PROCEEDINGS

OF THE

15th ANNUAL MEETING

FERTILIZER INDUSTRY ROUND TABLE

1965

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Held at the
MAYFLOWER HOTEL
Washington, D. C.
November 10-11-12, 1965

Executive Committee

Vincent Sauchelli, Chairman
Housden L. Marshall, Sec'ty-Treasurer
Joseph E. Reynolds, Jr.
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Executive Committee

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Fertilizer Industry Round Table

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Wednesday Morning Session, Nov. 10, 1965

The Fifteenth Annual Meeting of the Fertilizer Industry Round Table

Dr. Vincent Sauchelli, Chairman
Joseph E. Reynolds, Moderator

Dr. Sauchelli:

Ladies and gentlemen: Welcome to the 15th Annual Meeting of the Round Table, 1951, the initial year of our organization, now seems so long ago. What changes have occurred since then in all areas of human activities! Remarkable changes have particularly characterized the fertilizer industry and our agriculture.

Change is nothing new, of course. What distinguishes recent innovations is the speed at which it occurs. But, then, aren't we living in the jet age? Speed is the order of the day. Ours is now a dynamic industry. It is exhilarating to be in it.

Change can be hard at times on the persons and organizations directly affected but I am sure none would have it otherwise.

Technological changes in agriculture act as an indirect force in causing changes in the fertilizer industry.

Fertilizer use is closely associated with the pattern of farming which prevails in the area it serves.

May I point out some data showing the remarkably dramatic changes in American agriculture during the period 1950 to 1964.

In that period production increased 38 per cent. The most effective factor in this increase was the more intensive employment of chemical fertilizers, an increase in consumption of 130 per cent during that period. That's on the basis of actual plant nutrients.

Breaking this figure down, the consumption of nitrogenous fertilizers increased by 279 per cent, phosphate fertilizers by 55 per cent, and potassic fertilizers by 124 per cent.

Improvements in technology on the farm and in the fertilizer plant kept fertilizer prices relatively constant and attractive to the farmer, with not much profit to the manufacturer, I might say.

In 1950, the total value of assets of American agriculture was $132.5 billion. In 1965, it was $237.6 billion, a 79 per cent increase. That's a tremendous figure, $237.6 billion of dollars in assets for American agriculture. It is the largest industry in the country.

In 1950, the production assets used in agriculture were $95 billion, of which machinery and motor vehicles were valued at $11.12 billion. In 1965, total production assets were $186 billions, an increase almost double in that interval.

Production assets, the tools with which farmers create their production: In 1950, American farmers spent $975 million for fertilizer and lime: In 1964, they spent $1678 million, about a 70 per cent increase. This is a big industry, almost one and three-quarter billion dollars used for the purchase of fertilizers and lime and most of that is for fertilizers.

Our highly efficient agriculture results from a combination of constant research and education that gives to our farmers the information and techniques for producing more on every acre of crop land harvested.

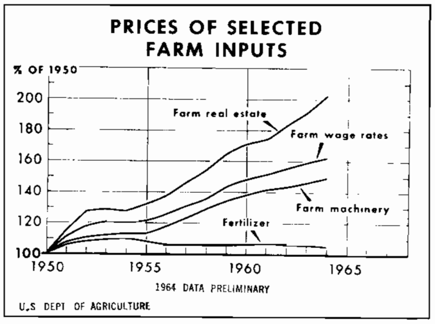
We are now using about 40 million fewer acres of crop land than we used in 1950, 336 million acres in 1950, 294 million acres in 1964. But our population in the interim increased from 152 million to 191 million persons.

Crop yields in 1964 exceeded all previous records. Corn, wheat, barley, peanuts, rice, all the important cash crops almost doubled in yield per acre in the interim between 1950 and 1964.

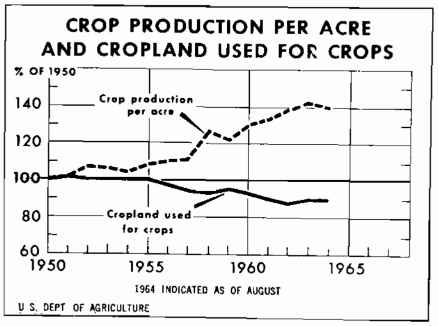
Of course, all credit for these currently high yields cannot be attributed to the use of fertilizers. It cannot, however, be refuted that, without the employment of adequate supplies of fertilizer, these record-breaking achievements could not have been realized.

This lesson about the indispensable role of fertilizers in promoting increases in crop yields is being driven home to those in the developing countries where food and nutrient difficiencies are desperately serious.

I have a slide here that will illustrate graphically the fertilizer picture.


PRICES OF SELECTED FARM INPUTS

1964 DATA PRELIMINARY
U.S DEPT OF AGRICULTURE


CROP PRODUCTION PER ACRE AND CROPLAND USED FOR CROPS

1964 INDICATED AS OF AUGUST
U S. DEPT OF AGRICULTURE

You will see 1950 and the present period. Here is the crop land. See how it has been decreasing and the use of fertilizer has taken the place of land. Labor on the farm has been decreasing with more efficient use of that labor being made. Fertilizer is taking the place of land and labor.

Here are farm imputs, wages, machinery, but the price of plant nutrients has gone rapidly down from 1950.

We have a remarkably fine record.

So much for general remarks. I want to refer now to our program. Your Executive Committee, mindful of the changing technology and techniques in the chemical laboratories and materials of construction, has prepared a program based on suggestions and problems received from our members. We hope the papers and discussions will help you to be posted on many phases of what is going on in our industry.

The special feature this year is a panel on nitrophosphate processes. Participating on the panel are outstanding authorities from Europe and the United States. We have always welcomed visitors from abroad. American fertilizer personnel have only recently begun to make a serious effort to inform themselves about the technical developments in European countries. They do this through attendance at their conferences and by visiting their fertilizer plants. European technology has a great deal to teach us.- We can't forget that much of our present fertilizer processing originated in Europe. Despite the handicaps of relatively higher costs of raw materials — they have had to import phosphate and sulphur, for example—Europeans manage to compete quite successfully on the world market. Their large scale, often integrated chemical operations, modernized efficient technology and the use of the most economical processes permit economies that offset high costs of raw materials.

It is good for all concerned that we now have this two-way flow of personnel between Europe and North America. We feel honored that so many European companies think our Round Table is of such a stature that they are willing to cooperate by sending worthy representatives to take part in our program.

Fertilizer technology today is internationally developed. All world capitals recognize that a nation's economy is mightily strengthened when it is based on a vigorous agriculture sustained and nourished by an adequate fertilizer industry.

We are indebted to Mr. William Weber of Dorr-Oliver and to Mr. Travis Hignett of Tennessee Valley Authority for the splendid panel program on mixed acids in nitro processes which will take place later on in this program.

The other items on our program are important to us all. Granulation has been almost an annual subject on our agenda. It is one of the outstanding accomplishments among many in our technology. Mr. Frank Nielsson of IMC and Mr. Achorn of TVA start off the program with interesting disclosures in this field.

We are getting in step with conference procedures. This year we have provided for coffee breaks in the forenoon sessions. The demand for such breaks has been irresistible.

The discussions on crystal structural changes in ammonium nitrate by Bert Tucker and R. J. Harvey will help us understand better how such occur and may be controlled.

Potassium nitrate is a new and welcome addition to fertilizer materials. Rodger Smith of Southwest Potash has been identified with the new product from the start. His presentation should be of interest to all operational personnel.

The other subjects of concern are on trace elements in fertilizer manufacture, statistical quality control, phosphoric acid manufacture, effluents from fertilizer plants, sampling of bulk fertilizers, automated chemical analysis developments, rubber as a material of construction and safety measures in the fertilizer plant.

We have a rich and varied fare to suit most appetites. With your cooperation in the form of lively questions and answers from the floor, this 15th meeting could be one of our most memorable. I emphasize that. We need your participation through questions and answers in order to make our meetings more interesting and up to our tradition.

I now turn the meeting over to your moderator for this mornin, Mr. Joe Reynolds.

Remarks by Moderator Joseph Reynolds.

Thank you, Vince. Good morning. It is my privilege and pleasure to appear before you again and give you also an official welcome from my standpoint to the 15th Annual Meeting of our Fertilizer Industry Round Table.

As many of us can recall, the conference has changed in style of presentation but it has retained its recognition for the operating man. Many other meetings around the country compete for some of the more fundamental research activities, some more at the management level, but this one we have dedicated to the production man, the man in the plant.

The Round Table brings together highly qualified speakers to share their timely experiences and technical knowhow which these operators can take back to their plants for immediate use.

Many advances have been made during the past 15 years, and we are now in the midst of still further acceleration. A review of the past proceedings actually reveals the tremendous wealth of knowledge of our industry. It really shows the evolution that has taken place.

To move with our program this morning, we will start off here with our first speaker. Mr. Frank Achorn of TVA, who will stimulate our thinking concerning recent developments and changes that have happened in granulation, TVA's contributions to this field which are widely recognized and a tremendous amount of thanks and appreciation go to them for helping to keep us in the front.

Recent Developments In Granulation

Frank P. Achorn and J. S. Lewis, Jr.

THE number of granulation plants in this country continues to increase. Many companies with small plants that formerly produced pulverized mixtures have converted their batch ammoniators to batch granulation plants, and many producers with medium-size granulation plants have installed preneutralizers and scrubbers so that they now produce diammonium phosphate grades. Companies that have plants of the latter type now tend to have higher annual fertilizer production, and many of them are now marketing complete grades through bulk handling stations.

Producers that have converted their small pulverized-mix plants to granulation have accomplished this conversion by cutting away part of the flights in their batch mixers and installing ammonia and acid distributors below a rolling bed of material in the batch mixer. Figure 1 is a sketch of a typical batch mixer that has been converted to a batch granulator. The flights in the first half of the mixer have been removed, and a block sparger or drilled pipe-type spargers have been installed in this section. The flights in the latter half of the mixer are usually cut so that they are only about 6 inches deep. The material from the batch granulater is usually cooled in a rotary cooler. Coolers of this type vary in size from 6 by 12 feet to 7 by 50 feet.

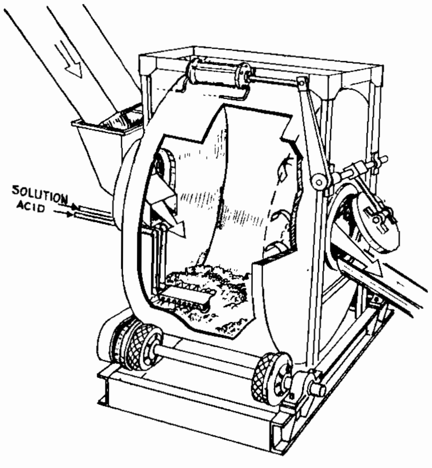


Figure 1.

Producers with granulation plants of this type formerly sold unscreened products or they removed the oversize only and sold the product as "semi-granular" fertilizer. However, since quality specifications of granular products have become more demanding, most of these companies have found it advisable to screen the product from the cooler and recirculate the fines from the screen to the batch granulator. Recently some companies have converted their batch ammoniators to granulators by enlarging the discharge opening from the ammoniator and operating it on a continuous basis. The operation would then be essentially the same as with a conventional ammoniator-granulator. *Most companies that have converted their 1-ton mixers or batch ammoniators to ammoniator-granulators have found that their production rate* is usually less than 10 tons per hour. Because of these production limitations and the demand for higher production rates, many of these companies now plan to construct conventional ammoniation-granulation plants.

The size of the conventional ammoniator-granulator has been increased in the past few years. The *Croplife* survey of 1961 indicated that the largest ammoniator-granulator at that time was 7 by 14 feet. Recently some companies installed ammoniator-granulators that are 12 by 24 feet. The larger ammoniator-granulators are usually found in those plants that produce granular diammonium phosphate. Most of the ammoniator-granulators are still constructed of mild steel. Many now have Hastelloy or stainless steel sparger pipes. Most operators have found that the extra cost of stainless steel or Hastelloy is worth the investment. They report that there is considerably less wear of the holes in the stainless steel distributor; therefore, the distribution of the ammonia and acid remains uniform in the bed of material in the ammoniator-granulator for longer periods of time. This uniform distribution in turn causes ammonia losses to be minimized and granulation efficiency to remain good. They report that the holes in the mild steel distributors become enlarged so that there are wet spots in the ammoniator-granulator that cause overgranulation and high ammonia losses.

Recent observations indicate that many operators are removing the retaining rings inside the ammoniator-granulator which eliminates the granulation section. Operators who have removed this dam in the granulator have found that its removal does not affect their granulation efficiency. They have found also that they can lengthen their distributors and that the longer distributors tend to lower the amount of nitrogen lost in granulation and to decrease the difficulties encountered with overgranulation of the higher nitrogen grades such as 13-13-13 and 16-8-8.

There are many new devices to prevent the caking of material on the walls of the ammoniator-granulator. Some companies use rubber-lined ammoniator-granulators to prevent this caking. Figure 2 is a sketch of this type of ammoniator-granulator. Strips of rubber about 3 feet wide are bolted to the walls of the ammoniator-granulator and are held in position with metal strips. As the ammoniator-granulator rotates, the rubber lining flexes and thus causes any buildup on the rubber to fall off. Other companies are now using ammoniator-granulators that have

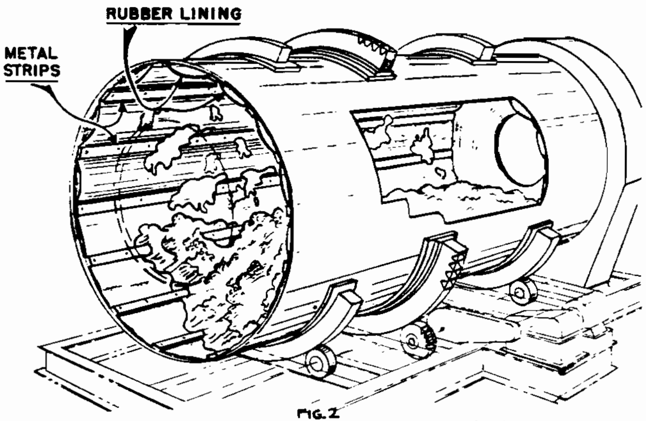


FIG. 2

A RUBBER LINED AMMONIATOR GRANULATOR

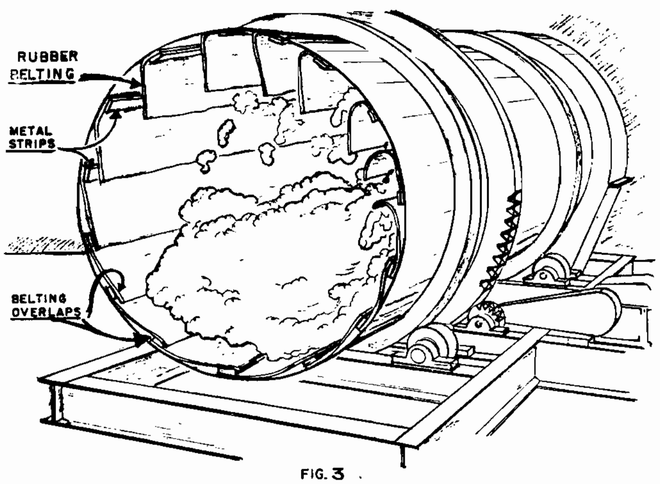


FIG. 3

AMMONIATOR GRANULATOR LINED WITH RUBBER BELTING

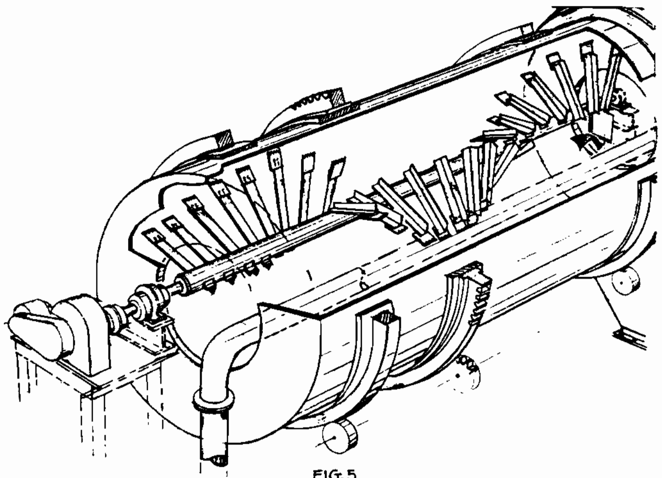


FIG. 5

AMMONIATOR GRANULATOR WITH SPIRIAL TYPE SCRAPER

rubber flaps inside. Figure 3 is a sketch of an ammoniator-granulator of this type. These flaps are usually made of 24-inch rubber belting, and they are installed so that the belts overlap each other when they are laid on the walls of the ammoniator-granulator. As the ammoniator-granulator revolves, the loose ends of the flaps drop. Any material that collects on them will drop off, and the flaps will remain relatively clean. Other plant operators have found it advisable to use an oscillating scraper to prevent this caking of material on the walls of the ammoniator-granulator. Figure 4 is a sketch showing a scraper of this type. The scraper oscillates back and forth across the walls of the ammoniator-granulatro, and its teeth dig the caked material away from the walls. This type of scraper tends to wear less than the normal stationary scraper bar. At TVA we have recently installed a spiral scraper in one of our new ammoniator-granulators. Figure 5 is a sketch showing a scraper of this type. This scraper is similar to a German design. It is driven by an electric motor through a speed reducer; as it revolves slowly its teeth dig away the caked material from the walls of the ammoniator-granulator. Most companies still use knockers to remove buildup from the walls of the ammoniator-granulator.

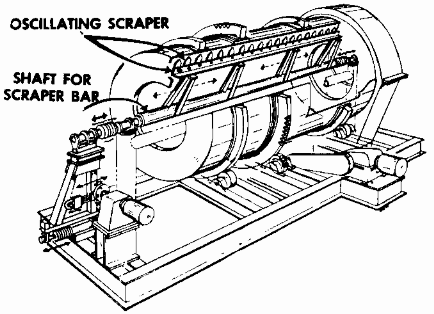


Figure 4.

Recently a company applied for a patent for a unique method of cleaning and positioning their sparger bars in the ammoniator-granulator. Figure 6 is a sketch illustrating this device. This mechanism will rotate the distributor bars that are normally used in the ammoniator-granulator. Many operators have reported difficulty with buildup and the positioning of the distributor bars in the ammoniation-granulation equipment. This rotating device provides a means whereby the distributor bars can be rotated out of the bed of material in the granulator so that they can be cleaned without shutting down the equipment. It also provides a means of positioning the distributor while the granulator is in operation. The rotating mechanism consists of an electric motor that drives a chain that causes the distributors to be rotated clockwise or counterclockwise. A brake drum is installed on one end of the distributor support bar, and this drum is used to lock the distributor at a desired position.

Many manufacturers with the larger granulation plants are now installing preneutralizers and scrubbers so that they can use large quantities of phosphoric acid and ammonia to produce diammonium

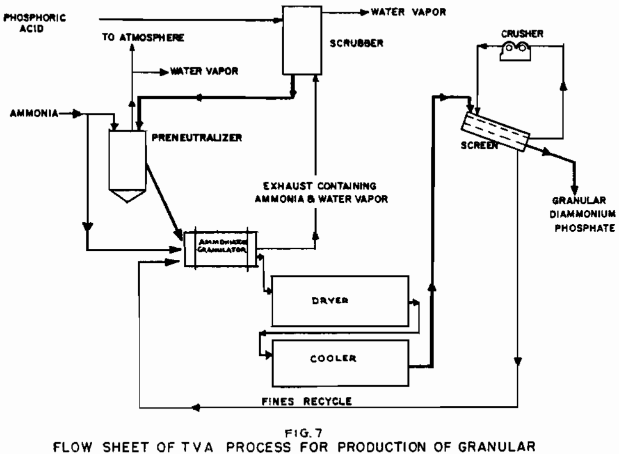


FIG. 7

FLOW SHEET OF TVA PROCESS FOR PRODUCTION OF GRANULAR DIAMMONIUM PHOSPHATE

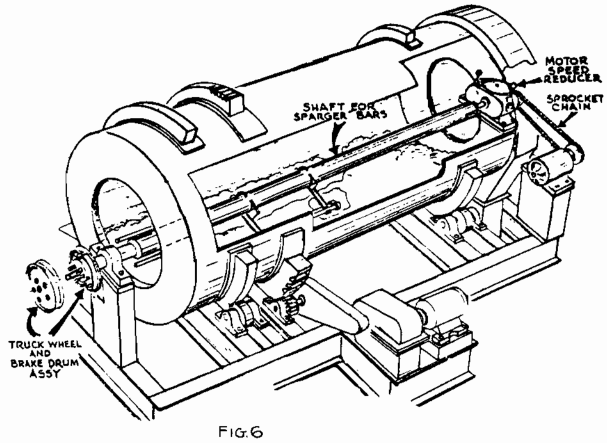


FIG. 6

AMMONIATOR GRANULATOR WITH ROTATING SPARGER BARS phosphate grades. Most of these are using the TVA process for the production of diammonium phosphate grades. Figure 7 is a flow diagram of this process. The process involves the partial ammoniation of phosphoric acid in a preneutralizer and the complete ammoniation to diammonium phosphate in the ammoniator-granulator. The phosphoric acid is ammoniated in the preneutralizer to NH_3:H_3PO_4 a mole ratio of 1.4 to 1.5. At this mole ratio there is a maximum solubility of the ammonium phosphate. Therefore, it is possible to obtain a concentrated slurry of satisfactory fluidity for the proper distribution of the slurry in the granulator. Further ammoniation of this slurry to diammonium phosphate in the granulator decreases the solubility of the salts, and this in turn results in a relatively low liquid phase in the granulator. These conditions are conducive to low recycle rates and high production rates.

Many manufacturers have found that by converting their conventional granulation plant to this process they can use over 900 pounds of phosphoric acid per ton of product. This quantity is far in excess of the usual 200 pounds of phosphoric acid per ton of product that was formerly used in the conventional plant.

When this process is used, a high degree of ammoniation of the phosphoric acid can be used—namely 9.6 pounds of ammonia per unit of P_2O_5. This degree of ammoniation of phosphoric acid is 33 percent higher than the 7.2 pounds of ammonia per unit of P_2O_5 that has been used in a conventional plant with an ammoniator-granulator. Because of this high degree of ammoniation, the economics of producing fertilizers in conventional granulation plants can be improved.

Some companies now produce high-analysis grades such as 8-24-24, 10-20-30, 12-24-24, and 20-10-10 by this process. Some of these companies are marketing their high-analysis grades through bulk handling stations. They have found that by producing high-analysis grades they decrease their transportation cost, and they market their products farther from their plants. A typical granulation plant of this type produces more than 70,000 tons per year, and these products are marketed through bulk handling stations.

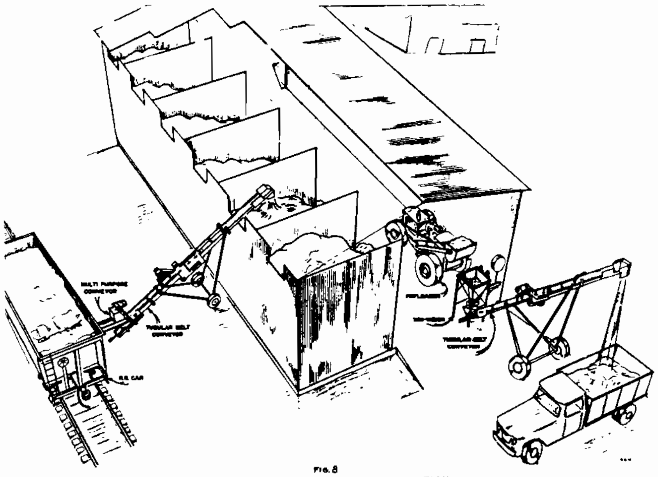


FIG. 8
GROUND STORAGE BULK BLENDING STATION

A typical bulk handling station is shown in Figure 8. At this station there is a 6-bin storage building. Each bin is about 12 feet wide and 30 feet long, and usually holds about 75 tons total capacity of the bins, therefore, is about 450 tons for all grades. These bins are usually used to store superphosphate, ammonium nitrate, potash, and three mixed fertilizer grades. The materials are usually transported to the bulk handling station by hopper-bottom railroad cars or by large transport trucks. A belt conveyor that fits under a hopper-bottom car is used to unload the materials. This belt conveyor empties into a portable conveyor that conveys the material to each of the storage bins. Materials are removed from the storage bins by means of a front-end loader. They are weighed in a scale hopper that is mounted above an inclined portable belt conveyor that empties into the bulk truck.

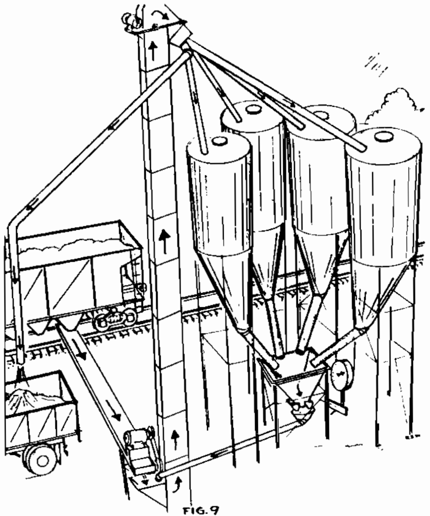


FIG. 9
BULK HANDLING STATION WITH ELEVATED STORAGE

Other types of bulk handling stations use elevated storage tanks. Figure 9 is a sketch of a typical station of this type. Such a station usually has six tanks, each of which holds about 50 tons. Materials are removed from the railway by a belt conveyor and are elevated to the storage tanks. The materials from the storage tanks are weighed in a hopper scale that discharges into the same elevator that is used to load the tanks. This elevator is used to convey the materials to the bulk truck.

Cost studies indicate that a bulk handling station of this type can be constructed for a cost of about $15,000. Cost studies indicate also that the high-analysis grades such as 10-20-30 can be marketed through a granulation plant with bulk handling stations at costs that are competitive with the cost of bulk blending. If a bulk handling system is to be competitive, however, it is imperative that the total movement from the granulation plant be as high as possible. Previous cost studies have shown that a granulation plant operating in conjunction with bulk handling stations cannot be competitive with bulk blending when only 30,000 tons of material is moved through these stations. Other calculations indicate however that with a 70,000-ton movement considered, the economics of this production and marketing system may very closely approximate those of bulk blending.

MODERATOR REYNOLD: Thank you very much, Frank.

I think we have time for some questions. I think this has been an excellent presentation, bringing us up to date.

Any questions from the floor?

A MEMBER: What was the mixer on that last bulk blender?

MR. ACHORN: I guess you missed the point or I must not have spoken plainly. We are talking in this case—can you put the last slide on—this is a bulk handling station, see slide #9 and what we are talking about here is to make complete grades instead of blending in a marketing plant. A complete mixture is delivered to the marketing plant. Because a high analysis grade is sold the transportation and handling cost per unit of plant food should be low, and by having a high enough movement through this marketing system a low fixed and operating cost should be realized, and this system may be competitive with bulk blending. It is imperative that you get your fertilizer movement high and our calculations show as high at 70,000 tons. So that is a bulk handling station. It is not a bulk blending unit.

MODERATOR REYNOLDS: There is another question, Frank.

A MEMBER: On your diammonium phosphate process, would you mind reviewing again why you can ammoniate to such a high degree by that method as opposed to the conventional method?

MR. ACHORN: Can you get us back to slide number 7. In this process, you feed your phosphoric acid to a scrubber. This is usually an impingement type scrubber, and the overflow from the scrubber goes into the preneutralizer and enough ammonia is added to bring the mole ratio, ammonia to phosphoric acid mole ratio to 1.4 to 1.5. This is the maximum solubility point of phosphoric acid and ammonia.

Therefore in this process water is evaporated in the preneutralizer which results in a concentrated slurry being delivered to the granulator so you keep your liquid phase low in the granulator.

MODERATOR REYNOLDS: Can you hear Frank in the back?

VOICES: No.

MR. ACHORN: Oh, I thought everybody could hear me.

At the NH_3: H_3PO_4 mole ratio of 1.4 to 1.5, which is the maximum solubility point and which, I might add, is where they make all liquid fertilizers so that they won't salt out. Therefore in this process we have the most concentrated slurry possible being delivered to the granulator. This slurry has a moisture content of less than 20 per cent.

This slurry is added to the granulator and additional ammonia is added to increase the NH_3: H_3PO_4 mole ratio in the product which lowers the solubility of the ammonium phosphate salts in the granulator, which lowers the liquid phase in the ammoniator-granulator. However at this degree of ammoniation ammonia is lost. This ammonia is captured by the incoming phosphoric acid in the scrubber.

I might add, I think these figures are close to being correct, and I will give you a good example, Ithink that about 110 pounds of a salt mix containing 50% MAP and 50% DAP will stay in solution at 32°F.; whereas, if MAP is dissolved in water, only about 30 pounds of salts will remain in solution and with DAP only about 35 pounds of salt stay in solution.

This gives you some idea of what you are trying to control, namely a high solubility in the preneutralizer by having a mixture of M.A.P. and D.A.P., in the preneutralizer and a low solubility in the granulator by ammoniating the slurry to DAP which has relatively low solubility.

A MEMBER: Frank, can you make monammonium phosphate or 13-52-0?

MR. ACHORN: Yes, in fact, that's an old standard process, really. You don't need the scrubber in that case because you won't be getting any loss from your granulation.

A MEMBER: But you're still maintaining NH_3: H_3PO_4 mole ratio of about 1.4 to 1.5 in the preneutralizer.

MR. ACHORN: I think that there are two methods of doing it, actually. One of them is to go to 1.45 in the preneutralizer and then after the slurry has been added to the granulator, phosphoric acid is added to bring the mole ratio of the product down to one.

Recently, it has been found there is another solubility point at a mole ratio of around 0.6 moles of ammonia per mole phosphoric acid. Then in this method a mole ratio of 0.6 is maintained in the preneutralizer, and then in the granulator this mole ratio would be increased to 1.0 by the addition of ammonia in the granulator.

A MEMBER: What happens with ammonia loss in your dryer? Do you lose the ammonia in your dryer?

MR. ACHORN: We have been operating and the people that we have been working with in the field have been keeping the drier temperature below 200 degrees Fahrenheit, and we haven't had an appreciable loss. We haven't measured it in the field. I know that in our plant we usually try to keep our diammonium phosphate plant dryers products temperature below 185 degrees.

Moderator Reynolds: We have one more question over here.

A MEMBER: How much ammonia do you lose in the preneutralizer? I see it doesn't go into the scrubber.

MR. ACHORN: We have had various opinions on how much ammonia you lose from the preneutralizer.

Actually, this diagram shows that it doesn't go into the scrubber. If this concerns you, you can always put your preneutralizer exhaust gas into the scrubber. But, personally, I have found out in starting off these plants that unless you exhaust to the atmosphere, when your scrubbber is cold, you have a difficulty with water collecting in the scrubber. So that, in a sense, you are chasing yourself around the plant with your water balance, and it takes a considerable length of time to get your plant settled down.

So what I usually recommend, is to vent to the atmosphere and then have a damper so that this preneutralizer exhaust can shift over into the scrubber after they get running.

But, I think, if you go around and look at the plants, that have got it, most of them are operating venting to the atmosphere without running in the scrubber and they are not showing an appreciable loss, but no measurement has been made.

We had some measurements made in a pilot plant. I believe that showed 5 per cent of the ammonia that was fed to the preneutralizer itself.

MODERATOR REYNOLDS: Thank you very much, Frank.

We will move along to our next speaker on granulation facilities, which were widespread in the Midwest 5 to 8 years ago and this type of processing spread further to the East. Shortly after that and more recently, it has penetrated the Southeast with greater acceleration than most of the forecasters of 5 years ago could even visualize.

We are fortunate this morning to have with us our good friend, Mr. Frank Nielsson, of International Minerals and Chemicals, with us to share IMC's experience in the Southeast.

MR. F. T. NIELSSON: (International Minerals and Chemicals): I would just like to steal some of Achorn's thunder with all these questions about DAP, in that I think it is the 1960 or 1961 proceedings of the Round Table where Federal Chemical gave a talk on the DAP process and if you will go back and read that one, you will be all set because they say in there that this is about the only process that no matter what the devil you do, you can't goof off, and this is so.

IMC's Southeastern Granulation Units

F. T. Nielsson

IN the fall of 1963, IMC made a study of fertilizer production trends in the Southeast area comprising the states of Tennessee, Mississippi, Alabama, Georgia, North Carolina, South Carolina and Florida.

Some of the findings were:

1. All indications point to a relatively rapid transition from pulverized products to granular products in the Southeast.

2. In the last three years, granular consumption has risen from 10% to 40% of total mixed goods consumption.

3. Forty-one granulating units averaging 38,000 annual tons each have been installed and ten additional installations are under construction.

4. Twenty-two companies including all of the major producers are now manufacturing granular fertilizers; and five additional companies are planning installations.

5. IMC at present (1963) has no facilities to produce granular goods of the *desired* type in this area.

Based on the above, a decision was made to install 30 ton per hour granulation units with necessary storage, shipping and loading components at Americus and Augusta, Georgia; Florence, Alabama; Winston-Salem, North Carolina and Spartanburg and Hartsville, South Carolina.

The Americus unit was to be on stream for the '64 fall season and the remaining units were to be ready for the '65 spring season.

Because of the time element involved, a critical path program for each plant was set up by IMC's Plans Division. After the board approved the Americus plant on January 9, 1964, the plant was scheduled to start up in seven months, allowing two and a half months for planning and design and four and a half months for construction. The items on the critical path were those where lack of performance would jeopardize the starting date. The items above and below the critical path were those that proceeded simultaneously with the main stream, but their performance had some leeway regarding completion. A sales program was set up concurrent with the construction program and the various sales functions became a part of the critical path diagram also. This type of planning paid off because Americus started on the appointed day.

FEECO of Green Bay was awarded the Americus, Hartsville and Winston-Salem contracts, while the Augusta, Spartanburg and Florence contracts were awarded to Sackett of Baltimore. Major design, awarding of contracts, and construction supervision were handled by IMC's Engineering Services group.

The granulation unit itself was set up in a separate structure, with dry base being prepared in the existing building and finished product moving also into the existing

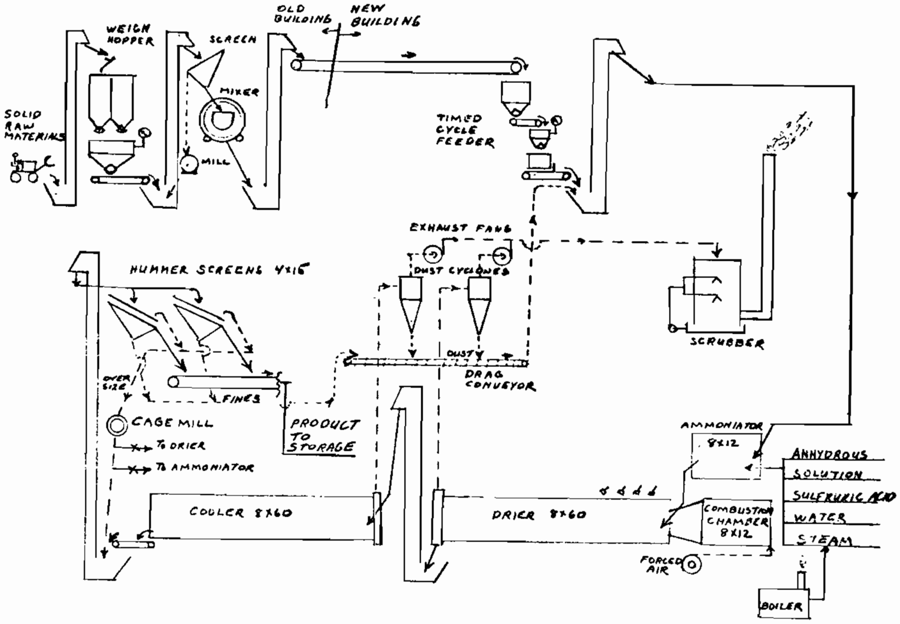


Figure 1.

building, or into a new storage addition.

This schematic of the Americus plant (Fig. 1) shows the old basing mill being modernized with a cluster hopper, followed by a mixing drum. The dry base is transferred to a time cycle feeder, then into an 8x12 ammoniator, an 8x60 cocurrent dryer, 8x60 cooler, over two 4x15 double deck Hummers, oversize through a 40 inch cage mill, screen aid cyclone fines back to the ammoniator feed elevator via a drag conveyor, 6x14 product to storage with dryer and cooler exhaust gasses passing through Buell cyclones and out through a wet scrubber. Rotameters are used to measure sulfuric acid and nitrogen solution, a magnetic meter is used for phosphoric acid and a turbine meter for ammonia. Combustion chambers are pressurized. A 150 Hp. Kewanee boiler is installed at each plant to generate steam as an aid to granulation.

The schematic of the Augusta plant (Fig. 2) shows the same setup as at Americus, except that the existing Atlanta-Utility weigh hopper on the existing base mill is used to proportion the dry materials.

All six plants substantially are similar except that at Spartanburg and Florence the dryer and cooler are "stacked" above each other because of the narrow land area available instead of being side by side as in the other plants.

The following slides will take you through the Augusta plant using construction photos as a guide.

First we see the kind of building to which the granulating unit was connected and next the kind of elevators that had to be replaced. Here we see a conveyor taking dry base from the old building to the time cycle feeder system, which is the start of the operation in the new building. Next we see the liquid unloading station followed by a view of the solution and acid rotameters. Next we have a partial view of the control board which is housed in a separate room. The buttons that activate the various motors are set in a pictorial sketch of the equipment involved. A flow sheet control board like this is a big help in teaching the proper sequence of starting and stopping equipment. Ammeters are in the circuit of every motor except those mounted on belt conveyors.

The time cycle feeder discharges into a 66 foot high elevator that feeds the ammoniator shown here being unloaded and then hoisted into place. Here we have a closeup of the sparger support in the ammoniator. The dam is 2 feet back to yield a 10 foot ammoniating section. Next we have a view of the dryer being unloaded and positioned on the trunnions followed by a view of the cooler being transferred onto its support. Here we have an end view of the dryer showing the flight design followed by a view of the dryer and cooler in position side by side. The dryer and cooler exhaust gases pass through cyclones, the one for the dryer being shown here. After the cyclones the gases pass through 25,000 cfm fans and into the wet scrubber. The scrubber, built of cypress, has a separate 2 pass system for the dryer and for the cooler. The inlet side contains wooden grids wet by recirculated water from the sump. The exit side contains polyethylene packing for demisting. The ducts to the scrubber and the exit stack from the scrubber are made of glass re-enforced epoxy resin and here we see the epoxy stack discharging water vapor.

Next we have the 6x14 mesh product going to storage from where it can be bagged or bulk loaded into box cars, side dump trailers, or pneumatic discharge transports.

Architecturally, the transite covered granulation buildings are quite impressive whether standing alone as at Augusta (Fig. 3) or when sandwiched into the main building as shown at Americus (Fig. 4). Most of the contractors used staging to erect the siding, but here we see one who used scaffolding. For a 70 foot high building this was quite a project, that almost delayed the completion date.

The superintendents and foremen from the new units were sent to existing granulation plants for training. Classes were held in formulation techniques and granulation technology. During start up, we

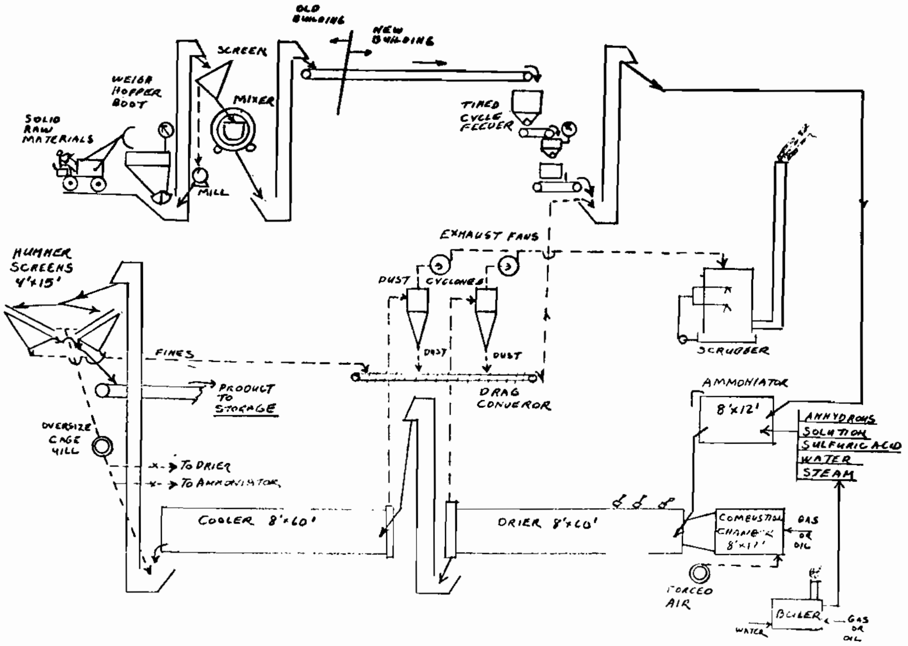


Figure 2.

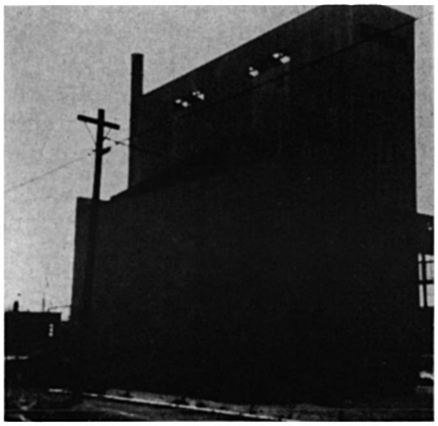


Figure 3.

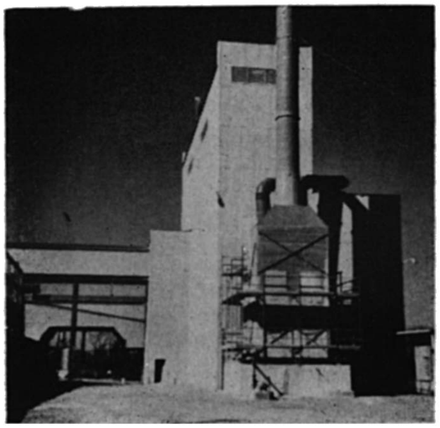


Figure 4.

borrowed experienced foremen from existing plants and called on IMC's technical service group for help. When Americus started up the entire technical resources of the Division were available to lend a hand. However, the other five plants came on stream within a period of a month of each other. This resulted in quite a stretching of experienced personnel to aid in start up because the entire division was busy filling up the house for the spring season.

Looking back, the building and start up of these six units within the alloted time interval made the word TEAMWORK a living symbol at IMC.

MODERATOR REYNOLDS: Thank you, Frank.

We have time for a few questions. Are there any questions?

Okay, if there are no questions, I think we'll go on to our next item on the agenda, which is the coffee break. This is something new with us. We have had breaks in the past, but this is the first time we have had an official coffee break. So when we pound the gavel and try to get you back in here, be sure that you respond. Okay, we will return in about 15 to 20 minutes.

MODERATOR REYNOLDS: I think you all are being very cooperative in getting us back on the program again.

Our speakers for the balance of the morning, discuss more the nitrate type of behavior in processing. As we all recognize, there is a trend to higher analysis which continues and one of the raw materials which is essential to increase concentration is ammonium nitrate in some form.

The use of ammonium nitrate brings about certain problems and certain things that we need to know more about. We get into such terms as increased hygroscopicity, increased liquid phase, heat sensitive materials and so on. So, as a result, we need to know more about what actually happens to the ammonium nitrate in processing.

We are very fortunate this morning to have a good friend, Bert Tucker of Solar Nitrogen Chemicals with us to discuss the subject Crystal Structure Changes In Ammonium Nitrate during processing.

Crystal Structure Changes in Ammonium Nitrate During Processing

H. H. Tucker

WHILE talking with Dr. Sauchelli at the recent Fertilizer Control Officials meeting at Clemson, I referred to some problems experienced in handling bulk ammonium nitrate in hopper cars. After Dr. Sauchelli had asked various questions, he then asked that I make some statements at the Round Table concerning our experiences. I felt that perhaps all of you have had similar experiences. However, Vince felt that this was something which might be worthy of discussion.

The problem I referred to was caking of ammonium nitrate. When thinking of caking I believe we most usually think in terms of moisture. However, customer complaints with hopper cars of ammonium nitrate showed most of the material to be in good physical condition. The only caked material was on the sides of the hopper cars. It is difficult to attribute this to moisture since caking did not take place over the top of the material.

There is published data, of course, to the effect that ammonium nitrate changes crystal form as it passes through certain critical temperature points. Published information will be shown in the first two slides.

Crystal Forms of Ammonium Nitrate

Modification	Temp. Range °F.	Crystal System
I	257-337	Cubic
II	184-257	Tetragonal
III	90-184	Rhombic
IV	1.0.4-90	Pseudo-Tetragonal
V	Below-0.4	Tetragonal

Slide 1.

This seemed to be a possible explanation for the hopper car caking difficulty, particularly since the hopper cars were painted black and constructed of steel which would absorb heat from the sun very readily. We have received reports which stated that caking was much thicker on the south side of the car then on the north side. When the hopper cars were opened, most of the material flowed freely and was in good condition, but the car did not completely unload.

While visiting a bulk blending plant I observed a sample of blended material which was placed in a glass fishbowl for demonstration purposes. This fishbowl had been standing in the window where it would be subject to temperature changes much as would the sides of hopper cars. The ammonium nitrate had disintegrated to various degrees at various points in the glass fishbowl. Greatest breakdown, or "sugaring" as it is sometimes called, occurred on the side next to the window. The top of the jar, where the heat from the sun's rays would be greatest, showed greater breakdown than did material in the bottom of the bowl. A second sample which had been stored on the opposite side of the room where it was not subject to the heat of the sun, was still in excellent condition.

To attempt to find out as to whether this heat cycling effect might be causing the problem and to determine as to the amount of time or number of heat cycles required to cause setting, we carried out some work in our laboratory. Blends were made using varying amounts of ammonium nitrate with diammonium phosphate and potash. Also, straight ammonium nitrate was included in the tests. The next slides show results of these tests. Of particular interest is the breakdown of prills and the expansion observed, both of which contribute to caking.

Changes During Crystal Transition

Transitions	Transition Temp. °F.	Volume Change
V-IV	-0.4	2.9% Shrinkage
IV-III	90	3.6% Expansion
III-II	184	1.3% Shrinkage
II-I	257	2.1% Expansion

Slide 2.

Summary

This is not an attempt to specifically present a solution to this problem, but merely a report of experiences. The following paper I believe will have something to say about the possibility of methods of solving this problem.

There is no doubt a number of things which would affect this degree of setting in addition to the cycling through this critical heat point of 90°F. These perhaps are; prill density, moisture content and diluents or contaminants in the ammonium nitrate as well as types of conditioners.

The amount of heat absorbed and its transfer into the ammonium nitrate would of course vary with the type of container or car; the amount of insulation; the color of the car, the size of prill which might determine the amount of air space and rate of heat transfer; and the amount of conditioner which might act as an insulator. Some cars have been insulated. One insulation material used was a polyurethrane -type of paint. This paint, as you know, expands after application and gives a good insulation affect.

Recent work has indicated that materials may be added to ammonium nitrate which will change the critical cycling temperature. However, this is not the object of this discussion. I am sure there will be other discussions about changing the critical cycling temperature.

MODERATOR REYNOLDS: Thank you very much, Bert.

I am sure that at the end of the next two papers, together with Bert's paper, we will have some questions thrown in, but are there any questions right at the moment here that you would like to ask?

There is a question in the back.

A MEMBER: Is there any loss of nitrogen due to the cycling?

MR. TUCKER: We have no record of any and I would anticipate none because it is merely a change in the form of crystal, but we didn't go into that study. This is just merely a report of experience and I could not see how there could be any.

A MEMBER: Do you know the loading temperatures of the materials?

MR. TUCKER: We have had some cases where the material was loaded hot and we find that where the materials was loaded hot and then it cools down we have immediately gone to one cycle change. Yes, you will have more setting if the material is loaded hot.

Joe has just asked me to redefine what we had as far as this cycling. As you saw, the critical cycling temperature that is most effective here or that caused the most effect here is this 90 degree temperature.

We consider the cycle a change from 70 up to 110 and back to 70 degrees, which was a complete cycle. That was going up through the temperature change and a critical point and back down and then we took our photographs at each cycle.

A MEMBER: How many cycle changes were possible for the material in the hopper cars?

MR. TUCKER: We frankly don't know because we don't know how the temperature causes the changes that took place. We just know that we had experiences of caked material. We also know that in our testing that we found some materials—We had one case where we had material where, I don't know that the difference was, but we even broke those jars on the fourth cycle. So we had quite a bit of compression. That is the reason why I made the statement that there are other things, no doubt, contributing to this, as to its critical moisture content. I have information to indicate that a three-tenths per cent moisture is much worse than even a two-tenths as far as affecting the cycling is concerned.

We don't know how many times they went through that but we do know that they went through enough that we had caked material on the sides of the hopper cars.

MEMBER: How many days in route were the hopper cars?

MR. TUCKER: We went back and tried to check this as to the three things:

First, how long were the hopper cars loaded before they were shipped?

How long were they in route and how long were they at a point before they were unloaded?

We have no consistent information on that but I would say it would be ten days or so.

MEMBER: Low density or high density material?

MR. TUCKER: We have had both and we experience this decomposition with both low density and high density prills.

MODERATOR REYNOLDS: One more question in the back.

A MEMBER: You mentioned the problem first became apparent in the hopper cars on the caking. Have you checked the moisture content of the ammonium nitrate? Do you know whether that moisture content—at what level was it?

MR. TUCKER: Most of the material goes out at about .13 per cent moisture, very, very low. Then we had one sample of material that was up about .25 and that material seemed to cake more readily than did the lower moisture content material. But it was considered very good material. We have all had experience, I'm sure, with ammonium nitrate caking in bags, perhaps due to the same thing. We probably most often thought it might be moisture but it was accentuated in these hopper cars because they were painted black and they absorbed heat so readily.

Moderator Reynolds: Thank you very much, Bert.

We will move along to our next speaker. As Bert has indicated, perhaps there are some other areas here that should be investigated and our next speaker has done some work in this field to determine the effect of potassium nitrate additive on nitrate conditions.

Mr. R. J. Harvey of the Southwest Potash Corporation will be our next speaker.

Effect of Potassium Nitrate Additives on Ammonium Nitrate Conditions

Robert J. Harvey

In order to broaden the market for potassium nitrate, we decided to investigate the effects of potassium nitrate addition to ammonium nitrate, not only in the small percentages for conditioning but up into the larger percentages for high analysis fertilizers.

This work is not new, the original phase diagram was done in Germany in 1932, work was done in Canada in 1941, in England in 1946, and has continued and the latest two papers are both by Coates and Woodword out of England in 1963 and 1965. However, most of this work was directed toward x-ray diffraction studies and not to how the properties of ammonium nitrate as modified by potassium nitrate affects storage conditions.

We will take a look at the first slide now.

Ammonium Nitrate

1 Density
2 Transition Temp.
3 Expansion on Transition
4 Cumulative Expansion
5 Critical Humidity
6 Degree of Hydration
7 Caking
8 Pressure Setting

Question Is:

How do all these properties relate to storage in the field—and how does KNO_3 addition affect these properties.

Slide 1.

(Slide I) Here are some of the properties that Mr. Tucker has been discussing. Number One is the density. Prills may be either high density, intermediate or low density, depending upon the degree to which the ammonium nitrate solution is concentrated and the height of the tower.

The surface condition of prills varies, the high density usually being harder and having a more glossy surface, the low density prill being somewhat more porous.

Next is the transition temperature. As Mr. Tucker discussed the important one is the one at 90 degrees Fahrenheit going from Form III to Form IV.

Connected with that is the expansion on that transition and as Mr. Tucker again showed you that in going from Form IV to Form III there is an expansion of about 3.6 per cent. Form IV is more dense than Form III.

This expansion as shown in those previous photographs is cumulative and is irreversible for practical purposes so that the number of times that you go through the expansion times the expansion factor is usually the net result that you come up with. As you can see, the volume increased for the ammonium nitrate quite considerably.

The critical humidity is the humidity at which the particle picks up moisture at a given temperature from the air but probably more important is the actual water content of the air in contact with the particle.

The degree of hydration or the so-called desiccant effect refers to how much water can the particle pick up and at what rate does it absorb this water.

Number 7 there is caking. Again density and surfaced hardness have an effect on caking as well as the hygroscopicity, changes in temperature will affect caking and the number of contact points between particles. So that, the smaller and finer particles you get, the more caking.

The last one there is pressure setting and primarily refers to the fact that in a bag the number of contact points increase as you go through the cycling transition and the resultant pressure build-up in the bag tends toward increasing pressure setting.

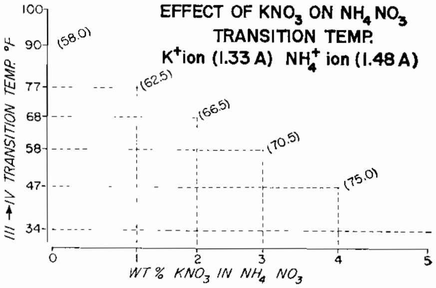
It is pretty difficult to differentiate completely between caking and pressure setting as such.

Now, let's talk about the effect of potassium nitrate on these properties.

Number 1, there is a slight effect on the density, with the density increasing as you add potassium nitrate. It is not particularly noticeable however.

The density again does have an effect on the particle breakdown when cycling through the transition temperature, the more dense prills being more compact when going through this temperature will tend to break up a little more than lower density prills.

Potassium nitrate lowers the transition temperature as shown on the next slide.



Slide 2.

(Slide II) Attempts have been made to raise this transition temperature and there is at least one substance we know of that does this. However, there are other properties that do not make it entirely suitable. Potassium nitrate lowers the transition temperature as is shown on the slide.

Potassium nitrate also lowers the expansion on transition and this will be developed a little more on the next slide and as a result of lowering the expansion, obviously, you are lowering the cumulative expansion.

The hygroscopicity is reduced. Now, potassium nitrate is considered a non-hygroscopic material, based on the usual laboratory criteria. With small percentages of potassium nitrate added to ammonium nitrate such as one per cent and two per cent, our data at 81 and 90 per cent relative humidity indicate that the hygroscopicity is reduced slightly. With greater percentages of potassium nitrate the reduction is more significant.

The degree of hydration, the effect of moisture on the prills is the same for ammonium nitrate with potassium nitrate added as it is with ammonium nitrate itself. We have a slide that we'll show later that will illustrate this a little better. The other common additive in the ammonium nitrate field is magnesium nitrate or a mixture of magnesium and calcium nitrates. These materials do have the property of being able to absorb a certain amount of water before they encounter this physical breakdown during the cycling.

Finally, potassium nitrate, of course, by reducing the hygroscopicity and preventing particle breakup due to transition reduces the number of contact points and it does reduce the caking.

Now, to pick out the items that are most important, we would pick out the transition temperature, the degree of expansion on transition and the so-called desiccant effect or how much water the particle can pick up and the rate at which it does pick it up.

This slide, here, does show the effect of potassium nitrate on the transition temperature. As you increase the per cent of potassium nitrate, the transition temperature is decreased from 90 to lower temperatures.

I must emphasize that this curve is drawn generally. Those are not fixed points you see there but rather a range of temperatures.

For instance, at four per cent potassium nitrate we indicate a temperature of 47 degrees for transition. We have actually run cycling tests from 36 up to 130 and back down again 12 times and never did pass through the transition temperature with four per cent potassium nitrate. So you can consider this as a generalized chart illustrating the point rather than absolute numbers.

The ionic radius of potassium is 1.33 angstrom units and for the ammonium ion it's 1.488 angstrom units. Because of this difference in ionic radius, the replacement of ammonium ion by potassium ion is favored in the ammonium nitrate III structure and actually potassium nitrate increases the range of temperatures for ammonium nitrate III to exist. Also because the potassium ion is smaller, the crystal lattice is shrunk and the shrinkage takes place clear on up to 38 per cent potassium nitrate at which time you not only get potassium nitrate as free potassium nitrate but you get a mixture of ammonium nitrate and potassium nitrate.

Effect of Moisture on Expansion Factor

Wt. % Moisture	Expansion Factor	
0.09	1.0333	After cycling
0.13	1.0598	12 times
0.023	1.0990	72°F→132°F
0.25	1.111	and at
0.33	1.114	constant pH

Slide 3.

(Slide III) This slide shows the effect of moisture content of a prill containing 2 per cent potassium nitrate on the expansion factor after cycling 12 times from 72 degrees Fahrenheit to 132 degrees Fahrenheit and with the pH being constant. We have investigated the effect of pH and generally in the desired operating range of 5 to 5½ there is essentially no effect of pH.

If you operate, however, at a pH of 3.8 your particle will show considerable breakdown in cycling tests.

This slide indicates what Mr. Tucker said, that generally as you increase the moisture content the expansion due to cycling increases and generally most people try to get moisture contents down to the 0.13 to 0.15 weight per cent range and we know some people who got down as low as .08. So it is important with ammonium nitrate and ammonium nitrate-potassium nitrate to get the moisture content down.

Normally, if the expansion after cycling does not exceed a factor of about 1.25, the material will have suitable storage characteristics. If it shows more expansion than that, then the storage characteristics may not be so good.

(Slide IV) This slide shows the expansion factor after cycling 12 times with one-tenth of a per cent moisture for ammonium nitrate plus one per cent potassium nitrate and ammonium nitrate plus two per cent potassium nitrate and plus three per cent potassium nitrate. It was cycled in two temperature ranges, one of them being from 72 to 135 degrees Fahrenheit and the other from 45 to 135 degrees Fahrenheit.

As you can see, for the cycling between 72°F and 135°F the material with one per cent potassium nitrate did go through the transition temperature. When you add two percent potassium nitrate, you did not go through the transition temperature, as indicated by the expansion factor.

Now when we lowered the cycling range down to 45°F, you can see, and as you saw from Slide II, that all of the material did go through the expansion. However, the effect of more potassium nitrate is to reduce the expansion factor.

Again, at any particular level of addition the transition temperature is a metastable change, somewhat irreversible but nevertheless metastable.

Expansion Factors . . . After Cycling 12 Times at 0.10% Moisture

Cycling Test	AN	+ 1% PN	+ 2% PN	+ 3% PN
72°F—135°F	1.46	1.29	1.022	1.022
45°F—135°F	1.62	1.43	1.42	1.36

Slide 4.

Effect of Cycling 12 Times on Bulk Density of Higher KNO_3 Mixtures Ammonium Nitrate

Nutrient Ratios	Wt. % KNO_3	Cycling Temp. Range, °F	Bulk Density g./cc.
2-0-1	31.7	72-135	0.97
		32-135	1.0
2-0-1	31.7	72-135	0.98
		32-135	1.0
3-0-1	22.6	72-135	0.96
		32-135	0.99
6-0-1	12.1	72-135	0.96
		32-135	0.98
6-0-1	12.1	72-135	0.93
		32-135	0.95

Slide 5.

(Slide V) This last slide will show the effect of cycling 12 times on the bulk density of materials containing a higher percentage of potassium nitrate. We have nutrient ratios of 2-0-1, 3-0-1 and 6-0-1 and they contain percentages of potassium nitrate by weight from 31.7 down to 12.1.

These were cycled through temperature ranges from 72°F to 135°F and from 32°F to 135°F. Basically what this illustrates is that with this amount of potassium nitrate the transition temperature is depressed so far that under ordinary ambient temperatures you do not encounter the Form III to Form IV transition at all. Actually, it is around 10 degrees Fahrenheit or somewhere down in there.

We feel that such materials with a high nutrient ratio will offer a marketing opportunity for the ammonium nitrate producer.

I would like to say in connection with this program that we have had four commercial tests on production type equipment and one test on a large-scale pilot unit other than the pilot work that we did. We have had difficulty getting a feedback of information in all cases. In one case they reported the results generally favorable on a two per cent potassium nitrate addition.- We are trying to develop that in a little more detail.

In one case the producer made a material of very low moisture content, uncoated, which caked badly and must be considered not satisfactory.

In the biggest commercial test the people made a 6-0-1 nutrient ratio and this material to date is standing up very well.

The fourth test, again we have not been able to elicit any results from the people.

There is a fifth test being planned.

In the way of operation, there doesn't appear to be any difficulty in adding the material to the ammonium nitrate operation.

In two of the tests the people dissolved potassium nitrate in hot steam condensate and then added it to their system and went right through the normal evaporation step with their ammonium nitrate and made the prill material.

In one case the operator dissolved it in 83 per cent ammonium nitrate liquor in a tank and then prilled that material after concentration.

In the fourth case the people merely added the material directly to the 99.7 per cent ammonium nitrate tank and then prilled it. This tank was equipped with an agitator which failed prior to the test but the material was added anyway and went into solution although there were only about four minutes holding time in the tank.

In the fifth test the material is going to be dissolved in 95 per cent ammonium nitrate solution and they happen to be using our prilled material as differentiated from our standard, the difference being that it takes about four times as long to dissolve the prilled material as it does the standard crystal form. The time for dissolution of two per cent with standard material is about three minutes and with prilled material is about 11.

This constitutes the work that we have done with potassium nitrate out in the field. We hope to get more reliable information back from the producers and especially as they relate to storage conditions in the field. As you are well aware, there is no laboratory test that will anticipate all of the problems you are going to have out in the field.

That concludes my remarks and I will be happy to try to answer questions.

MODERATOR REYNOLDS: We have time for some questions.

Let me ask a question. Has this behavior been investigated from the standpoint of the double decomposition of ammonium nitrate and potassium chloride, say, as in a mixed fertilizer operation itself?

MR. HARVEY: Normally most ammonium nitrate producers are concerned about the chloride level and the generally recommended standard, I believe, is 150 parts per million on prilling ammonium nitrate. Some people drop this as low as 60 and some people have gone as high as 300.

Our material normally contains about 200 parts per million of chloride ion as such and when added at the two per cent level it represents some four parts per million and that doesn't really have any significant effect on the decomposition or deterioration of ammonium nitrate. We have been pretty careful about this and the people who ran the material on the 6-0-1 nutrient ratio were careful about this also.

Does that answer the question you had?

MODERATOR REYNOLDS: This was one of them. What I was thinking of was, say, as in a mixed fertilizer formulation when you have ammonium nitrate either in solution as an 83 per cent solution or in an ammoniating type solution with anhydrous ammonia, when you are reacting with muriate of potash—In other words, you don't have any potassium nitrate present —we are always interested in a certain amount of transition between the ammonium nitrate and the KCl to obtain a less hygroscopic material.

In other words, the per cent transition over to potassium nitrate is the point that I am interested in, whether your work has been simulated in that field.

MR. HARVEY: No, I don't think I can answer that particular question.

MODERATOR REYNOLD: I know that several years ago there was considerable work done in the mixed fertilizer granulation area regarding the amount of potassium nitrate formed in the process as related to storage characteristics and I don't believe anyone did any work at that time on the same expansion factors. If they did, I am not familiar with that. But that would be of interest to see if there was similar work performed but not reported.

We will move on to our next speaker and then we promise to come back to the three of them.

Our next speaker is to give us a more or less progress report, to carry on in the same vein here using nitrate materials. During the past two or three years there has been considerable work in the use of potassium nitrate in mixtures not only in the specialty areas for tobacco fertilizers but also as an aid to improve granulation qualities, conditioning and to go to higher concentrations.

Mr. Rodger Smith of Southwest Potash Company will be our next speaker.

Granulation of Mixed Fertilizers Containing Potassium Nitrate

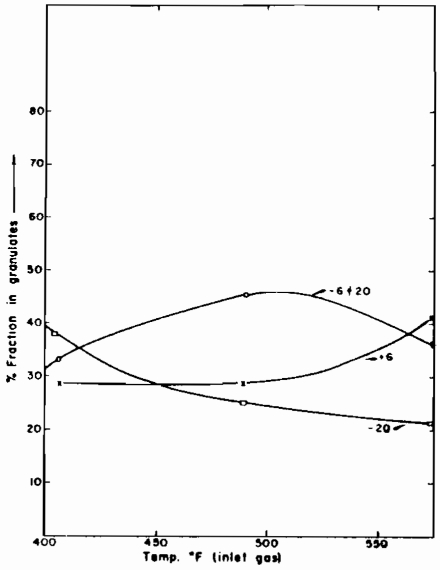
Rodger C. Smith

In 1964 a paper was presented at the Round Table by John Hardesty, then with U.S.D.A., on the solubility characteristics of fertilizer mixtures containing potassium nitrate. At the 1964 American Chemical Society Meeting, papers were presented by Iowa State University and the Colorado School of Mines Research Foundation on the granulation of certain mixtures containing potassium nitrate. A year has passed. In the few minutes available at this time we will attempt to bring to you information on the application that has been made to date of the data reported in 1964. Potassium nitrate has been used in granulation plants varying widely in size and equipment. Formulas presented are typical of those used.

First, for those of you unacquainted with the basic work.

Kamat, Iowa State University, pointed out the relationship of different moisture levels and the yield of 6-20 mesh product as well as the roundness and hardness and lowered the hygroscopicity of the granule. Slide 1.

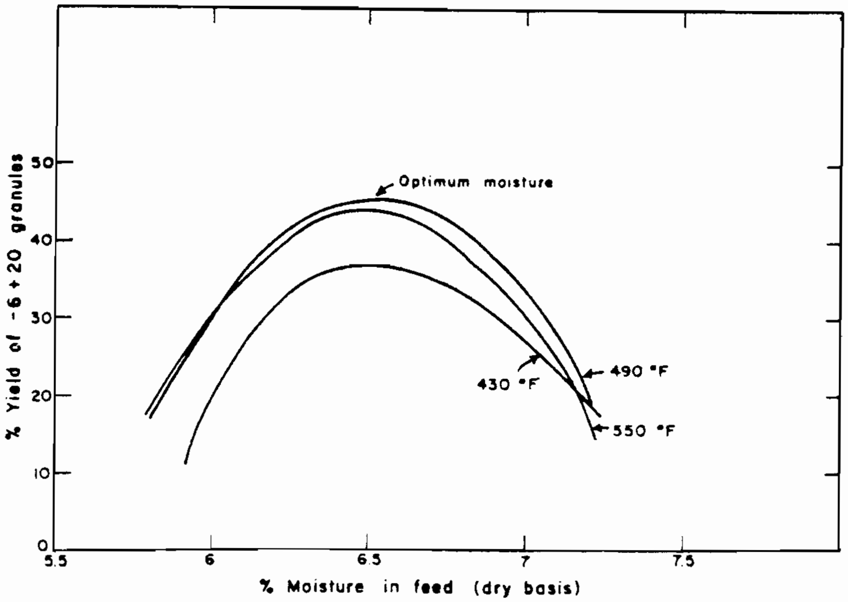
At the optimum moisture, 6.5%, under the conditions of the experiemntal work, temperature of the inlet gas was found to influence the yield of 6-20 mesh granules and the proportion of fines and oversize. It can be generalized that agglomeration increases with increase in temperature of mixtures containing potassium nitrate, a soluble salt. In the experimental work, maximum yield of 6-20 mesh granules occurred with inlet temperature of about 500° F. Slide 2.



Slide 2

You have probably seen this illustration of how the amount of liquid phase of mixtures containing potassium nitrate and other salts is affected by the temperature – moisture relationships prevailing in the ammoniator, dryer and cooler. Potassium nitrate—having a solubility curve twice as steep as ammonium nitrate – greatly encourages granulation in the ammoniator and setting of the granules as moisture decreases in the dryer and temperature drops in the cooler. Slide 3.

Now that agronomic research has proven conclusively that tobacco fertilizer requirements coincide with the properties of potassium nitrate, most tobacco formulas include it. Many of you shudder at granulating a three unit nitrogen



EFFECT OF MOISTURE ON YIELD FOR 5-10-15 MIXED FERTILIZER CONTAINING NITRATE OF POTASH.

Slide 1

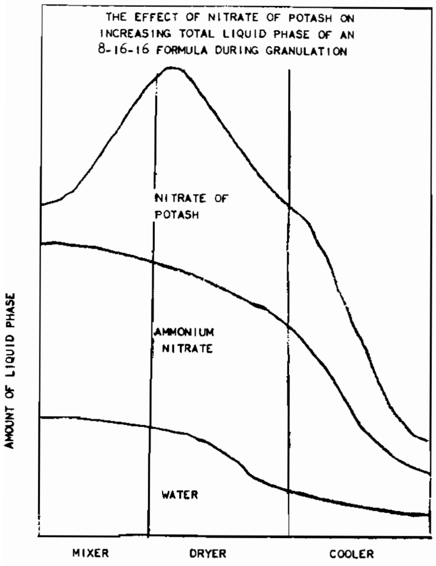
grade, but surprisingly good results are being obtained. Enough potassium nitrate is usually used to achieve 50% nitrate nitrogen. Slide 4.

8-0-24 is very generally used for sidedressing flue-cured tobacco. 100% nitrate nitrogen is recommended. This formula contains 67% nitrate nitrogen. Nitrogen-potash grades are readily granulated in conventional equipment utilizing the heat of reaction of a moderate amount of ammonia and sulphuric acid and the solubility of potassium nitrate. A pre-neutralizer is not necessary. Storage quality is excellent. Slide 5.

1-0-1 ratio grades are also used for sidedressing tobacco. Using essentially the same formulation as for the 8-0-24, this 15-0-15 contains 50% nitrate nitrogen and virtually no chlorine. 100 pounds or more fine limestone is included to neutralize any free acid in the product which may result from variation in rate of metering the nitrogen solution and acid. If dolomitic form of limestone is used, part of the magnesium contained becomes water soluble during granulation. Slide 6.

The market for non or low phosphate grades appears to be only dented. Fertilizing of apples, peaches, citrus in most areas and sidedressing cotton, corn and vegetables in some areas with nitrogen-potash grades is consistent with the findings of agronomic research. Since these crops are not very sensitive to chlorine, this formula uses muriate of potash and only enough potassium nitrate to facilitate granulation and improve storage quality. Slide 7.

Now to general farm fertilizers. This combination of nitrogen sources has been demonstrated to cause excellent granulation. Production rate was increased more than 30%. Product quality in the bin was excellent. 100 pounds potassium nitrate has been found



Slide 3

Slide 4 (3-9-9 Tobacco)

Pounds Ingred.	Ingredients	N	APA	K_2O	MgO	Ammonia Input
		Lbs. of Plant Nutrients				
92	Nitrogen Sol.	41				23
910	Superphosphate		182			
149	Nitrate of Potash	20		65		
223	Sul-Po-Mag.			49	40	
136	Sulfate of Potash			68		
40	H_2SO_4 60° Be.					
200	Fine Limestone					
300	Filler					
2050		61	182	182	40	23

Slide 5 (8-0-24 Tobacco)

Pounds Ingred.	Ingredients	N	APA	K_2O	MgO	Ammonia Input
		Lbs. of Plant Nutrients				
167	Nitrogen Soln. (25-69-0)	75				42
652	Nitrate of Potash	88		286		
223	Sul-Po-Mag			49	40	
298	Sulfate of Potash			149		
153	H_2SO_4 60° Be.					
100	Fine Limestone					
437	Filler					
2030		163		484	40	42

Slide 6 (15-0-15 Tobacco)

Pounds Ingred.	Ingredients	N	APA	K_2O	MgO	Ammonia Input
		Lbs. of Plant Nutrients				
325	Nitrogen Soln. (25-69-0)	146				82
210	Sul. of Ammonia	46				
225	Nitrate of Soda	36				
578	Nitrate of Potash	78		254		
223	Sul-Po-Mag			49	40	
302	H_2SO_4 60° Be.					
100	Fine Limestone					
97	Filler					
2060		306		303	40	82

Slide 7 (15-0-15 General)

Pounds Ingred.	Ingredients	N	APA	K_2O	MgO	Ammonia Input
		Lbs. of Plant Nutrients				
275	Nitronge Soln. (25-69-0)	123				69
743	Sulfate of Amm.	156				
357	Muriate of Pot.			215		
200	Nitrate of Potash	27		88		
253	H_2SO_4 60° Be.					
100	Fine Limestone					
122	Filler					
2050		306		303		69

Slide 8 (6-12-12)

Pounds			Lbs. of Plant Nutrients			Ammonia
Ingred.	Ingredients	N	APA	K_2O	MgO	Input
172	Nitrogen Soln. (25-69-0)	77				43
40	Anhydrous NH_3	32				40
1210	Superphosphate		242			
328	Muriate of Pot.			198		
100	Nitrate of Pot.	13		44		
170	H_2SO_4 60° Be.					
130	Dolomite					
2150		122	242	242		83

Slide 9 (8-12-12)

Pounds			Lbs. of Plant Nutrients			Ammonia
Ingred.	Ingredients	N	APA	K_2O	MgO	Input
344	Nitrogen Soln. (25-69-0)	154				87
22	Triple Superphosphate		10			
1150	Superphosphate		230			
333	Muriate of Potash			203		
100	Nitrate of Potash	13		44		
63	Brucite				41	
125	H_2SO_4 66° Be.					
2137		167	240	247	41	87

Slide 10 (5-20-20)

Pounds			Lbs. of Plant Nutrients			Ammonia
Ingred.	Ingredients	N	APA	K_2O	MgO	Input
116	Anhydrous NH_3	96				116
746	Triple Superphosphate		343			
366	Superphosphate		73			
611	Muriate of Potash			372		
100	Nitrate of Potash	13		44		
175	H_2SO_4 66° Be.					
2114		109	416	416		116

Slide 11 (6-24-24)

Pounds			Lbs. of Plant Nutrients			Ammonia
Ingred.	Ingredients	N	APA	K_2O	MgO	Input
46	Nitrogen Soln. (24-70-0)	20				11
100	Anhydrous NH_3	82				100
420	Phosphoric Acid		226			
353	Triple Superphosphate		195			
350	Superphosphate		70			
677	Muriate of Potash			413		
150	Nitrate of Potash	20		67		
2096		122	491	480		111

Slide 12 (10-10-10)

Pounds			Lbs. of Plant Nutrients			Ammonia
Ingred.	Ingredients	N	APA	K_2O	MgO	Input
340	Nitrogen Soln. (29.7-64.5-0)	159				100
134	Sulfate of Amm.	28				
1021	Superphosphate		204			
162	H_2SO_4 66° Be.					
254	Muriate of Potash			155		
59	Filler					
100	Nitrate of Potash	13		45		
2070		200	204	200		100

to be a satisfactory amount to include in general farm grades in which no claim is being made for any of the agronomic properties of potassium nitrate. Slide 8.

Observing the production of this grade was especially rewarding. In a carefully conducted comparison, the substitution of 100 pounds potassium nitrate for equivalent amount of nitrogen solution and muriate of potash clearly enabled a 50% production increase. Slide 9.

5-20-20 is commonly used when planting corn or small grains. In a large, well equipped plant 275 pounds sulphuric acid was regularly used to achieve optimum granulation. Adjustment of the formula to include 100 pounds potassium nitrate resulted in the reduction of the acid to 175 pounds with maintenance of the high rate of production and somewhat improved screen analysis. Slide 10.

Less experience has been gained with 6-24-24 than with 5-20-20 but improved granulation has occurred when using 100-150 pounds potassium nitrate per ton. Smoother granules and higher percentage of onsize granules have resulted. Slide 11.

10-10-10 is a grade that granulates very easily in some plants and with difficulty in others. This formula was used in a plant having difficulty with excess fines in the product. Adjustment of the formula to include 100 pounds potassium nitrate resulted in 30-35% increase in rate of production and at least as good range of product particle size. Slide 12.

The trend to high analysis mixtures continues. As in the past incorporating good storage quality into high analysis fertilizers is an important problem. This formula approximates that used in specialized equipment to produce several thousand tons in the southeast. Consistently good production and good physical condition in both bulk and bagged storage has been reported. Although potassium nitrate is very soluble at temperatures prevailing in the ammoniator, it is less soluble than muriate at temperatures below 70° F. It is less hygroscopic than muriate at

Slide 13 (12-24-24)

Pounds Ingred.	Ingredients	N	Lbs. of Plant Nutrients APA	K_2O	MgO	Ammonia Input
224	Anhydrous NH_3	184				224
889	Phosphoric Acid		480			
487	Muriate of Potash			294		
420	Nitrate of Potash	56		186		
2020		240	480	480		224

Slide 14 (20-10-5)

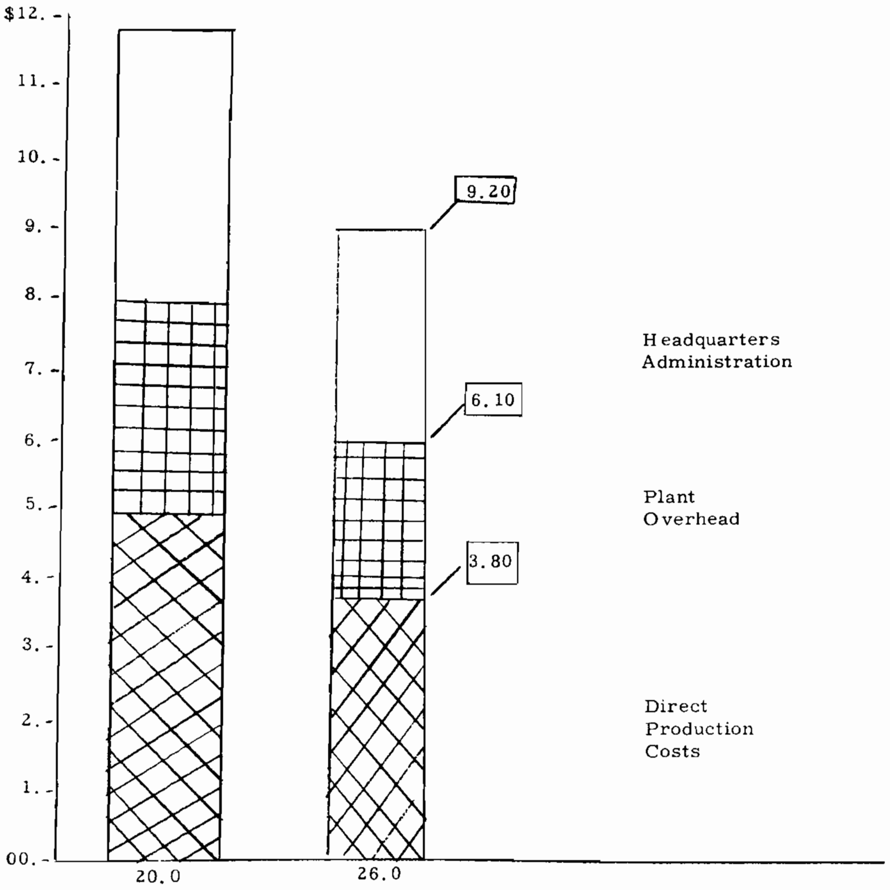
Pounds Ingred.	Ingredients	N	Lbs. of Plant Nutrients APA	K_2O	MgO	Ammonia Input
300	Nitrogen Soln. (30.5-0-43.3)	136				91
81	Sulfate of Ammonia	17				
30	Anhydrous NH_3	24				30
527	Ureaform	200				
70	Phosphoric Acid		37			
137	Triple Superphosphate		63			
512	Superphosphate		102			
261	H_2SO_4 60° Be.					
232	Nitrate of Potash	31		102		
2150		408	202	102		121

the higher and more troublesome humidities. Slide 13.

Light weight lawn fertilizers containing large amounts of vermiculite are difficult to granulate and the specialty fertilizer product manager tends to be demanding as to screen specifications. A formula similar to this one has been granulated in conventional equipment with about 95% on 16 mesh when the lower deck of the classification screen had openings equivalent to 16 Mesh. This 95% was much higher than when using a similar formula that did not contain potassium nitrate . Slide 14.

At this plant as well as at some others the required heat input was clearly less because of less water substituting formulas containing potassium nitrate.

The benefits of using potassium nitrate in mixtures can be shared by both production and marketing departments, and also the farmer. But our primary interest today is production. Rate of production affects direct costs, plant overhead and also general administrative costs. A 30% increase in production when using these types of formulas is realistic. Attempt has been made to obtain costs as affected by varying rates of production. If a plant that normally averages 20 tons per hour can comfortably operate at 26 tons per hour (30% increase) costs other than formula are affected as illustrated. Most plants can benefit financially by a similar expansion of capacity for a part of the year. All plants can benefit when the alternative is large capital outlay to meet growth of tonnage. Slide 15.



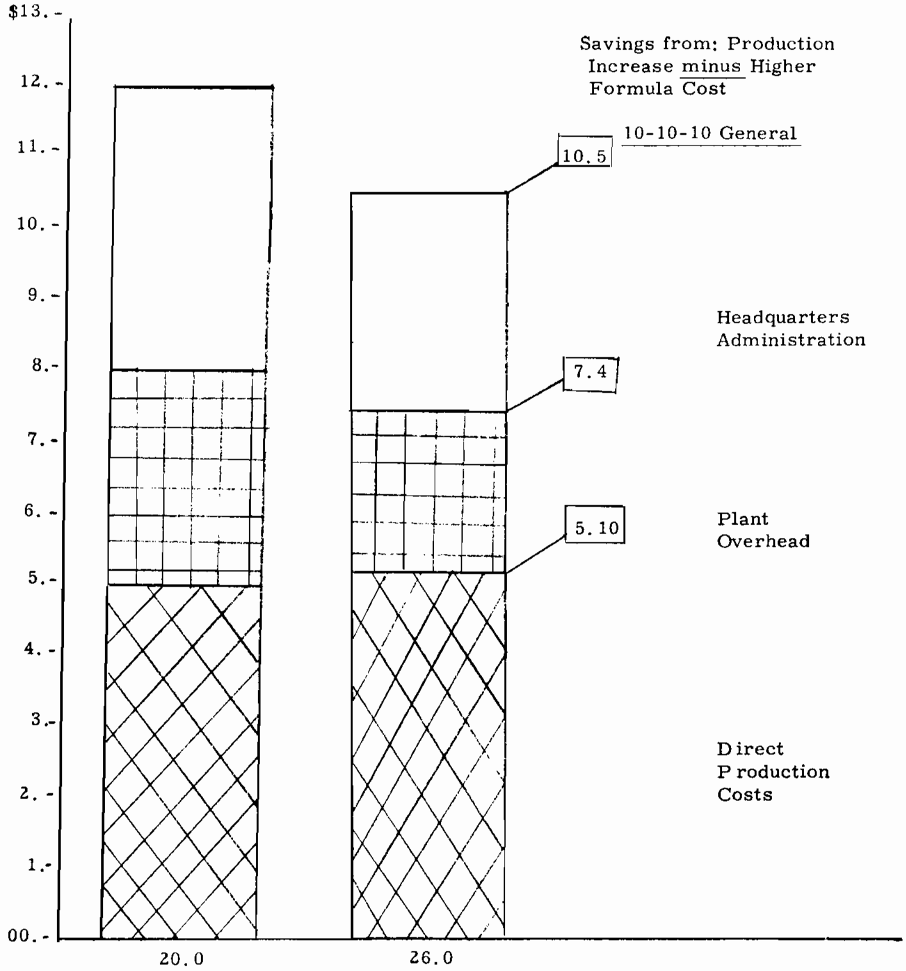
Slide 15

Effect of Increasing Production Rate on COST.

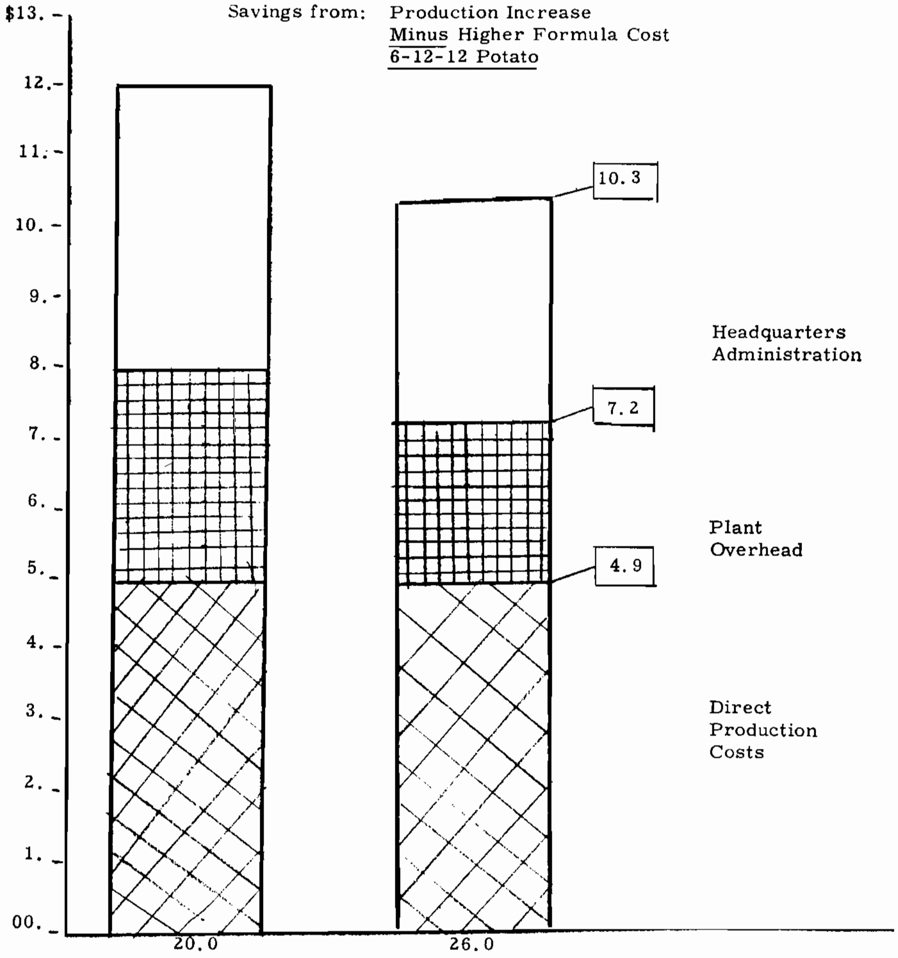
Base Rate: 20 tons Per Hour.

Using the previous manufacturing cost relationship as a base, it is adjusted in the next three slides as affected by changes in formula costs. Three formulas are used which are representative of three broad uses. Slides 16-17-18.

With general farm grades, such as 10-10-10, 100 pounds potassium nitrate is usually adequate to improve granulation as described. Substituting for 13 pounds of nitrogen from sulphate of ammonia and 44 pounds potash from muriate the formula cost increases about $1.30. Note that in this example the savings in overall manu-



Slide 16



Slide 17

facturing exist although the direct operating cost savings are about offset by increased formula cost.

In the formulas used for this cost comparison 80 pounds of potash (1/3 of total) is derived from potassium nitrate instead of from potassium sulphate, the nitrogen contained substituting for nitrogen solution. Although the formula cost increases about $1.10 note that overall savings prevail.

We have a typical flue-cured tobacco formula having 50% nitrate nitrogen. Note that the cost advantages are maintained. It should be pointed out that some manufacturers choose to have improved screen analysis of their product rather than to operate at a higher rate. This is especially significant at this time when screen specifications tend to be tightening.

This is a progress report. You can observe that potassium nitrate has application in widely ranging types of grades. The breadth of these advantages is increasing as more is known about the use of the material in both manufacturing and for specific crops.

MODERATOR REYNOLDS: Thank you, Rodger.

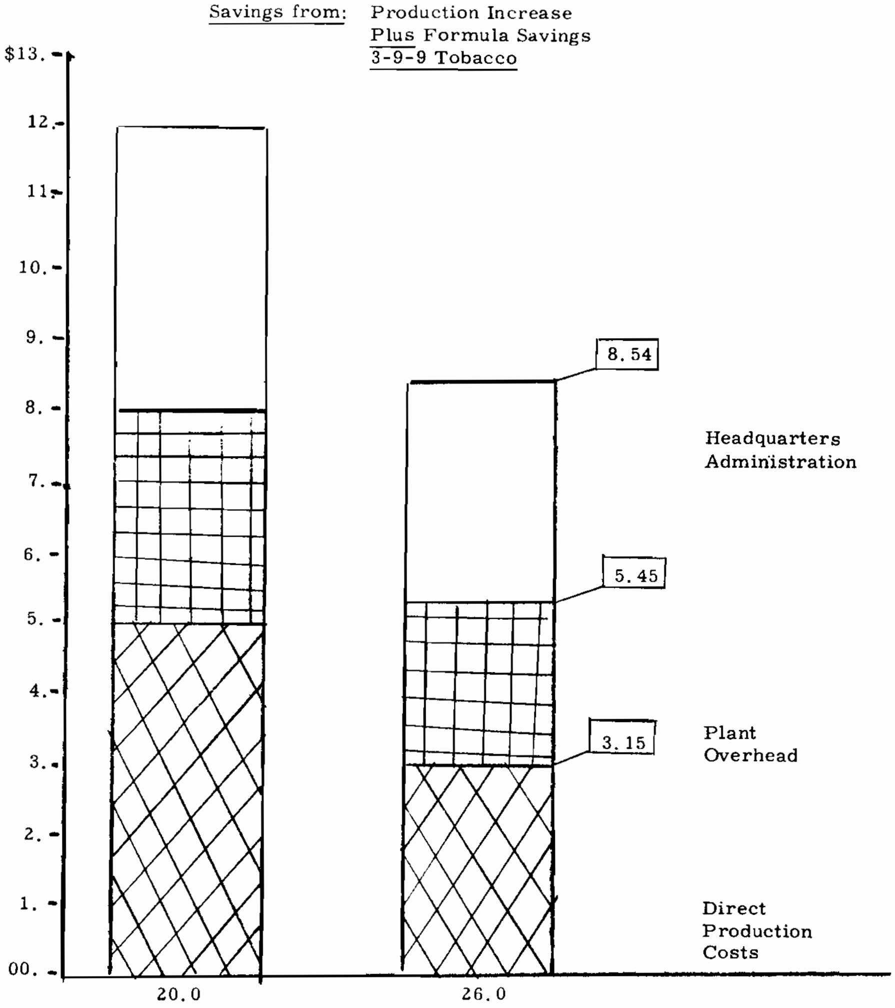
Are there any questions for any of the speakers this morning?

While you are thinking, I would like to remind the speakers to be sure to leave copies of their papers with us before we break off for the noon hour.

Let's have some more questions, I am sure that there must be some out there.

MODERATOR REYNOLDS: This is your last chance for any questions.

If there are no questions, then, we will adjourn until this afternoon at 2:00 p.m.



Slide 18 (3-9-9 Tobacco)

Wednesday Afternoon Session, November 10, 1965

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

Dr. Vincent Sauchelli and Albert Spillman, Moderators, presiding

MODERATOR SAUCHELLI: I think we can get started. I know it is not easy to get lunch within the short time that we had. Washington is very difficult in that respect but I am glad to see so many have been taken care of and are back here with us.

There is a change in the title of the next talk. It should be Trace Elements Usage in Mixed Fertilizers. Gordon Cunningham, our next speaker, is recognized as one of the best informed persons in the trade on the usage of trace elements. These elements are also known as micronutrients. Agronomists particularly insist that they be referred to as micronutrients, some of our foreign friends call them oligo elements. I think the general usage is still trace elements since most people understand what we are talking about when we refer to them as trace elements. So we are using trace elements in this title.

Last year Mr. Travis Hignett of the TVA gave us a progress report on the subject as to what TVA was doing in the way of investigating the usage of these trace elements in fertilizer manufacture.

Every year we learn more about the importance of these elements, how the incidence of their deficiency in soils is increasing. The more intensive types of agriculture in vogue draw heavily on the native supplies of these elements in our soil.

These technological changes in farming are creating a demand for the inclusion of trace elements in the fertilizer mixtures.

Mr. Cunningham has some very practical information to give us on the subject.

Trace Element Usage In Mixed Fertilizer

H. Gordon Cunningham

THE importance of trace elements for plant nutrition is now well recognized and thoroughly documented. Every state has reported deficiency of one or more of these elements according to several national surveys conducted in recent years. Early usage of trace or minor element carriers was by means of a separate application. Because of the small per acre requirements and the difficulty of making uniform distribution it was realized that with the increasing usage of these elements more efficient means had to be developed for applying them. Some twenty years ago the so-called premium grade fertilizers containing trace element carriers entered the market. This was generally done as a mixing operation just prior to bagging. Due to the relatively small tonnage involved and the large variety of formulations this seemed to be the only practical approach. Production and storage problems were minimized and since the largest tonnage was being used in areas where pulverized fertilizers predominated no serious difficulties were encountered. Today with the increasing usage of high analysis granulated fertilizer and the direct application of bulk blended materials many problems have appeared.

Some of the current problems include uniform mixing in order to prevent segregation, prevention of dustiness or caking, possible chemical reaction causing reduced availability, compatability with other ingredients and more complete information on what elements are required, and at what levels, for the major crops in various areas.

The ideal solution to uniformity of product would be incorporation of the carrier into the granule of a granular fertilizer. This would insure uniformity of product and distribution equal to that of the fertilizer. It would however require rather large tonnage to justify this approach. Other factors to be considered would be possible chemical reaction and with some carriers the danger of fusing due to the melting point of the carrier at elevated temperature. With the increasing trend toward bulk-blend fertilizer the problem of trace element addition has taken on major importance. The versatility of this type of operation for custom formulation makes it a natural for meeting the needs for inclusion of various levels of trace mineral carriers according to customer request. TVA has pioneered research on coating granular fertilizer materials with trace element carriers. Using a powdered material and oil or water they have applied such coating by a simple mixing operation. This gives good uniformity and prevents segregation of the materials. There are however several points which need further study. In order to include higher metallic content the more concentrated oxides have been used. There is some question from an agronomic standpoint as to the availability of these materials to the plant, especially under high soil pH conditions. Since a high soil pH generally aggravates a trace element problem this is a point which should not be passed over lightly. There is another factor which needs further study. The use of oil or other organic matter as an agent or binder in conjunction with a material such as ammonium nitrate may provide a hazardous situation. Unless already completed a full survey of the safety factors involved should be made. Even where water is used in the coating operation materials of high solubility may cause complications due to caking or lumping of material.

The use of raw materials containing trace element carriers poses a possible solution to incorporating them into mixed fertilizer. So far this approach has been only in the talking stage except for a few materials containing these elements as impurities. As the need and demands increase this avenue may well enter the picture.

For the bulk blend operation the trace minerals are now available in a granular form designed to be compatible both in size and density with other fertilizer raw materials. These are offered both as individual materials and in trace mineral combinations. Good uniformity has been experienced even where these materials are used at the one per cent level or only twenty pounds per ton of mixed goods. This approach lends versatility and simplicity since it is a simple blending operation.

This approach applies only for soluble, readily available carriers. Even under ideal conditions particle size is the governing factor for the insoluble or slowly available carriers. Like limestone their effectiveness is due to their finely divided state.

Dustiness and caking of mixed fertilizer can be eliminated to a great extent by coating the granules or by using the granulated trace element carriers. The addition of large amounts of the inorganic salts containing trace elements tended to cause caking and setting up of pulverized material. It could not be stored for any length of time. The current usage of granular materials either coated or mixed with granular trace element carriers has eliminated this problem in most instances.

The chemical compatability of trace mineral salts with mixed fertilizer is good where dry materials are used. Incorporating these salts into the manufacturing process may cause the formation of relatively insoluble metallic compounds. This is especially true for phosphates where all of the trace elements except boron form highly insoluble metallic phosphates.

When introduced prior to ammoniation the inorganic trace mineral salts decreased appreciably in water solubility but retained about 90% citrate solubility. After curing for a period of two weeks the water solubility was further reduced but the citrate solubility remained at a level of 85-90%.

TVA is currently conducting extensive research on the incorporation of trace element carriers in polyphosphates. Here the chelating action of the polyphosphate appears to improve the trace element availability.

The addition of trace element salts to liquid fertilizer can be accomplished with the soluble inorganic salts provided there is no phosphate present. All of these salts except the borates react with the phosphates or phosphoric acid to form finely precipitated metallic phosphates which tend to settle out. Due to their fine particle size they have reasonable availability. If some means of agitation is supplied to keep them in suspension while being applied they may be used effectively. It is possible to add the soluble inorganic salts to various forms of nitrogen solutions and keep them in solution. While less than 0.05% of the trace elements, with the exception of boron, can be kept in solution in a complete liquid fertilizer where soluble inorganic salts are used it is possible to increase the amounts considerably through the use of chelates. Due to their much higher cost this has not proved economically feasible except in isolated cases.

There appears to be no problem to incorporating trace element carriers into the slurry type fertilizers. Since the materials are uniformily distributed and held in suspension they may be evenly spread or applied.

In addition to the trace element content the inorganic sulfate carriers also contain from 15 to 20% sulfur in the readily available solution sulfate form. Thus in addition to the available trace element content part of the requirement for the secondary nutrient sulfur is provided.

Possibly the major factor to be overcome in expanding the use of trace elements in mixed fertilizer is determining what trace elements to use and at what levels. While their importance and necessity is well recognized the actual requirements for various crops under field conditions is a problem requiring much research and investigation. Now that the atomic absorption spectrophotometer and other instruments and methods of analysis for determining the extremely low levels of these elements in plants and soils are available it should be possible to advance our knowledge in this field quite rapidly. The levels of trace elements required will vary both with the crop and the area. This problem is solved to some extent by the use of combinations of trace element carriers in the fertilizer. Since most of these elements act as oxidation catalysts within the plant they can substitute for each other to some degree. In areas where the deficiency is incipient rather than severe and no concrete information is available the use of a combination of elements at safe and reasonable levels may prove the best and most economical approach.

Since the same conditions aggravate trace element deficiency in the soil for all of these elements except molybdenum it is possible to correct a deficiency of one element and aggravate that of another where application of a single element is made. Many research workers look down their nose at the use of combinations of trace elements as an insurance or maintenance level in mixed fertilizer. The fertilizer industry is more interested in making dollars for his customer than in saving him pennies. Any grower who is aiming at high levels of production and carrying out all good management practices but still not achieving his goal will be well advised to consider the possibility of the trace elements being a limiting factor.

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Reactions between Trace Element Salts and N-P-K Carriers in Fertilizers. Nikitin and Rainey, Agronomy Journal Vol. 14 No. 10 Oct. 1952 pp. 541-546.

Production and Use of Trace Element Salts in Fertilizers. A. A. Nikitin Chemistry and Technology of Fertilizers, V. Sauchelli, 1960 pp. 435-445.

Supplying Micronutrients in Solid Bulk-Blended Fertilizers. Travis P. Hignett, Commercial Fertilizer, Jan. 1964.

Problems in Adding Secondary and Trace Elements and Pesticides to Liquid Fertilizers. A. V. Slack, Commercial Fertilizer, April 1960.

Micronutrient Uses in Fertilizer. R. P. Thomas, Commercial Fertilizer, Nov. 1961.

MODERATOR SAUCHELLI: Thank you Gordon.

At this point I hope we have some questions to fire at Mr. Cunningham. This is, in my estimation, a very important subject and it will become increasingly important as the years roll by. I know that the incorporation of these materials in the fertilizer mixture presents many serious problems and if we can get any light on the subject through questioning Mr. Cunningham we should.

Who has the first question?

Here is a question.

A MEMBER: What are the major elements used in trace elements?

MR. CUNNINGHAM: There are essentially six of them that are recognized. The ones which are considered as essential for plant nutrition include boron, copper, zinc, manganese, iron and molybdenum.

Chlorine is sometimes considered as a trace element but that's in a little different category, not being a metallic element.

MODERATOR SAUCHELLI: Gordon, you mentioned something about chelating agents in the manufacture of liquid fertilizer. Do you want to say anything about polyphosphates or superphosphoric acid and so on?

MR. CUNNINGHAM: As I mentioned, in the work that TVA has done they do feel that the polyphosphates do have some chelating action and, of course, we know that superphosphoric acid does have some chelating action and I think that the use of superphosphoric acid is making up some of the bases that are used in liquid fertilizer manufacture, has been helpful in incorporating some of the trace elements salts into these materials.

MODERATOR SAUCHELLI: Any other questions?

(No response.)

Well, you did a good job, Gordon. There are no more questions.

Thank you very much.

The next talk is really divided into three parts. It is a very interesting paper. The complete title of the paper is Manufacture of Phosphoric Acid from AAC Black Rock Using Dorr-Oliver Single Tank Reaction.

Now, last year we had an informative panel on phosphoric acid. The subject is of major interest to our industry, particularly as it involves the production of ammonium phosphates and polyphosphates.

So this next paper is going to

deal with some new developments in the processing as worked out at a plant of the American Agricultural Chemical Corporation in South Pierce, Florida.

We are going to be able to hear three persons describe this development. When you consider how much time and effort is required to prepare these papers and how these men willingly give of their time to come before the Round Table and present their findings and their reports, it certainly pleases us since it reflects on the standing of the Round Table.

Mr. Leyshon will present the paper.

Manufacture Of Phosphoric Acid From A. A. C. Black Rock Using The Dorr-Oliver Single Tank Reactor

John G. Kronseder, Richard L. Kulp, A. Jaeggi, and David W. Leyshon

THIS paper describes two new and very modern phosphoric acid plants which are capable of producing large commercial quantities of 54% P_2O_5 phosphoric acid at the hightest efficiencies yet achieved in the industry. The plants which will be discussed are the two plants of the American Agricultural Chemical Corporation which were designed and constructed by Dorr-Oliver Incorporated.

The discussion is arranged in three parts, a general description, details of the equipment and design, and the results of operation.

A. GENERAL DESCRIPTION

The AAC Fertilizer complex in Florida is one of the largest in the world. Two Dorr-Oliver Titlestad Sulfuric Acid Plants produce in excess of 1,000 tons per day each of sulfuric acid at a sulfur conversion of better than 98% and provide more than enough steam for the entire complex. Figure No. 1 is a view of these Dorr-Oliver Sulfuric Acid Plants.

Figure 1.

The Phosphoric Acid Plants use *93% sulfuric acid directly without* dilution to react with the phosphate rock. The rock for which these plants were designed to operate is the so called "Black Rock" which has often proved to be a troublesome raw material in other phosphoric acid plants. However, prior to engineering the first of these plants, pilot plant runs were made by Dorr-Oliver to assure the design engineers that the rock could be successfully used, and to determine what the anticipated recoveries might be. On the strength of these tests, Dorr-Oliver engineers offered a SINGLE TANK REACTOR with a retention time in the reactor of five hours. A.A.C. preferred to increase the detention time in the reactor to eight hours and this is how the reactor was sized. Nevertheless, as the detail design of the plant progressed, AAC decided to avail themselves of the increased capacity that would result from a shorter detention time. An increase in cooling capacity was authorized to match the larger reactor if it were operated on a five hour detention time basis.

The fertilizer complex was engineered and constructed in two stages. The original plant consisted of one sulfuric acid plant and one SINGLE TANK REACTOR phosphoric acid plant which includes the 24B Bird filter and three single-stage forced-circulation evaporators operated in series. During the construction of this first plant, authorization was given for the addition of another train of sulfuric and phosphoric acid plants which would essentially duplicate the original facilities.

Common control rooms and common structures were provided for the two phosphoric acid plants as well as for the two Titlestad plants. The first phosphoric acid plant was designed to use air for cooling the SINGLE TANK REACTOR followed by a specially designed cross flow Gas Scrubber using a special packing called Tellerets and water sprays.

The second phosphoric acid plant was designed to use vacuum cooling and a cyclonic scrubber. Thus, the advantages and disadvantages of each of these systems in relation to the Dorr-Oliver SINGLE TANK REACTOR are readily demonstrated. Each plant uses the same raw materials and has the same dimensions, equipment, etc., with the single exception of the method of reactor cooling and scrubbing of the reactor vent gases.

Figure No. 2 shows a view of the two SINGLE TANK REACTOR phosphoric acid plants. The air-cooled SINGLE TANK REACTOR (the first plant engineered and constructed) is shown, in the right foreground. Beyond to the left is the vacuum-cooled SINGLE TANK REACTOR. The twin peaked building behind the reactors houses the filter and much of the equipment in the plant. The evaporators are supported at the opposite end of the building from the reactors. In the far background is the gypsum disposal and cooling water pond.

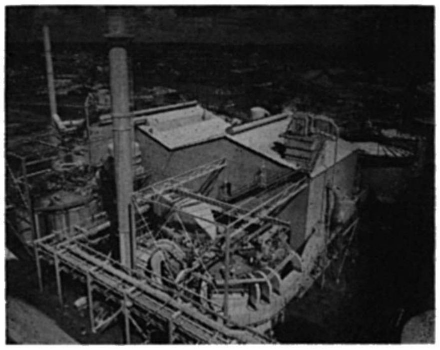


Figure 2.

I should like to point out some

features that are illustrated in this slide:

1. Note the duct leaving the building at the right which provides the air cooling. Vent gases from within the plant and from the plant tankage are collected and used for cooling to reduce the quantity of gases which must be scrubbed.
2. The vacuum-cooled reactor on the left is comparatively clear when the ducts are eliminated. The vacuum cooler may be seen directly behind the stack for the "A" plant.
3. The small sections on the roof of each plant house the dust collectors for the pneumatic system which supplies ground Palmetto rock to each plant.

Figure 3.

Figure No. 3 is a close up view of the graphic instrument panel for the vacuum cooled phosphoric acid plant.

Figure No. 4 is a view of the common control room for both phosphoric acid plants. Both semi-graphic instrument panels can be seen side by side. The window at the left of the slide gives the operators a view of the filter for the air-cooled train. A second window not shown in the left foreground gives a view of the filter for the vacuum cooled train.

Figure 4.

Figures No. 5 is the flowsheet for the air-cooled reactor system.

Ground rock is delivered to a large rock feed bin. From the rock bin the rock is discharged at a measured and controlled rate to a screw conveyor which delivers the rock to the proper point in the annulus of the SINGLE TANK REACTOR. At the point of introduction to the slurry in the reactor, the rock is caught in the vortex of a mixer and dispersed immediately. Note that a secondary rock dust feeder is available for feeding rock dust to the center compartment to reduce the free sulfate content of the slurry being filtered.

93% sulfuric acid is fed to the annulus of the reactor at a point somewhat removed from the point of rock addition. As the sulfuric is fed into the reactor, a stream of filtrate from the filter is mixed intimately with it and the mixture thoroughly distributed in the slurry in the reactor. The entire addition and mixture of rock and acid and recirculation in the reactor is such that analyses of the slurry do not indicate any sulfate gradient in the reactor.

Cooling air which includes vent air from the rest of the equipment impinges upon the surface of the slurry to remove the heat of reaction and maintain the desired temperature in the reactor slurry. Cooling air along with the fumes from the reactor pass through an entrainment separator and then through the gas scrubber.

Figure No. 6 is a flowsheet of the vacuum-cooled reactor system.

Exactly the same equipment is used as for the air-cooled reactor except for the method of reactor cooling and scrubbing of vent gases. For cooling and removing the heat of reaction, slurry from the reactor is continually pumped into the vacuum cooler where vaporization of water from the slurry reduces its tempeature and the cooled slurry is returned to the reactor.

The fumes from the reactor along with vent gases from the rest of the equipment is scrubbed in a cyclonic spray tower, The gases scrubbed in this unit are about half the volume of that scrubbed in the air-cooled system.

Figure No. 7 illustrates the filtration system which is conventional and exactly the same for both trains. Since concentrated sulfuric acid is used, ample wash water is available and only two stages of wash are needed on the filter.

Evaporation of all acid to 54% P_2O_5 is done in the Krystal

Figure 5.

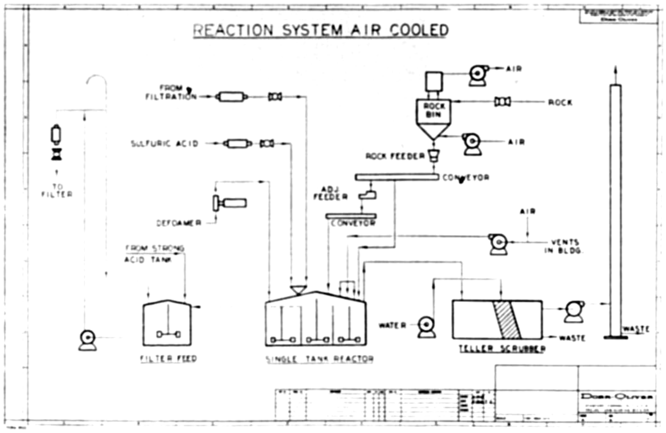
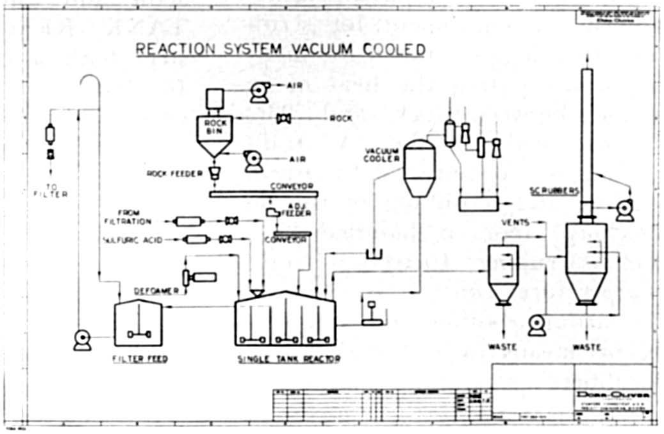


Figure 6.



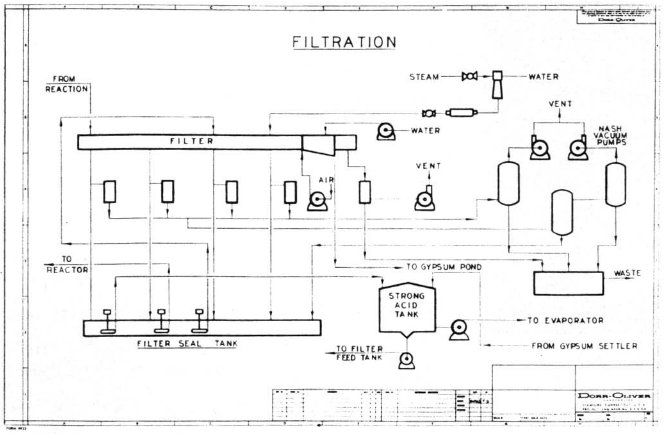


Figure 7.

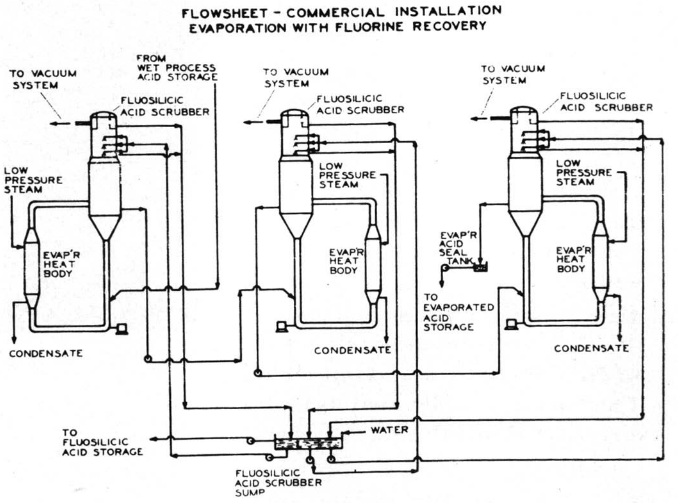


Figure 8.

evaporators as designed by the Struthers Scientific and International Company. The evaporators are intended to operate for long periods of time without the necessity of weekly washing of the units to remove scale.

Figure No. 8 is a schematic flowsheet of the evaporation system including the recovery of fluosilicic acid. The evaporators are operated in series with 30% P_2O_5 feed to No. 1 and 54% P_2O_5 product leaving No. 3.

Fluosilicic acid is recovered from the vapors leaving the evaporators by washing the vapors with a hot solution of fluosilicic acid. The fluosilicic acid product is about 25% H_2SiF_6.

B. *Phosphoric Acid Plant Description*

We have just given you an overall picture of the layout of the AAC plant. Now I will attempt to describe in brief some of the major components of the digestion filtration and evaporator systems.

As we pointed out, there are two substantially identical parallel trains. The only major differences are in the equipment for scrubbing the off-gases and in the method of dissipating the heat of reaction between rock and 93% sulfuric acid. In the "A" train, cooling is accomplished by air injection, and scrubbing of the obnoxious vapors is handled by a Teller scrubber. In the "B" train, temperature control is achieved by vacuum cooling, and scrubbing is by means of a Buffalo Forge scrubber.

Each train is furnished with a rock storage bin that receives phosphate delivered by a Fuller-Kenyon pump, and the dust laden air from this pneumatic conveying system is vented to Mikro Pulsaire dust collectors.

Thayer continuous type gravimetric feeders meter the rock to the reactors. For each feeder, the rate of delivery is controlled by a pneumatically operated pinch valve that discharges rock to a constant speed belt approximately 36″ long by 24″ wide. The metered rock is delivered to a screw conveyor for delivery to the reactor.

The return acids from the filters and the sulfuric acid feeds are metered by magnetic flow meters actuating pneumatically operated control valves. Antifoam reagent is fed to the reactors by Lapp Pulsa-feeder diaphragm type chemical proportioning pumps.

The parallel rock digestion systems each consist of a SINGLE TANK REACTOR and filter feed tank in series with the latter vessel providing surge between the reactor and filter. Each SINGLE TANK REACTOR is 49′ ID steel with a center compartment 16′ ID so that there is actually a tank within a tank. Overall depth of the tank is 20 ft. on steel. These overall dimensions after allowance is made for linings and operating levels accomodate a detention time of eight hours at 325 tons P_2O_5 per day or five hours at 500 tons P_2O_5 per day. The internal surfaces are lined with 3/16″ thick natural rubber, and the rubber is protected by carbon brick - 2-½″ thick on the bottom, 4-½″ thick on the walls.

The feeds of phosphate rock and mixed acids are added to the annulus, the zone where the reactions are substantially completed and where the detention is approximately nine times that of the center compartment. The function of the center compartment is to discharge the super-saturation of phosphoric acid to minimize scaling in the pipe lines and at the filter. Flow of slurry from this compartment is by launder to the feed tank.

The annulus is arranged with six agitators and suitable baffles to minimize short circuiting and to provide the optimum combination of slurry flow and turbulence for rock digestion. All of the agitators in these vessels operate clockwise so that the flow of slurry is predominantly in this direction. Transfer to slurry from the annulus to the inner compartment is accomplished by means of

Figure 9.

gravity flow through an opening - 265° clockwise from the rock feed - in the vertical wall of the inner vessel. However, the predominant fluid flow is recirculation around the annulus.

Figure No. 9 shows this opening in the vertical wall of the inner compartment. Note the pitched blade paddle agitator in the center compartment.

Figure 10.

Figure No. 10 gives a view of the annulus with pitched blade paddle agitators. Here you can see the rubber lined roof and also the contrast in arrangement of brick on the side wall and inner compartment. The walls and bottom of the tank are kept substantially free and clear of gypsum deposition.

I'd like to point out that, in the annulus, we are using about two and one-half HP per thousand gallons; and in the center compartment, two HP per thousand gallons. This may seem rather mild agitation to some designers, but we believe that the efficient use of the power input is the important factor rather than the magnitude of the power alone. Efficient phosphate rock digestion demands the proper combination of both flow and shear and our experience demonstrates that different combinations are required at different locations in the reaction system. We are saying that we have achieved a relatively high level of digestion efficiency with the style of agitation designed into our tank configuration. This we feel is quite important from the economic viewpoint. Based on an 8 hour detention time, one HP per thousand gallons is equal to about 13 cents per ton of P_2O_5 in power alone, thus if a digestion system consumes 5 HP per 1000 gallons rather than the 2.5 HP per thousand gallons specified earlier, the additional power cost is 33¢ per ton of P_2O_5. When maintenance and depreciation are added this figure approaches the equivalent of 1% loss of recovery on P_2O_5 figured at $50 per ton.

As we stated earlier, the "A" reactor is air cooled. There are nine type 316L stainless steel air cooling nozzles in the annulus as indicated in Figure No. 11 —

Figure 11.

Here we see a top view of the air cooled reactor with agitators, cooling ducts, and large exhaust duct. Note the grating on top of the reactor. — All of the coolers are fed from a common manifold system from a 150 HP stainless steel fan. Figure No. 12 shows this common manifold system. The duct system on the inlet side of this fan is the exhaust system for the entire plant which exhausts all tanks, both open and closed, and all other sources of possible noxious fume emission.

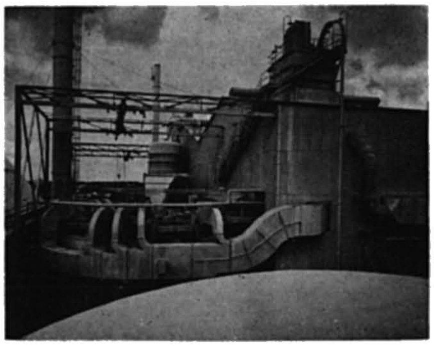


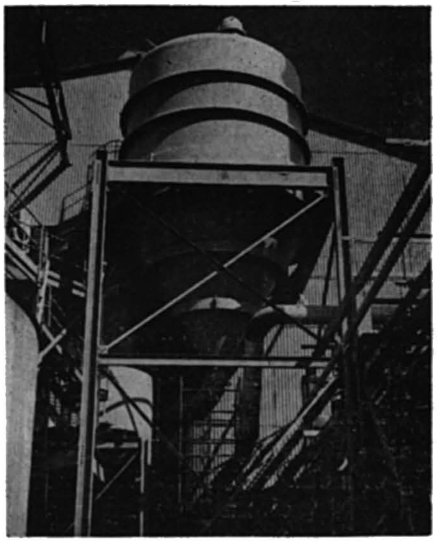
Figure 12.

The coolers are designed to direct contaminated air at the surface of the slurry, and since the nozzles are submerged they are relatively easy to maintain. Temperature control of the slurry is exercised by regulation of the slurry level in the reactor - accomplished by vertical movement of a gate installed in the launder delivering slurry from the inner reactor compartment to the filter feed tank.

The reactor tank is held at a slight negative pressure by a 250 HP stainless steel fan which exhausts the fumes through a Teller scrubber, and discharges about 100,000 CFM of washed gases to the atmosphere through a 120′ stack. The Teller scrubber contains three stages of open spray compartment and a final packed section, 4 ft deep of high density polyethylene Tellerettes. Approximately 1,700 GPM of water is used in the spray chambers and 800 GPM on the packed section.

In the "B" reactor, temperature control is achieved with a 17 ft. diameter upflow vacuum cooler of rubber lined steel construction. The rubber lining up to 18″ above the slurry level is protected by carbon brick. Delivery of slurry to the vacuum vessel is effected by means of a 14″ stainless steel Hazleton pump installed in a pump tank connected to the annulus of the main reactor by launder. The overflow from the cooler is sealed in a rubber lined steel vessel that returns overflow to the reactor by gravity. This arrangement of the equipment is designed to permit wash-

Figure 13.



ing and descaling of all of the components of the cooling system simultaneously and in place. I should like to add though, that this system has a high on-steam operating factor and washing has been required only infrequently.

Figure No. 13 shows this upflow cooler. Note the overflow system and seal tank.

The cooler vacuum system includes a rubber lined steel barometric condenser and a two stage steam jet ejector with alloy 20 nozzles and diffusers and a cast iron intercondenser.

Figure No. 14 illustrates the top view of the vacuum cooled reactor. The exhaust duct is, of course, much smaller than with the air cooled unit.

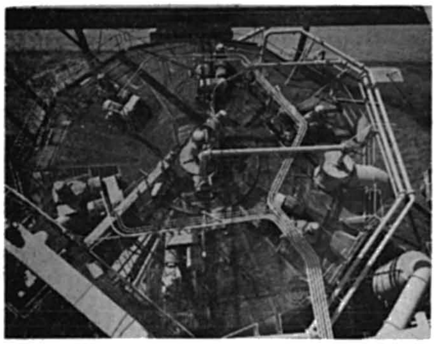


Figure 14.

Fumes from digestion and other points of emission from the "B" train are scrubbed in a Buffalo Forge two stage cyclonic scrubber handling 55,000 CFM of contaminated air. The first stage treats 9,000 CFM from the SINGLE TANK REACTOR and the discharge from this stage is rescrubbed with 46,000 CFM of air collected from various other sources, e.g. the filter, filtrate seal tank, filter vacuum pumps, storage tanks, etc. A 125 HP Buffalo Forge fan exhausts the cleaned gases to atmosphere through a 120 ft rubber lined steel stack.

Let me point out that the design and construction of these acid plants, a great deal of attention has been paid to dust and fume collection. We believe that our efforts have been well rewarded in that we have minimized dust and noxious fume emission to atmosphere and promoted operating efficiency and improved housekeeping.

The next unit operation is filtration and for this step Model 24-B Bird Prayon Filters are used. Slurry is pumped to the feed boxes above Floor El. 38′ by Wilfley K pumps through a constant head system. Slides 16 and 17 — Figure No. 15 gives a view of the filter with the hood and slurry feed system. Notice the magnetic flow meters and the hydraulically actuated Red Jacket pinch valves. — Figure No. 16 gives a view of the piping arrangement that accommodates the constant head system for the control on the filter feed slurry. You can see the vent lines at the top of the slide. The cake is subjected to two countercurrent washes, sucked dry, and discharged through a hopper to a launder carrying it to the gypsum pond.

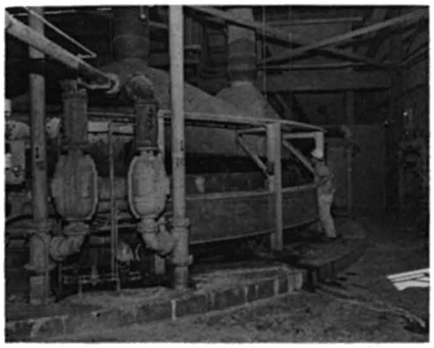


Figure 15.

Figure 16.

Figure 17.

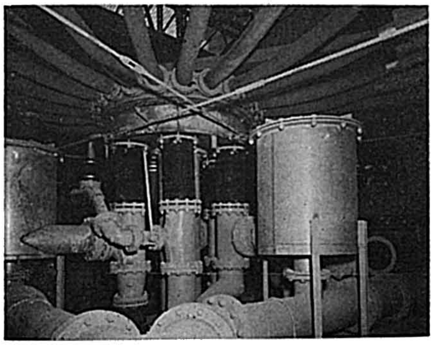


Figure No. 17 shows a view of the valve arrangement and receivers for the filter.

Two Nash vacuum pumps are operated per filter. One pump works on the cake form and washing stages; and the second pump is for cake drying. The filtrates are delivered through barometric legs to a four section rubber lined seal tank with carbon brick bottom and soldier course on the wall. In each section there is a 4″ neoprene line Galigher vertical sump pump. One of the pumps is a common standby for the No. 1 and No. 2 Filtrates. The No. 3 Filtrate is returned to the filter for cake washing; the No. 2 Filtrate is pumped to the reactor; and the No. 1 is pumped to a thickener tank providing acid storage ahead of the evaporators.

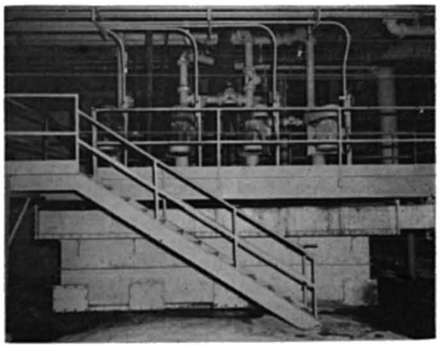


Figure 18.

Figure No. 18 shows this seal box with the four V-belt driven vertical pumps.

The filter is operated from El. 38′ and this floor is regarded as the main operating level for the entire plant. This we believe is the ideal location for our instrument control room—with the motor control room situated directly underneath.

Figure No. 19 shows the arrangement of the two filters on the operating floor.

I'd like to call your attention to the access bridge from the filter walkway to the center valve. This facility makes it convenient for operating personnel to make key inspection without enduring safety hazards.

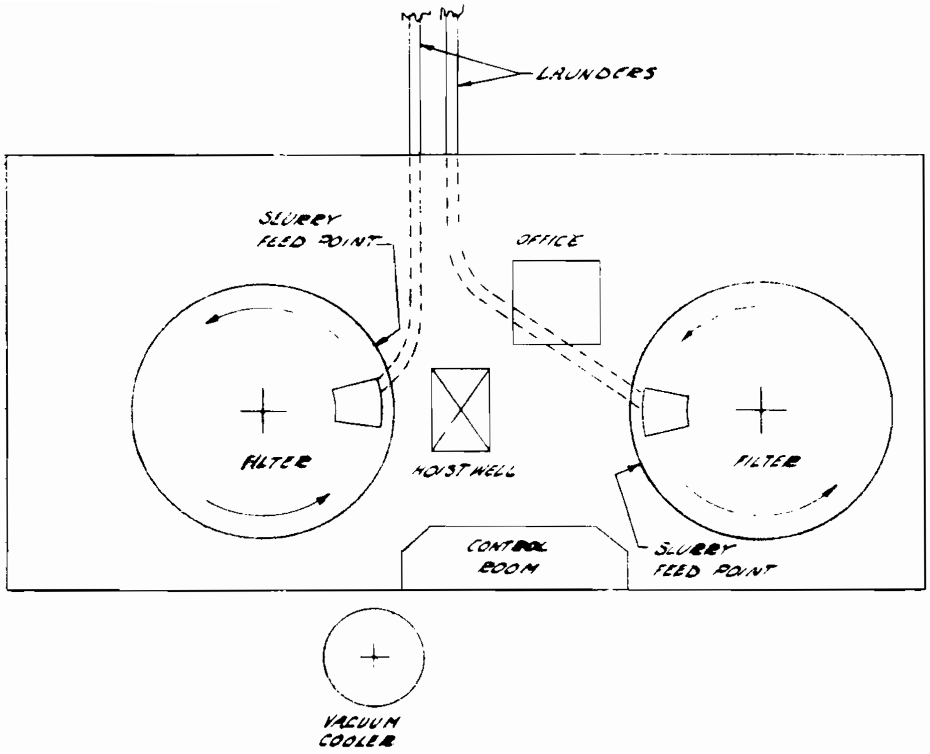


Figure 19.

Figure No. 20 illustrates this access bridge rather well.

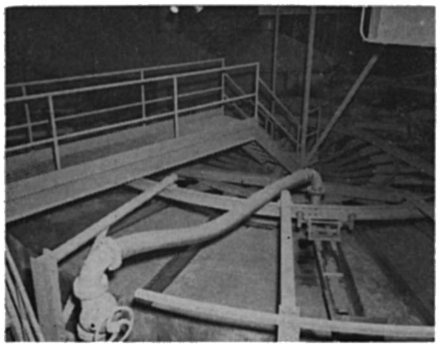


Figure 20.

EVAPORATION

Dorr-Oliver has pioneered the use of steam evaporators for concentration of wet process phosphoric acid. Almost all of the early steam vacuum evaporators were designed and developed for Dorr-Oliver plants. The Struthers Krystal Evaporators used in this plant for the first time are the latest development in forced circulation vacuum evaporation.

In recent years, the operation of new and very large wet process phosphoric acid plants with greatly improved reaction and filtration systems has again focussed attention on the relatively poor performance of the evaporators. Where once five days without cleaning was excellent, now it is a nuisance.

These evaporators were designed on the princples that the concentration of the acid involved crystallization. Let us review some of the principles which were utilized to solve the problem:

1. To produce and grow crystals a stable supersaturation in the solution is necessary.
2. After the supersaturation is created, crystal surfaces must be available so that the supersaturation can be discharged on these surfaces.
3. The release of supersaturation is not instantaneous but time is required to effect complete discharge of the supersaturation.

The key to any crystallization system is the control of supersaturation. If the crystallizer (or evaporator) can be designed and operated to maintain a very low degree of supersaturation throughout the system, it then becomes possible to make the solution discharge the supersaturation on crystal surfaces rather than form excess nuclei, scaling and deposition on surfaces of the evaporator. With such control of supersaturation, large and uniform crystals can be formed.

The evaporators were designed to make the most use of these principles. You have already seen a diagram of the three stage evaporation of phosphoric acid. Figure No. 21 is a diagrammatic flowsheet of one of the evaporators and is typical of each of the evaporators.

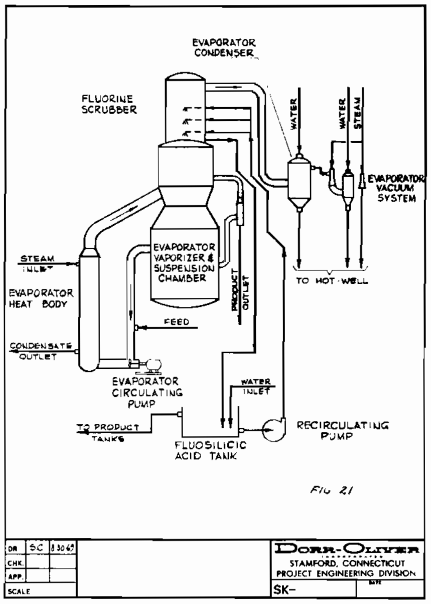


Figure 21.

A large quantity of acid (10,000 to 15,000 GPH) is circlated in each stage of evaporation. Dilute acid or acid from the preceding stage is introduced into the circulating stream and is relatively small (120 GPM) compared to the large volume recirculated. The degree of concentration per pass (and therefore the supersaturation per pass) is quite small and within the limits of control. The concentrated and slightly supersaturated acid leaves the vaporizer and passes down into the suspension chamber. Here it is rapidly mixed with acid in the chamber and comes in contact with a large amount of crystals. Tests to date indicate that the crystal size being obtained is of the order of 95% plus 50 microns.

The elapsed time from the introduction of feed to the circulating stream to its entrance and mixture in the suspension chamber is a matter of a few seconds. The elapsed time in the suspension chamber, however, is considerably greater and is sufficient to permit essentially all the supersaturation to be released before the acid enters the recirculation system. The suspension solids content of the recirculated acid is maintained at a minimum of 3% to provide ad-

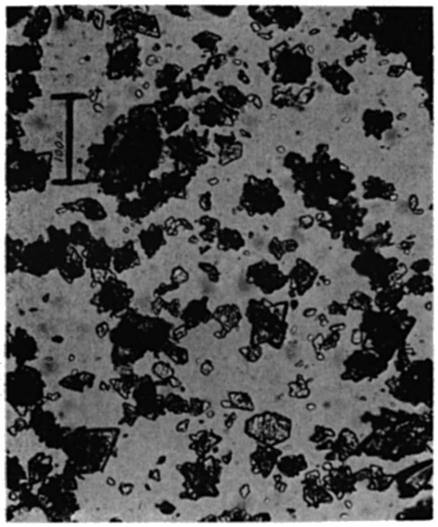
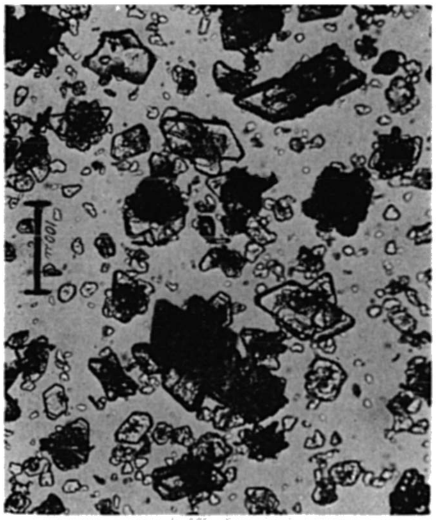


Figure 22.

equate nuclei upon which the precipitated solids can deposit to form large crystals.

Figure 23.



As the vapors leave the vapor head of the evaporator, they pass through curtains of recirculating hot fluosilicic acid. During the passage through the scrubber the fluorine content of the gases is absorbed by the liquid scrubbing medium. The operation is conducted so that the recirculating acid strength is increased in three successive stages.

Operations of the first set of evaporators has demonstrated that long periods of operation between cleanings of the evaporators can readily be achieved. Although the period of operation (almost a year) has been inadequate to indicate what the full potential of these evaporators might be, they are running for anywhere from 31 to 51 days before cleaning is necessary. More experience with these units should lead to even more lengthy periods of operation before cleaning is required.

C. *OPERATING RESULTS*

We would now like to present some recent operating results which we believe demonstrate rather successful phosphoric acid production. The period represented is 5 days in September during which the average analysis of the Palmetto Black Rock fed to the plant was as shown in Table I. The rock fed to both A and B trains has been relatively uniform in grades; about 80% of the analyses have fallen within the range, 31.0% P_2O_5 to 31.4% P_2O_5 with iron and alumina at about 2.5%. The ratio of I and A as oxides to P_2O_5 shown is 0.080. This is possibly a shade higher than average for this rock. This rock has been very consistent in performance throughout nine month's of operation.

Table I. Chemical Analysis Palmetto Phosphate Rock

	%
P_2O_5	31.20
CaO	46.65
Al_2O_3	0.73
Fe_2O_3	1.78
F	3.72
Insol.	8.45
Moisture	0.70

Table II. Operating Results, B-Train, A.A.C.

Date	Shift	Tons P_2O_5 Fed	Losses, % of P_2O_5 Fed			% Recovery D & F	Tons P_2O_5 Prod.
			Insol.	Water Sol.	Misc.		
9/19	1		2.14	2.15	0.06	95.7	
	2	342	2.14	1.38	0.05	96.4	329
	3		2.00	0.50	0.08	97.4	
9/20	1		3.63	0.70	0.05	95.6	
	2	379	2.21	0.87	0.05	96.9	365
	3		2.40	1.05	0.06	96.5	
9/21	1		2.02	0.45	0.01	97.5	
	2	382	2.02	0.74	0.01	97.2	371
	3		2.07	1.25	0.01	96.7	
9/22	1		2.40	0.41	0.05	97.1	
	2	365	1.97	0.49	0.04	97.5	355
	3		2.26	0.64	0.04	97.1	
9/23	1		2.24	0.83	0.15	96.8	
	2	393	2.05	0.53	0.14	97.3	382
	3		2.00	0.46	0.13	97.4	
AVE.		372	2.24	0.83	0.05	96.9	360

Table II presents the results of 5 days of operation on the most recent train to be put on line, the system using vacuum cooling. Overall recovery over the digestion and filtration stations was very near 97%. Water soluble losses were under 1%, insoluble losses including about 0.14% citrate insoluble loss were slightly over 2%. The miscellaneous losses include the vacuum cooler condenser, vent gas scrubber system and filter condenser. The average insoluble P_2O_5 content of the dry gypsum was 0.46% P_2O_5. Digestor acid averaged 31.6% P_2O_5, product acid 31.2% P_2O_5. These losses are based on samples of the repulped gypsum slurry at 25% to 30% solids taken from the launder going to the pond. This, of course, contains all pan washings and dregs. Frequently, losses are reported on the basis of pan samples. Table III gives a comparison of pan samples versus repulp samples. With the exception of two analyses, pan samples are uniformly low. There seems to be no suitable correlation between pan samples and repulp figures.

Table III. Per Cent Water Soluble Loss

	% of P_2O_5 Fed	
Date	Cake	Repulp
3/23	0.33	0.78
3/24	0.28	1.10
3/25	0.43	2.44
3/26	0.85	1.06
4/7	1.09	1.49
10/13	0.44	0.78
10/14	0.31	0.45
10/15	0.40	1.02

Pan samples, we believe, give a false sense of security. Total measurable losses should include all measurable losses that can be conveniently included.

Table IV. Gypsum Losses

% of P_2O_5 Fed	Repulp Method	A.O.A.C. Method
Total P_2O_5	3.77	3.77
W.S. P_2O_5	0.64	1.47
C.I. P_2O_5	0.51	0.51
C.S. P_2O_5	2.62	1.79

The data which were shown in Table II report as water soluble loss only that P_2O_5 which is readily removable by reasonable quantities of water. The water soluble loss is a function of the gypsum shape and the efficiency of the filter. The method used here to determine water soluble losses simply involves P_2O_5 determination on the liquid in the repulp gypsum slurry. By contrast a substantial portion of phosphoric acid plant data is often reported as water soluble by the A.O.A.C. method which tends to report as water soluble some P_2O_5 which can't be washed out by methods short of dissolving the gypsum. Table 4 illustrates the difference in the values obtained by the two methods. These are analyses of gypsum done sometime ago, not from this plant. It has been our experience that the repulp method gives the most reliable and reproducible figures, and a true picture of filter performance. The A.O.A.C. method may report water soluble losses up to 1% high as per cent of P_2O_5 fed.

The gypsum produced by both trains has been remarkably uniform. Figure 22 shows gypsum made on the vacuum cooled side; Figure 23 gypsum from the air cooled side. The general opinion around the plant is that if a beauty contest were being run the air cooled side would win. However, overall filterability and water soluble losses are very similar for both trains.

About 4 lb. of defoamer per ton of P_2O_5 produced has been used on the air cooling side; about 5 lb. on the vacuum cooling side.

Both trains run at well above rated capacity (325 TPD P_2O_5 average) without strain. Rock feed rates of up to 70 TPH (equivalent to an instantaneous rate of 480 TPD P_2O_5) have been run to date. It has been difficult to establish whether there is a definite increase in soluble losses at the higher feed rates. There is possibily a few tenths increase in insoluble loss. It appears that neither train has been operated at maximum throughput at this time.

Each filter is on a wash schedule of about an hour a day. There has been very little filter cloth blinding and virtually no scale formed in the valve, receivers, or filtrate lines. Over a 9 month period the No. 1 filtrate receiver on the air cooled side has been opened only twice. On one of these occasions about an inch of buildup was found. It has been necessary to use a high pressure gun on the filter cloths very sparingly and it has never been necessary to use the spare No. 1 filtrate pump due to a scaled line or pump.

Referring again in conclusion to Table II, we believe the recoveries reported here using 68 BPL Palmetto Rock are outstanding. Such performance is better than might be expected from a 75 BPL rock. Comparisons with other systems, noteably multitank digestors, are always difficult because of different raw materials, different methods of analyses and so forth. However, from analyses and data we have seen, it does not appear possible to reduce the insoluble losses in multitank systems below 3.5% of the P_2O_5 fed by any reasonable detention or recirculation rates.

If we were to predict what we feel is the ultimate recovery potentrial of the Single Tank Reactor using the conventional dihydrate process, we would, at this point, say that it appears to be about 97.5%.

MODERATOR SAUCHELLI: Thank you, gentlemen.

Are there any questions to be fired at these gentlemen? We have plenty of interesting material.

A MEMBER: There are two questions that I have.

One is: On what scale was the original test work done, on which basis the single tank reactors were built?

Secondly, those two types of gypsum that were made in the two types of coolers, what were the relative filterabilities?

MR. LEYSHON: First of all, the size of the pilot plant that was used in the development work was a reaction station approximately 15 meters in size. This feeds about six pounds, I believe, six or seven pounds of rock an hour.

We have also put this rock through a smaller pilot plant which is about 32 liters capacity which takes four or five pounds of rock an hour.

The relative filterability of the two different gypsums, there is apparently at least a slight difference in the crystal habit and the shape of the gypsum made in the two different trains. The relative filterability is very, very close. I did a number of leaf tests to evaluate the gypsum produced by both trains at the plant and I could not really determine or detect a difference, in spite of the fact that they do look different. The over-all filterability is very similar and this is also true of the water soluble losses.

Another question?

MODERATOR SAUCHELLI: I saw a question down there. What is your question?

A MEMBER: As I understand your final concentration of your acid for use is 31 per cent P_2O_5?

MR. LEYSHON: Yes, during the period of time that was shown in this particular collection of data the product acid in the digester, let's say the digester acid, the liquid phase of the digester acid was 31.6 per cent P_2O_5. The No. 1 filtrate was 31.2 per cent P_2O_5, the difference being a slight amount of dilution in the filter.

MEMBER: Is that the concentration you would advise for the manufacture, say, of triple super? At that concentration?

MR. LEYSHON: No, at AAC the acid is used in both triple superphosphate and diammonium phosphate plants at approximately 54 per cent P_2O_5, as produced by the Struthers evaporators.

MEMBER: I understand, I believe, that the Pierce plant has both the electric furnace and your process too.

MR. LEYSHON: This is at Pierce. Now, our plant is at South

Pierce. This is some distance away and only wet acid is made at this particular location.

MEMBER: Now, is this a fair question? Assuming that you use 31 per cent P_2O_5 acid, how would the electric furnace acid at that concentration and your wet process acid compare economically?

MR. LEYSHON: Well, I haven't run a recent study on the economics of furnace acid versus wet process acid, however, I think that the price of sulphur could still go up quite a tremendous amount before the two processes could be similar in cost.

MEMBER: I can understand, of course, if you are going to ship the acid that the electric furnace acid would have some advantage.

If it was used right there on the spot to manufacture, say, ammonium phosphate or triple super, do you think that the wet process acid has a distinct economic advantage?

MR. LEYSHON: Oh, yes, I am sure this is true.

Any other questions?

A MEMBER: I am a little bit curious about the strength of the sulphuric acid used in the attack system and it is my impression that the 98 per cent acid was used rather than the 93. Am I incorrect there?

MR. LEYSHON: It's 93. We have used 98 per cent acid in some of our digester systems at some times. At Bunker Hill 98 was used because of the freezing problem: out there, it's very cold.

MEMBER: I know the sulphuric acid plant produces both the 93 and the 98 there at South Pierce and I was under the impression that they use a stronger acid.

MR. LEYSHON: No, as a matter of fact I think we checked this point and I would imagine it has varied slightly from 93 but never anywhere near 98.

MEMBER: Thank you.

MODERATOR SAUCHELLI: Other questions?

A MEMBER: Could you tell me what the fineness of the rock grind was and also what filtration rate was obtained in terms of production of P_2O_5 per active square foot of filter area?

MR. YEYSHON: The fineness grind of rock? I think both plants are operating at similar rock grinds, although the grinds are being produced and the rock is being ground in two different mill systems.

The guarantee was 55 per cent minus 200. I believe that the rock being supplied actually is—at this point has been slightly finer than that, possibly around 60 or a little finer than that, minus 200.

The active area of the filter is 650 square feet so at 300 tons a day of P_2O_5 it is being run at slightly over 25 tons of P_2O_5 per active square foot.

MODERATOR SAUCHELLI: A question?

A MEMBER: What was your temperature control in your agitators and did you have the same temperature control in each cooling section?

MR. LEYSHON: Temperature control in the vacuum cooler side is by means of a weir which raises the level of the slurry up to approach the tips of the nozzles.

In general, the air cooled side has run at about 78 to 80 degrees centigrade. The vacuum cooled side has been at about 75 to 78, something on that order.

Any other questions?

MODERATOR SAUCHELLI: We have time for one more question.

A MEMBER: How did your pilot plant tests compare to the final plant results?

MR. LEYSHON: I considered putting another slide of the gypsum which I had, another picture of it which we had made, of the gypsum we had made in the pilot plant, which was somewhat similar, in fact, quite similar in crystal habit to the final gypsum made in the commercial plant.

I would say in general that it is easier to make at relatively high filtration rates, or gypsum that will produce relatively high filtration rates in a commercial plant than it is in a pilot plant. Our pilot plant results tend to be a bit on the conservative side in terms of filtration.

MODERATOR SAUCHELLI: Thank you, Dave. I am sorry we haven't more time for questions. Apparently bigger and better is the order of the day, a thousand tons per day of acid, a thousand tons per day of ammonia and now it is going up to 1,500 and there is talk about 2,000 tons per day of ammonia. It is just terrific.

I am sorry we do not have more time for this very interesting discussion on phosphoric acid.

I will now turn the meeting over to my associate, Albert Spillman, who is going to moderate for the rest of the afternoon.

MODERATOR SPILLMAN: Thank you, Vince.

In order to save time, we will go right ahead with the program. Our first paper is titled Pinch-Pak Packaging. This is a comparatively new developed concept of openmouth paper bags and bag-closing equipment to improve some of the characteristics of the sewn open-mouth bags.

Mr. Harlow E. Lichtward, Manager of Packaging Machinery, Bag Division of the West Virginia Pulp and Paper Company, will give the introduction and Mr. Walter Stone, Superintendent of the American Agricultural Chemical Company plant at Seymour, Indiana, will discuss actual operating experience with the Pinch-Pak packaging system.

Will Mr. Lichtward and Mr. Stone come forward.

Pinch-Pak Packaging

Harlowe E. Lichtward

AS a representative of West Virginia Pulp and Paper Company, I would like to express our pleasure at having been invited to participate in this 15th Annual Fertilizer Industry Round Table. I am here with one purpose—to tell you about Westvaco's Pinch-Pak Bag System because we feel its use can benefit your industry.

We at West Virginia feel that one of the keys to a company's economic growth in a dynamic market is to identify a need—and then fill it. The Pinch-Pak System successfully fills the need it was designed for—The need for improved multiwall packaging of dry, free-flowing products.

The question may arise in your minds—"Do *I* have such a need?" And my answer is this — "Yes, you need Pinch-Pak if your sewn bags rupture from handling! Yes, you need Pinch-Pak if your product should be protected from contamination! Yes, you need Pinch-Pak if your bagging rates are low, and your bagging and maintenance costs are high, or if the merchandising of your product could be improved by a better looking package.

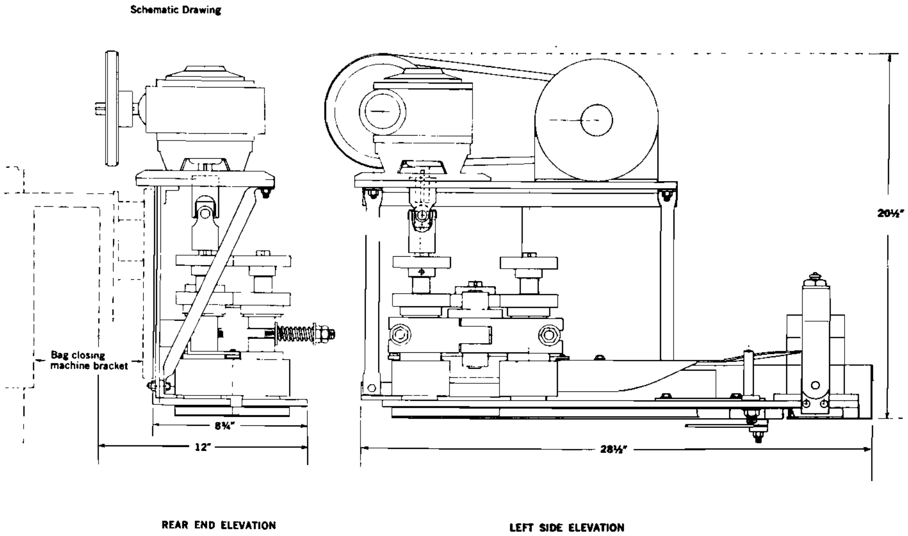
To sum it up, you need to know about Pinch-Pak if you want a multiwall bag system that can reduce your total packaging costs.

The Pinch-Pak Bag, very simply, is an open-mouth multiwall bag, which is available in most of the standard construction sizes and basis weights you are already familiar with. The distinctive characteristic of the empty bag is that the gussets are stepped, so that the front and back of the bag are offset from each other. This provides a flap which extends the full width of the bag. To close the bag, adhesive is melted and extruded on to the flap, which is immediately folded over and sealed to the opposite face by the bag.

This construction and method of closing provides a number of advantages. Neat appearance, with well filled-out corners, is one obvious advantage. We like this because we at West Virginia are convinced that "Packages Sell Products." This package can be printed on both ends as well as the face, back and gussets. Proper identification helps to sell your product.

Bag strength is not apparent to the naked eye, but it *is* important. In a sewn bag, 80% of failures occur at the sewn line. You know why — because a sewing machine needle punches holes in a bag, which weakens it. Pinch-Pak eliminate the holes, and reinforces the ends of the bag, which strengthens it. Pinch-Pak bags have been proven by drop testing to be from 3 to 5 times as strong as comparable sewn bags.

Pinch-Pak has made what was once the weakest parts of the bag now the strongest. Sifting, contamination, and moisture absorption of the product are all reduced because of the gusset step pattern, which is designed to provide effective sealing as well as high strength.



Slide 1.

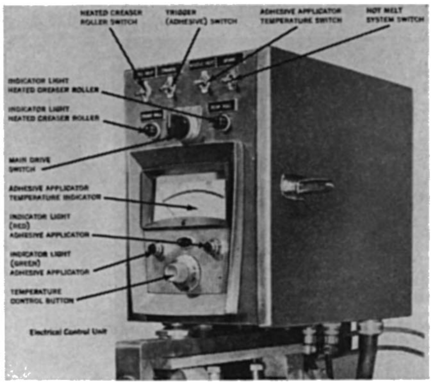
Both ends of the Pinch-Pak bag have the same construction and seal. We close the bottom in our factory, and the top of the filled bag is sealed by a Pinch-Pak Closing Unit. We would like you to see a film which illustrates the operation of this equipment. This movie was made in another industry, but we feel that the Pinch-Pak Bag System is of benefit anywhere that open-mouth bags are used.

We have prepared some slides for your consideration at this time:

(1) The first slide illustrates the compactness of the Pinch-Pak Closing Unit. You may be able to read the dimensions which indicate a total length, exclusive of the infeed guide, of 28½", a height of 20¼", and a depth of 12".

(2) The second slide shows the control panel. The four toggle switches across the top are simple On-Off controls for the roll heaters, the adhesive melting system, the adhesive pumping system, and the trigger which causes the adhesive to be extruded on the bag flap passing over the application head. The four indicating lights show whether heat is being applied to the front creaser roller, the rear creaser roller, and the applicator head. The three-position switch in the center controls the drive—Forward, Off, or Reverse, if at any time it becomes necessary to have a bag back out of the closing unit. The large dial registers the temperature of the adhesive applicator head. It normally indicates the actual temperature, which it controls very accurately. When the knob is pushed in to adjust the temperature setting, the dial then indicates the new desired temperature. Inside the box is the thermostatic control for the temperature of the adhesive hose,

Slide 2.



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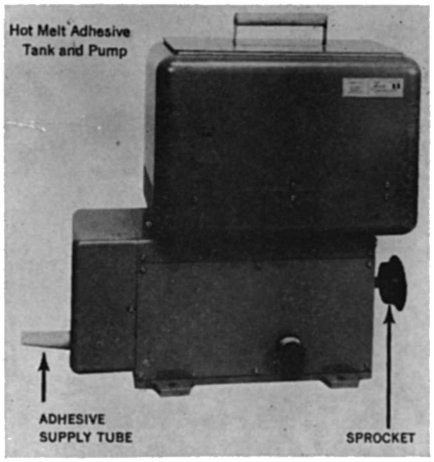
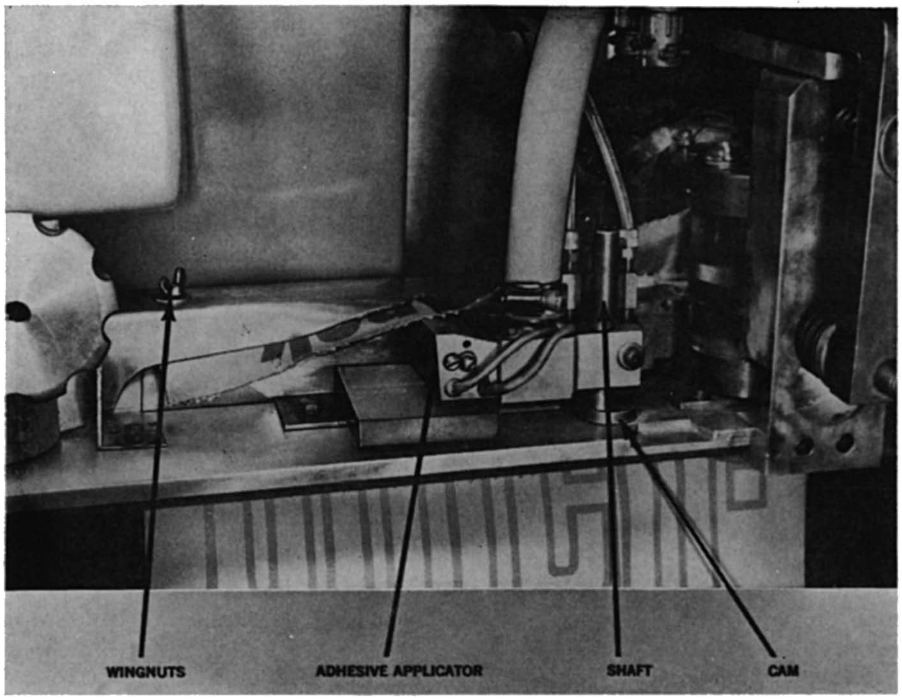


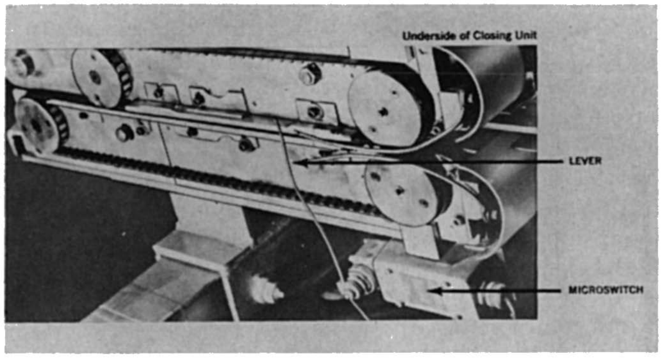


Slide 4.

as well as a rheostat to control the *amount* of adhesive being applied.

(3) The third slide shows the Hot Melt Tank, mounted over the adhesive pump. The sprocket on the right is driven at variable speeds for controlling the amount of adhesive. On the left is the Heated Hose which carries the melted adhesive to the Applicator Head. The Hot Melt Tank Cover is well gasketed to prevent contamination of the adhesive by foreign matter.

(4) The fourth slide shows the Heated Hose which brings the melted adhesive to the Applicator Head. The adhesive system incorporated into the Pinch-Pak Closing Unit gives the packer the utmost in flexibility. He has control over the type of adhesive used, the amount of adhesive used, and the temperature at which he applies it. Since it is an enclosed system it remains clean, and free of the detrimental effects of charring.



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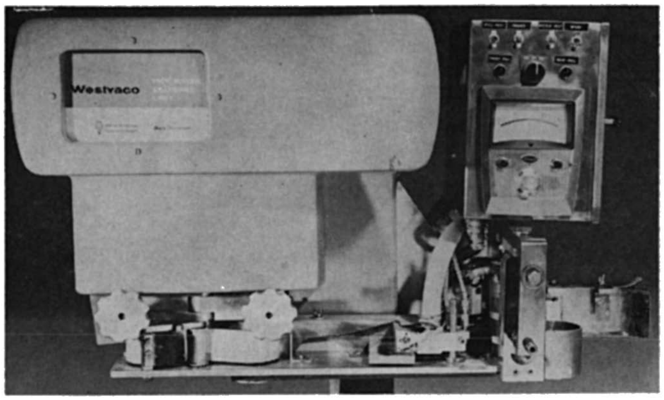
Slide 6.



(5) Looking at the underside of the Pinch-Pak Closing Unit, you can see clearly the timing belts which carry the bag through the Unit. The guards and the guides at the right clearly show their effectiveness of design and purpose. The rod which is marked "Lever" is the device referred to earlier as the Trigger, because it is activated by the bag coming through, and energizes the extrusion of the adhesive.

(6) We feel that the sewing machine, which for so many years has been the standby in open-mouth packaging is being replaced by the Pinch-Pak Closing Unit.

We have today a unique opportunity to hear from a man in your industry who has been using the Pinch-Pak System, has been living with it for months, and is here to tell of his experience in the field. It is my real pleasure to introduce to you Mr. Walter Stone, Superintendent of the Seymour, Indiana Plant, American Agricultural Chemical Company.

A User's Viewpoint of the Pinch Pak System

Walter K. Stone

LADIES and Gentleman of the Fertilizer Industry Round Table, it was with great pleasure that the American Agricultural Chemical Company accepted the invitation to participate in this discussion concerning the Pinch Pak style of packaging, and to share with you our experience with the Pinch Pak sealer.

Product packaging and handling, merchandising appeal, added safety, increased output with lower operating costs, have always been uppermost in the mind of our company. Consequently, when we heard that this fairly new concept of packaging, the glued open-mouth multi-wall bag, might solve some of our problems, Agrico decided to test this new form of packaging at our Seymour, Indiana plant.

Early last spring, therefore, we installed two similar systems, Pinch Pak from West Virginia Pulp & Paper Co. and Pinch-Bottom from St. Regis Paper Co. Both Westvaco and St. Regis manufacture the glued open-mouth multi-wall bag and provide equipment for sealing. The two systems differ in method but achieve the same results. The Westvaco Pinch Pak unit is a hot melt system that applies the melted adhesive to the lip of the filled bag, folds and seals the bag. The St. Regis Pinch Bottom Bag Field Closer reactivates, with heat, the adhesive that has been pre-applied to the lip of the bag by the bag manufacturer, then folds and seals the bag. Our intent has been to conduct a field evaluation of these two similar systems to each other and to other bag systems we have used.

While the comparison between Westvaco and St. Regis systems is not yet complete, the test has already revealed the benefits of this style of packaging, compared with traditional bags. Most of these advantages may be derived from either system since with the exception of the sealers themselves, the systems and packages are very similar. For the purpose of this discussion, I will confine by remarks to the West Virginia Pinch Pak system to avoid comparison between the two systems since our evaluation is not complete.

Let's take a look at our last eight months operation:

In our part of the country, southern Indiana, and along the Ohio River Valley, we have constantly contended with very high relative humidities averaging at 7:00 A. M. – 84% year round. As we all know certain combinations of fertilizer materials will absorb moisture from the atmosphere at much lower relative humidities. The completely sealed Pinch Pak bag has very effectively overcome complaints of hard knots and lumps at the closed end of the bag. The stepped gussets construction enables the Pinch Pak bag to be sealed so it is almost 100% airtight. This has effectively eliminated the absorption of moisture by the product from the atmosphere. We feel that this allows our bagged fertilizers to be stored for a much longer period of time.

We are operating our Pinch Pak system at a speed of 21-22 50 pound bags per minute. This speed is controlled by how fast our weighing unit can accurately cycle on different grades.

When packaging valve bags, our line crew consisted of two men, not including the palletizing operation. They were bagging 14-16 50 pound bags per minute.

Now, in bagging with Pinch Pak with one additional man on the bag line, we have achieved almost 50% increase in total output. This additional output more than compensates for the additional expenditure.

The lower speed of 14-16 bags can still be achieved with the smaller crew. This is useful in cases of absenteeism or during periods of low demand.

Pinch Pak line speeds compare favorably with sewn open-mouth bagging rates; however, I have found that operating efficiency of Pinch Pak is much greater. Most of us know the factors involved in a sewing operation which tend to seriously reduce operating efficiencies, needle replacements, rethreading needle and looper, mechanical adjustments—all of which result in lost production time. Our records indicate that our bagging lines are operating at better than 95% efficiency with the Pinch Pak style bags.

Maintenance is another expense that the Pinch Pak unit has substantially reduced. Our routine daily maintenance requires 15 minutes per day, and is performed by the operator during grade changes with no loss of production time. Maintenance by a mechanic has averaged less than 4 hours per month since installation.

We have, also, found that the training of closing unit operators requires far less time for Pinch Pak than it does for other bagging systems. Of course, we all recognize that performance and skills improve with experience under supervision.

Personal safety has been designed into the machine. As the bag is started into the bag guide, the operator releases the bag and the well designed protective guards prevent fingers from accidentally entering the unit.

Sifting, spilling and breakage waste money. They, also, create safety hazards on loading docks, truck beds and warehouse floors. The Pinch Pak bag effectively reduces these conditions because its complete closure is the strongest part of this bag. We are very pleased with our reduction in bag losses. Our records show that our bag losses from all causes have been less than one-half of one per cent since this installation.

Bagging costs involve many factors. A higher cost in our area may be more than offset in another area. We recognize that we could purchase several sewing heads for the price of one Pinch Pak closing unit and that the price of the Pinch Pak bags is no improvement over sewn-mouth bags. However, because of the considerations already discussed, we have found that total bagging costs have been reduced through use of the Pinch Pak system.

Product identification in our warehouses and dealer outlets is easily made because both butt ends of the Pinch Pak bag are printed to show brand and grade.

Palletizing, stacking and handling are not appreciably changed; however, the Pinch Pak bags are much neater in the pallet for warehousing efficiency.

I would now like for you to see some pictures of our installation at Seymour.

Narration On Slides

SLIDE 1:

This slide pictures a broad view of the bagging line taken from the rear of the pinch-pak unit. We are operating at 21 to 22 bags per minute requiring an additional man to straighten and fold bags ahead of the sealer operator. The pinch-pak unit pedestal is mounted on rollers and electrical and air connections are plug and receptical so that the unit can be rolled on and off the line at will. Height of the pinch-pak unit can easily be

Slide 1.

adjusted for different size bags by means of a screw-jack arrangement to raise and lower the unit.

SLIDE 2:

This slide shows a close up view of the bag folder as he straightens the bag gussets ahead of the sealer operator. This man can be eliminated by lowering the speed to 15 to 16 bags per minute.

Slide 2.

SLIDE 3:

This view depicts the front of the pinch-pak unit showing the sealer operator as he indexes filled bags into the sealer unit. This, also, shows the safety feature built into the unit to prevent accidental injury to fingers.

Slide 3.

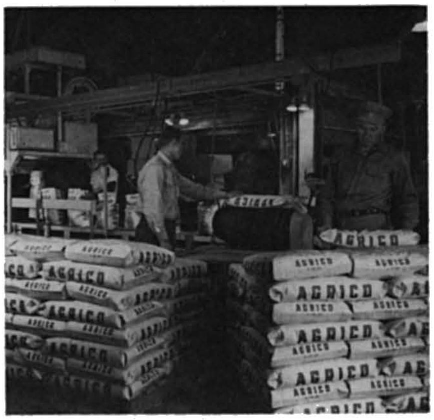
SLIDE 4:

This is another view of the operator as he indexes bags into the unit and, also, a good picture of the stepped-gussets construction of the bag which enables the bag to be sealed almost 100% air tight. Seen, also are the "On" and "Off" switches of the temperature controls for the pinch-pak unit.

Slide 4.

SLIDE 5:

This scene depicts the palletizing of the filled bags as they come from the bagging line. Branch and grade butt printing allow for easy identification on pallets for warehouse.



Slide 5.

SLIDE 6:

This scene depicts the palletized bags in storage. Again, the butt printing identifies the brand and grade and the squared end appearance of the bags which provides neat level pallets.

Slide 6.

SLIDE 7:

Another view of palletized bags showing butt printing.

Slide 7.

SLIDE 8:

General view of warehouse storage of the pinch-pak style bags.

Slide 8.

MODERATOR SPILLMAN: Thank you, Mr. Lichtward and Mr. Stone.

We are running short of time. If any of you gentleman want any information from either of these two gentlemen, they will be here most of the meeting and the information will be available to you on request.

Over on the table there they

have some literature that you may want to pick up on this particular system of packaging.

Our next paper covers a very important item of concern to all of us. City, state and Federal authorities are getting tougher on existing air and water pollution regulations. All of these agencies are demanding a better job of cleanup and compliance. They will no doubt request additional, more stringent legislation from their respective city councils, state legislatures, and Congress.

This paper will be discussed in three parts.

Plant Experiences by Mr. Larry Samuels, Assistant to the Chief Engineer of Federal Chemicals Company.

Types and Costs of Control Equipment by David E. Bonn, Manager of Dust Control Department of the American Air Filter Company.

Observations on Air Pollution Legislation by Mr. Huge Mullen. By the way, the name has been spelled wrong on the program. It is M-u-l-l-e-n, Vice President of Administration for the Buell Engineering Company. Mr. Mullen is also President of the Industrial Gas Cleaning Institute.

Please hold your questions until all three panelists have completed their discussions.

Observations On Federal Air Pollution Legislation

Hugh Mullen

I WOULD like to read to you an editorial that recently came to my attention, as sort of the basis for my remarks to you today. It reads as follows:

"It is a gloomy moment in history. Not in the lifetime of any man who reads this paper has there been so much grave and deep apprehension. Never has the future seemed so dark and unpredictable.

"In France, the political cauldron seethes and bubbles with uncertainty.

"England and the British Empire is being sorely tried and exhausted in a social and economic struggle, with turmoil at home and uprising of her teeming millions in her far flung empire.

"The United States is beset with racial, industrial and commercial chaos, drifting we know not where.

"Russia hangs like a storm cloud on the horizon of Europe—dark, menacing and foreboding.

"It is a solemn moment and no man can feel indifference, which happily, no man pretends to feel in the issue of events."

When do you suppose that editorial was written? Was it in 1965? Actually, it appeared before World War II, before the Great Depression of 1929, before World War I, before the panic of 1891 and even before the Civil War. That was an editorial in the *Harper's Magazine* of October 10, 1847,—118 years ago.

What does this have to do with air pollution? Simply that it emphasizes an important point. Like many other things, it is not a problem. The first recorded efforts to control air pollution were made in the 14th century. But today it has become a matter of extreme importance to the public. As such, politics, plays a major role in keeping the struggle for clean air before the public eye. Many people talk with borrowed authority without the slightest knowledge of the problem or the enormous sums required for effective controls. The number of so-called experts is staggering. Hardly a day goes by that does not bring a new book, a newspaper story or some announcement that another committee has been formed. State legislatures and congress are beehives of activity, and it almost seems that a new bill is proposed daily. And yet there is all too little consultation with the people who know most about the problem, the manufacturers of air pollution control equipment.

I have the honor of being the president of the Industrial Gas Cleaning Institute, an association of dust collector manufacturers. We are greatly concerned about this apparent head-long rush to pass some sort of control legislation. I do not mean to imply that all proposed legislation is irresponsible, but only to point out that political pressure can result in the premature passage of a bill before all aspects are fully investigated. The result could be overly stringent and impractical controls. On the whole, there seems to be reasonable thought behind currently pending legislation. However, even in areas where years of study have been devoted to the problem, impracticalities creep into the codes and laws. It was recently necessary for the San Francisco Bay Area Pollution Board to rescind a provision in a newly enacted law which prohibited the use of backyard barbecues. Directive A-11 of the Public Health Service of H.E.W. restricted the amount of sulfur in the fuel burned in new government installations to .9% in oil and .7% in coal. Pursued to its ultimate, this could have been applied to all fuel burning installations in the country. The results would have been catastrophic. First of all, the reduction of sulfur in coal would have rendered a great many of the precipitators now installed to collect flyash far less efficient. The solving of one problem would undo the solution of another. The effects of Directive A-11 would have reached far beyond air pollution. It would mean that those utilities that did not have natural gas available would have to burn the best grade of coking coal since only 5% of all the coal and oil in the country has a sulfur content below the required limits. The price of coking coal would soar and with it the price of steel. The steel industry would lose markets to foreign competition. In addition, it would shut down most of the now operating coal mines and cause greater need in an already poverty stricken area. There seems to be a vague inconsistency about pouring millions of poverty program dollars into Appalachia on one hand, and destroying the basic industry of the area on the other. Our economy is so complex that we must consider all the effects that may be caused by such regulations if we are not to do more harm than good.

Because air pollution is such a politically inviting subject, a rash of bills has been proposed. Most of them are reproductions of other bills or verbatim copies. To create the proper political atmosphere, we seldom hear the subject mentioned without reference to the 1948 episode in Donora, Pennsylvania, when 43 percent of the people became ill and 20 died; the 10-day temperature inversion in New York in 1953, to which 240 deaths are attributed; and the 1962 poisonous smog in London where the related death toll was 340.

These incidents have been used over and over again to dramatize the problem, but probably the most dramtic picture yet to be painted, which most of you read about in your daily newspapers, was by Dr. Morris Neiburger, professor of meteorology at UCLA. He predicted that, at the rate we are going, man will drown in his own waste within 100 years. He foresees 800 million Chinese driving automobiles and creating a world-wide smog worse than the current Los Angeles problem. Dr. Neiburger suggested that one solution to the problem would be the use of automobiles powered by electricity. Such a car is currently in development. The only problem is that the battery must be recharged every 75 miles, which is darn inconvenient. The obvious answer is long extension cords.

It is not my purpose or place to criticize Dr. Neiburger who is eminently qualified in his field, but to point out that there tends to be too much emphasis placed on the dramatic phase of the problem. No one wants to see a repetition of the incidents at Donora, New York, or London. But fortunately they were just that—incidents—few and unique. However, the real problem of ever increasing air pollution is with us constantly. The New York Herald Tribune gets a lot of publicity annually through its Fresh Air Fund. Each year they send hundreds of underprivileged children to the country to breath the fresh air. But what about the hundreds of thousands of children who remain behind; what about their parents—aren't they also entitled to breathe fresh air? Certainly, they are, and that is the overall problem. Not as acute as some people see it, but very real and very vital.

Several months ago I had the pleasure of discussing the air pollution problem with Mr. Donat, the Director of the Business and Defense Services Administration of the Department of Commerce. Mr. Donat evidenced some surprise that the dust collecting business had not increased fantastically since the passage of the Clean Air Act. As I explained to Mr. Donat, cleaning up the air will not be done without laws with some teeth in them and proper enforcement. It is difficult to sell equipment that is a pure expense and produces a worthless product that costs money to dispose of. No one is going to install such equipment because the government says, "Wouldn't it be nice if you did." That is why some collector manufacturers concentrate on the process industries where quality and performance are considered. When a user is buying strictly to comply with the law, he generally buys the least expensive equipment that will meet the requirements and delays the purchase as long as possible.

We of the Industrial Gas Cleaning Institute believe that:

1. Air pollution is a local problem and should be controlled by the cities and states. The many varying conditions throughout the country make an overall federal code impractical. The federal government should only enter the picture in the event of interstate disputes. This is the way the current legislation is written, but there seems to be a trend toward a federal code. For example, the water pollution bill which was signed by President Johnson last month specifies that if the states do not establish the proper water pollution standards by 1967, the federal government will.

2. We believe that in the case of particulate emission, there is adequate equipment on the market now and government research in this area is unnecessary. In the case of gaseous emission (SO_2), equipment has not been developed to the stage of particulate collectors because there is no market for it. If new laws change this, industry will develop the necessary equipment.

3. We believe that air pollution is a public matter and some of the cost of correcting the problem should be borne by the public. The best way to accomplish this is through tax relief in the form of a fast write off. There seems to be a good deal of thinking in this direction on the hill.

4. We believe any legislation must be practical and the requirements within the capabilities of the present technology. All aspects of the legislation must be explored beforehand so that it will not be overly oppressive on the marginal operator. In many instances the cost of control equipment could force a company out of business. Clean air at the cost of one's livelyhood is not a very good bargain.

Now let's take a look at the federal legislation as it stands today. First of all there is the *Clean Air Act* or law 88-206 which was signed on December 17, 1963. Under this law the federal government may:

1. Accelerate research on all aspects of the problem;
2. Award grants to state, local and regional agencies for the development and establishment of control programs;
3. Take action leading to the abatement of interstate pollution problems.

This law leaves to local authorities the main responsibility for administering air pollution problems. There are many, however, who feel that there may turn out to be as many codes as there are municipalities, and that the only solution is a federal code.

It is also well to remember what has happened in other fields. When the government grants funds to states or local agencies it often stipulates anything resulting from the use of such funds must be subject to government approval. If there is to be a federal code it is very likely to evolve in this way. This sort of creeping government control is insidious and difficult to combat and is now taking place in our school systems. It apparently is far easier to accept federal control than to refuse federal money.

There are three main aspects of air pollution that seem to consume the entire interest of congress at the present time. They are:

1. Tax relief
2. Automobile exhaust
3. The emission of sulfur compounds, or specifically, SO_2.

In Senator Ribicoff's words, and I quote: "If we are to clean up our air, a large part of the job must be done by private industry. But we can't simply point the finger at private industry and say, 'You are causing some of the pollution—do something about it.' The purchase and installation of equipment to control pollution is a big expense—bigger than private industry can bear alone. There must be some sharing with private enterprise of the economic burden of these expenses."

Currently there are ten bills before the Senate and the House covering tax relief. The principal difference being that some offer a 36 months write off and others permit air pollution control equipment to be expensed in the year it is installed with a 5 year carry over.

It seems when it comes to trying to get a bill passed, air pollution is not quite as universal as some experts claim. The farm states and plain states are not as desperate for the passage of such laws as the industrial states. So there is still the old game of "you scratch my back and I'll scratch yours;" particularly with tax relief which means a loss in revenue that must be made up some other way. As a result, these bills seem to be hanging around waiting for the proper vehicle. When some "sure thing" legislation comes along, the effort will be made to attach one of them as a rider. This will now have to wait until at least next year, and Senator Ribicoff has been working on his bill S1670 since 1963.

There were some five bills on controlling the exhaust from automobiles but this question was resolved last month with the passage of Senator Muskies' bill S306. The original bill was revised by the House and the revisions were quickly accepted by the Senate. The main revision struck the requirement that all new vehicles have control equipment by September 1, 1967, and left the exact date to be established by the Secretary of H.E.W. Apparently H.E.W. assured Senator Muskie that it would take action by 1967 and the revision was accepted. S306 also provides funds for a study of the disposal of solid wastes which is only indirectly connected with air pollution.

The bills covering the emission of SO_2 and the sulfur content of fuel are fewer, and two of them, S506 and HR 7429, are presently entangled in a disagreement involving the Public Health Service, Bureau of Budget, Bureau of Mines, and the coal and oil industries.

In regard to what is happening at the state level, there were 33 air pollution control laws passed in the period from January to July of this year. Thirteen (13) of these pertained to automobile exhausts and two were tax relief bills.

Another important thing has happened recently. The first enforcement case under the Clean Air Act has been requested by the Air Pollution Authority of Delaware. On its merits, the case is peanuts—but the principle is enormous. It provides the first test of the enforcement under the Clean Air Act, and how well the Public Health Service handles it may affect the course of future actions. The case involves odors from a poultry processing plant in Maryland crossing the border into Delaware. Under the law the Secretary of Health, Education & Welfare must call a conference when requested by a Governor. The formal request has been made and the conference convenes today. The results could be of great interest to all of us.

As you know, most work has been done and most controls effected at the municipal level. The outstanding air pollution districts are Los Angeles, the San Francisco Bay Area, and New York. Most other cities follow the lead of these three. City laws, typically prohibit the emission of smoke as dark or darker than No. 2 on the Ringlemann chart. This chart is also used to check and control emissions that are not black or gray. In such cases it is used to measure the "equivalent opacity." The use of such a completely subjective test that depends on the weather conditions, the direction of the sun, and humor of the inspector is vehemently opposed by collector manufacturers. But it seems that it is here to stay since it is the handiest, least expensive method and doesn't require many highly skilled technicians to run time consuming and expensive tests. Recently New York City adopted a law limiting emission to less than a Ringlemann No. 1. If this trend is followed or adopted by the federal government, it could have far reaching effects. New York has also set the tolerable level of sulfur in fuel at 3 percent through 1968 and 2.2 percent in 1970. In Los Angeles and Dade County, Florida, the use of sulfur-bearing fuels has been banned except that utilities can burn oil when natural gas is unavailable.

There are several approaches to smog control. One adopted by California sets ambient air standards. It recognizes three levels of air pollution.

1. An *Adverse Level* at which there will be sensory irritation, damage to vegetation and reduced visability.
2. A *Serious Level* at which there will be alterations of bodily functions or that may lead to chronic disease.
3. An *Emergency Level* at which acute sickness or death may occur among the more sensitive people.

Pollution levels are supposed to be maintained below the adverse level which means, for example, less than .3 ppm of SO_2.

New York City has adopted a code based on fuel quality and emission. It establishes fuel standards and sets a limit on the amount of sulfur that may be contained in the fuel – which is the 2.2% by 1970 mentioned previously. It also sets a limit to emission.

New York State applies the ambient air approach on a regional basis. It has set up four broad land use categories: industrial, commercial, residential, and rural.

The codes established by these air pollution districts must be considered in any appraisal of future federal legislation because they impose the highest standards and most stringent requirements. Undoubtedly, if the federal government follows any previous standards, it will follow these, particularly since Smith Griswold, the former Air Pollution Control Officer of Los Angeles County, has been appointed Chief of the Abatement Branch, Division of Air Pollution, Public Health Service, Department of Health, Education, & Welfare—which is quite a mouthful.

Fortunately, I have found that some Washington bureaucrats are far from incompetent. There are some dedicated people, particularly in the Business and Defense Services Administration of the Department of Commerce who are doing their utmost to protect the interests of industry and to prevent any disruption of our economy by overzealous legislators. Again, on the fortunate side, few of the proposed bills are really extreme. It is apparent from the number of bills proposing tax relief that there is general acceptance of the view that industry alone cannot and should not finance the entire program. The danger lies in the passage of overly restrictive requirements which are beyond the economic feasibility of the equipment now available. While this danger is very real, on the overall, there seem to be many sound heads working on the problem.

There is a difference of opinion as to what will happen next. The number of bills in Congress and the publicity given to the problem would indicate that there will be more legislation in the near future.- However, there is also the view that Congress has passed both an air pollution and a water pollution bill this year with a time schedule of 1967 and no further action is required until that time, particularly in view of the fact that more pressing legislation is pending. The course that federal air pollution legislation takes will be of vital interest to all industry, and it behooves all of us to keep abreast of it.

An Inside Look At Air Pollution And Dust Control In The Fertilizer Industry

Larry Samuels

Mr. Mullen has reviewed the general air pollution situation and in a sense given you a "weather report" concerning our industry. Now let's look at air pollution and in plant dust control from the industry's point-of-view.

First, I would like to make some general comments which I feel are especially pertinent. In my opinion, most fertilizer plants are dusty, dirty messes. But this is no excuse to accept the fact that the plants will always be dusty inside and out. Adequate knowledge and equipment now exist to properly exhaust and clean the air from dryers, coolers, ammoniators and granulators. Elevators, belts, screens, spill hoppers, bagging machines, loading spouts, etc. can also be handled with proper air engineering. Warehouse areas can be pressurized with clean filtered air which will prevent dust from entering from adjacent areas. Raw material storage bins can be enclosed and vented thru dust collectors, and that especially nasty problem, gases from superphosphate units, can be controlled and cleaned.

These things are possible; however, they depend on genuine interest in improved working conditions and improved community relations.

Of course, nothing can be accomplished without capital expenditures. Air pollution project budjets must be based on realistic cost figures, not wishful thinking dictated by preconceived overall budget totals.

Cost figures must, in turn, be based on complete engineering studies of the problem. For example, the actual cost of a wet scrubber for a dryer cooler combination may be on the order of $1000 per ton per hour of product. In other words, the dryer-cooler wet collector may cost $30,000 for a 30 ton per hour plant. But there are other items to be considered; namely:

1. Existing fan capacity
2. Plant electrical capacity
3. Availability of scrubbing water
4. Product recovery or disposal system
5. Contaminated water disposal
6. Material of construction specifications

As you can see *the actual wet scrubber represents only part of the cost and a minor part of the problem.* So it is with all air pollution projects. We are often guilty of at first over complicating the problem and later after we reconcile ourselves to the fact that a major project is needed and is feasible, we tend to over-simplfy and literally run out of time and money.

Air pollution poses no greater problem to our industry than the advent of granulation. We must simply make up our minds that we can and will solve the problem! It will be surprising to many that once we have successfully tackled the air pollution and dust control issue, the quality and inventory control problem will be much improved and our safety programs will seem a little less "sacriligious."

Good dust control and air handling will result in:

1. a more uniformly granulaed product, free of contamination and dust,
2. better inventory control
3. safer working conditions,

why, then, do most people think of air pollution and dust control projects as completely unprofitable? In my opinion, the answer is, that due to lack of complete planning, many of us have never had a good dust control project! Instead, we have experienced marginal operation or complete failures.

Most of us can probably think of more "home-made" collectors and systems in our plants than completely engineered "store-bought" systems. But very few of us try to build our own rotating equipment, meters, fans, screens, baggers, etc., because these are production items and "we want the best"!

Gradually we are beginning to rely on fertilizer equipment manufacturers for complete plant design, including dust collection equipment. I am always amazed at the capabilities of the men who represent these companies. They have many innovations and invent and construct good fertilizer equipment. Honestly, I envy their ability and I don't see how they accomplish so much so quickly. However, I have not been associated with a single fertilizer equipment manufacturer who talked fluently in terms of:

1. Dust loads in gr/cfm
2. Particle size in microns
3. Duct conveying velocities in FPM
4. System damper opening
5. Phycrometric charts
6. Humidifying efficiency of wet collectors
7. Solubilities of gases
8. Air to cloth ratios
9. Efficiency versus particle size
10. Collector design velocities
11. Iso-kinetic sampling
12. Velocity pressures, static pressure, total pressures.

These are the tools of the *Air Engineers.* These are things that "make or break" air systems and air engineering studies. Undoubtedly, there are some manufacturers who have people who are authorities on air engineering; however, most suppliers do not.

There are, however, many companies who specialize in dust control equipment, system design, etc. Many have large staffs of research and development people, application engineers, field engineers, test engineers and sales engineers. These people are not being used in our field enough! Why? Perhaps because our budget cut them out. Maybe we don't plan enough ahead and our timetables do not allow time to "dilly-dally" on "non essential stuff like dust control." If this is your reason, *wake up!* It takes twice the time and effort to work a collection system into the plant after it is built and the neighbors are up in arms.

But maybe the dust control companies are not used because the fertilizer equipment people think they can build a better "mousetrap" cheaper. Perhaps, but dust control machinery is a multimillion per year industry. If the fertilizer equipment suppliers can consistantly build better machines cheaper, they are "missing the boat." They are in the wrong business.

On the other hand, I have not seen many dust control sales engineers "haunting" fertilizer plants. I suppose the "grass is greener" or that it is only human to go where you are wanted. However, if the major collector companies expect to "crack" our industry, they must "see the people, and tell the story."

So much for generalities; now I would like to tell you of a case history concerning one of Federal Chemical's plants. Approximately four years ago, an existing plant was purchased and expanded by adding a granulation plant. Immediately complaints of air pollution and dust fall-out began. Of course, the scrubber manufacturer was summoned and some minor design changes were made. However, the complaints continued and finally in the fall of 1964, top management was asked to appear before the Township Board of Health, accompanied by legal counsel. They were informed that (1) Dust from our stack was creating a nuisance and that regardless of whether or not we were meeting the state code we would have to improve this condition or face court action. (2) Waste water from plant was contributing to stream pollution and we would have to correct this situation and (3) wind blown dust from our plant was also objectionable and must be eliminated.

The waste water problem was corrected by constructing a large settlement pond and the wind blown dust was satisfactorily controlled by constructing enclosed raw material unloading areas and insisting that the plant windows and doors be closed except for access. Of course, there was no quick simple way to improve the stack emission.

During several meetings between the Board of Health and executives of our company, we explained that we were most anxious to be good neighbors and would cooperate in any way possible, but we could not shut the plant down until after the Spring season of 1965.

Everyone involved put his shoulder to the wheel. John Surber, the Regional Production Manager, attacked the ammoniator fume problem. I reviewed the air handling piping and hoods. We asked Mr. Joe Sackett and Mr. Joe Prosser to give us their ideas. Heil Process Co., the scrubber supplier, was consulted and the following improvement plan was formulated and carried out.

1. *Furnace Modifications*

The furnace was lengthened 3 feet to create an air chamber between the furnace and dryer. This had the same effect as shortening the flame in that the flame no longer extended into the dryer with the possibility of decomposing fertilizer and creating fume.

2. *Product Chute*

The product chute which formerly passed directly through the furnace before entering the dryer was insulated and rerouted through the newly created air chamber. In addition, this chute was located behind a wall of fire brick, out of the direct path of hot air. This also eliminated a possible source of fume.

3. *The Dryer Discharge Plenum Chamber*

The existing chamber was completely replaced by a much larger chamber designed to lower the air velocity and return to the system by gravity dust which was formerly sucked out of the dryer and conveyed to the dust collectors. This reduced the load to the cyclone and scrubbers and thus the loss to the atmosphere.

4. *Cooler Plenum*

This chamber was renewed to obtain the result described above.

5. *Cyclone Air Locks*

Motor driven air locks were installed on the cyclones. These units replaced gravity operated flap gates. The results were a much better seal on the cyclone discharge and greatly increased cyclone efficiency. This also reduced the load to the scrubber and consequent loss to atmosphere.

6. Fans

The fan speeds were altered to restore the air flow to design conditions taking into account plant modifications.

7. Ammoniator Scrubber

A new medium pressure drop Venturi type scrubber was installed. This unit scrubs about 6000 cfm of air which had gone directly to atmosphere in the past. This installation most certainly reduced the fume from the stack.

8. Ammoniator Interior

All the interior ammoniator piping was removed and was replaced with redesigned piping in an effort to control the chemical reaction and the creation of unnecessary fume. At the same time, the bed was deepened for similar reasons. This modification included installation of a reciproating scraper which reduced the drag and allowed us to use the existing ammoniator drive.

9. Dryer-Cooler Scrubber

The dryer-cooler scrubber was modified to increase the efficiency of this unit from about 80% to about 90%. This represented a 50% reduction of inefficiency and thus, this improvement alone cut the stack emission in half.

The cost of all of the modifications was approximately $16,500. This is significant because it would have cost perhaps 4 times this amount had the problem been attacked by simply installing a collector with 99.99% efficiency. My point is, by reducing fume generation and unnecessary product carryover, and making minor improvements in the existing equipment, we accomplished the same effect as had we purchased a much more elaborate collector to remove the fume and dust from the stack. *The overall plant design does have a marked influence on the amount of collection equipment needed in a* given situation and, therefore, there is a need for air engineering in the original plant design.

Since resumption of operation, the subject plant has manufactured approximately 5,000 tons with only one dust fall-out complaint. This complaint was investigated and found to be of questionable validity. At present, stack tests are underway to determine the overall efficiency improvement; however, to date, the plant has passed the test of public acceptance and, in our opinion, this is the "proof of the pudding."

The next time your company builds or expands a plant, give your engineers or outside air engineers a chance to thoroughly design the air handling systems. Consider their recommendations in the same light as recommendations concerning major production equipment, because in reality, your air handling and scrubbing system is major production equipment. The best manufacturing equipment is useless when a court order concerning air pollution or a strike concerning working conditions prevents its operation.

I have certainly enjoyed talking to you and will be glad to discuss with any of you any specific problems you or your company might have concerning air handling, etc.

Equipment, Methods, and Controls for Fertilizer Air Pollution Problems

David E. Bonn

TO summarize from Mr. Samuel's talk, the main dust producing operations in mixed fertilizer plants are:

1. Material handling devices, conveyor belts, screens, elevators, and bagging stations;
2. Ammoniator or pug mills;
3. Dryers and coolers.

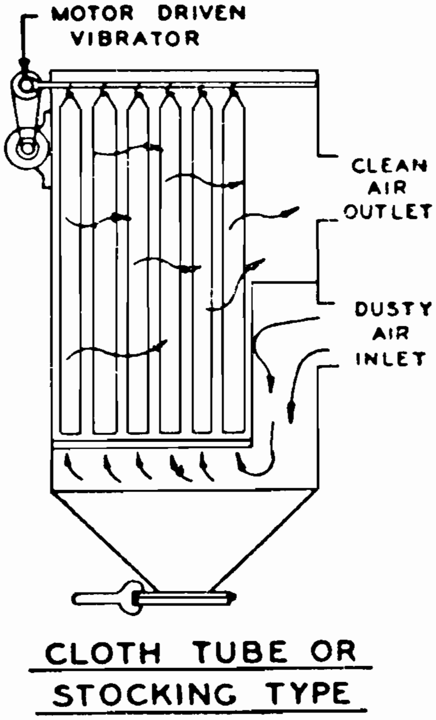
Control of the dust from material handling and bagging stations is relatively easy, since the dust is of rather large size and can easily be collected by dry centrifugal devices or cloth collectors. The dry collected dust can be returned to process.

Figure I.

The equipment shown in Figure No. I. can be used to collect the dry granular dust from material handling and bagging stations, and the dust discharged from the hopper back to the raw material elevator boot. This type of equipment cost is 10¢ to 15¢ per cubic foot of air.

Figure II.

A conventional cloth shaker type collector is often used to collect and salvage the dust from the material handling and bagging stations. Dust collected from this type of device also is returned to the elevator boot for re-use. The cloth collector will normally produce an invisible discharge while the dry centrifugal device will have some noticeable effluent. The cloth collector will range from 30¢ to 40¢ per cubic foot of air.



Control of dust from the ammoniator, dryer, and cooler is much more difficult and complex. It is usually the effluent from these devices that cause the neighborhood complaints or local air pollution problems.

Needless to say, it is also much more expensive. Conditions that make collecting the dust difficult are:

1. Temperature;
2. Moisture;
3. Corrosive materials;
4. Relatively large quantities of dust, plus, in many instances, large quanties of sub-micron fume;
5. Hygroscopic material.

The very materials that make fertilizer so good for crops make it extremely disagreeable to dust collectors.

There are almost as many different types of dust collectors as there are fertilizer grades. For simplicity these are catalogued into the three types that have been used most often or will solve the air pollution problem.

Wet Collectors—Medium Pressure 5″ to 6″ H_2O Gage

These types of collectors have relatively high efficiency down to the 2 micron range (A micron is 1/25,000 of an inch. For illustrative purposes the normal thickness of newspaper sheets is approximately 75 microns, and a human hair is approximately 100 microns.)

Many different types of wet collectors have been used with varying degrees of success. Most all well designed wet collectors will eliminate dust discharging from the cooler and dryer stack. But in the manufacture of many grades, the white or grey ammonium chloride smoke plume is produced. The ammonium chloride plume is basically less than 1 micron in size and very little of this sub-micron material can be collected by a medium pressure drop wet collector.

Two types of devices that have often been used in the collection of dust and fumes from the manufacture of fertilizer are shown in the accompanying photographs.

On the cooler and dryer if dust fall is the main complaint, a well designed high efficiency medium pressure drop collector can satisfactorily solve the problem.

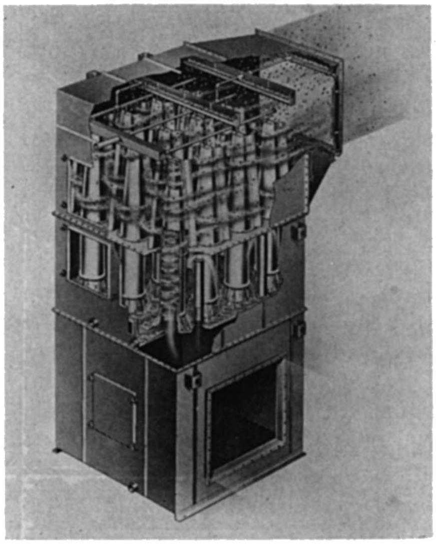


Figure III.

Figure III. is a rather new type wet centrifugal collector that operates on the wet impingement principle. Water introduced in each cone is carried to the periphery. The high velocity dust laden air entering the two tangential inlets of each cone. Clean air travels down the center of the tube while the dirty air and water are forced between the barrel and outlet cone. This type of collector will normally cost 30¢ to 35¢ per cfm manufactured completely of stainless steel.

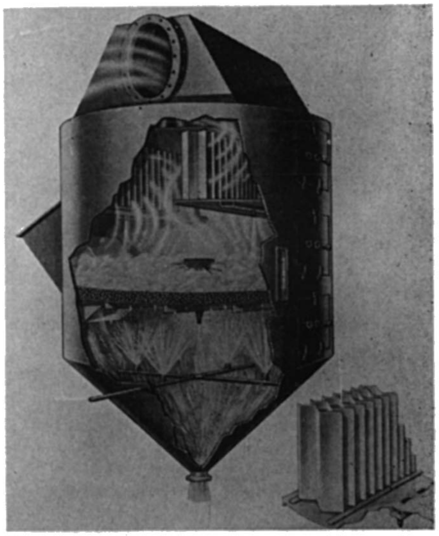


Figure IV.

Large particles of dust are removed on impingement of wet marble surfaces and contact with water spray in areas below the filter bed. Gas direction turns 90°, goes up through the filter bed where it is scrubbed. Baffle type of eliminators are used to remove the water before the clean air is discharged either to the fan or atmosphere. Dirt and water are drained from a conical type drain in the bottom of the unit.

But, if the complaint is visual discharge in addition to dust fall around the plant, there are certain grades that will produce a visible haze that will *not* be eliminated by the medium pressure wet collector.

Of course, more and more people want to see a smoke stack with nothing coming from it, and as long as they can see a plume they complain. It makes no difference that the dust under most conditions will not settle for 10 or 15 miles.

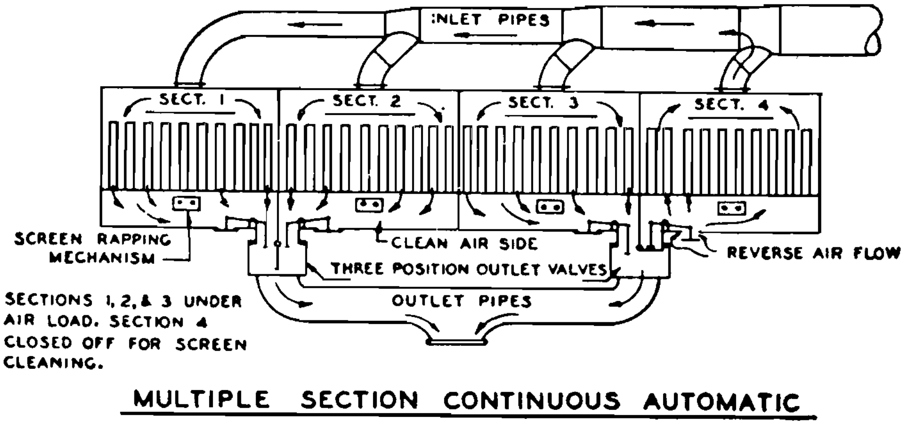
Cost on this type of unit is approximately the same—30¢ to 35¢ per cubic foot of air.

Use of a cloth collector will solve the problem of efficiency since the cloth collection will not only collect the dust but will also collect the fume. As long as the cloth tubes are in good conditions, there is no visible discharge.

However, there are many in-

Figure V.

Figure V shows a typical fabric arrestor of the continuous operating type. Cost of this type of collector will range from 55¢ to 75¢ per cfm. This does not include the cost of insulation which would be required.



Fabric type arresters.

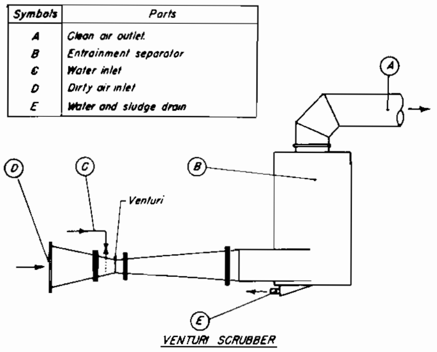


Figure VI.

Venturi collectors are the most efficient of all wet collector types. Where the efficiency normally begins to fall off at 2 microns for medium pressure drop wet collectors, the venturi can obtain 99+% on particles as small as ½ micron or smaller.
High collection efficiency is obtained by atomizing the water or other type scrubbing liquor by the high velocity gas stream.
Throat velocities range from 10,000 to 30,000 fpm or higher at the venturi throat.
113 to 340 miles per hour—this is compared to the normal 40 to 50 miles per hour for medium pressure drop collectors.
The scrubbing liquid is violently accelerated and dispersed in the throat section.
Collection efficiency is dependent upon collision and impaction of the dust particles with the liquid particles.
Colescence of the droplets occurs downstream from the throat resulting in liquid droplets large enough to be removed by various types of water eliminators.

herent problems in using cloth collectors on the discharge of dryers and coolers. The main problem is the high humidity of the gas stream causing condensation on the cloth tubes and walls of the collector. The ductwork and the collector must be heavily insulated to prevent this condensation. The connecting ductwork and collectors must be pre-warmed before running material and it is good practice to keep the temperature up and operate the system at the end of the day with feed for 30 or more minutes. Pre-warm up and shut down can reduce operating time as much as one hour per day.

The other problem is the hygroscopic nature of the material. If a cloth collector is to be left inoperative for any length of time, auxiliary heat should be added to keep the collector tubes from caking up.

A typical cloth collector for approximately 30,000 cfm would contain 1,000 synthetic tubes 9″ or 10″ in diameter and 10′ long.

While the principles of collection are the same for the medium pressure drop collector and the high pressure drop collector, the efficiency of the high pressure drop unit will vary as the pressure is increased or decreased.

While this type of collector has not been as widely used in fertilizer plants as the medium pressure drop unit, the venturi type can solve the dust and air pollution problem from the ammoniator, dryer and cooler.

The venturi will effectively collect the dust and fume and can produce an almost invisible discharge.

The only disadvantage with the venturi is operating pressure drop and the resultant high operating horse power. While you produce many different grades, the venturi collector operating at 30″ to 40″ pressure drop can normally provide you with a device that will meet today's and tomorrow's existing air pollution codes.

In the fertilizer industry dust control equipment has generally been regarded as non-productive equipment. Today this thinking is rapidly changing. In many areas of the country if a fertilizer plant doesn't have dust collection equipment, it will not be allowed to operate. In the very near future most all areas of the country will have laws requiring the control of dust producing operations.

What can you do about this as an owner or operator? Frankly, very little. However, there are some things that can be done to prevent laws or regualtions that are unduly harsh or restrictive. I'm not attempting to minimize the problems of air pollution; however, the law required for Los Angeles County may not be required in a rural area.

I'm afraid today that many states and local health departments are vieing with one another for government subsidiaries. Like most other types of give-aways, there are always strings attached to something you get for "nothing." If my understanding is correct, the fedaral authorities reserve the right to help in preparing the local code.

Frankly, I see no need for federal air pollution regulations except in disputes between states' boundaries. Certainly one state has no right to pollute its neighbors.

The following statement is taken from an article written by Mr. Herb Webber, an air polluion expert of the American Foundrymen's Society, who has aptly summed up some of the problems presented by air pollution ordinances.

"There have been all kinds of statements of position on air pollution such as:

Figure VII. Comparison of some of the important characteristics of the three types of collecting devices.

	Medium Pressure Drop Wet Collector	Cloth Shaker (Continuous)	Venturi (High Pressure Wet Collector
Size plan area	9′-0″ x 14′-0″	43″ x 12′-6″	7′-0″ x 22′-0″
Weight	8,000 lb.	30,450 lb.	11,000 lb.
Water requirement	75 GPM	None	240 GPM (not considering recirculating+15 GPM recirculating)
Dust disposal	Slurry	Dry	Slurry
HP/30,000 CFM	48 OHP	62.6 HP @ 200°F	220
Efficiency	92-98	99+	99+
Cost	$12,500	$19,887	$38,000
Maintenance	Wash down with hose (medium)	Replace tubes once per year (High)	Wash down with hose (medium)
Pressure drop	5-9″	5″	15-40″
Material of construction	SS or mild steel with corrosion protection	Mild steel orlon bags	SS or mild steel with corrosion protection

1. If an air pollution code forces a company out of business, it is indeed regrettable, but that cannot be allowed to stand in the way of progress. The greatest good for the greatest number of people must always take priority. So did the mechanical refrigerator put the ice man out of a job.
2. Every community wants an industrial plant that smells like Chanel No. 5; sounds like a Stradivarius Violin; looks like the Cathedral of Versailles; uses no freight cars or trucks; employs only executives; and pays all the school taxes.

So the State Labor or Health Department demands removal of dust and fumes from inside the plant. The air pollution department will not allow the dust and fumes to be emitted to the atmosphere. The water pollution control department will not allow the collected dust to be dumped into the sewer or streams.

Hence the solution of an in-plant dust problem begets an air pollution problem. Solution of the air pollution begets a water pollution problems. Solution of the water pollution problem begets a disposal problem. Solution of all four problems begets a financial problem."

MODERATOR SPILLMAN: Thank you, Mr. Samuels, Mr. Bonn and Mr. Mullen for those very fine papers.

We are running a little behind on our schedule and there will not be time for questions and answers today but we will have a question-and-answer period tomorrow and maybe some of the questions you have in mind can be answered tomorrow.

The meeting is adjourned until tomorrow morning at nine o'clock.

Thursday Morning Session, Nov. 11, 1965

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

Dr. Vincent Sauchelli, Moderator, presiding

MODERATOR SAUCHELLI: Good morning. We have another interesting program for you today. I hope it meets with expectations.

It's good to see this large audience at this early hour in Washington.

To many people statistical quality control, SQC as they refer to it, is a subject of mysteries. Quality control is something with which most persons are familiar, and is generally considered merely as a process inspection and control, a sort of culling process to weed out the obvious defectiveness in the production.

But SQC, statistical quality control, is much more than this. It involves taking corrective action resulting from the information gained during sampling in order to improve production.

Our next speaker, Mr. O. R. Weaver of Phillips Petroleum Company, has the unusual knack of presenting a difficult subject in an informal, understandable way.

I had the pleasure of listening to his talk this summer and I was quite impressed with the way he presented it. That prompted me to invite him to our meeting because I want more and more of our people to understand the importance of what is involved in statistical quality control. And I hope to see more of it used in the industry. It's a remarkable tool.

If you will pardon a personal reference: When I was in Taiwan recently I was impressed there that every industry, including the fertilizer industry of Taiwan, used statistical quality control in their operations.

The Japanese have taken it on too. They use it in all industries.

I hope the time will come when more and more of it will be applied in our own industry.

So it gives me much pleasure to call on Mr. Weaver as our next speaker.

Statistical Quality Control: Applying It To Fertilizer Production

O. R. Weaver

THE Book of Genesis tells us that Tubal-Cain was the first known cunning worker of metals. When he first began fashioning swords, he examined each of his masterpieces and determined whether or not he wished it to bear his name and to further his reputation. He inspected—accepted or rejected—each sword. Eons have passed since then, but articles which have been manufactured have been inspected by the worker or by his hired assistant.

Centuries ago, we are told, a certain king became extremely fond of games of chance. Like most of us who gamble, this king liked to win. In fact, winning became such a passion with him that he commissioned his court mathematician to devise methods whereby the king could always win. Not wishing to lose his head, the mathematician, it is said, spent many hours investigating the subject of chance and arrived at certain facts which have come to be known as "Laws of Probability." Properly applied to the king's pastime, these laws enabled him to win considerably although not all the time and probably did much to improve his financial status.

He found, for example, (Figure 1) that there were 36 possible combinations at which a pair of honest dice could come to rest, only one of which would yield an arithmetic sum of "2." There were two ways to shoot a "3," three ways to get "4," four to get "5," and five to get "6." In reverse order the same probabilities exist for "8" thru "12" and the chance of throwing a "7" is six out of thirty-six. Thus, if five is my point, the probability that I will throw it on any single cast of the dice is 4/36 while the chance of shooting a seven is 6/36. If I always bet the same amount that I'll "crap" before I make this point, I'll win one and one-half times as often as I'll lose over a long period of time.

Suppose you have just won the dice and on your first cast, you throw a seven. This is likely since seven is the most common single sum. What is the probability, then, that on your next toss you will get a seven? The answer is 6/36 or 1/6 just as it was before, since dice have no memory and none of the possible combinations have been removed. However, when you initially received the dice, the probability of throwing two sevens in succession was $1/6 \times 1/6 = 1/36$. Only $1/6 \times 1/6 \times 1/6$ or 1/216 is the probability of throwing three sevens in a row, and six successive sevens should occur only once in 46,656 tosses.

If your opponent should have this sensational success, you might suppose that he was using loaded dice. If you examined them carefully, you would usually find this to be true. Here your observations have established that it is highly improbable that the dice were performing solely by the Laws of Probability.

Now while shooting craps may be entertaining and, depending upon how you use the Laws of Probability, either profitably or costly, most of us must earn our livelihood in other ways so let's look at some other interesting history.

When Eli Whitney signed a contract with the U. S. Army to mass produce muskets during the War of 1812, he undertook a task which nearly ruined him financially but which may have planted the seed for statistical control of quality as we know it today.

Muskets had always been hand-made items. Each piece was individually fashioned to fit a specific gun. No parts were interchangeable and, when a part broke or wore out, a new piece was formed to fit. Whitney reasoned that if all parts were fabricated by a template or jig, then all the parts would be "exactly" alike and guns could always be assembled using any of the previously manufactured parts.

Mr. Whitney erred, however, in making the assumption that all parts would be "exactly" alike. To his sorrow he soon found that no two parts were exactly alike although in many instances they might be interchangeable. Thus he became acquainted with variability even though he probably did not use this term to define the condition.

Since that early date, product and process variability have been the subjects of much discussion in all phases of industry and many manufacturers of various kinds of product have faced the same financial ruin which plagued Eli Whitney because they, too, had assumed that parts could be made exactly alike.

Early in the twentieth century statisticians and engineers compared notes and found that the same Laws of Probability which applied to dice, cards, mortality, intelligence and other sociological, biological and statistical events were equally applicable to manufacturing processes.

Some observations which we are able to make regarding a manufacturing process if it is behaving in a normal manner include:

1. It will produce material which, if it can be measured, will have a central tendency commonly called "average," i.e., a mean, mode, or median.
2. This material will vary from the central tendency within certain limits which can be calculated.
3. Once the central tendency and the variation from it is ascertained, a probability can be established for the occurrence of material in any measurable distance from the central tendency.
4. Whenever material is being produced outside the measured limits calculated for the process, we can be sure (to whatever degree we wish) that chance alone has not caused change in the process but that some assignable cause is to blame for the variation.

While the field of quality control had its birth early in the 20th Century, it was not until just before World War II that it emerged as a youngster which showed some promise of survival in industry. As a youngster in the field, its outlook was necessarily restricted by the boundaries of its experience and capabilities. It viewed the functions of quality control and found that it could serve many of our plants by:

1. Advising management on quality conditions;
2. Assisting plant operations by:
    (a) Analyzing and reporting data
    (b) Performing process capability studies
    (c) Securing compliance with standard operating procedures
    (d) Assuring quality by tests and inspection
    (e) Approving raw materials
    (f) Using control charts
3. Assisting the Technical Departments by:
    (a) Designing experiments
    (b) Analyzing its methods
    (c) Modifying procedures

The most logical place for the use of statistics in the fertilizer industry and, in fact, the whole chemical industry, is probably in the control laboratory. The most profitable long-term application of statistics is in process improvement and research and development. Statistical methods can also be used profitably in design of equipment and processes and process control. The greatest immediate return from a program in many cases seems to come if we concentrate on the manufacturing control and problems in the control laboratory.

Initially, a quality control program has much to gain by showing immediate profits. A program for improving process control is outlined below.

1. Establish standard operating procedures
2. Use acceptance sampling
3. Make process capability studies
4. Design and use control charts
5. Plot frequency distributions
6. Set realistic tolerance limits on manufacturing specifications
7. Use designed experiments

In the control laboratory it will be profitable to perform tests of signficance, simple regression analyses, study confidence limits, analyze control data, and use other techniques for disclosing variability such as scatter diagrams.

Since World War II many manufacturing plants have expanded their use of quality control. While initially the pressure from government sources was their only encouragement, the profitability which resulted became an even greater stimulus to industry. We have grown up fast.

But we need to take a close look at where the big money is. Invention is a virtually unknown process. Whether this "invention" refers to a new product, an improved product, a new process, or a process refinement makes little difference to this thesis. The late Dr. Kettering is quoted as saying he "expected 95% failure in new ideas." But in the light of new knowledge and changing market demands which force short-term obsolescence on our processes, we must learn to take the results of new research and convert them into profitable production in a minimum of time, and we can't afford to be wrong anywhere near 95% of the time. The recent past years have shown us over and over again that we must squeeze every extra drop of product from our present processes and save every penny we can, in order to show profits.

Today we must look to the larger long-term gains offered by process improvement. This does not mean that we can rest on our laurels in the areas in which we have become involved, but we must ascribe our efforts in yet another direction. Techniques which can help us are:

1. Analysis of variance
2. Multiple regression
3. Curve fitting
4. Evolutionary operation
5. Tests of normality
6. Covariance
7. Discriminant functions

To some of you these may be familiar terms. To others they may elicit comments quite similar to those you expressed when you first heard of sigmas, "t" tests, "F" tests, and Chi square tests.

When working closely with a new acquaintenance it is well to have a formal introduction, so we now present a few of your colleagues in case you have not already met them. You will not gather from this cursory examination a complete familiarity, but only a casual recognition. First, meet a simple regression equation. These data represent observed gauge pressure of water in column x and at various temperatures in column y:

Regression Equation (Temp. vs. Pres.)

x	y	$x - \bar{x}$	$(x - \bar{x})\ y$	$(x - \bar{x})^2$
0	212	−22.5	−4770.0	506.25
5	227	−17.5	−3972.5	306.25
10	239	−12.5	−2987.5	156.25
15	249	− 7.5	−1867.5	56.25
20	259	− 2.5	− 657.5	6.25
25	267	+ 2.5	+ 667.5	6.25
30	274	+ 7.5	+2055.0	56.25
35	280	+12.5	+3500.0	156.25
40	286	+17.5	+5005.0	306.25
45	292	+22.5	+6570.0	506.25
Total 225	2584		+3552.5	2062.50

$$(y' - \bar{y}) = b\,(x' - \bar{x}) \text{ where } b = \frac{\Sigma\,(x_i - \bar{x})\ y}{\Sigma\,(x_i - \bar{x})\ 2}$$

$$y' - 258.4 = \frac{3552.5}{2062.5}\,(x' - 22.5)$$

$$y' = 1.7224x' + 219.646$$

From the formula any value of y' can be calculated when x' known.

May I next present an analysis of variance of a designed experiment.

Yield of Chemical A

Temperature (X_1)

Pressure (X_2)	150			175			200		
Concentration (X_3)	20	30	40	20	30	40	20	30	40
1.25	94.4	68.6	67.9	80.1	86.3	83.5	60.3	51.2	44.7
2.50	44.5	24.7	18.7	22.6	22.4	18.5	15.6	16.6	14.0
3.75	26.8	14.6	10.7	11.4	10.7	5.2	6.5	4.2	4.7

Here we wish to study the yield of a certain chemical A from a process which we believe to be affected by temperature, pressure and concentration. To do so we design an experiment in which we operate at three levels each of the three variables. The data we secure is entered as above.

We then prepare the following analysis of variance table.

Analysis of Variance Table

Source of Var.	Df	S. S.	M. S.
Temp (X_1)	2	1461.3356	730.6678
Pres (X_2)	2	512.4022	256.2011
Conc (X_3)	2	18430.4089	9215.2045
X_1 x X_2	4	476.4222	119.1056
X_1 x X_3	4	700.6489	175.1622
X_2 x X_3	4	23.3689	5.8422
Residual	8	131.7800	16.4725
Total	26	21736.3667	

In a table of F values we find that all of the actions and interactions have an effect on the yield except the interaction between X_2 and X_3 and the residual. If we break each of these sources of sum of squares into its linear and quadratic functions and rearrange them we can calculate a multiple regression equation whereby we can find the yield at any given value of temperature pressure and concentration and thus arrive at an optimum set of conditions.

Regression Equation

$$y = 3554.1056 - 37.04\,X_1 - 160.87\,X_2 - 1571.00\,X_3 + .1036\,X_1^2 + 3.1185\,X_2^2$$
$$+\ 305.8347\,X_3^2 + 1.9342\,X_1X_2 - .0377\,X_1X_2^2 + 17.1253\,X_1X_3 - 3.4048\,X_1X_3^2$$
$$-\ .0057\,X_1^2X_2 - .0486\,X_1^2X_3 + .000112\,X_1^2X_2^2 + .009728\,X_1^2X_3^2$$

Finally, we will take a look at one of the newer and more profitable techniques for improving processes — Evolutionary Operation. Evolutionary operation is a method of plant operation which has designed within its structure a procedure to both generate a product and provide information on how to either improve the quality, quantity, or efficiency of the product or process. Its basic assumption is that it is always more profitable to find out constantly means of bettering the process or product.

It uses the technique of the designed experiments which were discussed above but instead of "revolutionary changes," it uses small changes and runs many experiments during the regular operation of the plant. Very small changes in the cause variable can be detected in the effect variable because many, many pieces of data are collected over a regular production run.

These are some of the ways that by the use of statistical tools we are able to more easily control processes.

MODERATOR SAUCHELLI: Thank you, Mr. Weaver.

We have time for some questions.

I know it's quite an abstruse subject, but I know that quite a number in the audience here are quite familiar with SQC.

Any questions for Mr. Weaver? I'm sure he will be glad to answer them.

MODERATOR SAUCHELLI: You did a good job, Mr. Weaver. Thank you very much.

Our next subject I am sure is of direct interest to everyone here, and particularly to the operating personnel in fertilizer plants.

The subject is, Sampling of Bulk Fertilizers: Progress Report. We are going to have three very interesting speakers on this subject.

Little did the state regulatory officers foresee the headaches and embarrassments associated with sampling the bulk blends when these first appeared on the market.

Prior to the development of bulk blends, the administration of most fertilizer laws was a comparatively simple and orderly procedure.

Bulk fertilizer poses many difficulties, chief among which is the tendency of the various components to separate.

We shall hear from the next speakers as to what it is all about and how to meet the situation in a practical manner.

One -of the speakers, Bruce Poundstone, has previously appeared on our program, and we know he presents his information in a masterly manner.

None of us can forget how he told us about how he applied SQC in his work. You remember the "machine gun" that he used to demonstrate what he was talking about. I'm sure he will repeat in kind today.

The other speaker, Dr. Charles Gehrke of the University of Missouri, is known internationally for his research and scientific studies on chemical analysis.

He is an outstanding speaker and I'm sure we will all appreciate his presentation.

The third speaker on the program is Mr. Baker, also of the University of Missouri, who is in charge of regulatory work there in Missouri.

It has been my privilege to collaborate with these gentlemen on numerous assignments.

Our industry owes them a lot of gratitude for their unstinted services.

I call on Bruce to start the program.

Study On Sampling Bulk Fertilizers: Progress Report

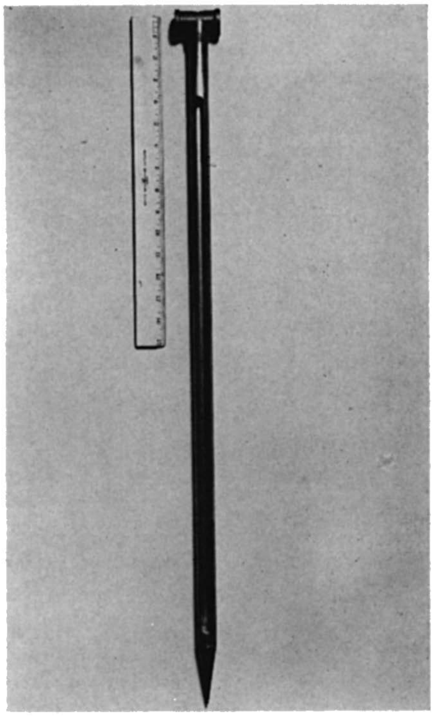
Bruce Poundstone, Charles Gehrke, W. L. Baker

IN quality control, quality is measured by considering samples. This is a preliminary report on sampling bulk fertilizers. This study will eventually lead to recommendations for official methods to the AOAC on the part of the Associate Referee on Fertilizer Sampling, Dr. Charles Gehrke.

We welcome the opportunity of sharing this with you and solicit your continued support and interest. We acknowledge with gratitude the cooperation of many of you who have helped us in this project.

Control officials have been sampling fertilizer for over 100 years. Until ten years or so ago, we considered only bagged fertilizer. With bulk distribution we are presented with an additional type of "package" for sampling.

What is it we want when we secure a sample of fertilizer? We sometimes speak of a representative sample. A representative sample is one that contains all of the elements of the sampled material in the same proportion, on the average, as in the entire lot. The answer to the question "What is wanted in a fertilizer sample?" is a representative sample. As we investigate sampling procedures, we are therefore testing and searching for procedures that will accurately represent all of the elements in the entire lot in the same proporations.



Slide 1.

Slide One pictures one of the regulation AOAC samplers. It is a single tube sampler. It is about 1" in diameter, a little less than 36" long, long enough to probe the entire diagonal of a standard fertilizer bag in a horizontal position. It has an open slot on one side. We take ten cores with this sampler from ten different bags and combine them into one sample.

The question is, how does this sampler perform in sampling bulk lots? Do we get a representative sample?

Individual states and many companies have been experimenting with this and other samplers. Results and comparisons have been inconclusive.

Early this year a program was planned to study this. Four states were involved, Missouri, Indiana, Virginia and Kentucky. Industry assisted in planning the program and provided the loads of fertilizer that were sampled.

What is wanted is a reliable procedure with reliable tools to sample truckloads and carloads. The plan called for sampling four types of fertilizer, pulverized, granular, a dry blend in which the particle sizes of the ingredients were matched and a dry blend in which the particle sizes were not matched.

Each lot of fertilizer consisted of from four to six tons. It was loaded into a spreader or a trailer truck in such a manner that the fertilizer would be 4-5 feet deep. As the fertilizer was loaded, a stream sampler was used to cut the stream at regular intervals throughout the discharge period (Slide 2) .

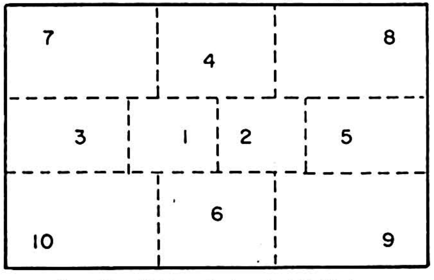
Slide 2.

We attempted to secure at least ten cuts. These were combined into a sample which, when analyzed was considered a reference sample or the true value of the material in the truck.

The sampling pattern for taking cores on each load of fertilizer is illustrated in Slide 3. The diagram represents the relative position of taking cores on top of the loaded truck.

Slide 3.

Bulk Fertilizer Sampling Study



Sampling Pattern in Loaded Vehicles

The first core, 1, was taken about 15″ from the middle of the pile. Number 2 was taken approximately 15″ to the other side of the center. Core 3 was secured half way between the center and edge of the truck and so on. Cores 7, 8, 9 and 10 were located about 18″ from each corner. Triers were inserted at an angle between 60° and 90° and as far into the fertilizer as possible. We had no difficulty in going to the bottom of the load with most of the triers we used.

Samples consisted of ten cores. These were taken with each type of trier, using one trier at a time, being careful to insert each in a different position so as not to enter the pile in exactly the same place previously sampled. Two samples were taken with each trier from each load of fertilizer.

Slides 4, 5 and 6 show the AOAC trier in use. We compared this trier with other triers. All of the others were long enough to penetrate the entire load.

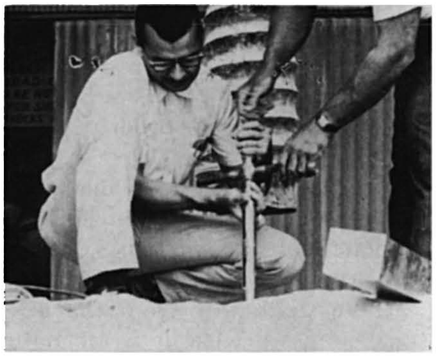
This (Slide 7) we call the Russell trier, since its use was suggested by Cecil Russell of Monsanto. This is a slightly modified grain trier 63″ long. It is a compartmental tube with a closing sleeve. Slides 7, 8 and 9 show this trier in use. It was our experience that two operators could more readily handle this trier. A long tray is needed to receive the sample.

Slide 4.

Slide 5.

Slide 6.

Slide 7.



Slide 8.

Slide 9.

The next trier is a modification of one that Jim Archer of International Minerals developed. This is 60″ long. A sleeve the entire length for opening and closing exposes an open slotted tube. It is inserted with the sleeve closed. Lifting the sleeve slowly, the sampler fills and when closed a column of the material is secured (Slides 10, 11 and 12). That is emptied through the handle.

Slide 10.

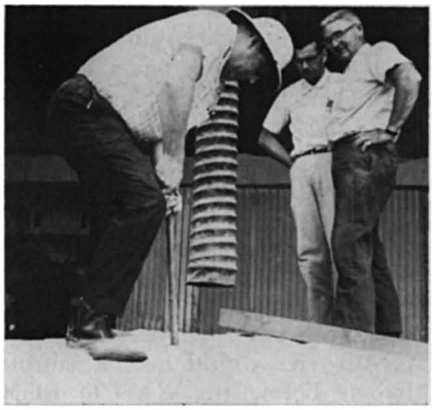
Slide 11.

Slide 12.

Another type of trier is the Missouri trier, designed by Baker of Missouri. This is similar to the grain trier, except it opens the sleeve by pulling instead of turning it. It is an interrupted compartmented double tube 59″ long. (Slides 13, 14 and 15). The tray is also needed for emptying this trier.

These are the triers that were used in all four states. We in Kentucky experimented with a fifth trier. I will show that shortly but first we wish to consider other work carried on only in Missouri.

Slide 13.



Slide 14.

Slide 15.

DR. GEHRKE: Thank you, Bruce.

Slide 16 (not reproduced) is a photograph taken at Charleston, Missouri. An experiment was set up with Monsanto and shows the commercial trailer and hoppers that were used. A special striated load of fertilizer was prepared containing superphosphate, ammonium nitrate, and potash. The load consisted of about 5 tons. In Slide 17 (not reproduced) are seen the respective triers. At the top the AOAC trier, followed by the Russell, Archer, and Missouri triers. These triers show the compartmented and segmented samples secured except for the AOAC and Archer triers.

The AOAC trier took a sample selectively from the top of the truck. The top layer (superphosphate) and second layer (ammonium nitrate), were found throughout the sample core.

Another special straiated sample was prepared in our laboratories, Slide 19 (not reproduced) shows the respective cores taken. The urea was green, muriate of potash (white), and superphosphate gray. Again, the AOAC trier filled preferentially from the top. The green urea top layer was found throughout the core. In this case, with the AOAC trier, the top urea layer slides right on down the tube and this trier takes most of the sample from the top of the truckload. This is not particularly so with the Russell, Archer, and Missouri triers.

Slide 21 (not reproduced) shows a spread out core taken with the AOAC trier. This shows that the potash, the top layer, has been picked up and goes all the way down to the bottom spreading all across that particular core, again non-representatively taking the sample.

These data represent a preliminary report. All of the samples have been taken, chemical and sieve analyses completed, and evaluations are now being made of this information. A complete report will be presented at the AOAC meetings in the Fall of 1966.

Table 1 shows the percent of the material in the core secured by the AOAC trier. This is from the special striated experiment.

Table 1. % of Material In Cores Secured With AOAC Trier from Different Parts of Load

% From

	Top 9″	Middle 9″	Bottom 9″
Ave %	65	22	13

The AOAC trier takes 65% of the total sample by volume from the top nine inches of the load, 22% from the middle and 13% from the bottom nine inches. This is a summation of data for a number of samples and convincingly shows that the AOAC trier takes most of its sample from the top of the load.

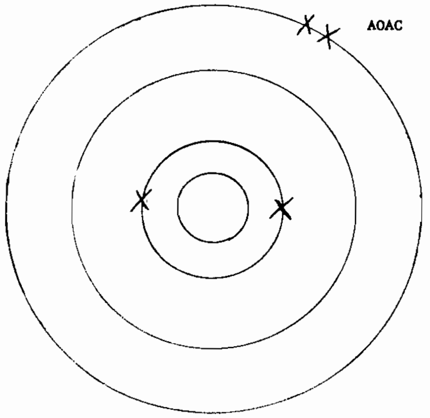
In Table 2, we have ranked the instruments on all of the lots A. B, C, and D. The lots were manufactured granular, a good blend, a very fine pulverized lot, and a "poor" blend.

The samplers were AOAC, Russell, Archer and Missouri triers. I should add that in regard to the AOAC trier, both a single and a double tube trier were used in some of the experiments. The evaluations were made for bias and precision. The AOAC trier was biased most, however, it was also most precise.

The AOAC trier can be described as "precisely inaccurate." As shown on the bull's-eye drawing, the AOAC trier was most precise in taking the two representative sets of ten cores each of that particular sample, but it was certainly far removed from the bull's-eye. Therefore, I would say that it was "precisely inaccurate."

Table 2. Rank of Instrument On All Lots

Sampler	Bias	Precision
AOAC	5	1
Russell	1	3
Archer	3	4
Missouri	2	2



Another example of precision is shown in the second set of scores. We are now evaluating all of the data on all of the lots of samples secured by the four triers. This is being done for N, P, and K. The bias values for the Russell, Archer, and Missouri triers are about the same and better than for the AOAC trier. The AOAC trier stands by itself having considerable bias. Therefore, the conclusion is that one certainly would not want to use a trier such as the AOAC in sampling bulk lots in trucks.

Table 3 gives the percent of the analyses by the respective triers falling below the stream values by more than the AAFCO tolerances. The stream value was used as reference point on all of the lots. We made the assumption that the stream analysis was the true value of that particular lot. Thus, we have tabulated the percent of analyses below the stream value by more than the present AAFCO tolerances. The first column lists the triers. It will be observed that all of the triers did quite well with the manufactured granular fertilizer. This was a uniform material. Secondly, in regard to the good blend, the AOAC trier selectively sampled the fertilizer from the top. This has been presented earlier with the striated samples. Forty-three percent of the time the AOAC trier would take a sample that is below the AAFCO tolerances. The data for the other three triers were quite good. The pulverized fine material was very uniform and apparently all of the triers did a good job in sampling this material. This is of course obvious. All of the triers did not take a representative sample of the poor blend. This lot was purposely segregated. The results are considerably below the AAFCO tolerances.

A summary evaluation is given for all of the triers. The average % of analyses below the stream values were 7% for manufactured granular, 20% for "good blend," 0% for pulverized, and 42% for "poor blend." Further, for the manufactured granular and the pulverized fertilizers, the calculated probability was greater than 95% for all triers that they would be within the AAFCO tolerances. In sampling the "good blend," the probability was 80% and for the "poor blend," approximately 50% (Table 3).

An average percent performance value is given in the last column of Table 3 for each trier on all lots. It will be seen that the AOAC trier performed poorly with respect to the Russell, Archer, and Missouri triers. These last three triers performed at about the same level.

Mr. Poundstone: Tables 4, 5 and 6 give some of the data from

Table 4. Bulk Fertilizer Study—Kentucky Comparison of Sampling Instruments

Pulverized Ammoniated Material Plus Single Nutrient Material

Grade	10.0	10.0	10.0
Sampler			
Stream Cup	10.1	10.2	10.2
AOAC	10.2	10.1	10.2
Archer	10.0	10.2	10.4
Missouri	10.3	10.1	10.2
Kentucky	10.3	10.1	10.3

Ky. Agri. Exp. Sta., November 1965 Preliminary

Table 3. % of Analyses Below Stream by More Than AAFCO Tolerances

Type of Fertilizer

	Mfg. Granular	Good Blend	Pulverized	Poor Blend	% Average
AOAC	3.7	43	0	54	26
Russell	7	10	0	39	14
Archer	7	17	0	35	14
Missouri	8	6	0	39	14
All Triers	7	20	0	42	
Meets AAFCO Tolerances	>95	80	>95	50	

Table 5. Bulk Fertilizer Sampling Study — Kentucky Comparison of Sampling Instruments Ammoniated Granular

Grade	5.0	20.0	20.0
Sampler			
Stream Cup	5.0	19.5*	19.8
AOAC	4.9	19.3*	20.2
Russell	5.0	19.7	19.6
Archer	5.0	19.5	19.9
Missouri	4.9	19.5*	19.9
Kentucky	4.9	19.5*	19.9

*Below Tolerance
Ky. Agri. Exp. Sta., November 1965 Preliminary

Table 6. Bulk Fertilizer Sampling Study—Kentucky Comparison of Sampling Instruments Dry Blended Granular Materials of Specific Particle Size

Grade	5.0	20.0	3.0
Sampler			
Stream Cup	4.7*	20.3	30.1
AOAC	4.2*	18.5*	31.6
Russell	4.9	20.7	30.4
Archer	4.6*	20.6	30.4
Missouri	5.0	20.7	29.6
Kentucky	4.7*	20.2	30.3

*Below Tolerance
Ky. Agri Exp. Sta., November 1965 Preliminary

the Kentucky portion of this study. Dr. Gehrke said that all samplers did a good job of sampling pulverized fertilizers. This is clearly indicated in table 4. Table 5 reports data on a granular 5-20-20. The stream cup showed the product to be a little deficient in P_2O_5. Notice the AOAC sampler at 19.3% did not do as good a job as the other samplers, although three of the other samplers showed deficiency greater than tolerance.

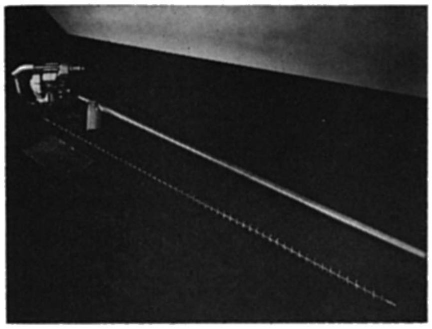
Table 6 reports the dry blend with matched materials. It is formulated to 5-20-30. The stream showed 4.7-20.3-30.1. Notice the AOAC sampler did the poorest job of approximating the stream value. The other samplers are all about the same. Since this was a little deficient in nitrogen it isn't surprising that two of the other samplers showed this.

In summary I emphasize this is not a final report. All samplers took a representative sample of the pulverized material. Difficulty was encountered with all triers, particularly with the AOAC trier as lots became less uniform.

All samplers seem to be somewhat biased, with regard to screen size. They all seem to pick up more of the fines. This warrants further study.

The AOAC trier is not useful for vertical sampling.

We in Kentucky experimented with a fifth sampler shown as the Kentucky sampler in table 4, 5 and 6. This is powered by an electric or a gasoline motor. The power actuates an auger inside a sleeve. The parts are shown in Slide 22. We are still in the process of perfecting this sampler. So far it shows real promise. Thank you.



Slide 22.

Mr. Sauchelli: This was a very interesting presentation and shows excellent team work. We are ready for questions.

Question: Was the material allowed to cone in the various trucks as they were filled?

Mr. Baker: Our intention was that there would be no special precautions to keep these loads from being segregated other than what the operator would do normally. This would vary probably from lot to lot and from state to state. A large proportion of our blenders in Missouri make some effort to avoid coning. Some of these lots were coned, some were not. In the case of the "poor" blend, we purposely allowed this to cone.

Question: Why do you think the samplers were inclined to pick up more of the fines?

Mr. Baker: You are asking what was the mechanism that gave particle size selection. There are numerous theories such as bridging of larger particles allowing the fines to sift in. Whatever it is, it is a flow characteristic of the material which we are sampling and I can't tell you much beyond that at this time.

Question: In sampling these ten cores of the bulk trucks, was any analysis made for information purposes of the individual cores?

Mr. Baker: In this study, no. This has been done numerous times. Bruce could give you a lot of information on that. We have done some of this at Missouri but not in this study.

Mr. Poundstone: We in Kentucky saved alternate cuts of the stream samples. These were analyzed as separate samples. Data on this will be available for comparison with the analysis from the combined cuts as called for in the outline for this study. We are the only state that did this.

Moderator Sauchelli: I told you they would have a very interesting presentation. This certainly shows excellent teamwork, and we're very pleased to have had it.

A Member: In this test work was the material allowed to cone as it fell into the various trucks, or was this prevented, in the loading of the trucks before sampling? Was it allowed to cone?

Moderator Sauchelli: Was the material allowed to cone in the trucks?

Mr. Baker: This would have to be answered by each individual state. Actually what we intended was that there would be no special precautions to keep these loads from being segregated, other than what the operator normally observed. This would vary probably from lot to lot and from state to state.

A significant proportion of our blenders in Missouri, at any rate, do make some effort to avoid coning; and some of these lots were coned, some were not.

Mr. Poundstone: The D sample was coned — was allowed to cone, definitely.

Where we were trying to illustrate a poor blend, it was allowed to cone in every case, I believe.

Moderator Sauchelli: Any other questions?

A Member: Why do you think the samplers were inclined to pick up more of the fines?

Moderator Sauchelli: Did you get the question?

MR. BAKER: I got the question. I don't know whether I have the answer or not.

You're asking what the mechanism was by which they picked up fines.

This is all in the theoretical stage as far as I am concerned. There have been numerous theories as to bridging of the larger particles, allowing the fines to sift in.

Whatever it is, it is a flow characteristic of the material which we are sampling, and I can't tell you much of anything beyond that.

MODERATOR SAUCHELLI: Other questions?

A MEMBER: In sampling these ten cores of these bulk trucks was any analysis made for information purposes on the individual cores?

MR. BAKER: In this study, no.

This has been done numerous times. Bruce could give you a lot of information on that.

We have done this, but not in this study. It was not part of our study.

MR. POUNDSTONE: We did do one more thing. As we took the stream sample in Kentucky—This is peculiar to Kentucky — we did take intermediate stream cuts and we kept them separate. This was to check the uniformity of the product as it was delivered into the truck. We have that data.

But we did not take individual cores with the samplers and compare those cores.

I don't know that any state did that. Do you?

MR. BAKER: No, I don't.

DR. GEHRKE: Fred, I might mention one other point.

In Missouri we conducted another experiment in which we took eight random bulk lots out in the field, and all of the data on all of the triers on all of the random bulk lots agreed with the other data that we took in the study itself of the respective lots and the respective triers and so on.

MODERATOR SAUCHELLI: There's a question out there.

A MEMBER: Did you find with any of these different triers a bias between your NP&K?

MR. BAKER: Yes, we found it, not with a specific trier, we found it with all triers. It was more pronounced with some than others.

But I feel in my own mind that this is probably just incidental. This trier can't identify a nitrogen particle or differentiate between a nitrogen and a phosphorus particle, except as to some very quizzical characteristic of this particle.

I would say that this will come out more clearly in our analysis of the sieve analysis.

MR. POUNDSTONE: In the work in Kentucky, in at least two of the lots, all triers were biased definitely in the direction of picking up more potash and less P_2O_5, for example.

There did not seem to be as much, or any, bias, just looking at the data in nitrogen, in our information.

MODERATOR SAUCHELLI: Did you have any reason for that, Bruce?

DR. GEHRKE: But then again, I guess the answer to that would be that triers are selected in regard to particle size, and the chemical analysis would then only be incidental. And, of course, the chemical analysis would change, depending on the particle size selected.

So there is a specificity, then, or a selectivity is a better word, in regard to particle size that these triers are for.

All of them in a way are biased in that direction. And we have a way to go, really, before we find a trier which is not biased in that particular regard.

The AOAC trier in the bulk lots is by far more biased, not only in regard to particle size, but also to flow into the trier.

MODERATOR SAUCHELLI: Other questions?

It's getting more interesting as we go along.

A MEMBER: To pursue this bias just a little more. In the case presented on the chart, the potassium appeared to be the greatest bias.

Was the potassium compound present in the finest material?

MR. POUNDSTONE: Fred, you have the answer to that. I think it was.

MR. BAKER: That's right. It favored potassium because in most of these lots potassium contained more fine material than the other materials being used.

MODERATOR SAUCHELLI: Other questions?

Down there. Would you make it loud enough so that the rest can hear.

A MEMBER: Was the Kentucky sampler also biased to the fines?

MODERATOR SAUCHELLI: Bruce.

MR. POUNDSTONE: It's a little premature to answer that question. But I would say that it was no different from the other type of triers.

MODERATOR SAUCHELLI: Was it biased in favor of the fines in Kentucky?

MR. POUNDSTON: Well, we think so.

Actually the trier that we used, the Kentucky sampler in our study, was the second one to be made. This is the third one.

The second one had a little more space between the auger and the sleeve. This meant that it actually did a little bit of pulverizing as it was getting the sample.

So this means that the data we have so far on this point is not reliable in terms of running a screen test.

However, this sampler we have here, we designed it to overcome that, — Bob Ludwig won't mind my telling you this, I guess — he actually took this out to his Baltimore plant to try it for this very purpose, to see if this auger sampler would in fact recover a material satisfactorily for screen sieving analysis.

His report on that was very satisfactory.

MR. GEHRKE: I wish to add one comment following Bruce here.

Bob Ludwig also was telling us last night about a new trier, a type of female trier. You'll have to ask him about it.

MODERATOR SAUCHELLI: Bob, are you willing to explain?

We have time for one more question. Any other questions?

A MEMBER: When this data is finally published, how do we get a copy of it?

MR. POUNDSTONE: Well, we'll leave that in the hands of the people who are working with the IBM computer. But there may be some preliminary work that we can report from time to time.

Charles, is this right?

Dr. Gehrke: I think the next report will be at the AOAC meetings in the fall of 1966.

Moderator Sauchelli: As I said yesterday, we have provided this year for a period for stimulation between halves of the session. The management has informed us that no caffeine has been removed from the beverage.

We will adjourn now for the coffee break.

Let's come to order. We want to get started again.

In answer to some questions that were asked in the interim, Mr. Poundstone wants to make a few remarks.

Mr. Poundstone: One of the things that came up during the intermission, and I thought it was important enough that I might share this with all of you.

In using any of these samplers where you have a double tube or a sleeve or something like that, I can tell you that about the third insertion, it will jam on you.

If any of you try to use these or experiment with them, you're going to run into this kind of trouble sooner or later, and from then on, you will always be trying to find ways to keep it from happening.

I'm sure there are many things you can do, but the thing that we have found works best is to spray it with silicone. You can get silicone in a pressure bottle, and if you will coat these triers with silicone, also the auger trier, and then about once a week take them apart and wipe them off carefully and spray it again with silicone, you will have had no trouble at all.

Moderator Sauchelli: Thank you, Bruce.

Now we will go on with our scheduled program.

The next subject is Automation in Chemical Analysis.

Speed, accuracy, reliability and cost consciousness are fundamental requirements of the modern control laboratory.

The major area for creative work by control chemists is to develop speed, that is to say the shortest possible time from sampling until the laboratory's results are reported.

A criticism frequently heard from the plant superintendent or manager is that control data from the chemists are received too late to permit corrective action.

To develop speed it will be necessary to emerge from the rut of doing things in the way they have always been done, the sanctified method, and to develop or accept new techniques, new procedures and better organization.

To do this, however, requires creative thinking by chemists and production management.

Chemical analysis is an important operation in all segments of the chemical processing industry. On this year's program we have given some time to chemical analysis, the previous speakers and those to come, because our feeling is that it is important to the operating personnel, the operating department. You can't sell one pound of fertilizer without the chemists' okay.

So we feel justified in giving time to this subject of Analytical Chemical Analysis.

Older methods are being replaced by instruments employing optics, electronics and other branches of science.

In the fertilizer industry we have been too conservtaive, but, hopefully, progress is being made.

On our program we have provided for a discussion of automation in the chemical analysis of fertilizers.

I was delighted, and impressed to learn about automated analysis that has been successfully installed at several fertilizer plants in Florida.

I had the privilege some time ago to participate in a panel discussion of the subject organized by Technicon Controls.

The first speaker will be Mr. Marten, and the second speaker, Mr. Baumann.

The first speaker is Mr. Marten, Mr. J. F. Marten. He is going to discuss kinds and costs of technical equipment.

Mr. Marten.

Automated Production And Quality Control Of Fertilizers

James M. Marten

I SHOULD perhaps mention first that we have been engaged in automating fertilizer manufacturing processes for some four years. We are being assisted at the present time in particular, by the rapid expansion of fertilizer production throughout the world.

I have attempted to review applications which are relevant to your interests today from this broad background.

We first applied the AutoAnalyzer in fertilizer control for orthophosphate (Fig. 1) This method was further developed in the U.S.D.A. Fertilizer Laboratory for direct available and total P_2O_5 (Ref. 1). Instead of the two tedious analyses required by the official AOAC procedure, a single weighing and appropriate dilution, followed by direct colorimetric analysis with a modified vanadomolybdate reagent, is all that was required for all types of fertilizers.

Research at the Missouri Experiment Station has also lead to the automation of the flame photometric method for potassium (Ref. 2). Anion exchange cleanup to remove interfering anions, laid down by the official AOAC method, has been found to be unnecessary for all fertilizers. Using an adjustable zero-range expander so that the upper end of the working curve could be expanded to read full recorder scale, high analysis potassium compositions can be analyzed from the "direct available P_2O_5" extracts with high precision.

We have thus, an automated direct and rapid system for phosphate and potassium which is as precise and accurate as AOAC official methods.

Increasingly also, ammonium

nitrate is being incorporated in binary and ternary fertilizers of the nitro-phosphate and nitro-chalk type. This gave us a further opportunity to simplify a complex manual procedure, in this case requiring two distillations and two titrations (Fig. 2). The combination of these basic analytical techniques leads to multiple, simultaneous determinations from single samples for complete analysis of multi compound products. (Ref. 3) Urea is, of course, one of these and is analyzed through its reaction with diacetyl. (Fig. 3)

It must be realized that a complete analysis takes only 3 minutes. In contrast, the chemical analysis of a single sample takes about 5 man-hours.

I think at this stage, it may be useful if I spent a little time explaining how these systems are used for production control.

As we all know, in most countries, regulations are laid down as to how the various plant nutrients should be determined in fertilizers. What the manufacturers do, therefore, is to go through the manual procedure for each of the fertilizers produced and then use these analyzed samples as standards for the AutoAnalyzer.

Take, for example, the start up of 22:11:11 fertilizer. Barring mishap, the product should be somewhat in this area. An analyzed sample, is therefore, run as the target composition and followed immediately by a production sample. If the two are identical, there is no arithmetic to be done; if they differ by only a small amount, a simple proportion of peak heights can be used. The further away the production sample from the ideal, the more obvious that the plant must be altered. This procedure would be tedious and expensive by hand but requires no extra work by AutoAnalysis.

Some may ask here for total quantities and not individual species and I may add a footnote to say that we are working towards a three channel system for total nitrogen, total phosphate and potassium. This system will incorporate automatic digestion to eliminate interference from color, convert phosphate to orthophosphate and nitrogen to ammonia. (Fig. 4)

What are the advantages of automation? Firstly, it makes better use of skilled analysts who are required for the official methods of analysts. In the second place, this new approach takes the pressure off the development of more rapid official methods. It also leads to the use of methods, which although too sensitive to variations in environment to be used manually, are quite satisfactory on the AutoAnalyzer under the standardized conditions described.'

What about other production control applications? Large scale manufacture of diammonium phosphate was not undertaken until the 1950's. In the TVA process, it is essential to keep the N:P in the preneutralizer at a mole ratio of 1.45 for maximum solubility. Finally, it is essential to check the product itself after final ammoniation for a mole ratio of 2.0, for ammoniation, unless carefully undertaken can cause some loss of P_2O_5 citrate solubility.

In this application, a solution of ammonium phosphate is split into two subsamples, one which is assayed for nitrogen and one for phosphate, using range expansion to give the necessary precision (Fig. 5)

You will see at the top of the flow diagram a device called a Solid Preparative System. This enables us to process solids, weighted manually into cups, Fig. 6), or automatically weighed (Fig. 7) and taken directly from a process stream. (Fig. 8)

Going back a little in the process, it is well known that close sulphate control of phosphate rocks break-down is desirable not only because of the cost of the raw material, but to give maximum solubilization of P_2O_5 and production of a rapid filtering gypsum. This control is now available using an automatically washed and standardized system (Fig. 9). The result (Fig. 10) taken from the original paper (Ref. 4), are accurate to within $\pm 3\%$ with an analytical lag-time of under 11 minutes.

Space does not permit me to describe other applications, such as the use of automation in soil analyses; to control ammonia losses during ammoniation; to monitor for the pollutant fluoride and to determine the unwanted impurities iron and aluminum in wet process phosphoric acid.

However, these brief descriptions perhaps will have shown you why automation of wet chemistry threatens to become a new technology. All industries can benefit from close control of intermediate processes and final product quality and a more thorough research. Automation will increasingly influence the direction of these endeavors especially as management take a harder look at the efficiency and usefulness of traditional laboratory practice.

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2. Elimination of Anion Exchange Clean-Up in the Flame Photometric Determination of Potassium in Fertilizers. J. R. Ussary and C. W. Gehrke, Proc. Technicon International Symposium 1965
3. Automatic Method of the Analysis of Fertilizers. A. C. Docherty, Fertilizer Society. Proc. No. 79 (London 1963); Proc. Technicon International Symposium 1964
4. Automatic Sulphate Ion Determinations in Wet Process Acid Systems, A. N. Baumann, Mr. Roberts, and B. P. Bell, Proc. Technicon International Symposium, 1964.

MODERATOR SAUCHELLI: Thank you, Mr. Marten.

For those who haven't seen the display -that the Technicon people have here, I recommend that you take a look. It's just amazing what can be done.

The next speaker, Mr. Al Baumann of International Minerals and Chemical Corporation is going to give us a very interesting talk and also show attractive slides on the installation at their IMC Laboratory in Florida. They are able to adapt automation to achieve speed, accuracy and reliability and lower cost per analysis of phosphate rock.

I had the privilege of hearing this talk and seeing the slides and I can recommend it to you.

Mr. Baumann.

Automatic P_2O_5 Analysis Of Phosphate Rock

A. N. Baumann — H. H. Roberts

THE term "Automatic Analysis" has been around for many years. In these years, it has been mis-applied many times and used when only parts of an analytical procedure were automated. In this paper, the term will be used in its true sense, for we are describing a system which is sampling phosphate rock as it is being loaded at a port facility and which splits the sample size to an analytical quantity, pulverizes, dries, weighs, digests and determines its BPL or if you like, it P_2O_5 content untouched by human hands. These seven processing steps require just 16 minutes. That means the first analysis is obtained only 16 minutes after the first sample is taken.

Normally, phosphate rock destined for overseas shipments is blended, dried and loaded on railroad cars inland. Samples of each car are analyzed while the train is en route to the port. Final grade adjustment of shipping parcels are made by adding a car of higher or lower grade material as needed, to make the parcel average out at a specific grade. With this automatic analyzer, we have the ability to maintain a runing average on the rock as it is being loaded. Changes in the blend can be made so that the specified grade is loaded and the customer obtains a more homogeneous shipment.

To understand how this is done, we will look at the International Minerals & Chemical Florida Phosphate Terminal at Port Sutton outside of Tampa, Florida. Here, (Figure 1.), the wet rock can be received by rail or truck from our various washer and benefaction plants located inland. It is unloaded according to grade in this 160,000 ton storage area. Shipments are withdrawn from the base of the piles and fed to a fluo solids dryer with a design capacity of 260 tons/hour.

The dried rock is then conveyed to dry storage silos having a capacity of 60000 tons. The dry material is blended to the customers' specifications as it is withdrawn from these silos and conveyed through the sampling tower and the loading gantry to the ships or barge at a maximum rate of 1800 tons per hour. The sampling tower is the beginning of the automatic analytical system.

The covered storage building in the left of the picture can contain 45,000 tons of the agricultural chemical products of I.M.C.'s Bonnie Chemical Plant. This material because of the quality control procedures used in its manufacture does not require the services of analytical instrument and is not sampled.

Figure 1.

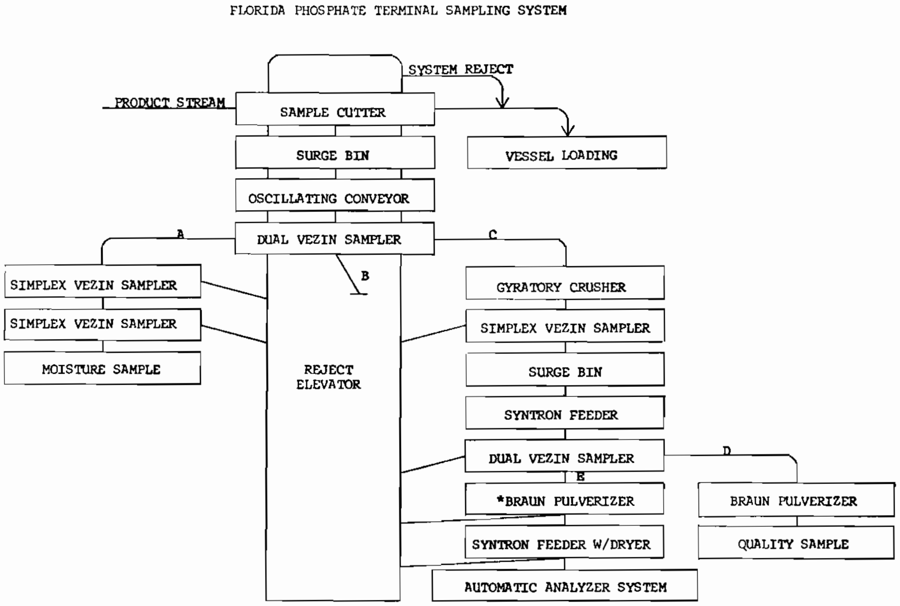


Figure 2.

The solids sampling system was designed by the Denver Equipment Company and is simplified by its representation in Figure 2. The sampler cuts the product stream at a rate regulated to take a set percentage of the shipment. The maximum sampling rate is 15 tons per hour. The material flow through the system is regulated by the surge bin and an oscillating conveyor.

The next unit, a dual Vezin Sampler, splits the sample into three fractions, labeled here A, B and C. Fraction A is the moisture control, fraction B is excess and is returned to the loading stream below the sampler by the reject elevator. Fraction C is the quality control sample.

Fraction A is further reduced in size by these two aditional Vezin

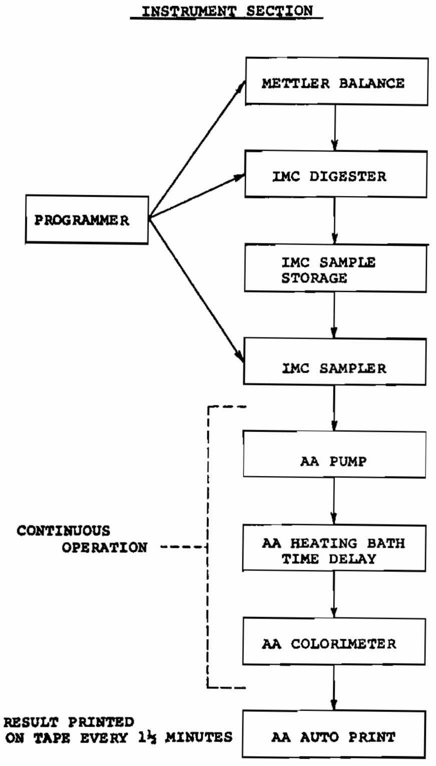
Samplers. Fraction C, the quality control sample, passes through a gyratory crusher, a Vezin Simplex sampler, a surge bin and syntron feeder to again even out the material flow and then to dual sampler.

Here the stream is separated into two fractions, D and E. Fraction D is collected and manually pulverized as the composite quality control sample. Fraction E is the automatic analyzer sample.

This portion is fed through the Braun pulverizer and conveyed and dried by a small syntron feeder with built in heater elements. Some of this pound-an-hour sample stream can be rejected while the remainder is used to feed the funnel on the Mettler automatic balance.

The complexity of this entire scheme is shown by the eight operations taking place in the instrument section alone as shown in Figure 3. The Mettler automatic balance Model DWA 10-5-C, of which a flow diagram is given in Figure 4, has many features which we take advantage of in this system. Its high sensitivity and great accuracy is accompilshed by feeding the pulverized dry sample across a vibrating pan at controlled rates to the weighing hopper. The rate of vibration is varied from high to medium to low as the weight in the hopper approaches the desired weight and stops automatically at the desired weight. If by chance, too much rock falls into the hopper and the total weight exceeds the tolerance chosen, the sample will be rejected and a new sample weighed. The sample, when of proper weight, is held in the hopper until the analytical programmer signals the balance to drop the sample into the digestion cell.

Figure 3.



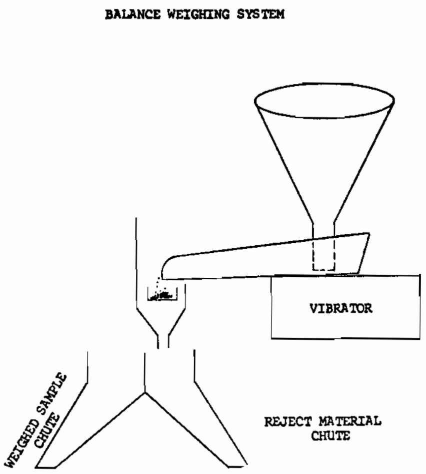


Figure 4.

The digestion system operates on a three-minute cycle. The weighed sample is digested in strong HCl, stored, and a clean degassed -sample submitted to the Auto Analyzer section every minute and a half.

The Auto Analyzer section takes the digested sample and determines its P_2O_5 content by the phosphovanadomolybdic acid colormetric procedure using the solution strengths recommended in the AOAC$^{(2)}$ approved procedure.

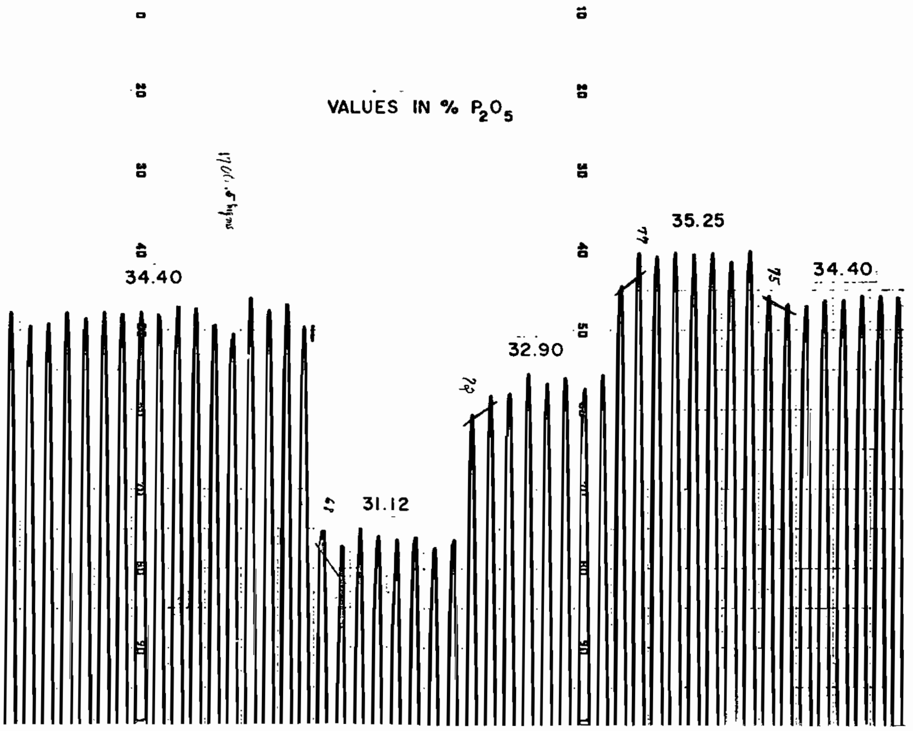
The methodology used is basically that described by Ferretti & Hoffman $^{(3)}$ in the Journal of the AOAC in 1962. The solution milligram loading was increased to 1.85 to 2.5 mg. P_2O_5/ml.

The P_2O_5 content of the sample as determined is printed out on tape in BPL units through the use of a Technicon Autoprint module. At present, a weighed average is manually calculated to determine the cargo grade.

In one of the lengthier tests made during the development of the analytical train, a sample of Florida phosphate rock was fed through the Mettler balance for one hour. Samples of standard rock were then run to determine instrument variation and then another 20 samples of the unknown rock were analyzed in the next hour and so on.

A portion of the recorder chart obtained during this part of the operation is shown in Figure 5. Here we can see the carry-over or "response time" needed when making concentration changes in this system. The concentration of

Figure 5.



the standard rocks analyzed here are 31.12% 32.90%, 35.25% and the unknown sample which averaged 34.4% P_2O_5. Volumetric results on a composite sample of this same rock indicaed a 34.5% P_2O_5 content.

The standard deviation determined with the results of this test of the equipment including the weighing, digestion and colorimetric variations, amounts to ± 0.22% P_2O_5. This accuracy is obtained by using the ten fold electronic expansion of range which makes each percent transmission on this chart equal to only 0.11% P_2O_5. These pointed peaks on the chart were obtained by slowing the chart speed to 10 inches per hour.

This sensitivity and reproducibility, which includes greater digestion and dilution errors than one gets in normal laboratory operations, indicated a possible successful application of the Technicon Auto Analyzer section for routine laboratory samples. We changed the P_2O_5 loading again so that the normal laboratory digested samples could be handled.

Results obtained when a series of phosphate rock check samples of various concentrations were analyzed is given in Figure 6. One gram weights of these samples were digested and diluted to 250 mls. manually. The solution was then presented to the Auto Analyzer. The range expander and chart speed are the same as in the previous chart.

As a result of these tests, we now have a Technicon Auto Analyzer in our phosphate minerals laboratory routinely analyzing plant control samples, 24 hours a day, 7 days a week.

In summary, we at I.M.C. have developed and put into operation, a truly automatic analytical system for solid samples.

Conclusion

Results to date, which include about six months operations, indicate that the standard of deviation first obtained in the laboratory testing was conservative.

The standard of deviation between the results obtained with the installed analytical train and the normal laboratory procedure average out to be only 0.20% P_2O_5 instead of the predicted 0.22%.

This accuracy, remember, is obtained automatically and is complete sixteen minutes after the last sample has been taken.

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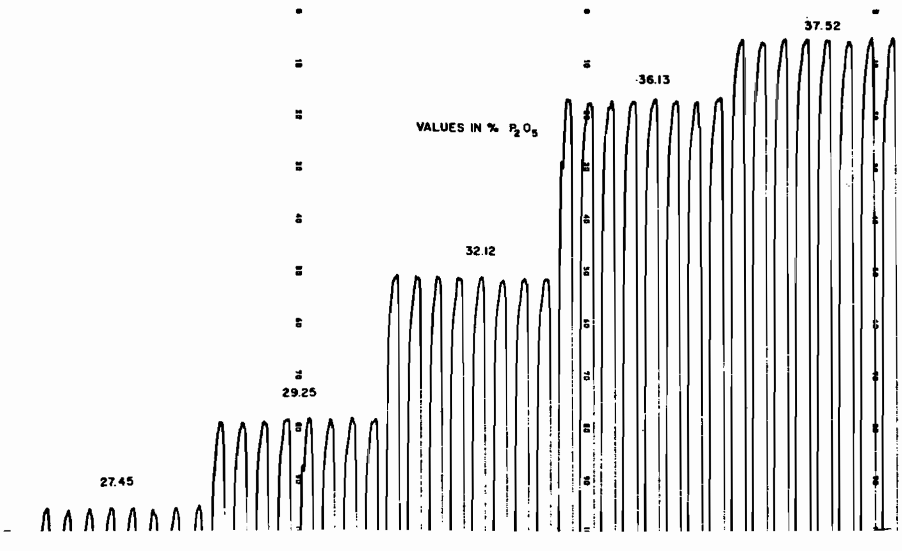
3. Ferretti, R. J. and Hoffman, W. M., Journal of AOAC, Vol. 45, *4* (1962).

MODERATOR SAUCHELLI: They said it couldn't be done, but it is being done.

We now have a few minutes for questions. The first question here.

Figure 6



A MEMBER: I wanted to ask a question of Mr. Baumann.

He cuts from 15 tons down to one pound and I wondered how he eliminated or prevented the problem of size segregation or checked it out to make sure that the composition of the fines or the larger particles coming to the sampler were, in fact, representative of the larger 15-ton or soil sample that came where he started?

MR. BAUMANN: The sampling system was designed and installed by Denver Equipment and is based on studies which were conducted by the Florida Phosphate Chemists Association down there for the last 30, 40 years and this type of system that we used here for sampling is used in all the port facilities in Tampa that I know of.

I did not check it myself. I accepted their word that this was giving us a representative sample.

MODERATOR SAUCHELLI: Dr. Gehrke, you had a question.

DR. GEHRKE: I have a question for Dr. Hofstader. In regard to the nitrogen work, did you use a nitrogen digester on the fertilizer sample and the applicability of that?

Did you do any work on the trace elements and perhaps trace element composition, and perhaps interferences in the chemistry of the nitrogen determination?

DR. HOFSTADER: No, we did not use the automatic digester at any point. We manually digested all our samples according to the regular Kjeldahl Digestion procedure with salicylic acid and there is one point, which I think might answer your second question, namely, that it is very important, we found out, when determining total nitrogen by the automatic procedure that the standards we are talking about running a series of standards of the same type material, that we are running through it and have been subjected to exactly the same distillation. This is very critical, and the acid strength is very important in this particular determination, too. That's one of the regular ones.

MODERATOR SAUCHELLI: Other questions?

A MEMBER: I'd like to ask Mr. Baumann what was his approximate investment for the solid sampler and the other equipment for the complete system of a solid sampler, a typical installation?

Mr. Baumann. Are you talking of our specific installation here or—

MEMBER: Any typical installation for taking a solid sample and processing it through.

MR. BAUMANN: I see. A lot of money was spent on development expenses here, but I would think that you can't get by with less than $75,000 to make an installation such as we have there. Cutting a sample stream at the rate that we're talking of and this would include the sample tower which is probably the most expensive part of the whole thing, because there are a number of splitters and mechanical parts in there.

MODERATOR SAUCHELLI: Dr. Gehrke.

DR. GEHRKE: I wish to add one comment in regard to the routine control laboratories, that as far as potassium is concerned, this can be routinely done on the sample aliquot or, as Mr. Marten mentioned, directly from the direct available extract. This obviates one complete sample preparation.

You can run it at 40 samples per hour. No cleanup, no ion exchange clean-up or any type of thing is necessary, as I reported in years past from 1958 up to 1965.

The phosphorus can also be done directly, automatically on the direct available P_2O_5 extract as the Vanderville photometric method.

I suppose total costwise, in regard to that, yours is quite expensive there but in regard to routine control laboratory I suppose one can set it up for $5,000 to $7,500.

Perhaps Mr. Marten or those people, there, might wish to add on that. I would say it would be roughly in that class for a routine control laboratory to set up a particular system and then you can run many, many samples and it works very well that you have your built-in standards and so on.

MODERATOR SAUCHELLI: Other questions?

As Dr. Gehrke has put it, in a couple of years from now you're not going to be able to find an analyst who can use the wet method.

DR. GEHRKE: I might make one further comment on that, that in regard to the analysts though, or the chemists that you need in the laboratories in this particular regard on automation, your top man must be better—and this is what you want anyway. So don't think that you're going to get away with the hourly help and so on, in regard to this, because you do need to know the techniques and how to handle the equipment, the electronics and all this type of thing.

But this is all well and good, it will really pay off for itself. This is in the general trend of things anyway. You do need this.

MODERATOR SAUCHELLI: Thank you.

If there are no further questions we will resume our discussions at two o'clock. Please be prompt. Mr. Spillman will be moderator.

Thursday Afternoon Session, November 11, 1965

The Round Table reconvened at two o'clock P.M.

Albert Spillman and Dr. Vincent Sauchelli, Moderators, Presiding

MODERATOR SPILLMAN: Rubber products for a long time, in all types of chemical plants, have been used in many difficult corrosive conditions.

Mr. J. J. Lemaire, General Rubber Company, assisted by his co-worker, Mr. Fred Drake, will discuss rubber as a material for construction and use in fertilizer plants.

Rubber — A Material Of Construction. "Flexicone" The Rubber Cyclone and Hopper Componement

J. J. Lemaire

Introduction

GENTLEMEN, I am gratified to be here today, because the Fertilizer Industry gave birth to the product I am about to discuss. The Flexicone idea originated four years ago in the Florida phosphate fields, by one of your number, who envisioned a solution to the problem of material build-up or bridging in dust collector cyclones. From this idea, General Rubber developed the Flexicone as it is presently known and used today by the Fertilizer Industry, as well as other process industries where material build-up and bridging and subsequent material handling problems raise havoc with production costs. Before the development of the Flexicone rigid steel cones were used exclusively. To remove the build-up on the inside of a steel cone, it was necessary to hit the cone at various points with a sledge hammer, Vibrators have been used, but sometimes the material would pack even greater. The resulting irregularities on the inside of the steel cone induced additional build-up. It was also necessary to remove the steel cone regularly for cleaning and scraping. During this time the entire unit must be shut down, with a resulting loss of man-hours and production tonnage.

The flexing action of General Rubber Corp. fabricated rubber cones drastically reduces the chance of material "bridging" on the inside of material handling equipment and dust collection systems, allowing the equipment to run continuously without choking off the flow. A moderate striking force, either physical or mechanical, on the outside of the rubber cone will release the build-up of hardened material on the inside surfaces of the cone. There is no damage to the rubber cone and it maintains its original shape because of its natural resiliency.

The Flexicone development, not unlike other good ideas, was initially tried and proven in actual service where controlled conditions simply did not exist.

Construction

1. *General.* At this point, I would like to describe the construction details. The Flexicone construction is very much like rubber hose, except of course, for its shape. It consists of a rubber tube or liner; a carcass of multiple plies of textile reinforcement to maintain strength and shape and a rubber outer cover to protect the textile carcass from damage and deterioration.

The end connections can be flanged, straight ends with flanges, or no flanges at all for a slip-over type connection. We prefer to make *round* flange connections at the ends, but we have on special jobs made the cones with square or rectangular flanges. The flanges are integral parts of the cone and we can effect a tight seal with split steel back-up rings behind the flange. We are equipped at present to produce Flexicones up to 10 ft. in length and 80″ in large outside diameters.

2. *Composition.* As a rubber manufacturer who compounds elastomers of many types, we can build Flexicones in natural rubber, neoprene, urethane, nitrile and butyl. The selection of an elastomer is contingent upon service conditions for a particular job. Once service conditions are established, our Engineering Staff recommends the elastomer to be used. I.E., Urethane is accepted as a leading abrasion resistant elastomer under certain conditions (150°F). Butyl-Dacron is used where high heat 180°F to 250°F is in evidence and also to resist certain chemicals. And so, while no two systems are the same, we can usually satisfy the specific requirements by our compounding techniques.

3. *Flexicone Shapes* are not restricted to the shape you see here. They can be made with straight away sections at top or bottom or at both ends, flanged or non-flanged. We can also build them with side ports in the wall to permit product evaluation or injection of another vehicle into the cone. In general, the shapes are round, conical or a combination of the two. We are not in a position to furnish a square or rectangular shape.

Installation

The Flexicone is easily installed as it is normally lighter in weight, more flexible and easier to handle than metal cones. Loss-time accidents have been reduced in installation and servicing Flexicones, and as a result plant safety departments have endorsed their use for this very reason. Serious accidents have been reported in plants installing large, heavy, cumbersome metal cones. The rubber Flexicone virtually eliminates this danger at the time of installation, also when cleaning.

Flanged or slip-over Flexicones are installed in a similar manner as are metal cones. For flanged ends, we furnish split steel retaining rings to effect a tight seal. The flanges are usually drilled to standard ASA drilling, but special flange drilling can be accommodated.

Special High Temperature (HT) Construction

The standard construction with cotton reinforcing fabric is designed to operate up to 180°F. The newly developed "HT" High Temperature construction is designed for systems operating continuously up to 250°F. "HT" construction uses butyl rubber throughout and Dacron for the body fabric. The Dacron offers strength as well as superior heat-resisting qualities.

MODERATOR SPILLMAN: Are there any questions for Mr. Lamaire?

Mr. Lamaire, I'd like to ask you one question. Do you specialize in cyclones on higher temperatures than 250 degrees?

MR. LEMAIRE: Not now.

What about rubber lining for fans and chutes, is that your specialty?

MR. LEMAIRE: No, not rubber linings.

A MEMBER: We didn't hear the question.

MODERATOR SPILLMAN: I asked what about rubber lining for fans and chutes and he said they're not in that specialty at the present time.

MR. LEMAIRE: Just one more word on that. We don't rubber line. Everything we make is an actual component which is either a flange slip-over type in large bins and so on which actually fits into the system, into the material handling system.

MODERATOR SPILLMAN: Thank you, Mr. Lemaire.

The next gentleman I am about to introduce really needs no introduction. He's a friend of all of us and has been around quite a while. He has helped many of us with fertilizer technical problems.

The gentleman is our good friend Elmer E. Perrine, Director of Technical Services, Nitrogen Division, Allied Chemical and Dye. Mr. Perrine will discuss "Safety A Way of Life."

Elmer has been a good friend and advisor to our Round Table. He has contributed many technical discussions on fertilizer manufacturing technology. He has a great respect for safety and has written many papers on safety for handling anhydrous ammonia, phosphoric acids, solutions, nitric acid and sulphuric acid.

Last year, in Raleigh, North Carolina, Elmer received the National Safety Council's Citation For Recognition of Ten Years of Service in the Advancement of Safety.

Elmer served as General Chairman for the Fertilizer Section of the National Safety Council during 1959 and 1960. He edited the Safety Council Newsletter for a number of years.

Elmer has been a featured speaker on the safe handling and application of agricultural chemicals at many meetings of the American Chemical Society. He has appeared on safety discussions at Governors Conferences and is the author of many safety articles for the National Safety Newsletter.

It is a privilege to have Elmer here to discuss Safety in Fertilizer Plants. Elmer.

Safety — A Way Of Life

Elmer C. Perrine

THROUGH the ages man has contended with two variables which determined his tenure on earth.

The conditions under which a man has existed may vary slowly or suddenly but enough to make his former activities downright hazardous.

What Makes Accidents?

The take-home explanation of an accident is stated by the National Safety Council as the result of an unsafe act committed in the presence of unsafe conditions. An equally satisfactory description is, "something waiting to happen." Much of the concern and responsibility for safety rest in those simple explanations.

Management determines the conditions at least in the initial stages even if the workers fail to understand, maintain or improve these conditions to their own sorrow. The worker has the most at stake, has the greatest immediate influence on accidents through his acts and he is the most variable of the factors.

The greatest safety device ever invented is the safe worker.

Nothing Is Constant

No man remains the same for very long, even for the space of minutes or sometimes even for a few seconds. The lives of normally safe workers have been snuffed out through a second's time of inattention or distraction. Distraction could be external or within himself while reflecting on the pleasures of the past or the future.

If it were possible to build a plant which would be safe for the most careless, inept workers without supervision it would not remain so very long. It would not be profitable to operate it. On the other side of the coin it becomes impractical to operate for very long any plant which is grossly unsafe or with many men who may be grossly unsafe workers.

We must build our industry and processes to economically use the materials of the trade. We must also use men much as we find them with the hope of improving their chances of survival. And men are often unpredictable in their thoughts and actions.

What Makes Accident Statistics? How Can They Be Controlled?

The National Safety Council's report on injury rates for 1964 shows the fertilizer industry as being 14th from the bottom of a list of 42 industries in disabling accidents. The average of all 42 is about 6.5 disabling accidents per million man hours of work with the fertilizer industry having about 10.

There are some good strong forces at work in our industry to control accidents. You have a very active Fertilizer Section in the National Safety Council. Many of you are members of the Council and many more should be. For its work in safety in 1964 the section won the Cameron Award which is the highest honor the Council can bestow on a section for effective safety work. There are many men elsewhere in the industry who are devoted to safety.

Some of the men to whom this message is addressed have the power and the ability to influence the conditions which have a bearing on safety. Others have the ability and the moral responsibility to influence the acts, or to make safe workers of the men; the greatest of all safety devices. Both management and supervision should gear their thoughts to the truism that an accident is the result of an unsafe act committed in the presence of unsafe conditions.

The factors which make the statistics, or the accidents are unskilled, unwarned, or inattentive workers, sometimes through rarely unsafe original equipment and processes, careless maintenance and operations which are permitted to deviate from a safe norm.

For a long time the injudicious and sometimes unknowing use of high heats in repairing equipment and in the processes probably was number one factor in serious accidents. This is still a very potent factor with some new acts and conditions crowding it for low honors.

We are saddled with the safety problems that are endemic in the handling of millions of tons of materials at the lowest possible cost. As these materials are moved several times it is probable that the fertilizer industry handles as much bulk as was handled in building the Panama Canal in less years than that task required.

Areas Of Concern

One thing, which stands out clearly, since it may be both a condition as well as an act, is the generation, existence, or unwise use of heat. This may be through intended efforts to attain a physical condition of the fertilizer such as in the use of large amounts of sulfuric acid of high concentration, of high dryer temperature, or temperature in the storage pile.

Ill-advised use of high heats include cutting and welding on equipment which has ever contained nitrogen solution without first thoroughly removing all trace of nitrogen deposits or any vapors. There is a sad history as well as a generally unrewarding record of applying torches and burning rags to free a system which has become blocked by deposits from the solutions. The first remembered fatal accident associated with the use of nitrogen solutions occurred about 25 years ago as an explosion when an acetylene torch was used to free a blocked valve. Within the past year a similar but less serious accident occurred.

The use of low pressure steam or hot water is usually a more practical and much safer method.

Improper condition of equipment through poor inspection, maintenance and operation can result in dangerous over-all or in locally large amounts of sulfuric acid being applied. In the presence of nitrogen solutions and potassium chloride with a small amount of moisture in the formula this situation continues to be a serious problem.

> Faulty metering is sometimes the root cause of the application of excessive amounts of sulfuric acid. Corroded or fouled distributor pipes add their evil influence.
>
> Failure of delivery of the dry ingredients into the mixer tends to concentrate the acid-solution relation.
>
> Recycle failure has the same effect. A factor which is sometimes corrected too slowly in the sliding or rocking of the mass instead of its being mixed as intended.
>
> This permits direct contact of large amounts of sulfuric acid and solution. Operators should be constantly alert for this possibility and be prepared to correct it immediately.
>
> There seems to still be some installations which make it possible for acid and nitrogen solution to move from one tank to the other through the system. These systems should be totally separated even to using separate distributor pipes in the mixer. We hope the industry has learned to never arrange any system to permit any product to enter the water system. This has happened and may at times be a tempting thought. Banish that thought forever.

Excess heat in the dryer has generated so much noxious fumes that the fan could not carry all of it away.

Blasting in hot storage piles has ended in the eventual thermal decomposition of storage piles of considerable size. There are no known cases of actual explosions of hot complete mixed fertilizer under these conditions. It is a good practice to know the temperature of all fertilizers at all times. Rises of more than 10°F or 15°F in the storage pile should arouse concern. Many good operators make every effort to keep the storage pile temperatures below 135°F and even lower for some grades.

Effects Of Deterioration

When sulfuric acid corrodes steel or any other metal it renders the equipment unsafe. Breakage can occur. Dangerous mixtures can result from improper metering through damaged equipment. This corrosion generates hydrogen which has a very wide explosive range when mixed with air. Only acetylene of our common gases has a little wider range. High pressure can develop during the corrosion if the gas is trapped in closed equipment such as in piping and tanks. A trained and equipped safety attendant should maintain constant vigil from outside when any man enters a tank. Better yet, leave the servicing of tanks to professionals.

Spraying of victims with nitrogen solution, anhydrous ammonia, and acids is still far too common in this industry.

This type of accident results from poor hoses or to hose connections, failure to release all pressures, failure to drain the system of all contents and failure to lock out all controls before any work is performed on the equipment.

These accidents become far more serious than they need to be when the victim fails to wear any or all of the prescribed safety equipment. This equipment may include ammonia type gas masks with full view and speaking diaphragm. Chemical type goggles or full face shields may be appropriate where anhydrous ammonia or nitrogen solutions are not involved.

Rubber gloves and rubber shoes with the trousers outside of the shoes and full length sleeves with protector head gear are minimum requirements for exposed personnel.

Tragic Water Shortage

We are not now speaking of billions of gallons or of cubic miles or of 36 inch mains. We may not be considering a gallon or even a pint as creating a tragic water shortage. For a few very critical seconds, perhaps only one second this shortage can be successfully met with as little as a few spoonfuls or perhaps a few drops of water. Many eyes and in some fated persons both eyes have been lost when some acid, caustic nitrogen solution or even some household standby has gotten into the eye when water, even a spoonful, was within reach of the victim to give the first second's aid by flushing the eye with water.

A man may be temporarily blinded and alone far removed from any water or other help in an accident.

Every person who may conceivably be exposed to chemical eye injuries should carry on his person at all times a small plastic squeeze bottle of water. There should be some restriction in the flow from the usually large opening of the bottle for maximum effect from a small amount of water. Variety and ten-cent stores usually carry a nice assortment of these bottles.

This first second's self aid should never be considered as a complete treatment. The victim's eyes and other affected areas should be flushed immediately with running water or frequently renewed water for at least 15 minutes, actually timed. Open tanks filled with water or deluge type showers used immediately are recommended. They should be placed away from likely accident areas but readily accessible. Immediate professional attention should then be given. Never delay the use of water for even a few seconds. Let the doctor prescribe the use of any substance beyond the water treatment.

In the Far West another man is campaigning for this personal, small supply of water to be carried at all times. We have hammered this point home for several years from the East. Both of us fervently hope to see this thought spread from shining sea to shining sea.

MODERATOR SPILLMAN: Thank

you, Elmer, for that very fine paper.

I was asked two questions before you came up here, Elmer. One was: How do you become a member of the Safety Council and, number two, what are the costs?

MR. PERRINE: For a small plant this may be as little as $25 a year and it is based on the number of employees you have. Just write in to the Fertilizer Section of the National Safety Council and they will be very happy to make you a member.

It's very simple.

MODERATOR SPILLMAN: Thank you.

Are there any questions?

If not, I shall turn the meeting back to Dr. Sauchelli. Thank you all.

MODERATOR SAUCHELLI: In Europe the nitrophosphate processes are rapidly gaining favor. Nearly every country on the Continent has or will soon have one or more plants of this kind. At least 8 different nitrophosphate processes are in operation, some of which have several variations.

Some of the more important processes will be discussed in the panel so ably organized by Mr. Weber and, as I said in my opening remarks yesterday, by Mr. Weber, of Dorr-Oliver and Mr. Travis Hignett of TVA. We have a most interesting, well-organized panel and I am sure the discussion is going to give us important information and a good cross-section of these processes rapidly becoming important.

I turn the meeting over now to Mr. William C. Weber, Dorr-Oliver, Incorporated, who will be the panel leader.

Panel Discussion On Nitrophosphates

William C. Weber

Panel Leader

MR. W. C. WEBER: Before opening this discussion I would like to say that I am not up here because I'm any expert on this subject. I'm up here because I stuck my neck out and suggested that this would be a very timely subject for discussion at the Round Table, so I got the job.

OUR subject today—Nitrophosphates — is very timely and we are exceedingly fortunate to have a distinguished international group of experts to enlighten us on this somewhat complicated subject. By nitrophosphates we mean compound or complex fertilizers containing soluble P_2O_5 *which has been derived from the digestion of phosphate rock with nitric acid.* Let me repeat—by definition, a nitrophosphate process, and the N-P or N-P-K nitrophosphate produced thereby, is not merely one containing nitrates or ammonium nitrate unless a substantial part of the P_2O_5 has been obtained by attacking phosphate rock with nitric acid. The nitric acid so used ends up in the complex fertilizer, or as a by-product, in the form of ammonium nitrate or by reaction with the potash constituent as potassium nitrate. The P_2O_5 ends up as water soluble monocalcium or ammonium phosphate, or as citrate soluble dicalcium or iron and aluminum phosphate. It is possible to produce the same complexes by mixing ammonium nitrate or nitrogen solutions with soluble phosphates derived from the sulfuric (or phosphoric) acid digestion of phosphate rock. Our definition excludes these ramifications from our discussion today because they would lead us away from our primary objective which is to examine the possibility of eliminating or minimizing the use of sulfuric acid in the production of phosphate fertilizers by utilizing the acidic properties of the nitric acid which is now wasted when producing ammonium nitrate by direct neutralization.

Nitrophos processes are used extensively in Europe and have been popular for many years, and we are fortunate to have speakers from Holland, Germany and France who can give us the benefit of this experience. To date, the production of nitrophosphates in the U. S. A. has been very limited. Probably the main reason has been the ready availability and low cost of sulfur. Possibly another consideration has been that nitrophos processes presume the acceptance of rather high nitrogen complexes and a very hygroscopic constituent, namely ammonium nitrate. The trend in this country in recent years has been to raise the nitrogen content and to use increasingly large amounts of ammonium nitrate in compounds; hence these objections, if they existed, have become less valid. On the other hand, sulfur is now in limited supply and the price is rising sharply.

It was, therefore, the opinion of your Executive Committee that nitrophosphates was a very timely subject for discussion at this meeting. If sulfur remains in short supply and the price high, the economies in the substitution of nitric acid will become of great interest, and we may see the construction of many nitrophosphate plants, especially as part of integrated nitrogen-phosphate production facilities.

In using nitric acid to attack phosphate rock the unique problem, compared with sulfuric acid attack, is that the calcium salt of nitric acid—to wit, calcium nitrate — is water soluble and cannot be separated readily from the phosphoric acid. If the insoluble tricalcium phosphate in phosphate rock is to be converted to soluble forms, for each mole of P_2O_5, one mole of CaO must be removed in going to citrate soluble dicalcium phosphate, two moles in going to water soluble monocalcium phosphate and three moles in going to water soluble ammonium phosphate. Furthermore, phosphate rock also contains calcium as carbonates and fluorides which must also be removed. It is in the method of removing or converting the excess calcium that the processes differ. These alternates can be categorized very simply as follows, but will be explained in more detail by the speakers.

1. Part of the calcium nitrate can be crystallized out of the digestion liquid by cooling and produced as a separate product, or converted to am-

monium nitrate or nitrochalk. The remaining calcium reports in the fertilizer complex as dicalcium phosphate. This is the "Odda Process." There are several variations to this approach.

2. Carbon dioxide can be used to precipitate in the product the unwanted calcium as calcium carbonate. This is the PEC so-called "Carbo-Nitrate Process."
3. The digestion can be done with a mixture of sulfuric and nitric acids so that the unwanted part of the calcium is precipitated in the product as calcium sulfate, and the remainder is converted to dicalcium phosphate. This is known as the "Sulpho-Nitrate Process."
4. The digestion can be done with a mixture of phosphoric and nitric acids in the proper proportions to convert all the calcium to dicalcium phosphate. In this case, however, calcium is discarded as calcium sulfate in the phosphoric plant. This is the conventional "Phospho-Nitrate Process."
5. The calcium nitrate can be precipitated as dicalcium phosphate with diammonium phosphate or triple superphosphate and ammonia. In this case also, calcium is discarded as calcium sulfate when producing the phosphoric acid used in making the superphosphate.
6. Ammonium sulfate or potassium sulfate can be used, if available, in sufficient quantity to react with the unwanted calcium to produce calcium sulfate, the remainder of the calcium reporting as dicalcium phosphate in the complex.

Alternate 1 above, the Odda Process and variations thereto, will be discussed by Mr. Piepers and Drs. Banthien and Nees. Alternate 2, the PEC Process as well as the Sulpho-nitric and Phospho-nitric processes, will be discussed by Mr. Berquin. Mr. Young will discuss TVA work on Alternates 3, 4, 5 and 6.

You will see from the above very sketchy review and later from the detailed papers that the bulk of the P_2O_5 in these nitrophos processes is converted to dicalcium phosphate which is citrate soluble-water insoluble. The water solubility of the P_2O_5 in most nitrophosphate does not exceed 30 to 40 percent, although there are some possibilities of obtaining higher percentages which will be discussed by the panel members.

There has been considerable disagreement on the need for water solubility, but in general, agronomists now feel that 40 to 50% water solubility is quite acceptable and that dicalcium phosphate is a good source of nutrient phosphorus under most soil conditions.

In Great Britain and some other areas, nitrophosphates are not acceptable as fertilizers are sold on a water-soluble basis. This is one of the problems associated with the production of nitrophosphates. What is probably needed is a new process that will use little or no sulfuric acid and produce a product that is mainly water-soluble.

In presenting our speakers, Dr. Sauchelli and I decided that probably the best procedure would be to have all of the papers first before having any question and answer periods, because these papers are all rather interrelated and it might be well to have all of the questions at once.

So we will proceed to go through the papers and then when we have finished, which will probably be sometime tomorrow morning, we will have, we hope, a good discussion and lots of questions.

I might say that, as Dr. Sauchelli mentioned, there are 8 different nitrophosphate processes in use in Europe. I didn't count them up myself. We, therefore, have a rather representative group of speakers here but there are other processes and I have been approached by some people who had their feelings hurt a little because we didn't ask them to speak on this panel.

Now, I will turn the meeting over to Mr. R. D. Young who is Chief of the Process Engineering Branch at TVA who will speak on the Conventional Processes that have been studied by TVA.

Nitric Phosphate Process Utilizing Supplemental Acid

Ronald T. Young

PROCESSES using nitric acid to decompose rock phosphate have been used in Europe since the early thirties. Today they comprise a major part of the fertilizers produced on that continent—totaling 4 to 5 million tons annually. In the United States such processes have not been used widely, although there has been considerable activity in development work and at least five commercial-scale plants are now in operation plus several small plants that make only slurry fertilizers. The TVA has studied processes of this type quite actively over a period of almost 20 years. There are some sound reasons for interest in these so-called nitric phosphate or nitrophosphate processes. The main one is a matter of economics since formulation cost for nitric phosphate is considerably lower than for fertilizers based on superphosphates or ammonium phosphates. Recent estimates from Europe and this country show a moderate but consistent over-all cost advantage for nitric phosphates as compared with ammonium phosphates. The current concern over price increases for sulfur has focused further attention on the nitric phosphate route for decreasing requirements of sulfur for the world's rapidly expanding fertilizer production.

The favorable economics for nitric phosphates results from two main factors shown below.

Use of comparatively cheap phosphate rock directly in process to supply a large part of the P_2O_5. Storage and handling of intermediate materials such as superphosphate are avoided.

Use of nitric acid for the twofold purpose of solubilizing the phosphate rock and supplying a large part of the nitrogen in the finished fertilizer.

There are several main types and variations of processes that commonly are referred to as nitric phosphate or nitrophosphate. This discussion is concerned with those that may be referred to as the mixed acid or supplemental acid types since phosphoric or sulfuric acid is used together with the nitric acid. My remarks will be concerned mainly with TVA's work on processes of this type. Similar processes have been developed and put into use by others *(9,3)*.

Chemistry of Nitric Phosphates

Nitric acid alone in proper proportions will readily convert the P_2O_5 in phosphate rock to an available form. This reaction can be expressed as follows.

$$\underset{\text{(Phosphate rock)}}{Ca_{10}F_2(PO_4)_6} + 20HNO_3 = 10Ca(NO_3)_2 + 6H_3PO_4 + 2HF$$

The main components after acidulation are an impure phosphoric acid, a large proportion of calcium nitrate, and a small amount of fluorine compound. On ammoniation the following reaction can be expressed.

$$10Ca(NO_3)_2 + 6H_3PO_4 + 2HF + \underset{\text{(Ammoniation)}}{14NH_3} =$$
$$3Ca(NO_3)_2 + 6CaHPO_4 + 14NH_4NO_3 + CaF_2$$

A considerable amount of objectionable calcium nitrate would be left in the ammoniated product. This would cause the fertilizer to be extremely hygroscopic and too unstable to dry properly. For satisfactory products, the various nitric phosphate processes must remove this excess calcium nitrate physically or chemically.

There are proved processes for removing part of the calcium nitrate from the extract by cooling, crystallization, and centrifugation to avoid this problem. Some of these that are utilized in Europe will be discussed by other speakers. A convenient method is to use supplemental phosphoric or sulfuric acid with nitric acid to deal with the excess calcium in the rock. Thus, on ammoniation, no calcium phosphate more basic than dicalcium phosphate will form and all nitrate will be fixed as ammonium nitrate.

The use of phosphoric acid to adjust the extract is expressed in the reaction shown below.

$$\underset{\text{(Phosphate rock)}}{Ca_{10}F_2(PO_4)_6} + \underset{\text{(Acidulation with mixed acid)}}{16HNO_3 + 4H_3PO_4} = 6H_3PO_4 + 2Ca(H_2PO_4)_2 + 8Ca(NO_3)_2 + 2HF$$

$$\text{(Ammoniation with } 17NH_3 = 9CaHPO_4 + NH_4H_2PO_4 + 16NH_4NO_3 + CaF_2$$

Thus, the calcium nitrate is eliminated in the ammoniated product that consists mainly of dicalcium phosphate, ammonium phosphate, and ammonium nitrate.

Surfuric acid can be used similarly as shown below.

$$\underset{\text{(Phosphate rock)}}{Ca_{10}F_2(PO_4)_6} + \underset{\text{(Acidulation with mixed acid)}}{12HNO_3 + 4H_2SO_4} =$$
$$6H_3PO_4 + 4CaSO_4 + 6Ca(NO_3)_2 + 2HF \text{ (Ammoniation with) } 13NH_3 =$$
$$5CaHPO_4 + NH_4H_2PO_4 + 4CaSO_4 + 12NH_4NO_3 + CaF_2$$

When sulfuric acid is used as the supplemental acid, the same compounds are formed on ammoniation, but the product is diluted with some calcium sulfate and lower grades result than when phosphoric acid is used.

The stoichiometry of nitric phosphates is not exact. By varying the proportions of acids within reasonable limits, the water solubility of the phosphates in the product can be varied. The water-insoluble portion is mainly dicalcium phosphate and the water-soluble portion is ammonium phosphate or monocalcium phosphate. With minimum proportions for solubilizing the rock and adjusting the excess calcium, the water solubility would be 20 percent or lower. By use of additional phosphoric acid, for instance, the water solubility can be increased to 40 percent or higher. This increases the formulation cost, however. The following tabulation shows how the requirement of phosphoric acid varies with water solubility of the nitric phosphate product.

Water solubility of P_2O_5 in nitric phosphate, %[a]	Proportion of P_2O_5 from phosphoric acid, %
50	69
40	62
30	56
26	54
20[b]	38

[a] Grade 20-20-0.

[b] Grade decreased to 19-19-0.

There are other methods similar to use of supplemental acid for controlling the excess calcium oxide. Carbon dioxide can be used to precipitate excess calcium as calcium carbonate, or a solid form of sulfate such as potassium sulfate can be added instead of sulfuric acid. These procedures are not used as widely as is addition of phosphoric or sulfuric acid.

The TVA Slurry Process

TVA's first nitric phosphate process of the supplemental acid type was a slurry-type process developed in pilot-plant work in the late forties (*6*). A flow diagram of this process is shown in Figure 1.

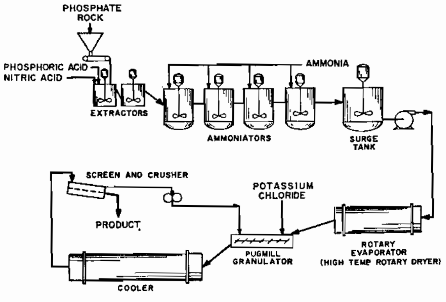


Figure 1.

Flow diagram of original TVA slurry process for nitric phosphates

Phosphate rock was extracted with nitric and phosphoric acids in two tanks in series and the resultant slurry was ammoniated with anhydrous ammonia in four reactions tanks in series. All of the reaction tanks were provided with thorough agitation. The proportioning of ammonia among the four stages was quite critical to obtain high availability of P_2O_5 in the product. The optimum was about 57, 26, 13, and 4 percent to the respective stages. Use of less than four stages or appreciable increase in proportion of ammonia added in the latter stages gave considerable reversion to citrate-insoluble P_2O_5. The fluid slurry from the ammoniation train that contained about 30 percent water was fed through a high-temperature rotary dryer. This unit was actually an evaporator, since the material remained fluid throughout and discharged as a melt. It was possible to evaporate the slurry to a very low water content, so that it granulated readily in a pugmill where the offsize material was recycled and potassium chloride was added if an N-P-K product was desired. In the pilot plant only cooling was required to obtain satisfactorily low moisture content. In those days granulation was not particularly critical and screening to remove the plus 6-mesh oversize was considered to be satisfactory. Closer screen sizing as required today would increase the recycle to the pugmill. Typical grades produced in the pilot plant were 17-22-0, 14-14-14, 14-28-0, and 11-22-11. These were considered very high analysis at that time.

The use of supplemental sulfuric acid was also practical in this process (*10*), although not so much water could be evaporated from the slurry in the rotary evaporator because of the calcium sulfate content. Drying of the product was required. Grades included 14-14-0, 11-11-11, and 8-16-0.

Potassium sulfate was used effectively to adjust the excess calcium oxide to avoid calcium nitrate in the product in another modification of this process (7). By adding part of the potassium sulfate in the ammoniators, problems in preventing reversion to citrate-insoluble phosphate were decreased.

The use of carbon dioxide in later stages of ammoniation to convert the calcium nitrate to calcium carbonate and ammonium nitrate was also demonstrated in pilot-plant work with the TVA slurry process (*8*). Grade of the product was 14-11-11 and water solubility of the P_2O_5 in the product was very low—only about 1 percent.

T. P. Hignett has summarized the TVA work on the slurry process (*4*).

The phosphoric acid modification of this process later was used in a commercial-scale plant at Sheffield, Alabama. It is still operated by the Tennessee Farmers Cooperative with some modifications and with use of supplemental solid feed materials such as triple superphosphate and diammonium phosphate. Plant-scale experience has shown that one or two additional stages of ammoniation would be needed to ensure high availability on complete ammoniation, and that drying and cooling of the pugmill product is desirable to ensure adequate process flexibility.

Process Using the TVA Continuous Ammoniator

Nitric phosphate work at TVA was not very active for the next few years until the TVA ammoniator-granulator came into the picture (*11*). With the demonstarted efficiency and versatility of this rotary drum unit for mixing, ammoniation, and granulation in one operation, its applicability in nitric phosphate processes was investigated (*5*). As somewhat of a surprise it was found that complete ammoniation of nitric phosphate extract slurry in the TVA ammoniator could be readily accomplished without any concern over reversion of phosphate to citrate-insoluble form. Feeding the slurry above the bed and ammonia beneath through the usual type sparger, with recycle used to control granulation, consistently gave good granulation and high availability of product. Apparently the TVA-type continuous ammoniator acts like several ammoniation stages in series. Conditions in this unit apparently are not conducive to localized overammoniation, a probable cause of reversion, and retention time is quite short.

A flow diagram of the complete process using the continuous ammoniator is shown in Figure 2.

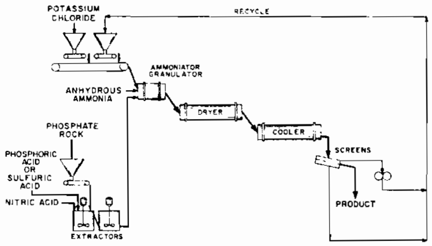


Figure 2.

Flow diagram of nitric phosphate process using TVA ammoniator granulator

The previously developed two-stage extraction system for reacting rock with nitric and phosphoric or sulfuric acids was used. The extraction slurry was pumped and sprayed onto the bed in the ammoniator drum. Ammoniation and granulation were carried out with recycle as the main control of granulation. The product was dried, cooled, and sized in a conventional manner. When N-P-K grades were produced the potassium chloride was fed with the recycle to the ammoniator-granulator. Typical grades produced in the pilot plant were 14-14-14, 12-12-12, and 10-20-15. Recycle ratios in the pilot plant ranged from 3:1 to 6:1. Pilot-plant tests showed that triple superphosphate could be used instead of supplemental acid to adjust the extract. It was effective when fed to the ammoniator drum.

This process utilizing the continuous rotary ammoniator was put into commercial use in a few plants in Europe (*1*). Operation of these plants has been generally satisfactory, but production rate has been lower than desired because of high recycle requirement. This has been partly the result of using nitric acid at concentrations lower than 60 percent HNO_3. Some of the main grades produced include 6-12-18, 14-14-14, 13-13-21, and 10-15-20. Recycle ratio has been 6 or 8 to 1 giving comparatively low production rates of 8 to 12 tons per hour for most grades. Use of supplemental solid feed materials, such as superphosphates and ammonium sulfate, increased the production rate for some grades.

Latest TVA Process Modification

When the preneutralizer came into common use for neutralizing acids prior to feeding to the continuous ammoniator, the applicability of such a unit in the TVA nitric phosphate process was investigated (*2*). It was expected that evaporation of water by heat of reaction in the preneutralizer and removal of heat prior to the continuous ammoniator should decrease the recycle requirement. The extent to which the reaction could be carried out in the preneutralizer was uncertain because of problems that are experienced in obtaining high availability in slurry ammoniation.

Pilot-plant tests of the preneutralizer exceeded our expectations for this unit. It was practical to feed 75 to 85 percent of the total ammonia to the preneutralizer and utilize the reactions to decrease the water content of the extraction slurry to a low level without appreciable loss of availability and with good fluidity of slurry. Below is shown the effectiveness of the preneutralizer in removal of moisture.

Ammonia to preneutralizer, % of total	0	53	70	77	85
Temperature of slurry, °F.	140	269	275	280	290
Moisture content of slurry, %	24	12	9	8	4

After practicality of the preneutralizer was established, it was included as an integral part of the complete pilot-plant system. A flow diagram of the process is shown in Figure 3.

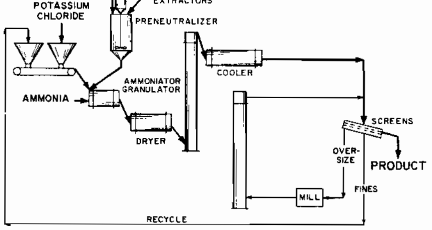


Figure 3.

Flow diagram of modified nitric phosphate process

The previously proved two-stage extraction system for treating the phosphate rock with nitric and phosphoric or nitric and sulfuric acids was employed. The tanks were equipped with thorough agitation and with mechanical foam breakers. The slurry flowed by gravity through the extractors and into the preneutralizer. When phosphoric acid was used as the supplemental acid, 70 to 85 percent of the total ammonia was fed to the preneutralizer, decreasing water content of the slurry from about 26 percent to about 6 percent. Use of gaseous ammonia provides greater heat of reaction and results in greater evaporation of water from the slurry. Gravity flow from the preneutralizer to the ammoniator was tested at first, but surging was a serious problem. Later the slurry was pumped at a controlled rate using a magnetic flowmeter. It was distributed on the bed by spray nozzles of the Whirljet type. The remaining 15 to 25 percent of ammonia was fed through a drilled-pipe sparger beneath the bed. When three-component grades were produced, the potassium chloride was fed to the drum with the recycle. The positive control of slurry feed rate to the ammoniator drum by pumping and metering showed distinct advantages by eliminating surging. Recycled undersize at a ratio of about 4:1 was satisfactory for 20-20-0 grade and about 3:1 was sufficient for 15-15-15.

Tests were made with hot and cooled recycle. There was some advantage for cooled recycle since a somewhat lower ratio was required. However, operation with either cooling of the entire throughput or only the sized product (as in granular ammonium phosphate systems) should be feasible. Single-deck screens and chain mills are preferable for sizing and crushing operations. Passing of all recycle through the undersize screen is considerably more efficient than use of appreciable amounts of coarser material. For this reason it is desirable to maintain granulation "on the fine side" with just the amount of minus 6 plus 8 or minus 6 plus 10 that can be taken as product at the required recycle ratio.

With phosphoric acid as the supplemental acid, N:P_2O_5 ratios from 1:2 to 2:1 were satisfactory. Some grades with and without potash for the various ratios are shown below.

Ratio	Grade without K_2O	Grade with $K_2O = P_2O_5$
2:1:X	26-13-0	20-10-10
1:1:X	20-20-0	15-15-15
1:2:X	14-28-0	10-20-20

Steam was needed to increase the temperature in the extractors for good extraction and satisfactory fluidity of slurry when producing the N:P_2O_5 ratio of 1:2; some water addition was required when highest concentrations of feed acids were used. Most pilot-plant work was with 20-20-0 grade. Water solubility of the phosphate usually was controlled at about 40 percent by use of some excess phosphoric acid and a small amount of sulfuric acid.

Data from a typical pilot-plant test of 20-20-0 grade are shown below.

Formulation
  11 units N from NH_3
  9 units N from HNO_3 (65%)
  7.5 units P_2O_5 from phosphate rock
  12.5 units P_2O_5 from wet-process H_3PO_4 (54% P_2O_5)

Production rate, ton/hr.	0.5
Extractors	
Temperature, °F.	140
H_2O, %	24
Preneutralizer (85% of NH_3)	
pH	2.0
Temperature, °F.	285
H_2O, %	9
Lb. recycle:lb. product	3
Granulator product	
Temperature, °F.	180
H_2O, %	1.5
Screen analysis, %	
+6 mesh	6
−6 +10 mesh	25
−10 mesh	69
Dryer product	
Temperature, °F.	220
H_2O, %	0.7
Screened product	
pH	6.3
P_2O_5 availability, %	99
P_2O_5 water solubility, %	40

Advantages of the preneutralizer are less with the sulfuric acid modification since very little water can be evaporated without obtain-

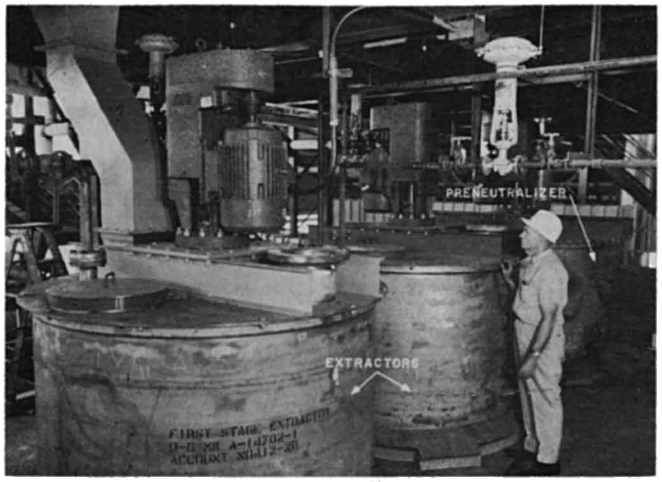


Figure 4.

Extractors and Preneutralizers Used in the TVA Nitric Phosphate Plant.

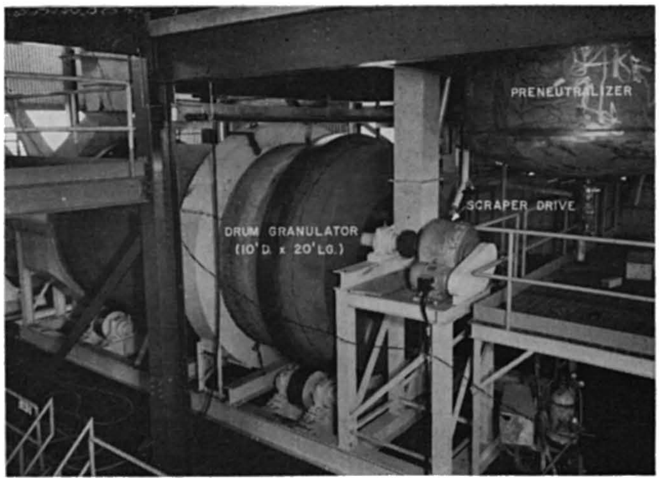


Figure 5.

Ammoniator-Granulator in the TVA Nitric Phosphate Plant.

ing slurry that is too viscous to handle properly. However, carrying out part of the reaction in the preneutralizer with addition of water to compensate for evaporation gave some decrease in recycle requirement due solely to decreasing heat liberated in the ammoniator drum.

Concentration of at least 60 percent HNO_3 is desirable in this process and the 70 percent HNO_3 now available commercially could be used to advantage.

The latest modification of the nitric phosphate process using a preneutralizer and continuous ammoniator will be used in a demonstration-scale plant that has just been completed by TVA. Production rate will be about 15 tons per hour for 20-20-0 grade and 20 tons per hour for 15-15-15. The next two figures are views of key process equipment in this plant. Experience and data from this plant unit should provide detailed design and process information for those interested in use of this process.

Some of the advantages for this process are listed below. Use of a preneutralizer to cut recycle requirement about in half, yet retaining advantages of the rotary drum ammoniator to avoid problems in availability.

Flexibility for production of N:P ratios from 1:2 to 2:1.

System is comparatively simple and conventional — quite similar to the widely used TVA granular diammonium phosphate process.

Summary

In summation, the mixed acid or supplemental acid processes for nitric phosphate production have demonstrated advantages of comparative simplicity, lower investment cost, and flexibility. A disadvantage is the reqirement of substantial amounts of either phosphoric or sulfuric acid that decreases savings in formulation cost. With the possible need for processes in the future that require little or no sulfur, the mixed acid processes do not fill the bill too well because of the sulfur requirement in producing the sulfuric or phosphoric acid. If water solubility of 40 percent is needed, about 60 percent as much phosphoric acid is used as in production of diammonium phosphate and only slightly less than in production of triple superphosphate. If only enough acid to adjust the extract is used and water solubility as low as 20 percent is acceptable, the requirement would be less than 40 percent of that required for diammonium phosphate. These processes are likely to continue to be used as nitric phosphate production expands, but if sulfur price and availability become acute, processes that avoid the use of sulfur likely will be sought.

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MR. WEBER: Thank you, Mr. Young. That was a very interesting paper.

I hope that all of you who are just itching to ask questions will make note of them so that we can have them when we have a question and answer period probably tomorrow morning and that you won't be too confused by hearing a lot of papers but I think it is more logical to do it this way.

We will next hear from Mr. R. J. Piepers who is with the Dutch State Mines in Holland, the so-called Staatsmijnen, who will give us a talk on the Odda Process and the variations that they have developed in connection with this.

The Odda process. the name comes from the fact that it was originally developed in Norway and used very extensively by the Norskhydro Company and then it has been adapted by many other companies.

Nitrophosphates

R. J. Piepers

Introduction

As is well-known, most phosphate rocks are of the so-called apatite structure, which means that the phosphate is present in such a form that it cannot be readily assimulated by plants. The most common structure of this type is that found in fluorapatite $Ca_{10}(PO_4)_6F_2$.

In the production of phosphate fertilizers this structure should first be broken down. This is achieved by dissolving the phosphate rock in an acid. The resulting solution can than be used in the manufacture of products, the phosphate in which can be readily taken up by plants. Suitable compounds of this type are ammonium phosphates and monocalcium phosphate, which are soluble in water, and also dicalcium phosphate, which is not water-soluble, but does dissolve in a 2% NH_4-citrate solution. This also guarantees that the phosphate will be readily available to plants.

In the above mentioned compounds the molar CaO/P_2O_5 ratio varies between 0 and 2, while in phosphate rock it mostly exceeds 3:3.

If sulphuric acid is used as the acidulant, the excess of CaO automatically precipitates as $CaSO_4$ during the decomposition, e.g. according to the equation:

$$3.5\ CaO \cdot 1\ P_2O_5 + 2.5\ H_2SO_4 \rightarrow Ca(H_2PO_4)_2 + 2.5\ CaSO_4.$$

By subjecting the mixture of monocalcium phosphate and gypsum to a few simple treatments, superphosphate with about 18% of P_2O_5 is obtained.

To make triple superphosphate (monocalcium phosphate with 40%-45% of P_2O_5), the gypsum has to be removed. The phosphate rock is then decomposed to phosphoric acid according to the equation:

$$3.5\ CaO \cdot 1\ P_2O_5 + 3.5\ H_2SO_4 \rightarrow 2\ H_3PO_4 + 3.5\ CaSO_4$$

The phosphoric acid left after the gypsum has been filtered off is then used for converting phosphate rock into monocalcium phosphate.

The phosphoric acid may, of course, also be neutralized to ammonium phosphate with NH_3.

The Decomposition With Nitric Acid

The decomposition to monocalcium phosphate can also be effected with nitric acid according to the equation:

$$3.5\ CaO \cdot 1\ P_2O_5 + 5\ HNO_3 \rightarrow Ca(H_2PO_4)_2 + 2.5\ Ca(NO_3)_2$$

The mixture of monocalcium phosphate and $Ca(NO_3)_2$ can be processed to an end product.

However, the presence of calciumnitrate. 4 H_2O has an adverse effect on the storage properties. Lonza improved this process by changing the reaction conditions in such a way that the $Ca(NO_3)_2$ is present in the trihydrated form.

To prevent the presence of $Ca(NO_3)_2$ in the end products, i.e. to remove the excess of CaO, the phosphate rock must — as in the process using sulphuric acid — be decomposed to phosphoric acid according to the equation:

$$3.5\ CaO + 7\ HNO_3 \rightarrow 2\ H_3PO_4 + 3.5\ Ca(NO_3)_2$$

Unlike the sulphuric acid process, this method of preparation yields phosphoric acid, in which the CaO is dissolved as $Ca(NO_3)_2$. Consequently, a separate operation will be required for removing the excess of CaO.

If the CaO is completely removed from the decomposition liquid, the phosphoric acid obtained may be re-used for the production of triple superphosphate or be neutralized to ammonium phosphate with NH_3.

To prepare fertilizers which are not completely water-soluble, but do dissolve completely in citrate, it is not necessary to remove all of the CaO, because the neutralization with NH_3 can be carried out in such a way that dicalcium phosphate is formed. To keep any $Ca(NO_3)_2$ out of the end product, the molar CaO/P_2O_5 ratio need (theoretically) be reduced only to 2. If more CaO is removed, $NH_4H_2PO_4$ will be formed in addition to $CaHPO_4$, and products with a higher water-solubility will be obtained.

Removal of Excess CaO

It will be demonstrated hereafter that phosphate fertilizers need not be completely water-soluble for agricultural reasons.

The following methods may be employed to remove the undesired amount of CaO from the decomposition liquid.

1. Crystallization of $Ca(NO_3)_2 \cdot 4H_2O$ by cooling the decomposition liquid and subsequently removing it by centrifuging. The calcium nitrate crystals can be processed to a valuable by-product. If the marketing possibilities are good, this product may render the nitric acid process much more economical. On this point there exists a definite difference with the sulphuric acid process, in which only the useless gypsum is obtained.
2. Precipitation to $CaSO_4$ with SO_4'' ions and, if so desired, removal of the gypsum crystals by filtration. Suitable precipitation agents are: sulphuric acid or soluble sulphates, such as ammonium sulphate or potassium sulphate. Using the latter product, an NPK-fertilizer is obtained. However, the use of one of the above mentioned agents may be considered as the introduction of sulphuric acid into the nitric acid process. Consequently, to retain the advantages of the nitric acid process, this will be done only if no more than a minor amount of CaO need to be removed, or if one of these products is present in a large amount as an inevitable by-product.
3. Addition of phosphoric acid. The molar CaO/P_2O_5 ratio in the decomposition liquid, which is at first 3.5 or higher, can of course also be reduced, e.g. to 2 or less, by addition of phosphoric acid. It is obvious that products thus obtained will not be completely water-soluble.

Production of NP and NPK Fertilizers

After removal of the undesired amount of CaO, the resulting solutions can be processed to NP and NPK fertilizers by simple procedures. The solution is first neutralized with NH_3, after which an amount of water is evaporated. The melt or slurry obtained can be processed to an end-product by prilling or granulating. To produce NPK fertilizers by prilling, a potassium salt must previously be added to the melt. The NP and NPK fertilizers are eminently suited for being shaped by these two techniques. After drying, cooling and powdering with a suitable anti-caking agent, they possess excellent storage properties.

The N/P and P/K ratios may, if desired, be varied within a wide range. The phosphate in the fertilizers may be completely or partly water-soluble. The water-insoluble part of the phosphate does, however, dissolve in a 2 % NH_4-citrate solution.

D.S.M.-Processes

In the D.S.M. plants two procedures are used for the removal of the excess CaO.

1. *Precipitation as* $CaSO_4$

This is effected by adding to the decomposition liquid a saturated $(NH_4)_2SO_4$ solution obtained as a by-product in the manufacture of caprolactam.

Such an amount of $(NH_4)_2SO_4$ solution is added that all of the CaO precipitates as $CaSO_4$, which is then removed by filtration.

In this way end-products are obtained the phosphate in which is virtually 100% water-soluble.

The N/P ratio in these fertilizers cannot, however, be less than 1:6. The product having an N/p ratio = 1:6 contains about 25% N and about 15% P_2O_5.

Shaping is done by granulation in a pugmill but can also be done by prilling.

A schematic view of the plant arrangement is shown in figure 1.

2. *Crystallization as* $Ca(NO_3)_2$ *4 aq.*

Using this process, an NP fertilizer is produced the phosphate in which is 50% water-soluble.

In this case, so much $Ca(NO_3)_2$ has to be removed by crystallization and subsequent centrifugation that, theortically, the molar CaO/P_2O_5 ratio in the remaining solution is 1. (Owing to the presence of fluorine, which also binds Ca^{++} as the insoluble CaF_2, this ratio may in practice be about 1:3.)

The N/P fertilizer obtained by this process contains 20% N and 20% P_2O_5.

By incorporating potassium sulphate an NPK fertilizer containing 14% N, 14% P_2O_5 and 14% K_2O can be made.

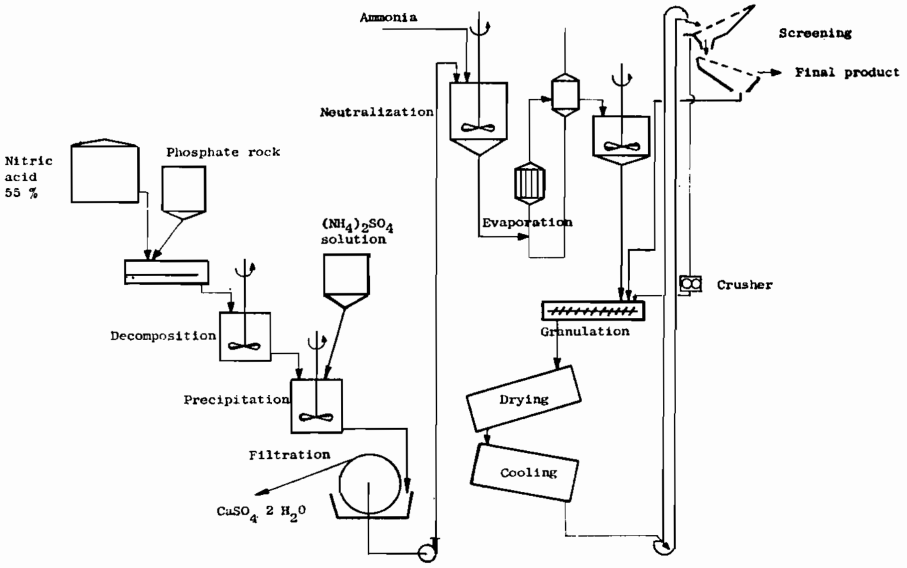
These products are prilled in air. A great advantage of prilling as compared with other granulation techniques is that the diameter of the prills varies between very narrow limits and that the amount of off-size product is less than 5%.

All the NP and NPK products produced by D.S.M. are coated with 2.5% of kieselguhr.

Figure 2 shows a flow-sheet of the production of NP + 20, while figure 3 gives a schematic view of the plant arrangement.

Figure 1.

SCHEMATIC VIEW OF THE MANUFACTURE OF NP 25-15



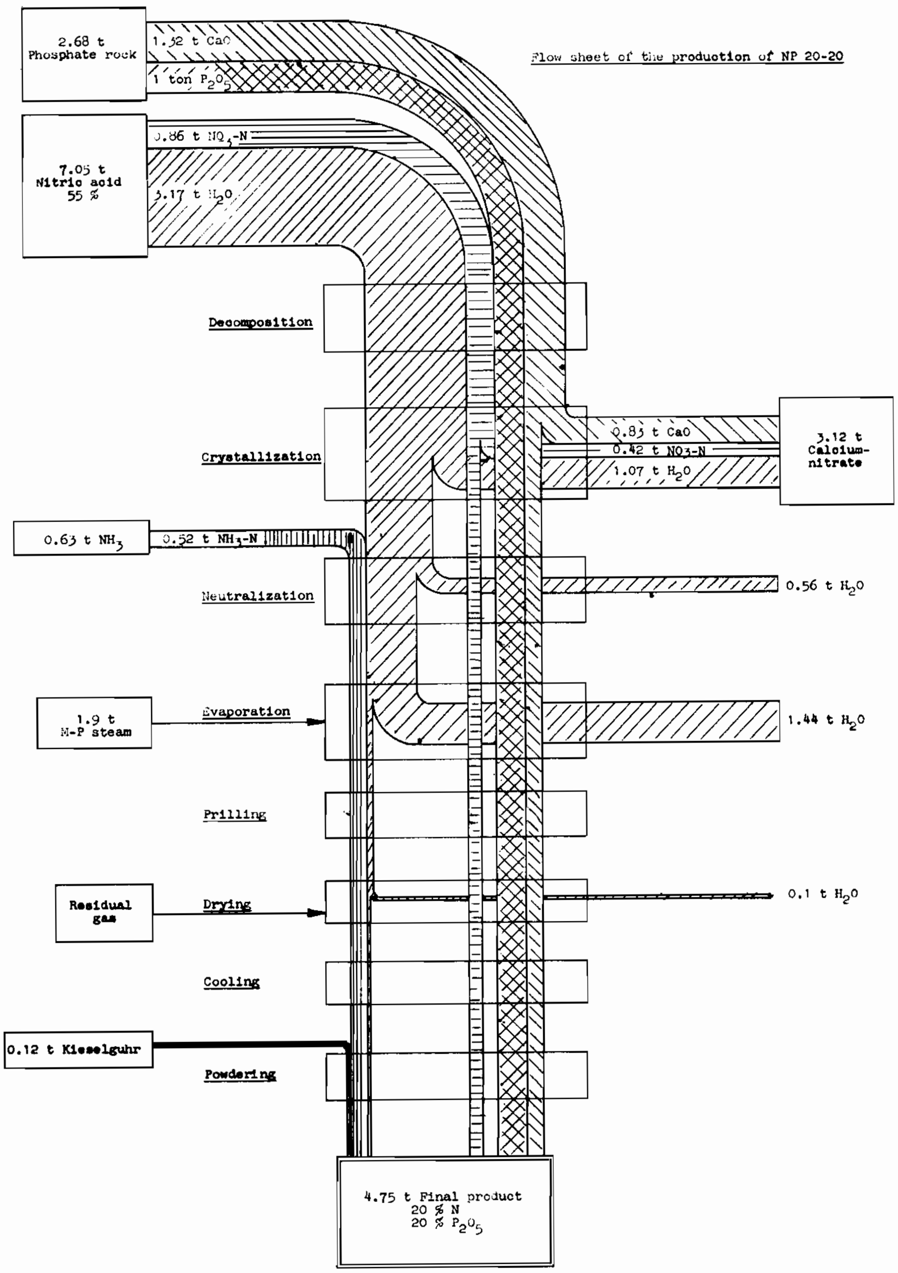


Figure 2.

SCHEMATIC VIEW OF THE MANUFACTURE OF NP 20 - 20

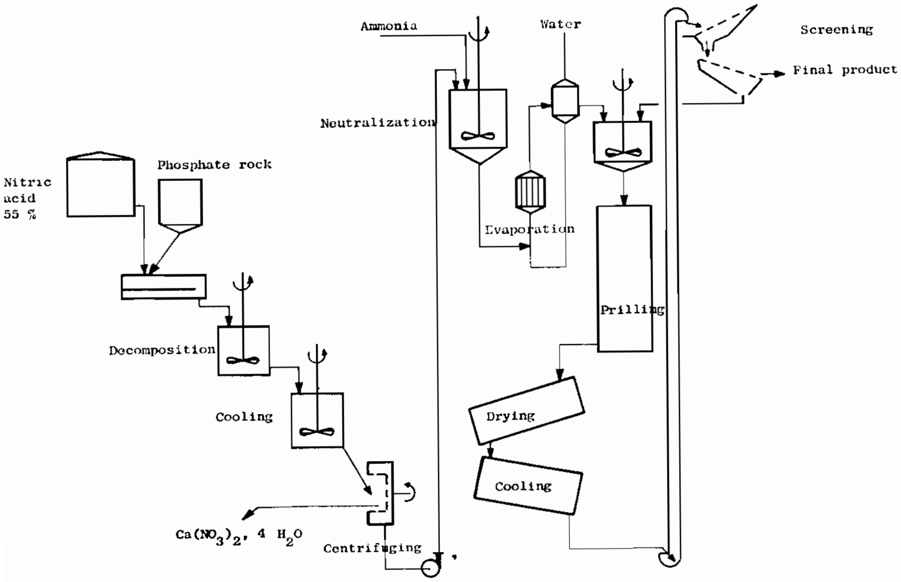


Figure 3.

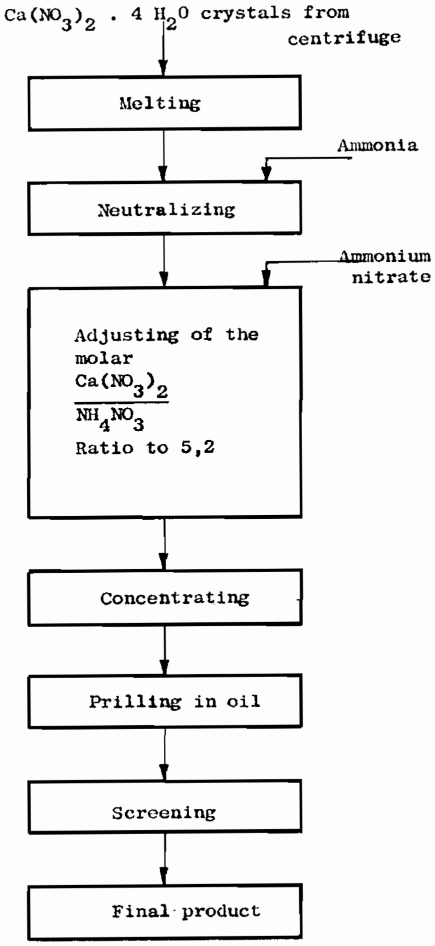
$Ca(No_3)_2$ As By-Product

The crystals removed by centrifuging can be converted into NH_4NO_3 and $CaCO_3$ with NH_3 and CO_2.

However, in the D.S.M. plant the crystals are at present processed to calcium nitrate. This product consists mainly of $Ca(NO_3)_2$ and furthermore contains a small amount of NH_4NO_3. Its total nitrogen content is 15.5%. Because of the very rapid fertilizing action of the nitrogen in the soil, the product is in very high demand in Europe i.a. for top-dressing.

The removed crystals are melted, while the adhering acid is neutralized with NH_3. After that, NH_4NO_3 is added to bring the molar $Ca(NO_3)_2/NH_4NO_3$ ratio to 5.2. The resulting solution is evaporated until it contains 15.5% N and then prilled in oil (see figure 4). Prilling in air is not very convenient because $Ca(NO_3)_2$ crystallizes only very slowly, so that very high prilling towers would be required. Therefore, prilling is done in oil, which moreover, offers

Figure 4.



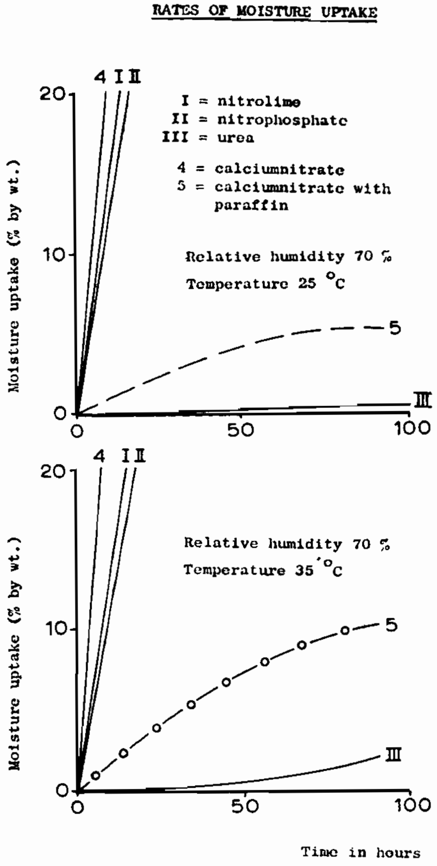


Figure 5.

another great advantage. Substances such as paraffin may be added to the oil, by which the prills are completely coated. The rate of moisture uptake will consequently be reduced. This is clearly shown in figure 5, where the rate of moisture uptake of the product prilled in oil is compared with that of the former flaked product and some commercial fertilizers. At a relative humidity of 70% and a temperature of 25°C, the rate of moisture uptake of the prilled product is even lower than that of nitrolime and nitrophosphate, and compares favourably even with that of urea. This also holds for the rate of moisture uptake at 35°C.

Figure 6 gives a schematic view of an oil-prilling plant in which two separate circuits can be distinguished, viz. the oil circuit and the circuit for the solution.

Thermal Instability

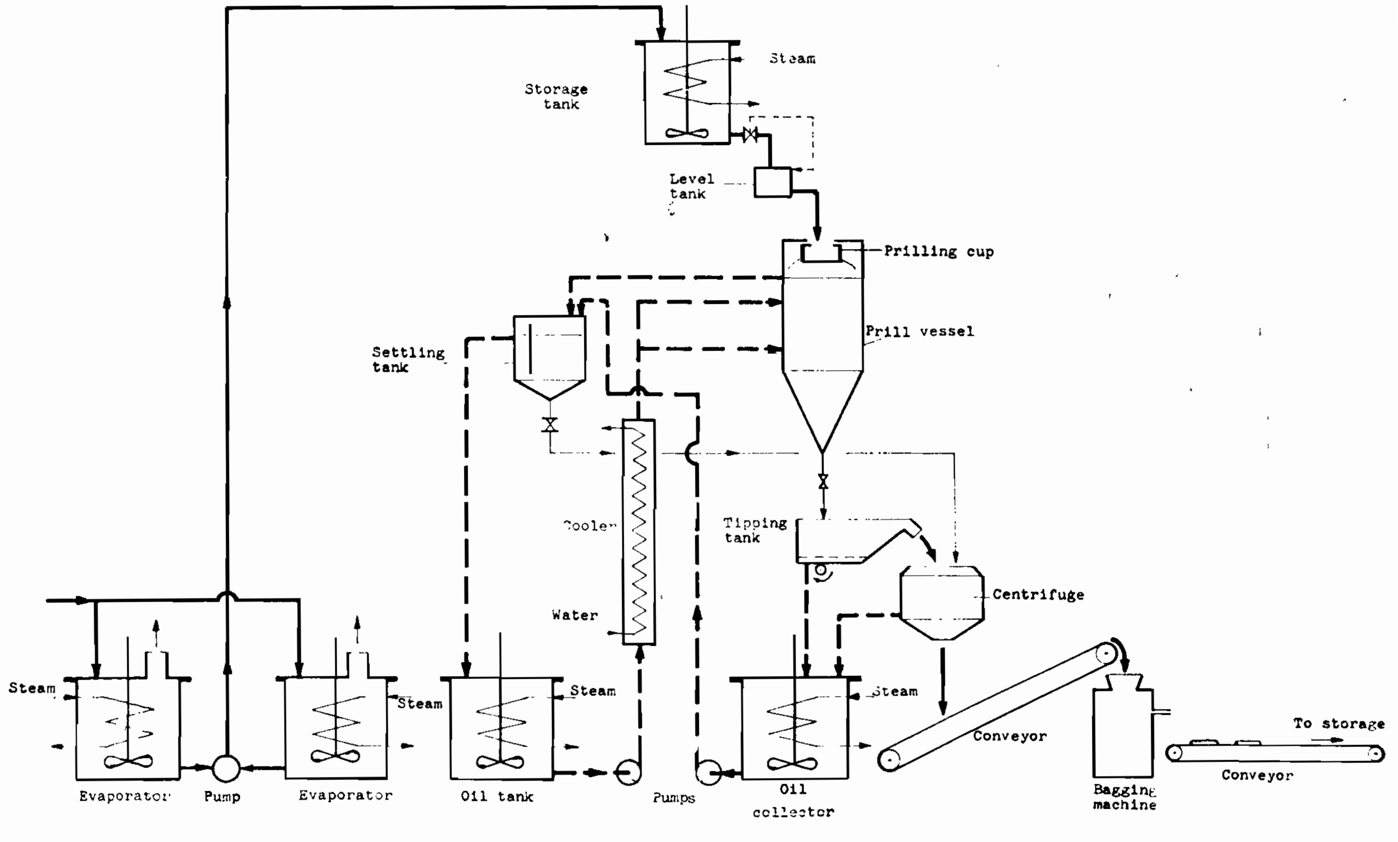
It is well-known that if muriate of potash is used to produce NPK fertilizers, a certain risk is taken owing to the thermal instability of products containing NH_4NO_3 and chlorides. According as more insight is gained into the mechanism of the decomposition reaction of NH_4NO_3 in the presence of Cl' ions, it becomes evermore clear that not all products are to be considered as dangerous.

It may be interesting to show the results of a series of experiments directly aimed at giving an answer to the important practical question: is it to be expected that, if a small portion of a material is heated to the decomposition temperature, the decomposition will propagate through the bulk of the material? This will indeed be the case if the amount of heat released per unit time during the decomposition is larger than the amount of heat which can be carried away. In the opposite case, the decomposition will stop.

In the experiments use is made of rectangular troughs made of wire gauze, which are open at the top. The dimensions are 50 x 10 x 10 cm or 50 x 20 x 20 cm. The troughs are filled with the product, which is then heated at one side with a gas flame until it decomposes spontaneously. If the decomposition propagates, the rate of propagation as a measure of the degree of instability of the product is determined.

The experiments have not been completed yet. The results obtained with chemically pure products consisting of NH_4NO_3, KCl and $NH_4H_2PO_4$ (100% water-

Figure 6.



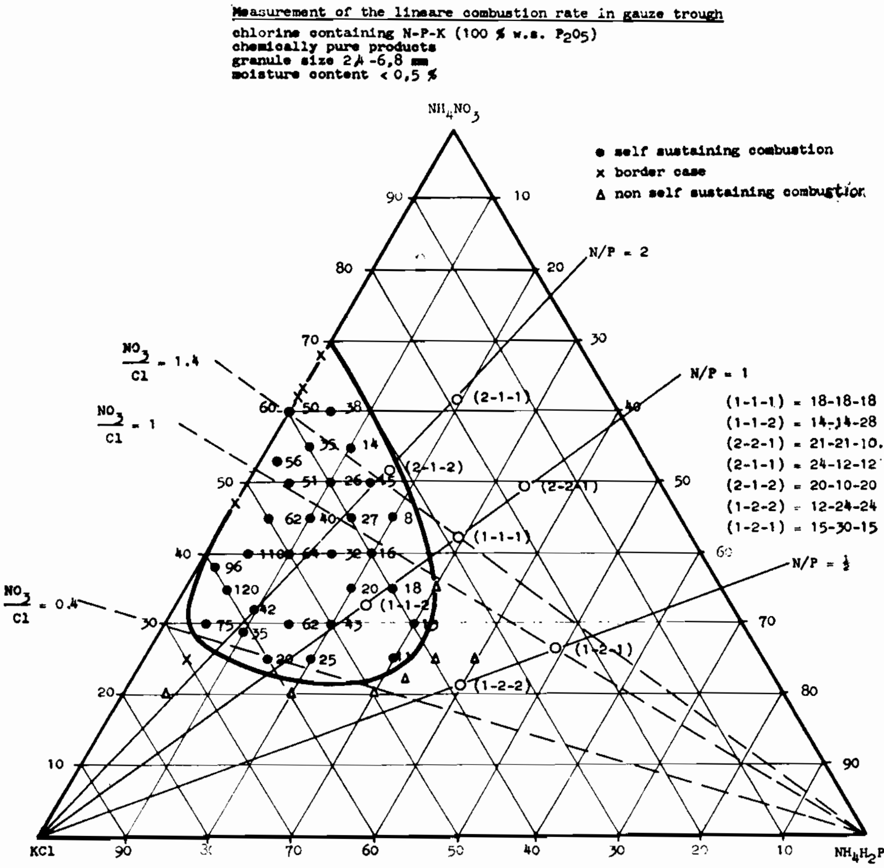


Figure 7.

soluble P_2O_5) are shown in figure 7.

The points in the triangular graph indicate the percentages to which the three components were present in the mixtures examined. Screen analysis showed that the grain size of the granulated mixtures was between 2.4 and 6.8 mm; the moisture content was less than 0.5%.

It appeared that the decomposition propagated only in mixtures having any of the compositions in the region bounded by the curve. The rate of propagation varied from about 8 to 110 cm per minute.

Mixtures having any of the compositions outside this comparatively small region, i.e. all products having a P/K ratio not smaller than about 1, are, consequently, to be considered as thermally stable.

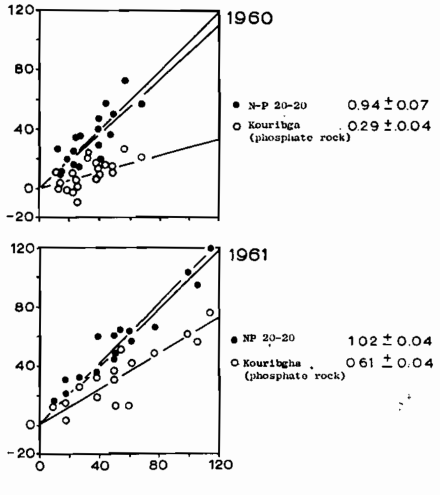
Agricultural Aspects

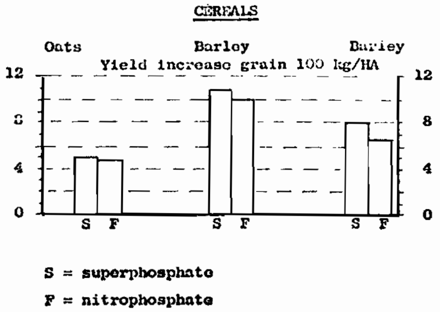
The most important property of phosphate fertilizers is of course their fertilizing effect. In the manufacture of products containing 100% water-soluble P_2O_5 by the nitric acid process, all of the CaO has to be removed. It will of course be more economical to remove only a portion of it.

Experiments made in different countries, including the Netherlands and the U.S.A. have shown that the fertilizing effect of products with about 50% water-soluble phosphate on most crops equals that of products with 100% water-soluble phosphate.

Figure 8 shows that the fertilizing effect of nitrophosphate containing 50% water-soluble P_2O_5 on grassland is equal to that of superphosphate.

Figure 8.





S = superphosphate
F = nitrophosphate

Figure 9.

This also applies to cereals (see figure 9).

In the case of potatoes, on the other hand, the use of completely water-soluble products is to be preferred in some cases, e.g. on phosphate-deficient or calcareous soils.

In estimating the fertilizing effect of a phosphate fertilizer, not only the percentage of water-soluble P_2O_5, but also the grain size must be taken into account.

It will certainly be known that, of fertilizers having a lower water-solubility (e.g. basic slag or phosphate rock) are used, the yield decreases according as the grain size increases (see figure 10). The fertilizing effect of a phosphate containing 0% water-soluble P_2O_5 decreases for instance by about 10% if, instead of a pulverulent product a product of 4 mm grain size is used.

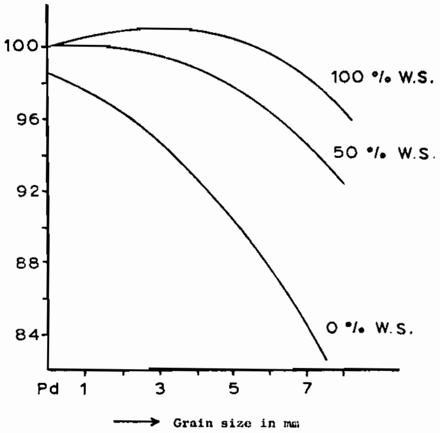


Figure 10.

This does not apply to the nitrophosphate with 50 to 100% water-soluble phosphate, at least not if the grain size is below 4 mm, which may be considered the maximum size of prilled products.

Mr. Weber: Thank you, Mr. Piepers.

We will now have the paper by Dr. Hans Banthien of Hoechst-Uhde, Frankfort, Germany.

Mr. Banthien.

Costs and Techniques Of Nitrophosphate Production

Dr. Hans Banthien

The present paper deals mainly with the ODDA process, which was developed by Erling B. Johnson of ODDA SMELTEVERK A.S., Norway. Compared to other methods of nitrophosphate production the ODDA process has the following unique features:

1) no requirements in sulphuric acid or phosphoric acid,
2) total recovery of calcium and P_2O_5 from rockphosphate in the form of dicalciumphosphate, ammoniumphosphate and calciumnitrate resp. ANL (conversion of calciumnitrate by ammonia and carbondioxide yields ANL),
3) NP products in the range from 15/30/0 to 25/13/0 preferably NP 20/20/0 can be produced,
4) application of NP products and calciumnitrate resp. ANL furnishes to soils neutralizing calcium equivalent to 150 kg $CaCO_3$/100 kg P_2O_5. This means substantial savings in the farmers budget.

Table 2. Figures in mt/100 mt P_2O_5

Process	H_2SO_4	H_3PO_4 P_2O_5	rock phosph. P_2O_5	HNO_3 N	NH_3	CO_2	Gypsum
1)	260-280	100	—	45	55	—	500
2)	160-170	55-60	40-45	45	55	—	300
3)	—	—	100	80-90	100	65-75	450 ANL
4)	500	100	—	—	100	—	500
	(ammonphosphate ammonsulfate)						

Table 3. Shows total investment cost of processes 1-4 for 230 mt N/d capacity. To be fully comparable an ANL plant is added in case of process 1) and 2)

Process 1)	nitric acid	96 t N/d	\$ 2.5 mio
	phosphoric acid	115 t P_2O_5/d	\$ 1.8 mio
	sulfuric acid	350 t H_2SO_4/d	\$ 1.2 mio
	NP/NPK	750 t 15/15/15/d	\$ 1.2 mio
	ANL plant	482 t ANL 22% N/d	\$ 1.5 mio
			\$ 8.2 mio
Process 2)	nitric acid	106 t N/d	\$ 2.7 mio
	phosphoric acid	69 t P_2O_5/d	\$ 1.5 mio
	sulfuric acid	108 t H_2SO_4/d	\$ 0.8 mio
	NPK plant	750 t 15/15/15/d	\$ 1.3 mio
	ANL plant	482 t ANL 22% N	\$ 1.5 mio
			\$ 7.8 mio
Process 3)	nitric acid	110 t N/d	\$ 2.7 mio
	NPK plant	750 t/15/15/15/d	\$ 2.2 mio
	conversion of $Ca(NO_3)_2$ to ANL	ANL suspension	\$ 0.6 mio
	ANL granulation	482 t ANL/d	\$ 1.5 mio
			\$ 7.0 mio
Process 4)	investment inclusive H_2SO_4		\$ 6.3 mio

Table 1.

a) *100% Phosphoric acid process*

$2\ H_3PO_4 + 3.55\ HNO_3 + 6.55\ NH_3 \rightarrow$

product: $NH_4H_2PO_4 + (NH_4)_2HPO_4 + 3.55\ NH_4NO_3$

fully water soluble P_2O_5 product NP26 /26/0

70% nitrogen in form of AN.

b) *60% Phosphoric acid process*

$P_2O_5 \cdot 3.6\ CaO + 3H_3PO_4 + 11.7\ HNO_3 \rightarrow$

$5\ H_3PO_4 + 3.6\ Ca(NO_3)_2 + 4.5\ HNO_3$

equal to

$2\ H_3PO_4 + 1.4\ Ca(NO_3)_2 + 4.5\ HNO_3$

after neutralization with 5.5 NH_3

product: $1.4\ CaHPO_4 + 0.3\ NH_4H_2PO_4 + 0.3\ (NH_4)_2HPO_4 + 4.6\ NH_4NO_3$

30%-40% water soluble P_2O_5 Product: NP21/21/0

85-90% of total nitrogen in form of AN

c) *100% nitric acid process (Odda process)*

$P_2O_5 \cdot 3.6\ Ca(NO_3)_2 + 9.0H\ NO_3 \rightarrow 2\ H_3PO_4 + 3.6\ Ca(NO_3)_2 + 1.8\ H\ NO_3$

2.2 mol $(Ca(NO_3)_2 \cdot 4H_2O$ are removed by crystallization and separation process.

Mother liquor:

$2\ H_3PO_4 + 1.6\ Ca(NO_3)_2 + 1.8\ HNO_3$.

Neutralization with ammonia gives the same product as under b)

NP product: NP 20/20/0 to NP 21/21/0

$2.2\ Ca(NO_3)_2 \cdot 4\ H_2O + 4.4\ NH_3 + 2.2\ CO_2 \rightarrow$

ANL product: $2.2\ CaCO_3 + 4.4\ NH_4\ NO_3 + 3\ H_2O$

The above mentioned advantages have created great interest in industry and among farmers. Presently 800.000 t P_2O_5/year and 1.1 million t N/y are produced by using the ODDA process.

Following recent statistics U.S. production of AN is expected to reach a top of 2.5 million short tons N/y by 1970 and will be largest outlet for ammonia.

This steep climb of AN encourages the introduction of the ODDA process to the U.S. industry and agriculture.

Table 1 gives survey on 3 nitrophosphate processes, which are subject to comparison. Chemical formulations show the special position of the ODDA process.

Table 2 shows the requirements of the above processes in sulphuric acid, phosphoric acid, nitric acid, ammonia and carbondioxide.

Table 3 gives review of investment costs. In each of processes 1)

Table 4. Utilizes labour and raw materials of Odda process 750 t NPK 15/15/15 t 482 t ANL 22% N

	total/day	per 100 kg N + 50 kg P_2O_5 in the products
l.p. steam	230 mt	100 kg
electricity	115 000 KWh	50 KWH
fuel oil	23 000 kg	10 kg
compressed air	25 000 m^3	10.8 m^3
process water	250 m^3	
cooling water	125 000 m^3	55 m^3
cooling requirements of crystallization (50°C–15°C)	60 mio kcal	26 000 kcal
(cooling requirements may be covered by evaporation of liquid ammonia and by water cooling)		
labour	1150 h	0.5 h
repair hours (incl. material)	1150 h	0.5 h
capital cost (10% investment)		\$ ~ 1.0
raw material		
ammonia	120 t $N\text{-}NH_3$	52.5 kg N
nitric acid	110 t $N\text{-}NO_3$	47.8 kg N
rockphosphate 36% P_2O_5	330 t	144 kg
carbon dioxide	90 t	39.0 kg
platinum loss	24 000 mg	10 mg
muriate of potash bonus:	187 mt	81 kg
steam production (ex nitric acid plant)	500 mt (40 atmg)	217 kg
calcium carbonate (extracted from rock phosphate, value low in case of ANL manufacture value high in case of recovery of $CaCO_3$ precipitated).	185 mt	80 kg

and 2) an ANL plant is added to be comparable with No. 3).

There is no large difference in investment cost for the 3 processes in question. ODDA process is on the lower side.

Table 4 contains consumption figures for energies and utilities, labour per 230 mt N/d capacity of ODDA nitrophosphate plant including conversion of calciumnitrate to ANL and nitric acid plant. This table may be useful to calculate final production costs. The ODDA process releases N and P_2O_5 in case of NP 20/20/0 and ANL 22% N in the ratio of 2:1 by weight. Therefore figures are given for 100 kg N and 50 kg P_2O_5.

Total production cost per 100 kg N and 50 kg P_2O_5 in the form of 250 kg 20/20/0 and 220 kg ANL, 22% N, will be around \$15.00 calculated from the above figures and assuming German conditions.

Process 1) (100% phosphoric acid) and process 2) (60% phosphoric acid) have more or less the same requirements in utilities, labour and capital, but have an additional consumption of

Present sulphur quotations on the world market are around \$45.- / mt S.

45 kg sulphur =
27 kg sulphur =

Odda process has approximately 180-190 t N/100 t P_2O_5 but succeeds in delivering 80-90 t N in the form of ANL fertilizer, whilst all other processes have the disadvantage to dispose of waste gypsum tailings.

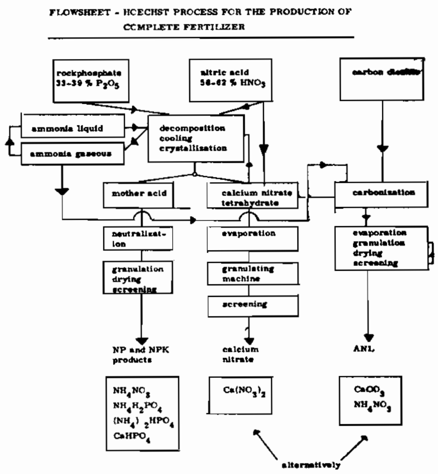
Techniques

Slide 5 shows a diagram from which the various types of NP - products depending on the rate of calcium extraction can be foreseen. Figures of diagram involve a variety of calculations which already are programmed to be calculated by simple computers. Calculations must be directed to find out how to make corrections of mother liquor after extraction of calciumnitrate mainly.

Neutralization of mother liquor and all finishing steps of NP-manufacture induce no problems of calculation or control of the process.

Slide 6 shows a scheme of equipment necessary for an ODDA plant.

Slide 7 is a material flow sheet, indicating the amounts passing in and out of the process. Slide 7 is typical for a rather low extraction of calciumnitrate.



Slide 7.

Details

Suitable types of rockphosphates:

Marocco, Togo, Senegal, Kola Apatite Concentrate, Florida various types, Israel, Jordan, Pacific islands.

\$2.-) per 100 kg N +
\$1.20) 50 kg P_2O_5

acid:

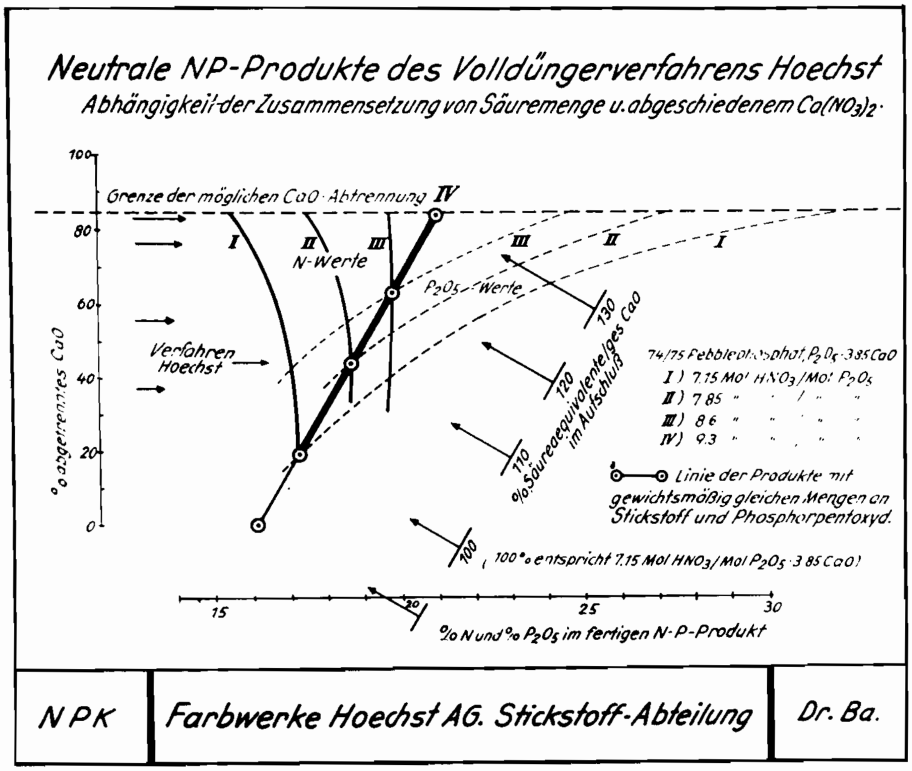
nitric acid from 55% to 65%.

Control of foam:

by use of calcined phosphates,
by use of foam breaking impellers,
by centrifuges.

Cooling and Crystallization

Any crystallizer with cooling coils is suitable. Cooling range of acidulated slurry is between 55°C to 10°C, or lower. Crystallization



Neutral NP — Products of Nitrophosphate Process Hoechst

Composition of products depending on amount of acid and grade of extraction of $Ca(NO_3)_2$

The upper limit of CaO extraction about is 85%

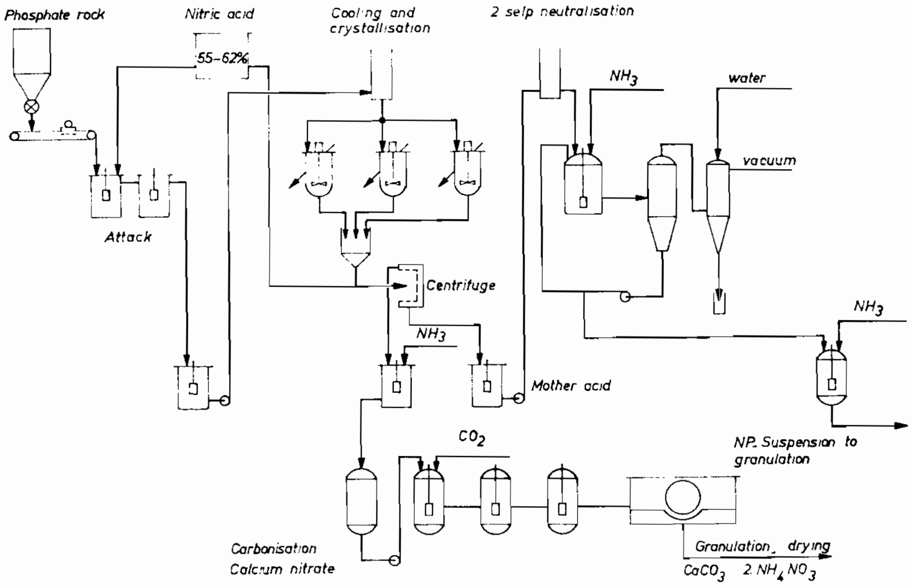
—○——○—	**equal weight per cent of N and P_2O_5 in the final NP-products**
———	**deviation of weight % N**
– – – – – –	**deviation of weight % P_2O_5 by extracting too much resp. too little amounts of $Ca(NO_3)_2$**
↖	**amount of HNO_3 used in % of amount equivalent to total CaO in rockphosphate**

graph according to 74/75 Pebble Phosphate

% N and % P_2O_5 in the final NP

Slide 5.

Slide 6.



may be continuous in several steps or batchwise. Measures are directed to yield crystals of uniform and large size to succeed in best filtrability of the rather impure mother acid.

Pushing type centrifuges or rotating vacuum sieves are used for the separation of crystals and mother acid.

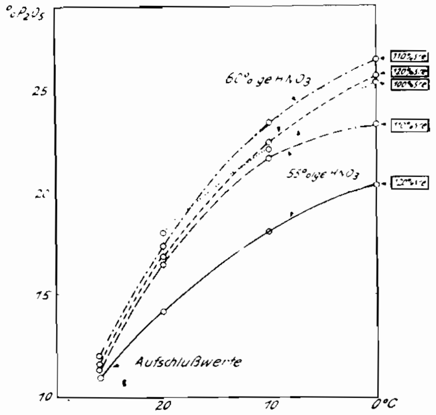
Neutralization: (slide 8 and slide 9)

Mother acid after checking on P_2O_5, N, CaO, free acids, is carefully titrated to show optimum composition. Corrections are made by nitric acid, acidulated slurry, rockphosphate.

Neutralization can be effected in 2 - 4 steps. Special experience is necessary to avoid pastyphases. Final step should reach pH values of 6.3 (sample diluted with water). Heat or neutralization is used to evaporate water. If necessary, final NP - slurry may be concentrated by disc-evaporator (UHDE) with hot gas, or by vacuum-evaporator.

Neutralization temperatures are from 100°C to 120°C.

Automatic control of neutralization makes use of pH value or of titration device.

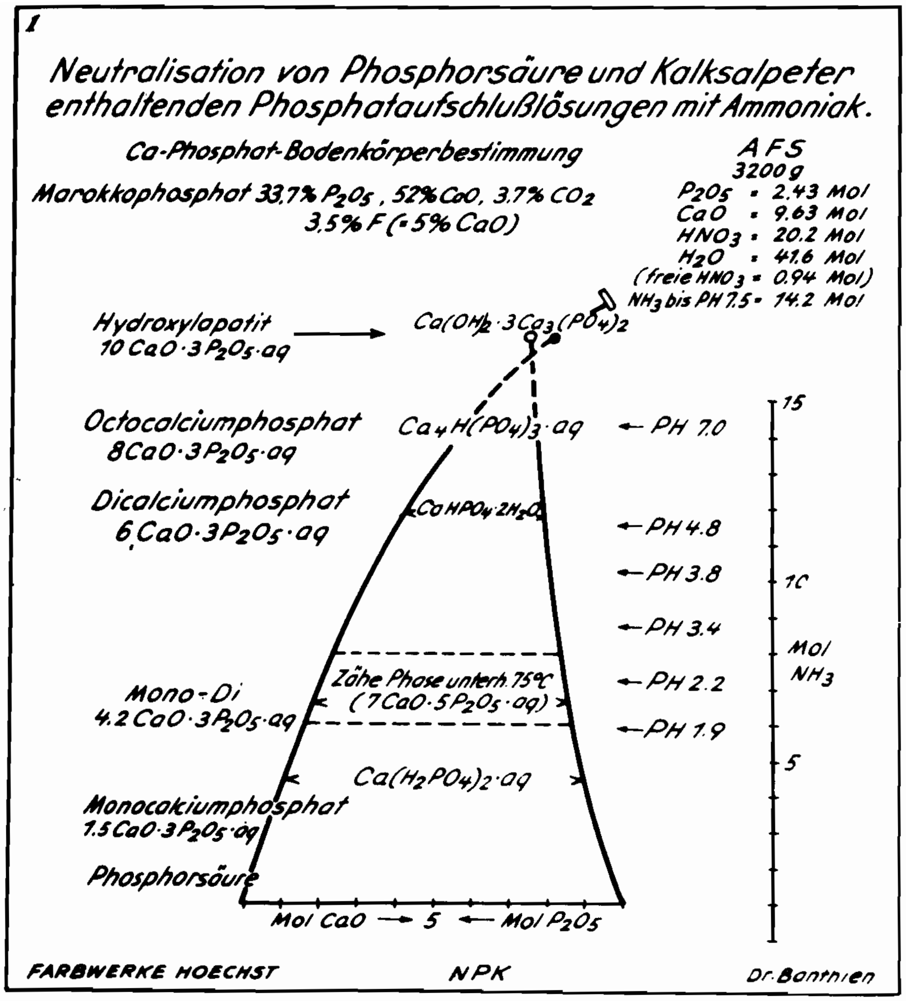


Slide 8.

Analysis of Mother Acid After Extraction of $Ca(NO_3)_2 \cdot 4\ H_2O$

Abscissa:	**cooling temperature**
Ordinate:	**% P_2O_5**

Diagram indicates dependency of analysis of mother acid, of acid concentration and amount of acid used in acidulation. Starting points indicate P_2O_5—contents of acidulated rockphosphate slurry.



Slide 9.

Neutralization of Acidulated Rockphosphate Slurries With Ammonia

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amounts of P_2O_5 = 2.43 mol

" of CaO = 9.63 mol

During ammoniation small samples of slurry were filtered off and after analysis indicated the precipitation of various types of calciumphosphates. With increasing pH the ratio of CaO/P_2O_5 in the precipitate increases.

Granulation

Neutral NP - slurry, milled recycle and fines are mixed in single shaft or double shaft pugmills. Well adjusted values of moisture content of NP - slurry and of granulation mix are necessary to avoid large spontaneous alterations of particle size. Dorrco- System of granulation with pugmills or Girdler Spherodizer equipment are suitable to produce granules of usual size. Farbwerke Hoechst AG. are using pugmills (system Friedrich Uhde GmbH), followed by rotating driers. One line of equipment produces from 600 to 850 mt/d on size product. Granulation is done also by use of prill towers. Water content of NP-, NPK - slurries in advance of prilling must be regulated to 2% (NP 20/20/0) to approx. 7% (NPK 12/20/20 with sulfate of potash). A secondary treatment of prills and drying is necessary to give prills a spherical shape and good storability. Prilling towers may have capacities of more than 1500 mt/d.

Sieving station, rotating mills (crushers) for oversize and feeding system to control the amount of recycle and to control the moisture during granulation, are essential equipment in the course of the granulation process. Large parts of know how apply to granulation.

Granulation temperatures in the pugmill depend on moisture and type of NP-/NPK-product and vary from 80°C to 95°C. Drying in the rotary kilns results in moisture contents of product in the range of 0.2 - 1.5%, preferably 0.5%. Storability can be improved by coatings, by special clay or by diatomaceous earth (Kieselguhr). NP - products have only little caking tendency whilst NPK (muriatic potash) incline to caking. Temperature of products prior to storage should not exceed 60°C.

Conversion of calciumnitrate to ANL resp. AN and $CaCO_3$:

The conversion of $Ca(NO_3)_2 \cdot 4H_2O$ byproduct with ammonia and carbondioxide is effected by thoroughly mixing of reactants in agitator vessels or in columns.

Farbwerke Hoechst AG. and Friedrich Uhde GmbH./ Federal Republic of Germany have developed processes for direct evaporation of water from ANL - slurry and to granulate the concentrated slurry with pugmills. A conversion plant of this type was designed and built for the first time by the engineering company Friedrich Uhde GmbH. for Scholven Chemie AG. in 1956.

Modified process allows full separation of AN solution from calcium-carbonate. Chemically calciumcarbonate results from the HOECHST process.

After evaporation of the solution, AN can serve for various purposes incl. fertilizers. Know-how of conversion processes includes large particle size of $CaCO_3$ crystals, complete conversion, avoiding of pasty phases, avoiding of decomposition during concentration.

MR. WEBER: Thank you, Dr. Banthien.

We have three more papers on this subject but we think you have probably had enough to sleep on so we'll have the remainder tomorrow morning.

And now I will turn the meeting back to Dr. Sauchelli.

MODERATOR SAUCHELLI: Thank you, Bill.

You have been a very patient and courteous audience. We must appreciate that some of our foreign visitors may have a little difficulty with the language but they have a fine message. When these papers are published in our proceedings, they will help make a very valuable contribution to the technology of fertilizer manufacture.

In connection with emphasizing the fact that these nitrophosphate processes are becoming important owing to the situation with sulphur, I have been asked by our good friends at the Sulphur Institute to call your attention to the Sulphur Symposium, sponsored jointly by the Tennessee Valley Authority and the Sulphur Institue, to be held at Wilson Dam, Alabama, next January 26th and 27th.

Sulphur is becoming a very important element. In no time we shall be talking about not the three major elements but of the four major elements, NPK and S. We are beginning to realize more and more the importance of sulphur as a plant nutrient. The use of concentrated fertilizers and the cleaning of the air of sulphur fumes and so on, we fear is causing sulphur to become quite deficient in many soils.

The sulphur symposium reflects that situation. It should prove very helpful to the industry.

I hope that we will see you tomorrow morning at nine o'clock. We have two more very interesting papers and a question and answer period and the Secretary's Report. We stand adjourned until tomorrow at nine o'clock.

Friday Morning Session, Nov. 12, 1965

Dr. Vincent Sauchelli Presiding.

The Round Table Reconvened at 9.45 A.M.

CHAIRMAN SAUCHELLI: Please come to order. We will resume our proceedings and I will turn the meeting over now to the panel leader, Mr. Weber.

MODERATOR WEBER: We will resume where we left off yesterday. We will have three speakers this morning, Dr. Nees from Chemische Fabrik Kalk, Mr. Berquin from Potasse et Engrais Chemiques, and Mr. Hignett from T.V.A.

We will start off with Dr. Nees.

The Manufacture Of Compound Fertilizers By The Kampa-Nitro Process

Dr. W. H. Nees and Dr. F. W. Brandt

Introduction

BEFORE I begin with my subject, please allow me to make a few remarks.

I should like to thank Mr. Weber sincerely for the invitation to present this paper at the 15th annual meeting of the *Fertilizer Industry Round Table.* His invitation reached us, when we had just finished our paper on the same subject for presentation at the *ISMA Technical Conference in Edinburgh.* There the paper was presented and discussed on September 15th, 1965. We were temporarely at a loss what to do, because we found it impossible to give more than one optimum representation of the same subject within a few weeks. But our minds were then put at ease by Mr. Weber's argument, that - compared to the Edinburgh Conference - we should meet an entirely different audience at Washington. So we consented to give almost the same paper here.

There is still another point to make. In Edinburgh the printed paper had been distributed to the delegates before presentation. For this reason the tables could be made up very extensively. This advantage of the Edinburgh situation now is disadvantageous for the Washington meeting, because the projected slides are hardly legible.

The *"Odda-Process"* for the reaction of phosphate rock with nitric acid and the related manufacture of an NP or NPK fertilizer together with a straight N fertilizer has been known for some 3.½ decades. The process is used by Norwegian, German, Dutch and French fertilizer producers. At least half a million tons of available P_2O_5, or more than four million tons of NP and NPK fertilizers, are manufactured annually by this process. Co-products of it are either calcium nitrate (15.5% N and 27% CaO) or calcium ammonium nitrate (22% N).

The *"Kampka-Nitro" Process,*

Table 1. P_2O_5 content and CaO/P_2O_5 molar ratios of orthophosphates involved in wet processes for fertilizer production

Material	P_2O_5 content (% by weight)	Molar ratio CaO/P_2O_5
Moroccan phosphate	∼33,5	∼3,9-4,0 : 1
Pebble phosphate	∼33,5	∼3,7 : 1
Togo phosphate	∼36,5	∼3,6 : 1
Taiba phosphate	∼37,0	∼3,5 : 1
Kalo phosphate	∼38,5	∼3,4 : 1
Fluor-apatite	42,22	3,3 : 1
Tricalcium phosphate (theoretical)	45,76	3,0 : 1
Dicalcium monohydrogen phosphate	52,16	2,0 : 1
Monocalcium dihydrogen phosphate	60,65	1,0 : 1
Orthophosphoric acid, anhydrous	72,43	0.0 : 1
Industrial phosphoric acids	e.g. 28	0,1 : 1
	54	0,0 : 1
Ammonium phosphates	53,74	0,0 : 1
	or 61,71	
Potassium phosphates	40,75	0,0 : 1
	or 52,16	

The trend of the P_2O_5 contents (% by weight) and of the CaO/P_2O_5 molar ratios is represented. The data given are consequently incomplete with regard to *all* types of phosphate rock.

The P_2O_5 contents and the CaO/P_2O_5 molar ratios of the rock phosphate types quoted are approximate values for air-dry material. The P_2O_5 contents of the commercial material deviate from these theoretical values within certain limits.

Table 2. Wet Processes for the Manufacture of Compound Fertilizers. (Nitrophosphates)

Classification of fertilizers according to plant nutrient content	Process Description	Raw materials Reaction	Raw materials Ammoniation	Ca ions fixed in the fertilizer as $CaSO_4$. aq + Cax (mol)	Ca ions fixed in the fertilizer as $CaCO_3$ + Cax (mol)	Ca ions separated from the fertilizer slurry as $Ca(NO_3)_2$. $4H_2O$ (mol)	Ca ions separated previously during H_3PO_4 production as $CaSO_4$. aq (mol)	Nutrient ratio N/P_2O_5 % (wt.)	Nutrient ratio $N/P_2O_5/K_2O$ % (wt.)	Finished fertilizer Ca compounds $CaSO_4$ + Cax (mol)	Finished fertilizer Ca compounds $CaCO_3$ + Cax (mol)	Finished fertilizer Ca compounds $CaHPO_4$ CoO (part) (mol)	Finished fertilizer Ca compounds $CaHPO_4$ P_2O_5 (part) (mol)	Ammonium phosphates P_2O_5 part	CaO/P_2O_5 Molar ratio linked to phosphate CaO / total P_2O_5	CaO/P_2O_5 Molar ratio total CaO / total P_2O_5
low-grade	a) Carbon dioxide nitric acid process with phosphate rock	RP HNO_3	NH_3 CO_2	—	2.0	—	—	16.6/14.1	13/11/13	—	2.0	2.0	1.0	—	2.0:1	4.0:1
	b) Sulphuric acid nitric acid process with phosphate rock	RP H_2SO_4 HNO_3	NH_3	2.7	—	—	—	13.5/13.5	11/11/11	2.7	—	1.3	0.65	0.35	1.3:1	4.0:1
medium-grade	c) Sulphuric acid nitric acid phosphoric acid process with phosphate rock	RP H_2SO_4 HNO_3 H_3PO_4	NH_3	1.7	—	—	1.0	15.0/15.0	12/12/12	1.7	—	1.3	0.65	0.35	1.3:1	3.0:1
				1.3	—	—	1.4	16.6/16.6	13/13/13	1.3	—	1.3	0.65	0.35	1.3:1	2.6:1
				0.7	—	—	2.0	18.3/18.3	14/14/14	0.7	—	1.3	0.65	0.35	1.3:1	2.0:1
high-grade	d) Nitric acid process with phosphate rock e.g. Odda process e.g. Kampka-Nitro process	RP HNO_3	NH_3	0.2	—	2.5	—	20.0/20.0	15/15/15	0.2	—	1.3	0.65	0.35	1.3:1	1.5:1
	e) Nitric acid phosphoric acid process with phosphate rock	RP HNO_3 H_3PO_4	NH_3	0.2	—	—	2.5	20.0/20.0	15/15/15	0.2	—	1.3	0.65	0.35	1.3:1	1.5:1
				0.1	—	—	3.2	21.8/21.8	16/16/16	0.1	—	0.7	0.35	0.65	0.7:1	0.8:1
				0.1	—	—	3.6	23.5/23.5	17/17/17	0.1	—	0.4	0.20	0.80	0.4:1	0.5:1
highest-grade	f) Nitric acid phosphoric acid process without phophate rock	HNO_3 H_3PO_4	NH_3	0	—	—	—	~ 24.7/24.7	~ 17.5/17.5/ 17.5	0.1	—	0	0	1.00	0 :1	0.1:1

RP = rock phosphate

developed by Chemische Fabrik Kalk GmbH, Cologne, is a modification of the Odda Process.*) The Odda Process and the Kampka-Nitro-Process belong to the group of so-called wet processes for the manufacture of compound fertilizers.

It has often been reported**) that the production costs of available P_2O_5 obtained by a wet process using only nitric acid in the reaction are lower than in the case of processes in which additional sulphuric and/or phosphoric acid are used. This cost reduction is chiefly caused by the saving in sulphur. Following the recent large increases in sulphur prices and the appearance of a sulphur shortage, processes which are independent of this raw material deserve particular attention.

A) Basic features of the wet process manufacture of compound fertilizers containing P_2O_5 .

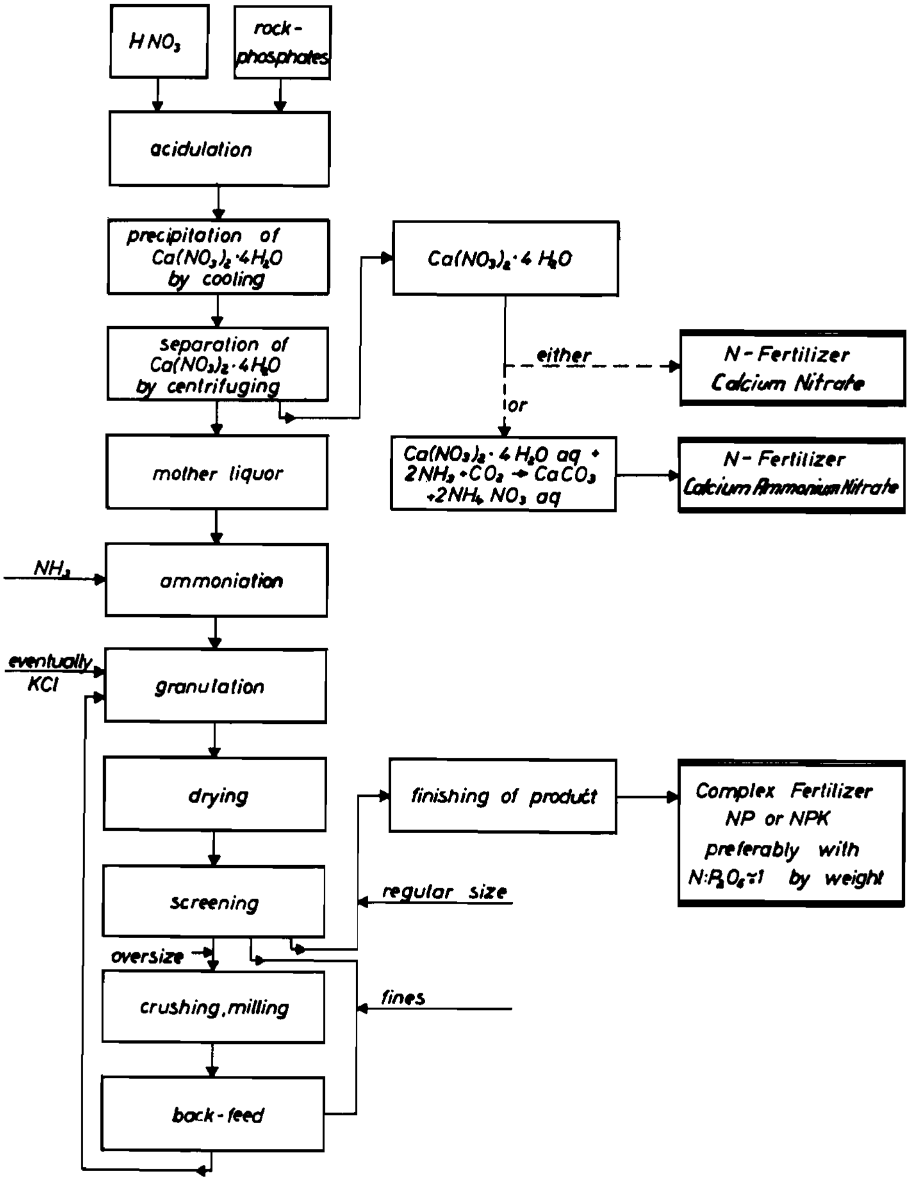
Phosphate rock is the essential raw material for the manufacture of phosphatic fertilizers by wet processes. It consists of apatite as well as other accompanying substances. The molar ratio of CaO/P_2O_5 in commercial phosphate rocks varies according to origin within the range of 3.4 - 4.1:1. Apatites are energy deficient and therefore very stable combinations of calcium orthophosphate and fluoride or hydroxide or carbonate, the phosphatic content of which becomes only very slowly available to plants.

The art of manufacturing phosphatic fertilizers by wet processes consists in breaking down the apatite contained in the phosphate by means of chemical reaction with acids and in so conducting the manufacturing process that the finished product will have a smaller CaO/P_2O_5 molar ratio than in the apatite. In this way fertilizers are obtained with their phosphatic components in a form which is available to plants.

Table 1. shows the P_2O_5 content and the CaO/P_2O_5 molar ratios of orthophosphates involved in wet processes for fertilizer production.

Table 3 ***General Scheme of the ODDA PROCESS***

Complex-Fertilizer without consumption of sulfuric acid



For the sake of clear representation the formulas of the rock phosphates have been simplified.

The following acids are currently used for wet process reaction with phosphate rock, either separately or in mixtures:

HNO_3
H_2SO_4
H_3PO_4.

During or after ammoniation, CO_2 is also introduced into the fertilizer slurry in certain processes.

If aq. $CaSO_4$ or $CaCO_3$, which are relatively insoluble compounds formed during the fertilizer production process, are left in the finished product, low-grade fertilizers result. But if the calcium salts formed during the reaction of phosphate rock with, for example, H_2SO_4 or HNO_3 - e.g.

or aq. $CaSO_4$
aq. $Ca(NO_3)_2$

are separated from the reaction slurry, either immediately by filtration or after cooling by centrifugation, one obtains phosphoric acid or a slurry containing phosphoric acid.

Table 2 is a compilation of almost all fundamental wet processes for the production of nitrophos-

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*) See patents DBP No. 1060411 and DAS No. 1047802

**) See papers by Banthien/Eimers and Brandt/Geiersberger, ECAFE-Fertilizer Conference, Bombay 1963, Item 7, 2, f, iv of Nov./Dec. 1963.

phates. It shows, in order of increasing plant nutrient content, the known processes for compound fertilizer manufacture which meet thees possibilities, the acids applied in each case, the distribution of the calcium-ion and the place of the Odda- and Kampka-Nitro-Processes within this order etc.

For the sake of clear presentation, the following simplifications are incorporated in table 2:

1. Only Moroccan phosphate, with a CaO/P_2O_5 molar ratio of 4,0, was used as the basis for calculations.
2. The ratio of $N:P_2O_5:K_2O$ in the fertilizers was limited to 1:1:0 (except item a) resp. 1:1:1.
3. For all fertilizers up to the 15-15-15, the proportion of water soluble P_2O_5 in the total P_2O_5 content of the fertilizers was put at 35% by weight (except item a).
4. In some cases, the calculated values were rounded.

B) Processes based on the reaction of rock phosphate with nitric acid and the separation of, e.g., $Ca(NO_3)_2.4H_2O$

Processes of this kind include the Odda-Process and its modifications. One of these modifications is the Kampka-Nitro-Process with its two methods of procedure - *with or without* the post reaction of phosphate rock.

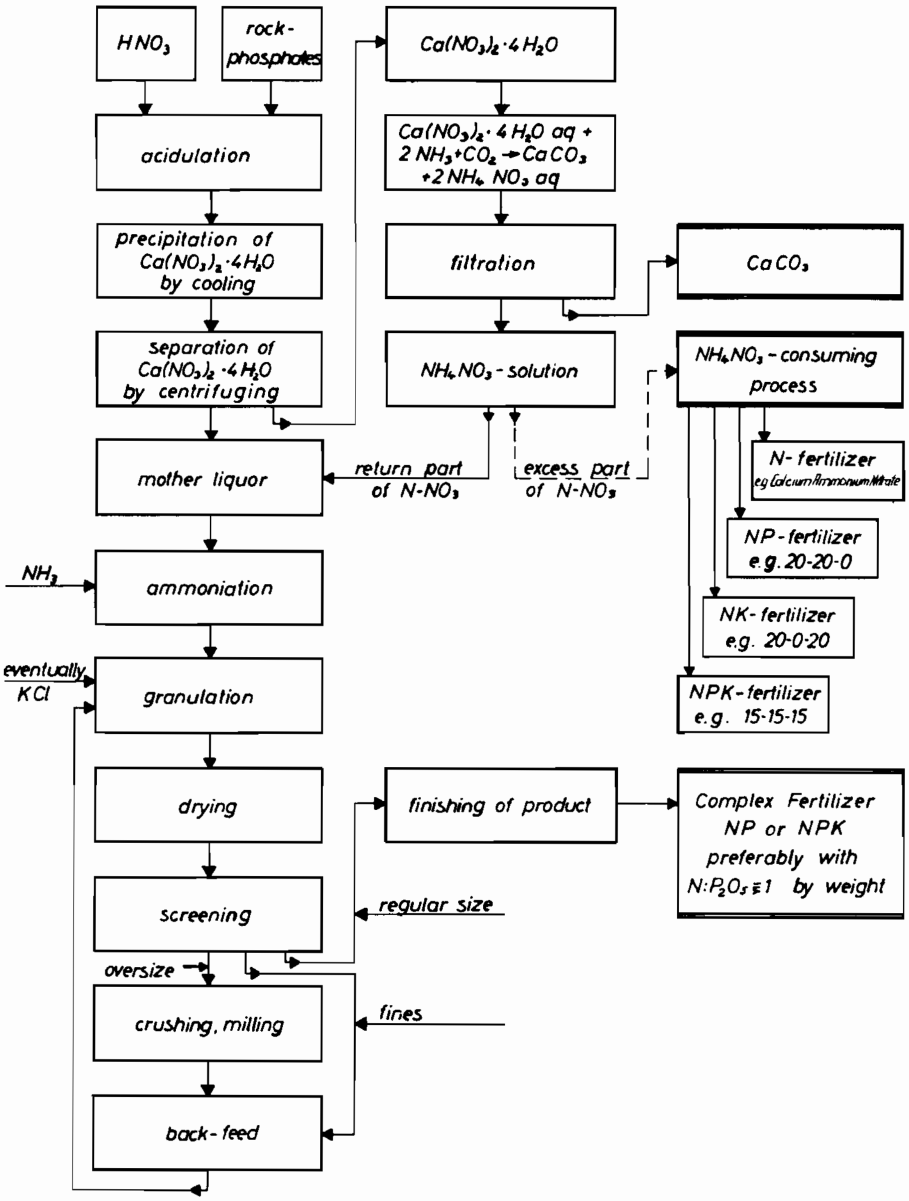
1) *The Odda-Process (c.f. table 3)*

The Odda-Process is designed for the manufacture of concentrated NP- or NPK-fertilizers (*primary fertilizers*) without the use of H_2SO_4. In addition to the compound fertilizer, a straight nitrogen fertilizer (calcium nitrate or calcium ammonium nitrate) *coproduct fertilizer*) is obtained. $Ca(NO_3)_2.4H_2O$ is separated off by cooling the reaction solution and by centrifugation.

2) *The Kampka-Nitro-Process (table 4)*

Table 4 **General Scheme of the KAMPKA-NITRO-PROCESS**

Complex-Fertilizer primarily without consumption of sulfuric acid



The Kampka-Nitro-Process is also designed for the manufacture of high-grade NP- or NPK-fertilizers primarily without the use of H_2SO_4. In contrast to the Odda-Process with the introduction of the full amount of HNO_3 required for both the compound fertilizer and the straight N-fertilizer into the acidulation step the Kampka-Nitro-Process has the following aims:

- with a given quantity of HNO_3 the ratio

$$\frac{\text{quantity of primary compound fertilizer}}{\text{quantity of coproduct fertilizer}}$$

is to be made as large as possible;

- The coproduced fertilizer is to be extended to NP-, NK- or NPK-formulations, in order to become free of the restriction represented by a coproduct with only nitrogen as its plant nutrient component;
- if possible, the production of a coproduct fertilizer is to be avoided altogether.

To achieve these aims, several steps in the process have been combined resp. technically worked out:

- the rock phosphate is treated with only the theoretical quantity of HNO_3 required for the completion of the reaction in the acidulation step;
- the $Ca(NO_3)_2.4H_2O$ which is separated by cooling and cen-

Table 5: Variants of the Odda Process

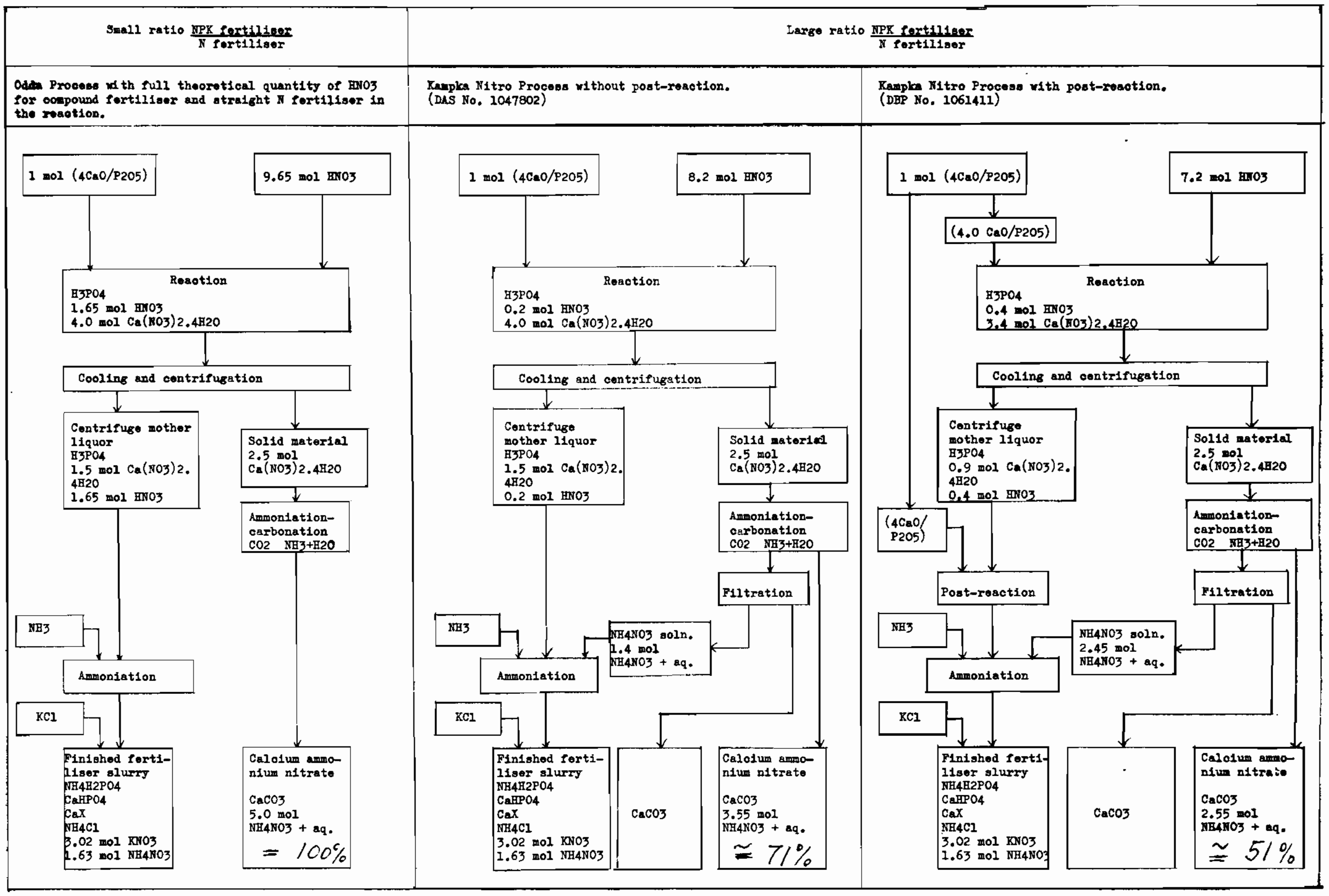


Table 6: Comparison of the variants of the Odda Process.

N-NO3 balance, and resulting amounts of Ca(NO3)2.4H2O, co-product fertilisers and free, usable CaCO3 per ton of primary fertiliser.

	Odda Process with maximum application of HNO3						Kampka Nitro Process without post-reaction					
N-NO3 for reaction mol HNO3/mol P2O5 Kg N-NO3/Kg P2O5	9.65 (≙ 100%) 0.95						8.20 (≙ 85%) 0.81					
N-NO3 balance	in the reaction	in the centrifuge mother liquor	in the primary compound fertiliser	Feed-back as NH4NO3	in Ca(NO3)2.4H2O	in the calc. ammon. nitrate as co-product fertiliser	in the reaction	in the centrifuge mother liquor	in the primary compound fertiliser	Feed-back as NH4NO3	in Ca(NO3)2.4H2O	in co-product fertiliser e.g. calc. ammon. nitrate
Kg N-NO3 /t primary fertiliser 13-13-21	122	59	59	—	63	63	105	40	59	19	63	44
Kg N-NO3/t primary fertiliser 15-15-15	142	69	69	—	73	73	121	47	69	22	73	51
Kg N-NO3/t primary fertiliser 20-20-0	189	92	92	—	97	97	162	63	92	29	97	68
Separated Ca(NO3)2.4H2O t												
t Ca(NO3)2.4H2O/prim. fert. 13-13-21	0.53						0.53					
t Ca(NO3)2.4H2O/t prim. fert. 15-15-15	0.62						0.62					
t Ca(NO3)2.4H2O/t prim. fert. 20-20-0	0.82						0.82					
Co-product fertiliser	calcium ammonium nitrate	NH4NO3 - Proportion for NP, NK or NPK co-product fertiliser					either calcium ammonium nitrate	or NH4NO3 - Proportion for NP, NK or NPK co-product fertiliser				
t co-product fert./t prim. fert. 13-13-21	0.59	—					0.41	0.25				
t co-product fert./t prim. fert. 15-15-15	0.67	—					0.47	0.29				
t co-product fert./t prim. fert. 20-20-0	0.91	—					0.63	0.39				
Free usable CaCO3	in the calcium ammonium nitrate co-product fertiliser						either in calc. ammon. nitrate as co-product fertiliser	or in NP, NK or NPK fertilisers as co-product fertilisers				
t CaCO3/t primary fertiliser 13-13-21	—						0.04	0.20				
t CaCO3/t primary fertiliser 15-15-15	—						0.06	0.24				
t CaCO3/t primary fertiliser 20-20-0	—						0.08	0.32				

Table 7. Comparison of production capacities and investment costs for a plant using the HNO_3—H_3PO_4 Process (see Table 2) and for one using the Kampka-Nitro Process

It is assumed in the comparison that

a) energy supply is available
b) workshops are available
c) an ammonia synthesis plant, including CO_2 compressors and tanks, is available.

The figures in the table are valid for specific investment conditions. They will vary according to country and circumstances.

Process	HNO_3—H_3PO_4 Process	Kampka-Nitro Process + Calcium ammonium nitrate and $CaCO_3$ section	
Output	200,000 tons/year of 13-13-21 = 615 tons/day	200,000 tons/year of 13-13-21 = 615 tons/day	60,000 tons/year of calcium ammonium nitrate (22% N) + 8,000 tons/year of $CaCO_3$ (dry)
	Capacity	Capacity	Capacity
A) Storage sheds			
Phosphate rock storage	20,000 tons	20,000 tons	—
Potash storage	4,000 tons	4,000 tons	—
Kieselgur storage	800 m^3	800 m^3	—
Phosphoric acid storage	800 m^3	—	—
H_2SO_4 storage	1,000 m^3	—	—
HNO_3 storage	500 m^3	500 m^3	250 m^3
Storage shed for NPK fertilizers	65,000 tons	65,000 tons	—
Storage shed for calcium ammonium nitrate	—	—	20,000 tons
$CaCO_3$ silo	—	—	1,000 tons
NPK fertilizer loading shed	200,000 tons/year	200,000 tons/year	—
Calcium ammonium nitrate loading shed	—	—	60,000 tons/years
B) Production plants			
NPK plant	200,000 tons/year	200,000 tons/year	—
Kampka-Nitro section	—	50 ton/day P_2O_5	25 tons/day $CaCO_3$
Calcium ammonium nitrate section	—	—	185 tons/day
HNO_3 plant complete	40 tons/day	40 tons/day	20 tons/day
H_3PO_4 plant complete	50 tons/day	—	—
H_2SO_4 plant complete	120 tons/day	—	—
Phosphate rock grinding plant	30 tons/day	—	—
Investment cost	ca. 38 milion DM	Total : ca. 44 million DM	
Plant nutrient production ($N + P_2O_5$)	52,000 tons/year	52,000 tons/year +	13,200 tons/year
Investment cost per ton of plant nutrient ($N + P_2O_5$)	ca. DH 720/ton/year ($N + P_2O_5$)	ca. DM 680/ton/year ($N + P_2O_5$) The by-product $CaCO_3$ is not included in this calculation	

trifuging is ammoniated and carbonated with NH_3 and CO_2 [$(NH_4)_2CO_3$] and is thus converted to a suspension of $CaCO_3$ in a solution of NH_4NO_3;

- the ammoniation-carbonation process is so conducted that the resulting $CaCO_3$ is filterable and can be separated from the NH_4NO_3 solution by filtration;
- the post reaction of rock phosphate may be executed as a method of procedure.

The ammonium nitrate solution, separated from the calcium carbonate by filtration, may be used in different ways as is shown by the following examples:

- 24-16-0 after complete return of the ammonium nitrate;
- 13-13-21, 20-20-0, 15-15-15, 20-0-20 etc., N solution and calcium ammonium nitrate with a N content = 20.5%

after partial return of the ammonium nitrate.

a) *Chemical and Technical Data*

Tables 5 and 6 show quantitative comparisons between the Odda-Process and the Kampka-Nitro-Process.

For the sake of clarity, these tables

- in some cases show only one of the process routes;
- quote figures only in terms of N-NO_3.

The Kampka-Nitro-Process can be used with advantage for compound fertilizers with a N:P_2O_5 ratio (by weight) of 1 to 1.5:1 and a N-NH_3:N-$N0_3$molar ratio — 1:1

As examples of fertilizers which can be produced by this process, we quote the following, most of which are already manufactured industrially:

13-13-21
15-15-15
20-20-0
12-12-20-S
12-12-16

12-12-24
24-16-0
18-12-15
18-12-12 S.

In the Kampka-Nitro-Process all, or almost all the HNO_3 which is fed into the process attacks the phosphate rock. Practically no nitric acid is fed to the process to combine only with ammonia.

After the ammoniation-carbonation of the separated $Ca(NO_3)_2 \cdot 4H_2O$, practically all of the NHO_3 fed into the Kampka-Nitro-Process was used both to react with phosphate rock and to fix ammonia.

If the precipitated $CaCO_3$ is not used in the formation of calcium ammonium nitrate, it can be processed to form a commercial product of its own.

For the ammoniation-carbonation step, by-product CO_2 from sod production can profitably be used.

Industrial experience has been gained with Kola, Moroccan and Taiba phosphates. The optimum concentration of the nitric acid for the reaction lies within the range of 55-61% by weight.

b) *Economic Data*

From *table 7* you may see, that a Kampka-Nitro-plant is economically advantageous compared with the process using wet phosphoric acid, because in terms of the quantity of $N + P_2O_5$ in the fertilizer produced, the *investment* for a complete Kampka-Nitro-plant with a calcium ammonium nitrate section, compared with a plant using the nitric acid-phosphoric acid-process, is smaller, if related to the amount of plant nutrient content in either case

DM 680/metric ton per year of $N + P_2O_5$ in the fertilizers
(Kampka Nitro)
DM 720/metric ton per year of $N + P_2O_5$ in the fertilizers
$HNO_3 + H_3PO_4$).

The figures in the table are valid for specific investment conditions. They will vary according to country and circumstances, but they show the typical trend.

The Kampka-Nitro-Process makes no direct use of sulphuric acid. The anion of the nitric acid used in the reaction passes into the primary fertilizer and the coproduct fertilizer, where it is paid for. On the other hand $CaSO_4$ from H_2SO_4, used in the production of phosphoric acid, is of no value.

Related to the same amount and the same plant nutrient content of the finished product the Kampka-Nitro-Process differs from the normal Odda-Process, with the introduction of the full amount of HNO_3 for both the compound and the straight N-fertilizer into the acidulation step,

- since there is less or no production of the coproduct fertilizer;
- since the coproduct fertilizers are not limited to straight N-fertilizers, and thus the Kampka-Nitro-Process may be independent of the straight N-fertilizer market;
- since the capacity of the HNO_3 plant and the cooling section of the Kampka-Nitro-plant can be smaller;
- since, with 1 ton of $N\text{-}NO_3$ in the form of HNO_3, up to 1.4 times more available P_2O_5 can be produced.

By using the Kampka-Nitro-Process with the post reaction which, for the same amount of HNO_3 used, consists in the treatment of an additional amount of rock phosphate with the mother liquor from the centrifuges, the ratio

$$\frac{\text{tonnage of primary compound fertilizer}}{\text{tonnage of coproduct fertilizer}}$$

can be still further increased.

If the coproduct fertilizer is to be a NP- or a NPK-fertilizer, the Kampka-Nitro-Process has to be used in combination with a conventional (wet process) phosphoric acid plant. By this way even NP- or NPK-fertilizers, falling outside the range offered by the Kampka-Nitro-Process alone, can be manufactured. All these fertilizers can take up the co-produced ammonium nitrate to such an extent, that no straight N-fertilizers need to be marketed. This is the method of operation practiced by Chemische Farbrik Kalk. It uses both the Kampka-Process and the Kampka-Nitro-Process.

c) *Equipment Data*

The design of equipment for the Kampka-Nitro-Plant incorporates new developments. The cooling of the reaction slurry takes place continuously in several stages. If these stages are accurately controlled, a coarse, crystalline calcium nitrate-tetrahydrate is produced. As a result the mother liquor can be easily separated from the salt by centrifuging. A comparative reduction in the required number of centrifuges can be achieved. With this process, the quantity of phosphoric acid remaining in the calcium nitrate-tetrahydrate can be reduced. A further reduction of the phosphoric acid content can, if desired, be effected in a special purification stage.

Cooling is fully automated. The control system regulates the course of the individual cooling stages and the intervals for cleaning the cooling surfaces.

For the ammoniation-carbonation of the calcium nitrate, a special apparatus has been developed in which the calcium carbonate can be precipitated in easily filterable form.

Only two men per shift are required for cooling, purification of the calcium nitrate, ammoniation-carbonation and ammonium nitrate concentration. Energy consumption and maintenance requirements are of the same order of magnitude as with complete compound fertilizer processes using nitric, sulphuric and phosphoric acids, or merely nitric and phosphoric acids in the reaction stage.

The plant, with a capacity of 250.000 tons per year of compound fertilizers, has been operating successfully since the end of 1963.

The PEC Company And The Problem Of Nitrophosphates

Y. F. Berquin

FROM the very outset. PEC engineers had spotted the present popularity gained by nitrophosphates by reason of savings they allow, both on equipment and sulphur consumptions.

As a matter of fact, world sulphur supply is critical again, and PEC people, thanks to a long experience acquired on the use of their processes — both in their own plants and in plants designed for their licenseees - are particularly apt to discuss the problem and share their knowledge with you. We think it fits to divide this report into the following sections:

(1) a brief review of the various existent PEC processes, with the potentials and the limitations for each of them.

(2) a summary description of the PEC plant, since the latter is perfectly versatile and may use any PEC process.

(3) an outline of outstanding research work and the first results from it.

(4) a summary of the solutions PEC is presently studying to solve a number of related problems raised by the production of complex fertilizers, especially as far as pollution questions are concerned.

Well-known as basic PEC processes are, we shall but review them as briefly as possible.

They are based upon dissolving rock-phosphate with nitric acid, eventually complemented—as the process may require — with either sulphuric or phosphoric acid. When this attack liquor is neutralized, di-calcium phosphate is precipitated.

The remaining calcium nitrate may then be converted into non hygroscopic salt in three different ways:

(1) *with carbon dioxide*
Both carbon dioxide and ammonia are injected directly into the ammoniated mass (minimum pH*8*) and a stabilizer is added to keep up the citrate solubility of di-calcium phosphate. Calcium is thus blocked as carbonate. This is the carbonitric process.

(2) *with sulphuric acid*
Sulphuric acid is added to the attack liquid progressively, and ammonia is injected at the same time. The final slurry pH goes up to about 5 and all excess calcium is present as calcium sulphate.
This is the sulphonitric process.

(3) *with phosphoric acid*
Operations are as described above, but calcium is precipitated as di-calcium phosphate. This is the phosphonitric process.

Many variants are possible, starting from the reactions triggered by the three processes described above.

For instance, carbon dioxide and ammonia may be substituted by ammonium carbonate or ammonium sexqui-carbonate. It was observed that such a substitution affects the thickness of resulting slurries.

In the same way, both sulphuric and phosphoric acids - and the relevant amount of ammonia - may be substituted by the corresponding ammonium salt and even, for the second acid, by a combination of either simple or triple superphosphate with ammonia. When the relative ratios of N -P- K nutrient elements are modified as compared to basic compositions, potassium salt may be substituted to the acid in all three processes.

Although in all-basic processes phosphoric acid is present in the final product as di-calcium phosphate, i.e. as a product soluble in ammonium citrate, but not in water, with the last two processes users may also obtain part of the phosphoric acid as a water-soluble product.

In the case of the sulphuric process, an additional amount of the sulphuric acid is injected after the attack, over and above the above-mentioned proportions. This excess acid blocks part of the calcium which should have normally been converted into di-calcium phosphate.

This calcium is then substituted by ammonia, and consequently part of the phosphoric acid is in the form of water soluble ammonium phosphate.

In order to prevent this ammonium phosphate from reverting, at a later stage, to di-calcium phosphate by reacting with calcium sulphate, here again precipitated salts should be blocked with a stabilizer. Up to 50% of P_2O_5 — depending on the relative amount of reagent — is in water soluble form.

In the case of phosphoric acid, it is clear that any excess acid — as compared to the amount required for reacting — will be changed into water soluble ammonium phosphate after neutralizing.

Moreover, one may always combine these processes with one another, and the range of formulations is thus fairly infinite, provided the necessary materials are available.

It remains to be seen how such processes as a whole are used in a PEC unit. We call it a "PEC unit" because we have done our best to engineer a single type of unit, sufficiently flexible to allow using the different PEC processes and their variants without any modification.

The present version of this plant — the result of a long period of continuous experience and improvement — looks attractive because its basic simplicity does not affect its flexibility in the least, but rather favours it.

The plant includes two strictly distinctive sections:

The first — liquid phase — section is the one where all the different reactions involved in the chosen process are carried out.

The 'core' of this section includes the battery of standard tanks we call 'U tubes' because of their peculiar shape. The tank is especially desgned to allow an extremely strong stirring action and high throughout rate of the mass in it. It may be used both to attack rock-phosphate with nitric acid — where strong stirring avoids any foam problems, even when phosphates with a high carbonate content are used — and to amoniate liquors — since here again their stirring system allows introducing a huge amount of ammonia for a given volume of liquor, without either reversion of the various present phosphates nor noticeable ammonia losses.

If potash is included in the formulation, the relevant salt is introduced at the required point in the reactors battery. The exchange of salts will generate a stable salt — potassium nitrate — at the expense of an unstable one — ammonium nitrate:

$$NO_3NH_4 + KCl \rightarrow NO_3K + NH_4Cl$$
$$2\,NO_3NH_4 + SO_4H_2 \rightarrow NO_3K + SO_4\,(NH_4)_2.$$

This section of the plant is completed by a set of measuring equipment designed for the input of solid, liquid and gaseous materials. As the whole plant is controlled automatically from a central instrument panel, the whole battery is easily operated, the more so as all operations evolve continuously over the three shifts.

It should be added that since the equipment of reaction tanks is made of high-grade stainless steel, such units are easily built, lightweight and rugged, and require practically no reasonable maintenance.

At the outlet of the battery, the slurry falls into a storage tank which acts as a buffer between the two sections of the plant and ensures a very smooth operation. The slurry is transferred from the buffer tank to:

— the second section of the plant, where granulating and drying operations are carried out.

This section may be designed in two ways:

1) In the conventional system, the slurry from the buffer tank is mixed in a paddle mixer to recycling fines in sufficient amounts to produce a still humid, of course, but not sticky granule, which is dried in a standard rotary kiln. Once dry, the product is graded; oversize and market sizes are cooled down, market size granules coated and sent to storage, oversize particles are ground and recycled with all fines back to granulating.

2) It is also possible to use a more up-to-date equipment, i.e. the 'Spherodizer' designed by our C&I friends. Since this device is now sufficiently popular, we need not describe it here in full detail. Let us just note that in this device, which is very compact, and much shorter than conventional driers, both granulating and drying operations are carried out simultaneously. The process consists in spraying the slurry onto a curtain of granules which cover practically the whole section of the Spherodizer. A stream of hot air flowing through the unit is used to dry continuously the film of slurry deposited upon the granules at each revolution. This device offers a host of advantages: simplicity, compactness and possible processing of fluid slurries with a high water content, since the recycling rate of fines required to generate the nuclei from which granules will be formed is very low and practically independent from the water content of slurries. With the conventional system, on the contrary, fluid and humid slurries — e,g, in phosphonitric processing — require huge recycling rates, often extending 10:1, and as a result, considerable weights — as compared to actual production rates—must be handled, with higher losses, bigger apparatus, — and larger capital investment, and higher power consumptions.

If we add to all this the outstanding physical specifications of the granule — very spherical, hard and finished granules, with a much lower water-content than after conventional drying, — it is quite clear why the PEC company considers this apparatus as an ideal component — in most cases in the layout of their unit. They are striving to reach maximum performance rates with this equipment by endowing it with any minute improvements recommended by the daily experience they acquired both in their own — or their licensees' — plants, and in their research and development facilities.

On the whole, and whatever the drying method, more than 20 plants have been or are being built to date to use PEC processes. This amounts to a capacity of 5 million tons a year, and more. However, even if it seems reasonable to develop the building of plants based upon carefully designed processes and devices, things should not be taken for granted, since science is continuously progressing at a rapid rate, and the best present solutions may look obsolete unless necessary developments are not carried out timely.

This is why both the test laboratories and pilot plants of the PEC Company are not only perfecting continuously such processes as may presently be used, but are ceaselessly carrying on research activities which take acount of any changes in industrial equipment and any new trends brought to light by agricultural research.

For example, one of the research items of our company covers the use of concentrated acids the industry is more and more currently supplying, more particularly the spectacular progress of nitric acid concentration. There are, of course, still many plants where nitric acid is produced under 50 per cent, but the pressure absorption process—which has made huge strides and is constantly perfected —is increasing the acid strength. A few years ago, 55-56 per cent strength had become current, but quite recently new increases were made possible, and strength in the range of 60-65, or even 70 per cent are in the offing. The use of such stronger acids, tempting as it may be because a smaller amount of water needs to be evaporated, will raise problems in most cases, especially when a spherodizer is used, because much too thick final slurries are obtained. It should be uneconomical, of course, to dilute them until they may be easily handled or pumped. The best solution will therefore be push the ammoniation of nitrophosphoric liquors as far as the viscosity of the medium allows in PEC reactors — characterized, as already seen above, by highly efficient stirring — and concluding the ammoniation process in a differently designed device.

After a number of tests in variously engineered devices, it was finally decided to choose, for this further ammoniation, a process in which small initial grains are covered with successive and individually ammoniated layers of slurry.

This is done in a cylindric horizontal drum apparatus. The inside surface of the cylinder is smooth, and the material moves in the cylinder as a rolling bed.

The unit is fed with recycled fines which act as primers for future granules. The preammoniated slurry is sprayed onto the bed of fines, either in one or more points, depending on the size of the unit.

Under the continuous impact of spraying and bed rolling, the particles get covered with a fine layer of slurry. Ammonia is fed from under the bed, at the point of maximum bed thickness.

Research was also devoted to the system of ammonia distribution under the bed, e.g. by substituting elements located in a plane at right angle to the cylinder axis instead of a manifold parallel to this axis. With this equipment, we have already been able — at the pilot stage — to design a large number of formulations, e.g. 16.14.0 or 13.10.12 with the carbonitric process — in which case the required CO_2 is also fed from under the bed through a second injection manifold, parallel and close to the ammonia manifold — and 13.13.0 with 50 percent of P_2O_5 water-soluble by the sulphonitric process.

On the basis of the results obtained with this equipment, our searchers tried and superseded the initial aim; in other words, they were able to produce, under good conditions, such non nitric fertilizers as 16.48.0, 16.20.0 and 15.30.0 by neutralizing both sulphuric and phosphoric acids.

In practically all such tests, the final granule was sufficiently dry to be used without further processing, since the reaction between ammonia and acids in the drum generated sufficient heat to strip any excess of water. In a few cases, however, a slight final drying stage should be provided.

An industrial sized plant is being built to carry out the tests at the actual production stage and assess the precise characteristics of material to be used.

However, such studies on how to prepare, strictly speaking, complex nitrophosphate fertilizers were not the whole picture, and we had to tackle another—and not less important — facet of the problem which will no doubt increasingly claim our attention in a near future, i.e. questions of sanitation and public health.

The fertilizer industry as a whole must face the problem of both gaseous and liquid waste, and complex fertilizers are no exception.

Complex fertilizers raise the question of nitric acid, and the problem of air-pollution by tail gases with a high nitrogen oxide content from the production of such acid did not escape us. Various processes have been designed to control the generation, but in most cases they boil down to some kind of oxide reduction—catalytic or not — between nitrogen oxide and a fuel (hydrocarbide, or even ammonia). In all cases, a considerable investment is involved, and the loss of both the nitrogen reduced to elemental form, and the fuel makes this a very costly proposition.

We have consequently explored and designed a process in which not only is the air purified, but the nitrogen is recovered from the oxide without increasing operating costs overmuch.

In this recovery process nitrous vapours are absorbed by a water-suspension of calcium hydroxide. This nitrogen is contained in the resultant solution as calcium nitrate. Sulphuric acid is then added to oxidize the nitrite. With 2.-2.5 moles acid to 3 moles nitrite, all the calcium nitrite may be quickly oxidized to give calcium nitrate, calcium sulphate and nitrogen dioxide. The calcium sulphate suspension in the nitrate solution does not hold any toxic nitric and may be either flushed or used, e.g. in complex fertilizer plants. If a higher proportion of sulphuric acid is used, e.g. 1 mole acid to 1 mole nitrite, nitric acid is generated, instead of calcium nitrate. After filtering the calcium sulphate, one gets then a nitric acid solution holding 10-20 percent of HNO_3, which can — for example — be recycled through the absorption apparatus of the nitric acid installation.

The nitrogen dioxide generated when nitrate is oxidized by sulphuric acid may be recovered, e.g. by recycling it too through the nitric acid installation.

However, this is a relatively simple problem, owing to the relative purity of nitrogen oxides in the waste of the nitric acid installation, as compared to gases produced during liquid phase reaction in the fertilizer unit.

As a matter of fact, such gases have a much more complex composition: nitrogen oxide, some ammonia, fluorous — and even silicofluorous-compounds, etc.

However, our studies on nitrogen oxide, reviewed above, together with the principles underlying them, helped us solve this new problem.

The principles of the process are as follows:

A first water-stripping of gases collected from the battery eliminates fairly all fluorous compounds and some nitrogen oxides. The stripping solution is recycled and its fluorine content is progressively increased. In order to limit this fluorine content in the water, it is necessary to provide a used water overflow and a fresh water intake to even up the volume of flow. Overflowing -water is sent back to the reactors battery, at a point where neutralizing is already advanced. In this way, no fluorine emission occurs, as would be the case if the fluorous liquor was introduced into a strongly acid slurry. On the contrary, calcium fluoride is precipitated when in contact with soluble calcium salts, but since neutralizing is not over at that point—i.e. the pH is still acid—this precipitation of fluorine does not involve any precipitation of insoluble-type phosphates.

Gases from the first stripping tower are then stripped with a sodium carbonate solution (slaked lime, exceptionally, when there are no carbonates in the phosphates) which stops both nitrous gases and such traces of fluorine as might get through the first tower.

Here again, we use a closed-circuit system with overflow and fresh liquor inlet, but the overflow, in this case, goes to the end attack tank. Thus the mixture of sodium — or calcium — nitrate and nitrite formed in the tower according to relation:

$$N_2O_4 + CO_3Na_2 \rightarrow NO_2Na + NO_3Na + CO_2$$

is put into contact with free strong acids; the nitrate remains in the solution, but the nitrite is broken down as follows:

$$2NO_2Na + 2NO_3H \rightarrow N_2O_3 + H_2O + 2NO_3Na$$

and further, in the presence of air in the piping:

$$N_2O_3 + O \rightarrow N_2O_4.$$

It is thus clear that at each cycle of nitrogen, half is recovered as nitrate and the other half is recycled, until no nitrogen oxides are left in the gases.

On the other hand, the gases are mixed with steam generated by the exothermal reaction of ammonia with acids. This is a useful phenomenon, since it reduces the work of the drying section proportionally, and a heater is therefore located at each stripping circuit to prevent this steam from condensing. One must just maintain the temperature at a level where the vapour tension of stripping solutions balance the partial pressure of the stream in the gases.

We hope this short report has helped demonstrate that the PEC Company is striving to rank, now and in the future, among the leaders of the 'nitrophosphate' complex fertilizers industry.

Moderator Weber: Thank you, Mr. Berquin, for that very interesting talk.

Our final speaker is well known to the Round Table, Mr. Hignett of TVA, and I hope that he will try to give us a little overall picture of the economics and money that we may save by going to some of these nitrophosphates.

Mr. T. P. Hignett: Thank you, Bill.

The position I found myself in this morning reminds me somewhat of a story by Mark Twain or perhaps O'Henry, about a character who achieved great popularity as a public speaker by seeing that he was always placed last on the program, whereupon he would arise and say: There has been so much said and so well said that I can add nothing to it. And he would sit down.

I am afraid, Bill, that Vince will not let me get off quite that light.

Mr. Hignett then presented his talk.

Nitrophosphate Processes Advantages And Disadvantages

Travis P. Hignett

THE world production and consumption of fertilizer is increasing at an unprecedented rate. Consumption in the 1963-64 season increased about 14% over the preceding year. Production and consumption of phosphate fertilizers increased by about 11%. All signs point toward a continued upsurge in fertilizer use, especially in parts of the world where the pressure of hungry people and increasing population demand greater food production.

Most of the world's phosphate fertilizer is made by processes that involve the use of sulfur. In the United States, an average of about 0.75 ton of sulfur is used for each ton of fertilizer P_2O_5. Moreover, the trend is toward an increase in this ratio. Ammonium phosphates, which are the fastest growing phosphate fertilizers, require about 0.9 ton of sulfur per ton of P_2O_5.

It has been estimated that the world consumption of sulfur in all forms will increase from 22 million metric tons in 1964 to 31 million tons in 1970 and 45 million tons in 1980. This estimate is based on the assumption that the ratio of sulfur to fertilizer P_2O_5 will be 0.75 to 1, and nonfertilizer uses will increase at the rate of 4% per year.

Sulphur prices are increasing, and a short supply of elemental sulfur is in prospect. World reserves of sulfur, including sulfides and sulfates, are fully adequate so only temporary shortages are predicted. However, new sources of elemental sulfur are limited and expected to be more costly to bring into production. Sulfides and sulfates are also more expensive sources of sulfuric acid. So the cost of elemental sulfur is not likely to return to its previous low level; it is more likely to rise to a point where pyrites and other sources are competitive in most of the world.

In view of the prospect for continued higher sulfur prices and at least temporary shortages of elemental sulfur, it is natural that fertilizer manufacturers should take a close look at prcesses that require less sulfur or no sulfur. The most attractive of these is a group of processes commonly known as nitrophosphates or nitric phosphate processes.

Nitrophosphate processes are those in which phosphate rock is treated with nitric acid rather than sulfuric. In contrast with the prospective rising costs of sulfuric acid, the cost of nitric acid is expected to fall because of the economics of producing ammonia in very large plants and because of technological improvements in converting ammonia to nitric acid.

The reaction of nitric acid with phosphate rock produces a solution containing calcium nitrate and phosphoric acid or monocalcium phosphate, according to reaction (1) or (2).

$$Ca_{10}F_2(PO_4)_6 + 20\,HNO_3 = 10Ca(NO_3)_2 + 6H_3PO_4 + 2HF \qquad (1)$$

$$Ca_{10}F_2(PO_4)_6 + 14HNO_3 = 3CaH_4(PO_4)_2 + 7Ca(NO_3)_2 + 2HF \qquad (2)$$

In some nitrophosphate processes, sulfuric or phosphoric acid is used in addition to nitric acid. These processes are sometimes called sulfonitric or phosphonitric processes, or mixed acid processes. In other processes, part of the calcium nitrate is removed by cooling, crystallization, and centrifuging. The purpose of these steps is to balance the amount of calcium that is available for combining with the phosphate so that upon ammoniation no calcium phosphate more basic than dicalcium phosphate will form. The mole ratio of CaO:

P_2O_5 in phosphate rock ranges from about 3.3 to 4.0 Since the ratio for dicalcium phosphate is 2, at least 40 to 50% of the calcium must be removed or combined with anions other than PO_4.

In practice, some water-soluble P_2O_5 usually is desired in the final product so the ratio of available CaO to P_2O_5 is adjusted to less than 2; part of the -P_2O_5 forms water-soluble ammonium phosphate or monocalcium phosphate upon ammoniation. If the water solubility is obtained by using increased amounts of sulfuric or phosphoric acid in the mixed acid processes, less sulfur is saved, and some of the economic advantage is lost.

It is the purpose of this paper to review in a general way the advantages and disadvantages of some of the present and proposed nitrophosphate processes in comparison with other popular processes that produce like amounts of nitrogen and phosphate fertilizer. For this purpose I have selected processes or combination of processes that produce 200 tons per day of fertilizer nitrogen and 100 tons per day of fertilizer P_2O_5, either in combination or as separate products. The nitrophosphate processes selected were those that produced at least 40% of the P_2O_5 in a water soluble form. This proportion is deemed sufficient for most agricultural uses. However, I do not wish to imply that fertilizers with lower water solubility are necessarily inferior.

The various combinations of products and their raw material requirements are listed in Table I. Following is an identification of the processes and their main advantages.

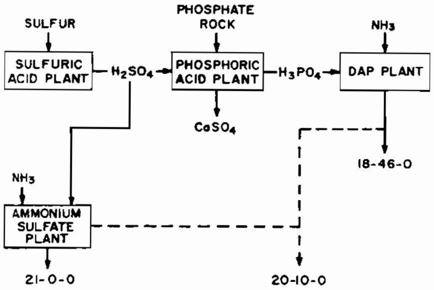


Figure 1. Diammonium Phosphate and Ammonium Sulphate.

These two products are popular fertilizer materials, both as separate products and in combinations such as 20-10-0 and 19-19-0. They also are a popular base for N-P-K grades such as 13-13-13 and 12-12-18. They are fully water soluble and relatively nonhygroscopic. Equipment for their manufacture is relatively simple. The outstanding disadvantage is the high raw material cost and relatively low analysis.

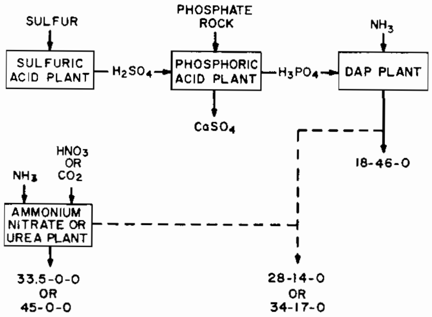
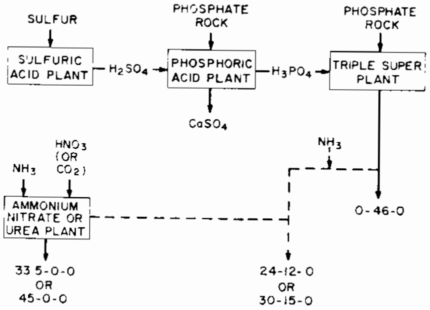


Figure 2. Diammonium Phosphate and Ammonium Nitrate or Urea.

These products are well known, popular fertilizers both in combination and separately. Combinations of diammonium phosphate and ammonium nitrate are sometimes known as ammonium phosphate nitrates; grades range from 30-10-0 to 25-25-0. N-P-K grades such as 17-17-17, 16-16-21, 23-11.5-11.5, 7-28-28, and 17-11-22 are popular in various countries. Urea-ammonium phosphate compounds are produced by several Japanese firms and are coming into use in North America. N-P grades range from about 20-40-0 to 34-17-0. Both the ammonium phosphate nitrate and urea-ammonium phosphate series have the advantages of water solubility, high analysis, and fairly good flexibility as to grades that can be made either as compounds or blends. The main disadvantage is the high sulfur requirement, about 0.94 ton of sulfur per ton of P_2O_5.

Figure 3. Triple Superphosphate and Ammonium Nitrate or Urea.



Triple superphosphate is a popular product which is widely used in blending or compound fertilizer manufacture. For best physical properties, it should be ammoniated or treated with basic conditioners, especially when mixed with ammonium nitrate or urea. Ammoniation reduces the P_2O_5 water solubility to a minimum of about 50%. One advantage of triple superphosphate is the wide range of grades that can be made; in combination with ammonia and ammonium nitrate, grades range from 8-32-0 to 24-12-0. N-P-K grades range from 6-24-24 to 15-15-15. No-nitrogen grades also may be made. The sulfur requirement is about 0.67 ton per ton of P_2O_5, appreciably less than for ammonium phosphate. Mixtures containing triple superphosphate are somewhat lower in analysis than those made with diammonium phosphate.

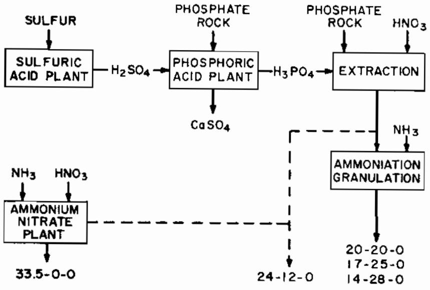
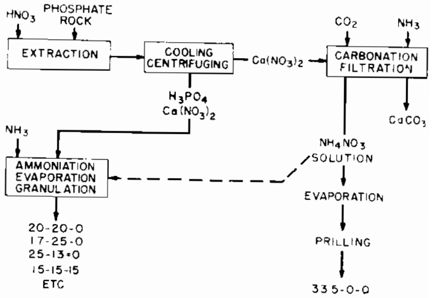


Figure 4. Mixed Acid Nitrophosphates.

Nitrophosphates made with phosphoric and nitric acid are produced commercially in several plants in the United States and Europe. Typical grades are 20-20-0, 24-12-0, 15-15-15, 10-20-20, 13-13-21, and 10-15-20. When formulated to contain 40% of their P_2O_5 in a water soluble form, the sulfur requirement is 0.6 ton per ton of P_2O_5, only slightly less than for triple superphosphate. The analysis of mixtures is about the same as

Figure 5. Odda Process



those made with triple superphosphate, but there is less flexibility as to grades. For instance, 1-4-x ratios are not possible.

Various modifications of the Odda process are widely used in Europe. Its outstanding advantage is that it requires no sulfur, and hence the raw material costs are low. The P_2O_5 water solubility depends on the proportion of calcium nitrate removed. Commercial products usually range from 35 to 50% water solubility. Typical grades are similar to those made by mixed acid processes. The minimum $N:P_2O_5$ ratio is about 3 to 4.

The calcium nitrate that is removed may be granulated or prilled and sold as such, or it may be treated with ammonia and carbon dioxide to convert it to ammonium nitrate and calcium carbonate. This mixture may be granulated without separation to make ammonium nitrate-limestone (21% N), or the calcium carbonate may be removed by filtration. The resulting ammonium nitrate solution may be concentrated and prilled, or used to prepare nitrogen solution, or recycled to the mixed fertilizer process.

Whereas processes that prepare phosphoric acid through the use of sulfuric acid produce gypsum as a waste product, the byproduct of the Odda process is calcium carbonate. Disposal of calcium carbonate may be less difficult than gypsum; in many areas it may be sold for liming farmland for a sufficient price to pay for the cost of disposal.

Despite the considerable flexibility in dealing with the calcium nitrate byproduct, there remains the disadvantage that the process necessarily produces nearly 2 tons of fertilizer nitrogen for each ton of fertilizer P_2O_5. This can be a serious disadvantage when the two elements are not needed in that ratio or where the nitrate form is not the preferred form.

The complexity of the Odda process and its relatively high investment cost are often considered to be disadvantages. However, if we include all of the facilities needed to make the same amount of fertilizer nitrogen and phosphorus by other methods (such as those illustrated in Figures 2, 3, and 4), there may not be much difference in complexity or investment.

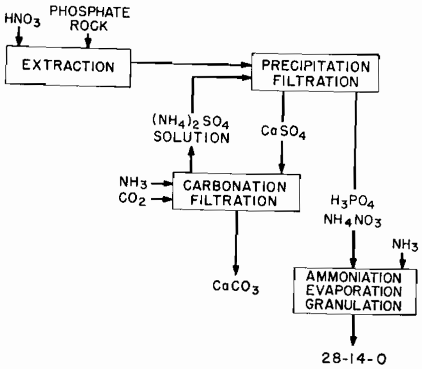


Figure 6. Sulfate Cycle Nitrophosphate Process.

This process (Fig. 6.) or similar ones have been proposed by Weber and Oliver (*2*) and by Strelzoff and Roberts (*1*), but it has not been carried out on a commercial scale. However, all of the individual steps have been proved in large-scale operation.

All of the other nitrophosphate processes thus far considered retain some calcium in the product. This calcium lowers the grade and limits the water solubility. It also prevents preparation of diammonium phosphate since at the pH required for diammonium phosphate formation the calcium will precipitate as hydroxyapatite which has dubious fertilizer value.

In contrast, the sulfate cycle process produces an entirely water-soluble product in which the phosphate may be present eitirely as diammonium phosphate. The most obvious disadvantage is the lack of flexibility as to $N:P_2O_5$ ratio. Unless some way of separating the diammonium phosphate from the ammonium nitrate is devised, the product will contain both in a fixed ratio of $N:P_2O_5$ of about 2 to 1 (28-14-0).

Another disadvantage is that much water is introduced into the process in the sulfate cycle, all of which must be evaporated. A rough estimate indicates that the cost of evaporation may be $2 to $3 per ton of P_2O_5 as compared with a saving of about $30 or more in sulfur cost.

This process (Fig. 7.) is a combination of the two preceding ones. After dissolution of phosphate rock in nitric acid, calcium nitrate is removed to whatever extent is feasible and converted to ammonium nitrate as in the Odda process. The calcium remaining in the solution is precipitated as calcium sulfate by addition of ammonium sulfate solution. If byproduct ammonium sulfate is available, the calcium sulfate may be discarded. Otherwise, the calcium sulfate can be used to regenerate ammonium sulfate solution which is recycled.

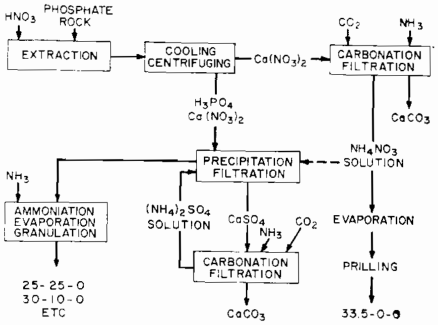


Figure 7. Odda Process with Proposed Sulfate Cycle.

This process has the advantages that the product has high water solubility and there is some flexibility in $N.P_2O_5$ ratio. For instance, the products might include ammonium phosphate nitrates ranging from 30-10-0 to 25-25-0. However, the total fertilizer nitrogen output would necessarily be about twice the P_2O_5 output. Although the process has more steps than the straight sulfate recycle method, the amount of calcium sulfate to be treated is no more than one-third of the total calcium. This step probably is the most expensive in operating cost.

Like the sulfate recycle process, this modification of the Odda process has not been carried out commercially in exactly this form, but all steps are known to be technically feasible.

The cost of the basic raw materials for the several processes are shown in Table I. Since the amounts of phosphate rock and ammonia required for all processes are similar, differences are mainly due to sulfur requirements. The raw material cost for the ammonium sulfate phosphate combination is highest, $82.40 per ton of N + P_2O_5. The ammonium phosphate nitrate is next highest at $61.20 per ton. Triple superphosphate-ammonium nitrate and mixed acid nitrophosphate are next at $57.90 and $56.70 per ton. The Odda

Table I. Raw Material Requirements and Products for Selected Nitrophosphate and Conventional Processes

Product	Grade	Tons per day	Basic raw material requirement, tons/day: Phosphate rock[a]	Sulfur	Ammonia	Cost of raw materials[b]: $/day	$/ton of $N + P_2O_5$
DAP and AS	18-46-0	217	334	228	251	24,715	82.40
	21.0-0	768					
DAP and AN or urea	18-46-0	217	334	94	261	18,375	61.20
	33.5-0-0	480					
	45-0-0	(358)					
TSP and AN or urea	0-46-0	217	327	67	261	17,360	57.90
	33.5-0-0	598					
	45-0-0	(446)					
Mixed acid nitrophos and AN	20-20-0	500	325	60	259	17,005	56.70
	33.5-0-0	299					
Modified Odda process	20-20-0	500	313	0	260	14,830	49.40
	33.5-0-0	299					
Modified Odda process with sulfate cycle	25-25-0	400	313	0	260	14,830	49.40
	33.5-0-0	299					
Sulfate-cycle nitrophos	28-14-0	715	313	0	260	14,830	49.40

[a] 33% P_2O_5.

[b] Assumed cost per ton: phosphate rock, $10; sulfur, $35; ammonia, $45.

processes and sulfate recycle processes are lowest at $49.40 per ton.

Investment Cost

We have attempted to make investment cost estimates for the several processes, but due to lack of time and authoritative information, we feel that our estimates are not sufficiently accurate to be useful. The equipment required for the Odda process and sulfate recycle process is complex and expensive. On the other hand, the need for production facilities for sulfuric and phosphoric acid is eliminated. As a result, there was not very much difference in investment costs. Weber and Oliver (*2*) have made estimates for similar processes, and their results are similar to ours.

Operating Costs

We have not attempted to make operating cost estimates since obviously much of the operating cost is related to investment cost. Probably the main difference would be the need for steam or fuel for evaporation in the sulfate recycle processes, whereas an excess of steam is available from sulfur-burning plants. The order of magnitude of this difference was estimated to be $3 per ton of P_2O_5, or $1 per ton of $N + P_2O_5$. Excess steam also is available from modern nitric acid plants, but not in sufficient quantity to supply the needs of the sulfate recycle processes. Requirements for power, cooling water, and catalyst for sulfuric acid production would be approximately offset by similar requirements for nitric acid production.

Conclusions

Of the several nitrophosphate processes that are available, modifications of the Odda process and the sulfate recycle process offer the greatest potential saving because they require no sulfur, while producing fertilizers of good quality containing a substantial proportion of water-soluble P_2O_5. Their greatest drawbacks are lack of flexibility in making a variety of $N:P_2O_5$ ratios and the fact that they necessarily produce fixed proportions of ammonium nitrate either as a separate product or in combinations. The latter point should not be a great handicap in the United States since ammonium nitrate, as such or as a component of solutions or mixed fertilizer, is the leading form of nitrogen

Research is in progress in several countries that may result in improved, more versatile nitrophosphate processes.

References

1. Strelzoff, Samuel, and Roberts, Edward S. (assignors to Chemical Construction Corporation). U. S. Patent 2,689,175. September 14, 1954.
2. Weber, Wm. C., and Oliver, R. H. "The Techno-Economic Aspects of Processes for the Acid Solubilization of Phosphates." Presented at Regional Meeting of the Economic Commission (ECAFE) for Asia and the Far East at Bombay, India, November 18-December 2, 1963.

Thank you.

MR. WEBER: Thank you, Travis.

We will now have a question and answer period and I would request all the speakers to come up to the Fertilizer Industry Round Table and take their places.

I thought possibly that we wouldn't let Travis Hignett have the last word and so I am going to ask the members of the panel whether they would like to comment or add to what he has said.

Do any of you gentlemen want to speak on that?

No response.

All right, there not being any questions from the panel, or comments, we will go to questions from the floor.

A MEMBER: I would like to ask anybody how much calcium nitrate can be left in the bagged fertilizer as calcium nitrate and still retain good properties?

MR. HIGNETT: How much calcium nitrate can be left in the product and still maintain good properties?

Is that your question?

MR. WEBER: I think the answer is none, but I will let the members of the panel answer it.

MR. HIGNETT: Approximately none, plus or minus two per cent.

DR. NEES: Yes, I agree with you, especially with fertilizers containing ammonium nitrate and ammonium chloride, for example, which is formed in fertilizer when you add potash and ammonium nitrate. You will get ammonium chloride and potassium nitrate.

In this kind of process, there shouldn't be any calcium nitrate because the calcium nitrate deteriorates the storability of the product.

Mr. Weber: Is there a question here?

A Member: Many valuable tables have been presented that could not be read either because they were in a foreign language or the measurements were in different units. My question is this: Is this information going to be presented in the proceedings?

Mr. Weber: Yes, the paper will be presented in the proceedings and the speakers have all agreed that they will furnish us copies of the tables and curves for inclusion in the transactions.

Dr. Banthien: I should like to respond to the first question.

Mr. Weber: All right. Dr. Banthien wants to speak on the first question.

Dr. Banthien: It is, of course, possible to have calcium nitrate in the final fertilizer, so it is possible to extract first the calcium nitrate, evaporate it, prill it in the usual manner and mix these prills with the prilled fertilizer.

We did some experiments of this kind and most unexpectedly found to be true what I just said.

Mr. Weber: Chris Pratt has a question.

Mr. Pratt: How many of these nitrophosphate processes are operating or under construction in North and South America? I would be interested in the number and also the type and size of these?

Mr. Weber: Is Enrico Pelitti here? Would you like to speak for that question?

Mr. Pelitti: I believe that Dr. Sauchelli pointed out yesterday in his introduction that there were only three plants in North America, in the United States, that have been built according to the nitrophosphate processes.

These plants were introduced in the middle fifties, originally because of the shortage of sulphur that developed in that period.

Two plants were built in accordance with the pilot plant tests done by TVA. One was the Allied Chemical in Ohio and the other was the Sheffield plant close to TVA.

Neither of these two plants, to my knowledge, ever produced to a large capacity. One of them was discontinued, the Allied Chemical Plant, after a fire developed in the warehouse a few years after they started operation.

The Chemical & Industrial Corporation had started looking into these units in the early fifties and made an agreement, it was a pact, to be able to produce and build these plants in the United States and in North America and, as a consequence, they built the first nitrophosphate plant for the California Spray Chemical Corporation in Richmond, California.

Subsequent to that, there were two more built also for the same company that later changed its name to the California Chemical and again only recently to Chevron Chemical. These two plants were built respectively at Kenewick in the State of Washington and Fort Madison in Iowa.

All of these plants use the phosphonitrate process, though they were equipped to possibly operate also by the sulphonitrate and the carbonitrate process. They were respectively — the first plant, in Richmond, was a nominal 500 tons, the second plant at Kenewick a nominal 200 tons per day. The third plant in Iowa was 600 tons per day based on triple 14.

The grades made by California Chemical gradually increased in analysis and the triple 14 was brought to triple 16, the 20-20-0 was brought to 22-22-0.

We have here on the stand a box of small samples of the triple 16 as made by California Chemical, now Chevron Chemical, in Fort Madison, Iowa.

One of the questions that you might ask is, Why were there not more of such plants built since there has been such an expansion in the fertilizer field. One of the reasons that has always been given was the lack of water solubility or complete water solubility of the nitrophosphate.

I believe that that has been already commented in part by Mr. Weber and Mr. Hignett. It seems to be something that no agronomist can reach a final agreement on. However, I would like to point out most of the products that are presently produced by these plants are more or less water soluble now.

The sample that is here and which you can take for yourself is, for example, 51 per cent water-soluble. This is the guaranteed analysis that is actually given by Chevron Chemical.

TVA has made a number of very interesting studies on the question of water solubility and by comparison I would like to call your attention to a paper that has just been published by TVA on quantitative analysis of mixed fertilizers by x-ray diffraction. I believe it is a fairly complete study of what the final components in the fertilizer material turn out to be actually after the process is completed.

One of these, the first tabulation of the study refers to ammoniated superphosphate. In that it is very clearly indicated that while initially the mixed fertilizer might employ a completely water-soluble phosphate, after it is treated with the ammonia, the water-solubility actually decreases to a great extent, in many cases well below the 50 per cent that is considered acceptable.

Therefore, the nitrophosphate, as presently produced in our system, actually at least an 18 point value, agronomically, even if the claims of the agronomists are accepted, which Mr. Hignett seems to have some questions on.

Mr. Weber: Fine. Thank you, Enrico.

I think that there is quite an agreement now that complete water-solubility is not necessary. I might mention that I don't think Mr. Hignett mentioned in this sulphate recycle process that he proposed that you would get a product that was 100 per cent water-soluble.

Would any member of the panel like to just comment on this question of water-solubility versus citrate-solubility?

Mr. Young: I think nothing has been said about the alkaline citrate method of determining solubility and the nitric phosphates, of course, stack up better in that respect. I believe there are some agronomic data that give comparisons that the water-solubility of the nitric phosphate will stack up better than that of ammoniated super phosphate.

MR. PIEPERS: I would like to make a few remarks concerning the water-solubility and the lack of solubility. In my opinion, it depends much on the climatic conditions, the soil conditions and the crops. So in many cases water solubility of 100 per cent is not necessary.

I can only say that in the Netherlands we now produce a product which has 50 per cent water solubility and a product with 100 per cent solubility and the 50 per cent product is mostly used on our farms on grassland and on cereals and the 100 per cent water-soluble product is mostly used for potatoes, tubercles and such products.

MR. WEBER: Any other questions? In the back, there.

A MEMBER: I'm Russell Coleman, of the Sulphur Institute. I thought I should identify myself before I make a few comments on this question. Actually, I have two questions.

One first comment. This item has been covered in Mr. Hignett's discussion and I want to congratulate the panel on a very excellent job. The presentation by Mr. Hignett in terms of alternatives I thought was really quite outstanding and the presentations of the other men were too.

I would be certainly reticent if I didn't rise to the occasion because sulphur seems to be the culprit in the case.

Number one, I would point out that although the records show that the price of sulphur has advanced rather steadily over the last year, the price of sulphur is still not as high as it was in the early fifties and the price of sulphur is still cheaper than the top soil that I buy to put in my flowers.

This has nothing to do with this particular question, the question that I wanted to ask deals primarily with the price of ammonia.

Does the panel feel that the price of ammonia, reducing the price of ammonia, assuming that price of sulphur stays constant, favors the nitrophosphate processes?

It has been my impression that as ammonia went down the farmer got cheaper ammonia whether it was in nitrophosphate or whether it was in the competitive process of an ammonium phosphate, urea and other products.

Now, my specific question is: Is there an advantage to the nitrophosphate processes if the price of ammonia goes down?

DR. BANTHIEN: This needs different considerations. It's a good question. Of course, I am of the opinion that it is an advantage of any process if the price of ammonia goes down but the main aim of nitrophosphate processes is the real saving in sulphur. All calculations that have been done together with engineering companies and practical manufacturers have shown that the cost difference is always given by the cost of sulphur introduced into the process.

MR. HIGNETT: Of course, as Dr. Banthien says, as the cost of ammonia goes down it favors all processes. That's quite true.

To some extent, it favors lower costs, or lower differentials between ammonia and nitric acid because the losses of ammonia in processing become less and less important. I think the recovery of ammonia in nitric acid processes ranges around 90 per cent and that 10 or 8 per cent loss becomes less important.

Of course, low cost ammonia makes it generally available in a great many places by transportation. The availability of the raw material might have some effect on this.

SAME MEMBER: Thank you very much.

Mr. Chairman, my other question—I don't want to dominate the questions here, but my other question deals primarily with a subject which was not covered, that is, transportation.

It has been my experience n the fertilizer industry that transportation costs amount to roughly 40 per cent of the total cost to the farmer. Now, there has been some excellent presentations here on capital costs and costs involved in producing the product but, if we are neglecting 40 per cent of the cost, so far as transportation is concerned, then this is a question that I think certainly should be discussed.

Does the panel know of or has the panel made any study of on-farm costs of nitrophosphates as compared with competitive products?

MR. YOUNG: Of course, the higher analysis products that are available by the ammonium phosphate route certainly would favor a lower overall handling and distribution cost and that would be a factor in the final analysis and would be a more or less consistent factor because of the difference in grades, I would say.

SAME MEMBER: Our preliminary studies would indicate that the transportation cost is much more of a primary factor than the cost of sulphur. This is the reason I asked the question.

Thank you very much.

MR. WEBER: Did you want to comment?

DR. BANTHIEN: The transportation cost is something that affects the farmer and the industry. But the saving in sulphur, I would think perhaps of nationalized farms, therefore, might incline me to favor still higher analysis fertilizers in the future and I think this will be both an advantage to the industry and farmers.

Nitrophosphates might be an intermediate stage.

MR. HIGNETT: I might mention that some of the nitrophosphates are about as high in analysis as the best fertilizers made by other processes. For instance, one visitor told me that they were making 23-23-0 by a nitrophosphate process and it is rather difficult. You can, of course, get a little higher than that by other processes but not much.

DR. NEES: I think this problem is very complex, because when you raise the concentration, you have higher costs per unit of nutrient and then you have smaller or comparatively smaller transportation costs, but the rate of water-solubility has to be changed by means of phosphoric acid.

Now, the fertilizers which don't contain that much phosphate, for example, part of it, they are physically soft and sometimes potassium must be put in these soils.

Then you have to pay, one, for the high cost of the high analysis, comparatively high cost of the high analysis product, of course. Then you have to pay for the application of the nitro chalk you have removed just from the fertilizer.

So it makes little sense just to look at the high analysis fertilizers and in our opinion, and it has been proven in many countries, and during three to four years in Germany, that about 35 per cent water solubility nitrophosphate or ammonium phosphate is sufficient for most average conditions in the Middle and Central Europe.

For example, the same thing holds in Central and North America, the climate found in North America corresponds with the European climate.

So I think, or we think that in each individual case such questions must be resolved from the beginning to the end. You just can't say let's make high analysis fertilizers or low analysis fertilizers. You must calculate from the beginning to the end and then you come to the right answer.

Going other ways is speculative. You can make speculations, you can talk a long time and you don't get the answer, you don't find the truth. We just talk and we don't come to the end of the problem.

Now, something as to the price of sulphur, the price of phosphoric acid, the price of nitric acid. On the one hand, in Europe, at least, we have the prices of nitrogen increasing generally and the prices of sulphur are going up generally, so, phosphoric acid will be more expensive than nitric acid, for example, and what it depends on is the price of each equivalent either in nitric acid or in sulphuric acid.

If you calculate on this basis and you make yourself clear as to what it means to have two acids with different prices and two methods in which on the one hand you get money for it, and the other one has to be thrown away on waste heaps. Some people are just growing too nervous and the public laws won't allow that any more. We can't just remove the gypsum by throwing it away and so forth.

I think all of these problems are quite complex and it is really dangerous to just make general talk about them. We have to calculate and only calculation in each case will give you the right answer.

Mr. Weber: This gentleman over here.

A Member: Are grades similar to, I believe Mr. Hignett said a 17-25-0 made in Europe, or is 20-20-0 the lowest NP ratio produced commercially?

By the Odda process?

Mr. Piepers: As far as I know the 20-20-0 is the lowest NP ratio but you can produce a product with about a P_2O_5 ratio of 0.6 through the 17-25, but especially in Europe we are going up to the highest P_2O_5 ratios. We produce the 20-20-0 and they produce the 20-15-0 and they are still going up in the NP_2O_5 ratio to the highest N contents.

Mr. Weber: Of course, in the mixed acid process you can go to lower NP ratios but you have to use sulphuric acid to go to them.

A Member: I would like to ask, what is it which limits the removal of calcium nitrate by refrigeration?

Mr. Weber: What limits the removal of calcium nitrate by refrigeration?

Mr. Piepers: This is quite a difficult question to answer, because it depends upon a lot of factors. First you have to deal with the question of the composition of the phosphate rock which may be all-important. Then also' the concentration of your nitric acid used for the acidulation is of importance too. As far as we know just now, you can remove about 60 to 70 per cent of your calcium nitrate by refrigeration.

If you want to remove more than that, it is possible but you have to do i tin any case in two steps, because, due to the formation of potassium nitrate crystals and due to the high viscosity of the remaining matter you need a very extended cooling surface to be able to get the heat fluxed through it and in that case it might not be economical to remove more than 60 to 70 per cent, in my opinion.

Mr. Weber: Does anyone else have a comment?

A Member: In the PEC process where a combination is used, I would like to know what the phosphate water solubility of the products are and what range of products did they produce?

Mr. Weber: In the PEC process, what degree of water solubility is attained in the combination with the carbonitrate process?

Member: And what grades?

Dr. Berquin: When using the process, we can manufacture, in the NP_2O_5 ratio, different grades but the lower ratio should be, according to the phosphate rock used, in the range of 1.2 to 1.3 nitrogen and $1.P_2O_5$.

Regarding the water solubility, we use the straight nitrocarbonate process. We have practically no water solubility. With the P_2O_5 it is in the form of di-calcium phosphate which is not water soluble.

I would add my comments to the first question put to the panel regarding the real need of water solubility, I would say it depends on many factors. The crops, the chemical condition of the soil and so on, but also the fertility of the soil. I mean, in fact, how much P_2O_5 is already in the soil before putting in your fertilizer.

If you have good soil, all the fertilizer you put on this soil has to be used as quickly as possible by the crops because it is nothing else but more generally what we do in normal conditions, that is put back in the soil the stock, a part of the stock, the nutrients that the soil had and the part of this stock used each year by the crops.

For instance, in a test made with elements and additives in France, which is, generally speaking, a country where the soil is normally fertile and kept fertile by the normal addition of fertilizer, such tests on corn, on wheat, for instance, have shown that in a year only 10 per cent of the P_2O_5 is picked up by the plants from the actual fertilizer put before on the crops, and that 90 per cent was derived from the stock in the soil.

This means that, if you have 100 per cent water solubility or much less, this does not make any difference in such cases.

This is why the PEC process, even with no water solubility is still used in many parts of Europe.

But if, however, you are going according to special conditions of soil, you need some water solubility, it is quite easy with this process to add, during the manufacture of the product itself at the end of the chemical part, some water-soluble form P_2O_5.

In such a case you want water solubility at the lower cost because the sulphur content we are to utilize to manufacture this water soluble P_2O_5, is just enough to the level of the P_2O_5 required.

Mr. Weber: Anyone else?

A Member: With regard to the calcium nitrate removal, would anyone comment on the mole ratio of calcium oxide to P_2O_5 in the slurry after the calcium nitrate has been removed?

Dr. Nees: Yes, that goes to 1:0 to 1:3 under the conditions we are working.

As Mr. Piepers told you already about the potassium chloride which is contained in the liquor, this binds calcium and the CO_2, so only calcium remains in the remaining liquor.

Mr. Weber: Thank you.

Mr. Piepers: I would like to comment on this question, that due to the fact that you have this phosphate rock, your mole ratio to P_2O_5 is about 3:5 in general and you get a product which is only dicalcium phosphate after the separation of calcium nitrate and that means that the mole ratio should be 2 theoretically and if you are going to have a larger part of the phosphate in the water soluble form, then you can go to one and that means that it is 50 per cent water soluble, theoretically, but, as explained by Dr. Nees, due to the chlorine which is present it depends also on the composition of the phosphate rock.

But generally speaking you can say that to have a product which is 50 per cent water soluble the CO_2-P_2O_5 ratio should be about 1:2 or 1:3.

Mr. Weber: Anyone else?

A Member: I'd like to ask where in Europe the nitro processes have been so extensively used, what is a typical delivered cost of sulphur, say, as of 1964?

Mr. Weber: In Europe, what is the typical delivered cost of sulphur in 1964?

Can anybody answer that?

Dr. Nees: From 80 marks a ton to about 160 marks, 130 marks at the present.

Mr. Weber: Did you get that?

Apparently it is from 80 to 160 marks, and 130 marks today.

Dr. Nees: It was about 80 marks a ton and now today it is about 130 marks a ton and it is expected to go up to about 160 to 165 marks a ton.

Member: Can that be put in dollars?

Dr. Nees: Divide by 4.

Mr. Berquin: In our country the price of sulphur is up a little bit more than one year ago to the range of $58 C.I.F. Europe and Hamburg and now it is in the range of from $40 to $42 and we expect $45 C.I.F.

Mr. Young: These prices would be at locations that could not receive direct shipment of sulphur by seagoing vessels, is that right? You would have to off-load and have rail transport to the final destination?

Mr. Weber: He said C.I.F., in the harbor port.

Mr. Young: Oh, that's in the harbor.

Mr. Hignett: Those are metric tons, no doubt.

Mr. Weber: Long tons.

Any other questions?

Member: Would you comment on the number of nitrophosphate plants in the United States and North America?

Would you also comment on the number operating now in Europe?

Mr. Weber: Has anybody on the panel any idea of the number of nitrophosphate plants in Europe?

Dr. Nees: Most of them are nitrophosphate plants.

Member: Most of them are?

Dr. Banthien: Maybe about 60 per cent of all P_2O_5 plants in the Western European countries are producing via nitrophosphate.

Mr. Young: I'd like to make one comment concerning the lack of nitrophosphate processes in the States. It is my personal opinion we have had the pattern of separate production of nitrogen material for one segment of the industry and the production of phosphates by another segment and potash by the third.

This has not been the case in Europe. I believe it was natural that the people who were basic in phosphates would take the lead in that and would make wet process acid but with the integration that is going on now I believe the nitrogen people will take a look at using their main products in acidulation as well as just supplying nitrogen.

Mr. Weber: I think the widespread adoption of nitrogen phosphates in the United States will probably have to be in the form of integrated nitrogen phosphate complexes, rather than producing phosphates in one place and nitrogen in another.

Mr. Weber: I think it might be interesting to have the panel, if they wish, to comment on the self-propagating or self-supporting decomposition or combustion of these nitrophosphates in PK products.

Mr. Piepers touched on this in his paper yesterday when he gave the diagram showing the conservation concentrations.

Would anyone like to comment?

Mr. Hignett: I'd like to remark and point out that the property of supporting combustion or propagative combustion is not the exclusive property of nitrophosphate. Many bulk blends made in the United States have this property as well as many mixed fertilizers.

As a matter of fact the material that was burned was not a nitrophopshate. A very good paper was given at the American Chemical Society at its meeting in September defining the compositions that are subject to propagative decomposition and those that are not.

Some nitrophosphates are not.

Mr. Weber: Anybody else wish to comment?

Mr. Piepers: As I showed you in my paper yesterday, there is a certain region of areas of composition which cannot decompose if they are heated from the outside, but there are very many factors which have an influence on the decomposition possibility and that means the water content is of importance. The solubility of the phosphate, is it dicalcium phosphate or is is ammonium phosphate? Also the possibility to use ammonium sulphate may have an influence over it.

It is impossible to predict even for certain if a ratio of one to one can decompose or not. That depends on the way of manufacturing of it and it depends on the composition of it.

So, as you well know, if a certain product can decompose or not, you have to make your own experiments because it is quite impossible to predict it only from the composition of the product itself.

MR. WEBER: I think that we're going to have to bring this discussion to an end. We are running out of time.

I do think we have had a very fine discussion and I think we are very deeply indebted to our foreign visitors for the trouble they have taken and the distance they have come to give us a lot of useful information.

I will turn the meeting over to Dr. Sauchelli.

CHAIRMAN SAUCHELLI: We are going to continue the meeting. We have the Secretary's report, and I will call on Dr. Marshall now to give his brief report.

Secretary-Treasurer Report

Dr. Housden L. Marshall

Your Secretary-Treasurer has been rather busy. As you folks know, in January when we can approximate the price of the proceedings, we write a letter to everybody who has registered this year and last year. In that letter we ask for questions and subjects for the next meeting.

Next years meeting will be in this hotel Wednesday thru Friday November 2,3, 4, 1966.

Financial Report

Cash on hand 10/31/64		$ 262.34
Income, 1964-65.		
Membership List.	$ 220.00	
Sales Proceedings (current & back copies)	1672.15	
Registration 1964 Meeting	3975.00	5867.15
Total Cash Handled		$6129.49

Expenditures 1964-65

1964 Meeting Expenses	$ 406.42	
Membership Lists	348.24	
1964 Proceedings (Printing Costs)	3474.72	
Mailing	129.15	
Operation expenses	751.19	
1965 Preliminary Meeting Costs	353.25	$5462.97
Cash on hand 10/31/65		$ 666.52

CHAIRMAN SAUCHELLI: Thank you, Mr. Secretary. I will make a motion to have this report accepted.

Has anyone any comments?

(No response.)

All in favor, please say aye.

(A chorus of ayes.)

We have a very informal organization, as you have noted, it has been so from the very start.

And I think our strength lies in keeping it informal.

We have a registration this year of 540 people. We had 11 persons from overseas and 26 from our neighbors above our northern border. It has been a very interesting session.

We are always glad to have and to welcome visitors from abroad and particularly visitors from Canada. They have always shown much interest in our proceedings. They come from Europe and from Central America and from Canada and we find that they think their visit is worth while.

I have a correction to make in last year's proceedings. A printer's error on Page 91 unfortunately escaped detection. Dr. Waggaman had asked Mr. Weber whether .8 per cent chlorine would be objectionable in a phosphate rock used for making phosphoric acid.

Mr. Weber replied that he had experience with rocks having much lower chlorine than this and its presence had caused very severe corrosion in the phosphoric acid plant.

The typesetter inserted "fluorine" in place of "chlorine" and, of course, Mr. Weber was razzed quite a bit because of the appearance in print of the misinformation.

We are very sorry.

I want to insert that correction in this year's proceedings.

We have had another worthwhile meeting of our Round Table. Your helpful cooperation made it possible. We need your help in every way. Let me emphasize that we depend on your suggestions and your problems to work up an agenda. You act as a committee of one. We don't have small committees and the usual type of organization because we feel that every one of you is a part of our organizing committee and, please, send in your suggestions of problems or topics that you would like to have discussed or suggestions regarding the organization or anything. But please be articulate and let us know your attitudes.

Write to me or to any one of the members of Executive Committee.

We always welcome members of the press, they work hard. They have had difficulties, I know sometimes, in getting the information that they would like to get but they are indispensable in helping us to serve the industry. We are highly appreciative of their presence at our meetings.

I want to thank my associates on the Executive Committee for their unstinted cooperation. Remember, none of us gets any pay for this work, it's voluntary. The only paid person is the secretary to our Secretary. He has a secretary on part-time and that's about the only money that is disbursed for services. The largest proportion of the money goes for the printing of the proceedings and for mailing them out.

Costs have gone up. We keep it down to a minimum and that is why it is possible for us to ask such a low registration fee.

I want to thank the International Minerals and Chemical Co., Technicon Controls and the Edw. Renneburg & Sons Co. for their cooperation in sponsoring the coffee breaks. I believe the coffee breaks have been very popular this year and I hope we can continue with them.

Our thanks to Tom Athey and his associates, the Raymond Bag Company for the lovely entertainment and cocktail party Wednesday evening.

Our thanks to the management of the Mayflower Hotel for their cooperation in making our sessions pleasant and comfortable.

Our sincere thanks to all the speakers and particularly to our foreign visitors who have given their time and money to be with us and to share their knowledge with our industry here in this country. I am sure that it has been one of the features of our 1965 Meeting.

Do I have any comments, anyone who has any good word for the order?

MR. RODGER SMITH: Mr. Chairman, I am sure that I express the feeling of the members who have attended this meeting and we again appreciate the arduous tasks that have gone into making this meeting possible and also for the quality of the program that has been conducted.

We also feel, as you have already expressed to Bill Weber and his group of people from several countries, have made a contribution which we appreciate.

We hope that all necessary steps can be taken to continue the Round Table over the years, and again it is much appreciated.

CHAIRMAN SAUCHELLI: Thank you, Rodger.

You know the dates for next year, Wednesday, Nov. 2, 1966 thru Friday, Nov. 4, 1966 and you have heard our pleas for your cooperation by sending in suggestions and problems. We stand adjourned until next year. Thank you all.

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