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END USE OF SUPERPHOSPHORIC ACID

By R.G. Powell  
(International Mineral &  
Chemical Co., U.S.A.).

Early in 1962, International Minerals and Chemical Corporation constructed a plant at its Bonnie, Florida chemical complex to produce a concentrated phosphoric acid containing 68-70% P<sub>2</sub>O<sub>5</sub>. The method used for manufacturing this product was explained in a paper presented by Mr. R.A. Shetler at the ISMA meeting in Avignon, France in September of 1962.

Since most of the production from this plant was originally scheduled for producing feed grade products, testing of the product in N-P-K fertilisers was not attempted until early 1964. At this time the decision was made to utilize approximately 1,500 tons of superphosphoric acid in plant tests to determine its characteristics when incorporated in liquid fertilisers and high analysis granular and semi-granular N-P-K fertiliser.

For the purpose of the evaluation to be made today, I will confine my remarks to the use of superphosphoric acid in the production of semi-granular and granular fertilisers. The use of this product in the production of liquid fertilisers has been thoroughly investigated and reported by TVA. Our use of super acid in the production of 10-34-0 liquid fertiliser followed the general production procedures established by TVA, and the results of our tests corroborate results obtained during the TVA investigation.

Since IMC has 42 fertiliser plants in the United States producing a wide variety of products, we decided to conduct the evaluation tests in our own plants. This permitted us to conduct the tests under actual plant scale operating conditions rather than bench scale or pilot plant conditions.

The acid used in these tests was typical of the normal production at our Bonnie plant, and no effort was made to change its physical or chemical characteristics prior to its use in mixed fertiliser production. A typical analysis of the acid used in all of the tests is shown in Table 1. The range of analysis for individual shipments is shown in Table 2.

Table 2.

## Analysis Range for Superphosphoric Acid

Total P2O5	69-70%
Ortho P2O5	42-45%
Combined Fe2O3 and Al2O3	5-6%
Viscosity at 75°F, cps	25,000-95,000
Viscosity at 150°F, cps	6,000-15,000

Although methods of reducing the viscosity are known, it was felt that it was not economically feasible to make the necessary process changes for the small amount of acid required for the tests. Therefore, a method of shipping and handling the more viscous acid was devised for the various test locations.

Because of the tendency of the product to become highly viscous as its temperature decreases, it was decided that the product should be shipped in insulated railway tank cars, and that the cars should have internal steam coils for reheating the acid at its destination.

At the point of consumption a water heater or steam boiler was added to provide heat for use in reheating the acid in the tank car and in the piping from the car to the process. Since all of our plants use compressed air for unloading liquids from tank cars, it was not considered necessary to install a pump for the purpose.

In April 1964, tests were conducted using superphosphoric acid in a TVA type granular fertilizer process to see if it offered any unique advantages over wet process, orthophosphoric acid or other forms of P2O5 in high analysis granular fertilizers.

These tests were conducted at our Plymouth, Indiana plant in the production of a 6-24-24 granular fertilizer. The process used is shown schematically in Sketch 1. As you can see, this is a conventional TVA type plant using a weigh hopper, time cycle feeder, ammoniator-granulator with spargers for liquids, drier, cooler, double deck screens, and a pulverizer for crushing oversize material from the screens.

The only alterations made to incorporate superphosphoric acid were the steam boiler, a magnetic meter for metering acid, and a sparger over the bed for adding the acid to the ammoniator.

Formulae used during these tests are shown in Table 3. From these formulae you can see that tests were made using 18, 14 and 11 units of P2O5 derived from superphosphoric acid.

In the initial tests using Formulae 1, 2, and 3, the formula containing 14 units of P2O5 from superphosphoric acid (Formula 3) was found to produce the most acceptable product. However, all of the formulae yielded

products containing an excess of minus 14 mesh particles.

Under normal operating conditions, using conventional sources of P2O5, the particle size can usually be controlled by increasing or decreasing the liquid phase in the granulator. This change in liquid phase can be brought about by changing the recycle ratio, water content, soluble salt content, or reaction temperature.

Efforts made to improve the product size by the addition of water to the granulator were not successful while the plant was operating on Formulae 1, 2, or 3. The operating personnel could not maintain adequate control of the liquid phase, and some damage was caused to the granulator drive mechanism when the bed of material in the granulator hardened during a temporary shut-down.

Because of storage space limitations in the plant, tests were discontinued using the first three formulae, and a new formula was written (Table 4) for a Super Rainbow 6-24-24.

At the beginning this formula made a product similar in screen size to that made with Formulae 1, 2 and 3. But as the operators gained more confidence and experience, they were able to add water and control both particle size and recycle. The resulting product was found to be somewhat coarser and more uniform in appearance than products made using 54% orthophosphoric acid. Screen analysis of the final product made from Formula 4 is shown in Table 5.

A chemical analysis of a composite sample made using Formula 4 is shown on Table 6. This product is within the tolerance of variation permitted for our plants.

Although all of the magnesium used was in a water soluble form as a raw material, approximately 50% was reduced to the water insoluble form during granulation. This change in water solubility was attributed to the formation of magnesium ammonium phosphate during the granulation stage. Magnesium ammonium phosphate would also tie up part of the P2O5 as water insoluble P2O5.

The Plymouth plant was designed to produce 6-24-24 at a production rate of 10-12 TPH. Under the conditions of the test with superphosphoric acid, the maximum production rate attained was approximately 10 TPH. The limiting factor, however, was the capacity of the meter used, rather than the inability to control the process.

Operating at 8-10 TPH, the following range of process data were found:

Table 7  
Process Data

Superphosphoric Acid Temperature, °F	170-195
Granulator Discharge Temperature, °F	190-210
Granulator Discharge Moisture Content, % H <sub>2</sub> O	3.0-4.5
Dryer Discharge Temperature, °F	210-250
Cooler Discharge Temperature, °F	110-125
Product in Storage, after 24 hours, °F	100-110
Recycle ratio	1/1

As a result of the tests conducted in our Plymouth plant, we have drawn the following conclusions concerning the use of superphosphoric acid in the production of high analysis, granular fertilizer.

1. Superphosphoric acid is unique in that it can be handled and ammoniated like wet-process ortho-phosphoric acid, yet adds no water to formulations.
2. Ammoniated superphosphoric acid behaves in a manner different from any phosphate which we have tested to date in that the granules appear to be formed more readily in the size range of -6 mesh +20 mesh.
3. The granules made from this acid, although more porous than those made with other phosphate forms, are harder by test and tend to maintain their firmness under conditions which normally cause degradation.
4. The bulk handling and distribution properties of fertilizers made from this acid are excellent, since the product contains very uniformly sized particles which are dust-free.
5. If superphosphoric acid is sold at a delivered unit price equal to 54% P<sub>2</sub>O<sub>5</sub>, ortho-phosphoric acid, savings of \$1.50 per ton on 6-24-24 and \$5.00 per ton on 8-40-10 granular fertilizer can be realized as a result of the increased use of normal superphosphate, increased production rates and decreased fuel cost for drying. If the delivered cost of superphosphoric acid is in excess of approximately ten cents per unit above the delivered cost of ortho-phosphoric acid, there is no apparent savings on the grades tested.

In many parts of the United States fertilizer manufacturers owning plants designed to produce a pulverized fertilizer find themselves in a position where they cannot compete with high analysis granular fertilizers which have superior storage, handling and distribution characteristics. In an effort to produce a more competitive product without making the large capital investment required for a TVA type granulation plant, many plants have installed equipment to permit them to manufacture a "semi-granular" fertilizer.

Although this product has granular characteristics, it is usually not screened to a definitive size. A scalping screen is used to remove particles larger than 6 mesh (Tyler) but no effort is made to remove the finer particles such as -16 mesh. Removing the finer screen fraction from the product is considered uneconomical. Since the batch mixers are limited in size, the addition of appreciable quantities of recycle to control particle size would reduce the production rate to a point where it would be uneconomical.

During our earlier studies on the use of superphosphoric acid in TVA type granular plants, certain observations were made which indicated that this acid produced a more uniformly sized particle and required less recycle for granulation control than the conventional ortho-phosphoric acid or sulfuric acid. This characteristic led us to the conclusion that superphosphoric acid may offer a solution to the problem of improper screen size in the semi-granular operation and may also provide means of producing a high analysis, semi-granular fertilizer at an economical rate of production.

In June, 1964, tests were conducted in an IMC plant at Buffalo, New York, to determine the characteristics of superphosphoric acid in a batch type, semi-granular plant producing high analysis N-P-K fertilizers. A flow sheet of this plant is shown on Sketch No. 2.

This sketch shows that the dry raw materials are weighed in a FESCO weigh hopper and are transferred by a bucket elevator to a surge hopper above the Sturtevant mixer. From the surge hopper, the 2500 pound batch is dumped into the mixer, where nitrogen solution, water and sulfuric acid are added through spargers located under the bed of rolling material. Superphosphoric acid is fed by air pressure from a hot water-heated tank car, through hot water-traced, and insulated pipe to sprays located above the bed of material. The acid quantity is measured with a stainless steel, positive displacement type meter, similar to a conventional water meter.

After adequate mixing and rolling in the Sturtevant mixer, the hot, plastic particles are gravity fed to a 6' x 20' rotary cooler. Product from the cooler is fed by an elevator to 4' x 10' double deck Hammer screens. The plus 6 fraction is removed, crushed in a chain mill and returned to the screen elevator. The minus 16 mesh particles are removed and returned to the weigh hopper as recycle. The product passing the 6 mesh screen and retained on the 16 mesh screen is transferred by conveyor belts to a bulk storage area.

Tests were conducted at our Buffalo plant on the following N-P-K grades: 8-16-16 (containing 2 units of MgO), 16-8-8, 10-20-20, 10-20-10 and 10-10-10. For purposes of our evaluation today I have chosen to discuss the formula, operating conditions and physical characteristics of the 10-20-10, since this is one of our most popular 1-2-1 ratio fertilizers.

Table 3

6-24-24 FORMULAE

GRANULAR

<u>RAW MATERIALS</u>	<u>POUNDS PER TON</u>			
	(1)	(2)	(3)	(4)
H <sub>2</sub> SO <sub>4</sub> , 60° Be°	-	130	75	70
NH <sub>3</sub> , 82.2% N	152	152	152	152
Superphosphoric Acid, 69% P <sub>2</sub> O <sub>5</sub>	520	310	400	400
Superphosphate, 20% P <sub>2</sub> O <sub>5</sub>	410	118	250	157
Triple Superphosphate, 47% P <sub>2</sub> O <sub>5</sub>	98	528	340	380
Muriate of Potash, 61% K <sub>2</sub> O	810	797	797	760
Sul-Po-Mag, 22% K <sub>2</sub> O	-	-	-	90
Borate 65, 20.2% B	-	-	-	2
Zinc Oxide, 56% Zn	-	-	-	2
Water	10	-	-	-
Evaporation	0	-35	-14	-13
TOTAL	2000	2000	2000	2000

Table 4

6-24-24 FORMULA

GRANULAR

<u>MATERIALS</u>	<u>LB/TON</u>
NH <sub>3</sub>	152
H <sub>2</sub> SO <sub>4</sub> , 60° Be°	70
Superacid, 69% P <sub>2</sub> O <sub>5</sub>	400
Normal Super, 20% P <sub>2</sub> O <sub>5</sub>	157
Triple, 47% P <sub>2</sub> O <sub>5</sub>	380
KOL, 61% K <sub>2</sub> O	760
SPM, 22% K <sub>2</sub> O, 18% MgO	90
Borate 65, 20.2% B	2
Zinc Oxide, 56% Zn	2
Evaporation of H <sub>2</sub> O	-13
	2000

Table 5

## SCREEN ANALYSIS

6-24-24

GRANULAR

<u>SCREEN SIZE</u>	<u>PERCENT RETAINED ON</u>
(TYLER)	
6 mesh	4.2
8 mesh	30.6
14 mesh	90.3
16 mesh	97.4
20 mesh	99.6

Table 6

## CHEMICAL ANALYSIS

6-24-24

GRANULAR

Total Moisture	2.50%
Free Moisture	1.78
Nitrogen	5.65
Total P2O5	24.57
(Hydrolyzed)	24.70
Total Ortho P2O5	22.45
Insol. P2O5	.16
Water Soluble P2O5	15.12
(Hydrolyzed)	15.38
K2O	22.92
MgO	1.07



Table 7

## PROCESS DATA

Superphosphoric Acid Temperature, °F	170-195
Granulator Discharge Temperature, °F	190-210
Granulator Discharge Moisture Content, % H <sub>2</sub> O	3.0-4.5
Dryer Discharge Temperature, °F	210-250
Cooler Discharge Temperature, °F	110-125
Product in Storage, after 24 hours, °F	100-110
Recycle ratio	1/1

Table 8

## 10-20-10 FORMULAE

## SEMI-GRANULAR

MATERIALS:POUNDS/TON

	<u>Formula 1</u>	<u>Formula 2</u>
Superphosphoric Acid (69.6% P <sub>2</sub> O <sub>5</sub> )	180	206
Nitrogen Solution 450 (26-68-0)	360	385
Ammonium Sulfate (21% N)	215	160
Normal Superphosphate (20% P <sub>2</sub> O <sub>5</sub> )	507	575
Triple Superphosphate (46% P <sub>2</sub> O <sub>5</sub> )	390	332
Muriate of Potash (60.5% K <sub>2</sub> O)	295	295
Sul-Po-Mag (22% K <sub>2</sub> O, 18% MgO)	100	100
Borate (65% B)	2	2
Zinc Oxide	1.5	1.5
Evaporation	<u>-50.5</u>	<u>-56.5</u>
	2000	2000

Table 9

## OPERATING DATA, 10-20-10

Superphosphoric Acid Temperature, °F	165-185
Ammoniator Discharge Temperature, °F	190-210
Cooler Discharge Temperature, °F	110-120
Product Temperature after 24 hours, °F	100-110
Recycle Ratio, estimated	1/1
Production Rate, TPH	10-12

Table 10

## CHEMICAL ANALYSIS, 10-20-10

## SEMI-GRANULAR

<u>GRADE</u>	<u>10-20-10</u>
Total Moisture, %	3.14
Free Moisture, %	2.30
Nitrogen, %	9.25
Total P2O5, %	20.30
Citrate Insol. P2O5, %	.18
Available P2O5, %	20.12
P2O5 as Ortho, %	18.80
Water Soluble P2O5, % of Total	73.84
K2O, %	19.76
Total MgO, %	1.10
Total Zinc, %	0.046
Boron, %	0.030
pH	5.6

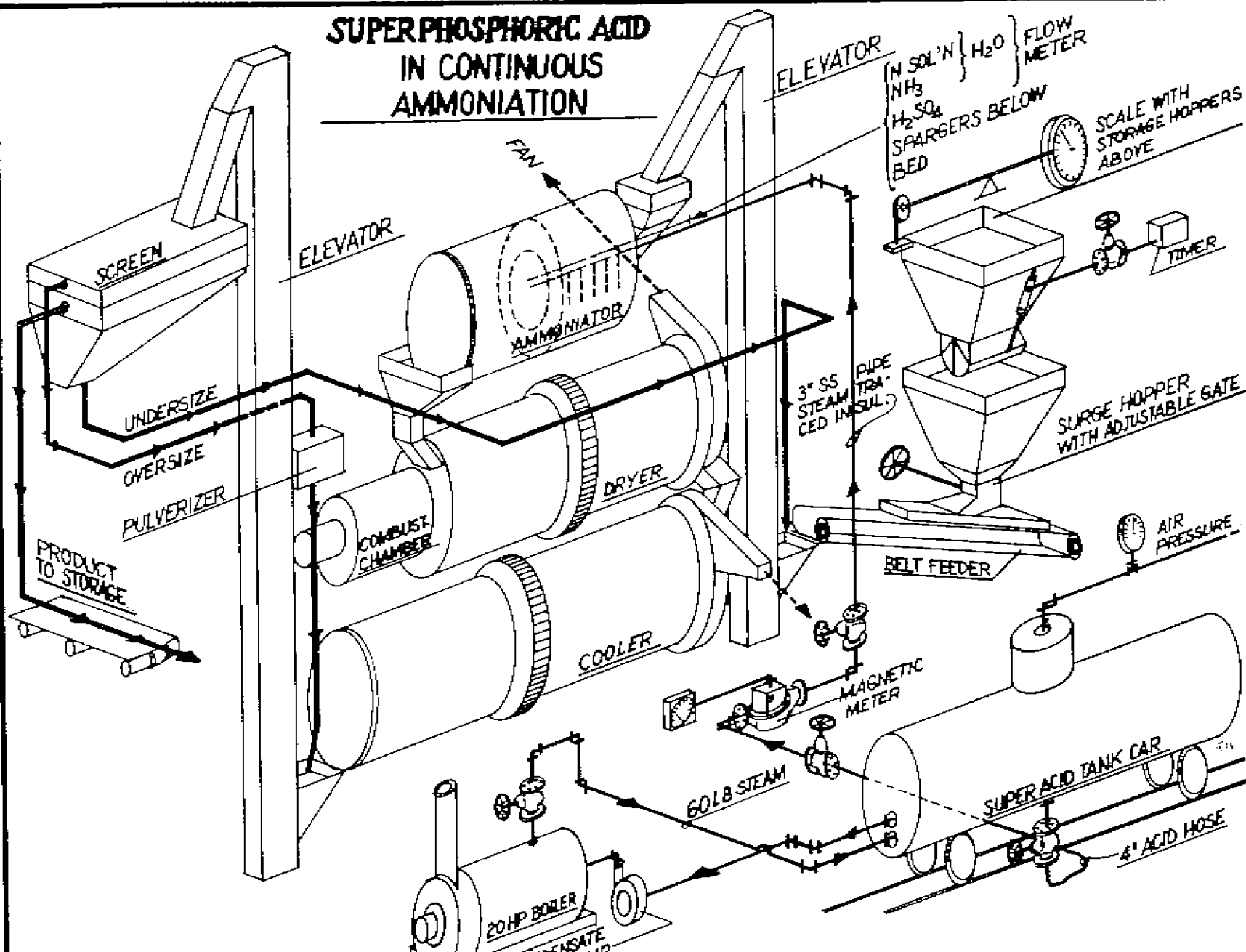
Table 11

## SCREEN ANALYSIS, 10-20-10

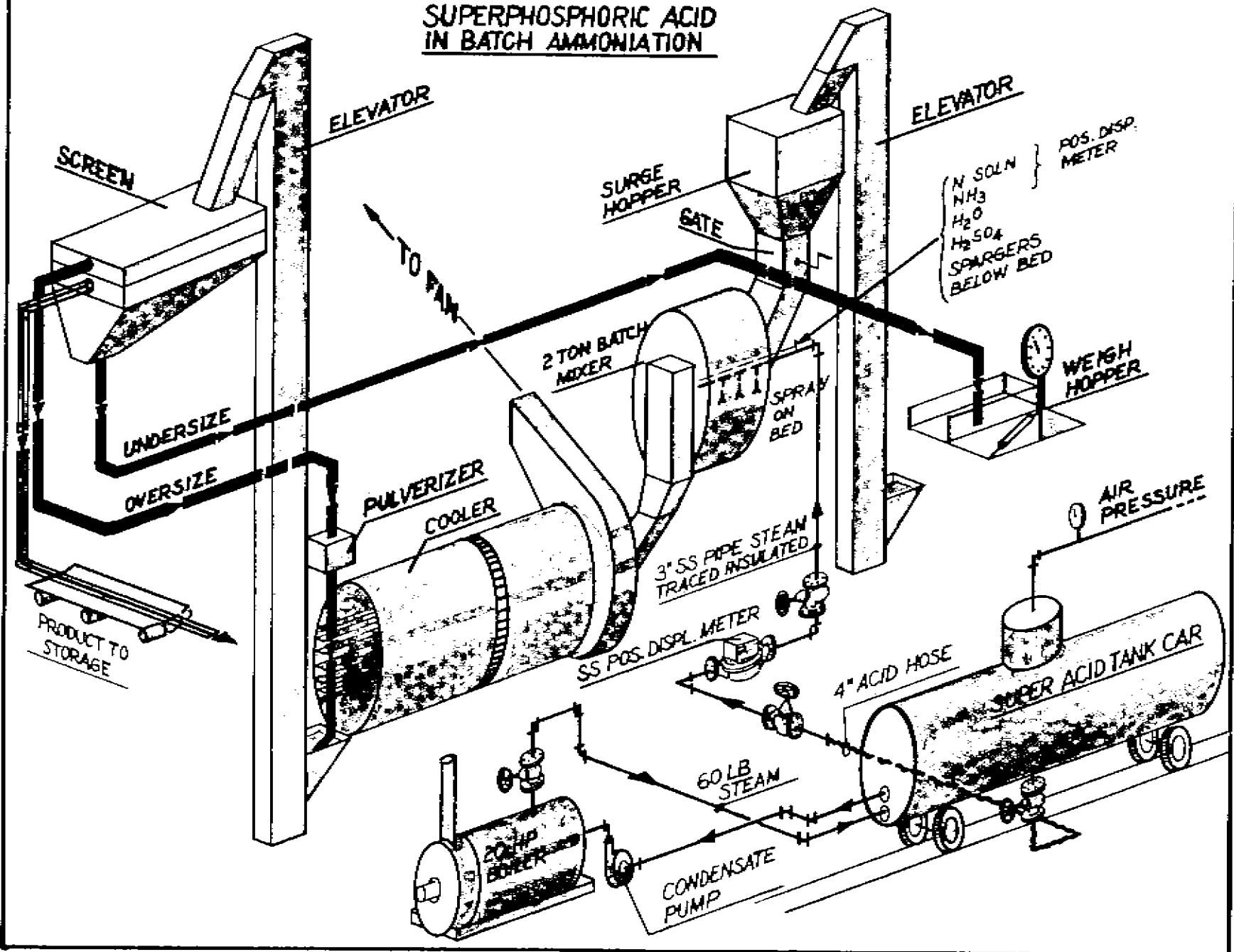
## SEMI-GRANULAR

<u>SCREEN</u>	<u>PERCENT RETAINED</u> <u>ON</u>
4 mesh	0.0
6 mesh	1.6
10 mesh	54.5
16 mesh	91.7
20 mesh	94.9
35 mesh	99.8

# SUPERPHOSPHORIC ACID IN CONTINUOUS AMMONIATION



# SUPERPHOSPHORIC ACID IN BATCH AMMONIATION



DISCUSSION

Mr. R.G. POWELL (International Minerals & Chemical Corpn., U.S.A.) :

The purpose of the work we have been conducting is of a rather general nature. It was not meant to be comprehensive. We were not studying superphosphoric acid per se, but rather the economics of using it in our own plants and processes, as well as problems of handling it. My company has 42 mixed fertiliser plants, with a wide variety of equipment, and we are keenly interested in any technique allowing us to continue to use the equipment we already have, without having to resort to new, more complex and more costly processes.

One of the reasons for our interest in using superphosphoric acid in a granulation plant and in what we call a "semi-granulation" plant is that wet process phosphoric acid in the U.S.A. is generally cheaper on a per unit delivered cost basis than electric furnace acid. However, owing to varying market conditions furnace acid occasionally becomes as cheap as wet process acid; and for the wet process acid producers this then becomes something of a problem. Whilst there is no difference in the  $P_2O_5$  content of thermal and wet process acid, the advantage of the thermal acid is that the free water constitutes virtually the only diluent, and in a granulation system, if one can drive off the free water, one can achieve a higher NPK formulation with furnace acid than with wet process acid. Consequently, since superphosphoric acid has, in effect, a negative water content, absorbing about 5 lbs. water per 100 lbs. of acid used in a formulation, it seemed that this would be a means to duplicate or improve upon what we can do with furnace acid. In addition we should be able to make use of phosphates high in iron and aluminium, which we consider to be of assistance in granulation.

Furthermore, in the U.S.A. we have "semi-granular plants" which are batch operations and which have been converted to produce a semi-granular product in order to remain competitive with the more costly and more extensive TVA-type granulation plants. But one can only have a certain amount of liquid in a batch mixer. Consequently, wet process phosphoric acid or electric furnace acid of 54%  $P_2O_5$  puts too much liquid phase in a batch mixer for practical purposes. In addition, very few semi-granular plants have driers following the batch mixer; usually they have only coolers.

Our test data are far from complete. But as indicated, we believe the following conclusions offer possibilities for the use of superphosphoric acid in our circuits:

1. Superphosphoric acid is unique in that it can be handled and ammoniated like wet-process ortho-phosphoric acid, yet adds no water to formulation.
2. Ammoniated superphosphoric acid behaves in a manner different from any phosphate which we have tested to date in that the granules appear to be formed more readily in the size range of -6 mesh +20 mesh. You will notice that our recycle rates were relatively low, and the limitation on increased throughput was due primarily to the metering equipment.
3. The granules made from this acid, although more porous than those

made with other phosphate forms, are harder by test and tend to maintain their firmness under conditions which normally cause degradation.

4. The bulk handling and distribution properties of mixed fertilisers made from this acid are excellent, since the product contains very uniformly sized particles, which are dust-free, and exhibits better storage characteristics. Some of the material made during the two test runs is still in storage, and periodic checks made against a similar formula made in our normal fashion indicate that the product is much more free-flowing after any prolonged storage period.

5. If superphosphoric acid is sold at a delivered unit price equal to 54%  $P_2O_5$  ortho-phosphoric acid, savings of \$1.50 per short ton on 6-24-24 and \$5.00 per short ton on 8-40-10 granular fertiliser can be realised. This is a result of the increased use of normal superphosphate, increased production rates and decreased fuel cost for drying. If the delivered cost of superphosphoric acid was in excess of about 10 cents per unit above the delivered cost of ortho-phosphoric acid, there was no apparent savings on the grades tested.

We are far from having completed our test work, although we have one of the largest superphosphoric acid plants in the world. Most of this acid currently goes into feed-grade phosphates. This business has recently been so good that we need all the defluorinated acid that we can get. For this reason, we have had to curtail some of our test work; but we shall continue to study the use of this acid in varying grades and ratios and under varying climatic conditions. We intend to investigate other process equipment in commercial use, e.g. the effect of using superphosphoric acid in conjunction with a pre-neutraliser, as well as in other processes such as slurry fertilisers. In addition, we are just beginning agronomic test work, and this will naturally take some time to provide definitive data.

Mr. Y. ARATEN (Israel Mining Industries, Israel) : What was the analysis of the feed acid for the data given in Table 2? I ask this because the term "superphosphoric acid" produced from wet process acid is used for different phosphoric acids, and their impurities depend, of course, on the feed acid, which is different if produced from different phosphate rocks, different grades of sulphuric acid and, particularly, if produced from calcined, as compared with uncalcined phosphate rock. In comparing the details in Table 2 with other superphosphoric acids, the analysis of the feed acid would be of great interest.

Mr. POWELL : Unfortunately, I cannot give you accurately the feed acid input. It comes from our regular phosphoric acid unit at our Bonnie, Florida, plant, consisting of 3 Prayon acid trains. They are running considerably in excess of their rated capacities, and so their efficiencies are slightly decreased. Two of the trains are rated at 300 t.p.d. and the other at 400 t.p.d.; but two of them are producing at the rate of about 450 t.p.d. and the larger one is producing about 600 t.p.d. We are using 64/66% BPL Florida rock with all its impurities. Our acid receives very little clarification prior to the superphosphoric acid system. The viscosity and colour

of the acid would be definitely improved if we had both the inclination and the time to further clarify our own 54% acid.

Mr. ARATEN : Again with regard to Table 2, could you indicate the amount of suspended solids in the superphosphoric acid and the corrosion rate of mild steel in the equipment used?

Mr. POWELL : As I said previously, we were not studying the superphosphoric acid itself in this work and did not try to obtain corrosion rate data. No attempt was made to measure the amount of suspended solids. The acid was viscous enough, and we were therefore not much concerned.

Mr. ARATEN : On page 3 you say : "Although all of the magnesium used was in a water soluble form as a raw material, approximately 50% was reduced to the water insoluble form during granulation." I believe that as long as the magnesium is available to the plant, 100% water solubility may sometimes be a disadvantage because of leaching. IMI has developed a process for the production of magnesium phosphate containing 37%  $P_2O_5$  and 40%  $MgO$  which is not water soluble but which is nevertheless in a form - both the P and the Mg - which is available to plants. I wonder, therefore, what you regard as the importance of your statement.

Mr. POWELL : We, for our part, firmly believe there are advantages for water soluble magnesium. We have a product called "Sul-Po-Mag", which is a double sulphate of potash-magnesia containing 18% water soluble magnesia. We feel it is beneficial to know when the magnesium is water soluble and when it is not. Some states in the U.S.A. do not require this information, but others do.

Mr. ARATEN : Have you tried making triple superphosphate of, say, 54-55%  $P_2O_5$  from superphosphoric acid? I recall that the TVA was making such triple superphosphate from highly concentrated furnace acid several years ago.

Mr. POWELL : We have done this in our pilot plant. We have also tried making other compounds of high  $P_2O_5$  content, such as 10-60-0.

Mr. ARATEN : Figures published by various firms concerning the cost of converting wet process 54%  $P_2O_5$  acid to 70%  $P_2O_5$  vary from \$3 per ton to \$12 per ton of  $P_2O_5$ . No details are given about the feed acid and no breakdown of the figures is supplied in the present paper. Could you give us more information ?

Mr. POWELL : We run our unit primarily to produce acid for feed-grade, and for this we concentrate up to only 65% and then cut back. Generally speaking we think in terms of about \$8 per ton  $P_2O_5$  as being the conversion cost.

Mr. R. BAUWENS (Ets. Kuhlmann, France) : When you concentrate phosphoric acid to the polyphosphoric state and when you obtain a strength exceeding what you require and you cut back with water, do you have the same state of complexation in the acid?

Mr. POWELL : When cutting acid back from one given strength to another, hydrolysis to the ortho-phosphoric state occurs very rapidly. In shipping acid, we have to be very careful to get as little water into the tank cars as possible, as the superphosphoric acid will hydrolyze en route.

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