I don't have them is to canvass around to find out who had so we could get them back. We are going to be a little bit lucky to get some back. But where I don't have the issue, I am willing to take our file copy down to the Xerox man and have them Xeroxed out at about ten cents a page and send you the Xerox copy with a small charge for handling. That means about two trips downtown and one to the Post Office and special handling.

We have had a rather successful business in back issues this year and I would like to take the Secretary's hat off and put the Treasurer's hat on now.

You will remember last year we reported only on 11 months because our meeting date was Novem-

ber 2 and you can't get information out of the bank on the October expenditures in time to get it into the Treasurer's Report. Therefore, last year's Report was only 11 months. This year's Report covers 13 months. Therefore, some of the charges are a little large.

To start off: On October 1, 1966, we had a cash balance of $883.18. Now, remember, that is the leavings from an eleven-month operation, that was 1965-1966.

Now the income for 1966-1967:

The Registration was $4780; Membership List Donations were $310; The Coffee Break—We had some folks contribute to that—was $175. Your Reprints and Back Issues Sales were $1388.57.

This made an Income Total of $6653.57, which means that from October 1, 1966 to November 1, 1967, your Treasurer had pass through his hands or available to him $7,536.75. That is our Total Cash Flow that we had during the year.

Now, how did we handle it? Our Disbursements:

The Bank Charges $1.75 for handling some foreign checks. I request U. S. funds but they don't always come in marked so that you can understand it, and we get charged for it, for the correction. We overcharged some people, some mixup in some charges and there was $8 that I had to refund. The 1966 Meeting Costs were $1,166.61.

The Membership List cost, printing, mimeographing and getting it ready and mailing, $276.15. Your Proceedings cost, now mark this figure, $4,220.46. Your Secretarial Office running 13 months was $988.64. Now, that includes postage which is for the back issues also.

The 1967 Meeting costs were $414.84. That takes care of everything up to November 1st.

Total Disbursements were $7,076.45 and when you recapitulate that cost you find we had $460.30 left as of November 1, which is not very much of a cash balance.

Your Treasurer has been alarmed at the way things are going.

magazine salesmen and, therefore, we may have to ask you, for several reasons, for $3 more next year, in other words, raise the dues to $15, because I don't think we are going to be able to have the good fortune to have some hosts for our cocktail party on Wednesday night and, of course, we only had one host for the coffee break at this meeting.

This is my Report respectfully

new dates, convention dates in any hotel in a reasonably located city, we have to know three or four years in advance where we want to do it because they are actually filled up that far in advance.

Thank you.

CHAIRMAN SAUCHELLI: Thank you, Mr. Treasurer. Usually the Treasurer's Report is not too interesting but those are the facts. We operate on a small margin. We are not a profit organization. We reflect the fertilizer industry in that respect.

Is there any discussion on the Treasurer's Report?

MR. WAYNE KING: I move we accept it.

CHAIRMAN SAUCHELLI: The motion is made that we accept the Report as presented.

(The motion was seconded.)
All in favor.
(A chorus of ayes.)
Contrary minded.
(No response.)

The question of hotel accommodations is always a problem. I know there are some dissident votes or voices in the group who would like to see the meeting held in other parts of the country but that is a problem. With a group of this size it isn't always easy to get hotel accommodations in various cities. The big hotels are usually booked in advance. We have been very fortunate in having good accommodations here and the majority of the people in the past have always voted for the meeting to be held in Washington becaues of its convenience.

Most people like to come to Washington not only to this meeting but to visit for other purposes too that they include in one trip. Our foreign guests find it very convenient to come to Washington. It might be different if they had to go to St. Louis or Chicago or some other place like Miami.

So every year we have a short discussion on this and I don't think we want to be different this year. What are some comments on a meeting place? I think we are committed for next year anyway here in Washington but let me hear some comments on this matter of location of the meeting.

Do I hear any comment or do I assume that there is general

TREASURER'S REPORT — October 1, 1966 to November 1, 1967

Cash on hand Oct. 1, 1966		$ 883.18
Income Oct. 1, 1966 to Nov. 1, 1967		
1966 Registration	$4,780.00	
1966 Membership List	310.00	
1966 Coffee Break	175.00	
1966-1967 Reprints, Back Issues	1,388.57	
Income Total	$6,653.57	6,653.57
Total Cash Handled—Oct. 1, 1966 to Nov. 1, 1967		$7,536.75
Disbursements—Oct. 1, 1966 to Nov. 1, 1967		
Bank Charges	$ 1.75	
Refunds	8.00	
1966 Meeting Costs	1,166.61	
1966 Membership List	276.15	
1966 Proceedings Cost	4,220.46	
1966-1967 Secretarial Office Cost	988.64	
Stenographic, Postage, Supplies		
1967 Meeting Costs (Preliminary)	414.84	
Total Disbursements	$7,076.45	$7,076.45
Balance Oct. 31, 1966		460.30

RECAPITULATION

Cash on Hand Oct. 31, 1966	$ 883.18	
Cash Income Nov. 1, 1966 to October 31, 1967	6,653.57	$7,536.75
1966-67 Disbursements		7076.75
Cash Balance, Oct. 31, 1967		460.30
Equitable Trust Co. Balace as of October 31, 1967		$460.30

ANALYSIS OF FERTILIZER INDUSTRY ROUND TABLE COSTS

Year of Report	Proceedings Costs	Back Issue Sales	Total Cash Handled
1963	$4,059.16	$1,675.38	$6,287.70
1964	3,202.66	939.26	5,079.11
1965	3,474.72	1,672.15	6,129.47
1966	3,861.50	1,001.35	6,888.37
1967	4,220.46	1,388.57	7,536.75

As you probably would realize from the Treaurer's Report, our big expenditure cost is the Proceedings.

Now, the thing that worried me most was the fact that we had only a $460 balance. Therefore, to be sure of a safe operation, we had to raise the dues $2. The figures were not available to us in time to announce it to you in advance.

I don't feel that we can bank on sales of back issues which has been a nominal income. We are not

submitted.

For next year our meeting dates are November 13, 14th and 15th and for 1969 they are November 5th, 6th and 7th at this hotel.

I would like to have a motion approving the Treasurer's Report and I would like to have a motion approving these dates so that I can tell the hotel we are willing to pick them up. We always do that. Fortunately we do have our dates set to 1972 here, if you want to continue. Bear in mind to get

agreement that we continue here in Washington?

Do you have some comments here, Dr. Strelzoff?

DR. SAMUEL STRELZOFF (Chemical Construction Corporation, New York, New York) : Yes. I would like to make a suggestion to all present here representing manufacturing companies and the rest of it.

I think we derive a great deal of profit from this Conference and I think that some voluntary contribution from these companies that are getting so much out of these meetings would certainly be in order, to help this Conference. This conference is very, very successful and is becoming more and more popular and is bringing each year more visitors from foreign countries and giving us a chance to listen to their experiences which are very valuable to us.

I am surprised that this can be carried on such a small budget, and I think the companies should help.

As far as the locations, well, the United States are full of locations but Washington is good, Atlantic City is good and New York City is good too.

CHAIRMAN SAUCHELLI: I know it is expensive here. I find it is expensive to have these hotel prices but that is characteristic of all of the big cities now. People who travel around find that it is hard to get accommodations at prices that some of us, looking back, remember with great pleasure when you could get rooms for $10 a day. This is speaking an ancient language now.

I am going to assume that the majority of the members here agree that we should continue here in Washington, at least for next year anyway.

What was your suggestion?

SECRETARY MARSHALL: I would like to call the attention of this group to the fact that this is the 17th Meeting and the 20th Meeting is coming up in three years. You had better start thinking over what you want to do at that 20th Meeting.

CHAIRMAN SAUCHELLI: That's too far ahead.

With the flux situation that we have in the industry, I think three years—even projections on sales and so on for 1975 are too far ahead. I think if we could project for at least one or two years, we would be safer.

Any other order of business to come before this group at this time?

MR. WAYNE KING: I rise to a point of order.

The Executive Committee has been living in sin. They have never been approved. This may sound a little silly but I'm an engineer and not a lawyer but let's make this legal.

On the back of your program is listed the expanded Executive Committee and with my limited ability to read—You all know these people.

Vince Sauchelli is Chairman, Albert Spillman, Joe Reynolds, Bob Heck and Billie Adams.

Now, I am probably the only one who has ever carefully read the Minutes of the meeting but Housden Marshall is our permanent Secretary-Treasurer and this was done of necessity on account of handling all of that money, you see.

So I will make the motion that this be accepted for the next three years. Can I get a second to that?

(The motion was seconded.)

All in favor say aye.

(A chorus of ayes.)

One thing, Vince. I just want to give you a little of my philosophy this morning. If everyone was as big around as I am the people in this world would be a lot closer together.

CHAIRMAN SAUCHELLI: I have nicknamed our good, lovable friend Wayne King the Inimitable Wayne or the Unpredictable Wayne. He's a great friend of ours and we are glad to have him around.

If there is no other order of business, we will proceed with our program. I know the folks here are very much interested in this morning's program, since it is concentrated on nitrophosphate and I think nitrophosphate discussions have been one of the most lively and generally accepted to be the most interesting item on the program and, in fact, for the whole fertilizer industry I think nitrophosphates are a big subject.

I think we are at the crossroads. American industry must look very carefully into the claims and the merits of nitrophosphates.

Last year we had a panel that was devoted entirely to this subject. Our good friend, Bill Weber, organized the panel. We had members on that panel from this country and abroad and it was an excellent discussion. But the subject has grown in interest and so this year we were fortunate also in getting some outstanding personalities and knowledgeable persons to accept our invitation to discuss this subject from different phases.

We are fortunate in having representatives from one of the outstanding organizations of Europe, the Badische Aniline & Soda-Fabrik. They are internationally known and have a splendid record. We usually associate Badische with synthetic nitrogen but they are in all sorts of things.

First we have Dr. Kurt Jockers and Dr. Gero Lüth and we apologize to Dr. Lüth for misspelling his name. His name is Lüth, L-umlaut u-t-h, instead of Lutch.

These foreign names sometimes are badly handled by our secretaries and others and we apologize because I think every man is interested in having his name spelled correctly and pronounced correctly. So it is Dr. Gero Lüth.

Then we also have Dr. Johannes Jung. Three gentlemen from Badische.

Dr. Kurt Jockers is going to introduce his associates.

Introduction by DR. KURT JOCKERS: Mr. Chairman, members of the Round Table Meeting: Last year Dr. Sauchelli was so kind to invite me to join the Round Table Meeting as a guest. This Meeting was so interesting to us that at the end of this 1966 Meeting I asked Dr. Sauchelli if it would not be possible for Badische Aniline & Soda-Fabrik to contribute to the Round Table Meeting some of our 40 years of experience in the NPK field.

BASF is producing in Ludwigshafen-Rhein, Germany, presently about 1.1 million metric tons of NP and NPK fertilizers. The trade name of these NPK fertilizers is Nitrophoska.

Apart from producing Nitrophoska, we manufacture in Ludwigshafen another one million metric tons of straight nitrogen fertilizers such as calcium-ammonium nitrate, ammonium - sulphate - ni-

trate, calcium-nitrate, ammonium-sulphate and urea.

At first I would like to thank you, Dr. Sauchelli, again, for making it possible to be here with you this morning.

Now I would like to introduce to you two gentlemen of BASF, Dr. Jung and Dr. Lüth.

Dr. Jung is our Chief Research Agronomist at our Agricultural Experimental Station in Limburgerhof, which was founded in 1914 for the development of mineral fertilizers.

Dr. Lüth is the Production Manager of all nitrates-containing

fertilizers. May I present Dr. Jung.

DR. JOHANNES JUNG: Mr. Chairman, Ladies and Gentlemen: First of all, I would like to thank the Executive Committee for making it possible to present this paper here in Washington. I hope that you will be able to understand my German-English.

But since I am trying to discuss here in this presentation how to go along with 40 per cent water soluble phosphates in NPK, it would be possible to even get along with maybe less than 40 per cent of the minimum language requirements.

erous tests over several decades have shown that the ammonium citate-soluble phosphate contained in a fertilizer (the problematical question whether soluble in neutral or alkaline citrate being left aside for the moment) is basically just as available to the plant as are water-soluble compounds. Certain qualifications will have to be dealt with later.

In Germany this knowledge has had a considerable influence on the farmers' choice of fertilizer as well as the range of fertilizers produced. In this connection it should be mentioned that German manufacturers of superpohsphate have gone over to producing phosphate fertilizers containing three components with varying solubility. In these new products 40 to 50% of the phosphate is in water-soluble form; according to the manufacturers the percentage content of the several forms of phosphate determines the very good overall effect of these fertilizers some of which, according to results received so far (2), are slightly superior to the superphosphate fertilizers.

40% Water-Soluble P₂O₅ in NPK is Adequate

Dr. J. Jung

1. *Introduction*

IN assessing the value of phosphorus as a fertilizer there is only one point on which all agricultural chemists are in absolute agreement and that is that this element is an indispensable nutrient for all plants. However in what chemical form this nutrient is best conveyed to the plant under the most varied agricultural conditions has been vigorously discussed for exactly 127 years without a unanimous decision being reached. That this apparently inexhaustible subject is still of topical interest and has become a "problem for each generation" is principally due to the fact that the action of the particular fertilizer phosphates on plant growth depends on various factors, the main ones being
   a) type of plant
   b) type of soil (especially the pH value and content of reactive Fe + Al)
   c) particle size of the fertilizer
   d) amount of phosphate available in the soil

It is therefore not surprising that when phosphate fertilizers are tested under various conditions, different and even contradictory results are frequently obtained. The difficulties encountered in objectively assaying the value of various forms of phosphate in agricultural application are, however, not infrequently due to the method of testing employed. In order to illus-

trate the differences in action as emphatically as possible, comparative experiments, especially in pots, are preferably carried out in soils very low in phosphate. Under these "model" conditions it is certainly easier to demonstrate specific relationships in the behavior of the various phosphates with the soil and plants. However, whether these relationships can be applied to agricultural practice is often questionable. It may be mentioned in passing that it has become very difficult in Central Europe to obtain the right reactive soils from normally cultivated areas for these comparative tests.

2. *Availability of water-soluble and ammonium citrate-soluble phosphates (as components of nitrophosphates) to plants*

The requirement that fertilizer phosphates should be completely water-soluble dates back to the time when mineral fertilizers were first used. Especially in Europe, the classical area for the application of mineral fertilizers, this requirement for complete water-solubility has long been superseded by the requirement for adequate availability to the plants. However in this connection the question can be justifiably asked, using a quotation from J. A. Brabson and W. G. Burch (1): "How available is available?".

Our reply is as follows: Num-

2.1 *Behavior in the soil, utilization by the plant and effect on yield*

When discussing the suitability of phosphate compounds with varying solubility as fertilizers we must bear in mind that the soil acts as a particularly effective barrier between the applied phosphate and the plant in the case of the nutrient phosphorus. Before the phosphate can be absorbed by the plant, by far the largest proportion of it reacts with certain components of the soil; the more readily soluble or reactive the phosphate compound, the higher the proportion that reacts with the soil. Particularly in the case of water-soluble phosphates this reaction takes place within a few hours or days (3, 4 and 5). Thus the plant generally absorbs the nutrient phosphorus not direct from these compounds but from their reaction products. However, since water-soluble and citrate-soluble phosphates differ principally as regards their reaction rate in the soil and less as regards the reaction products which they form, no great differences can be expected in the effect of these two forms of phosphate on plant yield.

Here are some examples:

From pot experiments carried out at our Limburgerhof Agricultural Research Station over the last 40 years we have obtained the following results on the influence of monocalcium phosphate (as the prototype of a water-soluble phosphorus compound) and dicalcium phosphate (as the prototype of an ammonium citrate-soluble phosphorus compound) on the grain yield of oats. 85 comparative tests were carried out on 18 different soils with a total of 40 different pH values and in some cases with a varying rate of phosphate fertilization (Table 1). Since the soils used were generally very low in phosphate, fertilization with this nutrient caused a very vigorous increase in the grain yield, in fact almost five fold. There were no appreciable differences in the action of mono- and dicalcium phosphate even under these extreme conditions. Similary results of several thousand tests compiled by S. Gericke (6) show that there is no difference worth mentioning in the action of water-soluble and ammonium citrate-soluble phosphates (superphosphate and the thermic phosphate "Rhenania") (Table 2).

In addition to these summarized data numerous individual results can of course be produced which speak for the superiority of either the one or the other form of phosphate.

This is illustrated by results of tests by Terman, Bouldin and Lehr (7) with certain North American soils. As can be seen from the phosphate uptake in Figures 1 and 2, dicalcium phosphate was best available to the plant in the pH range of about and below 7, whereas with pH values of about 8 there was an opposite tendency.

Apart from the fact that acidulated phosphates react with iron and aluminum compounds in acid soils and with calcium ions in calcareous soils in addition to the biological fixation by microorganisms and are thus converted to a very great extent into a form which is relatively difficultly or only slowly absorbable, there is only a very low degree of utilization during the first year. By far the greater proportion of the applied phosphate goes into the soil's "phosphate pool" from which almost all of it is supplied continuously to the plant via equilibrium reactions which are not adequately understood.
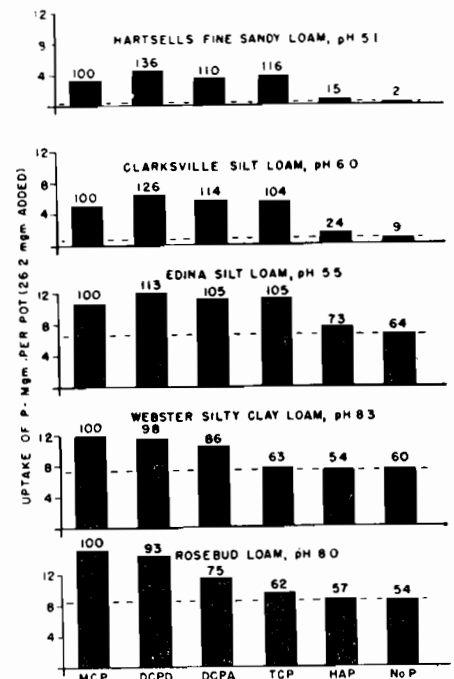
For example with cereals in

Figure 1. — Phosphorus uptake (actual and relative values by ryegrass from various calcium phosphates in 5 soils.

the first year one expects on an average only about 15% of the phosphate fertilizer to be utilized, with sugar beet about 25%, on grassland about 35% and in normal crop rotation in Central Europe about 20%. Even the total utilization over decades rarely exceeds 50% (8). Moschler, Krebs and Obeshain (9) found that 3/4 of the phosphate applied over a period of 40 years was still present in the soil as so-called "residual phosphate."

If for example a harvest of cereals removes 40-50 kg/ha of P_2O_5

Table 1. Influence of monocalcium phosphate (MCP) and dicalcium phosphate (DCP) on the grain yield of oats

(pot experiments with 18 soils and 40 different pH values)

Number of comparisons	Grain yield in gm of dry substance/pot		
	without phosphate	monocalcium phosphate (MCP)	dicalcium phosphate (DCP)
85	6.9	32.6	31.2

Table 2: Effect of water-soluble and ammonium citrate-soluble phosphates on various plants

(according to S. Gericke, 1966)

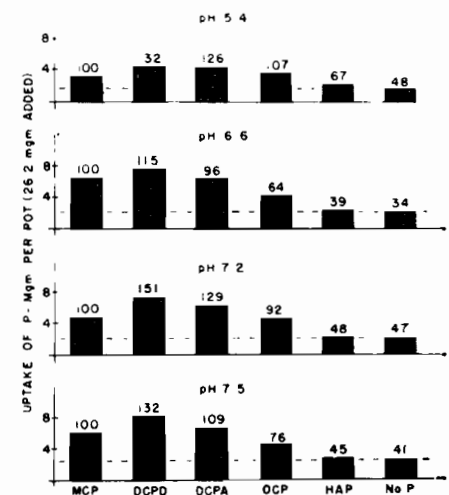|	Increased yields, 100 kg/ha		
	water-sol. phosphate	ammon.cit.- sol. phosphate	number of comparisons
Rye	3.8	3.4	1,444
Oats	3.5	4.0	1,182
Wheat	3.2	3.0	1,748
Barley	3.3	3.4	508
Cereals average	3.5	3.5	4,882
Potatoes	25.2	27.2	1,327
Sugar beets	31.7	30.9	301
Fodder beets	62.4	76.3	604
Meadow hay	12.0	12.5	1,508

Figure 2.—Phosphorus uptake (actual and relative values) by ryegrass from various calcium phosphates in Hartsells fine sandy loam limed to 4 pH levels.

109

from the soil, not more than $\frac{1}{4}$ to $\frac{1}{3}$ of this can be covered by the annual phosphate supply even with intensive fertilization. Consequently much greater attention must be paid to the residual effect when assessing a phosphate fertilizer than was hitherto the case.

3. Agronomic significance and effect of nitrophosphates

In Germany the term NPK fertilizer is nowadays very closely associated with the term nitrophosphate. Exactly 40 years ago BASF started production of its NPK fertilizer ® Nitrophoska, 14 years after the Haber-Bosch synthesis had been developed by our company for the recovery of ammonia. Since then the prototype of the modern NPK fertilizer has often been seen in Nitrophoska, which is perhaps confirmed by the fact that the term "Nitrophoska" has become part of modern Russian usage for NPK fertilizers. However in the early years the basis for Nitrophoska was not nitrophosphate; at that time it was thought that the phosphate component in this fertilizer ought to be completely water-soluble. It was not until later, after many experiments had been carried out, that it was realized that ammonium citrate-soluble phosphate in combination with a certain proportion of water-soluble phosphate generally has an equally good effect on plant yield. It was also found that the diammonium phosphate in the earlier Nitrophoska sometimes caused damage during germination especially in the case of cotton. The practical consequence was that Nitrophoska production was switched to a nitrophosphate base.

In view of the spontaneous increase in the application of nitrophosphates in Europe and the experience gained from this, it is surprising that there is sometimes a certain reticence toward this type of fertilizer in some other areas in which nitrophosphates are not yet so well known. Certainly the reasons for this are often other than agronomic. On the other hand it is in fact possible to arrive at different assessments of the action of nitrophosphates if the exact compositions of these products are not taken into consideration and no distinction is made between various types of nitrophosphates.

When extracted with a neutral (AOAC method) or alkaline solution the content of ammonium citrate-soluble phosphate in these fertilizers in Germany is practically the same. This seems worth mentioning especially as recent investigations by American authors have shown that commercial fertilizers in the U.S.A. often have a much lower content of phosphate which is soluble in alkaline citrate solution than phosphate which is soluble in neutral citrate solution. Thus Gilliam and Wright (10) come to the following conclusion: "For control purposes, a method more discriminating than the present AOAC procedure is needed to serve as a basis for quality control for fertilizer manufacturers and for protection of the consumer." The following view is held by Engelstad and Terman (11): "There is evidence that the alkaline ammonium citrate solution method provides a better guide to the agronomic effectiveness of phosphorus in ammoniated superphosphates than does the neutral ammonium citrate method."

As far as the nitrophosphates commercially available in Germany or supplied by BASF elsewhere are concerned, the ammonium citrate-soluble component in these fertilizers is readily available dicalcium phosphate and not difficultly soluble phosphate compounds which are soluble in neutral but not in alkaline ammonium citrate solution. From their previous experience German manufacturers of nitrophosphates will continue to maintain this high quality level of their products. That this principle has been accepted by farmers is best shown by consumption figures. Today in Germany about 30% of the phosphate applied as fertilizer is in the form of nitrophosphates whereas in 1950 it was only about 9%. This increase in the proportion of total phosphate sales should be seen in the light of the fact that sales of basic slag have also been very high (Fig. 3).

3.1 Effect of granulation and water-soluble fraction on the action of phosphate fertilizers

Now that it has been shown with the results given earlier that there are no fundamental differences in the action of the two com-
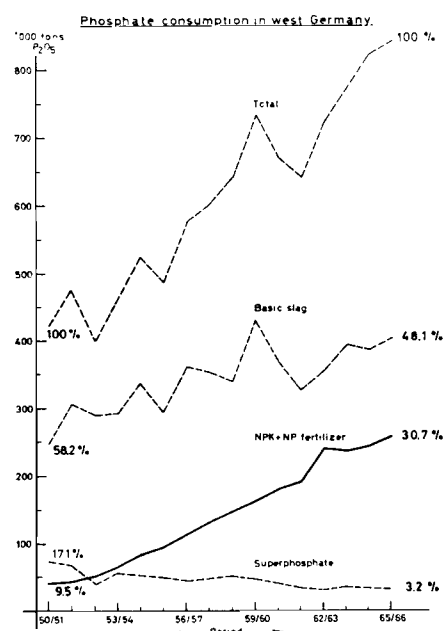

Fig. 3

ponents of nitrophosphates, i.e. the water-soluble phosphate and the phosphate soluble in alkaline citrate solution, the question automatically arises why nitrophosphates should need to contain water-soluble phosphate at all.

If the fertilizers were applied in powder form there would, in fact, be no agronomical justification for the water-soluble phosphate portion. However it is seen with granulated fertilizers which are becoming more and more popular because they are easier to apply and save labor that the ammonium citrate-soluble fraction has a slower initial action than the water-soluble fraction on soils which are low in phosphate and have a neutral to alkaline reaction. Here it must be particularly stressed that granulation of citrate-soluble phosphate has this effect only on these soils, otherwise one might come to a false conclusion.

Numerous experiments on soils low in phosphate have demonstrated, however, that about 30-40% of water-soluble phosphate is sufficient to compensate for this effect of the granulation (12). This can also be seen from the results, given in Table 3 below, of pot experiments carried out at our agricultural research station on 20 different soils with pH values ranging from 3.5 to 8.0.

The table also shows that granulation of the nitrophosphate has a positive effect on the availability

110

Table 3: Comparison of action of powdered and granular nitrophosphate fertilizers with 35% water-soluble phosphate fraction on different soils

Pot experiments with oats

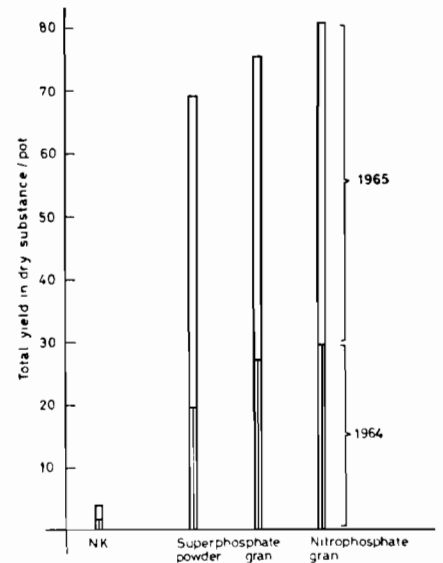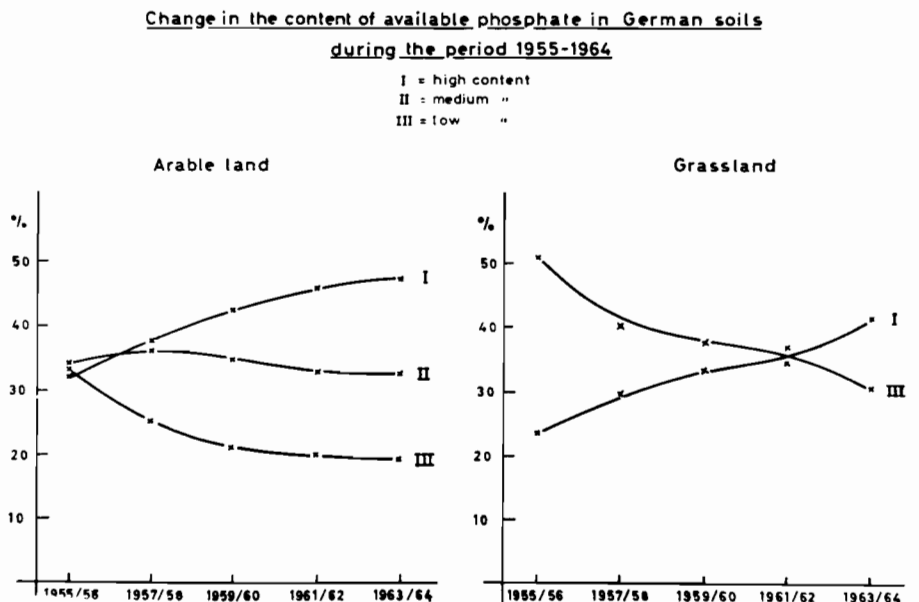| Soil | | | Grain yield in gm of dry substance/pot | | | |
| | | | | Nitrophosphate | | |
			(without P) NK	Powder	Granular (original)	difference in gm/pot
1.	Malaisia I	3.4	0.1	3.1	12.6	+ 9.5
2.	Malaisia II	3.5	0.1	1.0	8.2	+ 7.2
3.	Germ., Darmstadt	4.0	3.5	8.0	12.3	+ 4.3
4.	" Marzalben	4.2	0.3	8.5	22.1	+13.6
5.	" Kohlhof 56	4.2	39.9	42.5	44.4	+ 2.0
6.	" Steinbach	4.4	53.0	53.0	53.0	+ 0.3
7.	" Rollwaldhöfe	4.5	0.1	7.2	10.3	+ 3.1
8.	Costa rica	4.8	3.9	28.7	35.3	+ 6.6
9.	Germ., Baiersbronn	5.1	8.5	30.4	30.8	+ 0.4
10.	" Kohlhof 65	5.5	10.9	26.8	27.5	+ 0.7
11.	" Waldmauer	5.6	3.4	34.4	31.2	− 3.2
12.	" Löhlbach	6.3	0.9	37.6	42.0	+ 4.4
13.	" Kohlhof 64	6.7	11.7	33.3	31.2	− 2.1
14.	" Steinbach	7.0	1.4	18.0	19.2	+ 1.2
15.	" Merzalben	7.0	0.9	20.5	20.8	+ 0.3
	(with additional lime)					
16.	" Bruchfeld	7.3	31.2	34.8	36.6	+ 1.8
17.	" Limburgerhof	7.5	49.9	51.1	51.5	+ 0.4
18.	" Darmstadt	7.5	3.9	27.7	21.6	− 6.1
19.	" Gartelshausen	7.6	37.2	44.0	42.7	− 1.3
20.	" Gundersheim	8.0	39.9	42.5	42.4	− 0.1
Mean values		−	15.0	27.7	29.8	+ 2.1 = 7.6%

Fig. 4: Action of superphosphate and a nitrophosphate fertilizer (15-15-15) with a 35% water-soluble phosphate fraction on oats

Granite soil, Malaisia

pH = 3.5

of the phosphate at pH values lower than 6—an effect which is generally known from completely water-soluble phosphates. As a result of the high degree of fixation in acid soils, granulation of the water-soluble phosphate is an important requisite for its adequate effectiveness in such soils. Therefore with these soils the water-soluble portion of the phosphate should not be too high in nitrophosphates either, otherwise weaker action can be expected particularly in tropical soils as the following pot experiment with a typical soil from Malaisia shows (Fig. 4). The rate of phosphate supply can also be regulated by the particle size of the granulated fertilizers. This constitutes an important means of control—a particularly large particle size may be used for extremely acid soils and particularly small particles for alkaline soils.

3.2 Phosphate level in soil and action of nitrophosphates

With normal cultivation methods there are hardly any soils in which plants live "from hand to mouth" as far as the supply of

phopshate is concerned, i.e. where the requirement is met substantially or entirely by the applied fertilizer. This is theoretically only possible where soils extremely low in phosphate are fertilized with phosphate for the first time. In the second successive year of fertilization the residual phosphate is available to the plant as a result of the reactions taking place in the soil which were mentioned earlier and the slight extent to which the fertilizer phosphates were utilized in the first year.

An interesting example of this is the building up of the phosphate pool in German soils (Fig. 5) during the period 1955—1964 as illustrated by the results of tests by the official experimental station on several hundred thousand soil samples (13).

In the course of nine years the proportion of well supplied arable

Fig. 5: Change in the content of available phosphate in German soils during the period 1955-1964

Change in the content of available phosphate in German soils during the period 1955-1964

I = high content
II = medium "
III = low "

Arable land   Grassland

111

land increased from 32 to 48% whereas the proportion of poorly supplied land dropped from 33 to 19%. The corresponding figures for grassland are 24 and 42% and 52 and 31%.

It must be particularly borne in mind with these results that very little fertilization was carried out by farmers in Germany during and directly after the war and therefore the phosphate content of the soil at the beginning of the period under investigation was relatively low.

We are thus led to the conclusion that under agricultural conditions in Germany only on a small proportion of the soils in use can phosphate fertilization be expected to influence plant yields directly. The same applies to many soils in other parts of the world, whereas in areas with a low level of fertilization we can expect both the soil's phosphate pool to be further built up as the result of continued fertilization and the immediate effect of the phosphate fertilizer to become decreasingly important. Although the value of the acidulated fertilizer phosphate for the plant will not be diminished, the question whether a phosphate fertilizer which is completely soluble in alkaline ammonium citrate solution should contain a water-soluble portion of 30 or 50% will have to be regarded as academic and not of any appreciable significance for fertilization in practice. For the time being, however, a 30-40% water-soluble phosphate portion in an otherwise completely . ammonium citrate-soluble nitrophosphate should not be dispensed with as a safety factor, since experience has shown that with granular NPK fertilizers this guarantees optimum action in a wide range of variations in soil, climate and plant species.

This conclusion is substantiated by the results of 125 field tests (Table 4) in which the action of the NPK fertilizer Nitrophoska was compared with that of completely water-soluble straight phosphate fertilizers (12). The tests were carried out over the last ten years in various regions of West Germany, soils being used which were as low in phosphate as possible.

No difference between the actions of completely water-soluble phosphate and nitrophosphate with

Table 4: Action of Nitrophoska compared with that of straight fertilizers with water-soluble phosphate

(Straight fertilizer = 100)

Crop	No. of tests	Nitrophoska Low NPK rate	Nitrophoska High NPK rate
Cereals (grain yield)	39	100.3	99.4
Potatoes	76	100.2	100.4
Fodder beets	10	101.4	98.9

a 35% water-soluble phosphate fraction has been established.

1. Brabson, J. A. & Burch, W. G.: How available is available?, J. Ass. off. agric. Chem., 47 (3), 439-442 (1964)
2. — "Der neue Phosphat-Einzeldunger Novaphos," leaflet of German superphosphate industry, p. 3-4.
3. Nabijew, M. N. & Glagolewa, A.F.: Die Kinetik der Umwandling wasserlöslicher Phosphordünger in wasserunlösliche Verbidungen, Usbek. chem. J., No. 3, 9-14 (1959)
4. Bouldin, D. R. & Sample, E. C. Labor u. Gewächaus-Versuche mit Monocalcium, Monoammonium-u. Diammonium-Phosphaten. Ref. Z.f.Pflanzenern., Dgg., Bodenk., 90, 170 (1960)
5. Scharpenseel, H. W. & Concepcion, J. S.: Studien über die Pflanzenaufnehmbarkeit einiger Phosphordünger u. ihre Verteilung in verschiedenen Bodenschichttiefen an tropischen Bodentypen. Landw. Forschung, 10, 9-17 (1957)
6. Gericke, S.: Wert und Wirkung der Phosphatdüngung in der deutschen Landwirtschaft. Tellus-Verlag—Essen, p. 122-126 (1966)
7. Terman, Bouldin & Lehr: Calcium phosphate fertilizers: I. Availability to plants and solubility in soils varying in pH. Soil Science Soc. Proc., 22, 25-29 (1958)
8. Bader, B.: Phosphate sichern die Erträge und steigern die Qualität. Mitt. DLG 80, 622-664 (1965)
9. Moschler, Krebs & Obeshain: Aufnehmbarkeit des restierenden Phosphors aus langjähri-gen Anwendungen von Rohphosphat und Superphosphat zu Groseclose-Schlufflehm. Soil Soc. Proc., 21, 293-295 (1957) Ref. Chem. Centralbl. 1958, 5489.
10. Gilliam, J. W. & Wright: Quality of phosphorus in mixed fertilizer as revealed by solubility in water, neutral ammonium citrate and alkaline ammonium citrate solutions. Agr. Food Chem., 12, 205-207 (1964)
11. Engelstad, O. P. & Terman, C. L.: Water solubility of phosphorus fertilizer, Commercial Fertilizer, December issue, p. 32-35 (1966)
12. Buchner, A.: Zur Wirkung des Phosphats in Mehrnährstoffdüngern Lecture, Internat. Congress for Applied Chemistry, Brussels 1966
13. Riehm, H. & Wiechens, E.: Ergebnisse von Bodenuntersuchungen im Bundesgebiet 1955-1965 und ihre Auswirkungen auf die Düngeranwendung, "Die Phosphorsäure", 27, 36-46 (1967)

CHAIRMAN SAUCHELLI: Thank you, Dr. Jung. Dr. Jung's paper was, of course, primarily based on agronomic studies and the majority of our members are not agronomists. It is becoming more and more important, though, to evaluate these fertilizers agronomically because, after all, that is the purpose of the fertilizer.

The production man takes the attitude that: You tell us what fertilizer you want and we will do our best to produce that type of fertilizer.

As to the agronomic phase, of course, I don't know whether we can open it up for much discussion here because it is not a part of our main interest. This forum is primarily for operational personnel but it was started yesterday and we are going to have a study by one of our speakers on the program, Christopher Pratt, on the economics and the agronomics of this type of fertilizer.

But it is important to break down traditions in the farm business because there is where tradition is anciently established and one of the most difficult things to do is to change the general attitude

of farmers toward fertilizers. I go back about 50 years in experience and I can remember some of the attitudes that still persist towards fertilizers depending on whether it is synthetic and so on.

I think what we will do, Dr. Jung and Dr. Jockers, we will have a discussion on each paper and then we will have a general discussion at the end.

Are there any comments on Dr. Jung's paper?

Maybe there are some agronomists in the audience. Will you identify yourself?

MR. GROVER (Producers Chemical Corporation, Dallas and El Paso, Texas) : I would like to make clear first that I am not here to try to rebut anything; I am here to try to learn as a representative of an operating company, but I am puzzled.

Yesterday I listened to some comments that were in favor of the sulphur route to phosphate and I saw some natural gas prices of 40 cents per thousand cubic feet and I was happy that Mr. Strelzoff arose and rebutted this because that isn't really a representative price for the production of nitric acid or ammonia.

Most of the ammonia produced along the Gulf Coast comes from somewhere around 18 to 22 or 23 cents. Also, I noticed that the pH values that were given on all the charts that I saw varied from 3 to somewhere near 8 per cent. I am an agronomist, which I don't attempt to claim very often. I am an engineer, which I have to claim every day. And I watch this as an impossible range for agriculture in the United States.

If I understood correctly the material that was presented, there seemed to be a spread that is simply impossible for us in agriculture in these pH values. If I counted correctly, it is the third chart where the meaningful comparison was made between the superphosphate and nitrophosphate and I think the pH given at the top of the chart was 3.0.

Now, if my memory is correct and I saw this correct, this is tipping it as badly in favor of nitrophosphate as a 40 cent natural gas figure would have been in tipping it towards sulphur and I am won-

dering if 3 is an average value for the soil in Germany and if these are legitimate comparisons and, if they are, they are not very valid in the section of the United States that we are operating in.

I wonder if Dr. Jung could tell us why he has picked 3.0 as the pH value for his comparison charts?

DR. JUNG: The pH values of the soils in Germany are almost the same as in the United States, of course, and the table had to be smaller, and in the middle of the table there was the normal pH value. But I like to show the extremes too and I like to say, for instance, in connection with our production and our sales in the world, in the subtropical and in the tropical areas that most soils had a pH value between 3 and 4 and the pH value between 3 and 4 is realistic. Not for Germany at most and not for the States but for some other countries too.

MR. GROVER: But that chart you gave used only a pH of 3 and it was the one for nitrophosphate. It was the vertical type on the extreme righthand side of the chart. This is the one that drew the closest comparison in my mind between the two sources of phosphate fertilizers and I wonder if we could look at that again because I feel that a pH of 3, is just not meaningful in the United States in agriculture. I think we spend much money to avoid this sort of a situation.

DR. JUNG: Of course, you are right, but I would like to say principally we have that same condition in action in the range between 3 and 6 only with gradual differences. This is a tendency in the lower pH value range.

We have another type that has the high pH value and in this case there is no question, if the soil is poor in phosphate, in this case the action of full water, of 100 per cent water soluble phosphate is better and in the pH range below 6, 7 or 6, the action of water soluble or slightly soluble phosphate, at most or almost is slightly better.

MR. GROVER: Okay.

DR. RUSSELL COLEMAN (Sulphur Institute) : I would like to ask the question: What rate per acre of P_2O_5 was applied in the pots and

what rate is considered a low NPK rate in Germany and a high?

These are questions which I think are pertinent to the information which was presented.

DR. JUNG: In the pots the pH amounts applied were at most zero point twenty-five (.25) and .5 grams per ten pounds of soil and under field conditions the application rates are between 40 and 80 pounds per acre.

In the usual fertilization nowadays in Germany, of course, we have higher amounts of phosphate too but in most cases we get direct action in the first or in the second and third year because of the high level of phosphate in the soil.

CHAIRMAN SAUCHELLI: Dr. Burns, do you have any additional comments to make?

DR. G. R. BURNS: I am Bob Burns of The Sulphur Institute today and of USDA Monday.

The one thing I would like to say, and I remarked to Mr. Pratt too, as we were sitting there when he showed the data of the soil with the pH and I thought it was 3.5 and I told John I was surprised that the nitrophosphate of low water solubility wasn't even better than it showed there. I would expect a soil at pH 3.5, when nitric phosphate is applied, to be far superior to your water soluble forms because it serves, in addition to supplying phosphorus, it serves to lime the soil and it neutralizes the soil.

But generally this condition is not one which, at least I would follow, if I were a farmer and I had a soil of pH 3.5, which is likely to be toxic in aluminum and it may have high manganese in it. My suggestion to the farmer would be to lime the soil at least up to 6.5 and managing, at least in this country, the trend toward liming to higher pHs is much greater and I expect in the future for soils to be limed at near a pH of 7. In Iowa right now and in other states they are recommending a pH of 6.9 for corn.

So, if you lime a soil, then I would expect the situation to reverse itself. I would expect the water soluble phosphate to be better than the non-water-soluble, if you lime your soil up to, say, pH of 6.9.

If you leave it at 3.5 and you wouldn't let me lime, then I would take the nitric phosphate every time over the water soluble form. But that is really not a realistic situation, if you want to make money farming, and my interest is to help the farmer make money as well as the fertilizer industry.

The one other point I would like to make with respect to this is that there is a general attitude among agronomists as well as a lot of other people where they seem to think that as the soil becomes better supplied with phosphate then water solubility becomes less important.

I don't think this is really the proper way to logically reason this out. My answer to this is simply: That when you increase the supply of phosphorus in the soil, the importance of water solubility does not decrease but the need for adding phosphate fertilizer to the soil decreases. The citrate soluble decreases in importance, the water solubility decreases in importance, if you want to include them both together, but the important thing is that if you have a soil well supplied with phosphorus, you just don't need as much phosphate fertilizer.

It is not a fact that water solubility becomes less important, it is that phosphate fertilization becomes less important.

CHAIRMAN SAUCHELLI: Dr. Jung, have you been able to follow?

DR. JUNG: Yes.

I would like to mention only that the average values for the pH value in Germany on light soils is from 5.5 to 6 and on heavy soils in the range of 6 to 7, as a result of 100-year fertilization with chalk.

I don't think that you will get in the States in a few years at all pH values which range higher than pH 7.

We have a few agronomists here in the audience. It is not a question to be resolved here by us but I think discussion is valuable. It is inevitable that the agronomic phase comes forward in deciding whether to use nitrophosphate type or monocalcium phosphate.

Mr. Weber.

MR. WILLIAM WEBER: Thank you, Vince.

CHAIRMAN SAUCHELLI: Mr. Weber has had a lot of experience as an engineer and is familiar with agronomics.

MR. WEBER: I am not an agronomist so I am not going to speak on the agronomic angle of this thing.

I think Dr. Jung's paper was a very excellent one primarily because I think he brings into proper perspective this question of water solubility about which there has been a great deal of nonsense, in my opinion.

My company has worked with nitrophosphate processes and is working with them and we are developing a process which would produce a very high water solubility.

But when people talk for the United States generally on an average of something like 80 to 85 per cent water soluble, I think this is really nonsense and completely unnecessary. It is an important consideration because if we, because of the sulphur shortage and the trend toward high nitrogen fertilizers, are going to adopt nitrophosphate processes in this country, which I predict, you are putting the nitrophosphate processes under a considerable handicap when you insist on an astronomical and unnecessary water solubility because they are at their best economically with relatively low solubility. They can produce 30, 40, 50 per cent water solubility very easily, which, I think, is the range in which we should be thinking.

But when you put 80 per cent water solubility, then it becomes very doubtful whether you should use nitrophosphates and, therefore, I think the conclusion on this water soluble question is a very important economic one.

CHAIRMAN SAUCHELLI: Economics finally catches up with everybody.

We will continue this discussion later, if we have enough time, but I think we will proceed now with the next speaker, Dr. Gero Lüth.

40 Years NITROPHOSKA

Dr. Gero Lueth

FIRST of all I should like to thank the Executive Committee and the members of the Round Table for the invitation to speak about the experience which BASF have in the development and the manufacture of complex fertilizers.

Ludwigshafen-Oppau is the traditional birthplace of synthetic fertilizers. Ludwigshafen saw the first commercial-scale production of ammonia by the Haber-Bosch process, nitric acid by combustion of ammonia, urea and—what intersts us today in particular—complex fertilizers containing all nutrients in each granule.

In giving you an outline of the history of the production of complex fertilizers over the past 40 years, I shall endeavour to show you the processes we used in Germany to provide our farmers with the most efficient and at the same time the least expensive fertilizers.

In these 40 years four different processes for the production of these fertilizers have been used in Ludwigshafen. In this connection I should like to mention that the name "NITROPHOSKA" used since 1927 for these compound fertilizers is a BASF trade-mark which has been registered in almost all countries of the world. A feature which has characterized these fertilizers from the very beginning is that they contain all nutrients in practically the same ratio in each individual granule. The danger of separation and segregation during storage, transport and application is therefore eliminated.

One point which I feel is important for a full understanding of the situation is the number of different grades marketed in Germany. Thanks to an agricultural research and service program carried out at a very early date, we in Germany are able to get along with an extremely small number of grades. The economic advantages of the small number of

standard grades for production and storage costs have always been passed on to the farmers. For this reason special formulations offered by small regional producers of fertilizers have never been able to establish themselves. Four formulations: 13:13:21:, 15:15:15, 12:12:-20 and 12:12:17 + 2% MgO, the last two of which are based on potassium sulfate, account today for about 85% of the consumption of complex fertilizers in Germany. About 40% of these NPK fertilizers is produced by BASF.

Let us now look back 40 years:

In 1927 we took the first step with phosphoric acid-based NPK fertilizers. Potash was granulated with a slurry of diammonium phosphate and ammonium nitrate. This was carried out in pugmills. The diammonium phosphate was produced from phosphoric acid obtained from both the electric and the wet process acid.

In 1933 we took the second step using the mixed acid (phospho-nitro) process. On the basis of experience gained in the preceding 6 years we decided to produce a grade with only $\frac{1}{5}$ water-soluble P_2O_5 and $\frac{4}{5}$ citrate-soluble P_2O_5 in addition to the grades with completely water-soluble P_2O_5. Germination damage by diammonium phosphate and a comparison of the efficiency of diammonium phosphate and dicalcium phosphate, as well as economic considerations, spoke so strongly in favour of these new fertilizers that two years later—1935—the production of NITROPHOSKA containing completely water-soluble P_2O_5 was discontinued for the home market.

This new type of fertilizer was produced by the mixed acid process: phosphate rock was attacked by a mixture of phosphoric acid and nitric acid. The solution obtained was neutralised with ammonia, and the resulting slurry was granulated with potash. Numerous other processes which were also available did not succeed in establishing themselves.

You will be interested to hear that the gypsum obtained as by-product in phosphoric acid production was already converted as early as 1932 with ammonia and carbon dioxide to ammonium sulfate and

calcium carbonate. The development of this process was laborious because the by-product gypsum is far more difficult to convert than natural gypsum. The lime obtained in the process was sold in the moist state to farmers at a low, but nevertheless profitable, price. This lime was preferred to natural lime because it was more efficient due to its fineness, and also because of its content of nitrogen and P_2O_5, although this content was low.

In 1947 we took the third step using a sulfo-nitro process. Owing to the destruction of the phosphoric plant during the war we had to produce fertilizers without using phosphoric acid. For this reason we used the sulfo-nitro process to produce a fertilizer with the formula 11.5:8.5:18. In the process sulfuric acid was added to a solution of phosphate rock in nitric acid. The suspension of gypsum in phosphoric acid and nitric acid was neutralized with ammonia to give dicalcium phosphate, mono- and diammonium phosphate, ammonium sulfate and ammonium nitrate. The magma was then granulated with potash, forming fertilizers with 35% water-soluble P_2O_5.

In 1949 we took the fourth step, viz. the Odda process. This was a decision which involved at

that time a strong element of risk: the BASF began to design the first commercial-scale plant to operate the Odda process which was patented in Germany in 1930 by the Odda-Smelteverk. The plant went on stream in 1952 using calcined Moroccan phosphate rock. A calcining plant was erected in Morocco specially for the BASF. The strong demand for efficient fertilizers to enable the farmers to increase their per-acre yield, and the excellent quality of the fertilizers produced by our process, which are ideal for rotary spreader application in view of their special, coarse granulation, resulted in a steady expansion of the Odda plant. The production grew from

60 tons P_2O_5 per day in 1952
to 180 tons P_2O_5 per day in 1956
to 240 tons P_2O_5 per day in 1961
and
to 400 tons P_2O_5 per day in 1965

Today we produce in Ludwigshafen about 1.1 million metric tons of fertilizers per year by this process.

In 1960 we completed the fourth step by developing a process for the conversion of the by-product calcium nitrate to calcium carbonate and ammonium nitrate. In this manner we were able to eliminate the disadvantage of the Odda process, which gives a by-product with a low nutrient

Slide 1

NITROPHOSKA process flow sheet   Lüth

115
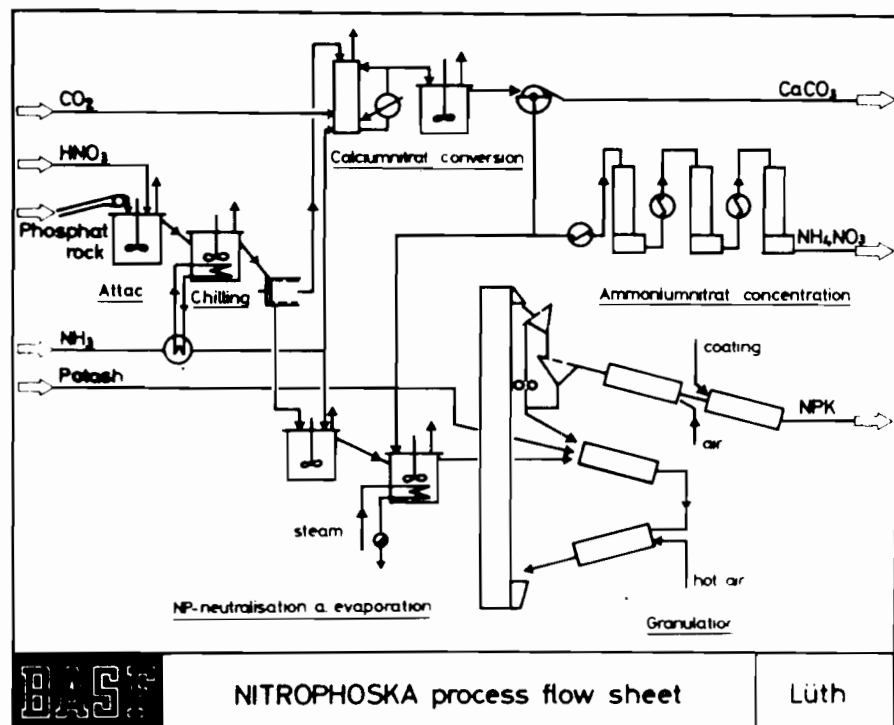
content consisting exclusively of the expensive nitrate nitrogen.

A plant for this conversion went on stream in 1960. The two materials ammonium nitrate and calcium carbonate were used as raw materials for the production of calcium ammonium nitrate (nitro-chalk). In Germany we have severe restrictions governing the storage of ammonium nitrate ever since the explosion in our factory in 1921. For this reason a calcium ammonium nitrate with 23% nitrogen is the only form in which ammonium nitrate can be marketed in Germany today.

Now, having outlined the history, I should like to discuss some details of our present process.

Slide 1 shows you a simplified flow sheet of our NITROPHOSKA production system today. We started, as mentioned above, with calcined Moroccan phosphate, then learned to use Kola, Taiba and Togo phosphates, and finally we developed methods of using exclusively Florida concentrate with 72 BPL. We have been doing this for the last two years. The coarsely ground phosphate rock is dissolved with 55-60% nitric acid. A special method of operating and a special design of the vessels help to control foam formation. Chilling is at present carried out batch-wise by means of brine. The heat of evaporation of the ammonia required for neutralization and conversion of the calcium nitrate in the process provides the necessary refrigeration. When liquid ammonia is used, the process requires no additional cooling.

The separation of the calcium nitrate is carried out at present, as mentioned above, in multi-stage pusher-type centrifuges. By using a special procedure we are able to prevent the screens of the centrifuges from being blinded by sand. The separated calcium nitrate is at present melted, and converted with ammonia and carbon dioxide, cooled ammonium nitrate being recycled during the process. We are able to vary within certain limits the size of the lime crystals obtained. The coarsest grade at present contains about 70% of crystals measuring 80-100 microns.

The ammonium nitrate can be concentrated to 99% by treatment

in multi-stage evaporators of a special design. We have had no trouble with crusting.

The mother liquor from the calcium nitrate separation is mixed with the necessary amount of ammonium nitrate and neutralized with ammonia or with off-gases from the urea plant in several stages. In this manner we are able to produce magma whose viscosity is so low that it can be evaporated at temperatures below 130°C to a water content of less than 8%. This magma, whose $N:P_2O_5$ ratio is adjusted precisely, is now granulated without or with varying amounts of potash to fertilizers of the type 20:20:0, or 13:13:21 or 15:15:15, respectively.

We have many years of experience on a commericial scale with both prilling and granulation by recycling. For economic and also for safety reasons we decided to adopt the hot recycle process. Prilling is, in our opinion, uneco-

nomical except possibly with magma containing less than 1% water. For safety reasons we decided to reject the use of hot melts of ammonium nitrate and potassium chloride and other components at 160-180°C. The quality of prilled products depends far more on the characteristics of the raw materials used than the quality of products obtained by a recycle process.

We are often asked what our recycle ratio is. It is between 1:3 and 1:5, or in American terms 3:1 and 5:1. I must emphasize that recycling is not a disadvantage at all; it is actually useful. Once you realize this, all you have to do is to provide the plant with bigger elevators and screens. The relatively small extra costs involved are more than offset by the advantages of a hot recycle process.

Slide 2 shows two graphs. In the lower graph the softening temperature of the granules is plotted against the water content. The

Slide 2

Theoretical calculation of the magma : recycle ratio — Lüth

116
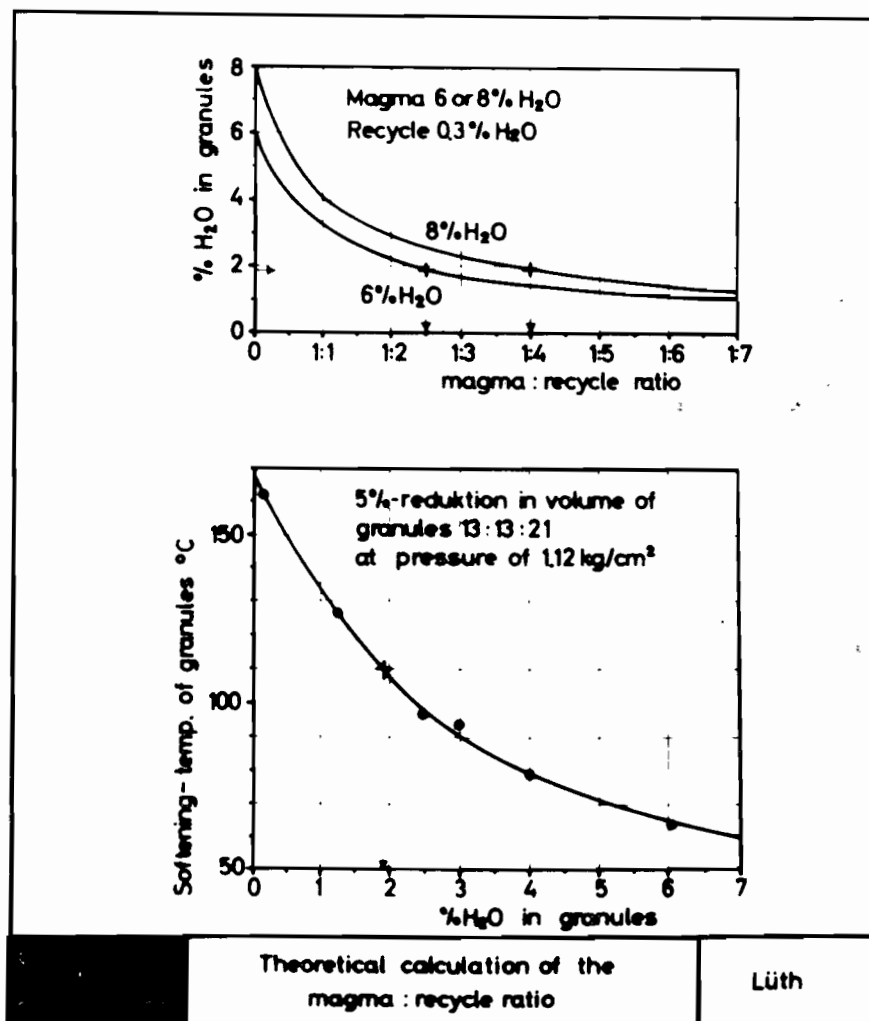
softening temperature is defined in this case as the temperature at which the volume of a column of granules decreases at a pressure of 1.12 kg/cm² by 5%. This is an arbitrary measure, but it corresponds roughly to the pressures occurring in the granulating drum. As you can see, a water content of 1.9% is suitable for granulating at 110°C. for instance. This water content can be adjusted by mixing dry, hot recycle with about 0.3% water and NPK magma with approximately 6% or 8% water. In the upper graph, the resulting water content has been plotted against the recycle ratio. As you can see, a ratio of 1:2.5 is necessary to obtain a water content of 1.9% when using magma with 6% water. A ratio of 1:4 is necessary when using magma with 8% H_2O. We generally use somewhat higher ratios than these. The advantage of this is that the magma applied to the surface of the recycle wets mainly the surface of the granules obtained. A water content as low as 0.1 to 0.4% can then be achieved with one dryer. With our hot recycle process without a second drying, we obtain material with excellent characteristics. When the fertilizer is stored at temperatures below 40-50°C, it can be piled to a height of 20 m and more. We store these fertilizers in bulk, but a large proportion is shipped in bags. We have a bagging and shipping capacity of 1200 metric tons per day.

Allow me to repeat the main features of our present process:

1. Use of a relatively low-grade Florida phosphate rock
2. No waste by-product when the by-product is calcium ammonium nitrate; and a low-grade, but in some regions usable, by-product lime when the main by-product is ammonium nitrate.
3. Low investment in the solid-state part of the plant because of the high capacity of the dryer due to the use of a magma with very low water content (1,200 metric tons per day in a drum with 4 m diameter)
4. Good storage characteristics of the product due to the low water content of the product

5. Flexibility to produce formulas with $N:P_2O_5$ ratios between 0.8 and 2.

CHAIRMAN SAUCHELLI: Thank you very much, Dr. Lüth.

We are really proud to know that for the first time in 40 years this process has been disclosed to the public and we are proud that he chose the Round Table to explain the Nitrophoska process to a group of engineers. Thank you very much, Dr. Lüth.

Any questions? We have time for a couple of questions. We are going to have a general discussion later after Mr. Christopher Pratt's paper.

DR. STRELZOFF: May I ask one question?

CHAIRMAN SAUCHELLI: One question, yes, sir.

DR. STRELZOFF: With this process and the way you conduct it, can you make a product higher than 15-15-15, let's say 17-17-17 by lowering it maybe to the temperature crystallization of calcium nitrate to get so much more calcium nitrate before you proceed to neutralization and the other steps?

DR. LUETH: We have no need for this formulation in Germany but we are able to produce formulas with higher water solubility. We have made this to 75 to 80 per cent water solubility and the resulting formulas are close to 17-17-17.

A MEMBER: You mentioned that you store this material in bulk. Do you store this in an ordinary warehouse or do you have to use airconditioned warehouses as some of the people do here?

DR. LUETH: We use normal warehouses but we have capacity of warehouse in Germany of 50,000

to 70,000 tons. These warehouses are not airconditioned.

CHAIRMAN SAUCHELLI: Many of us sort of envy these multi-lingual or polyglot members who are fluent in different languages. How many Americans could go to Germany and give a talk in German as intelligibly and as effectively as these gentlemen here did this morning?

I think the time will come, though,—There is a great interest in languages in our country—and the time will come when that will be accomplished.

MR. WILLIAM WEBER: Using low-grade Florida rock, what happens to the silica? Does it stay with the calcium nitrate or do you have a separate separation step?

DR. LUETH: We were waiting for this question. But, excuse me, when I say this is something of knowhow we are not able to offer. I am sorry.

CHAIRMAN SAUCHELLI: These engineers have a way of sort of needling their confreres and I think agronomists do the same thing.

We will proceed and then I hope we will have time for a continuation of our discussion.

The next speaker is a man who is well known to a great many here. He has been a friend of the Round Table for many years. He has helped us with suggestions and ideas for keeping the Round Table effective and interesting. He has had wide experience in both Europe and in this country and he usually prepares splendid papers and it is a great pleasure to me to call on the next speaker, Christopher J. Pratt.

Comparative Agronomics and Economics of Nitrophosphates

Christopher J. Pratt

Introduction

Many millions of tons of nitrophosphates are used annually in Europe, and the lush farms plus a virile population leave no doubt as to their efficacy. Yet, in North America, use of these fertilizers has been limited and even interest has

been small. However, the growing shortage and rising prices of sulfur have now brought them into focus in the U.S.A. as likely alternatives to superphosphates and ammonium phosphates made via sulfuric acid.[1, 2]

But, we should not confine an

examination of nitrophosphates to a mere possible substitution for more-familiar fertilizers. We should also look for potential advantages, such as specific agronomic and economic benefits, or greater simplicity and convenience. In addition, we should recognize the numerous nitrophosphate products and processes now available, as well as the important technical advances made during recent years.[3] In fact, some of this sophisticated technology, especially regarding product finishing, could probably be used advantageously to make other types of fertilizer.

Accordingly, a brief review and comparison of the principal processes and products now commercially available will be given as a guide to the most suitable technology applicable to a given set of circumstances.
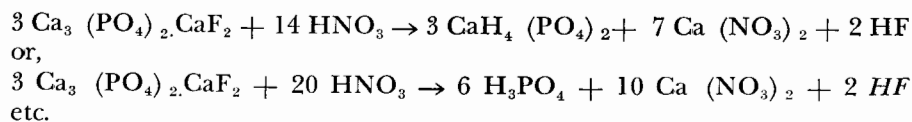
Process and Product Considerations

First, let us briefly look at some principal agronomic factors, beginning with the chemical and physical nature of nitrophosphates themselves.
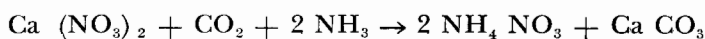
General

As is evident from numerous earlier and recent publications, a mysterious new group of fertilizers known as nitrophosphates in reality doesn't exist. These have been shown to be combinations of familiar materials such as ammonium nitrate, ammonium phosphate, dicalcium phosphate and calcium nitrate made "in situ" from phosphate rock, nitric acid and ammonia. In a characteristic human way, many people have taken sides for or against nitrophosphates with almost religious fervor, and some go to great lengths to support their views. However, we can be reasonably certain that a plant is indifferent to the name given to its source of fertilizer as long as there are sufficent nutrients to match the profiles of its needs! Therefore, when comparing various nitrophosphate processes and products with others, we must consider the entire fertilizer-soil-plant system in each case, and not just the apparent merits of a particular fertilizer, old or new.

Process Chemistry of Nitrophosphates

The reaction between phosphate rock and nitric acid (as an alternative to sulfuric acid) can proceed in several ways,[4] according to the ratio of reactants use, e.g.

$$3 Ca_3 (PO_4)_2.CaF_2 + 14 HNO_3 \rightarrow 3 CaH_4 (PO_4)_2 + 7 Ca (NO_3)_2 + 2 HF$$

or,

$$3 Ca_3 (PO_4)_2.CaF_2 + 20 HNO_3 \rightarrow 6 H_3PO_4 + 10 Ca (NO_3)_2 + 2 HF$$

etc.

Because calcium nitrate in a mixed fertilizer product results in eutectics of very low relative humidity, it must be removed in some 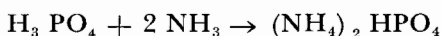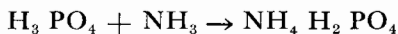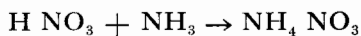manner prior to finishing. One method is to convert the calcium nitrate to dicalcium phosphate via the addition of ammonia and a mineral acid (or sulfate salt) on the following lines:[13]

$$7 Ca (NO_3)_2 + 6 H_3PO_4 + 2 HF + 14 NH_3 \rightarrow$$
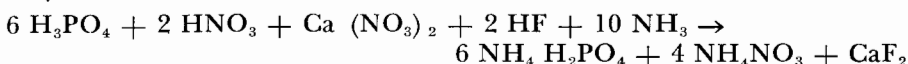$$6 Ca HPO_4 + 14 NH_4 NO_3 + CaF_2$$
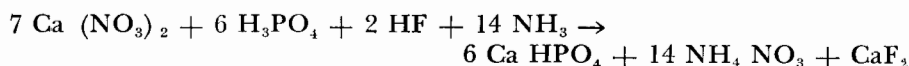
Carbon dioxide can also be used, but almost the entire phosphate content of the slurry is converted to dicalcium phosphate.

In a second method, the calcium nitrate can be largely removed by cooling, crystallization, washing with nitric acid and mechanical separation [14, 15]. Subsequent ammoniation yields a liquor which can be converted to a solid, stable fertilizer which is essentially all ammonium phosphate and ammonium nitrate according to the following reactions and the stoichiometric balance chosen:

$$H NO_3 + NH_3 \rightarrow NH_4 NO_3$$
$$H_3 PO_4 + NH_3 \rightarrow NH_4 H_2 PO_4$$
$$H_3 PO_4 + 2 NH_3 \rightarrow (NH_4)_2 HPO_4$$
$$Ca (NO_3)_2 + 2 HF + 2 NH_3 \rightarrow 2 NH_4 NO_3 + CaF_2$$
$$Ca (NO_3)_2 + H_3 PO_4 + 2 NH_3 \rightarrow 2 NH_4NO_3 + Ca HPO_4$$

For example, an overall reaction might be:

$$6 H_3PO_4 + 2 HNO_3 + Ca (NO_3)_2 + 2 HF + 10 NH_3 \rightarrow$$
$$6 NH_4 H_2PO_4 + 4 NH_4NO_3 + CaF_2$$

In a variation of the second method, most of the calcium nitrate remaining in solution after crystallization is precipitated as calcium sulfate and removed by filtration, following the addition of a sulfate salt[16]; e.g.

$$Ca (NO_3)_2 + (NH_4)_2SO_4 \rightarrow Ca SO_4 + 2 NH_4 NO_3$$
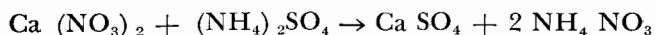
(In one sulfate recycle method, no crystallization is used.)

Calcium nitrate produced as a by-product from the second method is converted physically to a solid crystalline or prilled product in some plants, and sold as a nitrogen fertilizer containing about 15% N. In other cases, it is converted to ammonium nitrate and calcium carbonate by reacting with ammonia and carbon dioxide:

$$Ca (NO_3)_2 + CO_2 + 2 NH_3 \rightarrow 2 NH_4 NO_3 + Ca CO_3$$

The precipitated calcium carbonate is separated by filtration and sold or discarded, according to circumstances. The ammonium nitrate is concentrated and can be incorporated with the nitrophosphate liquor prior to finishing. Alternatively, it can be sold separately as a liquid or prilled nitrogen fertilizer containing about 33% N.

In a proposed further method, the calcium sulfate formed by removing calcium nitrate via ammonium sulfate is converted back to ammonium sulfate by reacting with ammonia and carbon dioxide, to result in a closed cycle operation, apart from a little sulfate make-up.[16]

Principal Nitrophosphate Fertilizer Components

Table I shows the major commercial nitrophosphate processes in use and the principal components in their products. (The ammoni-

TYPE	PRINCIPAL COMPONENTS IN PRODUCT (Ranked, and prior to addition of any potassium salt)	TYPICAL PRODUCTS $N-P_2O_5-K_2O$
Non-Separatiaon Calcium Nitrate Removal Via:		
1. CO_2	Ammonium Nitrate	16-14- 0
	Dicalcium Phospate	13-11-12
	Calcium Carbonate	
2. H_2SO_4 and/or H_3PO_4, XSO_4 salt	Ammonium Nitrate	20-20- 0
	Dicalcium Phosphate	
	Ammonium Phosphate	16-16-16
	Ammonium Sulfate	
	Calcium Sulfate	
3. Crystallization (normal)	Ammonium Nitrate	20-20- 0
	Ammonium Phosphate	15-15-15
	Dicalcium Phosphate	
4. Crystallization (intensive)	Ammonium Nitrate	23-23- 0
	Ammonium Phosphate	17-17-17
5. a. Crystallization plus gypsum removal or b. Sulfate recycle only	Ammonium Nitrate	25-15- 0
	Ammonium Phosphate	20-20- 0
	(zero Dicalcium Phosphate when required)	
6. Co-Products from 3, 4, 5	Calcium Nitrate	0-15- 0
	and/or Ammonium Nitrate	0-33- 0
	plus Calcium Carbonate	0- 0- 0
from 5	Calcium Sulfate plus (perhaps) Calcium Carbonate	0- 0- 0

um phosphate is the mono compound in most cases.)

Future possibilities include (1) the extraction of phosphoric acid for other purposes from the nitric phosphate liquor, via solvent extraction, ion exchange or other means, and (2) the conversion of calcium nitrate to nitric acid for recycling to the process, which is understood to have been undertaken on a pilot-plant scale.

It should be mentioned that, with the exception of Method 2, no sulfuric acid is required in the above processes.

As can be seen, all of the above components are familiar fertilizer materials. However, as already stated, the complete fertilizer—soil—plant system should always be considered in each specific application.[5,6] Hence, corresponding factors such as fertilizer water solubility, particle size, soil pH and other characteristics, as well as plant nutrient needs and profiles, need to be studied, so that the maximum benefits can be obtained for the minimum applied fertilizer cost.

Agronomic Factors

General

To ensure optimum growth, the nutrient needs of a plant must be met in terms of time as well as quantity. If the requirement profile for a particular element demands a high initial rate, failure to meet this immediate need is likely to result in permanent retardation, even if ample amounts are furnished later. On the other hand, excessive nutrient availability may result in "luxury uptake," where the amount used by a plant is greater than the corresponding results. An excess of fertilizer can also induce damaging or lethal changes, due to high osmotic pressures, large pH changes or poisoning of the plant.

For example, it is well known that some tubers such as potatoes have a heavy phosphorus uptake in the early growth stages, whereas many young tree seedlings and transplants may suffer severe "burning" or be killed by an overabundance of ammonium and phosphate ions in the soil. In the former case, readily-available phosphate fertilizers are usually needed for best results, while in the latter, slow-release compounds are advisable.

Nutrient Soil Patterns

An adequate review of soil chemistry is not possible here, because of space limitations; nevertheless, a brief account of nutrient movement patterns in typical soils is helpful in a comparative assessment of nitrophosphate fertilizers. Basically, the problem is one of ensuring an adequate supply of nutrients to the plant roots in accordance with the requirement pattern or profile. Although root systems are remarkably skilled at finding food and water, there are limits to this ability, especially when young and tiny. Hence, much can be done to ensure healthy crop growth by the proper choice of fertilizer, soil conditions and fertilizer placement from the outset.

A soil should not be regarded as a mere system of small pipelines whereby fertilizers are conveyed, unchanged, to the roots of a plant. Instead, a series of complex chemical and physico-chemical changes usually occur, which often tie up much of the applied nutrients to a greater or less degree, and release them in a different form to searching plant roots. An exception is ammonium nitrate, which is able to penetrate the soil and reach the roots unchanged. In fact, unless precautions are taken, this can happen so rapidly in some light soils, that losses due to leaching may occur. On the other hand, some nitrogen compounds such as urea (and to some extent, ammonium sulfate) undergo transformation into complex ions, especially in clay soils, and the ammonium ion is subsequently re-

leased at a moderate rate, usually in keeping with plant needs. Potash salts often perform in a similar way.

The behavior of phosphate fertilizers in soils is also complex and is affected by:

Fertilizer properties, such as phosphate water and citrate solubilities, chemical composition and attendant ions, physical properties and particle size range.

Soil properties, e.g. moisture, chemical characteristics and pH, physical characteristics.

Ambient conditions, such as intensity of application (lbs./acre), pattern and method of application, type and nature of crop sown, climatic conditions.

Phosphate Water Solubility and Related Performance

Much work has been undertaken on pot and field tests with phosphate fertilizers, and still continues. A useful summary was made a few years ago by Tisdale and Rucker[7] who concluded that even highly water-soluble phosphates such as monocalcium phosphate undergo a fairly rapid transformation into less-soluble compounds. When in contact with moist soil, MCP first changes into a strongly acid solution, plus some dicalcium phosphate dihydrate. The solution diffuses into the soil and reacts with iron, aluminum and other salts, with the eventual precipitation of highly-insoluble compounds. Phosphates in this solution are more-readily available to plant roots than from the less-soluble dicalcium phosphate, or the metal phosphates resulting from soil reactions.

Addition of a water-insoluble (but citrate-soluble) fertilizer, such as dicalcium phosphate, to a land does not rapidly yield a phosphate soil solution, and the plant root must rely on finding more-slowly soluble particles of dicalcium phosphate. The high pH of a calcareous soil will usually retard phosphate solubility further. Accordingly, fertilizers containing appreciable quantities of dicalcium phosphate give best results when applied to acid or neutral soils, and

the chances of phosphate ions being found by plant roots are increased by:

1. even dispersal of fertilizer in the soil
2. small fertilizer particle sizes
3. extensive and bushy plant-root systems.

Phosphates which are both water- and citrate-soluble are ineffective, except in soils which are sufficiently acid to achieve slow solubility.

Agronomic Comparisons

Based on the foregoing desiderata, it is possible to make an agronomic comparison of various types of phosphates in terms of water solubilities. Provided citrate solubilities approach 100%, it can be said that:

1. Low water-solubility (say 0 to 33%) suffices for pastures, trees and other long-season crops, especially when soils are acid or neutral and high in residual phosphate. The fertilizer should be of small particle size and preferably broadcast.

2. Medium water - solubility (e.g. above 33% to 67%) is suitable for crops having bushy root systems and a phosphorus uptake which corresponds to the rate of P_2O_5 release. The fertilizer should be of small granule size and evenly dispersed in the soil. The use of phosphates in this category can often be extended over a wide range by applying in conjunction with highly water-soluble "starter" fertilizers and/or maintaining high residual soil P_2O_5.

3. High water solubility (above 67%, and especially over 80%) is satisfactory for all crops and soils, except where "burning" may be a problem. The fertilizer can be of relatively large granule size (especially on acid or neutral soils), and is preferably applied in banded or localized patterns.

Notwithstanding a preference in some countries for highly water-soluble fertilizers, dicalcium phosphate (supplied as nitrophosphates) has many supporters in Europe. They contend that it is
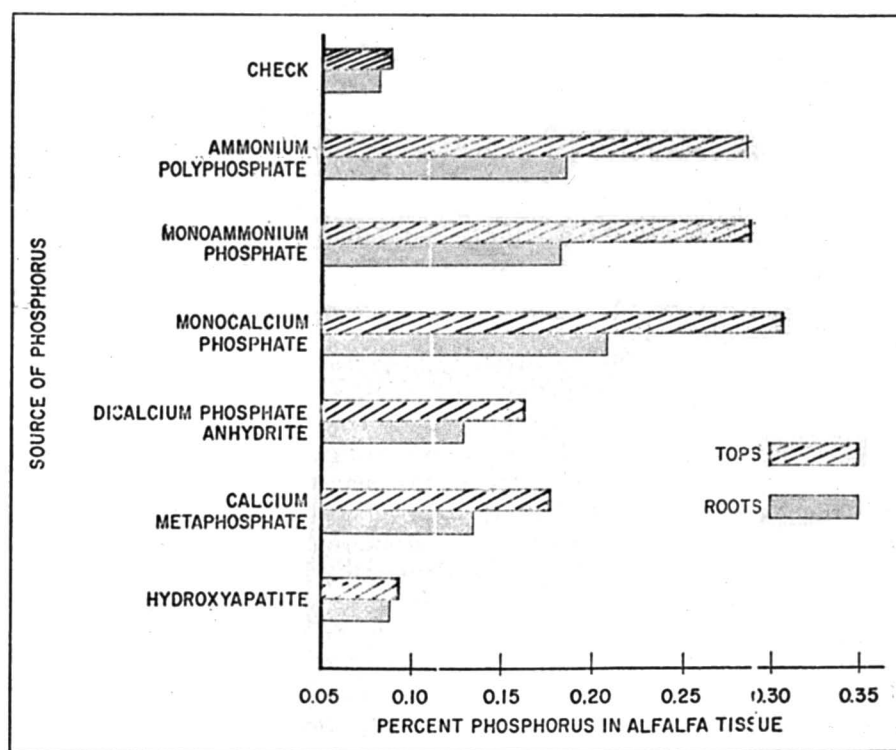

Figure 1
Effect of type of phosphatic fertilizer on phosphorus content of tops and roots of alfalfa. Ammonium polyphosphate, monoammonium phosphate and monocalcium phosphate all are water-soluble. (Beaton et al.)

Courtesy—Sulphur Institute

120

a better policy to maintain a high soil residual P_2O_5 content via dicalcium phosphate than to apply periodic doses of water-soluble P_2O_5, of which two-thirds or even more may be wasted by being rapidly converted to highly insoluble soil metal phosphates. Furthermore, the water-solubility of dicalcium phosphate far exceeds the optimum P_2O_5 content of a soil solution (1.2 mg. per liter or 0.00012%), as the following Table shows:

Table 2. Water Solubilities of Various Phosphate Compounds

COMPOUND	WATER SOLUBILITY
Phosphate Rock	Insoluble
Soil-Metal Phosphates	Insoluble
Tri-Calcium Phosphate	0.002%
Di-Calcium Phosphate	0.02%
Mono-Calcium Phosphate	1.8%
Di-Ammonium Phosphate	13.1%
Ortho Phosphoric Acid (pure)	All proportions

At the risk of over-generalization, one P_2O_5 uptake pattern (for N. Amer. alfalfa) from different phosphate compounds[8] is shown in Figure 1. With the same reservations, a crop-yield pattern corresponding to different application rates and phosphate water solubilities[9] is indicated in Figure 3,4,2, A vast amount of analogous data for European crops and conditions is also available.[7, 10]
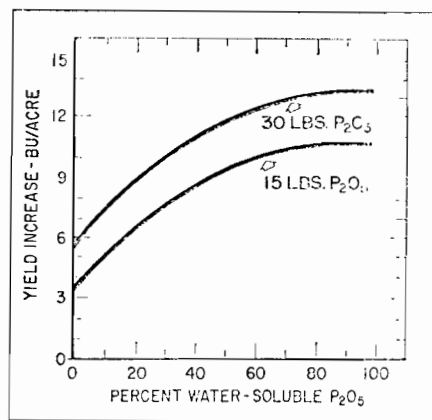
In accordance with the various

Figure 2

Corn yield as influenced by rate of application and water solubility of phosphatic fertilizer applied in the hill. The data summarize the results of 16 experiments conducted in Iowa from 1952 through 1955.

Courtesy—Sulphur Institute

Table 3. Agronomic Comparison Between Various Nitrophosphate Processes and Products

PROCESS	PRINCIPAL PRODUCT COMPONENTS (Ranked, and prior to addition of any potassium salt)	APPLICATIONS (Indicative only)
Non-Separation Conversion via:		
1. CO_2	Amonium Nitrate Dicalcium Phosphate Calcium Carbonate (approx. water solubility 0 to 5%)	Pastures, long season crops, perennials, acid or neutral soils
2. H_2SO_4 and/or H_3PO_4, XSO_4	Ammonium Nitrate Dicalcium Phosphate Ammonium Phosphate Ammonium Sulfate Calcium Sulfate	As above, plus medium season crops with bushy root systems; acid or neutral soils
Separation	20% to 67%) (approx. water solubility	
3. Crystallization (normal)	Ammonium Nitrate Ammonium Phosphate Dicalcium Phosphate (approx. water solubility 40% to 67%)	As above, plus medium season crops with bushy root systems; acid or neutral soils
4. Crystallization (intensive)	Ammonium Nitrate Ammonium Phosphate (approx. water solubility 67% to 85%)	Most or all crops and soils
5. a. Crystallization plus gypsum removal or b. Sulfate recycle only	Ammonium Nitrate Ammonium Phosphate (zero Dicalcium Phosphate when required) (approx. water solubility 67% to 95%)	Most or all crops and soils
6. Co-Products From 3 4, 5	Calcium Nitrate	Vegetables, Fruits, Soil conditioning,
From 3 4, 5	Ammonium Nitrate	solid and/or liquid source of N. soil liming
From 3 4, 5	Calcium Carbonate	
From 5	Calcium Sulfate plus (perhaps) Calcium Carbonate	Soil conditioning and a source of S

nitrophosphates processes and agronomic principles outlined, it is possible to make an empirical comparison between the major groups as shown in Table 3. It should be added that all proprietary processes are able to make granulated N-P and N-P-K products in a fairly wide range of particle sizes. One process also produces prilled N-P materials, while another is able to make both N-P and N-P-K prills in numerous formulations.

As regards phosphate water solubility, in general, a minimum level of 50% is increasingly accepted as being adequate for many purposes, especially on acid or neutral soils.[3] Low water-solubility nitrophosphates perform well in Europe, under conditions of high residual soil P_2O_5 and where pH is 7 or less.[11]

Economic Considerations
General

Economic comparisons between various nitrophosphate processes and products, and with

other fertilizers, can be made in terms of the producer or the consumer. However these relative results may differ, because of product transportation and application costs per unit of plant food. At the producer level, the principal cost items are:

1. Raw Materials
2. Ancillary Materials and Services
3. Direct and Indirect Labor
4. Utilities
5. Maintenance
6. Depreciation
7. Management and Overhead
8. Working Capital, Corporate and Sales Expenses

Naturally, the total production cost is also a function of the process efficiency and product yield.

Additional factors determining the ultimate cost to the farmer include:

9, 10 Manufacturer's and Distributor's Profits
11, 12 Transportation and Application Charges Per Unit of Plant Nutrient
13 Crop response per Unit of Nutrient Used
14 Financing and Other Expenses

Relative Production and Consumer Costs

Regarding primary raw materials, phosphate rock, ammonia and nitric acid are common to all nitrophosphate processes. Secondary raw materials for calcium nitrate conversion range from nil in the case of separation via cooling to low-cost CO_2, medium cost sulfuric acid and even relatively costly phosphoric acid. Obviously any process requiring sulfuric or phosphoric acid has a potential cost handicap compared to one which does not need these materials. Direct and indirect labor costs per unit of output are not only affected by plant size, but often by the number of plant sections and design. Thus, it can be expected that a simple, non-separation process comprising one reaction section and a single finishing unit as in Figure 3 requires fewer operations than a plant which includes calcium nitrate separation and perhaps conversion to re-
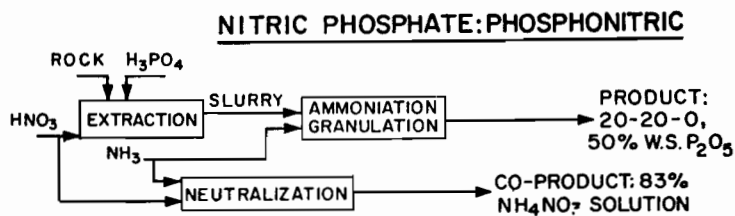
NITRIC PHOSPHATE: PHOSPHONITRIC

Figure 3
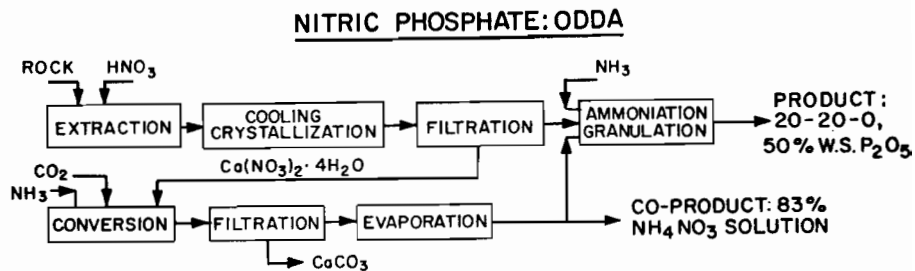
NITRIC PHOSPHATE: ODDA

Figure 4

cycled materials or co-products as indicated in Figure 4.

Similarly, utility and maintenance costs can be anticipated to be relatively greater in a more complicated plant. Capital costs and depreciation charges will also be higher, compared to a simpler plant of equivalent output. Other indirect production costs and corporate expenses should be affected to a lesser extent.

Relative process efficiencies and conversion factors are also im-

Table 4. Comparative Nitrophosphate Production Data
(Calculated on basis of 1,000 short tons solid N-P per day)

Process Product Co-Products	1 Phospho-Nitric 20-20-0[1]	2 20-20-0[2] Odda-Type +600 tpd AN[2]		3 25-16-0[2] SO₄ Recycle
Raw Materials, T/T product		N-P	AN	
Phos. Rock 73 BPL	0.27	0.6	—	0.50
Nitric Acid 100%	0.44	0.43	0.47	0.50
Phosphoric Acid P_2O_5	0.11	—	—	—
Ammonia 100%	0.14	0.15	0.14	0.16
CO_2 100%	—	—	0.20	0.14
Gypsum	—	—	—	0.05
Labor				
Operators/shift	5	5	2	7
Utilities				
Power, kwh	80	53	18	45
Water, M gallons	1	3.5	1.5	20
Steam, M lbs.	—	2	—	3
Fuel, MM Btu	3	0.9	—	—
Miscellaneous				
Coating T/Ton	0.02	0.02	0.02	0.02
Ancillary Items $/Ton, say	1.0	1.0	0.5	1.00
Financial				
B/L Cost $MM	5.5	6.0	2.5	5.50
Royalties	incl.	incl.		incl.

[1] Granulated   [2] Prilled

Notes: Process 1 does not include sulfuric and phosphoric acid in manufacture
Processes 2 and 3 yield by-product calcium carbonate
Potassium chloride or sulfate can be added as desired
Data are approximate and based on U.S. installed plants

122

portant when comparing different processes, as only a 1% N or P_2O_5 loss on a large plant can add $20,000 to $30,000 annually to raw material costs. For this reason, a nitrophosphate process with an attainable P_2O_5 recovery of about 99% is at an advantage, compared to a combined ammonium phosphate-wet process phosphoric acid plant which in most cases rarely achieves P_2O_5 recoveries greater than 92 to 94%. However, larger comparative savings can result from the avoidance of using sulfuric acid (and hence sulfur) to solubilize phosphate rock.

Ultimate costs to the farmer depend on transportation and application charges, and also crop yield, in addition to fertilizer sales price. These items are largely functions of fertilizer nutrient content, chemical composition and physical properties. Hence, economic comparisons at farmer levels in terms of specific cases.

The large variety of nitrophosphate processes and products possible makes an overall cost comparison very difficult. Useful data has been published by Banthien[12], Hignett[12], Slack[3] and others[12]. As a guide, basic production requirements for three major types of nitrophosphate processes (calculated on a U.S. installed basis) are given in Table 4. Comparative fixed capital costs and other data are best obtained from experienced plant suppliers in accordance with the specific parameters of an envisaged project.

Economic Comparisons Between Nitrophosphates and Other Phosphate Fertilizers

Sulfur Savings

On the basis of modern, high efficiency plants, primary nutrient costs in terms of phosphate rock, ammonia (and potash) will be about the same in each case. However, those nitrophosphate plants which use no sulfuric or phosphoric acid can show a cost saving which is closely related to the corresponding sulfur needed by other processes, (and which is usually discarded as waste gypsum). Naturally, the saving is also dependent on the difference in capital costs,

conversion costs and process efficiencies between the nitrophosphate unit and a sulfuric acid—phosphoric acid—phosphate fertilizer complex. Accordingly, rising sulfur prices will give a non-sulfur-using process and its products an increasing cost advantage.

Cost savings also depend on product grade and delivered sulfur prices. For example, in the case of a 20-20-0 formulation, made (a) as a highly water-soluble nitrophosphate by the Odda route and (b) as a granulated mixture of triple super and nitrophosphate, and using the conversion costs published in The Sulfur Institute Technical Bulletin No. 8 as a basis*, these savings can be expressed typically by:

$$\text{\$ saving per unit of } P_2O_5 \text{ in product}$$
$$\text{equals}$$
$$\frac{\text{\$ per delivered long tons } -5}{170}$$

Thus, a delivered price of $40 per long ton of sulfur would give a cost advantage of $\frac{40-5}{170}$ or $0.21 per unit of P_2O_5. The corresponding saving for a 20-20-0 compound would be $4.2 per ton of product. This formula includes an allowance for a 20% pre-tax return on plant investment in each case. (*Revised Edition, 1967.) On this basis, to compete with a nitrophosphate, a sulfur-using complex would have to obtain sulfur at $5 per ton. (If the tax allowance were not included, this price is reduced to about $2.75 per ton and the corresponding savings would be proportionately greater.)

The cost advantage would be increased, if comparisons were made with a product made via a route which required relatively more sulfur, e.g. if an ammonium phosphate—ammonium sulfate base were used. Other comparisons have been published by Slack et al.[3]

Capital Costs

The installed cost of a large nitrophosphate plant (together with an associated nitric acid unit in some cases) is of a similar magnitude to the total cost of separate sulfuric acid, phosphoric acid, ammonium phosphate and ammonium nitrate units having an

equivalent output. Furthermore, operation, maintenance and control are simpler than for several inter-dependent units.

Distribution and Application Costs

On the basis of nutrients applied to the soil, higher analysis fertilizers are obviously advantageous because of lower relative distribution and application costs. Latest developments of the Odda-type process in Norway enable grades such as 20-30-0 and 17-17-17 to be produced, which compare not unfavorably with 18-46-0 or 0-48-0 as regards transportation and application costs, especially in domestic markets. Although it is difficult to generalize, one recent study[3] indicated that fixed distribution costs would have to rise at least $0.70 per ton of product to be equivalent to a $1 rise in the price of sulfur, and a corresponding cost advantage to a nitrophosphate product.

Summary and Conclusion

Nitrophosphates are not a radically new class of fertilizer, but are composites of orthodox plant nutrient compounds such as ammonium nitrate, ammonium phosphate and frequently some dicalcium phosphate. Modern processes enable grades containing some 50% of plant nutrients to be made in the form of granules or prills having water solubilities tailored to meet agronomic needs, and ranging from 0 to 95 per cent. Some of these processes entirely avoid the use of sulfuric or phosphoric acid, which results in an increasing cost advantage in times of rising sulfur prices. The newer processes and their wide product ranges offer considerable manufacturing and agronomic flexibility.

In view of the availability of such technology, and the need to insure against limitations being imposed on phosphate fertilizer manufacture by a sulfur shortage, the newer nitrophosphate processes and products can be recommended under appropriate conditions as a good way of meeting expanding fertilizer needs in both the developed and developing countries of the world.

REFERENCES

1. Slack, A. V.—T.V.A. Fertilizer and Marketing Conference, Knoxville, Tenn., Oct. 4 to 6, 1967
2. Pratt, C. J.—Chemical Engineering Progress, p. 37-46, October 1967
3. Slack, A. V. et al.—Farm Chemicals, April to July, 1967
4. Plusje, M. H. R. J.—Proceedings, Fertilizer Society, London, No. 13, 1951
5. Huffman, E. O.—Proceedings, Fertiliser Society, London, No. 71, 1962
6. Cooke, G. W.—Proceedings, Fertiliser Society, London, No. 92, 1966
7. Tisdale, S. I. & Rucker, D. L.—Crop Responses to Various Phosphates, Sulphur Institute, Washington, D.C., June 1964
8. Beaton, J. D. et al.—Canadian Journ. Science 42, 254 to 265, 1962
9. Tisdale, S. I. & Rucker, D. L.—Ibid, p. 14
10. Van Burg, P. F. J. & Mattingly, G. E. C.—Proceedings, Fertilizer Society, London, No. 75, 1963
11. Turvund, L. & Kolrud, J.—T.V.A. Conference, Knoxville, Tenn., Oct. 4-6, 1963
12. Banthien, H. — Proceedings, Fertilizer Round Table, Washington, D.C., November 1965
13. Berquin, Y. F.—Proceedings, Fertilizer Round Table, Washington, D.C., November 1965
14. Anon—Phosphorus and Potassium, No. 30, London, July/August, 1967
15. Anon—Phosphorus and Potassium, No. 21, London, 1965
16. Anon—Phosphorus and Potassium, No. 26, London, 1966

CHAIRMAN SAUCHELLI: Thank you, Chris. I know that Chris has spent a lot of time burning the midnight oil and in other ways preparing this paper. He is quite a student on these problems and we appreciate his appearing on our program.

As I said at the beginning, Christopher Pratt has been of great help to the Round Table in the past. He has been in the background and this is the first opportunity we have had of getting him out on the platform.

Any questions? We are going to have some general remarks now on the three papers for a few minutes. I promised Mr. Strelzoff to give him a couple of minutes to make a statement.

Comments On Nitrophosphates

Samuel Strelzoff

First of all, gentlemen, I would like to invite all of you to give a standing ovation to Dr. Sauchelli and his committee for their excellent organization of these kinds of meetings, the very friendly atmosphere and open and frank discussions. The Round Table has succeeded in bringing quite a number of very distinguished guests from Europe and other countries. I would like all of you to join me in this.

(Standing ovation.)

Gentlemen, I was born 67 years ago in South Russia and I was educated in the southern part of Belgium and I have lived in the southern part of New York, so some of you Yankees will have to excuse my accent. It is a little bit too heavy.

I have the honor today to celebrate 26 years as an employee of Chemico. We in Chemico don't take any position on sulphur versus nitric or the nitrophosphates. We have got to build as many sulfuric acid plants, as many nitric acid plants and as many phosphate plants as possible. But personally I spent about 42 years in this field of nitrophosphate. The day I joined SPA staff in Belgium the general manager told me to forget about sulfuric acid, use only nitric acid. I spent quite a number of years waiting until it came to the point today that we can discuss so openly the various ways of doing this.

That is what they have done in Europe. They actually have about ten million tons of various types of nitrophosphates produced by various methods.

It is always difficult to persuade a farmer in a country which has never used a new type of fertilizer to try to use it this time, here in the United States as well as in other countries.

When I joined Chemico 26 years ago, this was a subsidiary of American Cyanamide. I told the Cyanamide people to use ammonium nitrate now. I was told it was a very dangerous and explosive material. It would never be used in the United States. As a matter of fact, we don't use any fertilizers in many parts of the United States. We have too much virgin land.

Well, things have changed and today we are looking at what we can do if sulphur becomes short in supply. I don't believe sulphur will be short. There is plenty of sulphur. As a matter of fact, some of you probably know that in Iraq they have about a billion-ton deposit and some American companies are being involved in trying to get some kind of concession to work the sulphur out.

But the price, that's the main thing. At what price will sulphur be delivered to the consumers? While at the same time we have needed to reduce the cost of ammonia with the large producers of ammonia and nitric acid they have come down to practically $10 a ton for production cost and so on.

You have got to face it. Nitric acid becomes a very serious competitor to sulfuric acid. In addition, all this discussion about water soluble versus citrate soluble is a very old discussion. But it is entirely irrelevant because there are nitrophosphate processes where you can make water solubility as high as you want it. These are based primarily in ammonium sulphate cycles.

I had the pleasure to have this study made about 12 or 14 years ago and with some people this seems to be of great interest. I will make the statement that Chemico's process is as flexible as possible because you can separate as much ammonium nitrate as you want and you have a P_2O_5 to nitrogen at any ratio you want.

There are also other processes

that, well, we don't know but I will have the pleasure of describing more in detail in St. Louis in February at the meetings which is a special symposium of the American Institute of Chemical Engineers, where we are going to compare all of the processes to make nitrophosphate.

But I do not like to overlook elemental phosphorus.

Today power is cheap enough, low enough and available at strategic locations so that elemental phosphorus might become a very serious competitor to all other methods for making phosphate products.

And nobody is going to tell me that you cannot make 100 per cent water soluble fertilizers starting from elemental phosphorus. As a matter of fact, I was involved many years ago in a very interesting work where we converted phosphorus directly to phosphoric acid and hydrogen, to make hydrogen available to make ammonia. There are plenty of ways of doing it when one is really pinned against the wall.

My professor in 1924 told me that there are no more inventions to be made. Well, we have made more inventions in the last few years than before 1924 and there will be more and more possibilities in the future and I don't see any sense in saying in advance that something will not be acceptable here just because it was not used up until now. The United States, as far as fertilizer consumption, is not number one in the world. As a matter of fact, it is number 13. I can give you figures showing how much Holland is using, how much Japan is using, how much Taiwan is using for comparison with the United States. There is a long way to go before it can be said that there are no more inventions to be made in the fertilizer field.

I invite you, gentlemen, to think about this next year and I would like very much, Dr. Sauchelli, to suggest that the discussion next year would include elemental phosphorus in comparison with the other methods to make cheap phosphates.

Thank you.

CHAIRMAN SAUCHELLI: Thank you, Mr. Strelzoff.

We respect the remarks of a man of that experience such as yourself.

We would like some more comment. I know there is a wealth of information in this group that I am facing, if we only have time to bring it out.

I am amazed that we have one representative here of the agronomists, who has been quiet, and that in some ways astonishes me. Dr. Arthur M. Smith.

Agronomic Comments

Arthur M. Smith

Thank you, Vince.

DR. ARTHUR M. SMITH (Agronomy Consultant): Thank you, Vince. Shall I make a comment?

CHAIRMAN SAUCHELLI: Yes, can you make your comment brief?

From my 52 years of experience — ten years as an experiment station soil chemist and teacher, and 42 years with the fertilizer industry, I will try to clarify the borders between some of these differences of opinions.

The methods used to manufacture fertilizer have in the past, and I presume in the greater part always will be determined by the economics of the cost of raw materials at the locations where the fertilizers can most conveniently or, from a power or labor standpoint, most economically be made.

We have one very important exception here in the United States; namely, our alkaline soil areas in the Western States, beginning with the calcareous soils in Western Missouri and Iowa and extending through the soils which in California, Colorado and other Western States very often have an actual, working pH as high as 10.0. In other words, they contain sodium carbonates.

Now, with reference to the matter of water solubility, I have sold in my career every type of fertilizer that was ever made, including 14 years promoting and selling the original German Nitrophoskas all over the Atlantic seacoast and Cuba and other related areas, and I can tell you that, if you are a potato grower anywhere along our Atlantic seaboard, you had better have water soluble P_2O_5 in your fertilizer.

I have seen the comparisons, both commercially and experimentally, and, in fact, got into that work because of certain experiments that I made on early potatoes over on the eastern shore of Maryland.

That goes for a lot of our vegetable crops all along our Eastern seaboard. It also goes if you are top dressing winter grain. But, remember, in our Atlantic seaboard states ammoniated superphosphate still supplies a large part of the fertilizer and a large part of the phosphorus by that process is dicalcium phosphate.

It is very true, when you get back from the lower coastal plain and into the upper coastal plain with heavier soils and into our uplands and limestone valley areas, that the acidity of the soils generally is such that your dicalcium phosphate is just as good as any other phosphorus.

I have sold and tried to promote both kinds in both areas.

Now, with reference to pH. Our low pH areas in the United States are mostly in our South Atlantic states and the crest extending through the Gulf Coast area as far as Houston, Texas. In other words, from Houston, Texas, east, including Long Island, we have these low pH soils. But the agronomists in most of those states tell the farmers, I mean the college agronomists and the extension agronomists, "Brother, if your soil pH is as low as 4.5, you'll be better off if you don't try to plant a crop. You'd better lime it."

Now, why is that? Because you cannot find varieties that will grow at that pH? No, not necessarily. But those soils that have the low pH in our Atlantic coastal plain areas are also high in total maganese and primarily the advice is given on the basis that the crop

will suffer from manganese toxicity.

Now, we are much hepped up about minor and trace elements but I can tell you from my experience, including U.S. Soil Survey and some other things, that there are probably as many crop acres at least east of the Mississippi River that even today are still suffering from manganese toxicity as there are acres that suffer from manganese deficiency.

Now, with reference to ammonium phosphates. I spent 14 years promoting the sale of diammonium phosphates. In January 1926, I was going all over the cotton South giving away 16-32-16 for demonstrations; that is, giving it to county agents and teachers and other such people, supervised experiments or demonstrations, and I have spent 16 years promoting the sale of mono-ammonium phosphate; that is, before I was graduated by the company I was with at age 71, and the four years since I have been a consultant. I know the difference between diammonium phosphate and mono-ammonium phosphate and I can tell you that if in the South Atlantic coastal area you are planting cotton or corn, diammonium phosphate banded in the row at planting time is positively dangerous. I know, I have paid damages for crops that were not made with diammonium phosphate.

That same fertilizer on that same soil top dressing winter oats is a world beater. Take it up in the red clay soils of the Piedmont and I could bet anybody's fertilizer salesman a Stetson hat, and often did, that pound for pound of plant food a' diammonium phosphate would beat anything that they could make.

On the other hand, on those soils where diammonium phosphate proved dangerous, mono-ammonium phosphate is safe. It is not always better but under those conditions it is safe simply for the reason that that second ammonia is not held as tightly as the first.

So there is something in what one of the men said yesterday. You should know where you intend to market your fertilizer when you decide on which process you will use in manufacturing.

But by and large it is the matter of materials economics that has first consideration, everywhere except our really alkaline soil areas and I presume other equivalent soil areas in other parts of the world.

Thank you very much.

CHAIRMAN SAUCHELLI: Thank you, Art.

This is a forum to give both sides. We want to keep an open mind. After hearing all of the arguments, then you can come to some conclusion.

Dr. Lüth wants me to announce that they have samples of Nitrophoska down there on the tables that are available to anyone who wants to pick up a sample of their fertilizer.

Any other comments?

A MEMBER: I would like to ask Mr. Pratt a couple of questions about the cost data which he presented. I'm afraid I couldn't see at the back.

In the capital cost figures you showed, have you included in the phospho-nitric approach to 20-20-0 the capital cost of the associated phosphoric acid plant? Because this must be included in such a capital cost comparison to make it in total comparability to the truly neutral phosphate processes such as the Odda and the sulphate recycle.

CHAIRMAN SAUCHELLI: Who that question directed to?

SAME MEMBER: Chris Pratt.

And there is a second one on the same chart, going on from there. And the cost you pay for the sulphate recycle route to make 20-20-0.

Did you also include there the capital costs associated with the ammonium nitrate facility? Because you can't make a 20-20-0 simply by sulphate recycle, you merely get 23-15-0 and to get down to 20-20-0 or 22-22-0 formulation, you have got to remove some calcium nitrate or add phosphoric acid, one or the other, and either of those is going to incur further chemical cost that wasn't included and have you in fact put those figures in?

CHAIRMAN SAUCHELLI: Thank you.

MR. PRATT: I didn't hear the

entire question but I can guess what it is.

If one is comparing a phospho-nitric process against another or a sulphate recycle, where does the phosphoric acid come from? Well, it comes from a phosphoric acid plant but it need not necessarily be yours. This can be reflected in the total raw material cost or the capital investment cost, whichever way you go. Of course, he is absolutely right that it has to be cranked into the total economics for the comparison.

That's about all I can say. These things are so obvious.

CHAIRMAN SAUCHELLI: Thank you, Chris.

Dr. Lüth.

DR. LUETH: To the question what are the costs to produce fertilizers in Europe, I can say that our specialist for capitalization figured out that at today's prices for sulphur it would be cheaper to waste the calcium nitrate to the ocean than to use the mixed acid process.

That means that when you use the Odda process and you do not use the byproduct calcium nitrate, it would be cheaper than using sulphuric acid in Europe now.

CHAIRMAN SAUCHELLI: A question here.

MR. BRUSH (Foster-Wheeler): With regard to Mr. Bennett's remarks, you can, as Mr. Weber, I believe, pointed out yesterday, make a 20-20 grade or a 1-1 grade with the sulphate recycle process with a modest Odda type step. Using that, I think you can achieve high water solubility, higher than with straight crystallization. You can hit up to, as Mr. Pratt pointed out, 95 per cent in a sulphate recycle process.

CHAIRMAN SAUCHELLI: Thank you.

I get the impression that the fertilizer companies had better add a good agronomist to their staff so I would put in a plug for agronomy and agronomists here. I think it is essential for a fertilizer company today to have a good agronomic staff to meet the conditions.

MR. STRELZOFF: I think, as far as the sulphate recycle, gentlemen. —I don't think you are well in-

formed if you say that you can make products as high as you want and in the ratio that you want.

I can have a private discussion, I don't want to do that in public discussion, and prove it to you and I will bet you any money you want that it can be done. Sulphate recycle is a process that can be used. As a matter of fact, Stamicarbon found that after removing so much they liked the way they did that because after removing so much calcium nitrate they removed the balance by ammonium sulphate and they claim that they can get products very high in ratio of P_2O_5 to nitrogen, which I believe they do.

There are many different methods to use that ammonium sulphate cycle. But I feel we are just arguing just for the pleasure of arguing because it can be proved on the blackboard, if you want, any time.

CHAIRMAN SAUCHELLI: Now, I think that time is getting along and I want to take this opportunity to thank all of the speakers for their fine cooperation.

I think we don't always appreciate the amount of work that goes into these papers and the expense and when our foreign guests come to share with us their experience and information, that is at a great expense and we certainly do appreciate it.

So I want to thank all of the speakers. I want to thank my associates on the Executive Committee for their kind cooperation in helping to make this Meeting such a success. I think it has been a very successful meeting.

We have added to our Executive Committee Robert Heck of the IMC who, unfortunately, could not be with us; also Billie Adams of Allied Chemical. Billie, will you come out in front here.

(Mr. Adams came to the front of the room; applause.)

I want to thank Miss Withers, here, for her patient work in taking notes. Sometimes she is confronted with foreign languages that sort of bewilder her but she gets along all right with them.

I want to thank the Mayflower Hotel personnel. They have been very courteous and very helpful in making our stay a pleasant one.

I particularly want to thank our Secretary-Treasurer. As I have said in the past, he is a beaver for work. It is hard to keep him down. He just seems to be a dedicated soul and even under the handicap that he had yesterday, he persisted in participating in our program, you couldn't keep him away.

I want to thank the trade press representatives who are another group of hard workers and who have given us splendid cooperation in the past and in the present and we are really grateful to the press.

We need suggestions from you for this coming year. This is your Meeting. Our policy has always been to consider the members here as a committee of one. The success of our meetings has been primarily attributable to your cooperation and, unless we have your cooperation in giving us suggestions, for and against and so on for improving our programs, we will not have any programs.

Now, let me say something about the proceedings. They take about 85 per cent of the income that we get through registration. Do you as a whole like the proceedings as they have been or should we just prepare abstracts and make abstracts available? What is your wish on the proceedings?

The proceedings become a valuable library of information. There is such a big demand now for some of the past proceedings by newcomers to the industry. They are valuable and a low-cost book on technology and on other subjects pertaining to the industry.

Should we continue the proceedings as they are?

VOICES: Yes.

CHAIRMAN SAUCHELLI: They represent a lot of hard work but we have been very glad to do the work and, I don't know, in the future we might have to make some changes regarding the printing and so on. But that is a matter for us to decide.

I have no further comments. I simply want to thank you for being a patient and a fine audience and we stand adjourned until next year.

Thank you all.

(The Round Table Meeting adjourned at eleven-fifty-five o'clock a.m.)

Index of Participants in Program

Adams, Billy E.
Allied Chemical
Agricultural Division
Hopewell, Virginia 23960

Archer, Jim R.
Quality Control Manager
Int. Min. & Chem. Corporation
1507 Willingham Drive
East Point, Georgia

Athey, Tom
Raymond Bag Company
3403 Rodman Street, N.W.
Washington, D. C. 20008

Barrett, Ernest E. Jr.
Senior Chemist
Int. Min. and Chem, Corporation
1507 Willingham Drive
East Point, Georgia 30044

Bennett, Michael J.
Director — U. S. Operations
Humphreys & Glaskow Intl. Ltd.
22 Carlisle Place
London, SW 1, England

Berg, Gordon L.
Editor
Farm Chemicals Magazine
37841 Euclid Avenue
Willoughby, Ohio 44094

Bixby, David W.
Chemical Engineer
The Sulphur Institute
1725 K Street, N. W.
Washington, D. C. 20006

Boutan, Pierre J.
Technical Liaison Representative
Peachiney-Saint-Gobain
220 East 42nd Street, Suite 1220
New York, New York

Bowers, Quentin D.
Manager, Process Engineering
Dorr-Oliver, Inc.
Highway 17 South
Bartow, Florida

Burns, Dr. G. R.
The Sulphur Institute
1725 K St. N. W.
Washington, D.C., 20006

Carr, John E. Manager
Denver Equipment Co.
Division of D. W. Joy Mfg. Co.
1400 17th Street
Denver, Colorado 80002

Coleman, Russell, Dr.
President
The Sulphur Institute
1725 K. Street, N. W.
Washington, D. (. 20000

Countess, James E.
Consultant
1134 East Belvedere Avenue
Baltimore, Maryland 21212

Davis, Charles M.
Process Chemist
J. R. Simplot Co.
P. O. Box 912
Pocatello, Idaho 83201

Detuncq Yves
"DT" Section-Pechiney-Saint-Gobain
Boite Postal N°4
76-Grand-Quevilly-France

Dorland (Kanar) Eleanore
Technical Editor
Agricultural Chemicals
Box 31
Caldwell, N. J.

Garman, W. H. Dr.
Vice President
N. P. F. I.
1700 K Street N. W.
Washington, D. C. 20006

Gibson, A. E.
Vice President Production
Red Barn Chemicals, Inc.
7018 Red Barn Road
Freeport, Texas 77541

Giles, Clem B.
  Vice President
  CPI / Girdler
  256 McCullough Street
  Cincinnati, Ohio

Grover, Kenneth M.
  Vice President
  Producers Chemical Corporation
  375 Park Avenue
  New York, New York

Hammett, James A.
  Special Project Supervisor
  Int. Min. & Chem. Corporation
  1507 Willingham Drive
  East Point, Georgia

Harding, Charles T.
  Senior Vice President
  Wellman-Lord, Inc.
  2402 Newport Avenue
  Lakeland, Florida 33803

Hignett, Travis P.
  Director, Chemical Development
  Tennessee Vally Authority
  Muscle Shoals, Alabama 35660

Hofstader, Robert A.
  Esso Research & Engineering
  Linden, New Jersey

Janovac, Stephen J.
  Application Engineer
  W. S. Tyler Co.
  8200 Tyler Boulevard
  Mentor, Ohio 44060

Jockers, Kurt, Dr.
  Badische Anilin and Soda Fabrik
  Ludwigshafen/Rh., Germany

Jung, Johann (Dr.)
  Badische Anilin und Soda Fibrik
  6703 Limburgerhof
  Ludwigshafen, Germany

King, Wayne W.
  Assistant Vice President
  W. S. Tyler Co.
  803 Kingston Road
  Baltimore, Maryland 21212

Lagarias, John S.
  President
  Resources Research, Inc.
  11455 Newton Square South
  Reston, Virginia 22070

Lambillotte, G. J.
  Kalium Chemicals, Ltd.
  200 Parlce IWE
  New York, N. Y. 10017

Legal, Cass C.
  Manager
  Grace Research Co.
  Route 32
  Clarksville, Maryland

Lehr, James R.
  Proj. Leader, Fundamental Research
  Tennessee Valley Authority
  Muscle Shoals, Alabama 35660

Leister, Elmer J.
  Vice President
  Edw. Renneburg & Sons Co.
  2639 Boston Street
  Baltimore, Maryland 21224

Levitsky, Serge L. (Dr.)
  Texas Gulf Sulphur Company
  200 Park Avenue
  New York, New York 10017

Leyshon, David W.
  International Division
  Dorr-Oliver, Inc.
  Havemeyer Lane
  Stamford, Connecticut

Long, Larry A.
  Editor
  Croplife
  2501 Wayzata Boulevard
  Minneapolis, Minnesota 55440

Lueth, Gero F. (Dr.)
  Badische Anilin und Soda Fabrik
  8 Muehldorfer Strasse
  68 Mannheim, West Germany

Marburger, Grant C.
  Armour Agricultural Chemical Co.
  P. O. Box 1685
  Atlanta, Georgia 30301

Marshall, Housden L.
  Consultant
  1604 Walterswood Road
  Baltimore, Maryland 21212

Marten, James F., Dr.
  Manager
  Technicon Corporation
  14 Marks Road
  Riverside, Connecticut 06878

McManus, James M.
  Asst. Mill Superintendent
  Southwest Potash Corporation
  Box 279
  Carlsbad, New Mexico 88220

McNally, Richard D.
  Editor
  Agricultural Chemicals
  Box 31
  Caldwell, New Jersey 07006

Miller, H. Vise
 Vice President — Sales
 Kalium Chemicals Ltd.
 4 Executive Park Drive
 Atlanta, Georgia 30401

Nielsson, Frank T.
 Mgr., Fertilizer Technology
 Int. Min. and Chem. Corporation
 5401 Old Orchard Road
 Skokie, Illinois 60076

Osguthorpe, John E.
 Special Asst. Agriculture
 State Dept. A.I.D.
 1711 Newport Ave.
 Washington, D.C.

Pelitti, Enrico
 Vice President
 C & I / Girdler
 256 McCullough Street
 Cincinnati, Ohio 45226

Phillips, A. B.
 Asst. Mgr. Office Ag. & Chem. Dev.
 Tennessee Valley Authority
 Muscle Shoals, Alabama

Plate, Henry
 Agronomist
 Agway, Inc.
 Box 1333
 Syracuse, New York

Pratt, Christopher J.
 Manager Agric. Development
 Mobil Chemical Company
 150 East 42nd Street
 New York, New York

Rosenbloom, Wm. J.
 Technical Manager
 Mobil Chemical Co.
 150 East 42nd Street
 New York, New York

Russo, Vincent J.
 Director R & D
 C & I / Girdler
 256 McCullough Street
 Cincinnati, Ohio 54226

Sackett, Walter, Jr.
 Executive Vice President
 A. J. Sackett & Sons Co.
 1701 South Highland Avenue
 Baltimore, Maryland 21224

Sauchelli, Vincent, Dr.
 Consultant
 303 Overhill Road
 Baltimore, Maryland 21210

Schall, E. D. Dr.
 State Chemist
 Purdue University
 Lafayette, Indiana 47907

Smith, Arthur M., Dr.
 Fertilizer Industry Consultant
 216 East 39th Street
 Baltimore, Maryland 21218

Smith, Galen B.
 Eastern Advertising Manager
 Farm Chemicals
 355 Lexington Avenue
 New York, New York 10017

Strelzoff, Samuel, Dr.
 Senior Vice President
 Chemical Construction Corporation
 320 Park Avenue
 New York, New York 10022

Surber, John H.
 Mfg. Services Supervisor
 I.M.C.
 5401 Old Orchard Road
 Skokie, Illinois 60076

Swanson, Vernon F.
 Administrative Staff
 W. R. Grace & Co.
 101 North Charles Street
 Baltimore, Maryland 21201

Truitt, Paul
 President
 National Plant Food Institute
 1700 K St. N.W.
 Washington, D. C., 20006

Van Sant, John B.
 Technical Service
 Southwest Potash Corporation
 1270 Avenue of the Americas
 New York, New York 10020

Waggaman, Wm. H.
 Chemical Engineer
 Box 111
 Alexandria, Virginia 23313

Weber, Wm. C.
 Director, Intl. Project Services Div.
 Dorr-Oliver Co. Ltd.
 185 London Road
 Croydon, Surrey, England

Whittington, Joe
 Agricultural Chemicals
 202 Cedarcroft Road
 Baltimore, Maryland 21212

Zilenziger, Rod
 Sales
 Agricultural Chemicals
 41 East 42nd Street
 New York, New York 10017

Zoellner, J. H.
 Manager, Mfg. Services
 I. M. C.
 Old Orchard Road
 Skokie, Illinois

Note: Many more participants who did not announce
their names when asking or answering questions.