PROCEEDINGS

OF THE

13th ANNUAL MEETING

FERTILIZER INDUSTRY ROUND TABLE

1963

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November 5-6-7, 1963

Executive Committee

Vincent Sauchelli, Chairman
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Fertilizer Industry Round Table

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Wednesday Morning Session, Nov. 6, 1963

The Thirteenth Annual Meeting of the Fertilizer Industry Round Table.

Chairman Vincent Sauchelli presiding.

CHAIRMAN SAUCHELLI: Welcome to the Thirteenth Annual Meeting of the Fertilizer Industry Round Table. It certainly is good to see so many old familiar faces and to see many new faces.

Before I proceed with my comments, I want to emphasize that we are anxious to have you send in your questions for our question and answer period. I think you have been given cards and we hope that you will help us by sending in problem questions and then we can handle them through our panel on Thursday afternoon.

Many important things have happened in our fertilizer industry since our initial meeting back in 1951. Since our industry is founded upon chemical science and technology and is closely linked with agriculture, it was natural that the winds of change blowing across the chemical and agricultural fields would be felt also by our industry. The ferment of change is still going on and, in our case, it is affecting not only the technology but also the corporate structure of our industry.

A tremendous impetus was imparted to all units of our economy during and following the First World War. Perhaps the most outstanding event of that period was the achievement of Fritz Haber, in Germany, of synthesizing ammonia from atmospheric nitrogen. That success stands as a shining milestone in man's struggle to secure himself against the threat of famine.

Having this small economical source of nitrogen available, the fertilizer industry made rapid advances in its technology and produced economically many important nitrogenous materials, among which are anhydrous ammonia, ammonia solutions, ammonium nitrate, calcium nitrate, urea and cyanamide.

Other equally important developments included the commercial production of ammonium phosphates by reacting ammonia with phosphoric acid, the thermal processing of phosphate rock, acidulation of phosphate rock with nitric acid in combinations with other mineral acids, and the several ammoniation and granulation processes. Marketing services to farmers were improved and the cost of plant food to farmers has been kept down below that of other inputs used to produce crops.

The rapid development of ammonium phosphate technology is a recent occurrence. The construction of facilities for and the production of diammonium phosphate for use in formulations of mixed fertilizers, both solid and liquid, are such as to constitute a trend.

Another major development during the past five years is the growth of the so-called bulk-blending business which has been greatly helped by the availability at attractive prices from old line manufacturers of component materials of fairly uniform granule size.

Thus we see another trend in the making comprising the marketing of bulk fertilizers, custom servicing on the farm of bulk-blend and liquid mixed fertilizers and the parallel dependence upon soil testing as a basis for determining specific nutrient recommendations.

Another feature of recent developments in the industry is the increasing emphasis on marketing in its broadest sense. Management is being forced to study and apply principles of marketing to serve the new agri-business type of farmer. This does not mean the subordination of the production department in any way, but rather a strengthening of the business along modern merchandising practices.

Granulation and ammoniation undoubtedly will continue to expand and steadily supplant conventional fertilizer processing operations in the older fertilizer manufacturing areas of the country.

Let me cite some statistics relating to fertilizers in the United States:

Since 1950 the consumption of fertilizers in the United States jumped from 18 million to 25 million tons and the plant nutrient content increased from 3.9 millions to 8.3 million tons.

The average nutrient content of mixed fertilizers has increased from 22 per cent to 32 per cent. Liquid fertilizers and bulk-blending with custom service have become big business.

Total nitrogen consumed in 1950 was one million tons as N.; in 1962 three million 378 thousand tons. Total production of phosphate rock mined in 1950, 11 million; in 1961, 19 million long tons.

Triple superphosphate production increased by about 250 per cent in that interval.

Total farm expenditures for lime and fertilizers in 1950 amounted to $978 million; in 1961 to $1.5 billion.

Ours is a big industry.

Although much of these remarkable increases may be attributed to the Second World War and the Korean War, the upward trend during the life of our Round Table has been continuous. It may be well to note, moreover, that there is hardly a commercial crop grown now in our country which is being fertilized as high as could profitably be done. Agronomists have pointed out that for some crops, for example forest crops, it would pay to increase the nitrogen application three- to five-fold over the present rate, other nutrients to balance, of course.

It is important that we remember this: the increase in farm productivity did not occur because people work harder, but because agricultural industry as a whole utilized science to develop energy, machines, products and processes, all of which make it possible for fewer persons to produce more and better things with less physical labor.

In 1961 each acre of cropland in the United States was producing 65 per cent more than an acre did in 1920. Technology made the difference.

Thus we see that science and industry constitute an essential partnership whose ultimate purpose is to promote the welfare of mankind. Ours is a world industry and its potential for continuous growth is vast. In 1961 approximately 31 million tons of plant nutrients were consumed by world agriculture. Of this grand total, the United States accounted for about 25 per cent, and we have only about six per cent of the world's population and only about 13 per cent of the world's arable land.

Authorities estimate that in order to produce the extra food and fiber required by the expected population of the year 1980 world consumption of plant nutrients should be about 70 million tons, an increase of some 50 million tons over last year's consumption.

So the fertilizer industry worldwide has no reason to be down in the mouth. It has wonderful prospects.

Although the production of food in most countries is rising, at least half the world's population, we are told, is hungry or badly undernourished. The fertilizer problem in developing countries is chiefly one of capital rather than production. These countries are beginning to learn that a first requirement for national success is a prosperous, productive agriculture. This is precisely what communism has universally failed to achieve.

Now, permit me to make this observation. Our purpose in coming here is to pool our thoughts and experience toward increasing efficiency in fertilizer technology. This is a forum where operating personnel, particularly, assemble for this main purpose. The ultimate aim of our pooled efforts is to provide farmers with improved fertilizer materials with which they will be helped to grow food, feed and fiber at lower pre crop unit cost of production.

Advances heretofore and those to come in the future have been and will be contributed from many sources such as improved varieties of plants and livestock, radical innovations in agricultural machinery, lower cost and the freer availability of electrical and fossil fuel energy, better utilization of water resources and improved agricultural chemicals comprising fertilizers, pesticides and weed-killers.

As Sir John Russell, world authority, put it recently: hunger need not be feared for the next 40 years, if we apply our present knowledge to the full. Of all the factors necessary to that end none is more essential than an abundant supply of fertilizer materials, the indispensable tool for agricultural success.

So much for historical review. Now to turn to our program. A few preliminary remarks are pertinent to this opening session.

It has always seemed to me that in developing a fertilizer that the technologist and operating personnel at the manufacturing plant should know or be familiar at least with some of the important soil-fertilizer chemical reactions and the specific crop demands for certain nutrients. In other words, the dull, repetitive routine of plant operations would become greatly more tolerable and interesting if the operators could know more of the end application of the product they manufacture.

For such information and guidance, competent counsel from agronomists and soil scientists is available and should be sought and, vice versa, the latter would broaden and deepen their knowledge of the use and behavior of fertilizer materials by acquainting themselves with their physical and chemical characteristics through discussions with manufacturing personnel. The gain would be mutually beneficial.

The behavior of the fertilizer in the soil environment is the principal aspect of fertilizer use over which the fertilizer technologist can exercise some measure of control. He has means at his disposal for adjusting the reaction pattern of the fertilizer in the soil and is thus responsible for the behavior of his product in the fertilizer-soil reaction.

At the same time, he must provide those nutrient elements required by the cultural practices in the area in which the fertilizer is marketed.

It has happened that in the development of suitable economical processes for concentrating and granulating high analysis fertilizers the fertilizer-soil reactions of the end product and plant needs have not generally received adequate consideration.

For example: in the commercial crop area of the southeastern region, in fact, throughout the Coastal Plains area of the Atlantic seaboard calcium and sulfur are generally in minimum supply. Consider that generally the amount of calcium and sulfur in the whole plant exceeds the total amount of phosphorous and it seems obvious that instead of being regarded as of secondary rank these two nutrient elements are entitled to be classified as of equal rank with nitrogen, phosphorous and potassium; hence; it would seem reasonable to consider that triple-superphosphate, which has had its calcium-sulfate component removed during its manufacture might not be as appropriate for the southeastern region as is normal superphosphate which has a high proportion of calcium-sulfate.

This may explain why many agronomists in this region and further north along the Atlantic seaboard continue to recommend medium grades of mixed fertilizers which can be formulated with single super and why the middlewest favors high analysis mixtures formulated with triple super and phosphoric acid.

Other factors are involved, I know, but I am now considering only the agronomic aspect.

We are honored in having with us for today's session the very competent staff of the United States Fertilizer Laboratory of the U.S.D.A. at Beltsville, Maryland. This is an unusual innovation and a treat. The Director, Mr. W. L. Hill, our good friend of long standing, needs no formal introduction here. He has been with us on our program before. He has kindly consented to prepare a comprehensive discussion of the physical and chemical properties of fertilizer materials in which his entire staff will participate.

In 1933 the Tennessee Valley Authority Board of Directors was authorized by an Act of Congress to establish and operate laboratories and experimental plants for the purpose of improving and cheapening the cost of nitrogen and other fertilizer products.

I dare say you are all familiar with the efficient research in products and processes subsequently conducted at Wilson Dam. Not all of you perhaps are as familiar with the work and achievements of the U.S.D.A. Fertilizer Laboratories conducted first when they were located at Arlington, Virginia and later when they moved to Beltsville. They have a great tradition of service to our fertilizer industry:

Initial research in the synthesis of ammonia processes, investigations into processes for high analysis, complex or chemically combined plant nutrients, segregation of components, reduction of useless filler and the number of grades, initial studies leading to commercial processes of granulation, improvement of methods of chemical analysis, compilation of statistics of production and consumption, research on many phases of phosphate rock and derivatives, thermal processes on defluorination of phosphate rock, initial studies utilizing radio isotopes in agricultural research, and many other achievements too numerous to recount at this time.

I refer to these accomplishments to remind you and particularly the younger members of our industry that the U. S. Fertilizer Laboratory and its distinguished Director have a long and honorable record of service to agriculture and to our industry. Their willingness to participate in our program is heartily appreciated.

Developments in Fertilizer Materials

W. L. Hill, Panel Leader

Mr. Chairman, I appreciate the kind things you have just said; especially do I appreciate them because I didn't know you were going to say them.

Indeed, this program is an experiment, folks. It started out as a typical experiment, being originally conceived as a half-day session and then was immediately stretched to a full day by order of the Board. I hope you do not find it too thin.

I am supposed to be an expediter here. I do not know exactly what an expediter is supposed to do, but one woman told the other, "If *we* did it, it would be called nagging." (Laughter.)

I would like to make some contribution to this day. I am very much in the position of the very small man on the bus. A very, very fat lady got on a crowded bus and glared: "Isn't some gentleman going to give me a seat?" And this very small man rose and said, "Madam, I'd be willing to make a contribution." (Laughter.)

I'd like to make some sort of a contribution, and it seems that I can very well show some figures that will enable you to make your own comparison of what we are doing in this country with respect to the world situation.

First, I shall indicate the ground we are going to cover. May I have the first slide. These slides were not made for you folks in the back of the room, but we will do the best we can with them. Copies will be available at the close of the session.

Fertilizer Materials
Development Categories

1. Raw materials – N, P. K and auxiliary necessities
2. Kinds of consumer materials
3. Quality improvement
4. Manufacturing procedures
5. Trade specifications and test methods
6. Distribution patterns
7. Consumption trends

Slide 1.

The development of fertilizer materials can be considered from the standpoint of seven or eight development categories. One not on the slide is the location of facilities, the disposition of the facilities in the country. These meetings have in other years stressed number four. You are going to stress some aspects of it tomorrow and next day. We shall not touch the subject today. Like the gadfly, we shall drop down and touch first one and then the other of the other listed categories and try to make a fairly well-balanced program.

Now, we shall take a look at the size of the industry we are part of, which is indicated in the next slide.

Production and Consumption, 1960/61

Coverage			
Area	Nutrients	Production	Consumption
World	N, P_2O_5, K_2O	33,000,000 m. tons	29,500,000 m. tons
N. and C. America	N, P_2O_5, K_2O	29%	26%
USA	N	38%	26%
USA	P_2O_5	33%*	23%
USA	K_2O	23%	23%

* Exclusive of phosphate rock.

Slide 2.

The world had some 33 million metric tons of N, P_2O_5 and K_2O produced in 1961. North and Central America did a little less than a third. The USA accounted for somewhat more than a third of the nitrogen, about a third of the phosphorus and a little more than a fifth of the K_2O.

We didn't do bad on consumption either. You will observe that the countries in which a lot of fertilizer is produced also consume a lot of fertilizer. The moral is that exportation is something that spills over after we supply our own people. Perhaps Europe is the exception to this rule.

Let's see what the nitrogen situation is, in regard to the con-

Continent- to Continent Traffic in Nitrogen Fertilizer, 1961
Total 1,384,000 m.t. of N

		Share going to—						
Continent	Share	Europe	Asia	Africa	Oceania	S. Amer.	N. (C.) Amer.	Undetnd.
	%	%	%	%	%	%	%	%
Europe	78	=	51	16	1	7	16	9
Asia	3	24	=	18	10	13	35	—
Africa	—	—	—	=	—	—	—	—
Oceania	<1	—	79	—	=	—	—	21
S. America	11	34	2	3	1	=	60	—
N. (C.) America	8	<1	58	<1	—	8	=	33

Slide 3.

tinent-to-continent traffic in nitrogen.

Just a word of explanation. The first column of figures represents the continent'es share in the total traffic in nitrogen continent-to-continent traffic. For example, Europe takes 78 percent of it, South America comes second with 11 and we fell third with 8. The other columns tell you where it goes. For instance, the Europe exportation went: 51 percent to Asia, 16 percent to Africa and so on. South American, 34 percent went to Europe and so on. We sent 58 percent to Asia and 8 percent to South America and then about a third of it went to undesignated destinations. You see, nitrogen moves.

Now let us look at the nitrogen in materials and mixtures. With this type of information it is difficult to separate what we think of as a mixed fertilizer and what we have as multi-nutrient materials. Furthermore, some of these things are called complex fertilizers over in Europe, thus I lumped them all together under two and three nutrient fertilizers.

Farm Nitrogen Consumption by Materials, 1961

	Percentage share in consumption in—	
Fertilizer	World	USA
2- & 3-nutrient fertilizers*	24	38
Am. Sulfate	22	4
Am. nitrate	30	16
Anhyd. & aqua NH_3	7	25
Urea	5	3
Solutions	—	10
Other	12	4

*Mixed and compound fertilizers and 2-nutrient primary materials.

Slide 4.

We show up pretty good on these multi-nutrient things. We do not look so good on ammonium sulfate, though ammonium sulfate has a slug of the world's business. We do not look too good with ammonium nitrate, but we shine with anhydrous ammonia and solutions.

There are some things of interest that are hidden in the first and last items. They are shown in the next slide. I need not make any comment; after all you folks can read.

Slide 5.
Some materials included in first and last items in the table above

	Percentage share in consumption in—	
Fertilizer	World	USA
Calcium nitrate	4	0.3
Cyanamide	3	0.3
Nat. organics	—	0.6
Am. phosphates	2	4
Sodium nitrate	1	2.2
Other	4	0.4

You are aware, I am sure, that I have not given you anything to show trends; I have only compared patterns. My associates wouldn't let me say anything about what's happening from one year to the next, and I am perfectly happy to leave that part to them. Dr. Clark will now pursue this nitrogen thing further, commenting on such developments as in his judgment merit comment in the allotted time.

Nitrogen Fertilizer Developments

K. G. Clark

DURING the last half of the 19th century the principal sources of nitrogen for agricultural use were the natural organics comprising miscellaneous seed meals, animal and bird manures, and waste products of the fishing and meat packing industries. In the mid-nineties development of the by-product coke oven provided small quantities of ammonium sulfate for fertilizer use. However, at the turn of the century organic materials supplied about ⅞ of the nitrogen in fertilizers, with Chilean nitrate and byproduct ammonium sulfate largely supplying the balance.

Since then, development of the arc, cyanamid, and synthetic ammonia processes for the fixation of atmospheric nitrogen has provided agriculture with increasing amounts of chemical nitrogen for fertilizer use so that by 1950 the natural organic materials as a class supplied less than 1/25 of the total fertilizer nitrogen and in 1962 supplied less than 1 percent.

The arc and the cyanamid processes were developed in Europe around 1900. The cyanamid process was established in Canada in 1909, and during World War I the United States constructed a cyanamid plant at Muscle Shoals, Alabama. The plant at Muscle Shoals went through a short test period and then was maintained in a stand-by condition until it was remodeled by the Tennessee Valley Authority in the 1930's to become a phosphate furnace plant.

Synthetic Ammonia

The first synthetic ammonia plant went into production in Germany in 1913, and the first in this country at Syracuse, New York, in 1921. By 1928 eight such plants had been constructed in the United States with an estimated annual productive capacity of 116,000 short tons of nitrogen. Between 1928 and 1940 the number of domestic plants varied between 8 and 11, but in 1940 the productive capacity of 8 plants then in operation had risen to 380,000 tons N. The

Slide 6.

Table 1. Hydrogen source and estimated annual capacity of synthetic ammonia plants[1]

Hydrogen Source	Number of Plants	Estimated annual capacity 1000 tons N	Percent of total
Natural gas	49	4940	81.1
Oil refinery	6	628	10.3
Chlorine plant	10	295	4.8
Acetylene plant	2	103	1.7
Coke oven gas	2	94	1.5
Fuel oil	1	33	0.5
Total	70	6093	99.9

[1] Compiled from Advances in Nitrogen Fixation in Fertilizer Technology and Usage, 1963, Soil Science Society of America, and other sources.

number of plants increased to 18 in 1945, 19 in 1950, 35 in 1955, and to 70 in early 1963 as indicated in Table 1.

Productive capacity which was rated at 1,327,000 tons N in 1945, rose to 2,920,000 in 1955 and to 6,093,000 tons in 1963. The November 2, 1963, issue of Chemical Week lists 75 active synthetic ammonia plants with an estimated annual productive capactiy of 6,409,000 tons N with further increases in numbers of plants and capacities imminent.

As shown in Table 1 the hydrogen required for ammonia synthesis presently is derived from six different sources. Natural gas is the hydrogen source in 70 per cent of the 70 plants listed with 81 per cent of the total rated capacity. Water gas which was the hydrogen source for 89 per cent of the plants in 1926-1927 is not a source today. The average capacity of the six oil refineries and the 49 plants using natural gas as the hydrogen source exceeds 100,000 tons N per year in comparison to 35,000 tons for plants deriving hydrogen from the other four sources. Capacities of the 70 synthetic ammonia plants range from about 9,000 tons N per year to 380,000 tons with a median capacity of some 91,000 tons.

Nitrogen solutions were introduced to the fertilizer industry in 1928 for use in the ammoniation of superphosphate and the superphosphate content of mixed fertilizers primarily to reduce their acidity and improve their physical condition, but also as a means of decreasing the unit cost of nitrogen and increasing the nutrient content of fertilizer products. A plant for the direct synthesis of urea from ammonia and carbon dioxide went into production in 1932. Anhydrous ammonia was first used for direct application in irrigation water (nitrogation) and injection in the soil (nitrojection) in 1937 and 1938. The direct application of solid ammonium nitrate was initiated about 1945.

The production of synthetic ammonium sulfate first equaled or exceeded the production of byproduct ammonium sulfate in the period 1951 to 1954. In the mid-fifties some of the coke oven plants began the production of ammonium phosphates to improve their marketing situation. Other segments of the fertilizer industry are now producing these materials in appreciable tonnages.

The Wisconsin Process for fixation of atmospheric nitrogen as nitric oxide by a thermal method was studied at Lawrence, Kansas, in 1953 and 1954 in a plant designed to fix about 9 tons of nitrogen per day. This process for the production of nitric oxide and its conversion to nitric acid was found to be less economic for nitrogen fertilizer than the direct synthetic ammonia processes.

The geographic distribution of fertilizer nitrogen facilities by regions is shown for 1963 in Table 2. The upper portion of the table indicates that there were 57 byproduct ammonia, 27 synthetic ammonia, 9 ammonium nitrate, 15 ammonium phosphate, and 11 urea plants east of the Mississippi. The lower portion of the table shows that there were 6 byproduct ammonia, 43 synthetic ammonia, 14 ammonium nitrate, 19 ammonium phosphate, and 8 urea plants west of the Mississippi. Byproduct ammonia plants are concentrated in the Middle Atlantic and East North Central regions, whereas synthetic ammonia plants are concentrated in the West North Central, West South Central, and Pacific regions.

Production

Equivalent ammonia production increased from about 1,797,000 tons NH_3 in 1950 to about 5,952,000 tons in 1962, or an average increase approximating 340,000 tons per year. Ammonia production index numbers for the period 1950 for selected years through 1962 are presented in Table 3. Byproduct sources accounted for about 13 per cent of total ammonia production in 1950, but only about 3 per cent in 1962. Byproduct materials exhibited a decrease of some 6,000 tons equivalent NH_3 per year during this period; aqua ammonia

Table 2. Geographic distirbution of fertilizer nitrogen facilities, 1963[1]

Region	Ammonia Byproduct	Ammonia Synthetic	Ammonium Nitrate	Ammonium Phosphate	Urea
	No.	No.	No.	No.	No.
New England	1	1			
Middle Atlantic	21	6			2
South Atlantic		4	3	5	2
East North Central	26	7		7	2
East South Central	9	9	6	3	5
Sub-total	57	27	9	15	11
West North Central	1	12	6	3	4
West South Central	1	17	4	4	2
Mountain	3	3	2	4	
Pacific	1	11	2	8	2
Sub-total	6	43	14	19	8
United States	63	70	23	34	19

[1] Compiled from Advances in Nitrogen Fixation in Fertilizer Technology and Usage, 1963, Soil Science Society of America; U. S. Department of Commerce, Bureau of the Census Current Industrial Reports; and other sources.

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Slide 8.

Table 3. Equivalent NH_3 Production—Index Numbers, 1950 = 100[1]

Calendar Year	Aqua Ammonia	Byproduct Plants[2] Ammonium Sulfate	Total	Synthetic Ammonia Plants[3]	Total
1951	106	108	108	114	113
1955	71	122	117	208	196
1956	76	110	109	216	202
1960	64	78	82	308	279
1961	57	74	77	333	300
1962	58	74	75	369	331

[1] Computed from U. S. Department of Commerce, Bureau of the Census Current Industrial Reports Series; and U. S. Department of the Interior, Bureau of Mines Minerals Yearbook Coke and Coal Chemicals and Nitrogen Compounds Series.

[2] 1950 production: aqua ammonia 23,387 short tons HN_3, ammonium sulfate 207,754 short

[3] 1950 production: 1,565,569 short tons NH_3.

production decreased 42 per cent and ammonium sulfate 26 per cent. Synthetic ammonia production increased 269 per cent in the period 1950 to 1962, or an average of 346,000 tons NH_3 per year. The rate of growth of synthetic ammonia production, however, was about 50 per cent greater in the period 1960 to 1962 than in the period 1955 to 1960.

Consumption

Fertilizer nitrogen consumption by kind of material is shown for selected years in Table 4. The use of fertilizer nitrogen increased from 1,960,500 tons in 1955 to 3,379,400 tons in 1962, or an increase of 72 per cent. The straight line annual increase or trend over this period amounted to 210,000 tons N. The rate of increase between 1960 and 1962, however, was more than twice that of the 1955 to 1960 period.

The annual upward trend in tons of N during the 1955-1962 period was as follows: anhydrous ammonia 68,000, mixed fertilizer 51,000, nitrogen solutions 49,000, ammonium nitrate 18,000, urea 12,000, ammonium phosphate products 9,000, aqua ammonia 6,000, ammonium sulfate 2,000, ammonium nitrate limestone 1,000, and natural organics 500. Similarly, annual downward trends in N tonnages were exhibited as follows: sodium nitrate 4,000, calcium cyanamide 2,000, and calcium nitrate 200. During the 1955-1962 period the use of nitrogen in mixed fertilizers increased 41 per cent from 804,000 to 1,129,000 tons N in comparison with the following percentage increases in the chemical nitrogen applied to the soil in various forms: nitrogen solution 887, urea 331, anhydrous ammonia 169, ammonium phosphate products 116, aqua ammonia 115, ammonium nitrate limestone 32, ammonium nitrate 27, natural organics 24, and ammonium sulfate 5. Percentage decreases in the use of calcium nitrate, sodium nitrate, and calcium cyanamide were 15, 34, and 54, per cent, respectively. Increased use of materials in 1,000 tons N between 1955 and 1962 were: anhydrous ammonia 490, nitrogen solutions 341, mixed fertilizers 325, and ammonium nitrate and urea 102 each. The percentage of the total nitrogen supplied by mixed fertilizers declined from 41.0 in 1955 to 33.4 in 1962, whereas the percentage supplied by anhydrous ammonia, aqua ammonia and nitrogen solutions increased from 19.2 in 1955 to 38.0 in 1962. In addition to the three last-mentioned materials, only ammonium phosphate products and urea supplied greater proportions of the total N in 1962 than in 1955.

Specialty Materials

Urea-form, a slowly available high analysis synthetic nitrogen material of low solubility, was marketed by three United States manufacturers for the first time in 1955 after several years of experimentation and development. Subsequently, France and the Soviet Union independently developed processes for the production of similar urea-formaldehyde reaction products. Small quantities of these products are reported to be in use. Urea-form is a specialty material and be-

Table 4. Nitrogen consumption, by kind of material, year ended June 30[1]

	1955		1960		1961		1962		Trend[2]	
	1,000 tons N	% total N	1,000 tons N	% total N	1,000 tons N	% total N	1,000 tons N	% total N	1,000 tons N	% total N
Mixed fertilizer	804	41.0	1,017	37.2	1,071	35.3	1,129	33.4	51	–2.5
Ammonium nitrate	375	19.1	416	15.2	447	14.7	447	14.1	18	–0.9
Anhydrous NH_3	290	14.8	582	21.3	661	22.0	780	23.1	68	3.3
Ammonium sulfate	109	5.6	112	4.1	116	3.8	115	3.4	2	–1.1
Sodium nitrate	99	5.1	73	2.7	66	2.2	66	1.9	–4	–2.0
Ammonium nitrate limestone	74	3.8	55	2.0	50	1.7	98	1.4	1	–0.5
Phosphate products	53	2.7	94	3.4	102	3.4	114	3.4	9	0.4
Aqua NH_3	47	2.4	85	3.1	86	2.9	100	3.0	6	0.3
Nitrogen solutions	38	2.0	195	7.1	293	9.7	379	11.2	49	2.3
Urea	31	1.6	65	2.4	92	3.1	133	4.0	12	0.6
Natural organics	14	0.7	13	0.5	17	0.6	17	0.5	0.5	–0.2
Calcium cyanamide	14	0.7	9	0.3	8	0.3	7	0.2	–2	–0.8
Calicum nitrate	9	0.4	8	0.3	8	0.3	7	0.2	–0.2	–0.1
All materials	1,961	99.9	2,738	99.6	3,031	100.0	3,379	99.8	210	—

[1] Compiled from U. S. Fertilizer Laboratory report series: Consumption of Commercial Fertilizers and Plant nutrients in the United States.

[3] Straight line annual increase or decrease

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cause of its higher raw materials and manufacturing cost necessarily commands a higher price per unit of contained nitrogen than more soluble chemical fertilizers.

In 1961, magnesium ammonium phosphate (8-40-0) was introduced as an insoluble material with delayed availability. Since the finely divided material exhibits quite rapid availability, the delayed availability of the product largely results from an increase in particle size. This product is marketed in three particle size ranges to provide varying rates or availability.

Considerable effort has been expended since the introduction of urea-form and magnesium ammonium phosphate in developing other slowly available sources of chemical nitrogen. Among the alternatives examined are (a) reaction of urea with aldehydes other than formaldehyde, (b) coating granular soluble materials with moisture resistant materials, such as elemental sulfur, resins or plastic films, (c) encasement of soluble fertilizer in perforated plastic bags, (d) incorporation of soluble material in a tarry or asphaltic matrix, and (e) screening of other nitrogen compounds of low solubility with reference to their suitability for agronomic use.

Workers in Germany appear to have concentrated on the reaction of urea with actealdehyde and crotonaldehyde. Crotonaldehyde, an unsaturated aldehyde, is reported to react with two moles of urea and to rearrange into a definite chemical entity, crotylidene diurea, without polymerization. On the other hand urea-forms are considered to be mixtures of several polymethylene ureas of different degrees of polymerization.

Recently gylcoluril a reaction product of the dialdehyde, glyoxal (CHO.CHO), with two moles of urea has been suggested as suitable for specialty fertilizer use in the United States. The theoretical nitrogen content of this material is 39.4 per cent.

Plastic coated urea already has appeared on the market as have coated mixed fertilizers. In such cases the rate of dissolution of the soluble component may be controlled by the thickness of the coating, by the degree of coverage of the individual granules, or by both. Reports indicate that the coating material constitutes 10 to 15 per cent of the product. Since such products cannot be considered as water-insoluble nitrogen sources, attention will need to be given to laboratory methods for evaluation of their dissolution characteristics for purposes of quality control and to correlation of these characteristics with crop response or the needs of the crop. The same considerations apply to soluble materials encased in perforated plastic bags or incorporated in an insoluble matrix.

The Tennessee Valley Authority has studied the preparation and agronomic properties of oxamide. This material may be produced from ammonia and natural gas with hydrogen cyanide and cyanogen as intermediate products. Oxamide has a theoretical nitrogen content of 31.8 per cent and is insoluble in water, but like magnesium ammonium phosphate largely owes its delayed availability to the particle size effect rather than to its chemical nature.

An uncoated urea sulfur mixture containing 40 per cent nitrogen and 10 per cent sulfur was marketed this past season on the West Coast. The sulfur is incorporated in this mixture as a nutrient rather than as a physical means for decreasing the rate of dissolution of the contained urea. Similarly, an anhydrous ammonia-sulfur solution, 10 to 15 per cent elemental sulfur and 70 to 74 per cent nitrogen, was introduced this year for use as a direct application material in sulfur deficient areas of the Northwest.

Now, unless there are questions, I will close and thank you very much for your attention. (Applause.)

Chairman Sauchelli: Let's have any questions of the speaker?

(No response.)

Dr. Clark: No questions, Vince.

Discussion Leader Hill: Everybody apparantly believed what he said about nitrogen falling out of mixed fertilizers. I have heard some complaints that they weren't selling ammoniating solutions but they were selling nitrogen for direct application. Perhaps that is the way it is going to be.

Now, we shall leave nitrogen for a while and talk about phosphorus. Nitrogen, being in the atmosphere, is scattered all around the world, and it is available to anybody who has the facilities to win it. Nature's storehouse of phosphorus, on the other hand, is piled up in a few places. The next slide shows the world situation with respect to phosphate reserves.

Phosphate Rock Reserves and Production, 1961

World reserves, nearly 47,600 million long tons of rock

World production, 46 million long tons of rock

Location of producing fields	Share in world reserves %	Share in world production %
N. Africa	52	24
USA	29	42
USSR	16	19
Total	97	85

3% of reserve provided 15% of production

Slide 10.

You will notice that North Africa has more than 52 percent of the world's phosphate rock, and the United States has 29 percent. The United States, North Africa and Russia have 97 percent, and they produce 85 percent of the supply. The point I want to make is that 3 percent (we get it by difference) of the reserves are providing 15 percent of the supply. This means that the few small deposits scattered around in faraway places, but lying close to points of need, are being mined out at a disproportionately rapid rate. Consequently, these people are looking for new phosphate deposits close by, and when you have a find, the next question is: How does it react? Will it make superphosphate? Can you use it for direct application?

For some years now, we have been fiddling around with this problem of trying to find a way to get some idea of the value of a new phosphate, or an old one for that matter, without going to the rather expensive procedure of running it through a lot of acidulation tests and doing a lot of field tests. Some years ago we took a look at rocks from the known producing fields and came up with a reactivity scale of a fashion which was roughly about like this: bone is the most reactive, then some of the North African rocks, Florida pebble next, then some of our western rocks, and the compact apatites, such as the Kola apatite and apatite from Brazil and other scattered places, at the bottom of the scale.

Recently, rock has been discovered in Peru, in Lower California, and in South Africa here and there. We have made tests on specimens of these and come up with what we think is a good indication of just what the rock is good for. Mr. Caro will tell you something of what we are doing now and have been doing.

Character of Phosphate Rock: Variation With Geographic Origin And Changes Induced By Heat Treatment

J. H. Caro

ACTUALLY, I am going to report this morning on two phases of our program on characterization of phosphate rock. One, as Mr. Hill has mentioned, is the establishment of a reactivity scale for rock, and the other is a study of the properties of rock as affected by calcination.

It is a well known fact, and I am sure most of you are aware of it, that phosphate rocks mined from different geographic deposits exhibit differences with regard to their behavior in reactions with acids, both mineral acids such as sulfuric acid in fertilizer plants and soil acids when the rock is applied directly as a fertilizer.

The differences are especially prominent with respect to rate of reaction, or as we call it, reactivity. In our laboratory, we have been studying and measuring the properties of the rocks that cause these differences in reactivity and we have been able to set up, by means of a number of classification tests, a relative scale for direct comparison of different deposits.

Chemically, the components of rock that are known to affect reactivity are fluorine and carbonate. In general, the higher the degree of fluorination the higher the crystallinity of the material and the lower its reactivity; conversely, the greater the degree of carbonation, the more carbon dioxide is evolved on acid attack and the higher the reactivity.

We have found that the carbonate that is an actual part of the apatite crystals in the rock has a greater effect on reactivity than does carbonate that is present as a separate compound; that is, as free calcium carbonate.

As a matter of fact, the content of apatite-carbonate is one of the basic indexes from which we derived our relative reactivity scale.

Let's look at these indexes as applied to a series of well-characterized rocks.

In the body of this slide, the relative reactivity is given a letter rating from A to D in decreasing order of reactivity. Across the top are shown the various tests to which we put these rocks.

The second column represents a quick reaction with a 30 per cent solution of phosphoric acid. It is a laboratory test designed to indicate how much phosphate is made available in 10 minutes' reaction with dilute phosphoric acid. In the third column is the two per cent citric acid test for available P_2O_5 which is used in Europe. The American neutral ammonium citrate test for available P_2O_5 gave the relative results shown in the following column. Next is a relative ranking based on measurement of a physical property, the specific surface area. The heading "carbonation" in the next to last column refers to the apatite-carbonate content which I mentioned before, and in the last column is shown the relative buckwheat yield obtained in a greenhouse test. We have found that yield of buckwheat is also a very good measure of reactivity.

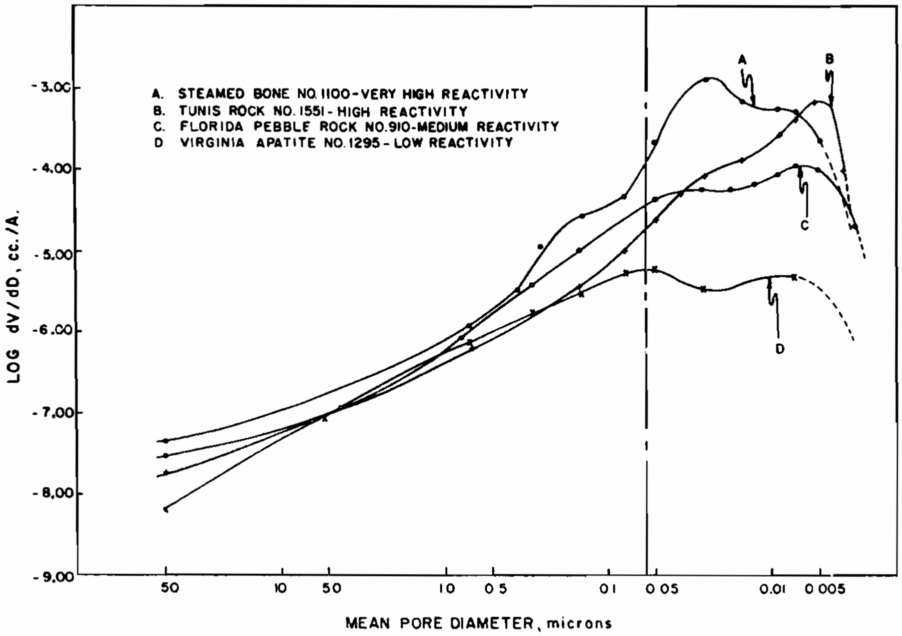
The rock varieties that were initially subjected to these tests are shown in the first column. These are very well characterized rocks and they form the basis for our scale. We have a supply of each in the laboratory and we are able to compare new and less well known deposits with these.

As you see, Tunis rock exhibits high reactivity no matter how it is measured. The reactivity decreases as we proceed down the ta-

Slide 11.

RELATIVE ROCK REACTIVITY INDICATED BY DIFFERENT TESTS

ROCK TYPE OR SOURCE	CLASSIFICATION BY TEST PROCEDURES					
	30% H_3PO_4	2% CITRIC ACID	NEUTRAL AMMONIUM CITRATE	SPECIFIC SURFACE	CARBONATION	BUCKWHEAT YIELD
TUNIS ROCK	A	A	A	A	A	A
CURACAO ROCK	-	A	B	C	A	B
FLORIDA ROCK I	B	B	B	B	A	A
FLORIDA ROCK II	-	-	C	B	B	B
IDAHO ROCK	-	C	C	C	B	B
TENNESSEE BROWN ROCK	C	C	C	B	C	C
VIRGINIA APATITE	D	D	D	D	D	D



Slide 12.

ble, with the rocks falling roughly into the order shown. Virginia apatite is the least reactive in every case.

We noticed in comparison of these tests that the measurement of surface area is not quite as good an index as the chemical tests or the greenhouse test. The letter designations, as you can see, are in a somewhat different order, and yet we felt that physical properties must indeed have some effect on reactivity. We consequently decided to examine the porosity of the rocks, looking to possible relationships to reactivity.

This is the type of thing we came up with. The figure exhibits the pore distribution in various types of phosphates. Pore diameter is shown on the horizontal axis, while the vertical axis denotes the volume of pores of each diameter, expressed logarithmically.

The figure shows four curves, comparing the porosity of steamed bone with that of three of the natural phosphates—the Tunis rock of high reactivity, Florida pebble of intermediate reactivity, and relatively unreactive Virginia apatite.

I might mention in passing that steamed bone, being the most reactive calcium phosphate known, would have an assigned letter designation in our scale of AA. It reacts almost instantaneously with acid, thus providing an excellent reference standard.

The vertical line in the middle of the slide shows the point at which we had to change measuring methods. Pores to the left of the line were measured with use of a mercury porosimeter, the procedure involving the simple forcing of mercury into the pores of the rock under a known pressure. To the right of the line, a much more complex and involved method is necessitated, in which nitrogen desorption isotherms are used to measure the volume of the extremely fine pores.

It is quite evident that in the coarse pore region there is little to choose among the four calcium phosphates shown. The differences are all in the fine pore region to the right of that line, and you can see quite quickly that the higher porosity materials in the fine pore region are also the most reactive materials.

Steamed bone has a very high porosity throughout the fine pore region. The Tunis rock has a peak at about .005 microns, which is approaching molecular dimensions in pore size. The Florida specimen has somewhat less porosity in the fine region, but the pores are still concentrated at the extremely fine end of the scale. The Virginia apatite has obviously fewer fine pores than the other varieties.

We concluded from these measurements that the distribution of the pores in a rock has a definite bearing on reactivity, and so we can measure the porosity of any rock and predict its reactivity on the basis of this general pattern.

Quite apart from the development of our reactivity scale, Mr. Hoffman and his associates, working independently a few doors from us, developed a reactivity scale for rock based on consecutive extractions with a two per cent solution of citric acid. Agreement between the two scales is excellent and, actually, either one is valid.

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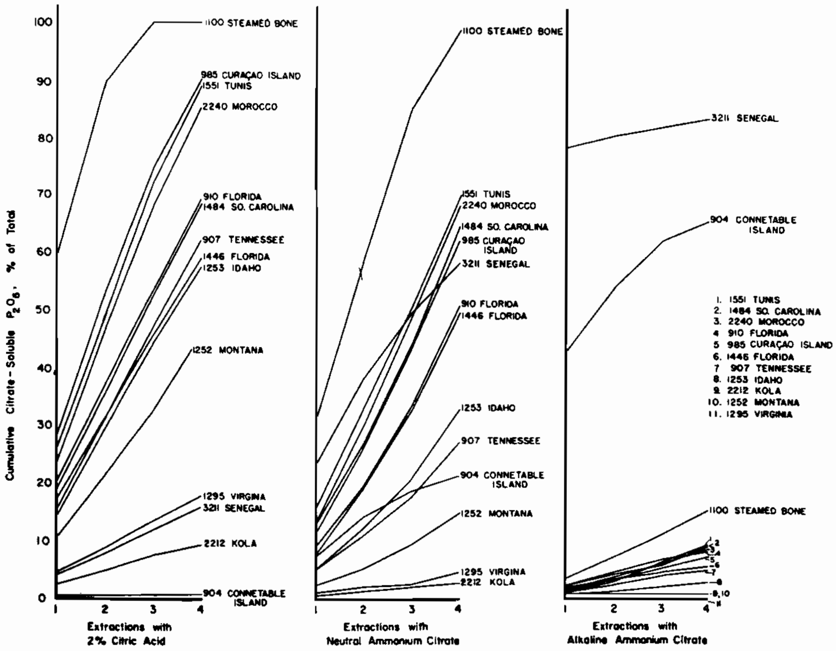

The basis for the consecutive extraction scale is shown in this figure. The vertical axis shows the cumulative percentages of soluble P_2O_5 and the horizontal axis shows the number of extractions by three different extractants. Mr. Hoffman at this time was comparing extractants as a measure of available P_2O_5.

Proceeding from left to right in the figure, the panels show extractions with two per cent citric acid, neutral ammonium citrate, and alkaline ammonium citrate, respectively. The citric acid and the alkaline ammonium citrate methods are used in Europe to evaluate available P_2O_5.

The citric acid puts the rocks in a definite order, which doesn't change with consecutive extractions. On the other hand, both neutral ammonium citrate and alkaline citrate give inordinately high rankings to high-alumina phosphates (from Senegal and Connetable Island) and there are changes in rankings with succeeding extractions.

Mr. Hoffman observed that after four extractions with two per cent citric acid, a convenient reactivity scale ranging from zero to 100 was obtained. Steamed bone gives a value of 100 on that scale, while the Connectable Island aluminum phosphate is close to zero. This, then, was the basis for his reactivity scale.

By dividing the figures on the left by 10 Mr. Hoffman set up a scale of zero to 10 and ranked the various rocks and calcium phosphate on that scale, as shown in the next slide.

Index of Solubility Based on 4 Repetitive Extractions with 2 percent Citric Acid

Index Value	Representative Varieties or Source of Mineral Phosphates
10	Steamed bone
9	Curacao and Tunis Morocco
8	
7	South Carolina land Florida pebble
6	Tennessee brown Idaho, Conda
5	
4	Montana, Garrison
3	
2	Virginia apatite
1	Kola apatite
0	Connetable Islands ($AlPO_4$)

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Steamed bone has a ranking of 10, followed by the North African rocks and then the domestic deposits in South Carolina, Florida, Tennessee, Idaho, and Montana. The lower reactivtiy rocks include Virginia apatite, Kola apatite and the Connetable Islands aluminum phosphate.

The interesting thing here is that Kola apatite, which Mr. Hill pointed out comprises 16 per cent of the world reserves of phosphate rock, is a very low reactivity material and yet this is the material that people in the Soviet Republics are largely using as their base fertilizer phosphate.

Source of Rock	Index of Solubility Rating
Christmas Island	7
Peru	10
Florida	7
Utah	6
Ocean Floor	9
Togoland	6
Phalaborwa	1
North Carolina	8

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Now we see what use can be made of a ranking scale of this nature. Here are some of the prominent deposits ranked along with some new finds and some less well known deposits. The ranking is, of course, on a scale of ten.

The Christmas Island rock has a ranking of about 7, which is characteristic of island phosphates. In Peru, on the Sechura Peninsula, there has been a relatively recent find of great extent and importance. This is a highly reactive rock, as you can see, ranking close to steamed bone. The Florida rock has a ranking of 7, Utah 6, ocean floor phosphate 9. This last represents material obtained off the coast of California, where a large deposit of phosphatic nodules exists on the ocean floor; commercial exploitation of these nodules is being considered. In Africa, in Togoland, there is a deposit now being mined commercially. It has a ranking of 6. The Phalaborwa rock, which has ranking of 1, is a deposit in South Africa which forms the basis for the South African phosphate fertilizer industry. This deposit is being actively exploited commercially and yet it is a material of very low reactivity. Many of you, I am certain, are interested in the new deposits in North Carolina which will be on the market in the near future; as shown, this is a highly reactive material having a ranking of 8.

I should point out that many of these high reactivity materials are unfortunately of relatively low grade and considerable beneficiation has to be done by means of flotation and calcination to bring them up to acceptable grade levels.

We turn now to the second phase of our project. As you well know, much of the rock that is marketed today is calcined by the producer to upgrade the product and to remove objectionable organic matter. Commercial calcination is accomplished in a variety of kiln devices throughout the world. Processes differ with respect to reaction temperature and retention time of the rock in the calciner.

In order to provide basic information on the effect of these

Effect of Calcination on Physical Properties of Phosphate Rocks

Source	Treatment	Particle Density	Pore Volume	Surface Area	Fine Pore Portion
		g/ml	ml/g	m^2/g	% of total pores
Morocco	Uncalcined	2.26	0.104	16.1	79
	Calcined (910°)	2.72	0.049	1.4	70
Peru	Uncalcined	2.34	0.080	29.9	80
	Calcined (900°)	2.67	0.043	0.6	17
Florida	Uncalcined	2.39	0.095	16.5	83
	Calcined (815°)	2.36	0.083	7.1	65
Idaho	Uncalcined	2.54	0.053	5.6	34
	Calcined (775°)	2.57	0.053	1.2	20

Slide 16.

processes on the properties of rock, we measured in the laboratory such characteristics as surface area, porosity, and density both before and after calcination. We also measured the volatilization of carbonate in the rock during calcination.

Here are some of the data. On the left are listed four commercial deposits of importance which are being calcined presently—in Morocco, Peru, Florida and Idaho.

The second column shows the treatment and the temperature of calcination. These are commercially calcined materials and you can see that the calcination temperature for the various processes varies from 910 degrees for the Morocco rock down to 775 for Idaho rock.

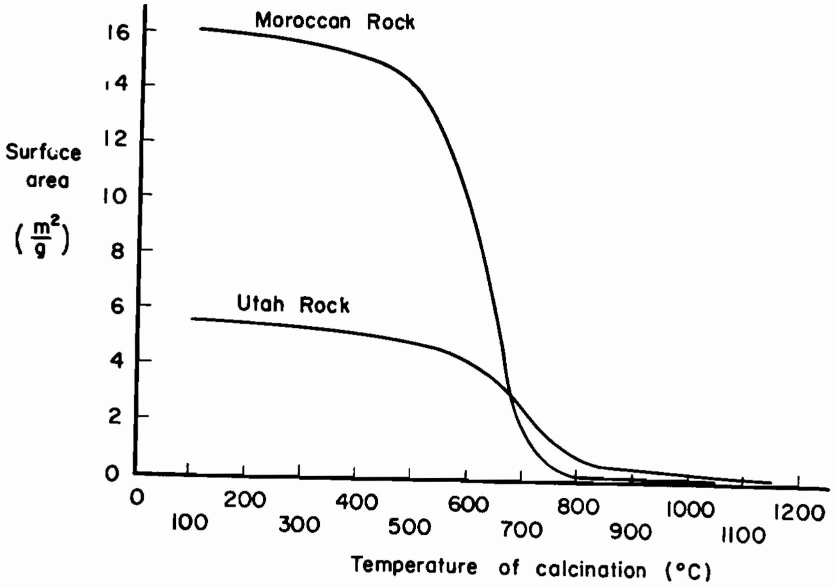
What happens to the rock when it's calcined at these temperatures? In the third column we see the effect on particle density. Obviously, there is a rather marked effect on density in those materials calcined at higher temperatures; conversely, there is relatively little effect at the lower temperatures.

The same observation applies with respect to pore volume. A sharp decrease is seen in pore volume for calcinations at the higher temperatures; a relatively lower decrease at the lower temperatures. No change at all was found in the Idaho material.

The surface area shows a very sharp change. The Morocco rock drops from 16 down to about 1½ square meters per gram on calcination at 910 degrees C. The Peruvian rock drops all the way from about 30 to 0.6 square meter per gram on commercial calcination. The reactivity in these materials is obviously lowered by calcination. The effect on the last two in terms of surface area is less pronounced but it's there, 16½ down to 7 for the Florida and from 5½ down to around one square meter per gram for the Idaho material.

The last column indicates the proportion of the total pores that occurs in the fine pore region that you saw to the right of the vertical line in the earlier slide. Obviously, the decrease in fine pores brought about by calcination is greater than that in coarse pores.

Since the effect of temperature was apparently quite marked, with a direct relationship between temperature and size of effect, we undertook systematic study in the laboratory of changes in temperature, to determine just what changes occurred in the physical character of rock.



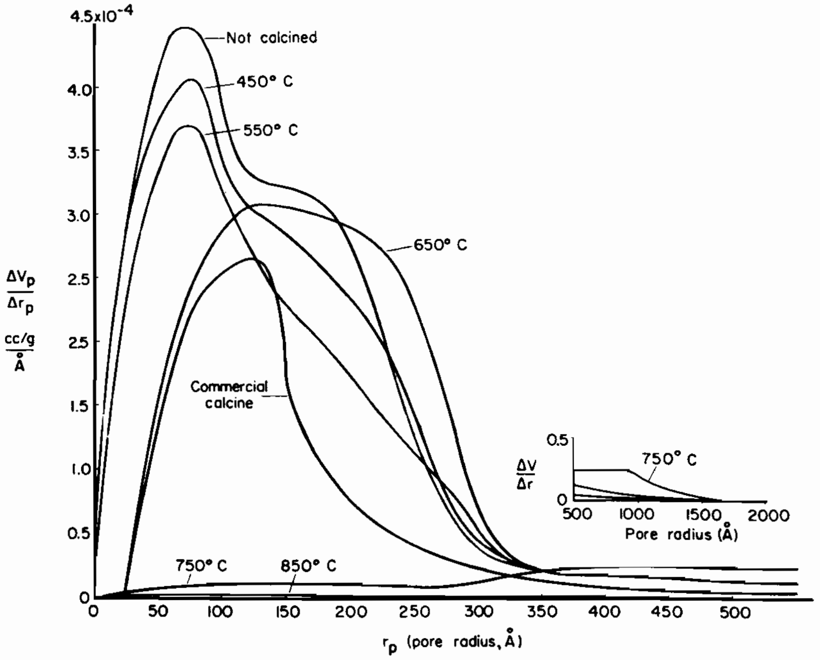
Effect of temperature of calcination on the surface area of Phosphate Rocks (100-150 Mesh).

Slide 17.

Here is one result, typical of many others we obtained. The figure shows the change in surface area of Morocco and Utah rocks with increasing temperature. The temperature of calcination is shown along the horizontal axis. This temperature was increased for each series of test specimens in 100 degree increments. The vertical axis denotes specific surface area in square meters per gram. It is quite evident that there is a sharp break at around 550 to 600 degrees for the Morocco rock, with the surface area practically disappearing in calcinations at 800° and above.

Utah rock also shows a break in the same region but it is less pronounced. As a matter of fact,

Slide 18.



Effect of temperature of calcination on the pore distribution of Moroccan Rock (100-150 Mesh).

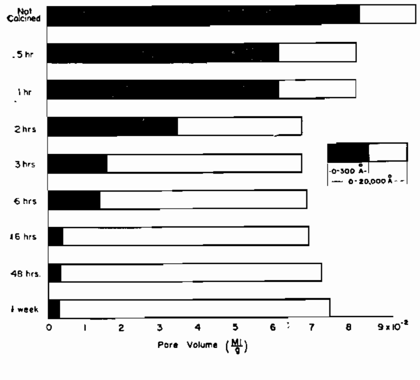
for any calcination temperature above 700 degrees, the Utah rock has a more open structure than does the Morocco rock. This constitutes a reversal from their natural state.

In terms of porosity, we have the effect on pore distribution of change in calcination temperature. On the vertical axis pore distribution, change of pore volume with pore size, is shown, while the horizontal axis indicates the pore size, increasing to the right. The small insert is merely a completion of the lines in the major part of the graph.

As you can see, the uncalcined material has relatively high porosity and relatively fine porosity, with a distribution peak at about 50 to 60 angstroms pore radius. Calcination at 450 degrees decreases the porosity, but the peak remains at about the same pore size. Higher-temperature calcinations produce still further decreases in porosity. At 650 degrees, a shifting of the pore distribution in the direction of more coarse porosity becomes evident. Between 650 and 750 degrees the sharp break in structure noted in the previous figure occurs. At 750 degrees, there are very few pores in the fine region, and at 850 there are practically none at all.

Interestingly enough, the commercially calcined material appears to have been treated under conditions corresponding to the verge of the structural collapse. We observed this repeatedly in the commercial materials that we measured. Companies calcining rock on a production scale apparently have found, through force of experience, the optimum conditions of temperature and retention time. Maximum benefit of calcination is achieved, yet the undesirable collapse of the physical structure is avoided. The point I want to make is that these processors are on a narrow edge; a slight increase in temperature will produce a much less satisfactory material.

Slide 19.



The final slide I have shows a further extension of our work on calcination. Morocco rock was calcined at 650 degrees and the time of calcination at that temperature was varied. The total length of the bar indicates the total porosity in the material; the black bar indicates the fine pores that exist in the rock, these from zero to 300 angstroms pore radius, corresponding to the area to the right of the vertical line in the earlier slide.

The uncalcined material has high porosity and has a large number of fine pores. With increase in time at 650 degrees the total porosity does not change very much. As you can see, there is a small regular decrease to about the three hour treatment and then a small regular increase down to one week treatment. We also performed a two-week calcination, not shown in the figure, which showed a continuation of the effect. A slightly higher total porosity was obtained than in the sample calcined for one week. On the other hand, the fine pores decreased regularly and practically disappeared after long-time treatment.

As a result of these observations, it becomes evident that three types of physical structure in phosphate rock can be obtained. They include a high-porosity material having mostly fine pores, such as the uncalcined material at the top; a high-porosity material with very few fine pores, such as the long-term calcination sample at the bottom of the figure; or a low-porosity material with few fine pores, such as that obtained by calcination at a higher temperature.

When future research shows us just what type of rock is best for a specific use, I think it will be possible by manipulation of manufacturing techniques to arrive at the exact type of material desired.

This is the kind of thing we are doing today in our laboratory; we hope to continue investigations of this type as specific problems in the area of rock characterization and calcination arise.

Thank you.

(Applause.)

Discussion Leader Hill: Thank you, Mr. Caro.

Now, are there questions? You see, you folks are going to have a little participating to do here.

Member: In the first slide there was an indication of two different kinds of Florida rock being used. One was indicated Florida I and the other Florida II.

The question is: What is the difference in composition of those two Florida rocks, and why are they labeled in two different ways?

Mr. Caro: They were two different grades, actually.

Member: Can you give us some details on the chemical analysis of P_2O_5 and iron and aluminum in Florida rock?

Mr. Caro: Not at the moment. I can get it for you but the basic differentiation was in grade of phosphorus. The one at the top is higher grade.

Discussion Leader Hill: Any other questions?

Mr. Christopher Pratt: I think that those of us in the phosphoric acid industry would very much like to know how the relatively unreactive rocks could be tickled into high reactivity by, say, some added catalysts or perhaps choosing lesser rocks where there is some indigenous catalyst. I wonder if this is on the research program?

Discussion Leader Hill: Mr. Caro had no comment on that angle of it.

I shall comment in the best way I know. That would be a very worthy goal. We have not had this angle in mind, although we have recognized the need for something. The main problem is that we haven't had any ideas that were worth pursuing. You see, the folk who make superphosphate are not too much concerned, or were not in other years, with moderately small differences in reactivity, because they throw the stuff out on a pile and let it lie there until next spring. As time goes on they will be more and more interested in that sort of thing. The man who is making phosphoric acid, of course, is pretty well in a box, and he has to get whatever P_2O_5 he is going to get while the slurry is being sloshed around. To him, reactivity really means something. We should keep this need in mind and perhaps someone can get an idea of how to do it. At one time I though that calcination of certain rocks would trickle them up, as a consequence of pore formation from CO_2 evolution, but these fellows have about exploded my theory.

Any other questions?

(No response.)

We shall look at phosphorus materials with the aid of a slide. I have done the same thing here that I did for nitrogen.

Farm Consumption of Available Phosphorus by Materials, 1961

Fertilizer	Percentage share in consumption in— World	USA
2- & 3- nutrient fertilizers*	37	85
Normal superphosphate	35	4
Triple superphosphate	4	8
Basic slag	12	0.3
Phosphate rock (dir. appl.)	7	0.9
Other	5	2

*Mixed and compound fertilizers and 2-nutrient materials.

Slide 20.

Normal superphosphate makes a pretty big splash world-wide; it's not splashing at all in this country. Basic slag is no particular item in this country but world-wide it really counts up, and most of that, of course, is in Europe.

The next slide shows some things that we are more interested in. I do not have the world picture for a lot of these materials, but you can see the comparisons that I have made.

Some materials included in first and last items in table above

Fertilizer	Percentage share in consumption in— World	USA
Monoam. phosphates	—	6.4
Diam. phosphates	3	3.1
Calcium metaphosphate	—	0.6
Nat. organics	—	0.4
Bone meal	—	0.1
Phosphoric acid	—	0.7
Other	5	0.2

Slide 21.

Any fertilizer that has phosphorus in it has to be analyzed, which means any one of these things listed in the last slide and mixtures containing them. We have talked a great deal in years gone by about method improvement. As a matter of fact, it has been going on since I can remember, and, if you can rely on published papers, it goes all the way back. Indeed, we have improved things, especially have we improved precision and accuracy. Nevertheless, the one thing that would count for the most, and mean the most to the industry and to people who have to do analytical work, is to find a way to save the time of the analyst. We haven't done too well in this sphere of effort.

There are some things going on now that should enable us to save more time than we have in the past. One of our men, Mr. Ferretti, has been playing around with the idea of an automatic determination of phosphorus in fertilizer. He will tell you something about his findings with an automatic analyzing instrument.

Automatic Analyser for Phosphorus

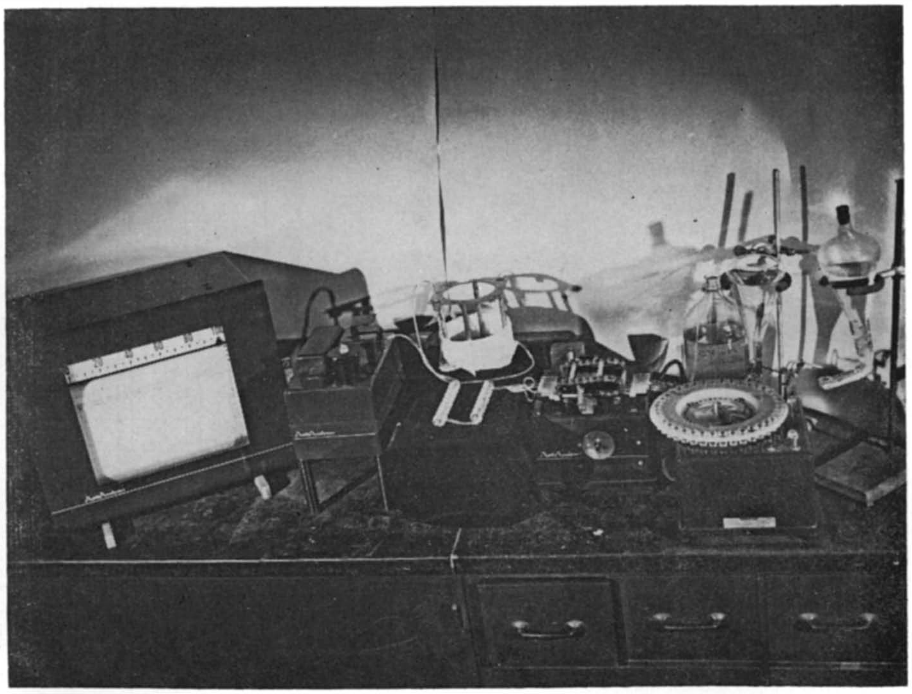
R. J. Ferretti

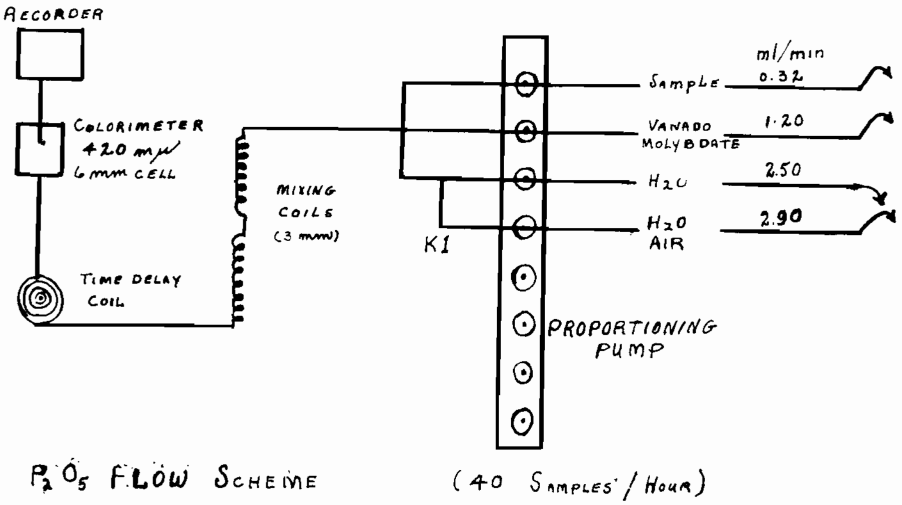
THE object of this study was to develop a simple, rapid and accurate automated method for the determination of phosporus in fertilizier materials.

The Technicon Autoanalyzer, looking from right to left, consists of a sampler, proportioning pump, colorimeter and a recorder. The sampler has a turntable that holds 40 sample cups. The only sample preparation required is a 20-minute acid digestion of one gram of fertilizer material made to 500-millimeter volume. The acid-insoluble material is allowed to settle, then the solution is poured into the cups.

For materials containing more than 35 per cent P_2O_5, one gram is digested and diluted to one liter. Known standards are interspersed with the unknown samples at periodic intervals. Since they are pumped into the same flowing stream and are treated alike under

Slide 22.





Slide 23.

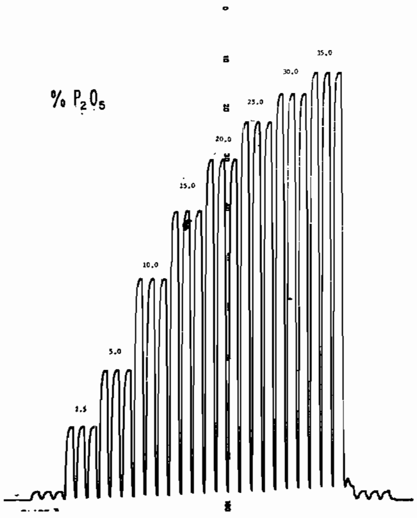
ideal conditions and identical conditions, the comparison is absolute.

The sample solution, the vanado-molybdate reagent, diluent water and air are aspirated into this system from their receptacles through the action of a pump and converge into a common line by means of a glass fitting. The air-segmented stream is pumped through two mixing coils, a time-delay coil, through a continuous flow cuvette in the colorimeter and then the percent transmission is registered on the recorder.

A water wash is also pumped through the system between each sample. It takes approximately 10 minutes for the first sample to get through the system and be recorded. Each sample thereafter takes one and one half minutes or 40 samples per hour.

This is a typical chart recording obtained on a series of triplicate standard solutions covering a range of two and a half to 35 per cent P_2O_5. Each peak represents a sample. The chart paper is graduated in 5-10ths per cent transmission. These lines aren't visible on this slide.

Slide 24.



The difference in peak heights between duplicate samples of a one-tenth per cent transmission unit is equal to the per cent of P_2O_5 shown on this next slide.

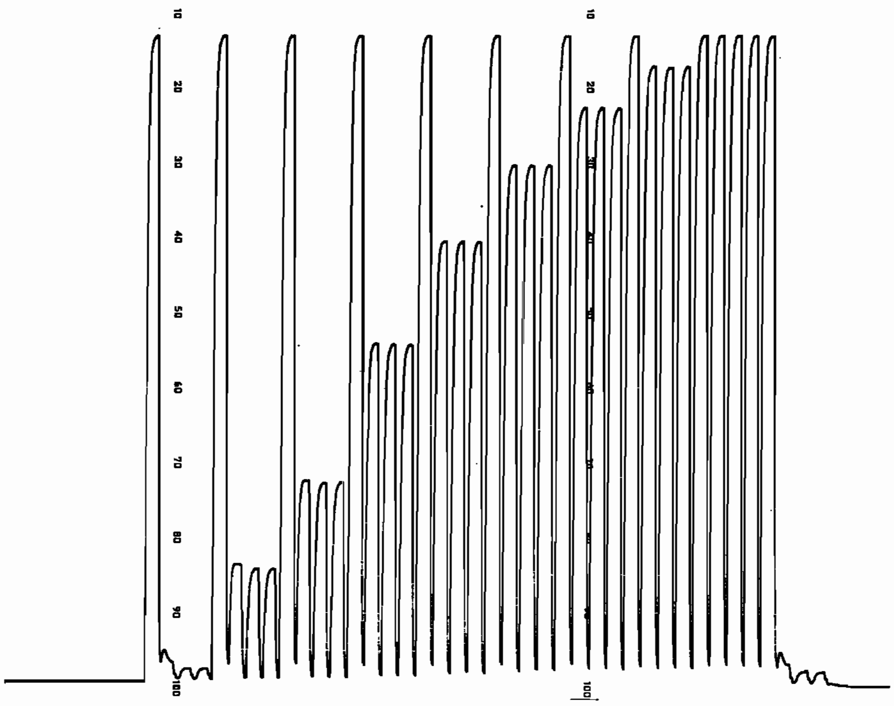
% P_2O_5	0.1 % T = % P_2O_5
2.5	.02
5	.02-.03
10	.03
15	.04
20	.06
25	.07-.08
30	.10
35	.13

Slide 25.

For example, the difference in peak heights of one-tenth per cent T between duplicates at the two and a half per cent level is equal to a difference of 0.02 per cent P_2O_5 between those two samples, while at the 35 per cent level, the difference is 0.13 per cent P_2O_5. Differences in peak heights of one-tenth per cent transmission occur frequently. Differences of two-tenths per cent transmission occur occasionally, and very rarely, differences of three-tenths per cent T or more.

This slide shows a series of standards, in triplicate, each series preceded by a high P_2O_5 standard. Carry-over of phosphorus due to contamination of the sample tube is apparent in the blank, two and a half, five and ten per cent P_2O_5 levels. In this particular run, at the two and a half per cent level, there is a difference of 6-10ths per cent transmission or 0.12 per cent P_2O_5 between the first peak and the other two. At five per cent P_2O_5, there is a difference of 3-10ths per cent T or 0.07 per cent P_2O_5 and at the ten per cent level, the difference is 2-10ths per cent T or 0.06 per cent P_2O_5.

Slide 26.



There are three ways to overcome this contamination: one, a selenoid attachment that would permit the sample tube to dip into a container of distilled water immediately after it comes out of the sample cup, thereby flushing out the tube.

The second, would be alternating cups of distilled water with the samples. The disadvantage of this procedure is that the number of determinations is reduced from 40 per hour to 20 per hour.

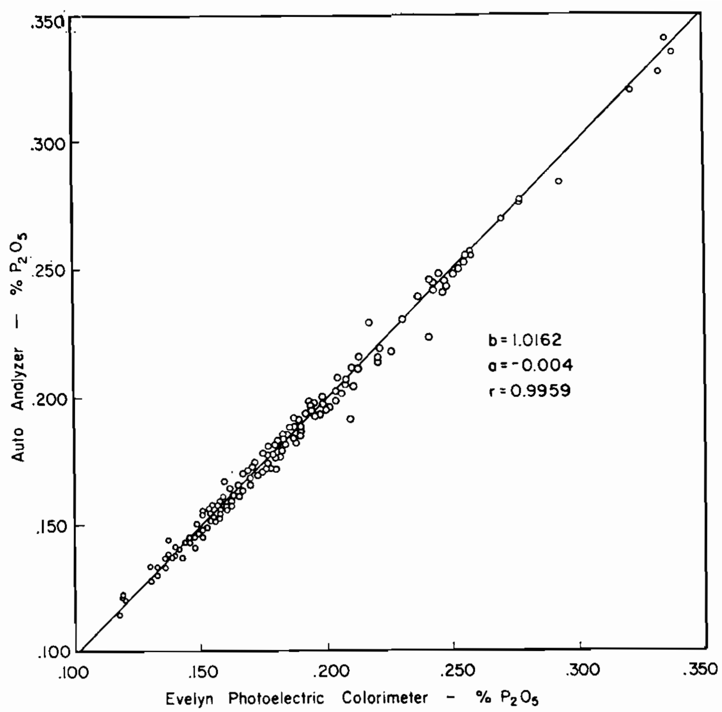
The third, and the one that we use when the approximate concentration of the P_2O_5 in the samples is known, is to group the samples so that a very high sample does not precede a low sample.

This is the way we grouped 10 Magruder samples analyzed in duplicate for total P_2O_5. Four standards, in duplicate, were also interspersed in this run. The only precaution taken was not to have a low P_2O_5 sample follow a very high one. To check the precision of this instrument, this run was made in the morning and again in the afternoon on three successive days for a total of six analyses on each duplicate sample.

These were also analyzed twice by the Quimociac method. The results are given in the next slide. These ten Magruder samples were grouped for this table from low to high P_2O_5 content. They weren't analyzed in this order, but in the order shown on the previous slide. A and B are duplicates of each sample. Good agreement was obtained between the Quimociac method, which is the first line across, and the autoanalyzer which is the second line in each group.

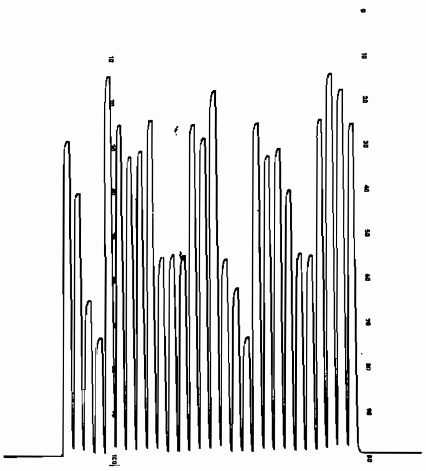
The accuracy on these samples was obtained using a method requiring only one weighing, one dilution for each sample, covering a range of approximately 8 to 48 per cent P_2O_5 and analyzed at the rate of 40 samples per hour.

These data and other data obtained over the past year have shown the autoanalyzer to be sufficiently accurate for routine pur-



Slide 29.

Slide 27.



Total P_2O_5

	8-8-8 (Liquid)		20-10-5		5-15-30 (Synthetic)		15-15-15		0-20-20	
	a	b	a	b	a	b	a	b	a	b
QM X	7.56	7.52	10.08	10.10	9.90	9.68	15.41	15.33	21.41	21.50
AA X	7.54	7.54	10.11	10.16	9.95	9.78	15.41	15.45	21.41	21.61
" S.D.	.024	.030	.038	.044	.027	.047	.054	.082	.065	.083
" C.V.	.318	.398	.376	.433	.271	.481	.350	.531	.304	.384
" Range	.06	.08	.09	.11	.07	.13	.15	.16	.17	.26

	5-20-20		Rock		0.46-0		18-46-0		18-46-0	
	a	b	a	b	a	b	a	b	a	b
QM X	19.23	19.13	34.21	34.25	48.54	48.58	46.95	46.89	47.56	47.56
AA X	19.31	19.21	33.90	33.98	48.75	48.69	47.08	47.18	47.58	47.65
" S.D.	.061	.100	.104	.113	.152	.158	.168	.161	.216	.160
" C.V.	.316	.521	.307	.333	.312	.325	.357	.341	.454	.336
" Range	.18	.29	.30	.30	.40	.42	.50	.40	.62	.38

Slide 28.

poses. Greater accuracy and precision could be obtained if the samples high in phosphorus were diluted to a larger volume or half gram samples used instead of one gram.

The differences in standard deviations between duplicates as seen under the 5-20-20 sample in the lower lefthand corner and the 18-46-0 over on the right were occasioned by one low value on each sample. No results were discarded.

The analysis of plant material such as corn, alfalfa and beans containing less than one per cent P_2O_5 was no problem. This work was done by Bill Jackson and Carl Erickson in our group. Three to five grams of plant material were dry-ashed at 525 degrees centigrade for four hours, the residue was taken up in dilute hydrochloric acid, made to a volume of 100 ml, and the acid-insoluble residue was allowed to settle before pouring into the sample cups. As a reference procedure, aliquots of the same sample were taken and the phosphorus determined by a modification of the method of Barton using an Evelyn colorimeter. This method has been used in the Fertilizer Laboratory for a number of years.

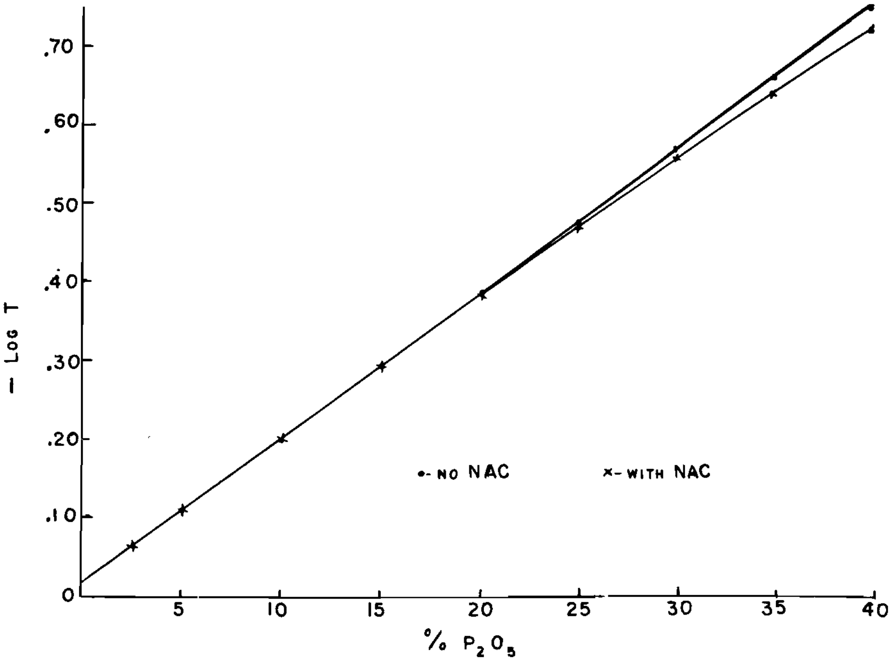
This slide shows very good correlation between the two methods on over 150 analyses of plant material. The results illustrate the high degree of accuracy that is obtained when analyzing samples having a P_2O_5 concentration within a narrow range.

Preliminary data on neutral ammonium citrate extracts of fertilizer materials obtained with the Autoanalyzer and the Quimociac method showed good agreement at concentrations of phosphorus pentoxide below 15 per cent. Above the 15 per cent concentration agreement was poor. This is shown in the next slide.

Standards containing neutral ammonium citrate show citrate interference at approximately 20 per cent P_2O_5 and become progressively worse as the phosphorus content increases. We hope to study this problem very thoroughly because a rapid procedure for the direct determination of available phosphorus would save a lot of time and money for laboratories having a large number of samples to analyze each day.

A group in Missouri is working on a method for potash in neutral ammonium citrate extracts with the use of a flame attachment with the autoanalyzer. If both methods are developed, then phosphorus and potash can be simultaneously determined on the same sample. The equipment needed for this simultaneous determination would be a sampler, a pump, a colorimeter, a flame attachment and a dual pen recorder.

Slide 30.



We have never analyzed soil samples for phosphorus, but since the phosphorus content of most soils is very low, it would be necessary to increase the sensitivity. With this instrument there are a number of ways to do this. For example, by using a sample tube with a larger bore diameter and thereby aspirating a larger sample into the system, or by eliminating the water diluent tube, or by inserting a 15 millimeter flow cell into the system instead of the 6 millimeter flow cell that we use here.

I would like to mention a few other considerations. This automated method eliminates a great deal of human error, which occurs when it is necessary to pipette aliquots, prepare standard solutions, titrate, filter and so forth. While samples are being analyzed, the operator can be doing something else, such as weighing and digesting additional samples. There is a permanent record of the analyses.

In approximately one and a half years of operation we have had no breakdowns of the intrument, and very little maintenance was required. The cost of the reagents per thousand analyses is $38.

DISCUSSION LEADER: Any questions?

A MEMBER: What wave length are you using?

MR. FERRETTI: 420 millimicrons.

DISCUSSION LEADER HILL: Other questions?

A MEMBER: What is the cost of the equipment?

MR. FERRETTI: There are two other parts. There is a dialyzer and a heat bath that comes with this equipment. The total cost would be around $5,000, but we don't need those two pieces in this procedure, because no heat is required to develop the color. As I understand it, $5,000 for the total estimate, but for what we have here, it is around $3,800.

DISCUSSION LEADER HILL: Other questions?

I think many of you have seen this thing and maybe some of you have one of your own, in place.

By the way, is there anyone here who has one of these or a similar thing in his shop? Is there?

We would like to see your hand.

(No response.)

They haven't bought them yet.

Other questions?

MR. FERRETTI: I would like to say one more thing.

This instrument can be used for any colorimetric method. It's very easy to change filters; it's not only for phosphorus. Commonwealth Edison in New York has, I believe, over 30 of these instruments where boiler water is analyzed for iron, silica, calcium, phosphates, etc.

A MEMBER: Perhaps I missed a point, but is this autoanalyzer good for analyzing phosphate rock samples?

MR. FERRETTI: Yes, it's just a matter of diluting it to the range of phosphorus content, which is one gram to five hundred. But, if you were analyzing phosphate rock, or triple super, or similar materials, you could increase the accuracy and precision of the instrument by diluting into a range where these slight differences in peak heights make little difference in P_2O_5 content.

DISCUSSION LEADER HILL: Would you like to comment on where the instrument is being studied?

MR. FERRETTI: Yes. C. H. Perrin, of Canada Packers in Canada, is working with it for nitrogen. I don't know the latest on that. And C. W. Gehrke has adapated it to potash in ammonium carbonate solution. He is also attempting to use it on neutral ammonium citrate solution.

DISCUSSION LEADER HILL: Any other questions?

A MEMBER: What is the name of it?

Mr. Ferretti: Technicon Autoanalyzer—made by Technicon Instrument Corporation, Chauncey, New York.

DISCUSSION LEADER HILL: Any other questions?

(No response).

We shall pursue analytical methods a bit further and Mr. Hoffman will speak to us briefly on methods for analytical control, particularly with reference to status of methods. I would like to apologize to these gentlemen. They were supposed to speak in the reverse order. When we had the caucus the other day, I got the order on the paper wrong, and so they're speaking in the order that I have it on the paper rather than in the order they preferred.

(Laughter.)

Analytical Control and the Fertilizer Industry

W. M. Hoffman

Actually it is probably better that Ren did precede me, because it makes my talk a little easier, now that you have seen one of the instruments that I am going to mention here.

The role of the fertilizer control chemist has changed significantly in the last 35 years. Then his duties involved the analysis of low to medium grade fertilizers and raw materials, such as, tankage, 16-20% superphosphate, and kainit. The production of fertilizers was nothing more than a mixing operation and the control chemist worried only about sampling and the details of the various determinations used in his laboratory. He had time to develop and practice good workable, precise techniques. Unfortunately, this utopian way-of-life was not to last and the position of the analytical laboratory was destined to become more and more important in the fertilizer industry.

The practice of ammoniation of superphosphates ushered in an era of techninological advances, which elevated the manufacture of fertilizers from an almost "alchemical" art to a highly scientific operation. These revolutionary changes in processes and techniques did not extend to the analytical laboratory. There, it was still necessary to determine nitrogen by Kjeldahl distillation, phosphorus by the volumetric ammonium molybdate method, and potassium by the gravimetric Lindo-Gladding method. The lot of the laboratory was not an easy one. They were dealing with large volume, bulk materials, varying in chemical and physical characteristics and with materials which varied tremendously in composition before, during, and after processing. With management calling for more and closer control, there was no time available for the study and adoption of new and faster methods of analysis.

The control chemist found ways of improving his operation. An idea or a quick test, picked up during conversations with other chemists, from industry, or state control laboratories, or the Federal government often found its way into his routine. His attendance at meetings, such as the Conference of Chemical Control Problems sponsored by the NPFI, the American Chemical Society, or the AOAC exposed him to other important development in the field of analytical chemistry. Constant perusal of the literature, both scientific journals and fertilizer trade organs, was necessary. The paucity of publications concerning analytical procedures by fertilizer chemists is further evidence that either there was no time to make the necessary measurements or that company policy did not allow these publications. However, this was a very minor inconvenience when one realizes the real role of the control laboratory. They are there to protect the manufacturer's most priceless asset, its reputation, its brand name.

Management's attitude toward the control laboratory has also undergone changes during this period. Formerly, the laboratory was looked upon as a necessary evil but has now risen in stature to a point where it is considered a very important member of the team. This change is taking place and can be shown by reviewing the addresses of management on the general topic "Management and the Role of the Chemical Control Laboratory." In 1957, at the first Conference of the Chemical Control Problems, M. D. Sanders, Swift & Co., answered it in this way. "I think you will agree that he can be a varsity player on the management team if he will cultivate and apply his specialized skills and knowledge to both the day to day operations and troubles of his plant, and to the long-term hopes and plans of his company." Two years later at the same conference, Nelson C. White, International Minerals & Chemical Corporation, spoke in this manner: "It (the control laboratory) should be one of the strongest links in the management chain, connecting research, production and sales, acting as an extension of each and insuring a strong safe bond to the customer." If one notices the choice of the words 'can', in one case, and 'should' in another, it can be inferred that recognition of the laboratory's merit was not completely accepted then. This year, and again at the same conference, Elwood I. Lentz, Western Phosphates, Inc., tells how to obtain this recognition. "Speed, accuracy, reliability, and cost consciousness will win higher esteem for the control chemists." How can the chemist achieve these goals?

Chemical analysis in the fertilizer industry can be separated into three equally important operations — preparation of the sample, estimation of the particular component, and the interpretation of raw data.

In the fertilizer industry, from the time of exploration, the processing of the materials, their incorporation into fertilizer mixtures, and finally to the marketing of the final product, sampling is of paramount importance. If the small amount of material in the bottle that the analyst takes to the balance is not representative, all of the values obtained from it are worthless. There can be no compromise of speed or cost consciousness in sample preparation. In fact, more time might well be spent in studying the techniques of sample preparation than studying accuracy and precision of a particular analytical method.

The area, in which the control chemist must consider new techniques and organization, involves the present methods of analysis. The efforts of the various task forces of the Chemical Control Committee of the NPFI to improve the reliability and accuracy of our time-honored methods is commendable but they still have not decreased the time of analysis. The same thing can be said about the newer methods adopted by the AOAC. In the last two years, I have visited the phosphate rock mining operations in both Florida and the western states and in almost every laboratory, the conversations eventually centered upon the urgent need for speedier methods. The obvious answer to this problem is instrumentation, but this is only part of the answer since most instrumental methods suffer because of their manipulative requirements. The real answer is an instrument which will do the aliquoting, add the color reagent, mix, read the optical density, and record the result—or an automated instrument. The instrument should have application in the laboratory and as an onstream analyzer.

Many companies are now making just such instruments—chromatographs, colorimeters, mass spectrometers, pH analyzers, X-ray analyzers, flame photometers, automatic balances, etc. Their use in the chemical processing industries is on the increase since the payout period of the instrument seems so much shorter than the firms anticipated. For example, a $15,000 chromatograph in an alkylation unit in a refinery paid off the initial investment in 3 months by smoothing out operating conditions and cutting the number of daily control tests from 24 to four.

There are instruments applicable to routine control work in the fertilizer industry. The first one to come to mind is the Auto Analyzer manufactured by Technicon Controls, Inc., but there are others—the Robot Chemist by Research Specialists, Inc., the Titralyzer by the Fisher Scientific Co. or the Bausch and Lomb Data Acquisition System. It is true that some are not as fully automated as others but all can yield significant savings in time. We have had an Auto Analyzer for a year and a half and Mr. R. Ferretti reported on an automated method for phosphorus applicable to fertilizers and fertilizer materials at the 1962 AOAC meeting. Response from visiting analysts and requests for copies of the method have indicated considerable interest in this type of phosphorus analysis. Three weeks ago at the AOAC meeting Dr. C. W. Gehrke, of the University of Missouri, reported on the application of this instrument to the analysis of potassium in mixed fertilizers. The Technicon Co. claims that their automated system can replace the Kjeldahl method for the determination of nitrogen but I know of no confirmed data on fertilizers. They have also introduced a Solid Sampler which eliminates the preparation of solution from many determinations. So, you can see, what a boon an instrument like this could be to the fertilizer control laboratory.

The rock producing companies are starting the move to instrumentation and automation. Two companies (Swift and Virginia-Carolina) have looked into the use of X-ray flourescent spectrophotometers for their rock control work. Davison and Central Farmers are looking at the Robot Chemist and both American Cyanamid and IMC have Auto Analyzers. Baumann, Roberts and Bell, of IMC, reported at the September ACS meeting, on the use of the Auto Analyzer for automatic sulfate ion determinations in wet process acid systems. They reported sulfate analyses accurate to 3% in 12 minutes and further stated that they planned to use this system for complete automation of sulfuric acid control at the digestion step. This operation should lead to maximum extraction of the phosphate rock P_2O_5 and production of a rapid filtering gypsum cake.

In order to keep up with the tremendous advances in technology, automation of chemical control must make steps as the one just mentioned. For example, IMC opened a new giant phosphate acid plant in Bonnie this year. Producing acid at the rate of 900 tons of P_2O_5 per day, this plant uses closed circuit television and other electronic and mechanical refinements in a highly automated system. Four production employees per shift operate the whole plant. I wonder how many chemists are needed for the chemical control for this plant.

Since most states either have or will adopt the minimum tolerances set up by the AAFCO for the secondary and micro-nutrients, the fertilizer companies, to stay in active competition, will have to guarantee these nutrients. When it comes to deciding how to analyze for elements, such as Zn, Fe, Cu, Ca, Mg, or Co, serious thought should be given to a relatively new instrumental system — atomic adsorption spectrophotometry. It is rapid, accurate, and relatively free from interferences.

Other new techniques, such as gas chromatography, polarography, thermochemical titrations, X-ray fluorescence, and others may well find their way into the fertilizer laboratory.

Unfortunately, the move to automated control is not simple. Initial experimentation will probably be done in the company's research facility and the information gained must be made available to the control chemist. Lines of communication must be established and maintained. Armour Agricultural Chemical Co. opened a new research laboratory in Atlanta in April of this year. The analytical section is engaged in methods of analysis in their research and development program. Raw phosphate materials are analyzed by a combination of methods: photometric, X-ray fluorescence and diffraction, differential thermal analysis, flame photometric, and atomic adsorption analyses. This is a very worthwhile program. Let us hope that some of their research findings help the chemists in Armour's rock and mixed fertilizer production laboratories.

The adaptation of automation to onstream control is complicated by the sampling system. If the sample is removed manually from the reaction, treated, and carried to the instrument the problem is not too serious. This is not the case when continuous chemical monitoring is desired. Development work will be necessary to free the analytical value of sampling error.

The biggest deterrent in the move to automation instrumentation is the cost. The initial cost of most of the instruments is not cheap although most of the ones mentioned are priced below $10,000. There will also be developmental costs and these can be quite sizeable. While the proof of justification will be on the control chemist, management must study any proposals seriously and be willing to make some gambles.

In reference to the interpretation of data, there is little to say. All laboratories, I'm sure, use control charts of one kind of another for handling their results. Another aspect of automation which should be mentioned, at this point, is the coupling of digital readout mechanisms with the instrument system. The preferred technique is probably printing on tape or paper of measurements, such as milliliters of titrant or optical density. In many cases, the readout mechanism can be programmed to read directly in the percentage of the nutrient being analyzed.

In conclusion, I would like to say that now is the time for fertilizer chemists to apply the ever-increasing revolutionary changes in analytical control to their operations. In so doing, the laboratory will become a recognized, integral part of fertilizer manufacturing.

DISCUSSION LEADER HILL: Thank you, Bill.

Are there any questions on Mr. Hoffman's comments?

(No response.)

I notice that we have one of our people from the Department of Agriculture. Mr. Pate, our Branch Chief, is sitting over here. He doesn't get out to this type of meeting very often. I think I would like him to stand so that you can all see who Bill Pate is. He's been around Agriculture for a long time. Will you stand, Mr. Pate? He's an expediter too.

(Mr. Pate arose, applause.)

At this time I want to show figures that depict the world potash situation in a manner similar to the way nitrogen and phosphorus were presented. We shall take a quick look at reserves. Potash, you know, is piled up in a few places. Oddly enough, all the potash that we know of, except a little that comes out of Chile, is in the northern hemisphere. Perhaps there should be more potash in the northern hemisphere than in the southern hemisphere, because there is more land mass in the northern hemisphere. Probably 60 to 70 per cent of the land mass is in the northern hemisphere, but I am told there is no geologic reason why there shouldn't be potash in the southern hemisphere, if people would just look for it.

Potassium Reserves and Production, 1961

World reserves of bedded deposits, >70,000 million s. t. of ore
World production, 9.3 million s. t. of K_2O

Location of producing fields	Share in world reserves %	Share in world production %
Europe	62	74
Canada	26	1
USA	> 1	23
Asia	3	1
Other	8	1

Less than 1% of reserves provided 23% of production.

A few countries control the potash situation. You will notice that we have less than one per cent of the reserves, yet we produced 23 per cent of the supply in 1961. The picture is different now that the Canadian production is in. The showing in 1961 is a feather in our cap in one way; in another way we are using up our stuff. Sometimes when we pat ourselves on the back, it's like the man who had the checker-playing dog. Someone commented "That is a smart dog," and he replied, "Well, he's not so durned smart; I beat him three times out of five."

(Laughter)

The next slide shows how potash appears in our fertilizer. I do not have anything for the world. We do not know what others are doing. It is interesting to

Farm Potassium Consumption by Materials, 1961

Fertilizer	Percentage share in consumption in— World	USA
2- & 3- nutrient fertilizers	—	87
Potassium chloride	—	12
Potassum sulfate	—	1
Nat. organics	—	0.5
Potassium nitrate	—	0.1
Other	—	0.1

me that 87 per cent of our potash goes into these multinutrient fertilizers; 85 per cent of the phosphorus goes in there, and only 38 per cent of the nitrogen. As was noted earlier, the nitrogen has fallen out of mixed fertilizers.

That completes my slides, but I want to mention another element. Sulfur is such an important nutrient element that we ought to say something about it. World production in 1961 was 11½ million short tons of S. That includes both native and recovered. North America produced 68 per cent of it (we did 51, Mexico 12 and Canada 5), Europe produced 11, 9 per cent coming from France, and Japan 2 per cent, whereas 19 per cent was scattered around here and there.

The essential elements in plants come to us in triads. There are carbon, hydrogen and oxygen, about which we hear very little. We have the major fertilizer triads, N. P and K, and the so-called secondary ones: Calcium, magnesium and sulfur. We spent 40 years taking the sulfur out of fertilizer, and now, it looks like we're going to have to spend a little time trying to get it back in. Of course, they took it out as a sulfate. Some folks want to put it back as elemental sulfur.

Then we have iron, manganese and boron; copper, zinc, and molybdenum; fluorine, possibly vanadium and a blank space for future use. Finally, we have cobalt and selenium, which are needed for animals. Since the latter two are wanted in the forage, fertilizer people must take notice of them.

Thus, we have some 17 or 18 elements that are of importance in plant or animal nutrition. The next generation will have to rassle with all of them. They are going to have a good time. You see, the geneticists are giving us high-yielding strains. We are cutting down our acres and making more grow on an acre. We are irrigating and doing many things that tend to expand the areas of deficiencies in some of these less common elements. Consequently, some fertilizer people are getting excited about ways of handling the micronutrients. One man asked me yesterday, "How are you going to get those on the soil?" And my answer was, "I do not yet know." In any event, you are going to do it.

There are sundry carriers for these less common elements. The glasses, better known perhaps as frits, are just one type of carrier. Somebody asked the other day if they were any good. Well, we think they are. They have a place, and so Mr. Holden at this time will tell us something about the findings and his notion of frits and other carriers of boron and zinc.

Micronutrient Carriers for Fertilizer Use

E. R. Holden

RECENT surveys have shown that the incidence of micronutrient deficiency has been increasing. High yield-producing crops are drawing more heavily on nutrient supplies of the soil. Organic and other low analysis fertilizers, containing significant amounts of micronutrients, have been replaced with high analysis materials containing only negligible amounts of micronutrients. Crop rotation and land-resting practices which tend to maintain micronutrient supplies in the root zone are becoming a thing of the past. With these technological changes, it is clear that the micronutrients will have to be included in fertilizer programs on a somewhat increasing scale.

Before considering the micronutrient materials themselves, it should be recognized that the objective is to maintain micronutrient levels in certain normal ranges. Within these ranges, growth of the crop is unaffected by differences in uptake.

Below the normal range, the crop is deficient, and both yield and quality of the crop are adversely affected. Insufficient molybdenum slows conversion of nitrate to protein. Copper deficiency lowers sugar content and has an unfavorable effect on the flavor of citrus. Low boron levels lead to poor cell structure, dry or mushy spots, and other faults in fruit and vegetables. Iron, copper and manganese play an important role in chlorophyll formation. Each micronutrient is vital to the step-wise process of building plant compounds of higher and higher energy levels.

At high levels, the micronutrients can be toxic to the crop, toxic to animals consuming the crop, or otherwise affect quality of the ultimate product. Copper, for example, catalyzes oxidative changes, and less than one part per million impairs the taste of beer. (Laughter.) At such levels only one or two pounds of copper a day would ruin the beer supply of the entire country! This could be a serious matter to some people, maybe less so to others.

Of real concern to everyone, though, is a recent finding by Dr. Denham Harmon of the University of Nebraska. His studies have shown that copper content of the blood is significantly higher in men who have had a history of heart attacks than in men of the same age who have been judged to be free of heart disease.

Impurities in micronutrient materials pose some other far-reaching implications. Every year there are a number of cases of dementia that are traceable to lead-poisoning. The number of people affected subclinically would, of course, be unknown. Cadmium, which accumulates in the liver, is suspected of being the cause of some infant fatalities and of possibly shortening the life span. We do not have enough information concerning the physiological effects of nonessential elements to reach definite conclusions, but until we do, suspected impurities should be held to low levels.

Micronutrient needs are said to be very specific for different soils and crops. There are, of course, differences between the nature of a micronutrient problem and that of a major or secondary nutrient problem. Some of the differences become evident if we con-

Figure 1.

sider a case of sulfur deficiency and then compare it with a zinc deficiency problem.

Alfalfa was grown on a low sulfur soil, purposely adding no sulfur in order to observe the effects of sulfur deficiency. In the first two harvests, yields were a little lower than with added sulfur, but there was little difference in appearance of the crop. In the third harvest, yield dropped to less than one-half, and in the fourth harvest to less than one-tenth of that with added sulfur.

The appearance of the crop during the fourth harvest is shown in figure 1. On the left, the sulfur deficient plants, now yellowish green in color, simply stopped growing. The middle pot had received elemental sulfur, and the pot on the right, sulfate sulfur, each at the level of 80 pounds per acre. By this time, the normal plants had removed approximately 70 per cent of the applied sulfur. Considering the amount of sulfur used and its structural importance to major plant compounds, one wonders why sulfur has been relegated to the status of a secondary nutrient.

With the same amount of total growth, recovery of a micronutrient would ordinarily amount to only two or three per cent of the amounts used in correction of deficiency. Many crops that produce less total plant material remove less than one per cent of the amount added.

Figure 2.

Figure 2 shows Sericea lespedeza growing on two soils containing about the same amount of extractable zinc. On the left, the lespedeza on a western calcareous soil is severly deficient in zinc. There was only about 50 per cent survival past the small plant stage and the typical little leaf symptom of zinc deficiency is so pronounced that the plants look like a different species. On the right, the same crop is growing normally on neutral Florida soil. At the time that this picture was taken, two cuttings had been taken from the pot of normal plants, none from the zinc-deficient plants on the left. Finally, when a cutting could be taken safely from both pots, there was a six-fold difference in the accumulated total yield.

In parallel pots, alfalfa, lima beans and red clover grew vigorously from both soils with no symptoms of zinc deficiency. On the surface, it might seem that zinc was needed specifically by lespedeza, not by the other crops. As it turned out, this was not entirely true. The data showed that yields of alfalfa and red clover on the western calcareous soil had actually been limited by insufficient zinc.

The potential benefit from micronutrient fertilization, as indicated by these results, varies vastly with kind of crop. There are also very large differences in the tolerance to high levels of the micronutrients. The differences in tolerance narrow the range of application. However, there still remains a low range that is suitable for most crops, and micronutrient levels should be held within such range by whatever method is most practical.

In the development of micronutrient carriers, research efforts have been concerned largely with special purpose materials. Slowly soluble forms have been under study as a possible means of minimizing leaching losses. Metal chelates have been introduced for use

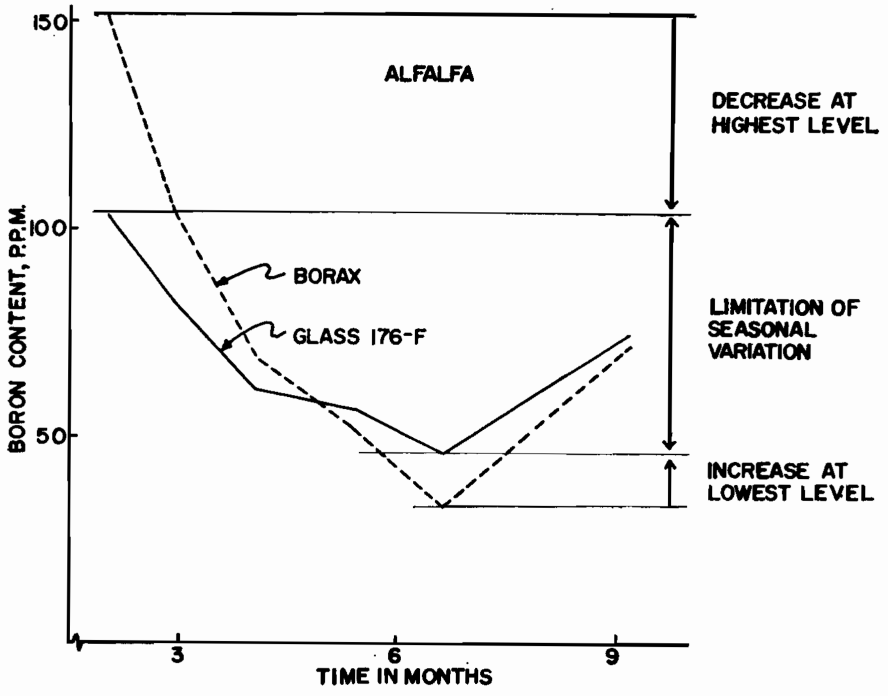


Figure 3.

more especially in areas where uptake is low because of alkaline soil conditions. These special types broaden the spectrum of micronutrient materials available to meet the widely varying needs of crops.

The advantage of using a slowly soluble carrier in a coarse texture soil is illustrated in figure 3. The effect of a boron glass on boron content of alfalfa over a nine-month period is shown by the solid line; results with an equivalent amount of borax, a readily soluable form, are shown by the broken line. As indicated on the right, use of the glass decreased boron content of early harvests and increased boron content of later harvests when uptake was the least. That is, the glass protects the crop from toxic concentrations in early growth and has more ability to prevent deficiency in late growth. The overall effect of the glass is to reduce seasonal variation in boron content of the crop.

Colemanite, a calcium borate mineral, has been used with some success in supplying boron to crops. In coarse form, it dissolves slowly enough to provide a measure of protection during the sensitive seedling stage of growth. However, dissolution is relatively rapid and its effect on uptake after a period of about six weeks becomes much the same as readily soluble boron.

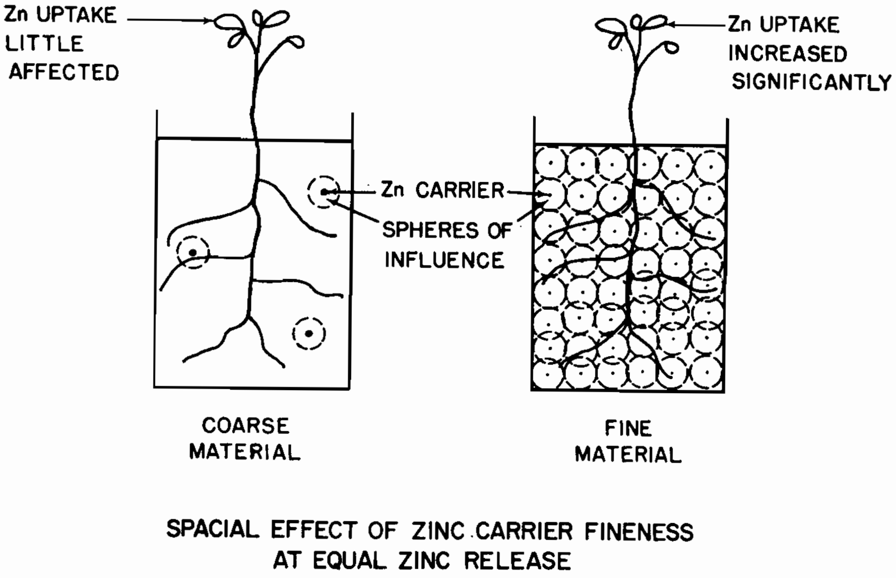
Figure 4 depicts the need for fineness when zinc is supplied in the form of a slowly soluble glass or other such carrier. Metal micronutrients are much less mobile in the soil than boron; consequently, the spheres of influence surrounding particles of the carrier are small. As shown on the left, a coarse glass, having much material coarser than 200-mesh, provides few particles, and there is little chance of root penetration into zones of high zinc concentration. Under this circumstance, the effect of a zinc glass on uptake is very low. The manner in which a finely-divided glass affects uptake is illustrated at the right. In this case, composition of the glass has also been altered so that it releases no more zinc than the coarse glass; that is, zinc release, as determined by extraction with ammonium acetate, is the same as that of the coarse glass. With the greater fineness, a much larger number of glass particles are added to the soil, so that plant roots penetrate spheres of influence no matter what direction they take in the soil.

Typical particle size distribution curves are illustrated in figure 5 by results obtained with a boron glass and those obtained with a multinutrient glass. Each point on these curves represents the percent of glass having a diameter in the range midway to the adjacent diameters enumerated on the horizontal axis.

Studies have shown that in the optimal range of release the largest particle diameter should not be greater than about 12 times that of the smallest particle. About 70 to 80 percent of each glass is within such range. Mean diameter can be shifted either to the right or the left with little consequence to the performance of a boron glass. That is, fineness of a boron glass can be varied provided that composition of the glass is also altered so as to compensate for differences in fineness.

Permissible variation of particle size is a great deal smaller with zinc or other metal micronutrients.

Figure 4.



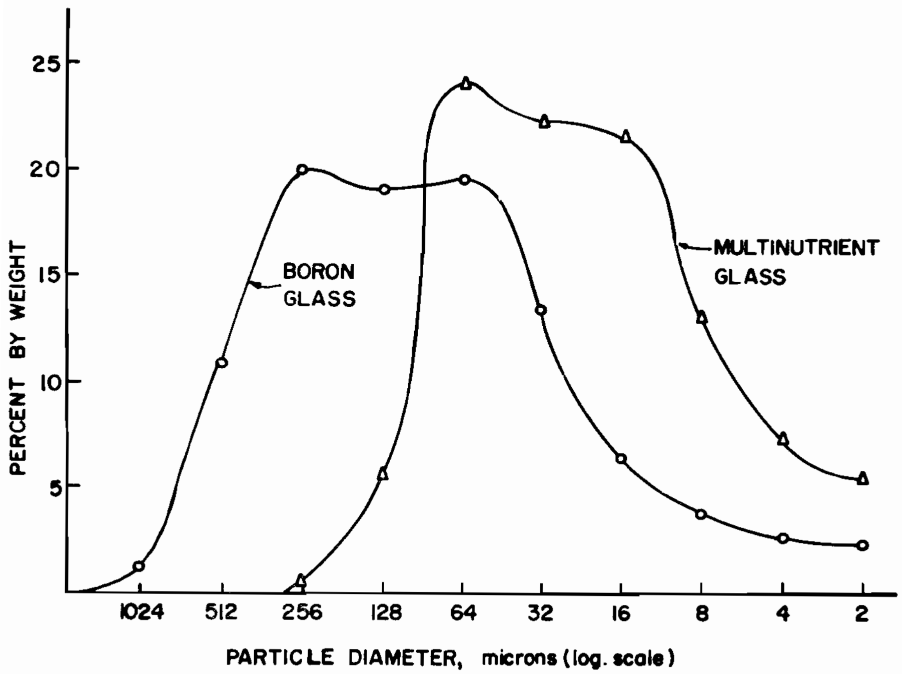


Figure 5.

A zinc glass is not suitable for crop use unless ground to pass 200-mesh, or below 74 micron size. With this limitation, fineness cannot be varied very much without an unreasonable increase in grinding cost. Thus, in making a zinc glass, composition of the glass, as it affects release rate, must be controlled closely in keeping with the required narrow range of fineness.

Extractable Zinc Vs. Crop Zinc

(Lakeland Soil + 3 PPM of Zinc)

Material	Am. Acetate Extr. Zinc, % of Total	Increase in Zn-Content of Alfalfa[a] PPM	%[b]
$ZnSO_4$	100	15.6	100
Hemimorphite	100	7.1	45
Willemite	30	3.0	19
Sphalerite	0	0.0	0

[a] Ave. of 3 harvests. [b] $ZnSO_4$ = 100

Zinc release from certain mineral materials, having a fineness of 41 to 47 percent through 200-mesh, is tabulated above, using zinc sulfate as the basis of comparison. Hemimorphite, a hydrated zinc silicate, dissolved completely when extracted 16 hours with ammonium acetate, pH 4.0 In vegetative tests, it increased zinc content of alfalfa about one-half as much as zinc sulfate. Willemite, anhydrous zinc silicate, released 30 percent of its zinc to ammonum acetate and increased zinc content of the crop 19 percent as much as zinc sulfate. Sphalerite, a zinc sulfide, released no zinc either to ammonium acetate or to the crop.

The correlation of ammonium acetate extractable zinc with zinc content of the crop suggests that the extraction method would be useful in rating zinc availability of mineral or byproduct materials. Extractable zinc, though not necessarily immediately available, could be regarded as an approximation of the amount of zinc that would dissolve in the soil over a period of a few months. When this test was applied to a few commercial grades of zinc oxide, extractable zinc was found to range between 70 and 85 percent of the total zinc.

Metal chelates have been of much interest and their use in correcting micronutrient deficiencies in crops has been increasing, especially in western states. It is almost impossible to have a complete understanding of the influence of metal chelates on crops because they affect uptake and within-plant mobility of other elements simultaneously. An excellent group of symposium papers on the subject was published in this year's March-April issue of Agricultural and Food Chemistry. This information, being available, need not be considered in detail here.

The value of a metal chelate is very dependent on method of application. The chelate can provide a much-needed increase in mobility when micronutrients are to be banded in an alkaline soil. The influence on uptake may also be somewhat greater than inorganic forms when the materials are mixed with the soil by plowing under broadcast applications. However, when the micronutrients are to be mixed with the soil, the use of a chelate would not ordinarily be necessary for other than very extreme soil conditions.

An interesting special use is made of a metal chelate in the growth of "acid-loving" plants such as roses, azaleas and hydrangeas. Apparently these plants require high iron levels, as would be available under acid soil conditions. Because of this high iron requirement, specialty fertilizers containing chelated iron are now being recommended for such plants.

Micronutrient deficiencies in orchard and nut groves present another special condition where chelates can be used with advantage. Soil applications of iron, copper, zinc or manganese tend to become fixed near the surface of the soil and fail to reach the depth of tree roots. Chelates can be used to overcome this immobility, but their application to soils for this purpose is not usually recommended because of the danger of severe toxicity.

Growers often prefer to spray the foliage. In this method of application, chelates offer the outstanding advantage of being less toxic than inorganic salts. Foliar application is growing in popularity, particularly where the metal chelate can be included with a necessary insecticide or fungicide spray treatment and very little extra work is involved.

In summary, the degree of benefit derived from micronutrient applications varies vastly with different crops. However, if soil supply of a micronutrient is low for one crop, it is probably low for most other crops. The tools for meeting special soil problems are slowly soluble carriers and metal chelates. Present information is sufficient to justify their careful use. Nutrient availability of mineral or byproduct materials can be estimated by extracting such materials with ammonium acetate, pH 4.0. Use of materials containing appreciable amounts of elements suspected of being detrimental to human health should be avoided.

Thank you.

(Applause.)

Discussion Leader Hill: Does anyone have a question? We have a minute or two.

(No response.)

Hearing none, we shall turn this thing over to the boss, and he will tell you what you're supposed to do for the next two hours.

Chairman Sauchelli: Thank you, Bill. It has certainly been a very interesting and worthwhile session.

(Announcement.)

We will stand adjourned until two o'clock, and we will start promptly at two.

(Applause.)

(The session adjourned at twelve-fifteen o'clock p.m.)

Wednesday Afternoon Session, November 6, 1963

The Round Table reconvened at two o'clock p.m., Chairman Sauchelli presiding.

Chairman Sauchelli: Let's come to order, please.

I think we will resume our interesting program that was started this morning. We will turn the meeting over to Director Hill once more.

Discussion Leader Hill: One agricultural thing high in the public conciousness and in the mind of Congress these days is the water budget. There's a limited amount of water in the country. Rain falls on the land; part of it soaks in, and part of it runs off. Sometimes we consume water in a way that it is returned to the streams, and then sometimes it's consumed in a way that it is not returned to the streams. There's a lot of talk and rassling in Washington as to who is going to get the money to do something about it.

Fertilizer people have not been too much concerned about water economy in the past, but I think they should be, because it could very well be that the next generation will be using one kind of fertilizer in a dry year and another kind in a wet year.

There's a water budget in the fertilizer plant. We know roughly what it ought to be, but we can't tell what it is without analyzing for water, and that is one of the most difficult things that we have to do. The next paper by Mr. Caro is concerned with methods for determining water. He is the Associate Referee in the Association of Official Agricultural Chemists. I think there is more interest among the fertilizer people in water determination now than there ever has been, and so it seems to me that considerable progress is being made these days.

Determination of Water in Fertilizers

J. H. Caro

THE water content of fertilizers is determined routinely in hundreds of laboratories and plants throughout the country. The determination is made for a variety of reasons, principally including the control of manufacturing processes, the prevention of caking, the attainment of proper chemical characteristics in the product, the minimization of freight costs, and the realization of nutrient guarantees. Yet in few other areas of analytical endeavor in the fertilizer industry is there so little true understanding of exactly what is being determined and exactly how to carry out the determination most effectively. This afternoon I shall attempt to shed at least some light on the situation so that you will better appreciate the problems confronting the control chemist at your plant.

Water occurs in inorganic compounds in an astonishing variety of combinations. Let's look at these combinations as they are commonly thought to exist. First, there is *water of constitution,* water that is an integral part of the molecule but not actually existing as water until released by heat or chemical reaction. A typical example is the heating of monocalcium phosphate to give off water, with the formation of calcium metaphosphate. Next, there is coordinated water, which includes the commonly Next, there is *coordinated water,* known *hydrate water* or *water of crystallization,* such as the hydrate in monocalcium phosphate monohydrate. This water is bound to the cation of the molecule by coordinate linkages, but the exact nature of the binding forces is not clear.

Complicatiing the picture is the fact that not all water of crystallization is coordinated water. Some, such as one mole of water in zinc sulfate heptahydrate, is combined as so-called *anion water.* This water is hydrogen-bonded to the anion of the molecule rather than to the cation and is more tightly held than coordinated water. Other water of crystallization may be neither coordinated nor anion water, but is present as *zeolitic water.* This water exists between layers in the crystal lattice and is sometimes rather difficult to remove. An example of this type is the hemihydrate of calcium sulfate. Still other water of crystallization may be considered as *lattice water,* bound to neither cation nor anion, or may be present in indefinite amounts in hydrous colloidal material.

All these modes of water comprise *bound water,* water that is held by intramolecular forces of one type or another. Binding energies vary from mode to mode and the release of water is continuous or step-wise, depending on the manner in which it is combined. Apart from all this, there is also *free water* on the surfaces of most solid compounds. This is, of course, water that is simply adsorbed on or near the surfaces and which is released quite readily on application of heat or vacuum. It is commonly known as *moisture,* although this term is often applied loosely to bound water as well as free water.

As you have undoubtedly gathered by now, the accurate, quantitative determination of water in inorganic materials is not quite the simple procedure it is supposed to be. While it is true that not all types of water occur in all fertilizers, enough of them occur often enough, and the stability of the fertilizer compounds varies enough, that no one analytical method will suffice for all types of materials. Thus, the analyst is faced with the proper choice of a method for his particular material.

What methods are available? Once again the profusion is astonishing. There are methods based on reaction with acyl halides, with acetic anhydride and other anhydrides, with calcium carbide, with calcium hydride, and with magnesium nitride. There are colorimetric methods based on reaction with cobalt chloride or cobalt bromide. There are methods utilizing polarography, chromatography, infrared and ultraviolet spectrophotometry, nuclear magnetic resonance, mass spectrometry, vacuum ultraviolet absorption, or glow discharge. There are radiochemical methods. There are physical methods, based on measurement of turbidity, density, vapor pressure or dewpoint. There are sonic techniques. There are thermal and electrical methods involving the measurement of thermal conductivity, heat of vaporization, heat of reaction, dielectric constant, or coefficient of friction. In short, there are enough methods available that one has a wide choice.

There are also six methods that I have not mentioned up to now, which happen to be those most commonly applied to fertilizers. Each of them may be applied to certain materials but each of them also has limitations that impair its usefulness. I would like to point these out.

First, there is the oven drying method. Now everyone has an oven and it is a simple thing to put a sample in it and measure the weight loss, but it takes the better part of a working day to obtain results and, after all, one measures weight loss, not water content. Obviously, if there is any appreciable decomposition of the sample so that volatile constituents of the fertilizer are evolved other than water, such as fluorine, ammonia or carbon dioxide, the weight loss would be higher than the actual water content.

Furthermore, complete removal of some of the more tightly held types of water is often very difficult, requiring temperatures far above those normally used in the oven method. Then, too, some dehydrated fertilizers are very efficient desiccants in themselves, so that they pick up water very rapidly after removal from the oven and can even remove water from some less efficient desiccants when they are placed in the desiccator to cool. Finally, ovens in different locations vary widely with respect to capacity, temperature uniformity, temperature control and the like.

All these factors contribute to loss of accuracy and precision in the oven method, yet it is still, as I shall point out shortly, the best method we have for many fertilizers and is at present the only official method for total water (free plus hydrate water) in fertilizers.

Next, there is the vacuum desiccation method, the procedure used most commonly for determination of free water in fertilizers. Don't expect an answer in a hurry with this one, because it takes at least 16 hours' drying to get an acceptable result. This method, too, depends on weight loss, so it is not specific for water.

The amount of water removed from the sample depends on the efficiency of the desiccant used as well as on the freshness of that desiccant. One inherent error which is often overlooked is the fact that even those materials in the sample that have low vapor pressure may be evolved in significant quantity during the lengthy time required for analysis. Yet, because of the relatively mild conditions, this procedure is often used to calibrate faster methods and is at this time the only official method for free water.

Third is vacuum oven drying. This method combines heat and vacuum, but once again weight loss is measured rather than water content. It does have an advantage, though, over straight oven heating in that heat-sensitive materials such as urea or diammonium phosphate may be dried without undue decomposition. Conditions may be adjusted in the vacuum oven so that weight losses corresponding to those obtained in the vacuum desiccator are achieved in only two hours, thus giving a faster method for free water. Vacuum ovens are already in use in numerous laboratories and we are now in the process of submitting the method to collaborative study, looking to its adoption as an official AOAC procedure.

Use of the thermal balance, or moisture balance as many call it, is another weight-loss method. The instrument is, in effect, an automatic oven in which relatively high heat is applied to the sample for a relatively short time. Although rapid, the procedure does not have the precision of the more conventional methods. Especially poor results are obtained on fertilizers having high free acid contents. Because the many thermal balances on the market have differing designs and are based on at least two different mechanical principles, rather extensive preliminary tests are required for each one to find the proper setting of the controls. Yet, with proper preparation, the thermal balance can be set to give results for free water that are acceptable for routine check work.

The last two methods are not weight-loss procedures, hence are more specific for water. The first of these is Karl Fischer titration. This involves a chemical reaction with Karl Fischer reagent—a combination of pyridine, sulphur dioxide, and iodine—to yield a measure of free plus hydrate water. The method is rapid, accurate and has wide applicability to both inorganic and organic compounds. It has been successfully applied to numerous fertilizer materials, but unfortunately has failed in other instances. Specifically, free carbonates and ammonia interfere with the titration, the water in hydrated calcium sulfate cannot be titrated quantitatively, and monocalcium phosphate monohydrate gives an obscure end point.

Where these difficulties do not exist, Karl Fischer titration offers an excellent solution to the problem of water determination. Results are usually slightly lower than those obtained by weight-loss methods because the inherent positive error of the latter is eliminated.

A promising method for free water alone which we are currently investigating involves extraction of the fertilizer with dioxane, followed by Karl Fischer titration of the extract.

Finally, we come to azeotropic distillation, in which the water in the sample is distilled out and trapped in a measuring cylinder with use of a water-immiscible carrier fluid such as benzene or xylene. Since the volume of water is read directly, the method is seemingly specific for water. However, other volatile water-soluble components will add to the aqueous volume and give high results. Moreover, excessively large samples are required for materials of low water content, and these samples are destroyed in the determination. For example, 100 grams of a material containing one per cent H_2O will yield only one milliliter of water in the receiver. Another difficulty is the adhering of water droplets on sidewalls of the apparatus, causing poor accuracy and precision.

In spite of these problems, distillation seems to be the best way to determine water in liquid fertilizers and phosphoric acid. An especially good procedure for use with wet-process acid involves distillation with heptane after precipitation of the phosphorus with aniline.

Those are the methods. It is quite evident that each is imperfect in its own way, and that no one method will give exact results in all fertilizers. The obvious question is, then: "Which method should be used on which fertilizer?"

In my capacity as AOAC referee on water, I am charged with the responsibility of answering this question in the best possible way in the light of present knowledge and present needs. I would therefore like to conclude my remarks with a summary of my recommendations for determination of water in the various fertilizer materials. I make these recommendations with full awareness of all the imperfections in the listed methods, and with the secure knowledge that the recommendations will change drastically as further research is conducted in this area.

Oven heating at 100°C for total water and vacuum desiccation for free water are the preferred methods for phosphate rock, superphosphates, mixed fertilizers not containing urea, monoammonium phosphate, and calcium metaphosphate. For ammonium sulfate, potassium salts, and sodium nitrate, oven heating at 130° is preferable to the lower temperature. Vacuum desiccation is best for free water in these materials also.

For diammonium phosphate, urea, and urea-containing mixed fertilizers, total water should be determined by Karl Fischer titration and free water by vacuum desiccation.

For liquid fertilizers and phosphoric acid, azeotropic distillation with heptane and aniline is recommended.

Two very promising methods for free water that have not yet been tested sufficiently to be recommended without reservation are vacuum oven heating and dioxane extraction-titration, both of which appear to be feasible for use with all solid fertilizer materials.

DISCUSSION LEADER HILL: Thank you, Joe.

Any questions?

Everybody knows how to determine water, I suppose.

It is an interesting thing. I believe there is some chance of getting people to use different and better methods now, but a few years back it didn't make any difference what you developed, they were going to use the drying oven.

Any comment that anyone cares to make on the water business?

There is a side to the farming business other than fertilizers. There is the lime side. We put on lime to adjust the acidity to some suitable level. The big thing in lime is agricultural limestone—22 million tons annually. That is a sizeable pile of limestone. Limestone is not shipped very far, but it is big business.

Dr. Whittaker will now give us some of his wisdom on liming materials and their characterization and whatever else in his judgment might be of interest to you.

Development in Agricultural Liming Materials

C. W. Whittaker

Developments in soil liming materials may well be considered in two categories; those things or events that affect the marketing or use of the industry's main product, agricultural limestone; and the minor or new materials now coming into new or increasing use. Agricultural limestone, or ground limestone, as it is often called, constitutes 90 percent of the total tonnage handled by the industry, perhaps as much as 95%.

Activity Ratings

Agricultural limestone must commonly meet specifications limiting two properties, the particle size or fineness and the potential or total neutralizing power commonly expressed as the calcium carbonate equivalent. We shall not be concerned here with the latter. The fineness is an index of the reactivity of the limestone or the rate at which it may be expected to react in the soil. This is based on the assumption that the finer the particles are the faster the material will react. While fineness may be the main factor governing reactivity it is not the only one. The chemical composition, especially the relative proportions of calcium and magnesium carbonates impurities, degree of crystallinity, and other factors may also play a part.

It would be very convenient if a chemical method for rating limestone reactivity could be found that would integrate the effects of all these factors in the same manner that they are integrated in the soil. A few years ago Professor Axley and a graduate student at the University of Maryland, proposed a method in which a limestone sample is reacted for a fixed time with the disodium salt of ethylenediaminetetraacetic acid (EDTA) under standardized conditions and the residual EDTA determined, thus obtaining an activity rating. This is not to be confused with the determination of total calcium and magnesium by means of this same reagent.

In a comprehensive collaborative study, reported in the July-August Agronomy Journal, this method was tried by 12 collaborators on 34 limestones. Results obtained by the collaborators varied but not more than would be expected of a group using a new method for the first time.

Twelve limestones selected from the 34 were incubated with 12 soils for various periods and readings of soil pH and of amounts of carbonate decomposed, or of lime requirement after incubation, were taken. These 12 were also rated by another EDTA reagent, the trisodium salt. Table 1 shows average correlations (r-values) of pH readings, 326 in all, with ratings by the two reagents and with the $CaCO_3$ contents of the samples. The averaging of the r-values was done by the "z" conversion as recommended by Snedecor. The ratings with the trisodium reagent correlated a little better than those with the disodium reagent. However, the percent of $CaCO_3$ predicted the activity in the soil about as well as the ratings by either reagent.

Table 1. "Averaged" correlations of activity ratings of limestones with Soil pH.

	28-39-Days	6 Months
Na_2 EDTA rating	0.85	0.81
Na_3 EDTA rating	0.89	0.90
$CaCo_3$ %	0.86	0.88

Table 2 summarizes the efficiencies of the two ratings and of the $CaCO_3$ content in accounting for the variations in soil pH and in carbonate consumed among the various limestones. The values in the table are coefficients of determination or the square of the correlation coefficient, and the range shown is that between results on the various soils. Ratings by the trisodium reagent appear to be slightly more efficient but the simple percentage of $CaCO_3$ is about as good. It would appear that the EDTA method, or some other, could be developed to a higher state of efficiency.

Table 2. Efficiencies of Ratings (Range of r^2 x 100)

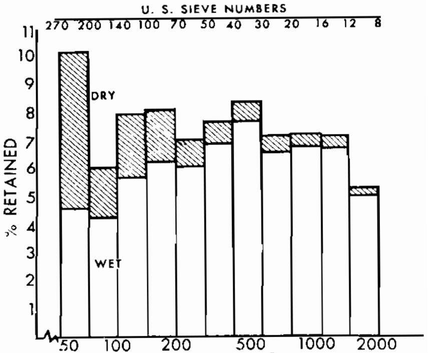
	Soil pH	$CaCO_3$ consumed*
Na_2EDTA	66 to 77	55 to 82
Na_3EDTA	81 to 83	61 to 89
$CaCO_3$ %	71 to 77	65 to 84

*Or lime requirements after incubation.

Wet Versus Dry Sieving

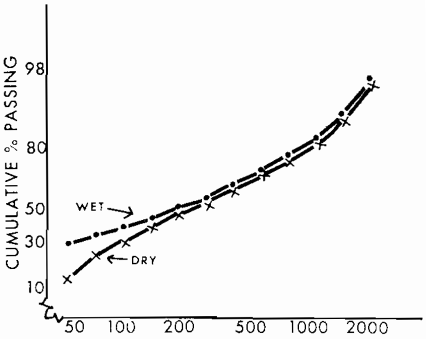
The question of wet versus dry sieving of agricultural limestones comes up repeatedly. Recently at Beltsville a study was made of the comparative results by the two methods on 30 limestones that had been chosen to give a range of magnesium content. These samples were (a) sieved dry in the conventional manner or (b) washed on a U. S. number 270 sieve, dried, and then sieved in the usual way. The latter procedure is referred to here as "wet sieving." Thirteen fractions were obtained in each case.

Figure 1* is a barograph illustrating the average results on the 30 limestones. As expected, the greatest differences were found in the finer fractions where the washing caused a great deal more material to pass. This may be attributed to the removal of very fine particles that tend to cling to larger particles and so do not appear in their proper size class, and to the slaking of aggregates that when unslaked would remain on the coarser sieve.



Average mechanical analyses of 30 agricultural limestones by wet and dry sieving.

Figure 1.



Average mechanical analyses of 30 agricultural limestones by wet and dry sieving.

Figure 2.

This is illustrated in a different manner in figure 2* where the average cumulative percent passing, a more commonly used method of expressing sieve analyses, has been plotted on a probability scale against the logarithm of the sieve opening in microns. On the average the method of sieving would not appear to be so important because the lines on the plot fall close together. Results on individual samples, however, varied widely. Figure 3* shows results on a Wisconsin limestone where the method of sieving would seem to be unimportant; but notice the wide differences on a Nebraska limestone shown in Figure 4*. Both these limestones are included in the average results shown in figures 1 and 2. Wet sieving would enable many limestones to pass particle

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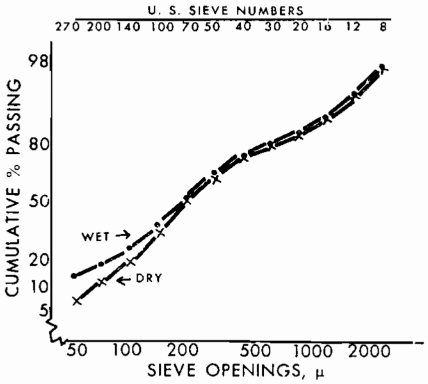
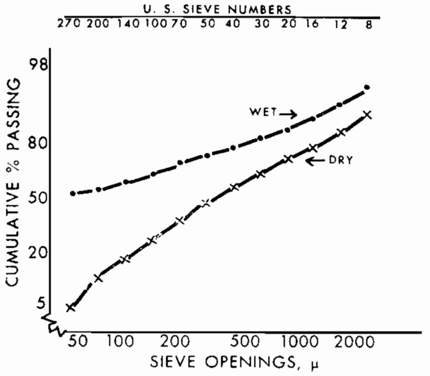
*Figures 1 through 5 are reproduced from the Journal of the Association of Official Agricultural Chemicals.



Mechanical analyses of a Wisconsin limestone by wet and dry sieving.

Figure 3.

size specifications that would otherwise fail.



Mechanical analyses of a Nebraska limestone by wet and dry sieving.

Figure 4.

The prewashing of the wet sieving may also increase the $CaCO_3$ equivalent of between-sieve fractions as shown in figure 5*.

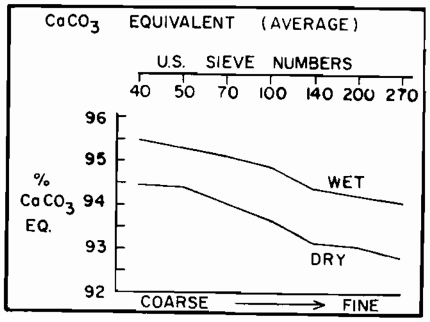


Figure 5.

This effect is probably due to the removal of some of the noncalcareous impurities in the prewashing. Since the determination of the $CaCO_3$ equivalent is normally made on the unsieved sample the method of sieving would have no effect on the value obtained. Washing of the limestone prior to marketing, if economically feasible, would however, enable some samples that would otherwise fail, to pass the minimum $CaCO_3$ equivalent requirement.

Gehrke and Johnson recently reported that some limestones that have been wet as in outdoor storage and then dried, tend to aggregate so that less passes the numbers 40 and 100 sieves. Addition of clay followed by wetting and drying had the same effect.

It would appear that wet sieving, with its greater reproducibility and more accurate estimate of all the fine particles, including those resulting from the slaking of aggregates, could well be a more realistic guide to the reactivity of a limestone than dry sieving.

Particle Size Specifications

This group is aware of the widely varying particle size specifications for agricultural limestone in the various States where the stone is handled under the Agricultural Conservation Program. The American Society for Testing and Materials now has a subcommittee on agricultural liming materials that is considering standard specifications and methods of testing. Dr. Stanley Barber of Purdue University, a member of that committee, has suggested five grades of agricultural limestone to be based on percentages passing the numbers 40 and 100 sieves, and a minimum $CaCO_3$ equivalent. These suggestions will be discussed and probably voted upon at the next meeting of the Committee in February. I shall not discuss these except to note that the Committee is anxious to get the views of as many interested persons as possible. It is hoped that the activities of this ASTM Committee will be a step toward the standardization of limestone specifications.

Slags

Blast furnace slag has long been used for soil liming but never in any great volume. The volume annually used in agriculture at the present time, some 69,000 tons, is about a quarter of one percent of the total processed slag. Studies are now in progress on the use of this slag, mixed with soil, peat, or sand as a subgrade for golf greens and lawns. This, of course, is hardly a liming operation in the usual sense. The per acre rates of application are many times what would be used for routine soil liming. I recently saw greens growing on these slag subgrades at Penn State. They looked very good.

Some 13,000,000 tons of open hearth slag are produced annually. About half of this is returned to the blast furnace for recovery of additional iron, but the other half is available for agricultural or other uses. We understand that a process for the granulation of open hearth slag is now being successfully developed. This should greatly facilitate the use of this slag in agriculture both for soil liming and as a phosphorus carrier. Experiments are underway on the use of both the air-cooled and granulated forms of this slag for soil liming and for other purposes at the New Jersey, Ohio, and Indiana Experiment Stations and perhaps at some other points. At Purdue it is being tried as a source of manganese in areas deficient in that element.

A recent arrival in the field of agricultural slags is low carbon ferrochromium slag. A byproduct of the production of low carbon ferrochromium, this slag is now being produced at the rate of about 100,000 tons annually. Many thousands are used annually for soil liming. This is a "falling" or disintegrating slag that breaks up into a fine powder as it cools due to a change in crystal form. Grinding or granulating is thus not needed. Ninety eight percent of the test sample passed 200 mesh. Table 3 compares the composition of the slag with that of a blast furnace slag and a high-calcium limestone. The data are for individual samples analyzed at Beltsville. Note the high $CaCO_3$ equivalent of this slag that makes about 1700 pounds of it equivalent in neutralizing power to a ton of pure limestone.

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*Figures 1 thriugh 5 are reproduced from the ournal of the Association of Official Agricultural Chemicals.

Table 3. Comparative Composition of Low-Carbon Ferrochromium Slag, Blast Furnace Slag and Limestone

	CaO	SiO_2	$\frac{CaO}{SiO_2}$	$CaCO_3$ Equiv.	MgO	Cr	
						Tot.	Sol.
	%	%	%	%	%	%	
Low-Carbon Ferrochromium Slag	55.0	25.5	2.15	117.9	9.2	0.88	.0015
Blast Furnace Slag	33.6	31.0	1.08	87.2	14.8	None detected	
High Calcium Limestone	(1)	(1)	—	99.2	(1)	None detected	

(1) Not determined.

The chromium content of this slag was a cause of some concern because of the possibility that chromium taken up by crops might be injurious to the crops, or render them toxic to animals. Recent experiments with corn and alfalfa at Beltsville, however, have indicated that the chromium is not taken up to any singificant extent by these two crops. No reports of chromium toxicity from the use of this material for soil liming have come to hand.

Cement Kiln Flue Dust

Approximately a million tons of cement kiln flue dust could be made available for use in agriculture annually. Table 4 shows the average composition of 21 dusts selected as being representative of the industry. Like the slag just described, it is a finely divided material. This dust has been used as a potash fertilizer. On the average however, its potash content is rather low for that purpose, although individual dusts may have potash contents up to 13% K_2O. Tests at Beltsville have indicated, however, that it is an excellent soil liming material, with the potash and sulfur contents as important plus values.

Table 4. Average composition of cement kiln flue dust

Lime (CaO)	45.04%
Magnesia (MgO)	1.97%
Total Potash (K_2O)	4.54%
Soluble Potash (K_2O)	2.85%
Silica (SiO_2)	15.43%
Sulfate (SO_3)	6.60%
$CaCO_3$ Equiv.	82.36%

DISCUSSION LEADER HILL: Thank you, Dr. Whittaker.

We have a few minutes for questions.

(No response.)

We are getting pretty smart these days and want liming materials analyzed. We used to determine the calcium carbonate equivalent and felt pretty well satisfied with that. Then, we began to state the amounts of calcium and magnesium. Now, people want to know how much of other things are there. Hence, we have an analytical job. Of course limestone carries a complement of micronutrients and I suppose the day is coming when we will have to determine the micronutrients as a routine chore.

Mr. Chichilo will describe the status of analytical methods for the odd elements in limestone and tell us some of the things he is doing.

Method of Analysis of Liming Materials

P. P. Chichilo

Introduction

MORE than 23,000,000 tons of agricultural liming materials are being applied annually to soils of the United States. The main objectives of these applications are to neutralize soil acidity and to supply calcium and magnesium. However, most liming materials are not pure calcium and magnesium compounds and in the application of these materials other elements which have agricultural significance, are being added to the soil.

Table 1 shows the tonnages of elements added annually to United States soils by the application of agricultural limestone. These elements are not spread uniformly over the land because of great variations in the composition of limestones. Through liming, some areas may be receiving enough of certain elements to meet crop needs, while in other areas, the amounts present in limestone may have no significance.

As fertilization and liming practices are put on a scientific basis, detailed knowledge of the total composition of such materials becomes desirable. At the suggestion of the Association of Official Agricultural Chemists we have been investigating methods for the determination of aluminum, iron, manganese, phosphorus and titanium in silicate and carbonate liming materials. The aim of the study is to select methods which are rapid, accurate, and suitable for routine use with ordinary laboratory facilities. Colorimetric methods seem most suitable at this time.

Table 1.
Tons of Elements Added Annually to Soils of United States Farms by the Use of Agricultural Limestone.

Element	Tons Added	Element	Tons Added
Calcium	6,900,000	Sodium	6,900
Magnesium	1,100,000	Fluorine	5,300
Silicon	540,000	Phosphorus	4,800
Aluminum	100,000	Zinc	710
Iron	98,000	Vanadium	250
Potassium	52,000	Boron	92
Sulfur	25,000	Copper	62
Manganese	7,600	Molybdenum	14

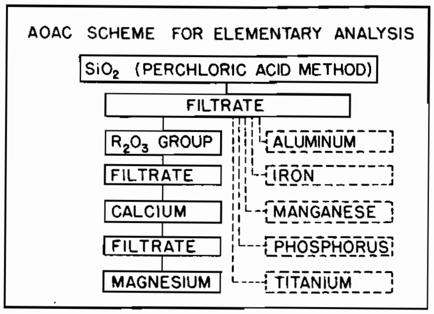


Figure 1.

Analysis of Liming Materials (Percent)

Material	Al	Fe	Mn	P	Ti
Limestone 1a	2.23	1.07	.035	0.60	.104
Dolomite 88	.05	.07	.003	.001	.005
Limestone 145	1.38	.87	.039	.027	.077
Blast Furnace Slag	6.53	.46	.668	.002	.235
Cement Kiln Dust	2.74	2.10	.140	.023	.158

Figure 2.

Methods of Analysis

Figure 1 shows where the methods selected fit into the Official Scheme for the analysis of liming materials. The Official Scheme is indicated by the solid lined blocks on the left.

In this scheme silica is dehydrated with perchloric acid. The R_2O_3 group and calcium and magnesium are determined in the filtrate from the silica separation. This same filtrate is used as the sample solution in the present study of colorimetric methods for aluminum, iron, manganese, phosphorus, and titanium.

Bases for the methods are: formation of a colored "lake" by aluminum with ammonium aurintricarboxylate (Aluminon); formation of an iron derivative of 2, 4, 6-tripyridyl-s-triazine (TPTZ); oxidation of manganese salts to permanganates with potassium periodate; reduction of molybdophosphoric acid to a heteropoly blue product; and formation of a chelate complex by titanium and disodium-1, 2-dihydroxy benzene-3, 5-disulfonate (Tiron).

The adequacy of the directions in the methods was established by the use of ruggedness tests. In these tests variations were made in the amounts and order of addition of reagents, duration of heating time, rate of cooling, etc. After the ruggedness tests were completed, liming materials including: limestones, blast furnace slag, and cement kiln dust were analyzed using the methods selected. National Bureau of Standards standard limestone samples were used to check the accuracy of the methods.

The following is a brief outline of the methods being studied.

Aluminum: — Transfer an aliquote of sample solution (<80 μg Al) to a 100 ml vol. flask and dilute to 20 ml with water. Add 2 ml thioglycolic acid solution (1% solution), 0.5 ml antifoam solution and 10 ml aluminon solution. Place the flask in boiling water for 20 minutes, cool and make to volume. Measure transmittance at 525 mμ and determine aluminum by referring to the standard curve.

Iron:—Transfer an aliquot of sample solution (<100 μg Fe) to a 100 ml vol. flask. Add 3 ml hydroxylamine hydrochloride solution (10% solution), 10 ml TPTZ solution, and ammonium hydroxide to a permanent violet color. Add 10 ml sodium acetate buffer solution and dilute to volume. Measure transmittance at 593 mμ and determine iron by referring to the standard curve.

Manganese: — To an aliquot of sample solution (<500 μg Mn) in a 150 ml beaker, add 25 ml of acid mixture ($HNO_3 + H_3PO_4$) and 0.3 g. potassium periodate. Bring to a boil and keep at boiling temperature for 10 minutes after the color appears. Transfer to a 50 ml vol. flask, cool, dilute to volume, and mix. Measure transmittance at 525 mμ and determine manganese by referring to the standard curve.

Phosphorus:—Transfer an aliquot of sample solution ($<75\mu$g P) to a 100 ml vol. flask. Add 5 ml ammonium molybdate solution, 5 ml hydrazine sulfate solution, and dilute to 70 ml. Place flask in boiling water for 9 minutes. Cool and dilute to volume. Measure transmittance at 827 mμ and determine phosphorus by referring to the standard curve.

Titanium: — Transfer an aliquot of sample solution (<75 μg Ti) to a 50 ml beaker and dilute to 25 ml. Add 5 ml Tiron solution and ammonium hydroxide dropwise until the solution is neutral to Congo red paper. Transfer to a 50 ml vol. flask, add 5 ml sodium acetate buffer and dilute to volume. Add 25 mg of dithionite and measure transmittance at 410 mμ within 15 minutes after the addition. Determine titanium by referring to the standard curve.

Results

Figure 2 shows the results of the analysis of five liming materials using the methods just outlined. Aluminum and iron are relatively high in liming materials. Aluminum ranged from 0.05% in dolomite to 6.53% in blast furnace slag. Iron ranged from 0.07% in dolomite to 2.10% in cement kiln dust. Manganese ranged from 0.003% in dolomite to 0.67% in blast furnace slag. Phosphorus and titanium are relatively low in these samples.

The methods for these five elements are now being subjected to a collaborative study among several laboratories.

Other Work

Finally, I would like to call your attention to a colorimetric method for silica which is more rapid than the classical gravimetric procedure and is more convenient for large numbers of samples. In this colorimetric method, the sample is fused for 5 minutes with sodium hydroxide. The melt is dissolved in dilute acid. A complex is formed between silicic acid and ammonium molybdate. This silicomolybdate complex is reduced to molybdenum blue and the transmittance of the solution measured and compared to standards. The colorimetric method was studied collaboratively among eleven laboratories in 1962 and is now an Official Method.

(Applause.)

Discussion Leader Hill: Thank you, Pete.

Any comments, questions?

(no response.)

I have a question. What is the interest in titanium in limestone?

MR. CHICHILO: We determined titanium just to have a picture of the total composition. If you determine calcium, magnesium, silica, iron, aluminum, manganese, phosphorus and titanium, you can account for 99.5 per cent of the sample.

DISCUSSION LEADER HILL: Some 15 years ago there was a rising interest in the use of radiophosphorus as a means for labeling phosphate fertilizers for use in field tests. A production program was started in a very, very small way about 1948 in Beltsville. The peak of interest was passed around 1952 and has fallen irregularly through the years until it is now pretty small business. There is still a sizeable number of people scattered around who feel the need for labeled fertilizer to conduct the experiments they have envisioned.

Mr. Wieczorek has been running the production show for the last 10 years. He will now tell you a little something about what he is doing and how the business is going.

Experimental Fertilizer Production at Beltsville

G. A. Wieczorek

TODAY you have heard of some of our work on nitrogen, phosphates, lime, micronutrients and many other things. We are also engaged in the preparation of numerous laboratory test preparations on a small scale, including those containing radioactive phosphorus.

About 1946 there was a mounting interest in the use of isotopes in medicine, industrial work, and in agriculture. About that time word went around that the atomic reactor could produce as byproducts many of the physiologically essential elements in quantities sufficient to do a reasonable amount of testing, and there were a number of meetings held here in Washington. A group of industrial and government men met and formed a committee and our Vincent Sauchelli, I believe, was the first chairman. They worked out the financial backing and research planning for the beginning of the broad program.

A decision was made at that time to centralize the work at Beltsville because of the hazards of the isotopes, the necessary regulations and authorizations, and waste disposal problems. It was also desirable to strive for uniformity of the radioactive, physical, and chemical properties of the materials, particularly those to be compared with one another. Licenses were issued by the Atomic Energy Commission on a project basis for awhile, and then on an annual basis to a radiological committee within the Department of Agriculture.

Figure 1 is a production record of the annual output in pounds of P_2O_5, a total of all the materials. It can be seen that initially there was a rather rapid increase in the output, because many of the experiments were on a large scale. Emphasis was on sources of phosphorus: superphosphate, monoammonium phosphate, calcium meta and other fused materials, and also phosphate rock. However, we were not able to use irradiated phosphate rock in agronomic experiments, because of the many different nuclides formed. Their presence greatly confused the interpretation of the results.

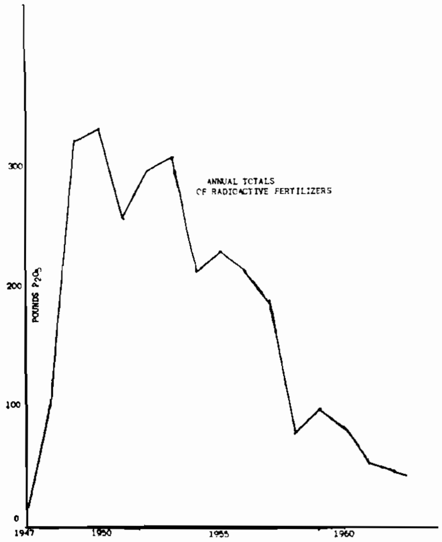


Figure 1.

About 1954 emphasis shifted to smaller experiments of better design. We began producing materials for uniform experiments and shipped them to several states simultaneously so that work could be done on a number of soils under different climatic conditions on one crop such as corn or grain. Then, interest shifted again to mixed fertilizers of higher analysis. Studies were made of variations in water solubility of the phosphate, differences in particle size, and the effects of adding nitrogen and phosphorus (simultaneously or alternately) on uptake and yield.

Recently, as Mr. Hill has said, interest in this country, has declined, though it has increased in foreign countries, particularly in water soluble materials such as ammonium phosphates. In the last couple of years we've shipped thousands of weighings of superphosphate by air to a group of cooperators under the auspices of the International Atomic Energy Agency. Studies were made of different types and rates of application in addition to irrigation practices for rice in Pakistan, Indonesia, the Philippines, Korea, India, and Hungary.

The plant occupies a small area at the west side of the Plant Industry Station. It consists of two 2-story cinder block buildings. The workers enter the plant and take off their outer clothing, and each puts on a special uniform, hat, faceshield, respirator, and shoes which are kept in the plant at all times. A film badge and sometimes also dosimeters are worn to indicate the amount of exposure received.

There are two main hazards incurred while working with isotopes. One is the radiation itself, which for P^{32} is a beta rediation, and the other is particulate contamination by ingesting dust.

Checks must be made continually on the total amount of radiation that each man receives, and frequent checks on dust concentrations. One of the tests is an analysis of the urine, which is done by precipitating the phosphorus and comparing the assay to that of a known amount of activity. The amount of P-32 that can be tolerated in the body is something like

10 microcuries, and the amount that can be breathed safely continuously is very, very small. In the room where the men change clothes there is a hand and foot monitor for checking possible contamination as they leave the plant.

The P-32 isotopes are supplied by the Union Carbide Nuclear Corp., Oak Ridge, Tennessee, as 'separated phosphorus', which contains no P-31 atoms, and in the form of H_3PO_4 dissolved in dilute HCl. The specific activity is quite high, but it is reduced at once by dilution to permit safe handling. The radio active solution is assayed by the supplier, and this permits quite close control of the specific activity of each batch.

For several years we were supplied P-32 as irradiated KH_2PO_4; we estimated the amount of activity it contained, and weighed the salt needed for each batch. Later on, the salt was supplied in an assayed solution. Now, sulfur is irradiated to produce pure P-32. Thus we have a supply of beta radiation uncontaminated with radioactive potassium, which is a gamma emitter.

The radioactive solution is delivered to Beltsville in a small bottle, centered in a tin can, which is in turn centered in a cardboard box. The package is opened behind a lucite shield, and the bottle is emptied and washed into a volumetric flask or directly into a container in which a batch is to be made. Large bottles of isotopes are placed in a lucite container which acts as a shield, and the solution is poured into shielded graduates. Close estimates of the amount of exposure per minute and the required time are prepared in advance of each operation.

P-32 is considered a moderately hazardous istope, and when ingested into the body it goes to the bone. It has a half-life of 14 days and an energy of about 1.7 million electron volts. This means that there is sufficient energy to permit experiments of considerable duration for crop work without having too high a specific activity at the beginning of the experiment. This is for our own protection as well as those who use it.

Figure 2.

Figure 2 shows the mixing equipment in which phosphate rock is acidulated with a tagged acid solution. Most of our requests have been for ordinary or concentrated superphosphate, or for materials in which one or the other is a source of the phosphate. Two operators work as a team, one or the other always monitoring with a beta-gamma survey meter.

The acidulations are carried out in an 8-gallon stainless steel can; the batch weighs about 15 pounds. The mixer rotates in one direction, the paddles in the other. We have experimented with different rocks, but mostly we have used a high-analysis, finely ground Florida rock. Some of the rocks which have come to our attention recently, such as those from Baja, California, Peru, and North Carolina, occur naturally in a rather finely divided condition. We have noted that fractions of the unground rock, such as the 100-150-mesh fraction, do not react nearly as rapidly as a similar fraction of the ground rock. Little or no difference in phosphate availability is noted after several days of curing, however. In the radioactive superphosphate, which we acidulate one day, cut out the next, then analyze, often ammoniate or incorporate in a mixed fertilizer, weigh field applications and ship, all within a week, we are concerned with the uniformity of the surface area of the phosphate source.

The curing oven operates at 70° C, with 90% of the air recirculated. It holds 6 of the 8-gal. cans. The cans are handled with a long bar with a cradle hook, to permit the man to keep his distance from the high activity.

Figure 3.

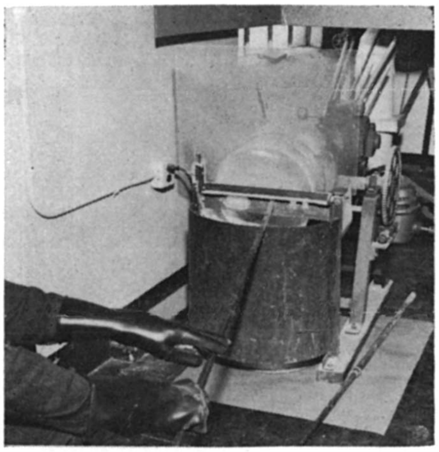


Figure 3 is a picture of the excavator. This is a framework into which a can of cured superphosphate is clamped. The frame is changed from a vertical to a horizonal position, and the can is rotated at about 40 rpm. A long bar with sharp edges is inserted into the center of the material and gradually moved outward to the edge. Thus the superphosphate is shaved into a hopper and falls into another can. The operator is protected by the upper lucite shield, through which he can see, and the lower metal shield which swings aside to permit removal of the canful of pulverant product.

All of our equipment is housed in masonite shielding with filtered exhausts. The exhaust pipes go out above the roof, and we frequently check for possible contamination of the outside atmosphere. This must be done also on water drainage from the sinks. In many of our preparations we have filtrates or some washing solutions, material overages, and paper trash which constitute the radioactive waste. This is stored in a shielded area through several half-lives before disposal in a designated area.

A disintegrator is used to further pulverize the superphosphate. It may not be completely cured, and it is difficult to grind superphosphate when it is not completely dry. The disintegrator is a stainless steel cylinder 18 in. diam., 12 in. long, with perforations in the outer surface equivalent to a No. 12 U. S. standard screen. There are about 30-35 pebbles, 1 in. diam., inside the cylinder, and they force the superphosphate through the perforations into a hopper which empties into a cement-type mixer on the floor below. The material is fed into the cylinder by means of a long-handled scoop, about ½ pound at a time. Infrared lights are mounted above the rotating cylinder, and they serve to dry the equipment if it should get clogged.

After the mixing operation, the material is stored in covered cans awaiting results of analyses. Based on the P_2O_5 content, the different weighings are made for the field applications.

Several other pieces of equipment are used for processing radioactive material. These include a V-shaped mixer, 1 cu. ft. capacity, equipped with a hollow tube in the axial position around which the mixer rotates horizontally. The tubing is perforated, and ammonia, steam, moist gases, etc. can be admitted from either end.

Materials of high specific activity are prepared in a hood which has three sliding panes of glass for frontal access. Inside there is a water bath in which a 10-gallon stainless steel can is mounted. Stirrers and blowers are provided for solution or air agitation, and the water bath can be operated from 0 to 100° C. Ammoniations, precipitations, and preparation of slurry mixed fertilizers are conducted in this equipment; also the production of small lots of individual phosphate salts, either soluble or insoluble in water. For example, tagged solutions of phosphoric acid or of a water-soluble phosphate are added dropwise to an agitated solution of a calcium or magnesium salt, or a lime slurry, with pH and temperature control. Ammonia is often used in these preparations. A suspension of dicalcium phosphate dihydrate is digested at 98-100° to convert it to the anhydrous form. Often the preparations are washed with acetone to remove excess water or phosphoric acid. Filtering is accomplished with the use of porous stainless steel discs, fritted glass, or porous clay tubes.

An evaporator for mixed fertilizers, which we call a grainer, and which was constructed by our shop, is seen in Figure 4. It is somewhat similar to the equipment in the hood but has a strong set of paddles that scrape the sides and bottom of the stainless steel can containing the batch. A small blower agitates warm air over the surface of the slurry, and a negative pressure is maintained in the enclosure by a strong blower which removes the evaporated water through a filtered exhaust stack. Infrared lights are mounted above the surface of the slurry to minimize the cooling effect of the evaporation.

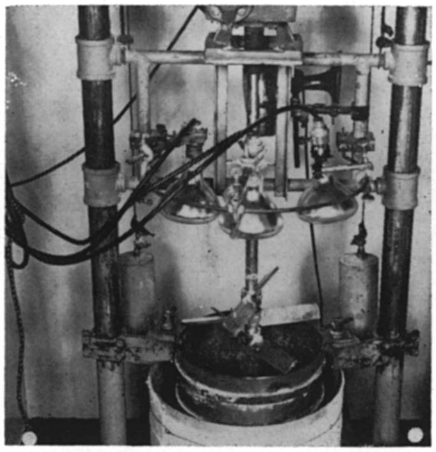


Figure 4.

Over the years we have had many requests from cooperators for mixed fertilizers with little or no variation in certain physical or chemical properties. However, they also wanted to know whether their tests were giving results close enough to those that would be obtained with the use of materials that were commercially available. We decided to make two kinds of slurry mixed fertilizers.

One we call the synthetic or mixed-salt type in which we start with pure, separately tagged dicalcium phosphate and/or mono- or diammonium phosphate. We then add other ingredients to give a series of mixed fertilizers in which a specific property such as the water- or citrate-solubility of the phosphate is varied stepwise. Combinations of nitorgen and potassium salts are used, and a filler which is usually diatomaceous earth. This filler does not contribute any appreciable differences in physical or agronomic effects as sand, clay, or limestone may do.

The other type is called the commercial type, since we start with a superphosphate, usually ammoniated, or an ammoniated nitric phosphate. Other salts and a filler are added to the slurry which is then evaporated to dryness. When the material is dry, it is ground in a hammer mill, mixed, analyzed, weighed, packaged, and shipped as pulverant material or it is granulated and reanalysed before shipment.

The granulator that we use is a simple framework on which stainless steel drums of different sizes can be mounted. The drum is rotated at about 30 rpm and can be tilted to any angle. Water is sprayed onto the tumbling mass of ground material. The operator stands behind a lucite shield and observes the course of the granulation; he uses long, thick rubber gloves to protect his hands and forearms. Some dry fines are kept until near the end of the spraying and are added to control the size buildup. Infrared lights are mounted around the can to provide some drying so the product can be screened and the yield measured. Further drying is usually necessary. Experiments on particle size require close control of chemical composition, so that 2 or 3 pre-runs are made to determine as closely as possible the conditions which give a satisfactory product throughout the particle size range.

In recent years there has been more uniformity among experimenters on the acceptable particle size spread. Six to twenty mesh is now widely used.

Variations in composition occur frequently among the various particle size fractions in a series in which many different fractions are represented. Some typical analyses are shown in Figures 5 and 6. Two sets of materials were prepared for experiments at Michigan State University. One series of the mixed salt type, 12-12-12 grade, was prepared at 6 different levels of water-soluble phosphate content. The ratio of the amounts of dicalcium phosphate and monoammonium phosphate was varied throughout the whole range. Results of analyses are shown in Figure 5.

12-12-12 Fertilizers
Mixed-Salt Type

Water-sol. P_2O_5 % of Total Intended range	Found	Total N %	Total P_2O_5 %	Total K_2O %	Granule size Mesh
0-3	1.8	11.4	12.6	11.7	4-6
	1.5	11.9	12.1	11.7	28-48
8-10	9.0	11.3	12.4	11.7	4-6
	9.1	12.1	12.2		28-48
18-20	18.0	11.0	12.7	11.7	4-6
	18.2	12.1	12.6	11.9	28-48
28-30	28.2	11.7	13.0	12.2	4-6
	29.6	12.0	12.1	11.8	28-48
40-45	41.2	10.9	12.0	12.0	4-6
	41.9	12.0	12.0	12.1	28-48
85-90	81.6	10.8	11.3		4.6
	81.6	11.5	12.1		28-48

Figure 5.

Results of analyses of a series of a commercial type of mixed fertilizer, ammoniated nitric phosphates in this instance, are given in Figure 6. The first member of the series, the low water-soluble one, is the true nitric phosphate. However this material always exhibits some water-solubility, because of the fact that some $NH_4H_2PO_4$ is formed in the ammoniation step, and there is some influence on the water solubility of the $CaHPO_4$ by the water soluble salts present. We have used magnesia to facilitate the preparations of materials of reproducible low water solubility.

A mechanized tablet machine is available for processing certain materials that are difficult to granulate, such as dicalcium phosphate or most of the water-soluble phosphate salts. Although the operation is not characteristic of commercial fertilizer manufacture, we have tabletted for tests in which it is desired to maintain close control of the weight of particle, or where a comparison is to be made among a large group of different materials of variable granulatability.

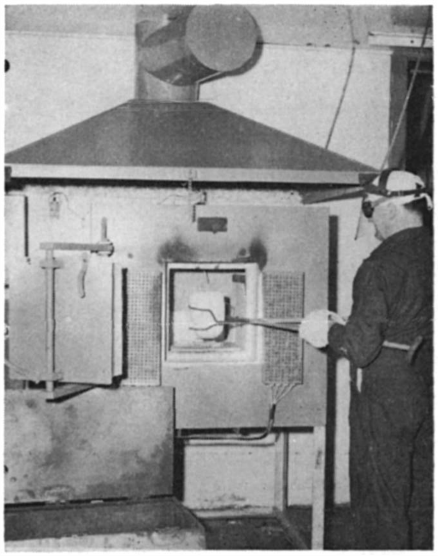
A series of tabletted materials was prepared and tested in the laboratory and greenhouse to determine the effect of soluble salts on the water-solubility of water-insoluble salts such as dicalcium phosphate. Most of the salts could be grouped into three distinct classes, depending on their effect, whether it was a severe effect on solubility, a moderate one, or a negative effect. Availability tests in the greenhouse were in good agreement with these results.

We also granulated a series of materials for the comparison of ordinary superphosphate with mixtures of dicalcium phosphate with either monoammonium phosphate or calcium sulfate in several different particle sizes. Rate of application and effect of the fixing capacity of the soil was studied; differences among the particle sizes were noted.

Figure 6.
Nitric Phosphates
Commercial Type

Water-sol. P_2O_5 % of Total		Available P_2O_5 % of Total	Total N	Total P_2O_5
Intended	Found		%	%
10	14.7	75.4	17.6	20.5
25	32.0	89.8	19.2	21.2
34	41.3	91.6	20.3	21.1
55	56.9	93.7	21.2	22.3
70	69.7	95.2	22.0	22.9
100	100	100	25.2	25.4

Figure 7.



An electric furnace is shown in Figure 7. It is heated by globar elements and is operated up to 1450° C. Calcium metaphosphate glass is tagged by adding alternate layers of ground $Ca(PO_3)_2$ and activity in a clay crucible and heating to 1100° C., holding for 30 minutes, and pouring onto a cold steel plate to quench. The glass is broken into fine lumps, and ground in a hammer mill to –40 mesh. Fused tricalcium phosphate is produced by preparing a charge consisting of a material with a CaO/P_2O_5 ratio of 1.40 and saturated with SiO_2, added in alternate layers with the labeling compound in a quartz crucible, and fusing at 1450°. The product is quenched by pouring the melt into an agitated water bath, broken up, and ground to pass a 40 mesh screen.

The large electric furnace holds 6 or 7 large crucibles each of 6 lb. capacity. We have two smaller furnaces which hold single crucibles, and a muffle furnace for heating platinum crucibles. Pyrophosphates and slags have been tagged on occasion.

After the radioactive materials are prepared and analyzed, they are weighed for shipment either in bulk amounts or in calculated portions for direct application in field experiments. The weighing operation is carried out in assembly line fashion. The first man stands behind a shield and removes some material from a can with a long-handled scoop.

He weighs into a weighing scoop on a shadowgraph scale, with an accuracy of ± ½ gram. The next man takes the scoop and dumps the portion into a mason jar, of ½ pint, pint, or quart capacity. A specially designed cap is used, which consists of a galvanized lid with porcelain insert, a round rubber ring without lip, and a cardboard disc which is waxed on one side. The waxed disc adheres to the jar top when the cap is removed, thus minimizing the possibility of dust coming out of the jar onto the user. The third man puts the capped jar into a cardboard telescope tube which he tapes and places into a cardboard carton for shipment.

The elapsed time between the receipt of isotopes at Beltsville to the date of shipping is usually 6 to 8 days. Since the half-life of P-32 is 14 days, and the user has his plants ready for the fertilizer as soon as it is received, significant results can be obtained for 3 or 4 months without the necessity of large rates of specific radioactivity during manufacture.

We have shipped something like 50,000 weighings in the 15 or 16 years of operation, and we have used about 230 curies and about 3,000 pounds of P_2O_5 during this period. There have been over 1100 separate shipments, generally in the spring of the year; and this is a good estimate of the number of experiments that have been conducted. There have been about 500 published papers reporting the results.

When the jars are received at their destination, they are again monitored, radiation levels are determined, and tests for contamination are made. A metering hopper designed by the Agricultural Engineering Division of the ARS is used to dispense each application onto a conveyor which is attached to a tractor. A uniform application can be made broadcast, in a furrow, or at a series of points.

Besides P-32 we use some other isotopes for agricultural research. One of them is S-35, with which we tag elemental sulfur or calcium sulfate. We also have used Ca-45 in calcium sulfate, and Sc-46 for tagging sand grains for work on the movement of sand particles in stream beds. A very high tagging rate of gamma activity was used. Gamma radiation is much more penetrating than the beta which is emitted by P-32. We use several different isotopes, rubidium, iodine, caesium, barium, and gold to tag fine glass beads for fallout tests.

The laboratory has been engaged in the preparation of numerous materials other than those containing radioactivity. Frequently we synthesize 100-lb. lots of mixed fertilizer, either slurried or dry-mixed. Sometimes commercial materials are used as bases to which other chemicals are added.

A few years ago a study was made of the effects of zinc compounds on the caking of fertilizers. A 4-12-12 mixed fertilizer was chosen for the tests, and zinc sulfate, carbonate, basic carbonate, or chelate was added. Slurry-mixing of all the ingredients resulted in a fertilizer which was non-caking until it was subjected to pressure such as in bag storage tests. The material was fine-grained, and when subjected to pressure gave cakes of rather high crushing strength. Ammoniation of superphosphate before incorporating it into the 4-12-12 reduced the caking. Use of ammonium nitrate increased the caking somewhat. Zinc chelates reduced the caking tendency.

Some work was done with coated fertilizers for control of rate of dissolution. We used road oils and similar materials, water glass, paraffins, and resins. It is difficult to characterize such materials.

We have added molybdenum in various percentages to superphosphate for work on alfalfa in the Southeastern States. Several mixed fertilizers were prepared for ion exchange studies, consisting of superphosphate mixed with calcium nitrate, ammonium sulfate, and potassium salts of the three mineral acids. These tests were also conducted in the South.

We have prepared glasses containing minor nutrients, and these have been incorporated into phosphates and mixed fertilizers for the study of effects of storage or of soil solutions on the availability of the glass components. At present we are working on the addition of elemental sulfur to concentrated superphosphate and to mixed fertilizers.

DISCUSSION LEADER HILL: Thank you, George.

One of the problems with the radioactive labeling work has been that you get ready to make 100-pound batches and folks want 5 pounds, or 500 pounds. The basic problem is to provide equipment of the right size to do the job we are asked to do.

Before presenting the next speaker I should emphasize two or three points that have emerged today, at least they have come to my mind as being the overall things that stand out.

If one compares our doings with the pattern of fertilizer business in the world, it will be seen that we have a very good standing in a good many particulars, but not in all particulars. We are not ahead in everything, and I think it is well that we realize that we are not. For example, we do not look so good on exports. Maybe some of the companies which you folks work for would like to change that; and perhaps if we get oiled up a little more, it will change.

Another thing is that fertilizers nowadays are being made for specific purposes. You are not just going out and making fertilizer and then trying to sell it, but you are making fertilizers for particular purposes. I think that's a good thing.

The last thing that I shall mention is that we have speeded up the production line. We have used automatic devices to produce our fertilizers, to run them through the line, but over in the control laboratory we are getting on with 50-year old methods and with 50-year old procedures. I am not thinking so much about analytical procedures, but we simply have not automated control procedures, and this is a job that management is going to have to do. I do not know whose fault it is that this feature has not received more attention, but it seems to me that updating control operation is a very, very important part of the business of making fertilizers.

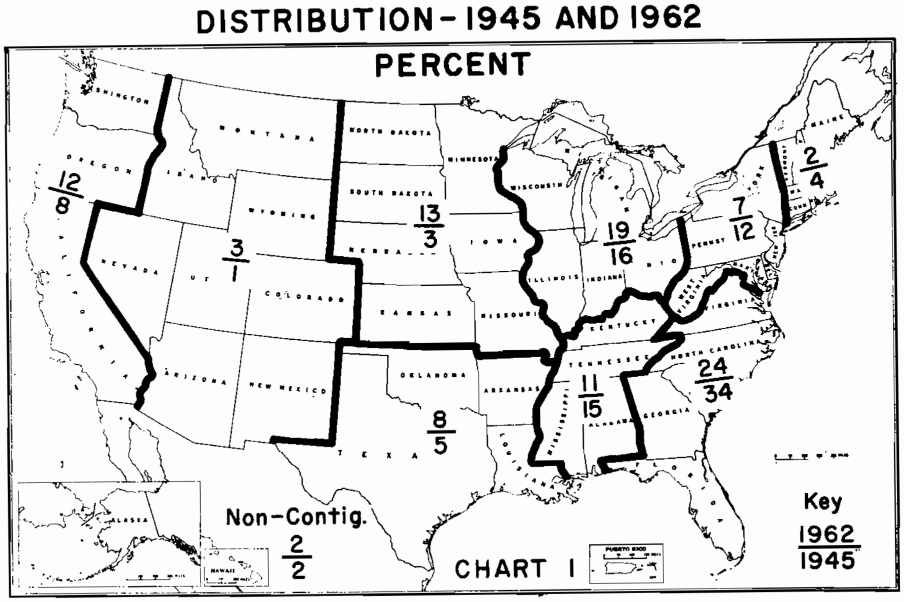
We have saved the best to last. The last speaker listed on the program is Mr. Scholl, but Mr. Scholl prefers to speak through Gordon Schmidt this afternoon. Gordon is Mr Scholl's running mate and what the one knows the other one knows. They speak the same language.

Trends in Fertilizer Consumption

G. W. Schmidt

DURING the next few minutes I want to discuss the different classes of fertilizers consumed, the proportions of nutrients in the fertilizers, the changes in the fertilizer materials and say something about the prices of fertilizers.

There are several approaches one can use in covering this. He could use the brassiere approach and cover a couple of points briefly, or use the slip approach and cover the whole subject lightly or use the girdle approach and cover the broad aspects of the matter. (Laughter.) I shall use the girdle approach.



This is a map of the United States showing the regional divisions which we use for showing our fertilizer consumption. I will be referring to these regions in subsequent charts. The first one in the upper right hand corner is New England, the next one down is the Middle Atlantic. The South Atlantic Region is located in the lower right section of the map. The East North Central region is next to the Great Lakes, and beneath this region is the East South Central. The area with the figures 13 over 3 is the West South Central. The Mountain region is west of these two and the last region on the left hand side of the map is the Pacific.

Each of these regions has a number above the line and one below. The upper numbers represent the percent consumption in 1962 and the lower numbers represent the percent consumption in 1945.

This chart shows that fertilizer consumption is shifting from the Eastern section of the United States to the West. In 1945, 81 percent of the total fertilizer consumption was used east of the Mississippi River; in 1962 only 63 percent was used in that area. The most decided change during the period 1945 through 1962 occurred in the West North Central region. Current consumption of all fertilizers in the West North Central region is 3,464,603 tons compared with only 462,265 tons in 1945. Fertilizer consumption is now higher in all regions of the U. S. except New England where consumption decreased slightly since 1945.

Chart 2 shows that more fertilizers are consumed as mixtures which are applied during the planting season followed by top-dressing materials. The greater spread in material consumption may partially be explained in that more materials, such as ammonia and nitrogen solutions are being used during the planting seasons. Also more materials used for bulk-blends are being reported as materials rather than mixtures. Consumption of fertilizer in 1962 totaled over 26 million tons — 16 million tons of mixtures and 10 million tons of materials. These tonnages represent an increase of 79 percent for mixtures and 137 percent for materials since 1945.

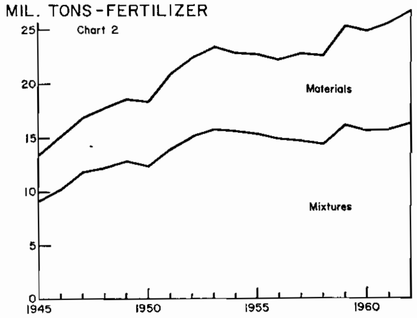
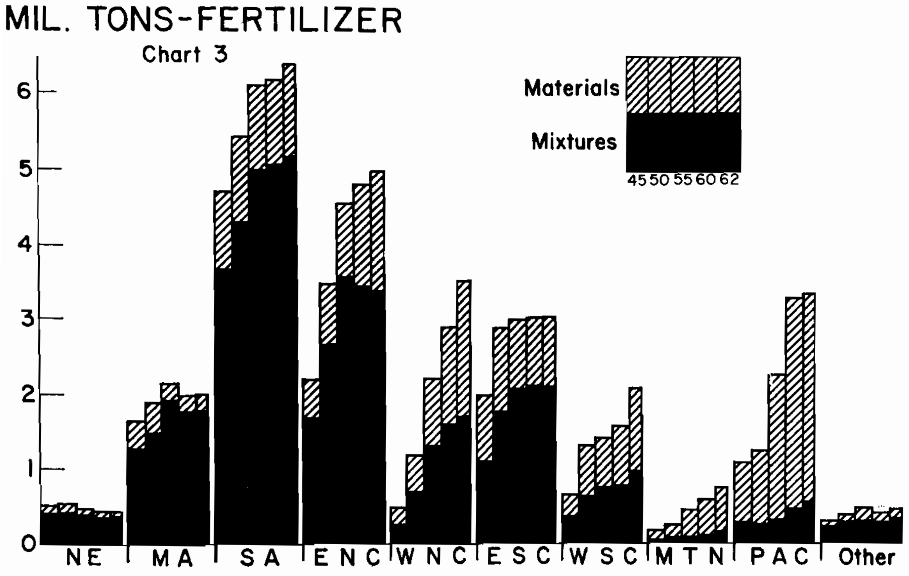


Chart 3 divides the national consumption by classes presented in the previous chart into regional consumption. Consumption in New England has generally decreased. During the period 1945 through 1955, there was generally a marked increase in all other regions. After 1955, regional consumption shows wide variations, some classes increasing and some decreasing. Mixture consumption has been about the same in the Middle Atlantic region since 1955. Consumption of materials in this region started decreasing in the early 1950's and has remained relatively unchanged for the last several years.

The South Atlantic region has consistently used the largest tonnage of fertilizer. In recent years the increase in mixture consumption has been slight but steady, al-



though not always exceeding the previous year's consumption. Changes in direct application material consumption have been insignificant throughout the period covered in this discussion.

In the East North Central region since 1954 mixture consumption has decreased slightly whereas consumption of materials increased. During the period 1945 through 1962 the greatest growth in fertilizer usage was in the West North Central region and was followed closely in the East North Central region. Consumption in these two regions, respectively, changed from about one-half million tons to about 3.5 million, an increase of 3 million tons and from 2.2 million to nearly 5 million, an increase of 2.7 million.

Not much change has taken place in the East South Central region since 1950 with either class of fertilizer. Consumption of both mixtures and materials has increased at a fairly rapid rate in the West South Central region. Mountain region consumption is still relatively low compared to other regions in the United States but shows increase in both classes. Direct application materials are increasing much more rapidly than mixtures in the Pacific region. Very little change has taken place in the noncontiguous areas with either mixtures or materials.

Chart 4 shows the increase in use of nutrients in mixtures in the United States. Available P_2O_5 has always been used in the largest proportion, followed by K_2O and nitrogen. One ton of mixed fertilizer in 1962 is equivalent to 1.5 tons used in 1945 as the composition of mixtures has shown almost continual increases in nutrient content. In 1945 the total primary nutrient content amounted to about 21 percent. In 1962 this had increased to about 33 percent.

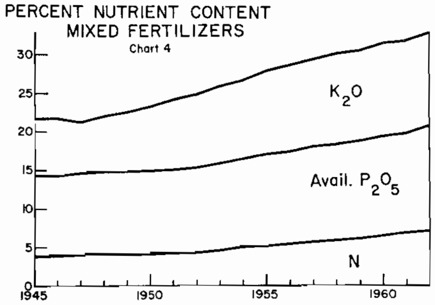
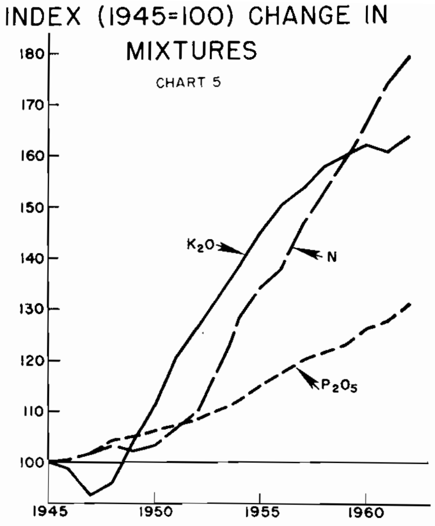
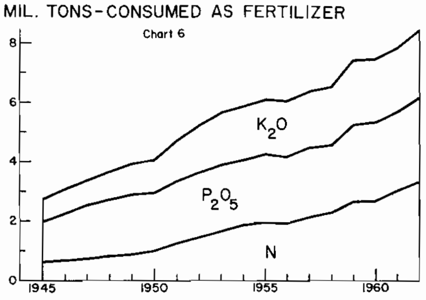


Chart No. 5 shows how the proportion of nutrients in mixtures has changed since 1945. In 1959, nitrogen surpassed the percentage of K_2O used in mixtures and has continued to be used in greater proportions since then. The percentage of available P_2O_5 used in mixtures has increased each year since 1945, but at a much slower rate. In 1962 the average primary nutrient content in mixtures was 7.01 percent nitrogen, available P_2O_5 13.48 percent, and K_2O 12.17 percent.



Nutrients in all fertilizers have increased considerably as shown in chart 6. Nitrogen increased continuously from 630 thousand tons in 1945 to 3 million 371 thousand tons in 1962. Tonnage of available P_2O_5 has more than doubled since 1945 and K_2O consumption has nearly tripled.



The next chart emphasizes the rate of nutrient consumption increase in all fertilizers. This index of nutrient consumption uses 1945 as the base year. The increase for nitrogen is greatest at 435. Available P_2O_5 at index 107 increased twofold from 1,353,027 tons to 2,807,039 tons in 1962. Index 211 for K_2O tonnage shows a three-fold increase since 1945 consumption of 729,439 tons to 2,270,537 tons in 1962.

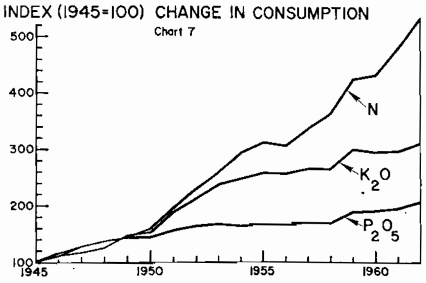
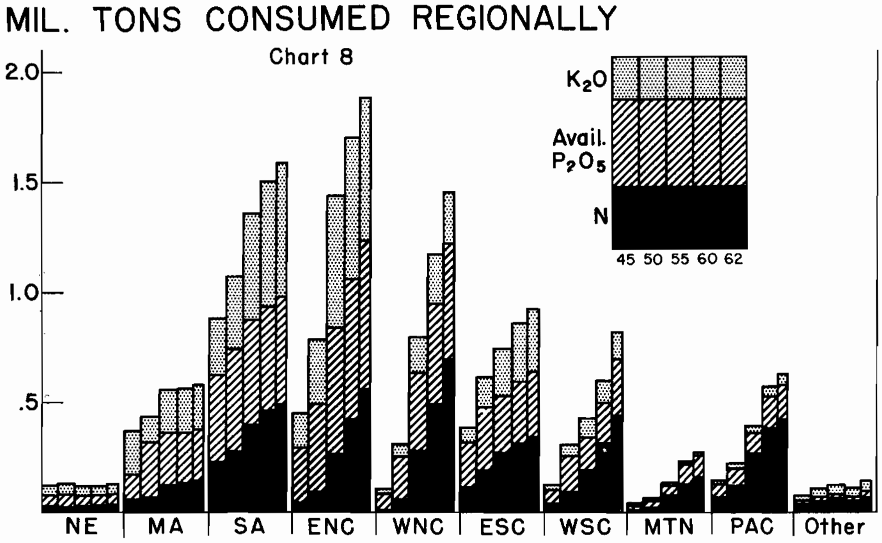
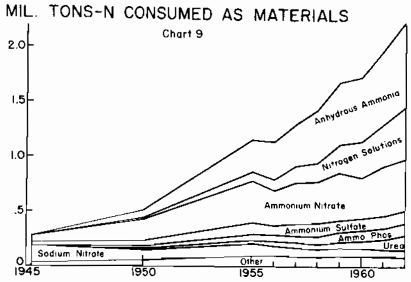


Chart 8 shows the use of primary nutrients in all fertilizers by regions. Years on this chart are by five-year intervals. Consumption of nitrogen has been increasing rapidly in all regions. In recent years the West North Central region has shown the most gain in nitrogen consumption. Seven hundred thousand tons of nitrogen were recorded in the West North Central in 1962. Current consumption of available P_2O_5 and K_2O is highest in the East North Central region.



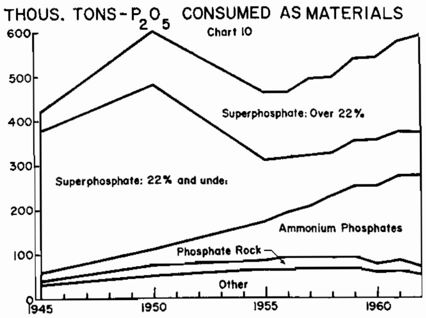
The increase of nutrients in mixtures and the increase of nutrients in all fertilizers has been shown. It is of interest to mention the more important direct-application materials used. Anhydrous ammonia consumption has increased rapidly as shown on chart 9. Ammonium nitrate has generally been a large supplier of nitrogen, but its rate of increase is much less than for anhydrous ammonia. Nitrogen solutions (including aqua ammonia) are increasing rapidly and the nitrogen tonnage now exceeds that of ammonium nitrate. The level of consumption of ammonium sulfate has dropped since 1957 and appears to have leveled off. Sodium nitrate has shown very little change for several years. Urea consumption has risen since 1958.

Tonnage of nitrogen in all other nitrogenous materials have remained about the same. These materials include ammonium nitrate-limestone mixtures, calcium cyanamide, calcium nitrate, the ni-



trogen in bonemeal, natural organics, phosphate and potassium products and other chemical nitrogen products.

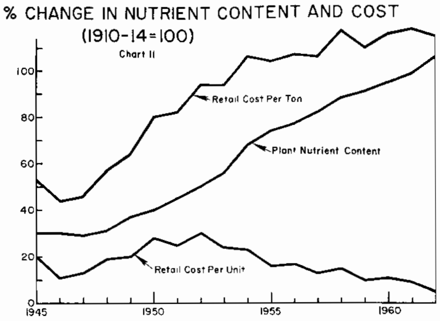
Chart 10 shows the use of some major phosphate products. In the past the majority of P_2O_5 from direct-application materials was supplied by normal superphosphate. Currently the major portion is supplied by triple superphosphate and nearly as much by the ammonium phosphates; that is 11-48-0, 13-39-0, 16-20-0, 27-14-0 and 21-53-0. There is very little change in the consumption of phosphate rock (including colloidal phosphate) and



other phosphate materials. Other phosphate materials include basic slag, calcium metaphosphate, phosphoric acid and the P_2O_5 provided by bonemeal, natural organics and other phosphate products.

I do not have a chart for K_2O direct application consumption. It has remained mostly unchanged. About 87.0 percent of the K_2O is supplied by potassium chloride, a little over 5 percent by potassium sulfate, around 4 per cent by natural organics and around 3 percent by other K_2O products.

The final graph shows the relationship of the retail cost per ton of all fertilizer with the average plant nutrient content and the retail cost per unit of fertilizer.



The percentages for the period shown is based on the years 1910-14 = 100. The top line on the graph represents retail cost per ton of fertilizer. The second line indicates that along with this increase in cost, the plant-nutrient content has generally paralleled this rise. The retail cost per ton was calculated by dividing the fertilizer expenditure by the farm consumption and expressed on the chart as percent change from the 1910-14 period. The average plant nutrient content was found by dividing the tons of plant nutrients by the total consumption (including secondary- and trace nutrients). Toward the ends of the top two lines, the space between them gets narrower. This is due to an increased use of lower priced, high analysis products going into the manufacture of fertilizers. A lower retail cost per unit results from an increased plant nutrient content as this was calculated by dividing the retail cost per ton by the percent plant nutrient content.

This covers my presentation, and if there are no questions or discussion I will yield control of the speaker's stand to Mr. Hill.

(Applause.)

DISCUSSION LEADER HILL: Thank you, Gordon.

Any questions or comments?

(No response.)

Hearing none, Mr. Chairman, our presentation has come to an end. I had very little to do with the organization of this program. The speakers deserve the credit. I was merely the expediter, who did as he was told. It has been a pleasure to be with you today. I hope you folks have gained as much from it as we have. I thank you for your attention and the opportunity of serving you.

(Applause.)

CHAIRMAN SAUCHELLI: As I said in my opening remarks, we were in for a treat and it has been a high privilege to sit through a presentation by the entire staff of the Fertilizer Laboratory, and we want to thank you very much Director Hill, and also the different members of the staff.

Are there any comments? This crowd certainly has been rather mute today. Our purpose, as I constantly have emphasized, is to have discussion from the floor, and we haven't had any discussion from the floor at all today.

Does anyone have any comments to volunteer or questions to fire at this round table group here?

(No response.)

Our Secretary tells me that the registration is 50 more than at this same time last year, but that the number of questions in that question box is still meagre. We need more questions for tomorrow afternoon's session. We want to make the question and answer period tomorrow as highly interesting as we possibly can, with your help, of course.

Since there are no comments and no questions, we stand adjourned until tomorrow morning at nine o'clock sharp.

(Applause.)

(The meeting adjourned at four-fifteen o'clock p.m.)

Thursday Morning Session, Nov. 7, 1963

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

J. E. Reynolds, Moderator, presiding.

MODERATOR REYNOLDS: Good morning. I think we might as well get started, everyone is ready to go and we're right on time, and our schedule that we maintained yesterday we will try to carry on through today and give you some time for discussion in the halls, corridors.

Since the Round Table began, we have discussed many subjects and highlighted many themes, but the one subject which has carried through from one year to the next is instrumentation and more specifically liquid and dry feeding equipment for continuous processing.

Other more immediately popular subjects have been discussed, dropped and reviewed at a later date but not so the subject of meters and scales. Process design and operating techniques have changed with great rapidity during the years and perhaps instrumentation, specifically for our industry, the fertilizer industry, is still catching up.

In any event, the expenditures for process improvements are not directed towards the major pieces of equipment but are concerned with improved control of liquid and dry raw material feed systems.

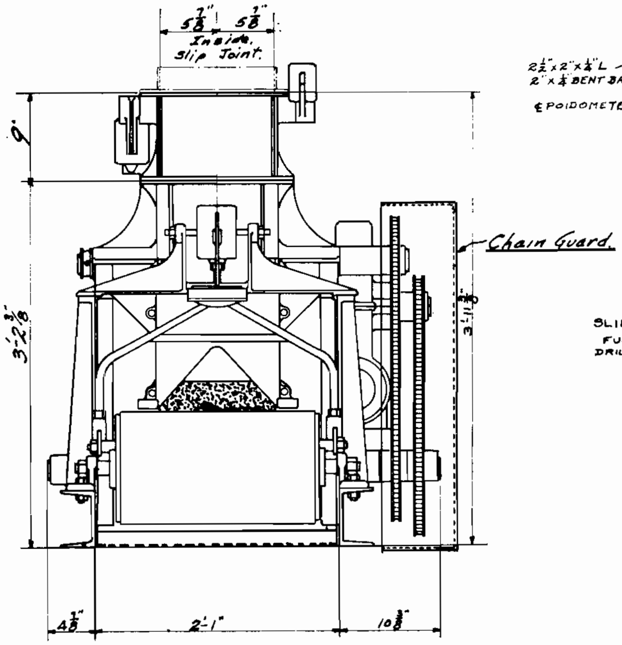
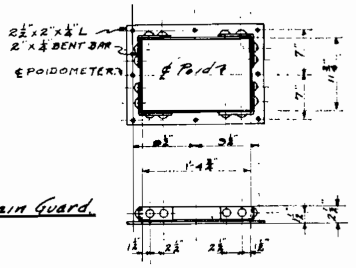


Figure 1.



SLIP JOINT FOR 20" POIDOMETER FURNISHED BY CUSTOMER - 9/16" HOLES DRILLED TO SUIT POIDOMETER HOPPER.

Figure 1A.

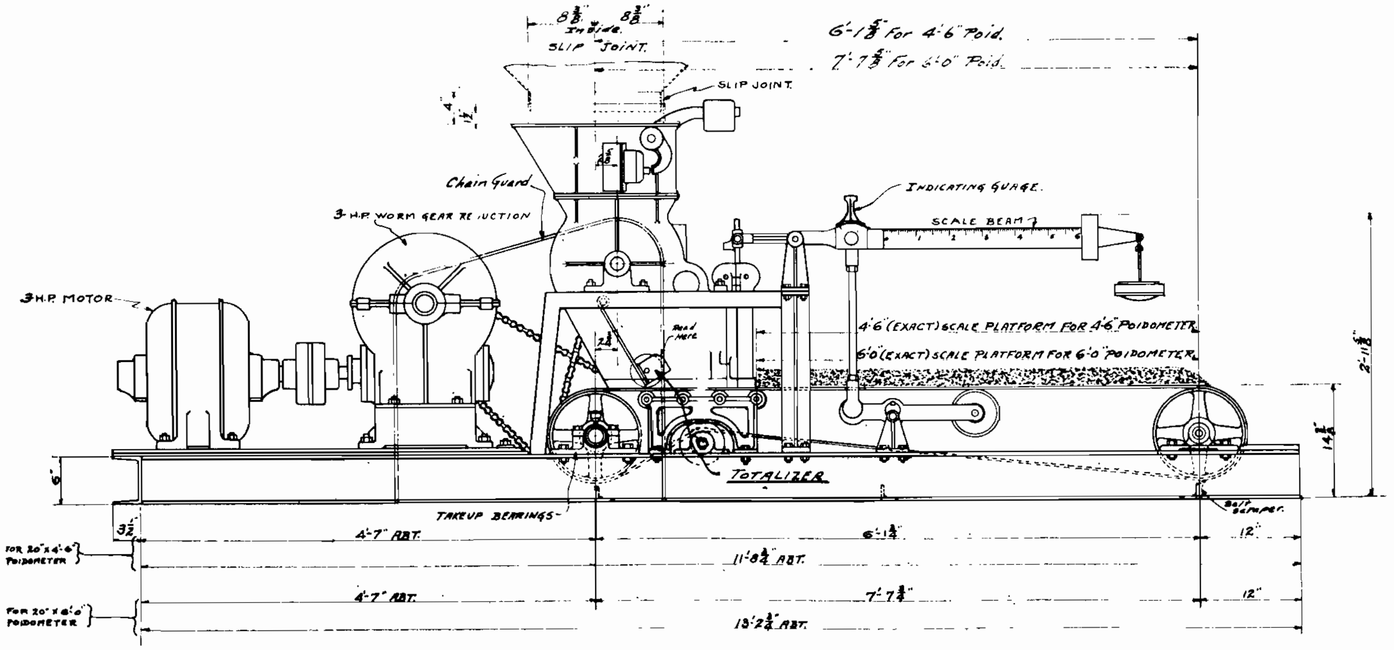


Figure 2.

Scales and proper weights have often been described as the backbone and vital nerve center of our industry. Without scales, either for calibrating or actually weighing. we are lost, completely lost.

Considerable progress has been made in all phases of instrumentation but have our plants actually kept pace with improved accuracy and control of our dry feed systems? The most accurate continuous feeder is no better than the preventive maintenance and the system for assuring its accuracy.

Our first speaker this morning is one of two gentlemen we are very familiar with who have been on our program in the past and they are coming again before us to discuss the hows and whys of calibrating and maintaining continuous feeding scale systems.

Schaffer Poidometer Continuous Weighing Systems

A. F. Cooke

Thank you, Mr. Reynolds; gentlemen.

We are not using slides because we feel that we can better interpret our Poidometer with this line drawing. Figures 1, 1A, 2.

Before I start, I would like to introduce the man that I call Mr. Poidometer. He is vice president and secretary of the Schaffer Poidometer Company and I am sure that many of you know him.

George Weiland, stand up, please.

Actually, he knows more about Poidometers than I do, but he says he's not used to making speeches, so it's: —"Al, you do it."

The Schaffer Poidometer is a gravimetric feeder, as opposed to a volumetric feeder. It feeds by weight any free-flowing, dry material.

The Poidometer has a simple weighing platform which runs from the idler roller to the tail pulley. The Poidometer shown in figure 2, has a scale platform of 4 feet, 6 inches; suspended in the middle is the weighing roller.

This weighing roller is hooked up by a series of mechanisms to the scale beam and to a gate which rides up and down inside the gate Box. Figure 1.

Very simply, you put the weight that you desire on the scale beam, that weight representing the amount of material per foot of belt. Then, the material comes down through the hopper (the hopper, figure 1A, on the Poidometer may be connected directly to your bin with a slip joint) and out over the scale platform. If you have set, let us say, 10 pounds on the scale beam, and nine pounds come out, the series of linkages will raise the gate, and vice versa; if 11 pounds come out, it will lower the gate. This control enables us to guarantee at least 99% accuracy,—sometimes better if all conditions are favorable.

I say it's simple; it is. One of our mottoes is: "Set it and forget it." We don't mean to forget it completely because any piece of equipment requires maintenance, but we think that this requires the least maintenance that is possible, but it does require an understanding of the machine so that you know just what you are supposed to get and what you are supposed to do.

We like to suggest that you make sure the machine is clean, that the knife edges are kept clean, and renewed when they become dull.

We like to suggest that the scale beam be kept clean and that it doesn't have a lot of dust hanging on it, since this will affect the weight.

We like to suggest that your rollers not collect dust, because, this, again, may affect your accuracy in your weighing.

I would like to call your attention to another thing, the ruggedness of this machine. It is built on the heavy, six inch ship channel. It is heavy all the way through. In fact, to go back a little, if I may digress, I would like to tell you that this Schaffer Poidometer is the oldest gravimetric feeder in the world. The first machine was built way back in 1912 and it has been built and sold ever since then. It has been improved, of course, as the years have gone along, but the principle has stayed the same.

We feel that this machine is simple, rugged and easy to maintain. We export a number of these machines, and one of our customers who exports them to the mountains of South America has told us "We like your machine because when it is installed in the mountainous areas of Peru, for instance, we do not have the machinists and the mechanics we have in the United States, we may have one man that's a mechanic, the rest of them are laborers. We like your machine because it required very little maintenance, it's very simple and even an Indian in Peru can operate it with a little bit of instruction."

Now, when it comes to testing this machine — Incidentally, before I tell you that, let me tell you that we build this, of course, in several sizes. We have what we call a heavy duty machine which is built on this six inch channel, which has a four-foot-six platform and we build a light duty machine which has a two-foot-six-inch platform.

The light duty and the heavy duty may have the same width belt. Incidentally, we designate 20 inch machine because it has a 20″ wide belt, a 30 inch machine has a 30 inch wide belt and a 10 inch machine has a 10 inch wide belt, and so on.

We build a 20 inch light duty and a 20 inch heavy duty machine. The reason for the light duty machine is that very often the capacity that is needed is only about half, or less than half, what a heavy duty machine will take, and, of course, we can build the light duty at a lower price, and while it is not as rugged as the heavy duty, it still stands up because it is not handling as much material.

If, when this machine is put into a plant, and you want to check it to make sure that your scale beam is in balance,—place a certain weight on the scale beam (either this slide weight or a weight on the weight hanger) and with a four-foot-six-inch machine, put two and a quarter times that amount of weight over this weighing roller and the Poidometer should be in perfect balance.

In other words, all you need to do is to put a weight two and a quarter times the weight that you have up there and that will balance your machine. You don't need a chain or anything else. That's all you need.

When we test the machines in our shop before shipping them, and we think this is even better, we run a certain amount of material over the belt, 10 feet or 20 feet, and then weigh it and check against the scale beam setting.

The testing is very, very simple. There's not much to it, but it will give you the actual weight that you are getting from the machine.

There are a few refinements we have made on the Poidometer. For instance, we have a little gate here, with a push button that comes down here, and as long as there is material being fed through the machine this gate is pushed forward so that the arm remains off of the push button. If, for some reason, the material from your bin into our Poidometer should fail, this gate will slide back and the arm will contact the push button and stop the Poidometer. It will stop it with material on the belt so that when you run again, you still have a full load on the Poidometer.

If you have two or three machines operating together, and if they are wired together, when one stops, all stops, therefore your mixture does not vary.

The drive end can be furnished to your specifications. In years past we have generally furnished a motor and a reducer. We can furnish you a motorized reducer, we can furnish you a variable speed motorized unit, we can furnish you any type drive that you want.

Now as far as maintenance is concerned, we have a number of things that we suggest that you do. First of all, the belt is endless, and that belt is made to our specifications by one of the rubber manufacturers. If your belt should wear out and you buy a piece of belting and put it together with the usual type of stitching you have destroyed the accuracy of that machine. You must have an endless belt that is uniform throughout.

This is one of the things that needs replacing occasionally, depending on the abrasiveness of your material and the sharpness of it. If it is more or less uniform material, the belt will last for a long time.

The only other item that needs replacing occasionally are the knife edges which are in this area that connects the linkage. There aren't too many of these, five sets to a machine; five knife edges and five knife edge bearings. They must be sharp and they must be properly maintained as far as cleanliness is concerned.

Another thing we get orders for occasionally is the bearings that are used in this machine. The Poidometer is ball bearing equipped, except the bearing on the pulleys. The head pulley and the tail pulley are equipped with bronze bushings, and after trying various types of bearing material, we find these are very satisfactory.

Actually, with the exception of those few items, replacements are practically nil, because, if the machine is properly kept, properly cleaned, properly taken care of, it is simple to maintain, and there is very little wear.

The installation of the machine is also rather simple. We send it to you on skids, partly crated, and all you need to do is to be sure that it is level when you build your piers or mounting. It must be level both this way and that way.

Then after it is level, make sure that your scale beam weight balances the weight that you set on here, and that is about all there is to it.

Now, we have a rather simple method of keeping a record of your run. We have here a Durant Productimeter whic his again built to our specifications, so it is dust-tight. It registers a foot of belt travel, and all you need to do at the end of the day is multiply the number of feet of belt travel by the weight up here on the scale beam, and you have the number of pounds or tons that have run.

In case you want this to register in tons we can furnish a Productimeter with such a recording.

Agitators are placed inside the hopper in case you have material that might stick in the hopper, or that might not flow very readily.. These agitators will keep the material flowing.

Again, as I say, if you give the normal maintenance that you give any piece of equipment, there is no reason why you should have any trouble with it, and there is no reason why it should not give you the accuracy that you desire.

If you are sure that it is properly set, that the weights balance, that it is level, this Poidometer should last for a long time and give you just the accuracy you desire with as economical a maintenance program as necessary.

MODERATOR REYNOLDS: Thank you, Mr. Cooke.

Do we have any questions? We have a few minutes here.

A MEMBER: Mr. Cooke, you have three or four capacity machines?

MR. COOKE: Three or four capacities, yes. We have—our smallest machine is a six inch which is a light weight, then we go to a ten inch heavy duty and light duty, a 20 inch heavy duty and light duty, a 30 inch heavy duty and light duty, and a 36 inch heavy duty and light duty.

We have also built a 48 inch heavy duty machine. I'm sorry, the 30 and the 36 do not have the light duties, the 30, 36 and 48 are the heavy duty machines. The range of capacities for these machines runs from about a ton per hour on the six inch Poidometer to about 350 tons per hour on the largest Poidometer.

Are there any other questions?

A MEMBER: What was the bottom range you said?

MR. COOKE: One ton per hour is about the minimum. This is a continuous operation 24 hours a day. If we get down below one ton we are a little afraid of the accuracy because the machine is not small enough.

One thing I would like to tell you is that this machine is being used in the cement industry as well as your fertilizer industry, and there are a number of them out in this industry. It is being used in the process industry, it is being used by the refractory people, such as General Refractories and Harbison-Walker. It has been used by a few concerns for filling railroad cars. They will set it to feed 40 tons into a railroad car, 50 tons or whatever that car will take and we furnish a cut-off, and when the 40 tons is reached the Poidometer stops, and the railroad accepts the weight of the car.

Moderator Reynolds: I have a question. How often should the machine be calibrated while it's in use?

Mr. George Weiland: It depends on how accurate *you* really are. I would say that at least once a week a mechanic should go up and check these various things and make sure the knife edges are pointed straight up and down. You can look in the machine here where each knife edge is and you can see whether it's vertical. If it is sort of lying to the side, then it isn't set properly.

Moderator Reynolds: What I was referring to was actually while you are, as in our case, granulating mixed fertilizer and you have your dry feed coming across the feeder. How often should the amount being fed across the feeder be checked?

Mr. Weiland: It wouldn't hurt to do that once a day.

Moderator Reynolds: Is that sufficient?

Mr. Weiland: Yes.

Moderator Reynolds: One time a day?

Mr. Weiland: What they can do there very easily is just take two pieces of sheet metal 12 inches wide, just cut down on the belt, scrape that off onto a little scale pan and weight it. It only takes a minute.

Moderator Reynolds: I think the industry is checking it much more frequently than that. That's why I was wondering. If once a day is sufficient, then we are doing an awful lot of unnecessary work.

Does anyone have any comment on this feature? Are you all only checking your dry feed once a day?

Mr. Albert Spillman: Joe, I have a comment.

We have a number of Schaffer Poidometer scales in several of our plants and we have a hopper above the scale which holds five tons. Any time we wish we can measure that five tons. We do it about three or four times a day.

Mr. Weiland: That again depends on how accurately you want to check your feed.

Moderator Reynolds: What is the accuracy of the Poidometer?

Mr. Weiland: 99 per cent. A lot of places it's even better than that.

Mr. Cooke: May I make a remark there?

Moderator Reynolds: Certainly.

Mr. Cooke: On accuracy, we have found in our shop, when we have tested these machines before shipment, we have been able to get 99.5 per cent. But don't forget what you get out in the field depends on conditions which are a little different than they are in our shop. They're actually perfect there, and so we will not stick our neck out and guarantee 99½ per cent. You may get it, but 99 is as far as we'll go, but they can get more than that.

Moderator Reynolds: In other words, what you are saying is plus or minus one per cent. I think that with liquid meters and so on they are coming down to stay within a half of one per cent, so you have one that is a half of one percent and one that is one per cent and you have some difference there between the two of them.

I think we should move on to our next speaker and after the next speaker we can come back if we need any followup.

Moderator Reynolds: Our next speaker will continue this discussion of dry feeding. Don Warren of Omega Scale has been with us before, so it is good to have him back and we will turn the program over to Don.

Omega Gravimetric Feeders in Formulation of Fertilizer

D. L. Warren

FIRST of all let's consider some desirable features to look for in a gravimetric feeder. It should be as accurate and sensitive as it can be made, while bearing in mind that it must offer a decent service life. The weigh belt should be driven positively by some sort of drive which will not allow slippage. The feeder should be supplied with a variable speed drive on the belt for changing rate. This allows a direct-reading totalizer. It offers the opportunity to use a constant heavy belt load which will be in a range of weight which will allow the scale section to operate at the most efficiency. The control gate should be operated by supplemental power and not depend on actual weight changes on the beam through leverage. The parts in contact with the material should be stainless steel. The finish should be corrosion resistant. The unit should be suitable for installation several ways, even the unorthodox ones, such as suspension from overhead structures by steel rods.

A few installation tips: Avoid excessive vibration, although some vibration will help. It seems to keep the feeder "loose." It helps to keep the various moving parts freed up. On the other hand, it should be isolated from excessive vibration which would be imparted to the unit, or its mounting structure from heavy conveyors, shaker screens, pulverization equipment, dryers, ammoniators, etc. A bin gate between the feeder and the hopper makes a lot of sense. If maintenance has to be done, such as changing a belt, it is very desirable to be able to isolate the feeder from the hopper. Always leave room to change the belt, catch samples and do routine maintenance around the unit. We realize that frequently the feeder has to be installed in an existing building where space is at a premium, but please bear in mind that your own maintenance man and, if you have a service engineer from B-I-F, are probably not former acrobats with the Barnum and Bailey circus.

They should have some means of approaching the feeder without having to hang from rafters, or stand in a pay loader.

Here is a must: The feeder should never be mounted directly over the ammoniator. The atmosphere found in a fertilizer plant with its corrosive vapors and abrasive dusts is bad enough by itself, please don't accentuate problems by allowing it to be directly exposed to the fumes and dust from the ammoniator.

Various methods of hopper agitation, such as plate agitators, pulsing sides of hoppers or pulsing air bladders may be used. Of, course, a vibrator is effective, too, but should never be used in a manner which would allow it to maintain vibration only when the feeder is running. It should at least be integrated with the feeder switch so that it cannot vibrate when the feeder is shut down. Better than this, a system of using a contactor on the feeder belt which would give a shot of vibration at certain intervals of feeding should be used. This could be further improved by the addition of a timer so that the frequency as well as the duration of the "shot" of vibration could be controlled.

Some sort of screen directly above the inlet chute is important. Many times fertilizer will build up in the corners of a hopper, become caked and then shake loose and drop down into the unit. This doesn't work very well. After all the gravimetric feeder is not a rock crusher.

Here are a few comments on calibration: Take a little time to read the instruction book. We realize that this is a breach of code for some people, but believe me it helps.

When calibrating the feeder I would like to propose the DWT theory (distance, weight and time) for calibration. This is very simple arithmetic and it goes like this: The poise on the scale beam is set to a certain value. This will determine the actual weight per unit of belt. Then with a variable speed drive the belt speed is changed for different rate requirements. Then lastly we check the number of units of belt we require per minute, so there is your formula. Distance or units of belt travel, weight which is the amount of product on a unit of belt and then units of belt per unit of time. When calibrating the unit is is well to take these separately. The first thing to do is set the poise on the desired unit of belt and in this case we recommend loading the belt as heavily as possible. The Omega scale can be set anywhere between 5 and 36 lbs. per foot and I would recommend a minimum of 20 lbs. per foot of belt because after all the scale is more accurate near the top of its capacity than near the bottom. After setting the poise the feeder should be run until it is controlling nicely. Then a sample should be caught. We would like to see at least 10 units of belt, or in this case, of course, 200 lbs. caught. If, however, this is not feasible catch as large a sample as you can. If 10 feet are run off and the sample weighs between plus or minus 1% of 200 lbs., and it does this three consecutive times then the weighing is all right. If it varies more than 1%, but the three weighings are still within 1% of each other this means that you are controlling all right, but the tare has to be adjusted until the output agrees with the poise setting. If, however, the three samples are not close together then you should start looking for trouble in the scale system. Look for friction in the system, a broken flexture in the weigh deck, a worn knife edge, perhaps a frozen bearing or looseness in the linkage from the weigh deck to the controller. After the load is established and the feeder is controlling at the correct setting per unit of foot it is very simple to go to the variable speed drive, set up the rate and check out through the use of the totalizer the units per minute so that the speed per setting can be calibrated over the range of rates required. This can be set up on a chart and expressed as lbs. per minute, tons per hour, whichever is more suitable for your operation.

Once a feeder has been checked out using the material weighing technique then it is a simple matter to make up some test chains, such as ½ or ⅝ inch coil chain which can be hooked on to the feeder for use in calibration. This is not quite as accurate as live samples, but is very good for a quick check.

On maintenance scheduling, of course, it should be obvious that the cleaner the feeder can be kept the better it is going to run. Of course, we realize these are not sitting in a nice clean doctor's office, but are in a fertilizer plant and therefore, recognize that it will always have a certain amount of dust and sticky materials in it and on it, but a few points to note in cleanliness are: the bottom of the side plates which can score and cut a belt if the material is allowed to build up on the bottom side, the area on top of the weigh decks, the area around the scale beam and scale leverage system and the area around the control gate.

As far as the chains on the side of the feeder belt are concerned, we highly recommend the use of the silicone grease prior to start up if possible, but in any case, after start up, because this extends the life of the chains tremendously. Note, we do not recommend regular grease because I can think of no better grinding compound than a mixture of fertilizer and grease and this would cut the chains out rather rapidly, but the silicone grease seems to get in there and do a good lubricating job while actually preventing the entry of dust.

In figure 1 we show the Model 37-04 Omega B-I-F Feeder with the various covers removed. On the left side you will notice a handwheel with the rate indicator attached. This controls the output speed of the variable speed drive which, of course, controls the belt speed. The unit can be furnished with a 0-100% setting, or a direct reading rate setter which can read in lbs. per minute, tons per hour, kilos per hour, etc. Moving to the right and higher we notice the gate raising and lowering mechanism and this gate is powered in both directions and does not depend on gravity to close. The cables are 1,000 lb. test stainless steel. Next to the right is our Sens-A-Gram mechanical controller which offers good accuracy and sensitivity and correction proportional to deviation. Looking inside through the top you will notice the stainless

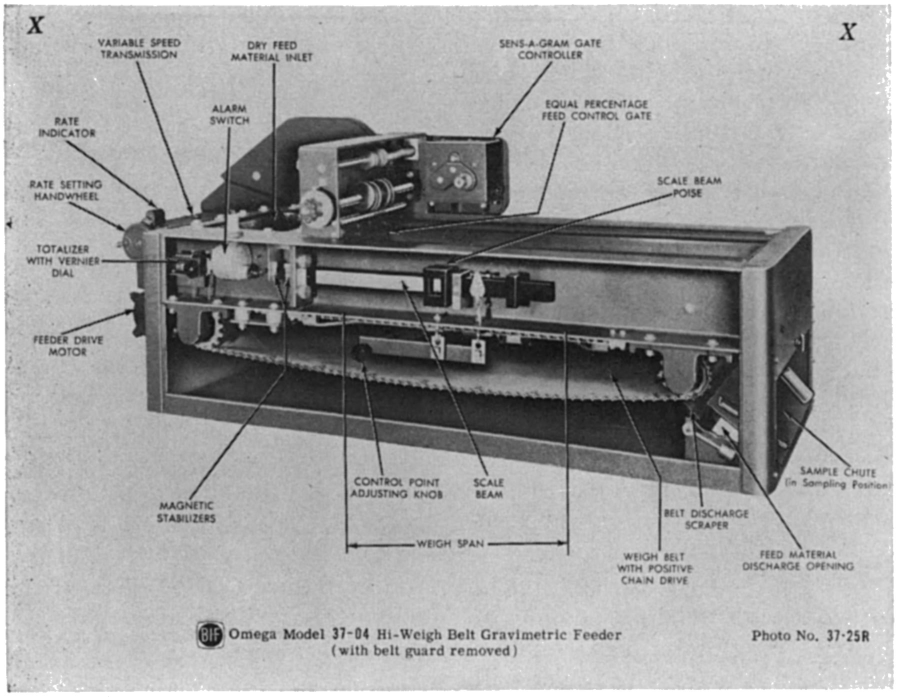
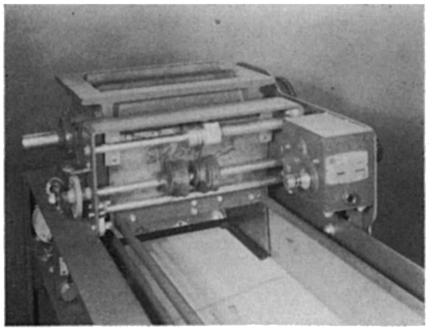


Figure 1.

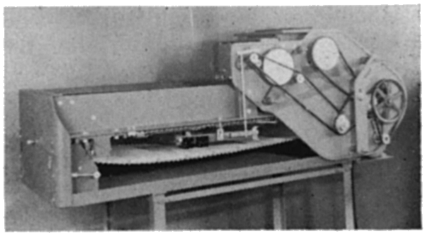
steel side plates which guide the material along the belt. Be sure these are adjusted with the discharge end slightly higher than the inlet end. Moving back to the left in the scale compartment you will notice the totalizer which actually reads in belt feet, but through sprocketing can be set up to read directly in lbs. Next is the alarm system. The alarm works directly off the scale beam which is the fastest and most effective way to do this. When the material supply is cut off the scale beam immediately drops and the alarm switch closes. Next are the adjustable magnets which are the stabilizers for the scale system. Next is the scale beam itself with the adjustable poise. The scale reads 0-36 lbs., but again we recommend loading it up as high as possible. Our rule of thumb for setting this up is to use a weight roughly equivalent to ½ cubic foot per foot of belt because that is the volumetric limitation. If, therefore, we were feeding dry fertilizer mix which would weight 50 to 60 lbs. per cubic foot we could easily carry a 20 lb. load, or 25 lbs. Next to the right is the adjustable tare weight and then dropping down to the belt compartment you will notice the sealed bearings, the sprocket drive, the belt with the attached chain, part of the scale leverage system and over to the right the discharge end sprockets. On the far right in the end of the feeder is the flop gate which enables samples to be caught.



Hi-weigh Feeder—Top View Showing Sens-A-Gram, Ton Tex Belt and Feed Gate Mechanism.

Figure 2.

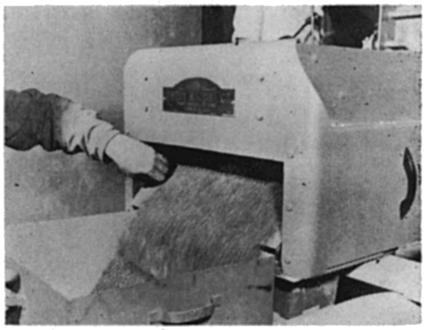
Figure 2 shows a closeup of the gate mechanism with the equal percentage drums which allow the gate travel to be approximately proportional to the opening. When the gate is operating down at a fairly low position the increment of change for a certain amount of correction is smaller than when it is wide open. This makes for a more stable feeding and less fluctuation. This particular one shows a non-flood rotor which we use when feeding rock dust. The rotor is driven by the output of the variable speed drive giving us a volumetric non-flood control directly ahead of the gate. This means its speed is proportional to belt speed. About 10% of the material is recirculated in the rotor and the gate takes care of trimming it out to the actual desired gravimetric rate.



Hi-Weigh Feeder — Side View With Chain Guard Removed.

Figure 3.

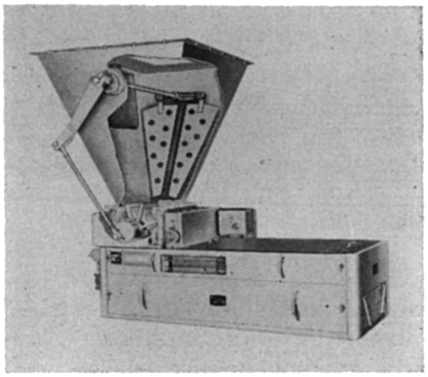
Figure 3 shows the drive compartment which is covered with a heavy duty fiberglass chain guard. You will note that all the components are driven by a roller chain so there is no possibility of slippage throughout the system. This also shows the linkage between the scale beam and the Sens-A-Gram controller.



Hi-Weigh Feeder—End View of Sampling Gate Open Discharging Feed Into Sampling Bin.

Figure 4.

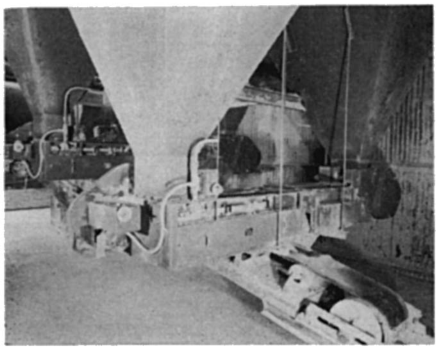
In figure 4 you can see the sample gate, or flop gate in action.



Omega Model 37-04 Hi-Weigh Belt Gravimetric Feeder (With Hopper Agitators and Rotolock.

Figure 5.

Figure 5 is a complete view of the 37-04 with the phosphate rock dust arrangement. The top of the hopper can be seen with a 9″ x 15″ access hole so that the feeder can be attached underneath the large supply hopper, or can be fed with some sort of a conveyor when feeding floodable materials like rock dust. We never want the feeder directly imposed or mounted under huge bins. We recommend a restriction between the supply bin and the "working" bin or hopper attached to the feeder. Over to the left or rear of the hopper you will notice a baffle and this is set up so that as the pockets of the rotor below rotate and fill with material the air in the pocket is allowed to go back up the baffle and not up into the material which would cause excessive aeration. On the back side of the hopper you will notice a pair of perforated plate agitators and there is a pair on the front side as well not shown. These oscillate in direct proportion to flow because they are driven off the same variable speed drive that drives the belt and the rotor. This makes a moving wall and effectively prevents arching, bridging and rat holing. The rotor itself as mentioned earlier will control flooding and furnish a volumetric supply ahead of the gravimetric gate.



Omega Model 37-20 Hi-Weigh Belt Gravimetric Feeders Feeding Various Dry Fertilizer Ingredients Onto A Conveyor Belt. This System Accurately Proportions the Dry Ingredients For A Granulation Process.

Figure 6.

In figure 6 we show an actual installation in a fertilizer plant which was installed in the Midwest about seven years ago. There are four feeders, one on superphosphate, one on triple super, one on potash and one on either recycle or solid nitrogen, depending on the formula. These feeders have had a rough life, but received a reasonable amount of maintenance and have given excellent service over the years. I'd like you to notice a sort of an outline above the variable speed transmission and on the back of the chute below the hopper. That is the angle of repose of fertilizer, gentlemen, the feeder was actually covered up with that much fertilizer and I brushed it off and also brushed a good deal of it out of the scale compartment before these pictures were taken. Perhaps I should have left it on to really show these feeders in their "working clothes."

In summary, I would like to say that with a minor amount of housekeeping and a little common sense maintenance the feeder will give you a long and accurate service life. Keep a good load on the belt and don't change it. Make all your changes by using the variable speed transmission when different rates are required. When catching samples catch your weight per unit of belt, don't ever bother with a stop watch until everything else has been brought in to the required accuracy and remember the DWT system of calibration — distance which is actually units of belt travel, the weight which is the actual lbs. of material per unit of belt and finally, time which is done last and entails taking the number of units of belt obtained per minute at the various settings on the variable speed drive.

Thank you.

A MEMBER: Don, have you done anything to keep the scale from building up, the use of Teflon or anything of that nature?

MR. WARREN: No, we haven't used any Teflon. We have used a thin stainless collar which has been applied to that with good success.

MEMBER: We have seen it with Teflon used, but the hygroscopic material will get built up on it.

MR. WARREN: That's a good idea, though. We've had questions about the chain, the chain will freeze up sometimes after the feeder has been shut down for a while and we have found that this silicon grease, I think it is made by Dow, will prolong the life of the chains.

I know that just ordinary grease is not very good because I can't think of a better grinding compound than grease mixed with fertilizer, but this silicon grease seems to stick down in there where it belongs and keep the dust out, and it is, of course, a very good lubricant.

I am talking about the chains which are attached to the belt.

A MEMBER: One thing you didn't mention that we have found contributes to inaccuracy is the build-up on your screen. You showed the stainless skirting. Have you ever considered Teflon on the skirting or using Teflon?

MR. WARREN: No, we have not considered using Teflon on the side plates, but it sounds like a good idea to me.

We have a model which we have been furnishing for the field which has a Teflon barb edge on it and that probably could very well be applied to these fertilizer feeds.

MODERATOR REYNOLDS:

Thank you very much, Mr. Cooke, and, Don Warren.

The foregoing discussions were concerned primarily with improved and assured control of dry raw material feed to a continuous process system.

Further control is often needed to check the tonnage of production going to the bin, to the storage bin. If overs or shorts occur when a bin is emptying, we often ponder whether the raw materials were weighed and metered properly, the plant food shrinkage was excessive, or if shipping weights could have been off.

A continuous weighing scale to check the indicated tons produced would provide a check point in our investigation to at least substantiate the tonnage of material which entered the bin to begin with.

Our next speaker, Mr. Dave Kennedy of the Toledo Scale Company, will discuss the subject of continuous weighing of bulk materials to storage bin.

Continuous Weighing Bulk Material On Conveyor Belts

David W. Kennedy

A SCALE is a bottleneck! A scale is a bottleneck in any production process. It is a consumer of space—of time—of labor.

Yet a scale is where I measure my production, where I count my dollars, where I meet my customer.

Many of you gentlemen have had these thoughts. These two conflicting sets of thoughts, these disadvantages and advantages of this very necessary piece of measuring equipment; it is these thoughts that have created the demand for a scale that provides weight measurement without being a production bottleneck. The answer is the totalizing belt conveyor scale.

Definition

Let's define this kind of scale. First, it is not a rate measuring device; it does not measure or control pounds per unit time. Rather it totalizes, we sometimes say *integrates,* the weight of bulk material that has passed over it. A typical example of such a totalizing belt scale is now shown on the screen. Figure 1. Notice the basic parts: weighbridge for weight sensing, belt speed pickup, and totalizing scale head with per cent of belt loading indication.

Legal Status

Now that we have defined this scale equipment, a more important matter to you is its legal status. The importance lies in the fact that the legal status of this equipment is not the same as that of a common dial or beam scale, and it is in a state of transition.

In most States scale equipment used only as a production tool is not subject to any form of inspection; it is a internal measuring device and has no legal status. However, where a commodity is bought or sold over a scale, the scale acquires a legal status which is governed by one or more legal and/or quasi-legal bodies. It then must meet specified accuracy requirements.

There is a variety of these governing bodies, so we will limit our discussion to those of concern to your industry. First among these are the State and local Weights and Measures authorities. These are agents of their respective governments and have full legal authority including condemnation of faulty equipment. Their accuracy standard is normally ± 1/10% and their other requirements are generally based upon National Bureau of Standards Handbook 44.

The other group of concern to you is the Railroad Bureaus. The railroads have established Weighing and Inspection Bureaus to supervise and contract for Weight Agreements with private and railroad-owned scales. These Bureaus are concerned with the tariff determination of commodities and materials shipped or received by rail. They have the right of approval of scale equipment both as to type and specific performance. There are four Bureaus and they have divided the nation geographically. The requirements of the Bureau appear to be in a state of transition.

What accuracy can be expected from a totalizing belt conveyor scale? Here we have a classic case of *caveat emptor*—let the buyer beware. Be sure that when you discuss accuracy with a vendor of such equipment that you have a clear definition of what is being discussed. A common habit is to discuss *instrument* accuracy rather than *installed* accuracy, and on this type of scale operating conditions affecting accuracy are of greatest importance: for example, on our own equipment we guarantee instrument accuracy of ± 0.2% but installed accuracy is ± 0.4%, and this latter is on approved installations only. These percentage figures are based upon full capacity, as is normal on single range scales. The factors affecting installed accuracy will be discussed later in this talk. Anticipated installed accuracy of belt totalizing scales will vary from ± 0.4% to ± 2% on approved installations, depending upon the make.

Generally the integrating belt conveyor scale will not meet the legal accuracy requirements for a buying or selling situation; in fact, from the figures given you so far, this would appear to be universally true. Yet we have said some of these requirements appear to be in

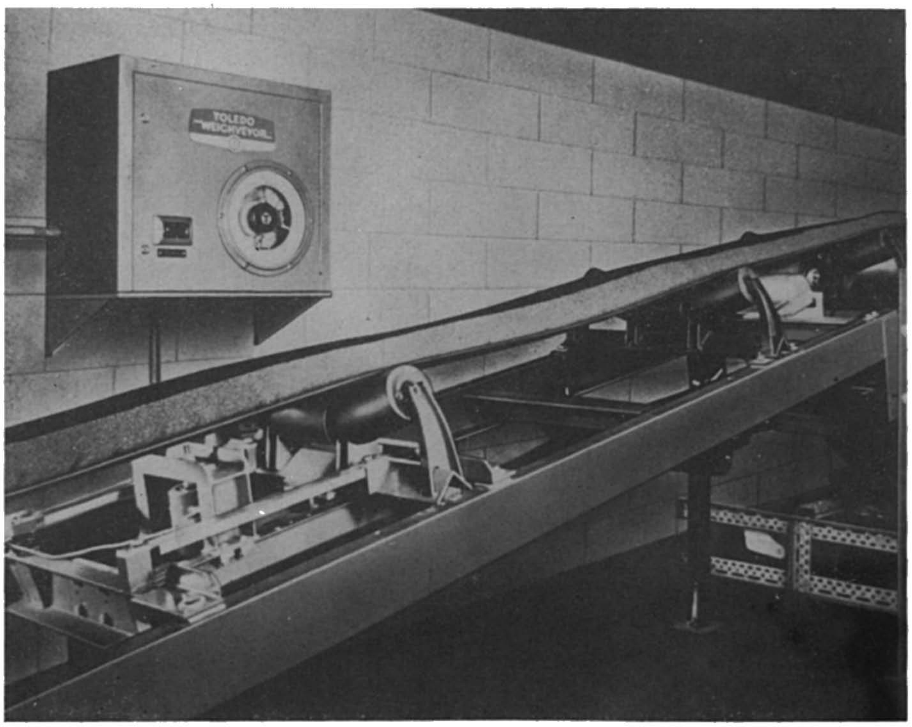


Figure 1.

a state of transition. In our own case we have recently had a totalizing belt conveyor scale in North Carolina accepted by the Southern Weighing and Inspection Bureau for certified weights for carloading of sand and crushed stone; however, this particular scale checked out at an amazing ± 1/10% accuracy.

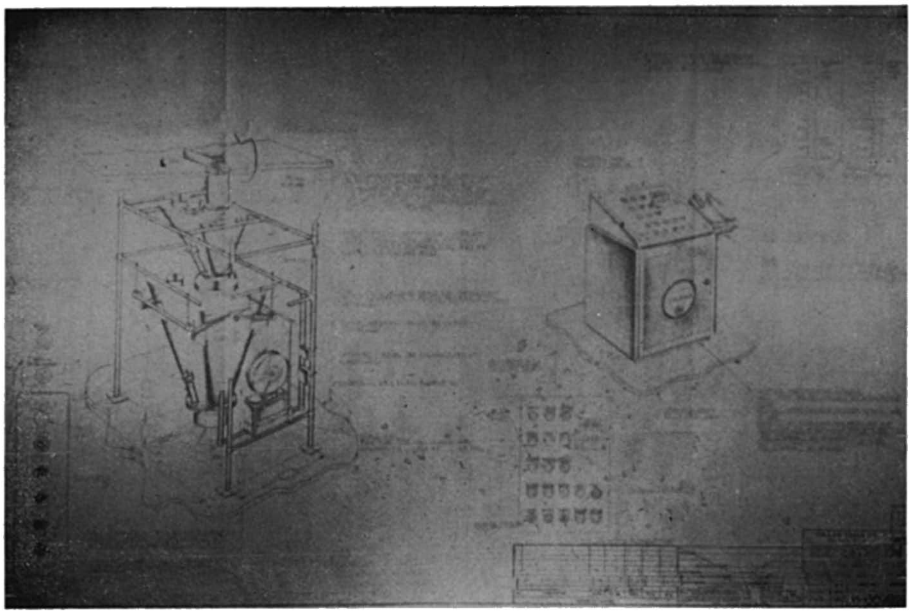


Figure 2.

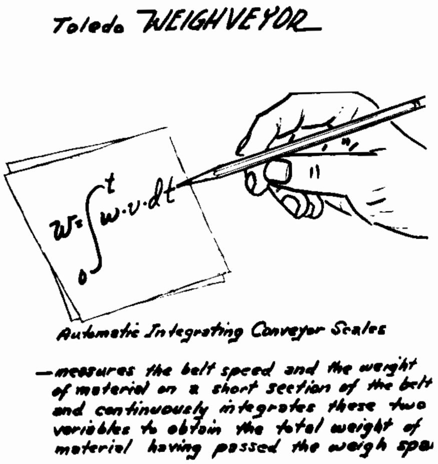
An alternative systems, figure 2, *guaranteed* to meet ± 1/10% accuracy and legal requirements, is now shown on the screen. This is a system of weighing a continuous flow of bulk materials, by breaking it into individual hopper drafts. It is called an Automatic Bulk Weighing System and it totalizes by in effect adding the net weights of each hopper load, through taking the difference between the full and empty weight of each draft.

Theory of Operation

Now let us look at the general theory of operation of integrating belt conveyor scales. There are two inputs: incremental weight and belt speed. The incremental weight is that instantaneous weight sensed by the scale weighbridge. Belt speed measurement is necessary even on a so-called constant speed belt, because belts do vary in speed with load.

These inputs are brought together in an integrator in the scale head. The resultant integration is displayed on an odometer type of counter as an indication of weight which has passed over the scale. As we now see on the screen, figure 3, this is expressed by the equation

$$W = \int_{0}^{T} w.\ v.\ dt.$$



Toledo WEIGHVEYOR

Automatic Integrating Conveyor Scales

—measures the belt speed and the weight of material on a short section of the belt and continuously integrates these two variables to obtain the total weight of material having passed the weigh spa

Figure 3.

Types of Integrating Belt Conveyor Scales

In examining the types of integrating belt conveyor scales, we will look at the basic elements of these units. The first of these is the weighbridge, figure 4, and a modern example is shown on the screen. This design utilizes a single weigh idler.

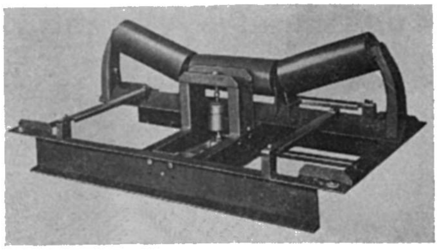


Figure 4.

There are others that utilize two idlers. The arrangement shown has the advantage that the complete assembly may be directly inserted in a conveyor frame in place of a single existing idler. Weighbridges range in design from pure mechanical to pneumatic-mechanical sensing. The unit shown is electromechanical, using a modest lever system to impart a tension pull to a bonded strain gauge load call; this type of arrangement has the advantage that there is essentially no deflection in the weight sensing process, a very important feature because it greatly reduces belt tension variations, a major cause of error in a totalizing belt conveyor scale. Use of the load cell increases corrosion resistance in the meauring system, and makes remote indication easy.

Notice the use of flexure stabilizers in thais weighbridge design, figure 5. These are very important to assure that the scale senses only true gravitational force; this we see now in a new slide. This weighbridge is constructed with rigid parallelogram stabilizers in both the longitudinal and lateral directions. In the upper half of the slide it can be seen that the longitudinal stabilizers prevent forces due to weigh idler friction from being transmitted to the weight sensing mechanism. In the lower half of the slide is described the lateral stabilizer parallelogram. The purpose of this lateral stabilizer arrangement is to eliminate any possibility of error due to uneven loading across the belt. These stabilizers enable the weight to be registered correctly regardless of its relative position across the belt, thereby eliminating a common source of location of the belt speed pickup is important; it should be on the under side of the carrying portion of the belt to prevent pick up of material, and it should be located close to the weigh section to accur-

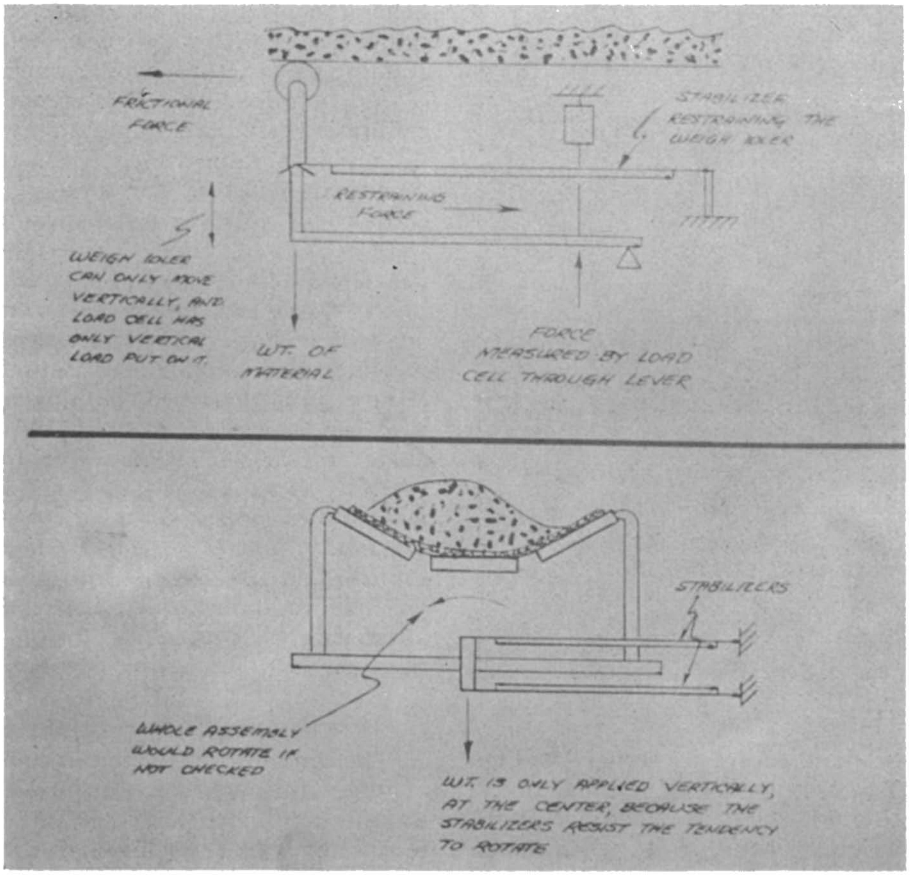


Figure 5.

error in totalizing belt conveyor scales.

The second basic input is belt speed and it is picked up by a roller in contact with the belt. The ately reflect speed to the weighing location, since belt speed is not the same at all points on a belt. Selection of the basic type of speed pickup, electrical or cable-driven mechanical, will depend upon the remoteness of the scale head. Electrical belt speed transmitters are of the selsyn or tachometer variety; the selsyn is preferred because it is absolutely accurate, while tachometers can have errors in the ½% range.

These two inputs of incremental weight and belt speed are joined in the scale head. Methods of doing this depend upon the form of the inputs and the type of integration used. Most manufacturers use one of a variety of mechanical integrators, in which belt speed is rotational motion and weight is a linear motion. In mechanical scale systems the weight becomes linear in the motion of the counterforce device, such as a pendulum, while in an electronic scale the weight is interpreted by a servo system.

The operation of one such mechanical integrator is shown on the screen in schematic form, figure 6. We can see the speed and load (incremental weight) inputs coming together in the ball and disc integrator, with the resulting integrated output to the weight totalizing counter. Notice that as the speed increases or as the load increases pushing the ball carriage to the right, the totalizing counter runs faster. This integrator is able to integrate negatively when weight indication is back of zero due to tare weight variations in the belt; this feature is very important in calibrating the zero of the scale, providing compensation thereafter for belt tare weight variations. Patented differential gearing, shown on the next figure of this integrator, prevents the double ball carriage from riding in the center at zero load, and thus prevents this major cause of wear when the belt

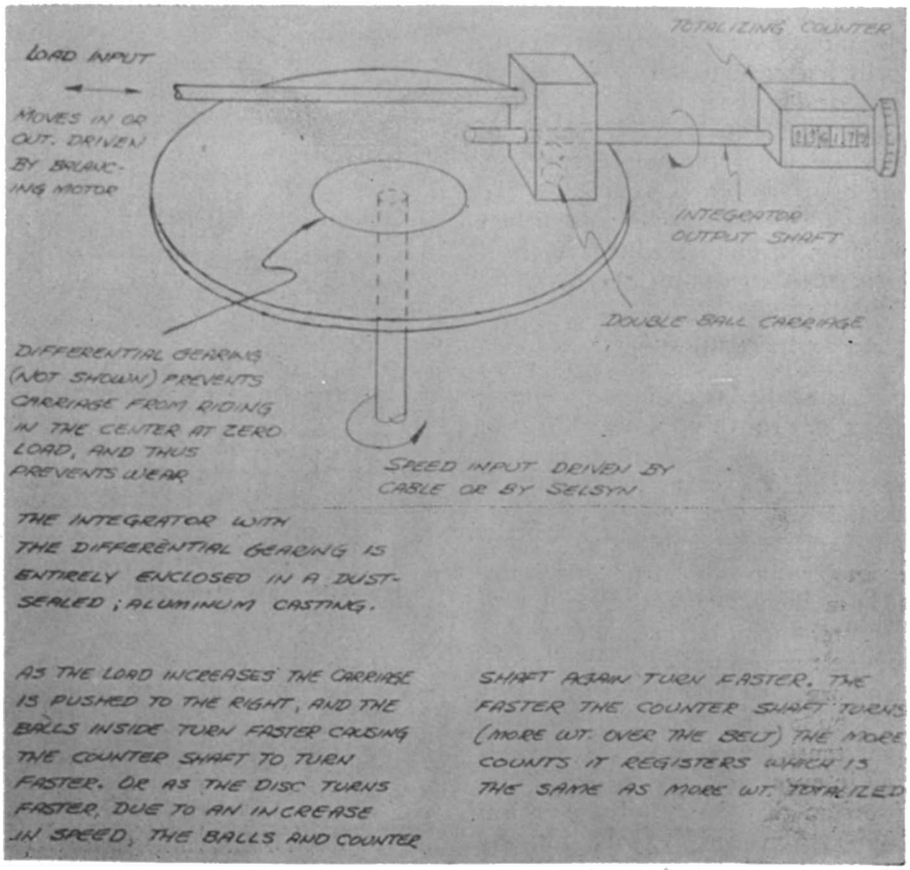


Figure 6.

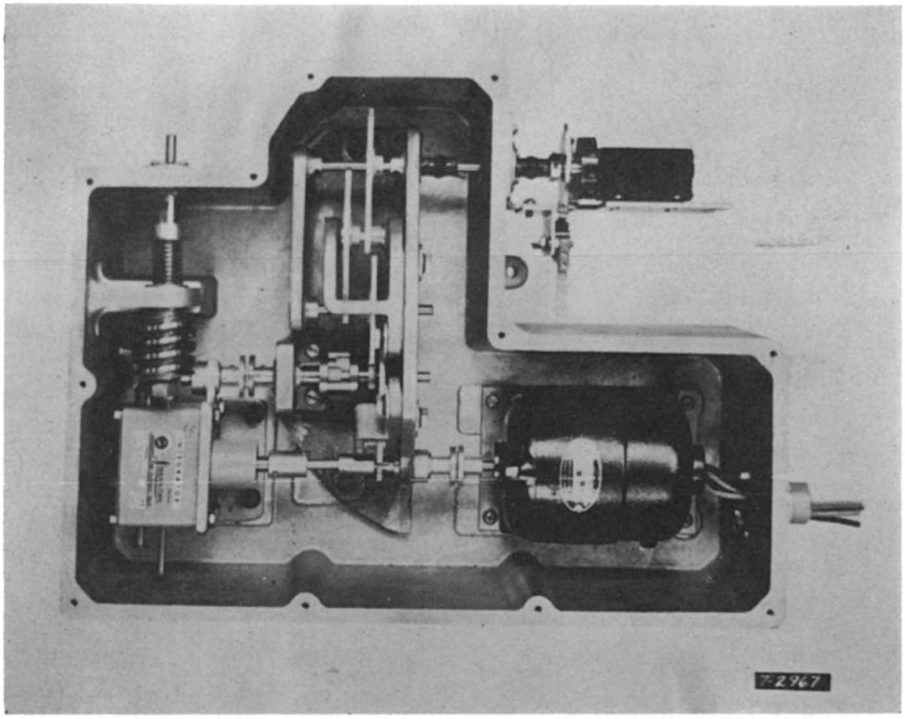


Figure 7.

runs unloaded. Figure 7, also shows the dust tight housing of this integrator, an important feature in the fertilizer industry.

The final item in considering types of integrating belt conveyor scales is a brief look at available accessories. There are a variety of remote weight information devices: digital totalizers, digital weight printers, analog chart load recorders, and analog load indicators. Control devices include cutoff of device feeding the belt after a preset quantity has passed across the scale, and analog control of belt loading through feedback control of the device feeding the belt.

Calibration

How does one calibrate a totalizing belt conveyor scale? This is a subject which has been much discussed. However, at the recent annual Instrument Society of America Conference in Chicago, there seemed to be agreement on calibration methods among the many represented manufacturers of totalizing belt conveyor scales. The problem centers on the fact that belt tension affects weight sensed, yet belt tension varies with belt loading in even the best conveyor. The problem then is one of simulating belt tension over the range of belt loading conditions, and this can't be done except by actual loading. The best method of *initial* calibration is to use live material as in weighing, running at approximately the 25% points from zero to full belt loading. This material is then captured and weighed on a conventional scale. Truly amazing accuracies are sometimes achieved by this method; we have experienced agreement of better than 1/10% in some instances. In this *initial* calibration, a test pan is then slung below the weighbridge and the test pan is loaded with weights, the belt running empty, through the range of the belt loading. This second calibration will differ from the first by a weight value wihch becomes a correction factor. For successive calibrations only the test pan and weights need be used, the established correction factor being applied. Of course, in the long run an actual check with material is recommended. Notice that the procedure just described eliminates the very expensive calibrated test chain, which still is not able to perfectly simulate belt tension effects under operating conditions. Obviously, if it is not practical to capture and reweigh the bulk material in your operation, there are alternative, less accurate calibration methods.

Application Engineering

In considering the application of integrating belt conveyor scales, there is a number of things to be reviewed. Before you buy be sure that you are considering all costs; for example, some manufacturers do not include the necessary new idler as part of the scale price, and some require modification of your conveyor bed by you. Then there are calibration costs; these and other costs would vary with the ac-

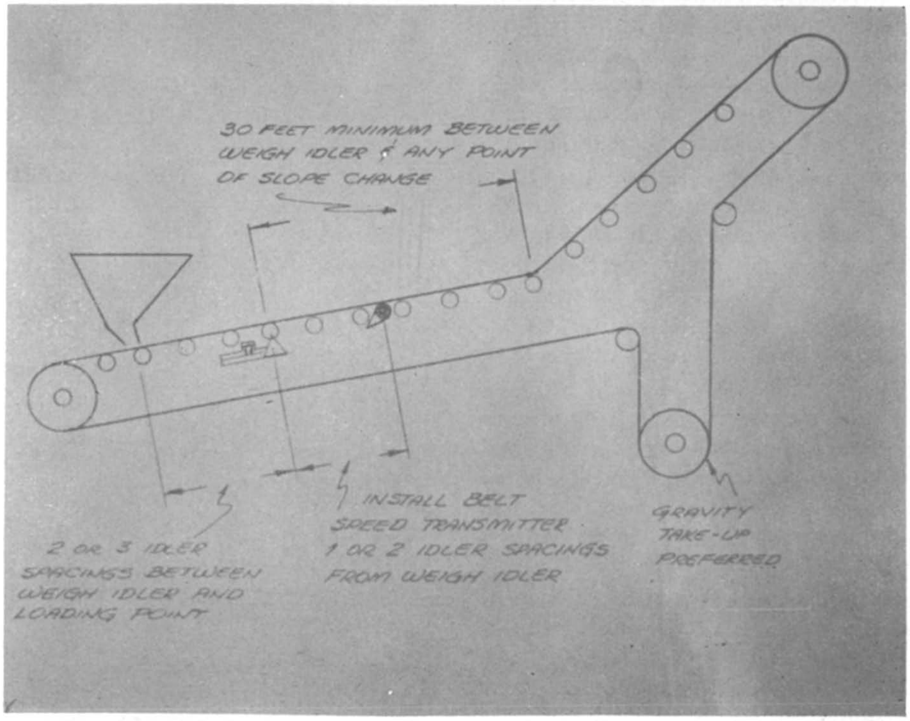


Figure 8.

cessibility of the selected installation point. You may want to modify your conveyor to include a gravity belt take-up, which is the preferred method for good weighing. For the long run consider the availability of service facilities for the unit you select.

The schematic on the screen, figure 8, contains tips for installing such a belt scale. We have already mentioned the gravity take-up and the proximate location of the belt speed pick-up. There should be 2 or 3 idler spacings between weigh idler and loading point (or tail pulley). We recommend 30 feet between weigh idler and any point of slope change. The slope itself may be up to any degree that will still carry the product properly. Belts may be any standard arrangement from flat up to 45° troughed. Try for a location relatively free from vibration, corrosive atmospheres, and winds which can cause weighing error.

Most important, consider the accuracy you will really get—that's what you are buying. In doing this remember that those units which have the least vertical movement will have the least belt tension variations, and that these variations are a major cause of error.

Conclusion

We have reviewed the continuous weighing of bulk materials on conveyor belts. It's been sort of a do-it-yourself kit for consideration of a totalizing belt conveyor scale. We have talked about advantages and disadvantages. Remember one powerful advantage; if this kind of equipment will meet your standards, it is the least expensive way to "beat the bottleneck."

MODERATOR REYNOLDS: Thank you very much, Dave.

Are there any questions?

I have a question concerning installation. The initial picture you showed looked like the belt was on an incline. Does it have to be horizonal or can it be on an incline?

MR. KENNEDY: The belt may be inclined up to any degree that will carry the load. In other words, it could be, for example, more than 20 per cent. Of course, the incline is taken into consideration in the design and calibration of the particular unit.

MODERATOR REYNOLDS: Thank you.

Any other questions?

A MEMBER: How do you compensate for variation in the weight of the belt?

MR. KENNEDY: How do we compensate or take care of variation in weight of the belt itself? In other words the tare weight of the belt. This is taken care of in the initial calibration because of the fact that this unit is able to integrate negatively and positively. So even if the weight variation of the belt would even be represented by a wave form, the unit could still take care of this.

What happens is, the belt is run empty and you simply let it run empty and make your adjustments until such time as there is no indication on the weight counter. At that point you know that you have properly compensated for the tare weight of the belt. Now, of course, we recognize that belts change. Some belts can even absorb moisture. There are problems which are not automatically taken care of but a regular check of the belt can take care of this.

MODERATOR REYNOLDS: We have time for one more question.

I believe they are all satisfied. Dave, you did a real fine job.

Thank you very much.

Our next speaker continues the discussion of our theme to achieve greater refinement in the techniques of our industry.

Automation is occurring in all ends of processing and has recently moved into the area of packaging and bag closing. Mr. W. R. Rumo of the Howe-Richardson Scale Company will review this subject and present a current report on the possibilities of relating this to the fertilizer industry.

Maintenance and instrumentation in the Area of Automatic Weighing and Bag Closing Equipment

W. R. Rumo

ALTHOUGH my presentation is called "Maintenance and Instrumentation in the Area of Weighing" we won't be discussing maintenance schedules and methods of caring for automatic bagging equipment, but rather how, through the use of instrumentation, Howe Richardson Scale Company developed advanced weighing equipment that requires low maintenance under the most rugged and severe operating conditions.

Approximately 7 years ago Richardson Scale Company realized that advances in weighing equipment were not keeping abreast with equipment advances being made in other major industries. It's true the weighing industry has developed automatic systems for proportioning materials by weight and provided various means to record, store and select formulas as well as several methods for the read-out at remote locations which permit complete automation of the weighing process. This, however beneficial, is not related to speed and accuracy consideration and ultimately maintenance benefits.

It is generally accepted that speed and accuracy in weighing equipment are not compatible. One is sacrificed for the other. For instance, if we are to obtain high speed, accuracy would be sacrificed. If we are interested in accuracy, we obtain this through the sacrifice of high speed operation.

In an effort to improve the relationship between speed and accurary, it was decided to investigate the factors which influence those two functions. Unfortunately, these factors occur simultaneously and over a very short time period of less than one second. It is impossible to observe all factors as they occur and much more impossible to detect small differences that occur in these factors from one consecutive weighing to the other.

We require some means of photographing or recording these factors as they occur so that comparisons between weighings in terms of weight differences and factors could be made to establish where weight inaccuracy occurred.

A rather thorough search of instrumentation available to industry at the time resulted in the selection of a device known as a recording oscillograph which, together with common transducers, permits conversion of forces, deflections, vibrations and other factors into electrical signals. The oscillograph records the several factors on a strip of paper as the weighing process takes place. After the weighing is completed and the actual weight of that particular weighing established, comparison of the trace and the weight is made to pinpoint origin of inaccuracy.

The recording oscillograph permits recording factors as they occur in time spans of less than one-thousandth of a second. Increasing the speed of the paper chart passing through the oscillograph permits expanding or magnifying these factors so they can be read easily.

The performance of a standard scale at the beginning of our investigation is shown in Figure (1). The trace patterns are of several factors influencing the weighing accuracy. An analysis of the trace permits evaluation of each factor and its contribution to the total scale performance.

By means of this instrumentation, it is possible to establish the areas of scale operation wherein the inaccuracy is generated and to what degree. With this tool, we can also evaluate quite well the effect, on over-all performance, of a design or component change.

Comparing the trace patterns of many consecutive weighings from a given scale results in an excellent index of the factors according to the degree to which they affect the performance of the scale. Concentrating on those factors which have the greatest adverse affect on performance resulted in a well defined scale development program.

New component designs when completed were incorporated into the scale and oscillograph traces of the performance permitted critical evaluation of the new design.

This approach to evaluation of existing weighing equipment provided the basis for generating a much better scale; one having a performance capability exceeding by far that which was available at the time.

In addition to equipment design, it was possible, through this instrumentation, to further research activity in related areas of material handling and material flow. The performance of weighing equipment, in general, depends to a considerable degree on the uniformity of material flow from storage to the scale. Research in this area resulted in new theories and concepts in material handling, which when put into practice, raised the level of scale performance.

Howe Richardson Scale Company, after five years of intensive research and development activity, established a design concept which resulted in the development of the "Speedac" family of scales. The term Speedac is usd to emphasize that the two functions speed and accuracy, while not compatible have been brought closer together permitting higher speeds with higher accuracy to be achieved in this scale to a degree not possible in standard equipment.

Speedac scales operate in excess of 20 weighings per minute on a single unit. The operation incorporates full flow and dribble feed permitting accuracy of 2 Sigma (95% of the weighings) to be within plus or minus 1 ounce or better. This speed and accuracy is accomplished in a stable operation. The stable operation is important since many standard scales are operated in excess of 20 weighings per minute but not in a stable manner. This reflects in the very poor accuracy obtained.

Originally the primary purpose of the development program was the improvement of the operating performance, specifically speed and accuracy. It was, however, through the accomplishment of this basic objective that an extremely valuable by-product resulted. This came in the form of substantial reduction in maintenance requirements for the Speedac scales.

One area of investigation revealed that components such as valves, air cylinders, switches, relays, etc. were required not only to operate at high speeds, but also with uniform, consistent action. Thorough research into available components from many sources of manufacture resulted in the selection of those which, in combination, gave the highest possible level of performance.

The history of several hundred

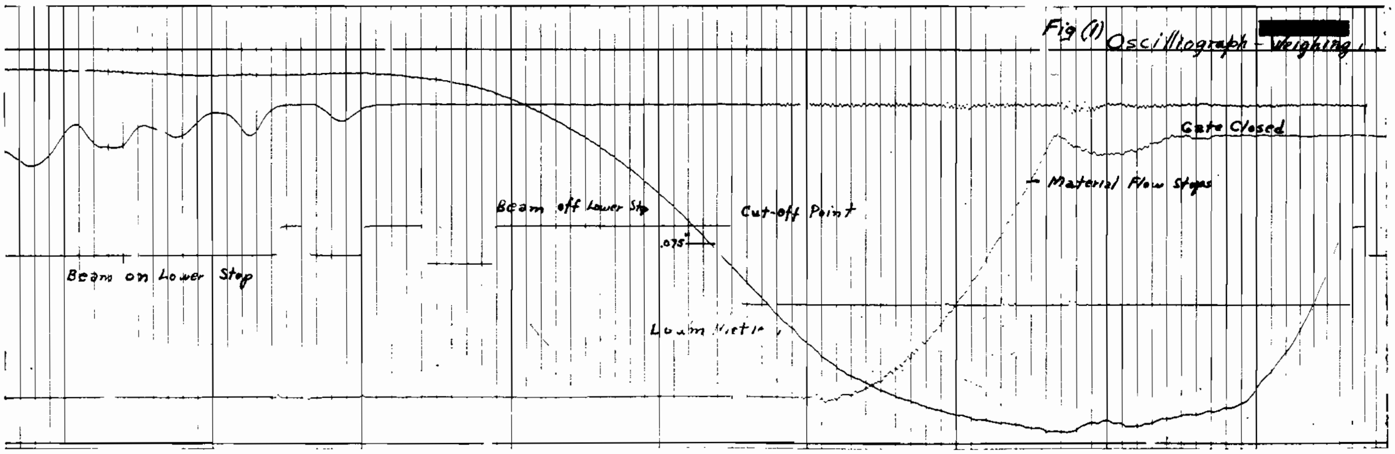


Figure 1.

Speedac installations during the past three years indicates that this method of component selection has substantially improved the service record for automatic high speed bagging scales. Users of Speedac carry less replacement components in stock and emergency service is rare.

Not every weighing equipment application requires high speed and accuracy. Every scale, however, should be able to sustain rugged operation with minimum maintenance.

Howe Richardson has built into the standard line of bagging scales, as many of the improvements, both in design and component selection, from the Speedac investigation as possible. The model E50-10B fertilizer bagging scale (see Fig. 2) has in this way benefited from the Speedac design. The fertilizer bagger is capable of 20 weighings per minute on 50 and 80 pounds with an accuracy of 4 ounces. It is designed specifically for the rugged environment of the fertilizer plant incorporating many features that enables it to put out the tonnage continuously throughout the season.

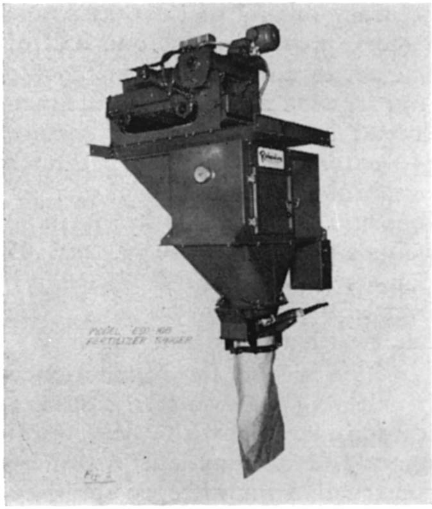


Figure 2.

Moderator Reynolds: Thank you, Mr. Rumo.

I think we will move on to our next speaker.

Steady continuous advancement has been made in the field of liquid flow control. The original simple flow meters were perhaps sufficiently accurate to satisfactorily meter the requirements for low analysis mixed fertilizers. However, with the double strength grades, improved accuracy is now required. A change in accuracy of even one half of one per cent can very readily substantiate direct contribution to our profits.

Our next speaker, Mr. Al Simmons, will discuss the recent advances in liquid flow metering systems.

Maintenance And Advances In Liquid Flow Meters

A. G. Simmons

From the title my subject would appear to be almost two different subjects, but in reality both phases, New Flow-Meter Developments and Flow-Meter Maintenance, are only part of a common fertilizer production concern, the best possible accuracy of liquid flow-metering. To maintain and improve uniformity of product existing flow instruments must have their inherent accuracy maintained and other more accurate flow-meters must be found if the existing instruments, even though properly maintained, do not supply the necessary precision.

In the process of seeking better accuracy and at the same time using only flow-meters that are truly compatible with the liquids of a mixed fertilizer plant, three basic types of flow-meters have come into use: first, the rotometer, second the electromagnetic flow-meter and third the turbine flow-meter.

The rotometer has at various times been used on all mixed fertilizer liquids. It has been found satisfactory or compatible with all of them except wet process phosphoric acid.

The electromagnetic flow-meter has again been used on all fluids and been found satisfactory on all of them, the only problem being the need for a non-standard lower conductivity unit for use on anhydrous ammonia. The turbine flow-meter, which is the newest and most accurate of the meters, is applicable only to anhydrous ammonia and water, due to the problems of solids, viscosity, and/or corrosion inherent in nitrogen solutions, sulfate acid and phos acid.

The operating principles of the rotometer and the electromagnetic flow-meter are by now quite familiar to you gentlemen of the industry, but even these meters had some new wrinkles added in the past year. Some fertilizer plants, looking for increased accuracy of simple flow-indicating meters have gone to a 25 inch scale rotameter which does offer increased accuracy. This meter is not truly a new meter in that it has been available to industry for more than 10 years, but its use in the fertilizer plants has only come about with this need for increased accuracy.

The magnetic flow-meters have not changed in basic operation but constant development has led to more compact and reliable recorder instruments of transisterized construction, smaller magnetic flow-meters themselves, and also a magnetic flow-meter whose lined pipe section can be removed and readily replaced in the fertilizer plants in the event that a liner is damaged during operations.

The flow-meter least known to fertilizer people and, therefore, really the only radical new development in flow-metering is the turbine flow-meter. This unit is extremely compact, a one-inch flange meter being only eight inches in length and having a diameter less than the flanges themselves. You can get some idea of the size of a one inch turbine meter from this unit in my hand which is one with pipe threaded end connections rather than flanges, but as you see it is extremely compact. The unit can be mounted in any attitude in a pipe line and produces an electrical output proportional to flow rate which can be fed to an indicator, recorder, totalizer or controller.

The flow-meter itself consists of a straight-through flow body, rotor support parts and a freely rotating rotor or turbine each blade of which creates an electrical pulse on passing the pickoff coil mounted on top of the meter. The rate at which pulses are created is proportional to the velocity of the fluid going through the flow-meter and so the turbine meter is a true volumetric flow-meter independent of density influences.

Its accuracy guarantee is plus or minus one half of one per cent of any flow rate over its range, and this range is considerable. This particular meter is a one inch meter with a range of .5 to 50 gallons per minute, and its error is only half of one per cent at any point on that range. This means it is half of one per cent at .5 gallons per minute as well as at 50 gallons per minute.

The turbine flow-meter also is not truly new from a use standpoint since it was developed for liquid fuel rocket testing as early as 1950 and has been used for high accuracy test work and missile flow measurement since that time. Only in recent years, however, has it been used widely in industry in applications requiring high accuracy. Since anhydrous ammonia is used as a rocket fuel, the turbine meter had experience with high accuracy metering of this fluid and it was only a matter of time before it began to be used in ammonia production plants and finally in mixed fertilizer plants themselves.

These are the newer developments in the field of liquid flow-metering. How, then, does one determine which type of flow-meter should be used in a given plant? This decision must be made on the accuracy required, the cost of the instrument, the maintenance required, and individual plant considerations such as the type of maintenance personnel available and whether a relatively clean and vibration -free area is available for high accuracy instruments. Since the subject of accuracy is a vital one in the choice of flow-meters and in their maintenance, let us review the accuracy guaranteed for each of the three types of flow-meters mentioned.

Here it might also be well to explain the accuracy statement somewhat since a great deal of confusion exists on this score. Accuracy listed by a manufacturer is the maximum error which may be encountered in a flow-meter when compared to a completely accurate calibration standard. The meter may, of course, give much better absolute accuracy than that which is guaranteed and it will most definitely provide repeatability of flow reading to better than one half of the accuracy guarantee.

The rotometer in its most commonly seen forms, the 10 inch and 5 inch metering scale without calibration, has a guaranteed accuracy of plus or minus two per cent of maximum flow reading. For a meter having a range of 1,000 to 10,000 pounds per hour, accuracy is plus or minus 200 pounds per hour at 10,000 and also plus or minus 200 pounds per hour at 1,000. The 10 inch or 5 inch scale rotometers can also be supplied with an actual flow calibration so that they give an accuracy of one per cent of the maximum flow rate. Then the error on a 10,000 pound per hour flow-meter would be plus or minus 100 pounds per hour at 10,000 and 100 pounds per hour at 1,000. The meter gives readings over a 10 ton range.

The 25 inch scale rotometer which I mentioned before as a higher accuracy instrument is considered a precision accuracy flow-meter rather than an industrial accuracy flow-meter. Its guaranteed accuracy is either plus or minus one per cent or plus or minus one half of one per cent of any flow rate on its scale, accuracy depending upon the number of calibrations run on the meter. Here the accuracy is stated differently and means a one per cent 2000 to 10,000 pound per hour flow-meter, the ranges are somewhat shorter on the long scale meters, has an error of plus or minus 100 pounds per hour at 10,000 but only plus or minus 20 pounds per hour at 2,000 This meter gives readings over a 5:1 range.

The magnetic flow-meter, on the other hand, has a guaranteed accuracy of at least plus or minus one per cent of maximum flow rate, which, again, means on a 10,000 pound per hour maximum flow plus or minus 100 pounds per hour at 10,000 or at 1,000 pounds per hour. However, when a magnetic flow-meter is supplied with a continuous range adjustment, its range can be changed by rotating a dial on the recorder and its accuracy can be maintained at close to plus or minus one per cent of any reading.

For example, if a certain formulation required a flow of 10,000 pounds per hour and the magnetic flow-meter is set for a full scale range of 10,000 pounds per hour, it will record this flow with an accuracy of plus or minus 100 pounds per hour. If later another formulation requires only 3,000 pounds per hour flow and the magnetic flow-meter range is not changed, accuracy of this flow will be plus or minus 100 pounds per hour at the 3,000 level. However, by changing the range knob in the recorder instrument so that full scale on the meter is now 3,000 pounds per hour, this flow can then be metered with an accuracy of plus or minus 30 pounds per hour. The magnetic flow-meter gives readings from 0 to whatever maximum flow is set on the recorder.

The turbine meter, as previously mentioned, has the highest accuracy of any of these available meters, plus or minus one half of one per cent of any flow meter rate over its wide range. A turbine meter can be supplied with a range of 10 to 10,000 pounds per hour over which the one half of one per cent makes it accurate to within 50 pounds per hour at 10,000 and .05 pounds per hour at 10. Readings over a 100 ml flow range can be made with the turbine meter.

The second factor mentioned in selecting a flow-meter, cost, varies considerably with the type of meter and its function. Assuming construction for nitrogen solutions with all welded parts of stainless steel, I would like to give you a general idea of what these meters cost. In a simple indicating unit the varities of meters that we have been discussing cost about as follows:

1) An uncalibrated rotometer, either the armored or the glass tube type, with a 10 inch or 5 inch scale, would cost approximately $225. Calibration of this meter so that

accuracy is plus or minus one per cent of maximum raises this price to $275.

2) The 25 inch scale meter with one per cent accuracy over the full scale runs $400, whereas a half per cent calibration on the type of meter adds another $100 to the price.

3) The magnetic flow-meter as a simple indicator costs approximately $1,000, with plus or minus two per cent of maximum flow accuracy.

4) The turbine flow-meter also can be supplied as a simple indicator at a price of roughly $800, for plus of minus one per cent of rate accuracy.

Since a large number of plants today are using recording devices, let us look at the prices of recording meters also.

1) A recording 5″ scale rotometer costs in the neighborhood of $600 to $700, with an additional $50 for one per cent calibration.

2) 25″ scale rotameters are not available with recordings.

3) A recording magnetic flowmeter approximately $1500.

4) A recording turbine meter approximately $1400.

The third factor mentioned in determining suitability of any meter was maintainence. As most of you know, indicating pyrex tube rotometers obviously need practically no maintenance, other than periodic cleaning and replacement of an occasional broken tube. Transmitting rotometers, on the other hand, require some periodic maintenance because they are handling air and slowly become dirty. Cleaning of the transmitters and filters and associated receiving equipment is necessary. Automatic controllers also require this type of maintenance. Most of the plant instrument people or maintenance people who have looked after instruments are capable of doing this type of work.

Magnetic flow-meter, routine maintenance can be done by most mechanics since it involves simple adjustments of the recording instrument. Complete periodic checks of the magnetic meter and its recorder are required to maintain accuracy and can be only done properly by a trained instrument man or a factory representative. Since this type of check is done in most cases only every three or six months, a service contract with the supplier of the instrument can take care of the necessity of having a trained instrument man to maintain the magnetic flow-meter.

Turbine flow-meter maintenance is of the same nature as that of the magnetic flow-meter. Day-to-day adjustments of the receiver instrument are easily done while a periodic complete check by a trained instrument man or factory repersenttaive is required for maximum meter performance.

These, then, are of the flow-meters being used today in fertilizer plants and some of the reasons why one meter is chosen over another. The most accurate flow instruments naturally require the most careful handling and maintenance, if they are to continue to be accurate. However, the cost savings through improved control of ingredients are so great with these higher accuracy meters that more and more fertilizer plants are taking the necessary steps in their facilities and operations to be able to use them.

MODERATOR REYNOLDS: Do we have some questions?

A MEMBER: What about remote indicating meters versus turbine meters?

MR. SIMMONS: All types of remote indicating equipment are available. The turbine meter puts out an electrical signal and this can be fed into almost any type of an indicator, totalizer, controller at remote locations.

MODERATOR REYNOLDS: Any other questions?

Any questions for the previous speakers? We have a few minutes here, we could entertain some questions.

Since we have no questions, apparently everyone is satisfied. We wish to thank you for your attention this morning, you've been a very patient audience.

We will adjourn now until our two p.m. session this afternoon.

Thursday Afternoon Session, November 7, 1963

The Round Table reconvened at two o'clock p.m., Mr. A. Spillman, Moderator, presiding.

MODERATOR SPILLMAN: Will the meeting come to order, please.

Gentlemen, I wish to take this opportunity to say hello to many of you old-timers attending this meeting; and on behalf of your Executive Committee we welcome all of you people who have come here for the first time.

Your Committee has had no easy task to arrange this program, with timely up-to-date subjects.

We have had many executive meetings during the year, analyzing the suggestions received from this membership for possible topics to be discussed.

The subjects we are discussing during this three-day meeting are the results of careful consideration by your committee, and we believe are representative of your suggestions.

I wish to take this opportunity on behalf of the entire membership to thank Tom Athey, a good friend of the Round Table, Tom's associates, and the Raymond Bag Company for the very fine party they gave us last night.

Immediately after the two subjects to be discussed this afternoon, we will have a question and answer period.

The first topic for discussion this afternoon is: Man-U-Pak Method of Fertilizer Production.

This paper will illustrate a concept of producing granular mixed fertilizers, bagging, palletizing, storing and shipping.

The paper will be given by Mr. Walter Sackett, Junior.

"MAN-U-PAK" Method of Fertilizer Production.

Walter J. Sackett, Jr.

Thank you, Mr. Spillman. Ladies and gentlemen.

We are pleased to have the opportunity to speak to you today on what we feel is the fertilizer plant of the future.

It represents a drastic departure from the fertilizer plant as we know it today. We feel that the old cliché, One picture is worth a thousand words, applies here, and therefore will make our presentation through a series of slides. (See Composite Drawing #1)

Man-U-Pak, a new concept in fertilizer production, in which granular fertilizer is manufactured, packaged and warehoused in one continuous operation.

Incidentally, we felt that the chicken and the egg was the best representation of exactly what we are talking about, manufactured and packaged in one operation.

The following shows a plant of this new design. Its capacity is based on 500 tons per day. Manufacturing goes on around the clock.

The packaging and warehousing are accomplished in one eight-hour shift.

Packaging shipments are made from warehouse. Bulk products are handled at the plant's bulk shipping terminal.

This plant offers better utilization of labor, greater product quality control, lower cost storage facility, improved working conditions.

This is a view of the overall plant.

How does it differ from other plants? We will try to show you.

Receiving solid-state raw materials.

Here we show materials being unloaded in bulk from either hopper bottom or box cars by means of an undertrack Bulk-Toter* (1).

This has the ability to convey and elevate the materials to a shuttle belt (2) which takes them to any one of five raw materials bins (3).

Receiving liquid-state raw materials.

Here we see our liquid storage system consisting of tanks for anhydrous ammoniating solutions, various acids that we will use in the process (4).

Transfer of solid raw materials.

Here we are charging by a front-end loader our various solid-state raw materials into a large boot hopper with grate (5) to an elevator (6) to the initial screening and batching part of our operation.

Screening, compounding and blending solids raw materials.

Here our materials go over our scalping screen (7) through a bin selector (8) to a six-compartment hopper system (9).

From the hopper system we drop the materials to our Blend-weigh* Scale Hopper (10) where they are mixed and weighed in one operation.

Transfer of solid material blend to process.

Our batch is then fed by gravity to another Bulk-Toter conveyor (11) which transfers it to a surge hopper over our continuous weighing machine (12).

Transfer of liquid raw materials to the process.

Here we are merely showing the pipelines for the various liquid raw materials from storage to the metering equipment (13).

Continuous weighing of solid blend to ammoniator.

Here we have our material in our surge hopper, transferring it across our continuous weighing machine (12) to our ammoniator elevator (14).

The ammoniator elevator then

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*U. S. and Foreign Patents Granted. Others pending.

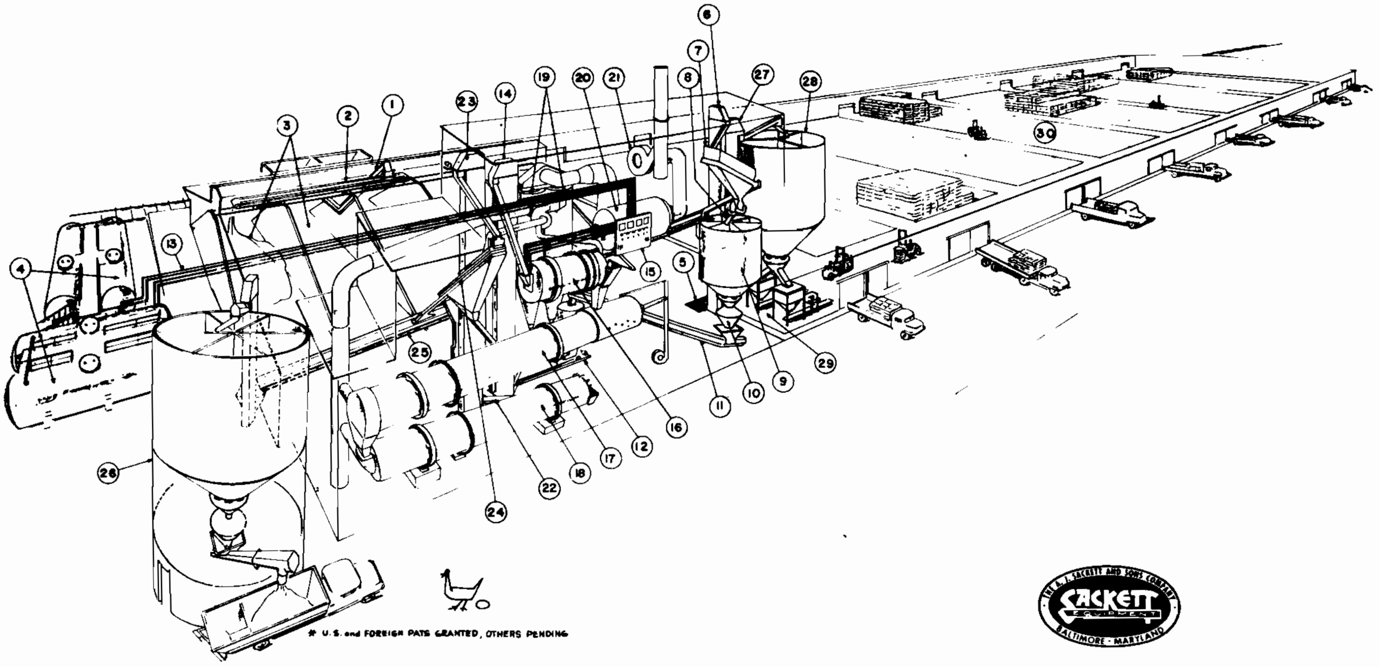

Fig. I. Manu-U-Pak Method of Fertilizer Manufacturing.

elevates the material to the ammoniator-granulator level.

Continuous metering of liquids to the ammoniator.

Here we show our panel board (15) and pipelines carrying metered liquids to the ammoniator-granulator.

Ammoniating reactions and pelletizing.

Here we show our continuous TVA-type ammoniator-granulator (16), where liquids are introduced under the cascading bed of solid raw materials.

Drying.

Here our plasticized mass is put through a rotary co-current dryer (17), either gas or oil fired.

Cooling.

The material then goes through a rotary counter-current cooler (18).

Cyclone air control.

Here we show our air system as handled through a common duct to twin cyclones (19).

Fume scrubbing system.

From the cyclones our air goes through a suitable wet-type scrubber (20), thence to the exhaust fan (21), and then into atmosphere.

Pellet classification.

Here we are taking our cooled material by way of a conveyor (22) to an elevator (23) and across a double-decked classifying screen (24).

Fines are spouted back to our ammoniator elevator (14).

Oversize is milled and returned to the screen, the ammoniator or dryer, as desired.

In this particular case, we are spouting them right back to the screen.

The product is spouted to a fixed-frame reversible belt conveyor (25).

Bulk product shipping terminal.

Here our product is being taken to our bulk shipping terminal, which is composed of an overhead six-compartment silo (26).

This will be the only place in the plant in which we will store finished goods in bulk.

New Revolutionary Man-U-Pak.

Reduces wasted man-hours, eliminates pile segregation, creates new high standards of product quality control.

We realize that it is pretty easy to make such claims, but we can back them up.

Up till now we have been talking in terms of a more or less standard unit, more modern and better designed than most, but still pretty orthodox.

From here on the Man-U-Pak plant is substantially different.

Product transfer from process to packaging reservoir.

Here we are reversing our product belt (25), taking the material to a stub-elevator (27) and to our packaging reservoir (28).

Product packaging.

Here we show our product going through our three-compartment reservoir (28).

Each compartment has the capacity to hold one complete eight-hour run from the manufacturing unit.

From this reservoir we are going to two bagging lines (29).

Product warehousing.

Here we show our fork-lift operators taking palletized bagged goods from the bagging lines to our warehouse.

All the area in green is low-cost warehousing (30) space. This is based on using a PVC bag.

Product shipments from warehouse.

Here we show bagged goods being loaded on trucks directly from warehouse by our fork-lift operators.

Shipping has no direct tie-in at all with our packaging operation.

Man-U-Pak study reveals amazing reduction in man-hours per ton of direct labor.

In our Man-U-Pak plant raw materials receiving and manufacturing will operate three eight-hour shifts per day.

Packaging, warehousing and shipping will be done on a one-shift basis, however, in this one shift we can handle all the material produced by the manufacturing unit in the previous twenty-four hours.

Here we show our receiving operation crew of two men, receiving at the rate of twenty-one tons per hour.

This material costs .0952 man-hours per ton.

Our manufacturing is done on the same three-shift basis, five-man crew manufacturing at the rate of twenty-one tons per hour.

The cost here is .2380 man-hours to a ton.

Total receiving and manufacturing cost, .3332 man-hours per ton.

At the same time we have a twelve-man crew in our packaging operation, packaging 63 tons per hour.

This is adding .1905 man-hours to our ton.

Our warehousing, two men warehousing at a rate of 63 tons per hour adds .0317 man-hours to our time.

Shipping from warehouse, two men shipping at the rate of 63 tons per hour, .0317 man-hours is added to our ton here.

Our total packaging, warehousing and shipping cost is .2539 man-hours to the ton.

For the entire operation our cost is .5871 man-hours per ton.

Non-productive labor and overtime wages due to seasonal consumer buying are sharply reduced by Man-U-Pak.

Here we are showing the typical labor utilization in a conventional plant, during an early seasonal period.

We have a crew of eleven men. We bring these men in at seven-thirty in the morning, and from a period of seven-thirty until eleven-thirty that morning, one truck shows up in the yard with an order of eight tons of fertilizer.

These men fill that order, they are all dependent on that order. They are going at a rate of two tons per hour for that four hours. So that fertilizer on the truck has cost of five and a half-hours per ton.

From the hours of twelve to

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*U. S. and Foreign Patents Issued.

four the trucks start coming in. They start to bag and ship at normal rate, thirty tons per hour.

During a four-hour period they ship a quantity of 120 tons. This fertilizer has cost us .3666 man-hours per ton on the truck.

But at four o'clock we haven't finished. We still have trucks in the yard. So we have to keep these eleven men for overtime.

During a three-hour period, three-hour overtime period, from four-thirty to seven-thirty we bag and ship at our maximum rate, thirty tons per hour. Our eleven man crew ships a total of ninety tons. This fertilizer is costing us .55 man-hours per ton.

During that day we had our eleven-man crew for eight hours of straight time. During those eight hours they shipped a total of 128 tons. This averages out to be about sixteen tons per hour.

This fertilizer has cost us .6875 man-hours per ton.

During the three hours of overtime we bagged and shipped ninety tons total. This fertilizer has cost us .55 man-hours per ton.

During this one particular day we had 31.0678 non-productive man-hours. And our total man-hour-per-ton cost for our shipping is .63007.

Non-productive labor and overtime wages due to seasonal consumer buying are sharply reduced by Man-U-Pak.

No seasonal problems with Man-U-Pak.

Here we show the same day in the life of a Man-U-Pak plant. During the hours of seven-thirty to eleven-thirty, we bring in a fourteen-man crew. This is for our packaging and warehouse operation.

Now, when they only have one truck in the yard, these people are not at all dependent on that situation. From seven-thirty to eleven-thirty they bag and warehouse at the rate of 63 tons per hour, a total of 252 tons during that four hour period. This fertilizer warehouse has cost us .2222 man-hours per ton.

From twelve to four the trucks start coming in, but these people don't know anything about it. They don't have to. They bag and warehouse at the rate, the same rate, the same constant rate of 63 tons an hour, quantity of 252 tons, constant cost of .2222 man-hours per ton.

Now our shipping. We do have a forklift operator during this period that is dependent upon orders. So during this period the first eight hours in this same day this forklift operator ships 128 tons, the same as in our orthodox unit. This is a rate of 16 tons per hour, but we only have one man dependent on these orders, so this cost amounts to .0625 man-hours per ton.

The forklift operator has to stay on overtime, the same as our full crew did with the orthodox plan.

From four-thirty to seven-thirty, he loads out at the rate of 30 tons per hour, a total of 900 tons. This fertilizer has cost us .05 man-hours per ton.

Our total non-productive man-hours during this day amounts to 3.7436 and our total cost of shipping is .0573 man-hours per ton.

Non-productive labor and overtime wages due to seasonal consumer buying are sharply reduced by Man-U-Pak.

Here we show the comparison between the conventional plant and the Man-U-Pak plant. Our shipping operation summary. During this same day in a conventional plant we have a total of 41.0678 total non-productive man-hours. In the Man-U-Pak system, we have 3.7436 non-productive man-hours. Our total shipping cost in the conventional plant .6307 man-hours per ton; in the Man-U-Pak plant a total of .0573 man-hours per ton.

Man-U-Pak improves working conditions and upgrades products.

In the conventional plant we have dust, contamination and attrition from open-bin storage. Man-U-Pak plants present no dust contamination or attrition from product stored in sealed bags.

Comparing the Man-U-Pak product quality control to existing methods.

Here we have some samples from bags. We have taken our sample from a conventional plant producing granular fertilizer. This fertilizer has come from the manufacturing unit, been dumped in storage bins, run over, picked up by payloaders, dumped into elevators, run across scalping screens and then put into a bag. We haven't got a Man-U-Pak plant in existence, but if we did the material would be coming off the belt and going directly to the bag.

Now in a conventional plant we find in a sample from a bag that is supposed to be granular fertilizer 7.175 per cent through a 20 mesh, but with the same product that would be coming off the product belt from manufacturing in the Man-U-Pak plant, we have .517 or a little over half of one per cent through a 20 mesh screen.

Man-U-Pak shows a 1400 per cent improvement in fines reduction.

Man-U-Pak eliminates seasonal problems, attracts better help, improves working conditions, produces higher quality products, reduces costly overtime and banishes duplicated effort.

That's it, ladies and gentlemen. We feel that the hen had a pretty good idea when she packaged her product the way she did. We think that our Industry could take a lesson from her.

MODERATOR SPILLMAN: There we have it, men. If this thing could be worked out according to the thinking of the Sackett Company, it looks like we could have one of the most economical operations.

Are there any questions? We ought to have some questions here for Mr. Sackett.

MR. SAM GUSHIN (Consumers Cooperative Association, Kansas City, Missouri): You mentioned the 500 tons a day, a 24-hour operation, and by rough calculation this would be about 150,000 tons a year.

I was wondering who had a plant that would do that, or whether this thing could be scaled down to, say, a 50,000-ton-a-year plant?

MODERATOR SPILLMAN: Walter, will you come up here and answer that question, please?

MR. GUSHIN: The big advantage is the continuous operation 24 hours a day, but you can't do that unless you have certain volumes and I was wondering whether you had different sized plants and could give us some idea of the cost of these plants?

MR. SACKETT: Sir, actually the plant has been worked out so far in theory—the theory of the idea more than anything else.

We would certainly be able to scale it down. But, so far as giving you a figure on what a plant of this size would cost right now, I couldn't do it. We have been working more on the theory of the idea and have not actually estimated the plant costs, as yet.

MODERATOR SPILLMAN: Are there any other questions?

Thank you, Walter.

Yesterday Mr. J. H. Caro, U.S. D.A. Fertilizer Research Laboratory, Beltsville, discussed all the possible methods for determining moisture in the chemical laboratory.

Our next subject to be discussed is moisture relationships in fertilizer production. This paper will be given by our good friend, James W. Lewis of du Pont.

The Effect of Certain Variables Upon the Condition of Granular Mixed Fertilizers

J. William Lewis

This report deals with results of a study of the effect of certain variables upon the condition of granular fertilizers. The study was a cooperative effort between Du Pont and a manufacturer of mixed fertilizers and was conducted under spring and summer conditions.

The objective of the program was to determine the relative importance of moisture, particle size, and quantity of nitrogen derived from ammoniating solution on the caking characteristics of several important grades of fertilizer. We were particularly interested in bag set during prolonged storage rather than primary pile set.

Manufacturing equipment used in the study was typical of a TVA plant. In consisted of a TVA ammoniator-granulator, dryer, cooler, double deck classification screens, and provision for complete recycle of crushed -over-size and fines. Grades were produced at normal production rates under normal operating conditions, except when necessary to control certain variables under study.

Grades chosen for the study were 8-16-16, 12-12-12, and 16-8-8. The variables were as follows:

a. Each grade was formulated at two solution levels. A low level, using 6 units of nitrogen from solution in each grade and a high level, using 8 units from solution in the 8-16-16 and 16-8-8 grades and 9 units from solution in 12-12-12.

b. Each solution level was made at two moisture contents. These levels were (a) less than 1 per cent and (b) greater than 1.5 per cent with a spread of at least 1 per cent between the maximum and minimum at each solution level. Moisture was determined by the vacuum oven method wherein the samples were exposed for 4 hours in a closed vessel heated to 60 degrees centigrade and evacuated to 20 inches of mercury.

c. Each moisture level was produced at two ranges of particle size. The first, designated as "standard" particles size, was produced using a #6 top and #16 bottom screens on a double deck hummer, while the second range, designated as "coarse," utilized a #6 top and #14 bottom. This, then, resulted in 8 samples with different characteristics for each grade. Figure 1 shows the samples and variables schematically.

The study consisted of two phases: (a) the laboratory phase, and (b) the warehouse storage phase.

The laboratory phase consisted of an accelerated exposure test wherein all samples placed under constant pressure in a controlled humidity room. The samples were exposed in a 40-mesh stainless steel, wire screen cylinder with a two-inch diameter. Polyethylene discs at the top and bottom of each sample restricted moisture penetration to the vertical walls of each cylinder. During exposure, all samples were subjected individually to a constant compacting pressure equivalent to material in the bottom bag of a stack 18 bags high. After exposure, the resulting cake was removed from the cylinder. Crushing pressure needed to dis-

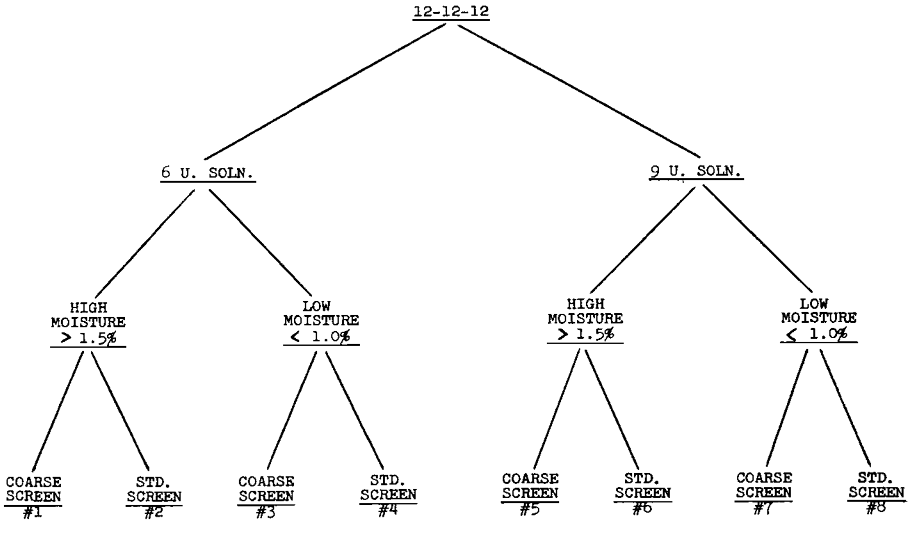


FIG. 1

Schematic Diagram -- Samples and Variables turb the cake was measured in pounds per square inch.

Exposure tests were made by running a set of samples in duplicate through a temperature-humidity cycle. A typical exposure was six hours at 90 degrees Fahrenheit with a relative humidity of 60 per cent followed by a 16-hour drying period at 80 degrees F. with relative humidity at 40 per cent. Separate sets of samples were run through a similar cycle at humidities of 70 and 80 per cent. Samples representing each of the eight production runs for each of the three fertilizers were always exposed simultaneously and in duplicate. Fresh test samples representing one group were used for each exposure and four exposure groups were tested for each of the three humidity levels. In total, this amounted to 576 samples tested.

At the time the sample material was shipped to the laboratory, a sufficient quantity was bagged to provide four stacks of each sample, 12 bags high and stored in the plant warehouse. These stacks were then examined at 2-, 4-, 8- and 12-week intervals. A total of 288 bags—96 for each grade—were examined and evaluated at the end of each time interval with particular concern for the evaluation at the close of the 12-week period.

The bags from warehouse storage were examined in several ways.

1. The first examination, termed the "spike test," was made on each bag in the stack. For this test, a device holds a spike about the size of a ten penny nail on top of a bag of fertilizer. The device is also equipped with a weight which drops a fixed distance on top of the spike. A measure of the relative bag set was determined by the number of drops required to drive the spike into the fertilizer.

2. After the spike test, the bags were removed from the stack and alternate bags were dropped once on the side from a height of four feet. Each bag, whether or not dropped, was then opened and poured across a four mesh screen and the per cent passing through the screen was determined.

After a little experience with the spike test, we soon learned to judge how hard the bag set would be and whether or not the fertilizer would be free flowing with or without the drop.

3. The contents of each bag were also examined visually and certain "judgment factors" were exercised in grading the product. However, for practical reasons, we relied principally on the results of the first two tests in arriving at our conclusions.

We are sure you can appreciate the difficulty in operating a plant to produce a product whose moisture and screen classification were within the ranges prescribed for these variables. Indeed, some samples did not meet the exact requirements. Nevertheless, we felt that the data obtained and the conclusions reached were reliable on a statistical basis.

We do not believe it appropriate, nor does time permit us to present the complete data to this group. We will, therefore, confine our remaining remarks to the conclusions reached as a result of this study.

Conclusions:

1. There was an extremely close correlation between the data obtained in the laboratory and that from storage bags. That is, samples which had the lowest crushing strength after the laboratory exposure also had the least bag set in storage. Likewise, those with the higher crushing strength had the harder set.

2. Product moisture influences the caking of a particular grade of fertilizer significantly more than any of the other variables under study. Low moisture samples caked approximately 35 per cent less than high moisture samples of a given grade.

3. Particle size in the two ranges studied was of secondary importance with the "coarse" samples caking about 15 per cent less than those with " standard" particle size. It should be noted, however, that we probably did not select particle size ranges with enough differential and it is quite probable that material with a higher percentage of fines would show a significantly harder bag set.

4. The level of ammoniating solution had the least effect and was masked to some extent by moisture and particle size.

5. Perhaps the most significant conclusion was that each of the three variables mentioned was overshadowed by the total nitrogen in the formula. In comparing the three grades is was found that the caking tendency increased substantially even though the moisture content decreased as the nitrogen increased from 8-16-16 to 12-12-12 to 16-8-8. This indicates that as the nitrogen content is raised, better granulation and lower moisture content is necessary to provide a free flowing product.

6. The effects of all these variables are additive. The hardest bag set was experienced with 16-8-8 material produced at the higher solution level, higher moisture content, and standard particle size. In contrast, the 8-16-16 at the lower solution level, lower moisture level, and coarse particle size was in the best condition.

7. From a practical standpoint, it was further concluded that to produce a fertilizer with the least tendency to cake, we should:

a. Have about 80 per cent minimum on #16 screen although some latitude may be exercised depending on the particular grade.

b. Moisture contents should range about as follows:

8-X-X and below	1.5% maximum
8-X-X to 12-X-X	1.0% maximum
12-X-X to 16-X-X	0.5% maximum

These conclusions are the consensus of people involved in performing and evaluating the test program. We hope that those of you, who may be experiencing difficulty with bag set, will find this information of value in solving your problem.

MODERATOR SPILLMAN: A good many of you have written in and asked for this topic, apparently some of you have had difficulty with your moistures. Now is the time to put the questions to Mr. Lewis.

Bill, I'd like to ask you a question.

On low nitrogen grades, 5-10-10 or 6-12-12, I understand that some folks can get by with three per cent moisture and we're drying down to one and a half per cent moisture.

Is it necessary to dry down that low on a 5-10-10 or a 6-12-12?

MR. LEWIS: I think on the basis of the results of this study the lower you get the moisture, that is down in the range of one and a half per cent, the much better guarantee you have that bag set is going to be reduced to an absolute minimum. You may never correct it entirely.

Certainly the way to reduce it is to get that moisture down in this case in the range of one and a half to two per cent, and as you go up with nitrogen you have to get progressively lower. That was what the data indicated.

A MEMBER: Bill, did you do any work with 1-4-X grades at all?

MR. LEWIS: No, just the grades mentioned.

MODERATOR SPILLMAN: Thank you, Bill.

We now come to the question and answer period and this part of your program will be off the record.

Question and Answer Period

Alvin B. Phillips

Panel Leader

Allen S. Jackson John H. Daniel, Jr. Myron E. Ruston Elmer C. Perrine Frank T. Nielsson John O. Hardesty	Panel

Questions Discussed:

1—Is it desirable to react sulphuric acid and ammonia or ammonium nitrate-urea solutions in a pre-neutralizer? Would it be preferable to use an ammonia-ammonium nitrate solution?

2—How can we figure a realistic moisture between raw materials and granulated mixer fertilizers? Are we interested in Total Water, Free Water or someplace in between?

3—Are there any advantages using liquid nitrogen containing carbon dioxide for manufacturing mixed goods from the standpoint of better mechanical condition, and to granulate and agronomic value?

4—Granulated mixtures dried down to 1½% moisture or lower, although containing clean classification — 6 + 16, appear to be extremely dusty when handled. Are there any known additives available to include in the formula to relieve the dusting.

5—How important is a rotary granulator following a rotary ammoniator? Or if a combination rotary ammoniator granulator is used how much granulation is accomplished in the granulator section?

6—Are there any new developments on screening between the dryer and cooler? How do higher analyses screen at this point.

7—What is the best method of introducing a pre-neutralized slurry into an ammoniator granulator?

Comments: This question and answer period was a highlight. The panel did an excellent job thoroughly discussing in much detail each of the questions posed. Many members in the audience got into the act discussing the questions. Discussion from the floor was spontaneous and revealed that these production men don't always agree on production methods.

After two and a half hours discussion this session was adjourned at 5 p.m.

MODERATOR SPILLMAN: Thanks Alvin Phillips for leading this question and answer period and congratulations to you and your associate panelists for a job well done and thanks to the members for their spontaneous questions and answers from the floor. This has been an interesting session and no doubt has highlighted this conference. Thank you.

Friday Morning Session, Nov. 8, 1963

Messrs. J. E. Reynolds and A. Spillman, Moderators, presiding.

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

MODERATOR REYNOLDS: Good morning, gentlemen.

The practical and specific processing techniques of our industry have always been a most heavily integral part of your Round Table, and this year is no exception. I think it was indicated yesterday afternoon during the panel when we had a lot of specific questions discussed—we really are glad that your questions came through and we only wish that we had had more.

This Friday's session is directed towards the everyday problem associated with the subject of ammoniation and granulation. During the past 10 years the need for increased plant food recovery and higher granulation efficiencies have become even more pressing. Originally product sizing of minus 4 plus 28 mesh was satisfactory, but this is no longer true. Granulated mixed fertilizer products must be much more uniform and patterned after the so-called BV's which are in the minus 10 plus 12 mesh range.

Our first speaker this morning will discuss granulation techniques of some of the most difficult grades, and particularly those in the 1-4-4 ratio. We have had discussion in the past concerning granulation techniques, ammoniation of these grades, and we are very happy this morning to have Mr. Joe Sharp of Spencer Chemical with us to discuss this subject.

A Study on Granulation of 5-20-20 and 6-24-12 at Different Ammoniation Ratios

Joe C. Sharp

This presentation will only deal with the effect of varying the ammoniation ratio and factors closely associated with the success or failure to achieve good granulation. Many things were tried before any real success was achieved. The studies were made by W. A. McPherson and N. E. Barr of Spencer Chemical Company Technical Department. The initial Pilot Plant run was made on July 8, 1957, and the concluding run on February 17, 1958. Thus, you can see this is a review, rather than a recent study.

It is hoped that the information will be of help to at least some of you. Many of you will recall what a struggle it was to granulate these two grades properly in the early days of granulation. Possibly there are days now when you run into problems because of lack of consistency of raw materials, faulty equipment or for some other reason. Even the weather may share in the blame and perhaps the cause of these problems.

The work on 5-20-20 was started, by deriving all of the nitrogen from 414 (19-74-0) solution, the P_2O_5 from the combination of normal and triple superphosphates and K_2O from muriate of potash. The ammoniation rate using this solution was 2.3 lbs. of free ammonia for each unit of P_2O_5 in the formula derived from the combined superphosphates. Steam was used as an aid to granulation. Even so, granulation was not good at this ammoniation ratio.

The importance of ammoniation ratio was recognized after several unorthodox experiments were made, so the authors report. In the first of these experiments 100 lbs. of sulphuric acid were added to the 5-20-20 formula and the superphosphates adjusted to balance out to the ton. This reduced the ammoniation ratio on the combined superphosphates to 1 lb. of ammonia per unit of P_2O_5. The product over-granulated and melted in the drier.

It had been noted previously that on startup, when the dry raw materials were added to the ammoniator in order to cover the sparger, before solution and steam flow was started, a period of the good granulation occurred before sufficient solution had been added to reach the calculated ammonia-tion rate. By the time the full ammoniation ratio was reached, granulation dropped off noticeably.

The next step was to use granular triple superphosphate without acid. The product over-granulated and showed signs of further agglomeration in the drier. To determine why over-granulation occurred with granular superphosphate at 2.3% ammoniation rate (2.3 lbs. of ammonia for each unit of P_2O_5) and that pulverized triple superphosphate at the same ammoniation rate under-granulated, free acid analyses were made on the two superphosphates. The granulated product contained 6.9% more free acid than the pulverized material. This meant that 700 lbs. of granular triple superphosphate would require 13 lbs. of free ammonia to bring it to the same pH of the pulverized triple superphosphate. It is believed that the difference in free acid content accounted for the difference in the granulation characteristics.

The above experience led to the conclusion that somewhere between an ammoniation rate of 1% and 2.3% good granulation could be achieved and the product could be heated to a sufficiently high temperature in the drier to remove the necessary moisture without destroying what had been accomplished in the ammoniator.

In order to verify this conclusion, a combination of ammonia and 318 (8-72-0) solution was used to supply the nitrogen in 5-20-20. To start with, a 5% ammoniation rate was used, then ammonia was decreased and 318 (8-72-0) solution increased in such a way as to keep the total nitrogen in the formula constant. As the ammoniation rate approached 2%, the product in the ammoniator changed from dry crystalline particles to smooth round granules. By altering the ammoniation rate, granulation could be made good or bad at will. It should be pointed out at this time that the ammonium nitrate content was changed along with the ammoniation rate. As the ammonium rate decreased, the ammonium nitrate content increased. Thus, there were two factors that contributed to better granulation. However, Messrs. McPherson and Barr did some later work on 12-12-12 that contained large quantities of ammonium nitrate on which they varied the ammoniation rate and obtained results similar to the 5-20-20 findings.

On 6-24-12, all the nitrogen was derived from 340 (12-69-0) solution. An extremely good granulation resulted. This was an ammoniation rate of 1.77%. When 490 (34-60-0) solution was used as the source of nitrogen and ammoniation rate brought to 2% with the use of sulphuric acid, poor granulation resulted. On another run, 490 (34-60-0) solution was used to obtain a 2 % ammoniation rate without the use of sulphuric acid. Ammonium nitrate was added for the balance of the nitrogen requirement. Very good granulation was obtained. When 448 (25-69-0) solution was used to obtain a 2% ammoniation rate and ammonium nitrate added to supplement the nitrogen, granulation was as high as 80% of particle size range between 6 and 20 mesh.

Other important factors in promoting uniform granulation were even solution and steam distribution, temperature and the kind of triple superphosphate used. While 5-20-20 could be satisfactorily granulated in the temperature range between 150°F. and 210°F., the temperature had to be very near 200°F. for 6-24-12. A 10°F. variation would seriously impair granulation. Success was never attained using pulverized triple superphosphate. What might be termed a medium-coarse potash was used throughout the study. A TVA-type ammoniator granulator was used.

Conclusions: From McPherson and Barr's work, there seems little doubt that amoniation ratio affects granulation of 5-20-20 and 6-24-12. Best results were obtained when the ammoniation rate did not exceed 2 lbs. of free ammonia per unit of P_2O_5 from the combined superphosphates and the supplemental nitrogen derived from ammonium nitrate. It made little difference whether the ammonium nitrate was part of the solution that furnished the free ammonia or whether it was added as a solid.

The formulas for optimum granulation are not the most economical insofar as raw material costs are concerned in most cases. Substantially all the P_2O_5 is water soluble which may or may not be a compensating factor.

MODERATOR REYNOLDS: Thank you, Joe.

Are there any questions of Mr. Sharp?

A MEMBER: What are the bag storage characteristics?

MR. SHARP: Bag storage tests were not run on this particular lot. This was just strictly a matter of trying to find the best way to obtain granulation.

However, in these grades bag set is not a real problem, because even with the amount of ammonium nitrate you put in here it is not enough to be of particular bother. You never run into any problem where you get the moisture content down as low as one per cent.

MEMBER: One per cent?

MR. SHARP: Yes, you probably can get by with a little higher per cent of moisture on these, but good safe moisture is one per cent.

MODERATOR REYNOLDS: Let's have another question.

A MEMBER: I would like to know what the particle size on the pulverized material was?

MR. SHARP: I can't give you accurate particle size but it was a coarse triple superphosphate and a medium coarse potash, and normal superphosphate was pulverized.

MODERATOR REYNOLDS: Does anyone else have any questions or comments to contribute on this subjects in relation to this 1-4-4 ratio? Are there any other techniques here that might contribute?

From a strictly granulation standpoint, this is probably one of the most discussed grades, like 5-20-20 or 6-24-12, it's one of the most difficult grades to wrap up to reduce your oversize, to reduce your fines.

Joe.

MR. SHARP: I'd like to make one other statement. This work is not intended to be the final way to make 5-20-20 or 6-24-12. I know a lot of you who do it other ways but this is just information that is a contribution to the knowledge on granulation of these two type grades. This is not intended to be the final analysis and the final formulas that you would want to use, but it is some additional information.

MODERATOR REYNOLDS: Any other information?

If not, we will move on to our next speaker. Chances are at the end of the session this morning, we can have some other questions that you will have thought of by that time.

Continuing on, as indicated early this morning, we are on the subject of ammoniation granulation so without any further comments, I will turn the session over to Mr. George Gilliam of the Nitrogen Division who will give us a general review and bring us up to date on ammoniation.

Ammoniation Summary

George R. Gilliam

Introduction

The practice of combining ammonia with acid materials in the manufacture of complete fertilizers is known as ammoniation. The ammonia may be added in the form of anhydrous, aqueous or as ammoniacal salt solutions. The amount of ammonia added per unit of P_2O_5 is known as the ammoniation rate.

Ammoniation of superphosphate is almost entirely an American development and is possible because our major crops show excellent response to citrate soluble P_2O_5. In areas where water soluble P_2O_5 is required, ammoniation is not used, or it is limited to very special cases. Although the basic principles on the use of ammonia as a source of nitrogen and as a neuralizing agent for acid phosphates were reported in the literature during the second half of the nineteenth century, commercial practice in the United States had its beginning in the early 1930's. This was at the time synthetic ammonia processes had been established and low cost nitrogen became available to the fertilizer industry.

For the fertilizer manufacturer, ammonia is the lowest cost and most concentrated source of nitrogen. However this product has its limitations. It is a gas at ordinary temperature and pressure and thus requires pressure equipment and special techniques for handling in the liquid state. Also, the amount of ammonia nitrogen introduced in any given formulation is dependent upon the capacity of the raw materials to absorb and fix ammonia. By converting anhydrous ammonia to an aqueous solution the need for pressure equipment can be overcome. This type of solution has had wide acceptance by fertilizer manufacturers. Limitations are high water content (about three units water per unit of nitrogen added) and capacity of other fertilizer ingredients for ammonia. Because of these factors the nitrogen industry developed at an early date the so-called nitrogen solutions.

This development, utilizing the high solubility of nitrogen salts in ammonia and water, gave the fertilizer industry a single liquid source containing both neutralizing ammonia and neutral nitrogen salts. These solutions offered a form of nitrogen which was easier to handle and cheaper than the combination of ammonia plus solid nitrogen materials. It was through nitrogen solutions and ammoniation practices that the nitrogen compounds of urea and ammonium nitrate became available to the fertilizer industry many years before they were available in solid form for agricultural use.

Early Commercial Practice

Prior to the time nitrogen solutions and ammonia became available to the fertilizer industry, mixed fertilizers were essentially a blend of solid materials. Their manufacture was basically receiving and storing raw materials and processing these materials through a batch mixer in weight ratios to produce a desired N-P-K grade. The material was denned for a sufficient time to allow it to reach chemical equilibrium, packaged and shipped in a form suitable for agricultural use. With these facilities the transition from solid sources of nitrogen; such as, sodium nitrate, ammonium nitrate, guano and other organic materials to the new forms of liquid nitrogen was relatively simple. All that was required for processing was to convert the mixer into an ammoniator by installing a sparger for dispersing liquids. Additional equipment included an air compressor or pump, a measuring tank, and piping to carry the liquid nitrogen from storage (usually the suppliers tank car) through the measuring tank to the ammoniator. The process then became batch loading of the solid ingredients into the mixer and ammoniating at a selected rate and time to give optimum absorption of ammonia. The batch was then discharged to a conveyor belt which transported the warm, moist goods to storage.

The bulk of the fertilizers made were of low nitrogen analysis and they contained normal superphosphate as the major source of P_2O_5. Ammoniation rates were limited to 20 to 30 pounds of ammonia per 1000 pounds of superphosphate to avoid P_2O_5 reversion in storage. Nitrogen sources in liquid form available at this time, other than ammonia, were composed of ammonia-sodium nitrate-water, ammonia-ammonium nitrate-water, and ammonia-urea-water. Total nitrogen ranged from 37 to 45%. Because of the low ammoniation rate, solution nitrogen allowable for any formulation was about 0.3 per cent per unit of P_2O_5. Use of anhydrous ammonia allowed only about one half this amount of nitrogen. In addition to benefit of low nitrogen cost, ammoniation improved physical condition of the fertilizer and reduced bag rot through neutralization of free acid. There was very little change in processing methods during the next fifteen to eighteen years.

Developments

Following World War II, the ever-growing need of American agriculture for more and better fertilizers, especially high nitrogen grades, resulted in a series of technical advances in fertilizer technology. Coolers were installed to remove heat developed from ammoniation. This resulted in a cooler and also drier product to storage, thus improving condition and reducing P_2O_5 reversion. With limited control of temperature, ammoniation rates were pushed upward with some operators balancing the cost of P_2O_5 reversion against the advantage of low cost solution nitrogen.

About this time work conducted in both government and private laboratories showed that pile moisture and temperature were the major factors affecting product condition and P_2O_5 reversion, thus exploding the theory that reversion was directly related to ammoniation rate. This was a signficant development, opening the door to greater use of ammonia and solution nitrogen and leading directly to higher nitrogen grades. As plant food content per ton of fertilizer increased, product condition became more and more a limiting factor. In each case where condition problems existed, reduction of moisture was proven to be the practical answer. Lower moistures were obtained through the use of improved superphosphate and nitrogen solutions having lower moisture content and the installation of dryers and coolers by the fertilizer manufacturer.

Although I have not mentioned granulation, this development was very much in evidence during this period. It was through granulation that the high liquid phase resulting from increased ammoniation rate could be tolerated and more low cost nitrogen could be added as solution.

One can readily see at this stage that fertilizer manufacturing was becoming much more complex than that which existed prior to 1950. Ammoniation rates had been doubled for normal superphosphate to the present 6.0 to 6.5 pounds per unit of P_2O_5. Rates of 2.5 to 3.5 pounds were being used for triple superphosphate. Dryers and coolers had been added and granulation was common practice rather than the exception.

The contribution from T.V.A. of the continuous ammoniator-mixer was a major advancement in fertilizer processing. This was the first continuous unit ever designed in which the ammonia absorption equalled that of the batch mixer. In addition, the rolling type action promoted granulation, and a continuous uniform feed to the dryer was possible. This unit has virtually replaced the batch mixer in full granulation plants.

In plants that did not have drying and cooling equipment, higher nitrogen solution usage was accomplished through semigranulation. Here sulphuric acid was added with the nitogen solution in quantities necessary to neutralize the excess free ammonia. The high heat of neutralization served both to remove water and promote granulation.

Phosphoric acid, both wet-process and furnace grade, has become important in ammoniation practices with high-analysis dry fertilizers and liquid fertilizers. In solid fertilizers it can be ammoniated to rates of 7.2 to 7.5 pounds of ammonia per unit of P_2O_5. The moisture in wet-process acid compares favorably with that of improved 20% superphosphate at about eight pounds of water per unit of P_2O_4. Ammoniation in liquid fertilizer manufacture is controlled to obtain the maximum solubility of the ammonium phosphate salts. The ammoniation rate normally employed is 7.7 to 8.1 pounds of ammonia per unit of P_2O_4.

Phosphoric acid has proven satisfactory for partial ammoniation in the pre-neutralizer. This practice was first introduced in 1957 by Virginia-Carolina Chemical Corporation. Ammoniation rates up to about 4.7 pounds of ammonia per unit of P_2O_5 can be obtained followed by further ammoniation in the mixer up to the normal 7.2 to 7.5 pound rate.

Current Practice

The various processes and developments which I have briefly described more or less cover ammoniation as it exists in the fertilizer industry today. The price differential initially existing between liquid and solid nitrogen exists today and it indicates the use of as much ammonia and solution nitrogen as possible. There are approximately eighty nitrogen solutions on the market, many of which only have slight differences in composition. Most have technical reasons for their existence. In general, the choice of solution for any given grade would be one having the ratio of neutralizing ammonia to nitrogen salts needed to satisfy formulation, production economy, and agronomic requirements.

Looking ahead, what is needed today are developments pointing the way to higher ammoniation without sacrificing economy.

Moderator Reynolds: Thank you, George.

Do we have any questions?

I think what we will do after the next speaker is ask all three speakers to come up to the center table. I am sure by that time we will have some followup questions from the floor.

We will move on to our next speaker continuing on with the subject of granulation. George gave us an excellent presentation here bringing us up to date on ammoniation from the beginning to the present. Bob Church of the du Pont Company is going to give us a similar summary here relating to granulation.

Formulation for Optimum Granulation

Robert J. Church

A simplified approach for evaluation of fertilizer formulas, with respect to their ability to produce the optimum degree of granulation, has been developed. This method is based on the amount of heat developed when anhydrous ammonia is reacted with the acidic ingredients commonly used in the granular type of fertilizer formulations (Table I).

In the granulation process, the more important variables are (1) the formula, (2) the manufacturing equipment, and (3) the operating conditions (Table II). Of these three variables, the formula is subject to the greatest variation in any given individual manufacturing plant. As illustrated, the ratio of liquid phase to solid materials is the basic variable in the formula. Considering these basic variables, there is an obvious correlation between the amount of liquid phase and solid materials required for granulation. Furthermore, there is the correlation be-

Table I. Rates and Heats of Ammoniation

Material Reacted With Ammonia	Rate of Ammoniation, lbs. of NH_3 Per unit of P_2O_5	Heat Released Per lb. of NH_3 B.T.U.s	Heat Released Per lb. of NH_3 calories
Normal Superphosphate	5.8	1430	39.7
Triple Superphosphate	3.8	1540	42.8
Phosphoric Acid	7.2	1780	49.4
Sulfuric Acid, 66°Bé	0.324	2940	81.7

Table II. Important Variables in Granulation

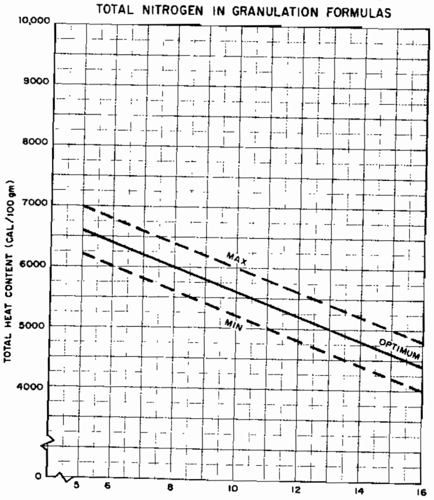
I. Formula
  A. Liquid Phase
    (1) Water
    (2) Water Soluble Salts
    (3) Heat Generated by Reaction of Ammonia with Acidic Ingredinets
  B. Solid Materials
II. Manufacturing Equipment
III. Operating Conditions

tween the specific components which make up the liquid phase, i.e., the amount of water, the water-soluble salts, and the heat generated by the reaction of ammonia with the acidic ingredients present in the formula.

A relationship between the total nitrogen of the formula and the total heat from the reaction of ammonia (primarily from ammoniating solutions) with the acidic ingredients, has been developed and is illustrated in Figure I. This relationship was developed from studies of published reports on granulation, and of many practical granulation formulas. As illustrated, the total heat required for granulation decreases as the total nitrogen increases. The curves labeled "maximum" and "minimum" describe the area where good granulation has been obtained. The "optimum" curve represents the average total heat that is described by the maximum and minimum curves. Though granulation may occur either above the maximum or below the minimum curves, the best granulation, as reported, has been found to occur in the area between the two curves. The total heat content is expressed as calories/100 grams, and can easily be converted to BTU/ton by multiplying by the factor 36.

FIGURE I

RELATIONSHIP OF TOTAL HEAT CONTENT TO TOTAL NITROGEN IN GRANULATION FORMULAS

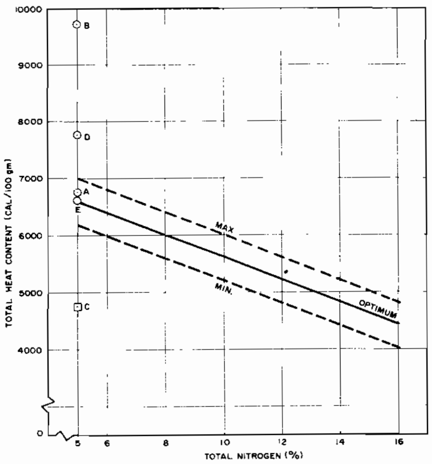


The curves were developed as follows:

1. The graunlation of a variety of formulations for a 5-20-20 grade fertilizer (Table III) containing triple superphosphate was discussed at the 1960 Fertilizer Round Table meeting.(2) As the author stated, the total heat for Formula A at 6,750 cal/100 gm., and Formula E at 6,610 cal/100 gm., was sufficient for good granulation. However, little improvement in granulation was found on increasing the total heat to 9,720 cal/100 gm. as in Formula B or in Formula D at 7,750 cal/100 gm. In Formula C, the decrease in total heat to 4,780 cal/100 gm. was sufficient for good granulation, even though the amount of water soluble salts was increased which presumably would have increased the effectiveness of the liquid phase. The relationship of the total heat to the described quality of the granulation of these formulas is illustrated in Figure 2.

FIGURE 2

VARIATION OF HEAT CONTENT IN 5-20-20 GRADE FERTILIZER FORMULAS



The heat for Formulas A and E was therefore used to describe the area of good quality granulatin for the 5-X-X grade fertilizers.

2. To complete the definition of the curves for good quality granulation, six additional formulas are illustrated in Tabel IV. Formulas F, G, H, and I, were used successfully to produce good quality granulation during normal production runs. Poor granulation was obtained from Formula J, having a total heat less than described for the minimum heat needed for good granulation. Formula K represents a formula having too high a total heat along with too much liquid phase which, when tested in laboratory-scale granulation equipment, produced a severely overgranulated product. The total heat

Table III. Formulation of 5-20-20 Grade Fertilizer

Materials	Analysis, % Moisture	Plant Food	Formula, (lb). A	B	C	D	E
Anhydrous Ammonia	—	82.3% N	125	125	84	84	84
Solution 440*	6.0	44.0% N	—	—	77	77	77
Normal Superphosphate	7.0	20.0% P_2O_5	439	25	514	98	262
Triple Supehphosphate	5.0	46.0% P_2O_5	696	876	663	844	773
M. Potash	—	61.0% K_2O	656	656	656	656	656
Sulfuric Acid 66°Bé	6.8	— —	118	348	43	275	182
Total (lb.)			2034	2030	2037	2034	2034
Ammonia Supplied, lb.			125	125	101	101	101
Ammonia Capacity, lb			125	189	102	169	143
Heat of Reaction, cal/100 gm			6750	9720	4780	7750	6610

*Solution 440 (22-66-0)

Table IV. Formulas Used to Describe Granulation Curves

	Formulas (lb.)					
Materials	F 8-16-16	G 10-10-100	H 15-10-10	I 16-8-8	J 10-20-20	K 15-10-10
Solution 455*	379	365	—	—	330	—
Solution 405**	—	—	257	297	—	—
Solution 435***	—	—	—	—	—	414
Urea 45%	—	—	—	—	125	—
Amm. Sulfate 20.5%	—	224	984	950	—	572
H_3PO_4 54.5%	—	—	295	294	—	370
H_2SO_4 60°Bé	180	208	—	41	132	—
H_2SO_4 66°Bé	—	—	—	—	—	134
ROP 20%	713	1038	229	—	—	—
CSP 46%	405	—	—	—	876	—
M. Potash 60%	550	343	338	267	667	338
Filler	—	56	3	257	—	288
Total (lb.)	2227	2234	2106	2106	2139	2116
Total Heat Content cal./100 gm	5610	6020	4650	4740	4500	8300

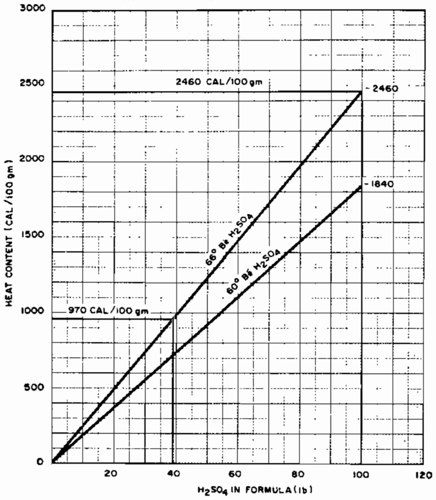
*Solution 445 (30-0-43) contains 10% CO_2.

**Solution 405 (38-0-38) contains 8.5% CO_2; 4% other material.

***Solution 435 (38-0-40-10) contains 9.2% CO_2; 10% ammonium sulfate.

FIGURE 4

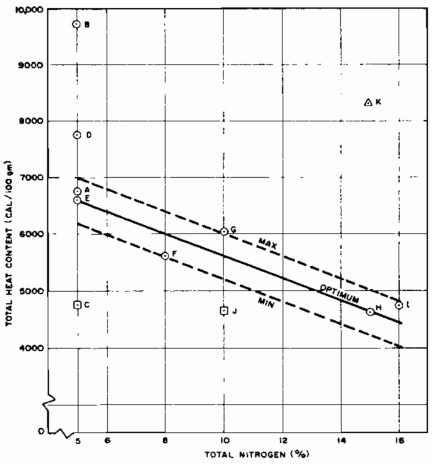
RELATIONSHIP OF HEAT CONTENT TO AMOUNT OF SULFURIC ACID IN FORMULA



of each of these formulas, as related to their respective total nitrogen, is illustrated in Figure 3.

FIGURE 3

ILLUSTRATION OF THE DEVELOPMENT OF THE OPTIMUM GRANULATION CURVES



Using Figure 1, in evaluating a particular formula with respect to its ability to produce a quality granular product, the formulator needs only to know (1) the amount of mineral acid available in the formula, (2) the units of P_2O_5, and (3) the ammoniation rate for the phosphate source. With this information, the total heat of the formula is calculated as the sum of the heats of reaction of the ammonia with the acidic ingredients. The granulation ability of the formula is then determined by relating the total heat to the total nitrogen through the use of these curves.

For example, the determination of the granulation ability of a 12-12-12 grade fertilizer⁽³⁾ would proceed as follows (Table V):

Table V. 12-12-12 Grade Fertilizer

Materials		Amount (lb.)	NH_3 (lb.)	Heat Content cal/100 gm
Solution 410*	(41% N)	451	+99	
Ammonium Sulfate	(20.5% N)	297		
Normal Superphosphate	(20% P_2O_5) **	415	–24	940
Triple Superphosphate	(46% P_2O_5) **	355	–31	1280
M. Potash	(60% P_2O_5)	480		
H_2SO_4 66°Bé		139	–44	3430
		2137 lb.		5640

*Solution 410 (22-66-0)

**Ammoniation Rate:

Normal superphosphate = 5.8 lbs. NH_3/unit P_2O_5

Triple Superphosphate = 3.8 lbs. NH_3 Unit P_2O_5

1. Determine the total free ammonia from the ammoniating solution; in this case, 99 pounds of free NH_3:

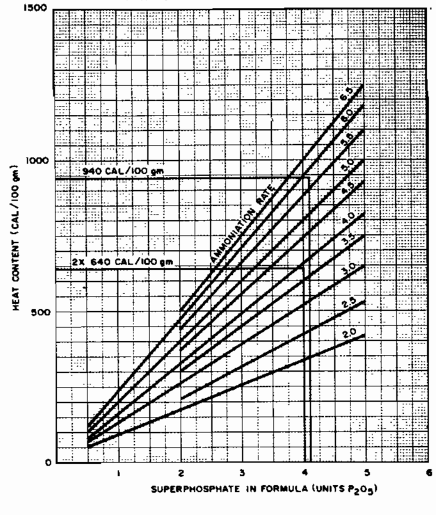
2. Determine the ammoniation rate and the units of P_2O_5 for the particular superphosphate source, in this case:

Normal super (ROP) = 5.8 lb. NH_3/unit P_2O_5 for 4.15 units.
Triple super (CSP) = 3.8 lb. NH_3/unit P_2O_5 for 8.00 units.

3. Using the calculating charts determine the heat liberated for 139 pounds of 66° Bé H_2SO_4 (Figure 4). The total heat liberated would be 3,430 cal/100 gm. for 139 pounds of the acid (i.e., 2,460 cal/100 gm. for 100 pounds of acid plus 970 cal/100 gm. for 39 pounds of acid). Further, the heat liberated for the ROP would be 940 cal/100 gm., and for the CSP it would be 1,280 cal/100 gm.⁽⁴⁾ (Figure 5).

FIGURE 5

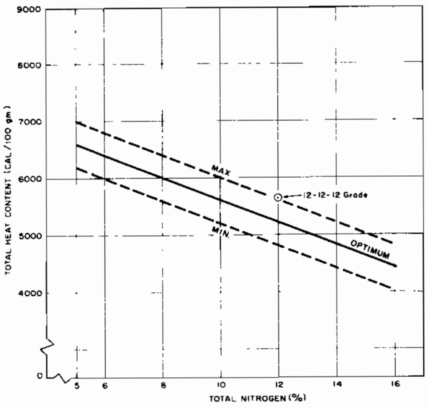
RELATIONSHIP OF HEAT CONTENT TO AMOUNT OF SUPERPHOSPHATE IN FORMULA



4. The total heat liberated would be 5,640 cal/100 gm. for the 12-X-X grade fertilizer and as seen, the total heat falls close to the maximum curve (Figure 6).

FIGURE 6

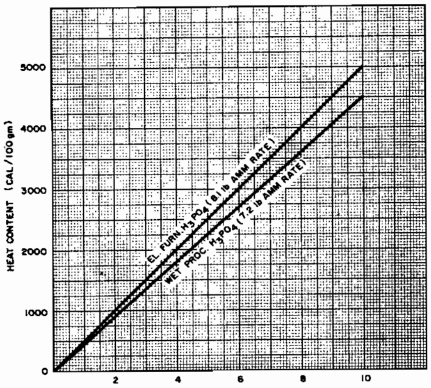
EVALUATION OF GRANULATION ABILITY OF A 15-15-15 GRADE FERTILIZER



Curves for the rapid calculation of the heat of the reaction of ammonia with phosphoric acid are illustrated in Figure 7. As in the case of the solid superphosphates, the formulator needs only to know the number of units of P_2O_5 supplied by the specific type of phosphoric acid in order to determine the desired heat value.

FIGURE 7

RELATIONSHIP OF HEAT CONTENT TO AMOUNT OF PHOSPHORIC ACID IN FORMULA



The subject of preneutralization has been discussed in a number of papers presented at the Fertilizer Industry Round Table meetings. The results of a preliminary study of a limited number of formulas, indicate the possible application of this evaluating method. For example, the manufacture of a 15-15-15 grade granular fertilizer was discussed at the 1962 Fertilizer Industry Round Table(5) (Table VI). The total heat of the formula was calculated to be 8,890 cal/100 gm., i.e., 6,750 cal/100 gm. at the preneutralizer and 2,220 cal/100 gm. at the ammoniator. For the normal granulation process this amount of liberated heat would be far in excess of the normal amount of heat required for good granulation.

Table VI. Preneutralization of a 15-15-15 Grade Fertilizer

Manufacturing Point	Materials	Amount (lb.)	NH_3 (lb.)	Heat Content (cal/100 gm)
Preneutralizer	Solution 440*	372	+88	
	H_2SO_4 66° Bé	275	–88	6760**
Ammoniator	Solution 440	210	+52	
	Amm. Sulfate	145		
	Diam. Phosphate	138		
	Triple Super.	310	–27	570
	H_3PO_4	127	–25	1650
	M. Potash	490		
	Total	2067 lb.		8980

*Solution 440 (27-70-0)

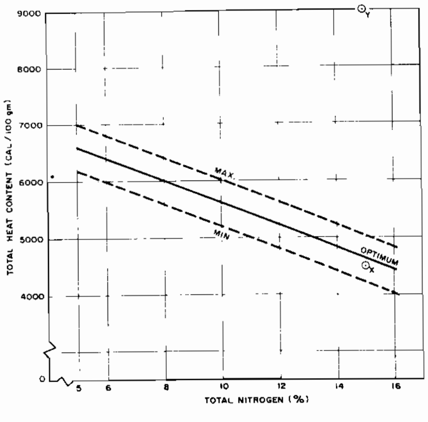
**Correction of Heat Content:

6760 cal/100 gm. calculated heat content
— 4480 cal/100 mg. 2/3 of above, as heat loss
2280 cal/100 gm. total effective heat from preneutralizer
thus 2280 cal/100 gm.
+ 2220
Total 4500 cal/100 gm. (or Point X, Figure 8)

If the preneutralizer is considered to be primarily a means of dissipating the heat evolved from the reaction of ammonia with a mineral acid, i.e., sulfuric acid, then it would be reasonable to assume that a substantial portion of the 6,760 cal/100 gm., formed in the preneutralizer, would be lost before the aqueous slurry was added to the ammoniator. Thus, for this specific case, it was assumed that at least two-thirds of the heat of reaction was lost during the preneutralization step. The total heat of the 15-15-15 grade fertilizer would then be 4,500 cal/100 gm. (point X, Figure 8) instead of 8,980 cal/100 gm. (point Y, Figure 8). The preneutralizer would now contribute only 2,280 cal/100 gm. to the subsequent granulation instead of the 6,760 cal/100 gm. as initally calculated.

FIGURE 8

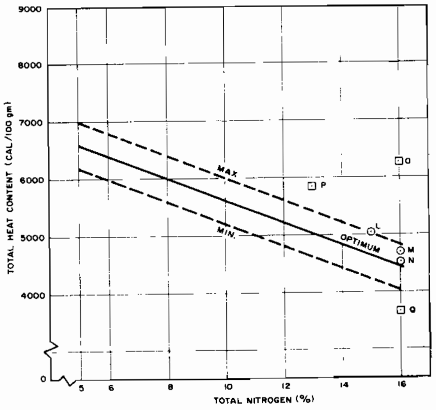
EVALUATION OF PRENEUTRALIZATION TYPE FORMULAS



Inspection of other preneutralization formulas indicates a reasonable degree of justification for the above assumption. For example, if the total heat for Formulas L, M, and N, are corrected for the heat loss as previously described (Table VII) (6,7) the resulting total heat of these formulas then show a promising degree of correlation with the curves describing optimum granulation (Figure 9). The results of evaluation of Formulas O, P, and Q, (Table VII) (7,8), as illustrated in Figure 9, show that further study of this particular type of granulation process is needed.

FIGURE 9

EVALUATION OF PRENEUTRALIZATION TYPE FORMULAS



The use of steam in graunlation is a third area where this method of evaluation of a formula

Table VII. Preneutralization Type Formulation

Example of Correction of the Total Heat Content

Formula L 15-15-0 Grade

Manufacturing Point	Materials	Amount (lb.)	Heat Content (cal/100 gm)	Corrected Heat Content (cal/100 gm)
Preneutralizer	Solution 448*	311	8350	2780
	H_2SO_4 66°	250		
	H_3PO_4	176		
Ammoniator	Solution 448	377		
	Normal Super.	1017	2240	2240
		2131 lb.	10590	5020
Formula N 15-15-15 Grade				
Preneutralizer	Solution 448*	302	9300	3100
	H_2SO_4 66°	242		
	H_3PO_4	272		
Ammoniator	Solution	386		
	Normal Super.	750	1600	1600
	M. Potash	175		
		2127 lb.	10900	4700
Formula M 16-8-8 Grade				
Preneutralizer	Solution 410**	596	8790	2930
	H_2SO_4 66°	353		
Ammoniator	Solution 410	205		
	Normal Super.	560	1580	1580
	Triple Super.	133		
	M. Potash	270		
	Filler	20		
		2137 lb.	10370	4510

*Solution 448 (25-69-0)
**Solution 410 (19-73-0)

Table VIII. Preneutralization Type Formulation

Formula O 16-20-0 Grade

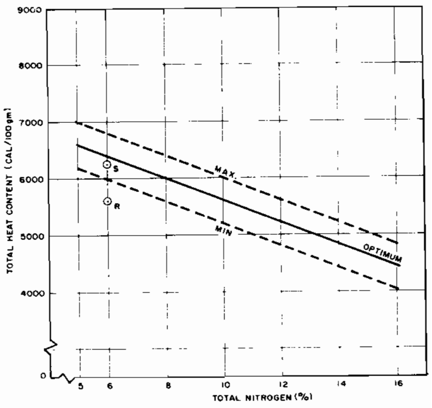
Manufacturing Point	Materials	Amount (lb.)	Heat Content cal/100 gm)	Corrected Heat Content cal/100 gm)
Preneutralizer	Solution 448*	384	7580	2530
	H_2SO_4 66°	308		
Ammoniator	Solution 448	349		
	Normal Super.	350	3720	3720
	Triple Super	718		
		2109 lb.	11300	6250
Formula P 13-39-0 Grade				
Preneutralizer	Solution 370**	488	5310	1170
	H_3PO_4	515		
Ammoniator	Analyzed NH_3	87		
	Triple Super.	1085	4050	4050
		2175 lb.	9360	5820
Formula Q 16-20-0 Grade				
Preneutralizer	Solution 370**	434	4500	1500
	H_3PO_4	405		
Ammoniator	Solution 370	325		
	Normal Super.	900	2160	2160
	Amm. Sulfate	190		
		2250 lb.	6660	3660

*Solution 448 (25-69-0)
**Solution 370 (17-67-0)

might be useful to the formulator. Two formulas are used to illustrate the simplicity of this method of evaluation.(9) Based on the assumption that dry steam is used, then for each pound of steam, 27 cal/100 gm. of heat will be available for the granulation process. Thus, in Table IX, it is seen that 105 pounds of steam are used in Formula R to supply about 2,840 cal/100 gm. In Formula S, 150 pounds of steam are used to supply about 4,050 cal/100 gm. The total heat of both formulas, as related to the curves describing the area for optimum granulation is illustrated in Figure 10.

FIGURE 10

EVALUATION OF GRANULATION FORMULAS USING STEAM



This method of evaluating the quality of the granulation of fertilizer formulas, produced in the conventional granulation process, has been used successfully over the past two years. The curves, as described in Figure 1, are adequate for use by any formulator. The effectiveness of this evaluating method could be greatly improved, however, through the development of similar curves for a specific manufacturing plant. These new curves would then reflect more precisely the effects of the liquid phase on granulation while holding constant the variables in the manufacturing equipment and operating conditions. For example, a more accurate measure of the quality of the granulation could be obtained by a study of screen analysis, heat content, and formulation data. Also, it may be desirable to study the effect of the producion rate and the physical nature of the solid materials on the quality of granulation.

In summary, a simplified ap-

Table IX. Granulation Formulas Using Steam

Formula R 6-12-12 Grade

Materials	Lbs.	Steam	Heat Content (cal/100 gm)
Solution 448*	273		
Normal Super.	1200		2760
M. Potash	393		
Filler	214		
		105	2840
	2080 lb.		5600
	Formula S 6-24-24 Grade		
Solution 448*	211		
D. A. P. (18-46-0)	155		
Triple Super.	888		2200
M. Potash	787		
		150	4050
	2041 lb.		6250

*Solution 448 (25-69-0)

proach to evaluating the quality of granulation as produced in the conventional granulation process, has been developed and its use in practical formulations has been illustrated. This method of evaluation is based on the relationship of the total nitrogen to the total heat liberated from the reaction of ammonia with the acidic ingredients present in a particular fertilizer formula. With further study, this method of evaluation may also find use in those processes utilizing preneutralization or steam.

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MODERATOR REYNOLDS: Thank you very much, Bob.

Let's hear some comments from the floor. I am sure we have some questions.

A MEMBER: I would like to ask Bob what consideration in the test work he did what sort of ratios he actually used and did he consider recycle at all?

MR. CHURCH: In this process?

MEMBER: Yes.

MR. CHURCH: No. Ratios and recycles were not considered. The amount of recycle was unknown in many of the illustrated examples. The subject of the paper presents a possible way for determining the ability or the capability of the particular formula to produce a good granular product.

As pointed out, in maybe a very rapid fashion at the latter end of the talk, these curves would represent, or we believe should be used as a guide in formulating a granular product. More precise curves could be obtained by evaluation of specific formula as based on the operation conditions in a specific plant.

These curves were developed as based in part on work reported by members in the industry.

We have no data on what the production rate was in any of these formulations because in most cases it was not reported.

MODERATOR REYNOLDS: Any other questions?

A MEMBER: Did you relate the heat liberated to bed temperature?

MR. CHURCH: No, we didn't, again because such information was not available.

MODERATOR REYNOLDS: Has anyone else tried to coordinate this information, tried to develop similar curves perhaps or charts? I think there has been quite a bit of discussion on this subject, as indicated by some of the questions yesterday and also some of the discussion in the halls, so apparently we are in fact interested in the relationship between temperature and some of the liquid phase studies.

Some work was done several years ago on the subject of liquid phase. I don't know whether temperature study with liquid phase was tied in or not.

George, do you have any comments to make on that?

MR. GILLIAM: The answer is yes, we tied in heat with liquid phases but I wouldn't want to get into discussion on it.

I do have one question I would like to put on the floor though. I don't know whether Bob has mentioned that we use steam as an aid in granulation. Steam has become important or of a great deal of interest you might say in granulation, as a source of heat.

Right at the moment I do not have a figure on how much of the heat that we supply as steam is actually recovered in your granulation process. That is, if we want 3,000 calories of heat, can we put in that amount of heat from steam and actually get 100 per cent efficiency recovery in the ammoniator, or do we have to put in more steam and take a 60 per cent factor and the other 40 per cent is lost.

That is, how much can we recover, how much heat of the actual steam added can we recover in the efficiency of granulation?

MODERATOR REYNOLDS: George is asking a question here concerning efficiency of steam.

Does anyone have any comments on that? Joe you did considerable work on steam several years ago also. Was your experience in a plant related to 100 per cent recovery?

MR. SHARP: Joe, I am not able to quote any data on that. I am sure that you do not recover it all and I certainly don't remember any data, but since steam is something that doesn't affect the formula itself, you just sort of adjust that to get the best granulation.

Now in the case of sulfuric acid or something like that, you've got to be more careful, or at least you should, some operators aren't. But so far as the steam, we really never did run a heat balance on it in the ammoniator.

MR. CHURCH: Steam was assumed to be of 100 per cent quantity and as such we made our calculations on that basis.

MODERATOR REYNOLDS: Thank you, Bob.

MEMBER: Was there any factor for water added in the formula. No.

MEMBER: Total water.

MR. CHURCH: Not on total water. Using only data as reported, in the majority of cases, there was no mention of the amount of supplemental water used, if any, in the granulation process.

MODERATOR REYNOLDS: We have time for a couple more questions. Perhaps many of you can go back to your plant during the next year and develop similar information and we can see if we can get some correlation here.

If there are no questions, then I will turn the program back to Dr. Sauchelli.

Thank you very much for your attention.

CHAIRMAN SAUCHELLI: That certainly is a very interesting approach to this problem of granulation. It certainly ought to stimulate must interest.

Our Thirteenth Anniversary Meeting is coming to a close. From the comments expressed and those overheard here and there, I judge we have another successful Round Table. We certainly hope so.

We trust each of you is taking home many ideas and suggestions that will help you in your work. It may not be amiss to re-emphasize that this Round Table is your forum, that you create the substance of the agenda through your submitted problems and suggestions. We, of the Executive Committee, are ever grateful for such cooperation which, in fact, is indispensable. I constantly emphasize that this is your meeting, not ours, yours, and if you want to make it really worth while it is necessary for your generous participation by sending in problems and suggestions that will be of use to the industry.

We have been your committee for many years; you have wanted it that way, and we are willing to continue. There is plenty of work connected with this Annual program. I would like to take this opportunity to pay tribute to my fellow members of the Committee for their unstinted cooperation. We give our time and energy to this work without any financial reward.

On behalf of the Round Table, I want to thank all of the speakers who have contributed to making these 1963 sessions a memorable success, and you all for coming and sharing with us your knowledge and experience in fertilizer technology.

We usually have a short business meeting at this time, and I will call on our Secretary-Treasurer for his report.

HOUDSEN MARSHALL -- (Secretary-Treasurer): Members of the Round Table, Your Secretary has been fairly active this year. I want to compliment everybody on their registration card fill-out because we only had 10 returns and I think maybe they switched jobs, and, really, that is phenomenal when you consider that we have a mailing of close to 1,000.

It has been the policy of the Secretary's office to mail notices to those who registered, of course, and also to those who have attended in the past two years, and we have been using those lists.

It is our feeling that these proceedings, as they accumulate, will develop into quite a textbook, and we are getting pretty close to 10 of them now.

There were three mailings last year, one a summary of the meeting and a solicitation of questions and answers. We didn't get too many replies back on the solicitation. We do hope that we will get more this year.

Then we wrote letters to 40 or 50 members and we got about a 70 per cent reply, which was very helpful in formulating our program.

Your membership list that you paid your $1.50 for will be out the first week of December. That's our target date on that, remembering, of course, that all of us are working our own spare time on this.

The Secretary's office has available for purchase '58 and '59 reprints of the proceedings. We have about 75 of each year left. We have no '60's, so please hold on to the '60's, as they are a collector's item right at this moment. '61 and '62 we have about 150 of each.

We also have a stock and we will put those four years (1958, 59, 61, 62) together for $10 as we did the others to fill out your file.

We also have reprints available of the Maxwell, the Hoffmeister and the Poundstone articles that were published last year in connection with the talk on blending, and blending materials. They are available, the three for $2.00. A lot of you people may want to have these reprints or give them away and the Secretary will be happy to receive orders therefor.

Our proceedings this past year were a little delayed through sickness and a lot of other things that happened, but we hope we can get again a target date of late March or early April.

Your Secretary is going to write you some more letters asking for questions. Please give us answers.

Now, we will get back to the critical situation regarding the money of the realm that keeps this organization going, the Treasurer's Report.

Last year, September 30th we had $1,007.33 cash balance. Remember,—though that last year we only reported for 11 months. This report covers 13 months. It was because of the meeting in October last year.

For this year, October 1, 1962 to October 31, 1963: Registration $3,354.99. Now, how come the 99 cents? We had a Canadian check.

The membership list $250.00 income. Here is a little item that you probably don't realize but it is a big item, 1962 to 1963 sales of proceedings. That is over and above the individual proceedings that each of you receives. $1,675.-38, some more of that foreign exchange in there. Making a total of cash received $5,280.37. Added to the bank balance, that means we had $6,287.70 to account for.

The meeting costs last year were $448.38, that's the projector and all the other incidental costs. The membership list costs, this is the year up went the red, $302.49. We have to have the membership list so we'll tolerate that little donation from the proceedings kitty. The proceedings costs, transcript $279.58, printing, and that includes the reprints, $3,406.35, mailing $217.03, supplies and handling, $156.20, making a total of $4,059.-16.

That is your meeting, your membership and your proceedings costs.

Now for operating your Secretary's office, your Secretary-Treasurer's office, the secretarial expenses, assistance, supplies, mailing and stationery supplies, of course, and meeting expenses, $918.35. Remember, that's 13 months this year, making a total of expenditures of $5,728.38.

Recapitulating the outlay, we had cash handled during the year $6,287.70; we spent $5,728.38; cash on hand October 1st, $559.32, and the bank balance is of the same figure.

That is the report of your Secretary-Treasurer.

Next year's meeting is set in this Hotel the second week in November after election, Wednesday, Thursday and Friday. November 11th, 12th and 13th, and I can assure you that we will be accommodated here and it is our plan, this next year, to move the meeting over to the Ballroom and we will have more of a Round Table than we have here. They have agreed to give us the Ballroom because we realize this is beginning to look like a revival meeting here and we don't want that. So we will get back to the circular seating of our Round Table next year.

Thank you.

Chairman Sauchelli: Thank you, Mr. Secretary-Treasurer.

I keep emphasizing that we are not in the book printing business and that the Proceedings are something that are byproduct but that the real substance of our meetings are the discussions. I want to refer to yesterday afternoon's session which has been widely acclaimed as something that goes back to our original purpose and intent where we had spontaneous participation and without recording.

I think the fact that the talks may be recorded acts as a damper on a great deal of discussion. People are reluctant to have their comments recorded and therefore are unwilling to get up and participate in the discussions.

After yesterday's demonstration, which proved our theory, we have decided that next year we will have at least two afternoon sessions similar to yesterday afternoon's session where problems will be handled and discussed frankly and fully by panelists and the membership and, of course, to have it succeed we would like to have problems and questions from you in advance so that we can make a selection, determine an appropriate panel and then organize it so that we can have a really lively meeting such as occurred yesterday afternoon.

I think every one of us who was here yesterday afternoon was buoyed up in spirit. That's the answer to making this a real lively Round Table Meeting as we used to have it prior to the formality that has crept into our meetings.

I see Mr. Wayne King down there just a little bit itchy. Wayne King, first let me say, is a good host and a great personality. We all like him, in fact, we all love him. But he has a way with him and as I say he has been itching to come up here on the platform as is his wont in the past.

Wayne, I'll give you an opportunity to get it off your chest.

Elections of Executive Committee

Wayne King

Thank you, Vince. This will only take a minute and a half. It pertains to the technicality of our informaritly. You have to have a plan even for informality, as they keep telling you every two years, when they have to elect who is to be greatest in the kingdom here.

With Doc bouncing that foreign exchange thing around here a minute ago, I just happened to think, as many of you, I have two master's degrees. I have one in mathematics and that entitled me to play with figures, see.

And we of the Nominating Committee met in solemn session on the third floor of the Gas Light Club last night—this is true. I don't know about the solemn part, but anyway, we came up with a very definite suggestion, and all you have to do is agree with me, because that's the way I'm going to do it anyway.

For Chairman—this is for a two-year session—and they are privileged to alter this and augment the Committee, I'll think he'll agree with us, that they have the power of attorney, anyway, and that would be Vince Sauchelli, chairman, and Albert Spillman and Joseph Reynolds, and then, as you probably know, Doctor Marshall, he was elected emeritus, or something, and he carries on on account of he's got that $560, you see.

So without getting into — Would you like to hear this story I told over at the Gas light Club last night?

Chairman Sauchelli: There are ladies here.

Mr. King: All right, I'll tune it up or down, as the case may be.

I don't think it's so damn funny, but they laughed.

Many years ago, a hundred years ago I had two grandfathers, both of them were colonels in the

Army, Colonel King and Colonel Wayne, that's where I got my name. Anyway, General Robert E. Lee came up in the front lines there near Petersburg during the siege of Richmond and he says—my grandfather was a captain and he says, Captain, how are you fixed for forces? Well, he says, There's me and this wounded corporal and this drummer boy. Lee says, How many Yankees are there out there? He says, There's about 5,000 of them. General Lee says, Charge.

That's the way it goes. Now, if you're in agreement with me, let's all say "charge." See how loud you can bellow. That's the committee for two years. Okay.

(A chorus of "charge".)

CHAIRMAN SAUCHELLI: Thank you, Wayne. He's inimitable. There's no one just like him.

It's always a pleasure to welcome guests or visitors from overseas to our meetings, and apparently the Round Table is being noticed overseas because, as the Secretary has indicated, the sale of proceeding is worldwide. We get requests from practically every country on the globe for our proceedings.

At our present session we have visitors from Korea, Australia, Puerto Rico, France, Mexico and Canada and there is one from one of the South American countries which has not been specified.

I think we would like to have these people rise and we will give them some applause to welcome our guests from overseas.

It is always a pleasure to have them and we hope more will come, because as I get around a little bit too, I find world-wide interest in fertilizers and in our fertilizer industry. There isn't a capitol of any nation on earth that isn't interested at the present time in fertilizers, because of the connection with food. The fertilizer industry is really gaining stature world-wide and we should be proud to be such a part of that world-wide industry.

Our thanks also to our trade press for their diligent coverage of our transactions. I am going to ask, as has been my custom, to have the members of the press rise so that we can see who they are. I guess you know all of them. But let's have a big applause for them.

They work hard, probably the only real hard workers at these sessions, and it isn't easy to record these meetings and we on the Executive Committee are always glad to have their help and sometimes our Secretary is particularly interested that they don't steal all his thunder, as he wants some of the papers for the proceedings.

Are there any questions, any comments from the floor that refer to this meeting or to our plans for next year? I would really like to have you express yourselves on it.

What do you think of the suggestion for a question and answer period two afternoon sessions next year and without recordings?

Let's hear some comment. We don't want to do anything that isn't in full agreement with the sentiments of the Round Table.

Joe.

MR. SHARP: Vince, I'd just like to pass along the comments that I have heard by other people. They think it was the highlight of this meeting, and I certainly agree with them.

CHAIRMAN SAUCHELLI: Thank you.

Does anybody else have anything to say for the good of the order? George Walton.

MR. GEORGE WALTON: I am very sure that all of us would hate to leave here without saying a very warm thank you to our Executive Committee.

CHAIRMAN SAUCHELLI: Thank you very much George, and I am sure I speak for the Committee in saying our heartfelt thanks for your confidence in us and your assistance.

Remember, our planning for next year is beginning right now. We need your help. Let us have your problems and suggestions. Remember the dates for next year and you'll be hearing definitely from us, and if there is nothing further, no further comments or anything else, we stand adjourned until next year, and good luck to you all.

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Note: Many more participants who did not announce their names when asking or answering questions.

Notes

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