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REPORT
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FERTILIZER RESEARCH AT
IOWA STATE . PART III

by Dr. D. Boylan
Director, Engineering Research Institute
Professor, Department of Chemical Engineering


and Dr. George Burnet
Head, Department of Chemical Engineering
Iowa State University

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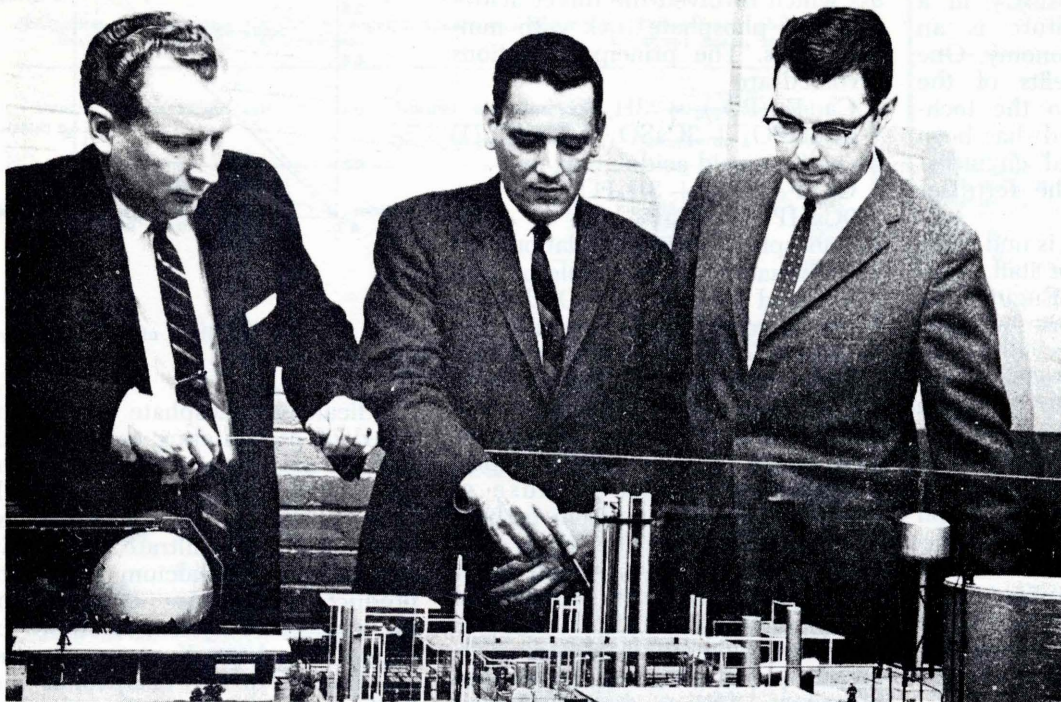
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PREFACE

Fundamental research on fertilizer technology has taken on a new significance in recent years as engineers and scientists worldwide move to meet the challenge of providing sufficient food for rapidly increasing populations. For many years a comprehensive program in fertilizer research has been conducted at Iowa State University in the Chemical Engineering Department. This work provides important support to the broad agricultural base which underlies the economy of Iowa and much of the rural United States.

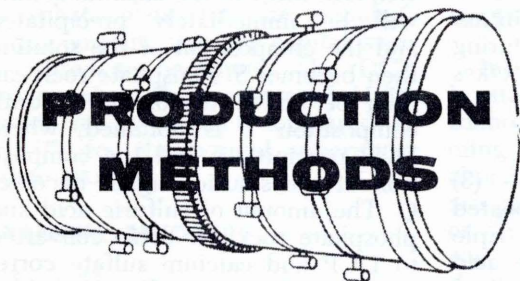
Papers reporting the results of fertilizer research appear in a wide variety of publications. This report consolidates under one cover papers which describe work done at Iowa State and which have appeared recently in several technical journals. The papers are reproduced with permission of the original publisher and copyright owner. For convenience of the reader, the papers are divided into groups by research area.



Dr. D. R. Boylan (left), Dr. John C. Reisch of Esso Research and Engineering Co., and Dr. George Burnet inspect anhydrous ammonia plant model built by senior students in chemical engineering plant design course.

IOWA STATE

Pioneer in Fertilizer Research



Since 1948 Iowa State has conducted a comprehensive research program in fertilizer technology unique to a university campus. The significance of this program to the fertilizer industry is reviewed in this special two-part report.

By DAVID R. BOYLAN and GEORGE BURNET

THE United States has about the same amount of crop land as 35 years ago and 60 million more people. Yet, today we eat better because food output is up 66% on those same acres. In no other nation do so few farmers produce so much food to feed so many people on a high quality diet at such a reasonable cost. This highly efficient agriculture results from a system of research and education that provides

farmers with the information and techniques necessary to be productive. A significant part of this transfer is in the production and use of fertilizers.

A 38% increase in crop production per acre occurred over the 1950 to 1963 period and was due primarily to the greater use of fertilizers. During this period fertilizer consumption increased about 130%, measured in plant nutrient content. Consumption of nitrogen fertilizers increased 278.6%, phosphates 54.8%, and potassium 124.4%. Improvements in manufacturing technology have kept fertilizer prices relatively constant so that plant food in almost any

form is one of the more stable items of cost in the farmer's purchases. Leading contributors of improvements have been research-oriented chemical companies, engineering and plant construction firms, agencies of the federal government, and a limited number of colleges and universities. One of the very few of the latter group at which a substantial program in fertilizer manufacturing research and development is underway is Iowa State University at Ames, Iowa.

A sustained program in this field was begun in the Chemical Engineering Section of the Engineering Experiment Station at Iowa State in

Dr. Boylan is professor of chemical engineering and associate director of Engineering Experiment Station and Dr. Burnet professor of chemical engineering and head of Chemical Engineering Department at Iowa State University, Ames.

1948. Its purpose was to carry out basic research and long-range interest to the fertilizer industry in a location where agriculture is an essential part of the economy. One of the important benefits of the program, in addition to the technical information derived, has been the training of chemical engineers for employment in the fertilizer industry.

The research program is under the supervision of four senior staff members in the Chemical Engineering Department, all of whom had considerable industrial experience before joining the staff at Ames. These men are Dr. D. R. Boylan, Associate Director of the Engineering Experiment Station, Dr. George Burnet, Head of the Chemical Engineering Department, and Drs. M. A. Larson and T. D. Wheelock. The various projects are carried out with the assistance of graduate students who use the results of their investigations in partial fulfillment of the requirements for their master's and doctor's degrees.

The program is supported by all the facilities of the Engineering Experiment Station which include a well equipped analytical laboratory, an x-ray diffraction laboratory, an electron microscope laboratory, and mechanical and electronic shops. Adequate space is available for both small-scale laboratory and intermediate-scale pilot plant investigations. In the spring of 1964 the Chemical Engineering Department occupied a new building, Sweeney Hall, which added substantially to the space available and provided several new facilities including an analog computer laboratory, an analytical instrument laboratory, a constant temperature-humidity laboratory, and a new reference library.

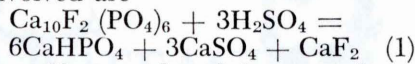
One of the advantages of carrying out research on fertilizer manufacture at Ames is the proximity of the outstanding College of Agriculture, now the largest in the nation. Excellent cooperation has been received from the Agronomy Department and other groups in the College.

University-related research can make its greatest contribution by providing a better understanding of the fundamentals of fertilizer technology. Work of this type completed at Iowa State prior to 1957 has been reported in two publications of the Iowa Engineering Experiment Station (1,2).

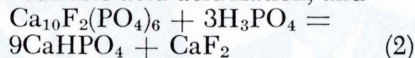
Dicalcium Phosphate

More work has been done on phosphate technology than any other

area. In 1956, Bridger et al. (3) reported a dicalcium phosphate process which involved the direct acidulation of phosphate rock with mineral acids. The principal reactions involved are



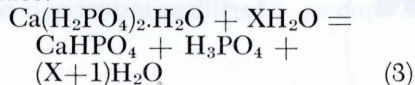
for sulfuric acid acidulation, and



for phosphoric acid acidulation.

In Equation (1) one mole of acid is required per mole of P_2O_5 derived from the rock. This is one-half that required for the production of monocalcium phosphate in the present normal superphosphate process. Actually about 2.6 moles of acid per mole of rock P_2O_5 is used in superphosphate production because of side reactions with calcium carbonate, calcium fluoride, iron, and aluminum compounds, and other constituents of the rock. In Equation (2) one-half mole of acid P_2O_5 is indicated per mole of the rock P_2O_5 for the production of dicalcium phosphate. This is one-fourth that required in the present triple superphosphate process. In actual practice, 2.3 moles of acid P_2O_5 per mole of rock P_2O_5 is used in triple superphosphate because of the side reactions.

From this work a cyclic process was developed which consisted of hydrolyzing a mixture of phosphate rock with monocalcium phosphate monohydrate, superphosphate or acids, followed by heating in an open container at 185°C . During heating the following reaction takes place:



The processing steps were repeated at least three times. When triple superphosphate or phosphoric acid was used, the acidulation required to produce the fertilizer was only 50% of that required for the production of ordinary triple superphosphate. When sulfuric acid or normal superphosphate was used higher acidulations were required.

Kaufman (4) studied this process on a pilot plant scale. The process was shown to be technically feasible and to offer the advantages of savings in acid requirements, high analysis products, elimination of the curing step in present fertilizer processes, and excellent physical properties of the product.

Later Feng (5) prepared a phase diagram for the $\text{CaO}-\text{P}_2\text{O}_5-\text{SO}_3-\text{H}_2\text{O}$ system which was used to develop a direct acidulation process

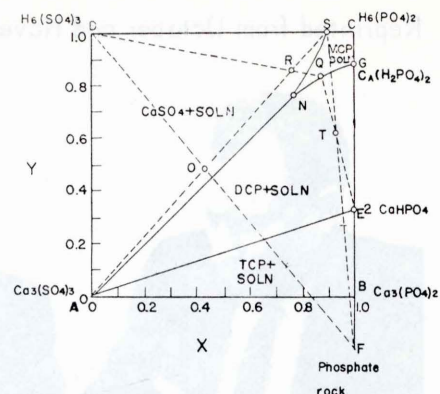


Figure 1—Phase equilibria of quaternary system $\text{CaO}-\text{P}_2\text{O}_5-\text{SO}_3-\text{H}_2\text{O}$.

for dicalcium phosphate which consisted of precipitating calcium with sulfuric acid, separating the insoluble calcium sulfate, forming dicalcium phosphate by adding phosphate rock to the filtrate and finally separating the dicalcium phosphate product. The phase diagram for the quaternary system is shown in Figure 1, where X represents the mol fraction of PO_4 compounds and Y the mole fraction of acid compounds.

The proposed process for the preparation of dicalcium phosphate (DCP) is indicated by dotted lines. Composition Q represents a saturated solution with respect to DCP at 145°C . Sulfuric acid may be added to this solution until the composition R is reached, the ratio of sulfuric acid to solution Q being QR/DR . Most of the calcium sulfate will be immediately precipitated and the composition of the solution then becomes S. Phosphate rock can then be added to solution S until composition T is obtained, where DCP precipitates and the composition of the solution again becomes Q. The amount of sulfuric acid and phosphate rock per cycle converted to DCP and calcium sulfate corresponds to Equation (1).

Interest in dicalcium phosphate as a fertilizer material stems from the fact that it is a neutral salt with good physical properties and, perhaps more important, the fact that significantly less acid is consumed than when monocalcium phosphate is produced. In Feng's process 2.3 moles of sulfuric acid are required per mole of P_2O_5 or 1.57 pounds of sulfuric acid per pound of P_2O_5 . The normal superphosphate process requires 2.6 moles of sulfuric acid per mole of P_2O_5 or 1.8 pounds of sulfuric acid per pound of P_2O_5 . These figures resulted from a pilot plant investigation.

Production cost estimates based on 1959 data for normal superphos-

TABLE 1.

Production cost estimates for normal superphosphate and the proposed di-calcium phosphate.
Basis: 20 tons/hour, 250 days/year
Location: Ames, Iowa

| Item | Unit cost ^a | Normal superphosphate ^b | | Proposed di-calcium phosphates | |
|------------------------------------|--------------------------|------------------------------------|----------|--------------------------------|----------|
| | | Quantity/ton | Cost/ton | Quantity/ton | Cost/ton |
| Raw material | | | | | |
| Acid | \$25.00/T | 0.371 T | \$ 9.28 | 0.308 T | \$ 7.70 |
| Rock | 15.0904/T | 0.594 T | 8.96 | 0.594 T | 8.96 |
| Water | 0.04/T | 0.341 T | 0.01 | 0.460 T | 0.02 |
| | | | \$18.25 | | \$16.68 |
| Labor | | | | | |
| Unskilled | 1.60/hr. | 0.150 man-hr. | \$ 0.24 | 0.150 man-hr. | \$ 0.24 |
| Semiskilled | 2.10/hr. | 0.150 man-hr. | 0.32 | 0.190 man-hr. | 0.40 |
| Skilled | 2.50/hr. | 0.100 man-hr. | 0.25 | 0.150 man-hr. | 0.38 |
| Supervision | 3.00/hr. | 0.0167 man-hr. | 0.05 | 0.0324 man-hr. | 0.10 |
| Reserve | 20% of above | | 0.16 | | 0.19 |
| | | | \$ 1.02 | | \$ 1.31 |
| Services | | | | | |
| Power | 0.02/kw.-hr. | 20.83 kw.-hr. | \$ 0.42 | | \$ 0.42 |
| Heat | 0.000 467/100 Btu | | 0.00 | 200,000 Btu | 0.10 |
| Water | 0.03/1000 gal. | 208 gal. | 0.01 | 500 gal. | 0.02 |
| Maintenance including labor | 20%/yr. of fixed capital | | 2.40 | | 2.26 |
| Packaging | 0.15/bag | | 3.60 | | 3.60 |
| Indirect costs | | | | | |
| Depreciation | 10%/yr. of fixed capital | | 1.00 | | 1.13 |
| Taxes and ins. | 3%/yr. of fixed capital | | 0.30 | | 0.33 |
| Overhead | 50% of labor | | 0.51 | | 0.54 |
| Total production cost | | | \$27.11 | | \$26.39 |

^a The unit cost and freight cost for sulfuric acid and phosphate rock are taken from Chemical Engineering News, June 29, 1959.

^b The manufacturing costs for the normal superphosphate plant are taken from Rounsley (20).

phosphate and the Feng DCP process are compared in Table 1. The fixed capital for the DCP process was estimated to be about 13% greater than for the conventional normal superphosphate plant, but the manufacturing cost and working capital were estimated to be lower. The DCP process showed an estimated 11.6% return on investment compared to a 9.0% for the normal superphosphate process.

URANIUM RECOVERY

In 1955, work was completed in the Chemical Engineering Division of the Ames Laboratory, USAEC, which is located on the Iowa State campus, that led to the development of a process for the recovery of up to 50% of the uranium found in phosphate rock during the manufacture of superphosphate (6). An organic solvent which dissolved the U salts present was mixed with the acidulated rock slurry and the phases then separated.

A major problem proved to be recovery of occluded solvent from the superphosphate. The work was later extended (7) to include recovery of uranium during the manufacture of wet process phosphoric acid. Material balances completed across two commercial plants demonstrated

that up to 80% of the uranium entering in the rock could be recovered from the product acid by solvent extraction.

WESTERN PHOSPHATE ROCK

Interest continues high in the Western phosphate rocks found in Idaho, Montana, Utah, and Wyoming. Generally the acidulation characteristics of the western rocks are poorer than those of the Florida or Tennessee rocks. In 1956, work was completed at Iowa State which dealt with the acidulation characteristics of typical Western phosphate rocks with sulfuric acid, and the development of treatment which would reduce the amount of acid required to achieve a satisfactory degree of conversion (8). Table 2 shows the analysis of two Western rocks used for these tests and that of two conventional rocks used for comparison purposes.

The effect of acidulation ratio and humidity during curing were thoroughly investigated. Typical results are shown in Figure 2 which demonstrates the effect of acidulation ratio on P_2O_5 conversion of all four rocks with curing taking place at 25% relative humidity, which was found to be optimum.

Four methods of treating Western

TABLE 2.
Analyses of phosphate rocks used
(from reference 8)
(dry basis)

| | Florida land pebble | Simplot | Anaconda | |
|--------------------------------|---------------------|---------|-----------|--------------|
| | | | Foot-wall | Hanging-wall |
| Total P_2O_5 , % | 35.5 | 35.8 | 30.3 | 31.5 |
| Citrate insoluble P_2O_5 , % | 33.6 | 32.2 | 29.6 | 28.9 |
| Moisture, % | 0.93 | 0.53 | 1.35 | 0.69 |
| CaO, % | 50.10 | 49.77 | 45.39 | 44.63 |
| Al_2O_3 , % | 1.23 | 0.68 | 1.22 | 1.57 |
| Fe_2O_3 , % | 0.87 | 0.44 | 1.21 | 1.37 |
| F_2 , % | 4.16 | 3.82 | 3.42 | 3.54 |
| SiO_2 , % | 3.56 | 2.90 | 7.89 | 10.52 |
| SO_3 , % | 0.62 | 1.74 | 1.31 | 0.38 |
| Co ₂ , % | 2.60 | 1.85 | 3.29 | 1.65 |
| Loss on ignition, % | 5.95 | 5.87 | 8.45 | 5.74 |
| Density, g/cc | 2.91 | 2.94 | 2.92 | 2.90 |

The latter were a high grade Florida land pebble and a hand-picked sample of rock from the Simplot Mine at Fort Hall, Idaho.

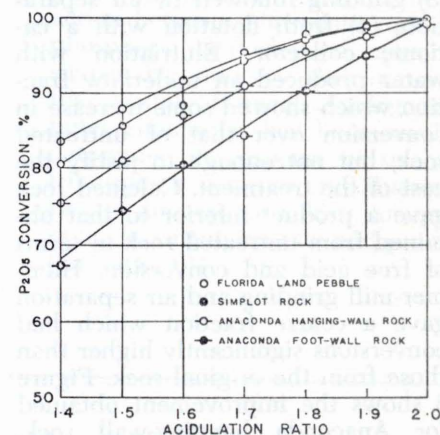


FIG. 2. EFFECT OF ACIDULATION RATIO ON P_2O_5 CONVERSION OF PHOSPHATE ROCKS CURED AT 25 PERCENT RELATIVE HUMIDITY.

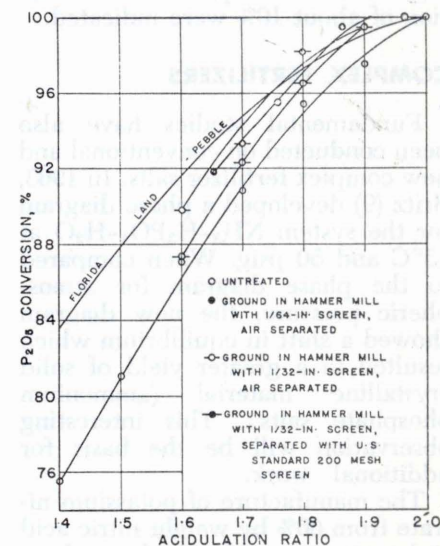
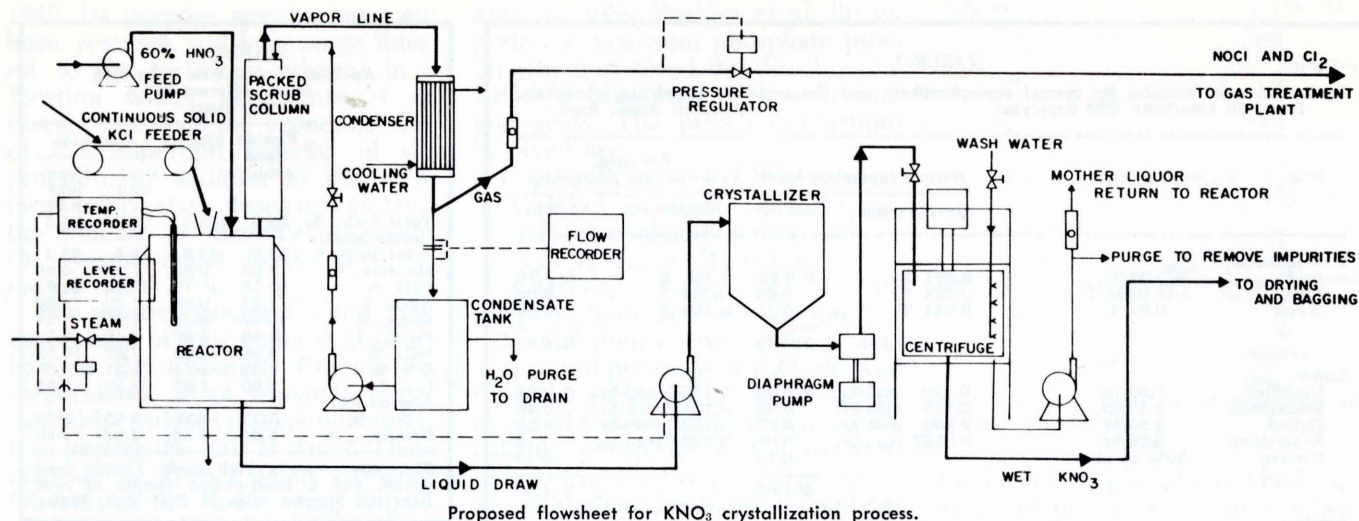


FIG. 3. EFFECT OF ACIDULATION RATIO ON P_2O_5 CONVERSION OF ANACONDA HANGING-WALL ROCK BENEFICIATED BY HAMMER MILL GRINDING.

phosphate rocks to improve their acidulation characteristics were investigated. The methods were (1) washing with water, (2) calcination,



Proposed flowsheet for KNO₃ crystallization process.

(3) grinding followed by air separation, (4) froth flotation with a cationic collector. Elutriation with water produced an underflow fraction which showed some increase in conversion over that of untreated rock, but not enough to justify the cost of the treatment. Calcined rock gave a product inferior to that obtained from untreated rock in terms of free acid and conversion. Hammer-mill grinding and air separation gave a coarse fraction which had conversions significantly higher than those from the original rock. Figure 3 shows the improvement obtained for Anaconda hanging-wall rock. Froth flotation using a cationic collector to remove siliceous impurities was highly successful on deslimed Anaconda hanging-wall rock. Savings in the acid required for acidulation of about 10% were indicated.

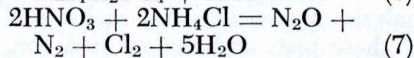
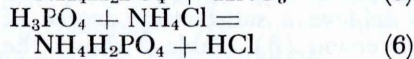
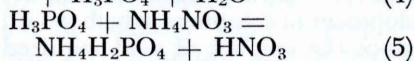
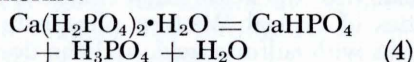
COMPLEX FERTILIZERS

Fundamental studies have also been conducted on conventional and new complex fertilizer salts. In 1963, Britz (9) developed a phase diagram for the system NH₃-H₃PO₄-H₂O at 25°C and 50 psig. When compared to the phase diagram for atmospheric pressure, the new diagram showed a shift in equilibrium which resulted in a greater yield of solid crystalline material (ammonium phosphate salts). This interesting observation will be the basis for additional work.

The manufacture of potassium nitrate from 60% by weight nitric acid and potassium chloride by a fractional crystallization process was recently studied by Gabrielson (10). Because potassium nitrate is several times more soluble than potassium chloride, it is possible to obtain an attractive yield of the nitrate from a solution containing both salts and various amounts of unreacted nitric

acid. Figure 4 shows a mutual solubility diagram prepared for the KNO₃-KCl-HNO₃-H₂O system. Above the solubility curve is the single phase region and below and to the right is the region where one or both salts and a solution exist. Point A is the composition of a solution in equilibrium with both salts. Based on these data and accompanying reaction rate studies, a process shown in Figure 5 was proposed.

A comprehensive study on the effect of composition on nitrogen loss from complex fertilizers during drying was recently completed (11). Most of the tests were conducted with a 12-12-12 mixture prepared using standard fertilizer materials. It was discovered that the key reaction in initiating decomposition was the hydrolysis of monocalcium phosphate which results in formation of dicalcium phosphate and phosphoric acid. The latter in turn reacts with ammonium nitrate or ammonium chloride to cause, as shown below, losses of nitrogen and chlorine:



Decomposition did not occur in the absence of chloride ion, but the addition of only 0.05 weight percent chloride caused substantial loss. In samples in which either the nitrate or ammonium ion was missing, no losses occurred. It made no difference whether these ions were supplied by ammonium nitrate or individual ammonium and nitrate salts; the losses were the same in either case.

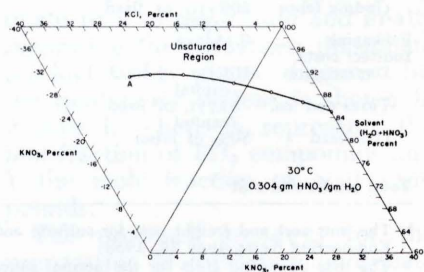


Figure 4—Mutual solubility diagram for system KNO₃-KCl-HNO₃-H₂O.

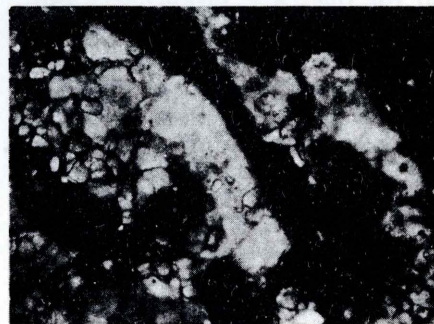


Figure 6—Photomicrograph of coated and then dried ammonium nitrate prill. 100X. Dark curving line is layer of diatomaceous earth originally on outside of wet prill.

When the effect of acidity was investigated, it was found that as the pH increased from 2.8 to 3.9 the losses dropped sharply and that the samples of pH 3.9 to 6.3 were stable. Of particular interest was the observation that the addition of potassium or ammonium sulfate to the mixtures effectively inhibited decomposition by preventing hydrolysis of the monocalcium phosphate and the subsequent formation of phosphoric acid.

A study of the drying characteristics of ammonium nitrate prills provided a practical application for the

new science of transport phenomena (transfer of heat, mass, and momentum) (12). It was discovered that wet prills coated with 3% diatomaceous earth dried from 3.0 to 0.2% water (dry basis) in about one-third the time required for uncoated prills. In the latter tests case-hardening was observed. During drying, ammonium nitrate solution moves to the surface where evaporation takes place and a dense crystalline layer is deposited which effectively obstructs the pores through which the solution must reach the surface. With the surface thus blocked, subsequent drying must take place by means of diffusion of water vapor through the crystalline shell.

The coating forms a porous layer which keeps the channels to the surface open until drying is complete. Figure 6 is a photomicrograph of a coated and dried prill which shows the deposit of crystalline material formed on the outside of the coating. Shorter drying times have been observed in both cabinet and rotary dryers.

Two current projects deal with

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the separation of controlled release fertilizers. In one case, various coating agents are being investigated and in the other, the effect of calcina-

tion on release. Consequently, work is underway on the development of a standard laboratory method for testing the velocity at which nutrients are released from fertilizer particles.

A relatively recent area of work deals with crystallization dynamics. An understanding of the dynamic changes which take place in the number and size of crystals during continuous crystallization is important in processes dealing with the production of several fertilizer salts including ammonium sulfate, ammonium nitrate, and potassium nitrate, and in the production of wet process phosphoric acid. In the latter case, the filtration characteristics of the gypsum formed from the reaction between phosphate rock and phosphoric acid depend upon the shape, size, and size distribution of the crystals formed. Analog computer simulation has been used to determine the response of size distributions in a mixed crystal suspension of ammonium sulfate to upsets in nuclei dissolving rate and production rate (13). ☆

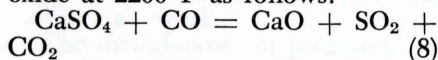
This final article in a two-part series reviews the fertilizer technology program at Iowa State University and its significance to the fertilizer industry.

By DAVID R. BOYLAN and GEORGE BURNET

IN the "thermal" processing of phosphate rock the P_2O_5 content is made available by heat treatment in contrast to acid treatment as is common in the manufacture of superphosphate and related materials. Most of the work at Iowa State has dealt with the fusion process in which the rock is heated to a molten state with certain addition agents such as silicate or sulfate without the removal of fluorine.

A typical project led to the development of a process for the manufacture of a phosphate fertilizer from the fusion of rock with gypsum (1). Products made by fusing a mixture containing 30% phosphate rock and 70% dehydrated gypsum contained at least 10.5% total P_2O_5 and 10.4% available P_2O_5 . Figure 1 shows a flowsheet for a proposed large scale fused phosphate rock gypsum plant. Later work showed that by-product gypsum from the manufacture of wet process phosphoric acid could be used (2).

Gypsum is also the source of sulfur dioxide and agricultural lime in a thermal decomposition process developed entirely at Iowa State (3). The calcium sulfate in gypsum or anhydrite reacts with a gaseous reducing agent such as carbon monoxide at $2200^\circ F$ as follows:



In practice the reducing atmosphere is produced by the partial combustion of natural gas and the reaction with finely divided gypsum carried out in a two-stage fluidized

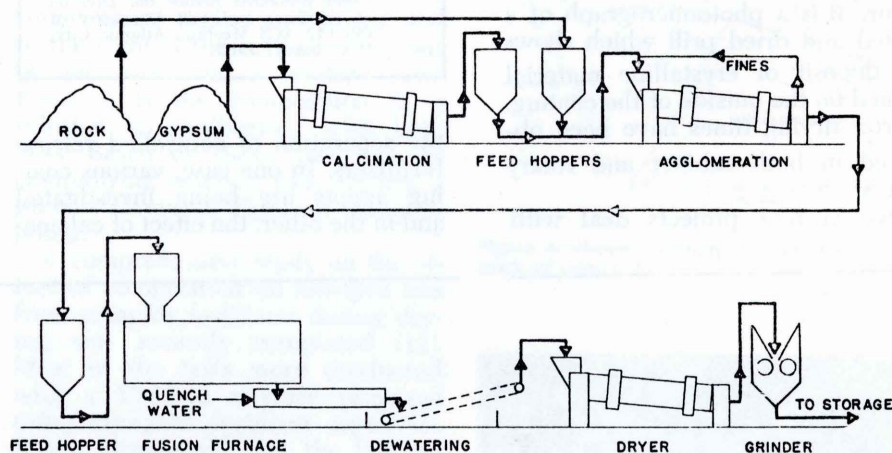


Figure 1 -- Proposed flow sheet for a fused gypsum-phosphate fertilizer plant.

bed. The SO_2 concentration in the effluent gas is high enough to make it a promising starting material for sulfuric acid manufacture.

Another investigation has led to a proposed process for the manufacture of phosphorus nitride containing a total of 84.8% phosphorus and nitrogen by heating liquid-ammoniated P_4S_{10} to temperatures in the range of $800^\circ C$ (4). The compounds formed easily hydrolyzed in water to produce monoammonium dihydrogen phosphate. The presence of potassium-containing salts catalyzed the hydrolysis and suggested a possible formulation in which the plant nutrients would become slowly available to plants in the soil. Approximately 30% hydrolysis was thus obtained in 45 days at $50^\circ C$. Table 1 shows the effect of temperature and various catalysts on the hydrolysis of phosphorus nitrides.

In work only recently undertaken, the very high temperature of a plasma torch is being used to cause

disassociation of phosphate rock to produce P_2O_5 . Preliminary experiments have shown a considerable increase in the availability of P_2O_5 in the residual rock as a result of the treatment. Optimum conditions for the treatment are now being sought.

MANUFACTURING OPERATIONS

The unit operations common in the fertilizer industry and process improvements have been an important part of the research program at Iowa State. Some studies in this area have been quite fundamental in nature such as those dealing with the theory and practice of filtration (5, 6). Significant improvements have been made in the accuracy with which commercial scale filtration performance can be predicted from small compression-permeability cell test data. The work could lead to improved filtration and lower costs in the manufacture of wet process phosphoric acid.

A recent granulation study showed

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Table 1: LONG-RUN AVAILABILITY OF PHOSPHORUS NITRIDES

| Catalyst for hydrolysis | Temperature, °C | Time, days | Percent hydrolyzed |
|--------------------------------|-----------------|------------|--------------------|
| No Catalyst | 25 | 30 | 3.1 |
| | | 45 | 3.2 |
| | | 50 | 38.2 |
| KCl | 25 | 45 | 44.0 |
| | | 30 | 2.9 |
| | | 45 | 3.1 |
| H ₂ SO ₄ | 50 | 30 | 29.6 |
| | | 45 | 34.0 |
| | | 50 | 5.8 |
| Citric acid | 25 | 30 | 5.8 |
| | | 45 | 6.1 |
| | | 50 | 90.3 |
| K ₂ SO ₄ | 50 | 30 | 90.6 |
| | | 45 | 4.8 |
| | | 50 | 5.5 |
| H ₃ PO ₄ | 25 | 30 | 74.1 |
| | | 45 | 81.5 |
| | | 50 | 4.6 |
| | 50 | 30 | 5.4 |
| | | 45 | 18.0 |
| | | 50 | 23.1 |
| | 25 | 30 | 5.4 |
| | | 45 | 5.7 |
| | | 50 | 85.8 |
| | | 45 | 92.5 |

Table 2: COMPARISON OF ESTIMATED RETURN ON THE INVESTMENT FOR STORAGE AND QUICK CURED TSP PLANTS

| Item | Storage cured | | Quick cured | |
|---|---------------|----------------------|-------------|-------------|
| | Cost/ton | Amount | Cost/ton | Amount |
| Annual sales ^a | \$76.80 | \$4,608,000 | \$81.60 | \$4,896,000 |
| Manufacturing cost | 63.86 | 3,831,600 | 67.53 | 4,051,800 |
| Gross profit | | 776,400 | | 844,200 |
| Administration and selling cost at 3% of annual sales | | 138,240 | | 146,880 |
| Net profit before taxes | | 638,160 | | 697,320 |
| Taxes, 50% | | 319,080 | | 348,660 |
| Net profit after taxes | | \$ 319,080 | | \$ 348,660 |
| Working capital | | | | |
| Raw materials inventory | | | | |
| Acid, 10 days | \$68.43 | \$ 108,390 | \$68.43 | \$ 102,508 |
| Rock, 2 weeks | 16.00 | 20,020 | 16.00 | 21,720 |
| In-process inventory | 63.86 | 383,200 ^b | 67.53 | 3,000 |
| Product inventory | 63.86 | 383,200 | 67.53 | 405,180 |
| Available cash, 30 days production | 63.86 | 383,200 | 67.53 | 405,180 |
| Credit, 30 days | 76.8 | 460,800 | 81.60 | 489,600 |
| Total working capital | | \$1,738,800 | | \$1,427,000 |
| Fixed capital | | \$ 671,400 | | \$ 626,100 |
| Fixed + working capital | | \$2,410,200 | | \$2,030,800 |
| Percent return on investment | | 13.2 | | 17.2 |

^a Based on sale price of 1.60 dollars per unit P₂O₅
^b Based on 30 days storage

that typical fertilizer mixtures which contained potassium nitrate gave granules which were more cohesive, less porous, tougher, and more spherical and uniformly shaped (10). Due to the relatively high solubility of potassium nitrate at the elevated temperatures of granulation, a 5-10-15 mixed fertilizer required only 6.5% moisture for optimum yield of product as contrasted to a comparable mix in which potassium chloride had been used and 16% moisture was required. The drying times were correspondingly reduced.

In 1958, an investigation was undertaken to determine the effect of grinding during the acidulation of phosphate rock (7). Bench-scale work lead to a successful pilot plant operation which demonstrated that a normal superphosphate product suitable for commercial use was obtained within an hour after the addition of acid. Both acidulation and drying were accomplished in a single unit to produce a product which required no curing. Conversions of 95% of the P₂O₅ in the rock were obtained. A later investigation resulted in several process improvements including the use of a rod mill in place of the ball mill originally employed (8).

More recently the pilot plant unit was used to investigate the manufacture of triple-superphosphate with similar success (9). Figure 2 shows a flowsheet for the pilot plant unit used in the investigation. The rod mill was 6 feet long, 1 foot in diameter, and contained 10 stainless

rods 1 inch in diameter. The interior lining was stainless steel as were four lifting flights installed to assure effective grinding.

Conversions of more than 94% were achieved with the use of Florida phosphate rock. (34.17% P₂O₅) and electric furnace phosphoric acid (66% H₃PO₄). The product contained more than 51% available P₂O₅ and left the mill as a free flowing dry material. Preliminary estimates of economic feasibility indicated that triple-superphosphate could be produced more profitably by this process than the conventional storage-

curing process. Table 2 shows a comparison of the estimated return on investment for a 200 ton per day plant in a midwestern location.

LOOKING AHEAD

As the world will become increasingly dependent on commercial fertilizers to provide the food requirements of its expanding population, the outlook for the fertilizer industry appears to be promising indeed. The years ahead will see important advances in the technology of fertilizers and in the economy and efficiency of their use. New kinds of products

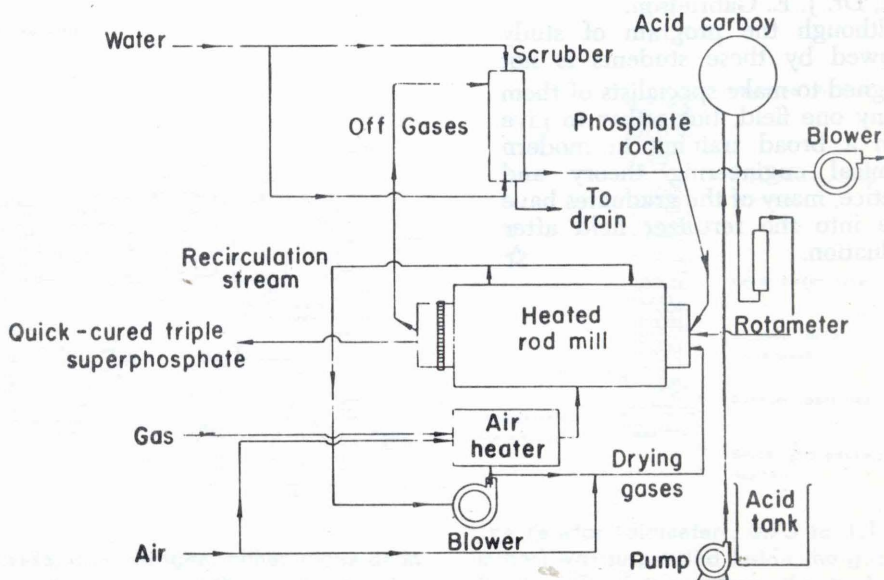


Figure 2 — Flow sheet of the pilot plant for quick-cured triple superphosphate.

will be developed, further improvements will be made in the physical condition of fertilizer materials, and new methods and means of application will appear. There would seem to be little doubt that the role of research and education will become even more important.

At Iowa State the fertilizer research program has been largely sponsored and financed by the Engineering Experiment Station with state appropriated funds. However, increasing support from industry has been forthcoming. For example, the nitrogen loss studies (11) were supported by the U. S. Steel Corporation and the potassium nitrate granulation work (12) by Southwest Potash Corporation. Also, graduate fellowships have been sponsored by Du Pont, Monsanto, Phillips, Union Carbide, and Esso. Needless to say, additional assistance of this kind would be welcomed by the University to expand the research program further.

One of the important benefits of the program, in addition to the technical information derived, is the training of chemical engineers in fertilizer technology. A number of Iowa State chemical engineering graduates have gone into responsible positions in the fertilizer and related industries. Among these are Dr. E. C. Kapusta of the Potash Company of America, Dr. C. R. Vander Linden of Johns-Manville, Dr. E. H. Brunsting of John Deere Chemical Co., R. G. Powell of International Minerals and Chemicals Corp., and Dr. J. W. Markey of Tennessee Corp. Dr. J. C. Reisch, now with Esso Research and Engineering Co., was joined last year by yet another graduate, Dr. J. E. Gabrielson.

Although the program of study followed by these students is not designed to make specialists of them in any one field, but rather to give them a broad training in modern chemical engineering theory and practice, many of the graduates have gone into the fertilizer field after graduation. ☆

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Reductive Decomposition of Gypsum by Carbon Monoxide

Sulfur dioxide and lime can be produced from gypsum under newly determined conditions. Process provides a new route for manufacturing sulfuric acid from gypsum

TREMENDOUS domestic reserves of gypsum and anhydrite constitute a potential source of raw material for sulfur-based chemicals. As in Europe today, calcium sulfate may become one of our principal raw materials for sulfuric acid. Several European acid plants are based on a process in which sulfur dioxide is freed from anhydrite by heating the latter with coke and shale to a sintering temperature (4). The sulfur dioxide is converted into acid and the clinker is used for portland cement.

In the work described here a simpler process for freeing sulfur dioxide was investigated. Calcium sulfate reacts with a gaseous reducing agent such as

carbon monoxide at elevated temperatures to produce sulfur dioxide and lime. The solids do not sinter and the lime may be a by-product of value. Because this by-product can be disposed of in more ways than portland cement, the process should be more flexible than the European process.

Thermodynamics

The principal reaction (Reaction 1) is endothermic and therefore favored by higher temperatures. Reaction 2, which is undesirable, is exothermic and is favored by lower temperatures and high carbon monoxide partial pressures. Above 2100° F., under equilibrium con-

ditions at atmospheric pressure, calcium sulfide cannot exist in the presence of calcium sulfate because of Reaction 3. Of course, the kinetics of this reaction may be unfavorable.

To show that a reducing agent is needed for decomposing calcium sulfate, equilibrium constants for Reaction 4 are included.

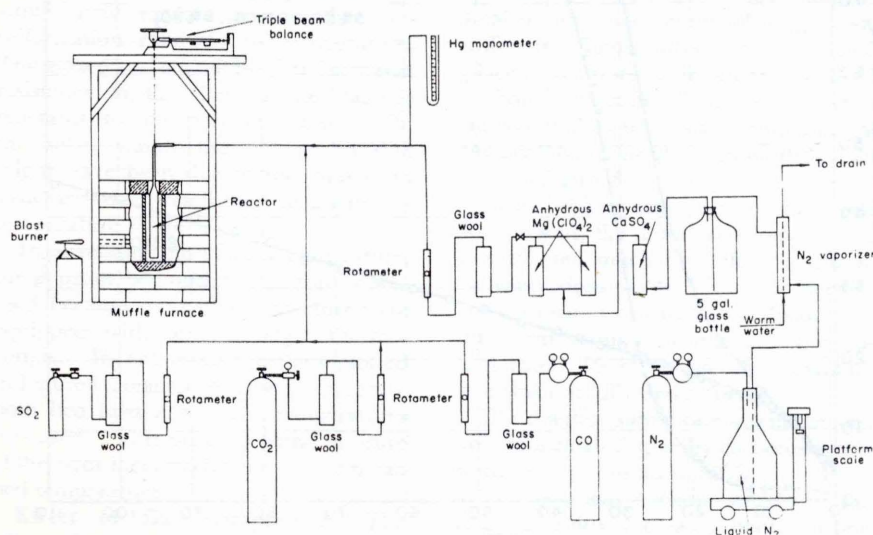
Experimental

For this study natural gypsum having the following composition was used. The gypsum was crushed and then separated by Tyler standard sieves into narrow-size fractions. The -7+8-mesh fraction was used for most runs.

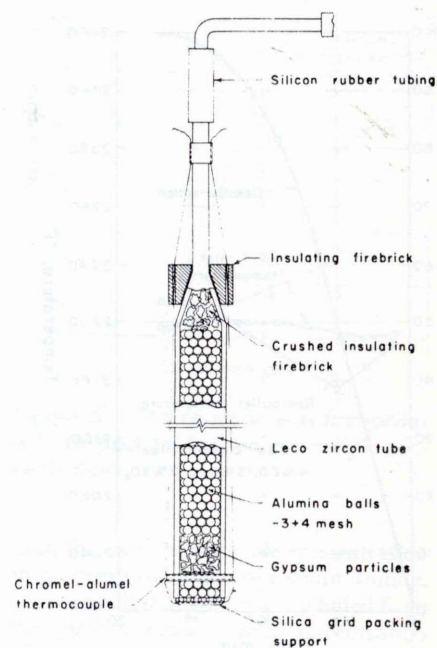
Both commercial and chemically pure grades of carbon monoxide were used. The carbon dioxide was specified as 99.97% pure, and the sulfur dioxide was refrigerant grade. The liquid nitrogen, which after vaporization served as a

Calculated Equilibrium Constants and Heats of Reaction for Reactions Involved in the Process

| Reaction | Log ₁₀ K | | | ΔH _R , Cal./ Mole |
|---|---------------------|----------|----------|------------------------------------|
| | 1200° K. | 1400° K. | 1600° K. | |
| 1. CaSO ₄ + CO = CaO + SO ₂ + CO ₂ | 0.31 | 1.48 | 2.28 | 43,400 |
| 2. CaSO ₄ + 4CO = CaS + 4CO ₂ | 7.92 | 6.69 | 5.66 | -48,400 |
| 3. 3CaSO ₄ + CaS = 4CaO + 4SO ₂ | -6.68 | -0.77 | 3.44 | 222,200 |
| 4. CaSO ₄ = CaO + SO ₂ + 1/2 O ₂ | -7.42 | -4.51 | -2.38 | 110,600 |



Carbon monoxide and dioxide, sulfur dioxide, and nitrogen, either alone or in combination, were continuously metered, mixed, and passed through the reactor containing gypsum



The reactor (diameters, 0.75 to 1.13 inches) was suspended inside the gas-fired muffle furnace from the triple-beam balance

Average Gypsum^a Composition (1)

| Constituent | Weight % |
|-------------------------------|----------|
| H ₂ O | 19.6 |
| CaO | 30.9 |
| MgO | 0.1 |
| SO ₃ | 45.1 |
| CO ₂ | 0.7 |
| R ₂ O ₃ | 0 |
| SiO ₂ | 3.3 |
| NaCl | 0.3 |
| Total | 100.0 |

^a United States Gypsum Co., Fort Dodge, Iowa.

diluent for the gaseous reactants, contained less than 0.1% oxygen.

The reactor, usually charged with a bed of gypsum 1 inch thick, was suspended inside the preheated furnace, and as its temperature rose, a mixture of sulfur dioxide and air was passed through to prevent the gypsum from decomposing. As operating temperature was approached, nitrogen and carbon dioxide were added. When the reactor temperature had leveled out, the flow of air was stopped and the flow of carbon monoxide was started. This marked the beginning of a run. At regular intervals of 1 to 10 minutes, depending on the rate of decomposition, the reactor weight was noted. Operating conditions were kept constant. After the reactor reached a constant weight, it was slowly withdrawn from the furnace, while nitrogen and a small amount of carbon monoxide were passed through it.

Undecomposed sulfate in the residual solids was determined gravimetrically (1). Sulfide and calcium were determined iodometrically and by Versenate titration (2), respectively.

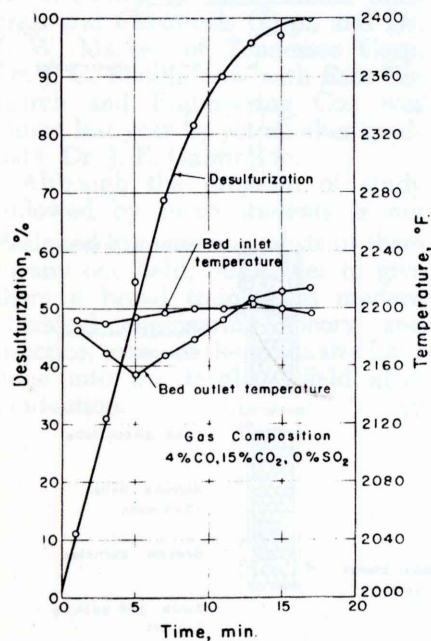


Figure 1. The desulfurization proceeded at a constant rate for much of the run when mixtures of carbon monoxide and nitrogen were fed

Results

Calcium sulfate in the gypsum could be quantitatively decomposed by passing a stream of nitrogen over the gypsum heated to about 2200° F. However, adding as little as 1% of the decomposition products, sulfur dioxide and oxygen, to the nitrogen prevented the decomposition. If several per cent of carbon monoxide were also present, calcium sulfate decomposed in the presence of as much as 7% sulfur dioxide.

Generally, calcium sulfate was converted to calcium oxide. At times calcium sulfide was produced. Consequently the criteria chosen for comparing the effect of operating conditions were the rate of desulfurization and the concentration of calcium sulfide in the residual solids. The conversion to sulfide was approximately proportional to the percentage of calcium sulfide in the residue.

The total desulfurization or conversion of calcium sulfate to calcium oxide was calculated from the composition of the final solids. By assuming that the instantaneous conversion was proportional to the weight lost by the gypsum charge, desulfurization curves such as those in Figures 1 and 2 were plotted. These curves usually had either one or two constant rate periods for which the rates could be reasonably correlated with reaction conditions. Generally the greater part of the desulfurization took place at a constant rate which corresponded to the maximum rate.

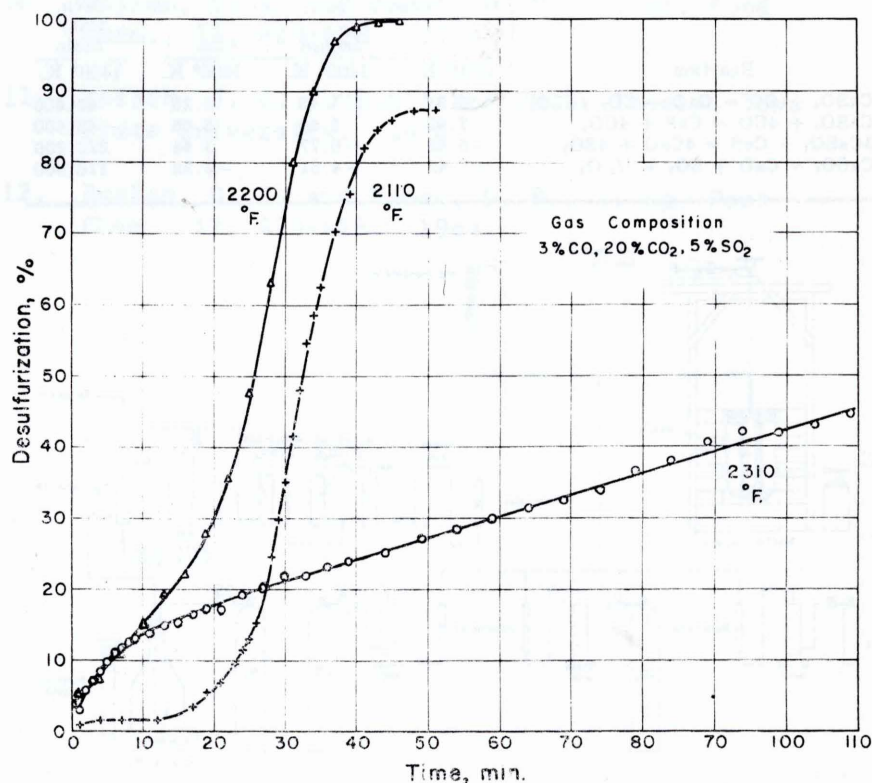


Figure 2. When sulfur dioxide was present in feed gas containing less than 5% carbon monoxide, S-shaped desulfurization curves were obtained

Effect of Temperature. The effect of temperature on the desulfurization rate and on the formation of calcium sulfide was studied between 2100° and 2300° F. using various gas compositions. When the gas mixture fed to the reactor contained 3% carbon monoxide, results were obtained as shown in Figure 2. At 2110° F. the gypsum passed through an initial induction period where little or no decomposition occurred. The reaction rate soon increased, and a relatively constant but rapid desulfurization rate was established. At the end the gypsum was 87% desulfurized, and the solids contained 11% calcium sulfide. Increasing the temperature to 2200° F. increased the initial desulfurization rate, but the maximum rate was unaffected. The total desulfurization was increased to almost 100%, and no calcium sulfide was found in the solids. When the temperature was raised to 2310° F., the initial rate was the same as for 2200° F., but after 8 minutes the rate fell to a much lower but constant value.

When the gas fed contained 4% carbon monoxide, the initial and maximum rates (Figure 3) and the per cent calcium sulfide in the residue (Figure 4) varied with temperature.

When sulfur dioxide was excluded from the gas fed, the maximum desulfurization rate reached a peak value at about 2150° F. with 4% carbon monoxide and 2250° F. with 2%. The variation in the rate with temperature was much greater

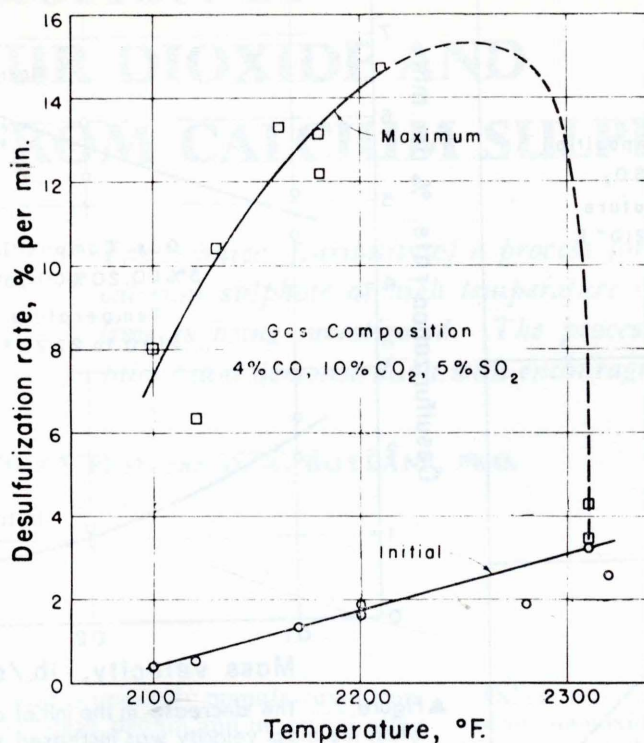


Figure 3. The maximum desulfurization rate reached a peak value at about 2200° F.

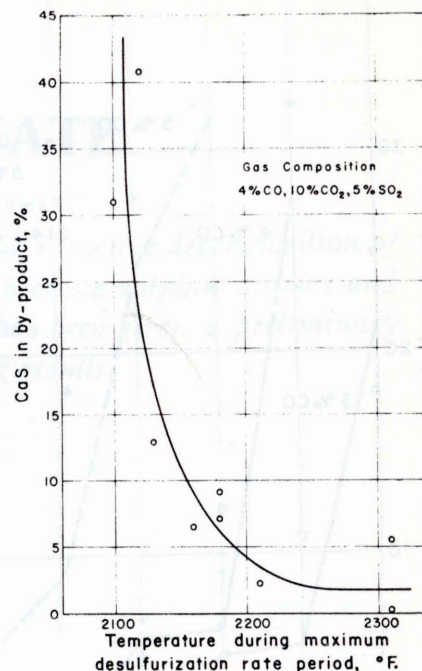


Figure 4. Production of calcium sulfide can be minimized by using high temperatures

for 4% carbon monoxide than for 2%. Again an increase in temperature from 2100 to 2200° F. sharply reduced the calcium sulfide produced.

Although the physical size and shape of the final solids were about the same as for the untreated gypsum, the surface of the treated particles was different in appearance. Gypsum has a relatively smooth surface, while solids recovered from a run made at 2200° F. had a porous surface and solids from a run made at 2300° F. had a glassy surface. The latter must have reached a state of incipient fusion, which may explain the smaller desulfurization rate at this temperature. The glazed surface might offer increased resistance to the flow of the gaseous reactants to the particle interior. On the other hand, the change in rate might have been due to the change in structure which reportedly occurs in this temperature range (3).

In correlating the effect of temperature, the gypsum bed outlet temperature was used because most of the reactors were equipped with only a single thermocouple. In obtaining the data plotted in Figure 1 a reactor equipped to measure both bed inlet and outlet temperatures was used. This provides some measure of the error incurred by not using a mean bed temperature.

Effect of Gas Composition. The effect of gas composition was explored at a temperature level of 2200° F. When a mixture of carbon monoxide, carbon dioxide, sulfur dioxide, and nitrogen was fed, the initial and maxi-

imum desulfurization rates varied linearly with carbon monoxide concentration (Figure 5). For these conditions the rate of decomposition was negligible with less than 1.8% carbon monoxide. With more than 5% carbon monoxide the data points probably fell below the plotted straight line because some calcium sulfide was produced.

When sulfur dioxide was left out of the gas fed to the reactor, the desulfurization rate was again a linear function of carbon monoxide concentration, but the rate of increase in the rate of desulfurization was smaller and the point of origin was different. Thus decomposition took place at an appreciable rate even with no carbon monoxide. With 4% carbon monoxide the rate was about the same as the maximum rate observed for the conditions of Figure 5.

When 4% or more carbon monoxide was present, the desulfurization rate was not affected much by sulfur dioxide in concentrations up to 7%. For smaller concentrations of carbon monoxide, sulfur dioxide reduced the initial desulfurization rate. Its effect on the maximum rate was not fully determined.

The desulfurization rate was influenced only to a small degree by carbon dioxide in concentrations up to 30%.

The per cent calcium sulfide in the residual solids increased with carbon monoxide concentration but decreased with carbon dioxide concentration (Figure 6). In the presence of 5% sulfur dioxide the concentration of carbon dioxide must be five to six times greater

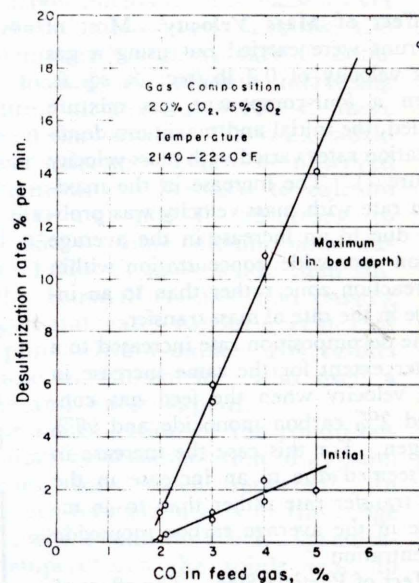
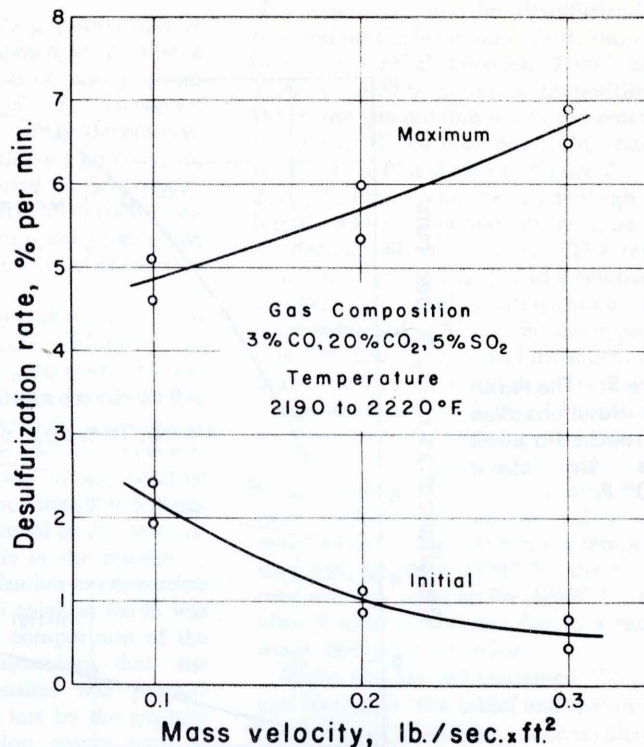
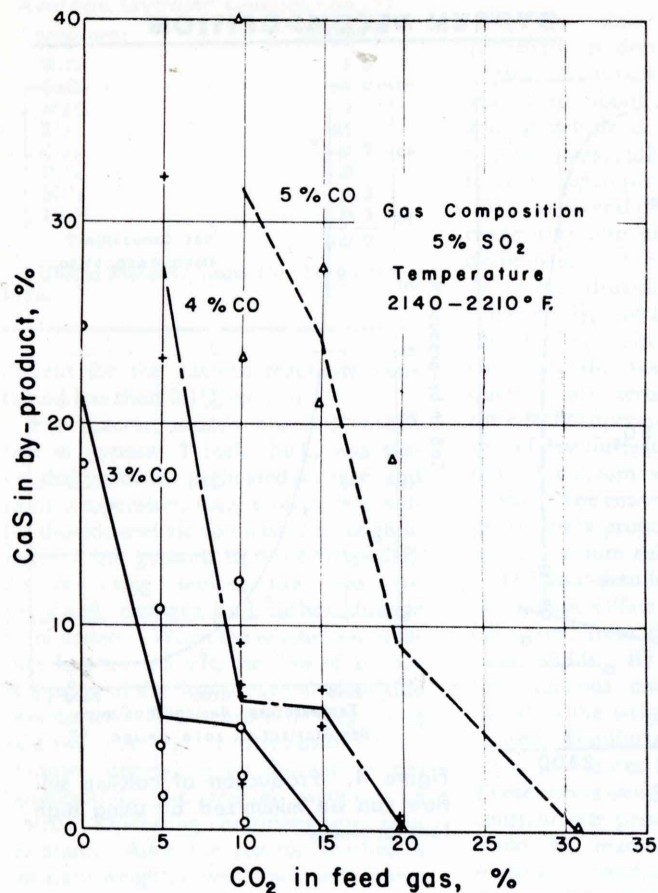


Figure 5. The reaction was first-order with respect to carbon monoxide concentration

than the carbon monoxide concentration to prevent production of calcium sulfide.

When sulfur dioxide was excluded from the gas fed, a much lower concentration of carbon dioxide was effective in suppressing calcium sulfide.

In correlating the results, the composition of the gas fed to the reactor was used, as it approximated the composition in the reaction zone and the latter could not be accurately determined.



▲ Figure 7. The decrease in the initial desulfurization rate when the mass velocity was increased was unexpected

◀ Figure 6. Production of calcium sulfide can be minimized by using small concentrations of carbon monoxide and large concentrations of carbon dioxide

Effect of Mass Velocity. Most of the runs were carried out using a gas mass velocity of 0.2 lb./sec. \times sq. ft. When a four-component gas mixture was fed, the initial and maximum desulfurization rates varied with mass velocity (Figure 7). The increase in the maximum rate with mass velocity was probably due to an increase in the average carbon monoxide concentration within the reaction zone rather than to an increase in the rate of mass transfer.

The decomposition rate increased to a greater extent for the same increase in mass velocity when the feed gas contained 2% carbon monoxide and 98% nitrogen. For this case the increase in rate seemed due to an increase in the mass transfer rate rather than to an increase in the average carbon monoxide concentration.

Effect of Particle Size. The effect of particle size on the desulfurization rate was determined by using three size fractions of gypsum: $-3\frac{1}{2}+4$, $-7+8$, and $-12+14$ -mesh. The initial and maximum rates are plotted against the average screen opening in Figure 8. Because the maximum rate increased with decreasing particle size, and mass transport in the gas phase did not seem to be limiting, the rate of internal diffusion might have been the rate-controlling mechanism during the maximum desulfurization rate period for the conditions common to both Figures 7 and 8.

Because the initial and maximum rates were not affected in the same way by

temperature, gas composition, mass velocity, or particle size, it is apparent that more than one mechanism is rate-controlling during the desulfurization of a single batch of gypsum.

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Reductive decomposition of gypsum using carbon monoxide in low concentration is both thermodynamically and kinetically feasible. The reaction appears to be first-order with respect to carbon monoxide concentration, and the optimum temperature is 2200° to 2250° F.

Desulfurization rate is a function of temperature, gas composition, gas mass velocity, and particle size. Side reactions yielding calcium sulfide can be limited by employing a high temperature, a low concentration of carbon monoxide, and a concentration of carbon dioxide five to six times greater than the carbon monoxide concentration in the reaction zone.

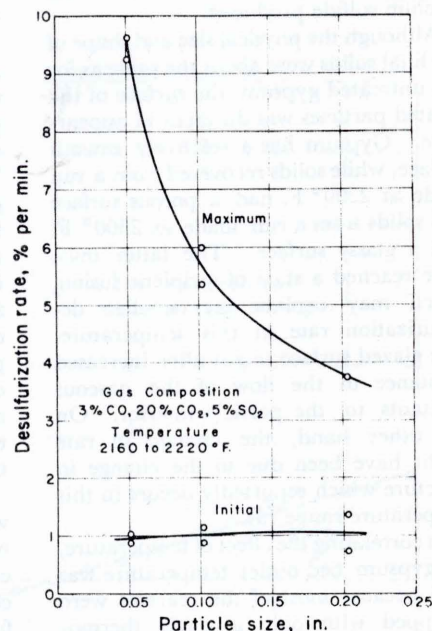


Figure 8. The maximum desulfurization rate can be increased by reducing the particle size

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Division of Industrial and Engineering Chemistry, 136th Meeting, ACS, Atlantic City, N. J., September 1959. Investigation carried out at the Iowa Engineering Experiment Station. Financial assistance received from E. I. du Pont de Nemours & Co., Inc., and the Ethyl Corp.

PRODUCTION OF SULPHUR DIOXIDE AND LIME FROM CALCIUM SULPHATE

The technical feasibility of a process for the reductive decomposition of calcium sulphate at high temperature to produce sulphur dioxide and lime is being investigated. The process has been given a preliminary pilot plant demonstration with encouraging results

T. D. WHEELOCK*, Ph.D., and D. R. BOYLAN*, Ph.D.

SULPHURIC acid is presently manufactured from anhydrite in Great Britain and in several other European countries by a process in which sulphur dioxide is released by sintering anhydrite, coke and shale in a large rotary kiln⁵. The sulphur dioxide is recovered from the kiln gas and converted into sulphuric acid while the clinker discharged from the kiln is used for Portland cement.

In some situations it might be more attractive economically to produce sulphuric acid from gypsum or anhydrite without at the same time producing Portland cement. For this, a process is needed which does not require the addition of shale or other materials containing silica or alumina to effect the decomposition of calcium sulphate. Such a process was patented by Fleck³, who asserted that quicklime and sulphur dioxide can be produced by heating calcium sulphate to temperatures in the range of 1,150 to 1,250° C. in a reducing flame. It was suggested that the process be carried out in a rotary kiln fired with coal gas or producer gas and insufficient air to provide complete combustion. Moreover, it was claimed that the lime would be high-grade and neither dead-burnt nor contaminated with calcium sulphide.

It is our purpose to re-examine this process, which was patented some 30 years ago, and to measure its present technical and economic feasibility. Although the work has not been completed, some progress can be reported.

Process Chemistry

According to a report of the American Gas Association¹, the partial combustion of either manufactured gas or natural gas will yield a gaseous mixture in which carbon monoxide and hydrogen are the chief reducing components. Hence, it would be anticipated that the first two reactions listed in Table 1 would be the principal reactions involved in the process patented by Fleck.

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Other reactions between calcium sulphate and carbon monoxide or hydrogen are possible. Thus, Hofman and Mostowitsch⁴ and Zawadzki, *et al.*⁸ reported the quantitative reduction of calcium sulphate to calcium sulphide according to Reaction 3 when a stream of carbon monoxide was passed over the solids at about 800° C. However, Zawadzki also observed that at temperatures above 825° C. some calcium oxide was formed, the amount increasing with the temperature, but even at 1,100° C. more sulphide was produced than oxide. When Zawadzki passed hydrogen over calcium sulphate he observed the latter to be quantitatively reduced to calcium sulphide between 600 and 800° C. according to Reaction 4. Above 850° C. some calcium oxide was produced and above 1,050° C. more oxide than sulphide was produced. Burwell² claimed that passing a mixture of hydrogen and water vapour over heated gypsum produced pure calcium oxide. His results were similar to those of Riesenfeld⁶, who used a mixture of methane and water vapour.

The results of our investigation of the conditions necessary for the reductive decomposition of gypsum by carbon monoxide have been reported⁷. In summary, the optimum temperature is in the range of 1,200 to 1,230° C., which confirms Fleck's specification. At higher temperatures the solids tend to sinter and the reaction rate decreases. At lower temperatures there is a tendency for calcium sulphide to be produced. Further to suppress the production of calcium sulphide it is necessary to employ a relatively small concentration of carbon monoxide and, at the same time, to have present either carbon dioxide or water vapour. Thus, where the concentration of carbon monoxide is 2 to 5 per cent. of the phase and the concentration of carbon dioxide is five or more times the carbon monoxide concentration, the reduction yields calcium oxide which is free of calcium sulphide. The gypsum desulphurization rate is a function of the temperature, gas composition, gas mass velocity and particle size. The reaction

appears to be first order with respect to the carbon monoxide concentration.

Equilibrium Conversion

Calculated values of the heats of reaction for some of the possible reactions between calcium sulphate and reducing agents are presented in Table 1, while logarithms of the calculated equilibrium constants are plotted in Fig. 1. Reactions 1 and 2, which produce calcium oxide, are endothermic and are favoured by higher temperatures, while Reactions 3 and 4, which produce calcium sulphide, are exothermic and are favoured by lower temperatures. In theory, calcium sulphate should be reduced by calcium sulphide at high temperatures according to Reaction 5. For a mixture of calcium sulphate and calcium sulphide to exist under equilibrium conditions at 1,150° C. the partial pressure of sulphur dioxide would have to be about 1 atmosphere. Calculated equilibrium data for Reaction 6 indicate that decomposition of calcium sulphate without a reducing agent is impractical.

The equilibrium conversion of calcium sulphate to calcium oxide and to calcium sulphide was calculated for two systems. In one the reducing agent was carbon monoxide, and in the other it was hydrogen. It was assumed that some carbon dioxide and nitrogen would be mixed with the carbon monoxide in the first system and some water vapour and nitrogen with the hydrogen in the second before the gases were contacted with the calcium sulphate. Furthermore, it was assumed that calcium sulphide and calcium sulphate could not both be present in

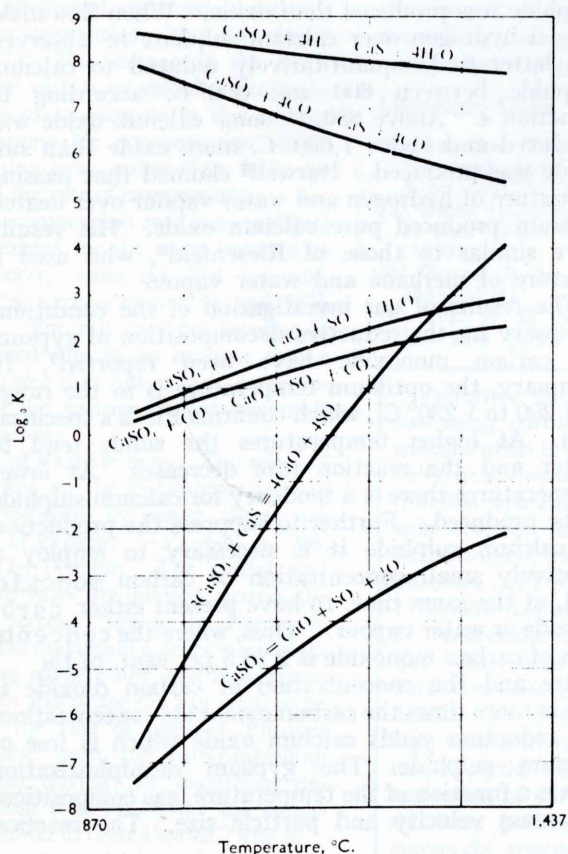


Fig. 1—Effect of temperature on the reaction equilibrium constants

Table 1
REACTIONS INVOLVED IN THE PROCESS AND CALCULATED HEATS OF REACTION

| Reaction | Heat of reaction, cal./g. mol | |
|---|-------------------------------|-----------|
| | 1,125° C. | 1,325° C. |
| (1) $\text{CaSO}_4 + \text{CO} = \text{CaO} + \text{SO}_2$ | 43,400 | 39,500 |
| (2) $\text{CaSO}_4 + \text{H}_2 = \text{CaO} + \text{SO}_2$ | 50,800 | 46,200 |
| (3) $\text{CaSO}_4 + 4 \text{CO} = \text{CaS} + 4 \text{CO}_2$ | -48,400 | -51,000 |
| (4) $\text{CaSO}_4 + 4 \text{H}_2 = \text{CaS} + 4 \text{H}_2\text{O}$ | -18,800 | -24,000 |
| (5) $3\text{CaSO}_4 + \text{CaS} = 4 \text{CaO} + 4 \text{SO}_2$ | 222,200 | 208,900 |
| (6) $\text{CaSO}_4 = \text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2$ | 110,600 | 106,200 |

the solid phase. When an excess of the reducing agent was added, it was necessary to consider the simultaneous equilibria of several reactions.

Figure 2 is the calculated equilibrium conversion chart for the carbon monoxide system. The upper half of the chart represents the region in which calcium oxide and calcium sulphide are present in the solid phase, while the lower half represents the region in which calcium sulphate and calcium oxide are present. When the initial mol ratio of carbon monoxide to calcium sulphate is 1.0 or less, the conversion is equal to the mol ratio of the reactants. For a reactants ratio greater than 1.0 the conversion is also a function of the temperature and the initial mol ratio of carbon dioxide to calcium sulphate.

Conditions which give complete desulphurization are of most interest. A comparison of such conditions shows that as the temperature and proportion of carbon dioxide increase the feed ratio of carbon monoxide to calcium sulphate becomes less critical. For example, at 1,325° C. and an initial carbon dioxide to calcium sulphate ratio of 4.0, complete desulphurization should be obtained for any reactants

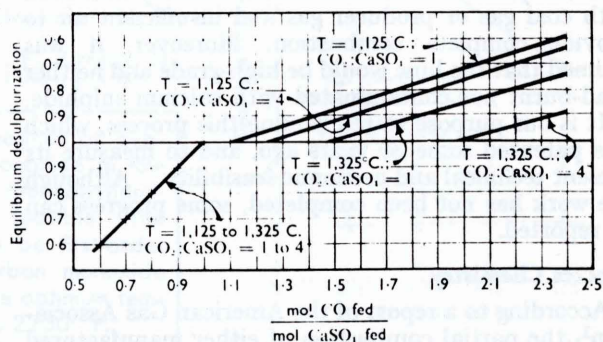


Fig. 2—Equilibrium conversion of calcium sulphate into calcium oxide using carbon monoxide

ratio between 1.0 and 2.0. At 1,125° C. the range is much smaller.

Equilibrium gas compositions were calculated for the conditions which provide complete desulphurization. For this purpose 10 mols of feed gas containing carbon monoxide, carbon dioxide and nitrogen were assumed to be introduced with each mol of calcium sulphate. This ratio of feed gas to calcium sulphate

Table 2
EQUILIBRIUM GAS COMPOSITIONS FOR 100 PER CENT.
DESULPHURIZATION OF CALCIUM SULPHATE BY MEANS OF
CARBON MONOXIDE
(10 mols feed gas/mol CaSO₄)

| Temperature, °C. | Gas composition, mol % | | | |
|---------------------|------------------------|----------------|-----------------|-------|
| | Feed | | Equilibrium | |
| 1,125 | CO | 10.00 | CO | 0.01 |
| | CO ₂ | 10.00 | CO ₂ | 18.17 |
| | N ₂ | 80.00 | N ₂ | 72.74 |
| | | | SO ₂ | 9.08 |
| | | | 100.00 | |
| 1,125 | CO | 11.25 | CO | 0.76 |
| | CO ₂ | 10.00 | CO ₂ | 18.58 |
| | N ₂ | 78.75 | N ₂ | 71.66 |
| | | | SO ₂ | 8.92 |
| | | S ₂ | 0.08 | |
| | | | 100.00 | |
| 1,125 | CO | 12.48 | CO | 1.88 |
| | CO ₂ | 40.00 | CO ₂ | 45.88 |
| | N ₂ | 47.52 | N ₂ | 43.24 |
| | | | SO ₂ | 8.92 |
| | | S ₂ | 0.08 | |
| | | | 100.00 | |
| 1,325 | CO | 14.82 | CO | 3.27 |
| | CO ₂ | 10.00 | CO ₂ | 19.36 |
| | N ₂ | 75.18 | N ₂ | 68.54 |
| | | | SO ₂ | 8.56 |
| | | S ₂ | 0.27 | |
| | | | 100.00 | |
| 1,325 | CO | 19.84 | CO | 7.88 |
| | CO ₂ | 40.00 | CO ₂ | 46.68 |
| | N ₂ | 40.16 | N ₂ | 36.61 |
| | | | SO ₂ | 8.56 |
| | | S ₂ | 0.27 | |
| | | | 100.00 | |

approximates to a value which might be used in practice. The assumed feed gas compositions and the corresponding equilibrium compositions are listed in Table 2. It can be seen that when the reactants ratio exceeds 1.0, the additional carbon monoxide remains largely unreacted. As the proportion of carbon monoxide is increased more of the sulphur dioxide is reduced to sulphur. However, in every case the amount of sulphur is small and the equilibrium concentration of sulphur dioxide is about 9 per cent. These concentrations are relative, for an increase or decrease in the proportion of nitrogen in the feed gas would result in a corresponding change in the equilibrium concentrations.

An equilibrium conversion chart was also prepared for the hydrogen system and it is shown in Fig. 3. It is similar to the previous one, but it differs in that temperature and the initial ratio of water vapour to calcium sulphate have less influence than do the corresponding parameters in the carbon monoxide system. The equilibrium gas compositions for conditions which would result in complete desulphurization by hydrogen are listed in Table 3. For the larger ratios of hydrogen to calcium sulphate small amounts of sulphur dioxide are reduced to sulphur and

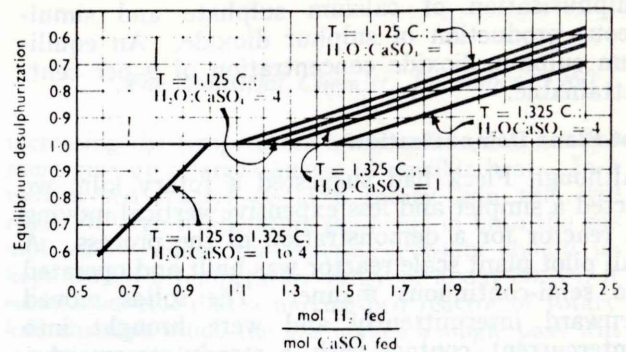


Fig. 3—Equilibrium conversion of calcium sulphate into calcium oxide using hydrogen

hydrogen sulphide, but most of the sulphur dioxide is unaffected.

These results show that for either carbon monoxide or hydrogen a range of conditions exists under which the attainment of equilibrium would provide complete

Table 3
EQUILIBRIUM GAS COMPOSITIONS FOR 100 PER CENT.
DESULPHURIZATION OF CALCIUM SULPHATE BY MEANS
OF HYDROGEN
(10 mols feed gas/mol CaSO₄)

| Temperature, °C. | Gas composition, mol % | | | |
|---------------------|------------------------|------------------|------------------|-------|
| | Feed | | Equilibrium | |
| 1,125 | H ₂ | 10.00 | H ₂ | 0.01 |
| | H ₂ O | 10.00 | H ₂ O | 18.18 |
| | N ₂ | 80.00 | N ₂ | 72.72 |
| | | | SO ₂ | 0.09 |
| | | | 100.00 | |
| 1,125 | H ₂ | 10.94 | H ₂ | 0.34 |
| | H ₂ O | 10.00 | H ₂ O | 19.07 |
| | N ₂ | 79.06 | N ₂ | 71.98 |
| | | | SO ₂ | 8.88 |
| | | S ₂ | 0.08 | |
| | | H ₂ S | 0.06 | |
| | | | 100.41 | |
| 1,125 | H ₂ | 11.78 | H ₂ | 0.85 |
| | H ₂ O | 40.00 | H ₂ O | 46.61 |
| | N ₂ | 48.22 | N ₂ | 43.94 |
| | | | SO ₂ | 8.80 |
| | | S ₂ | 0.08 | |
| | | H ₂ S | 0.15 | |
| | | | 100.43 | |
| 1,325 | H ₂ | 12.60 | H ₂ | 0.96 |
| | H ₂ O | 10.00 | H ₂ O | 19.42 |
| | N ₂ | 77.40 | N ₂ | 70.63 |
| | | | SO ₂ | 8.48 |
| | | S ₂ | 0.26 | |
| | | H ₂ S | 0.11 | |
| | | | 99.86 | |
| 1,325 | H ₂ | 14.60 | H ₂ | 2.36 |
| | H ₂ O | 40.00 | H ₂ O | 47.50 |
| | N ₂ | 45.40 | N ₂ | 41.49 |
| | | | SO ₂ | 8.35 |
| | | S ₂ | 0.26 | |
| | | H ₂ S | 0.28 | |
| | | | 100.24 | |

desulphurization of calcium sulphate and simultaneous production of sulphur dioxide. An equilibrium sulphur dioxide concentration of 9 per cent. is attainable.

Pilot Plant Demonstration

Although Fleck had suggested a rotary kiln, we selected a simpler and less expensive vertical moving bed reactor for a demonstration of the process. A small pilot plant scale reactor was built and operated in a semi-continuous manner. The solids moved downward intermittently and were brought into countercurrent contact with a steady stream of a hot, dilute reducing gas mixture.

Gypsum from the United States Gypsum Co. mine at Fort Dodge, Iowa, was crushed and sized with a mechanical shaking screen. The $-\frac{3}{4} + \frac{3}{8}$ in. size fraction was used in the pilot plant operation. This material was about 96 per cent. pure, a little less than 2 per cent. each of silica and calcium carbonate being the principal impurities.

The pilot plant reactor is shown in Fig. 4. It was essentially a cylindrical shaft $6\frac{1}{2}$ in. in diameter and 63 in. long, which was lined with chrome plastic refractory cement and insulated with insulating firebrick. A gas-tight steel shell enclosed the refractory materials. A manually operated screw conveyor was provided at the bottom of the shaft for discharging solids. A combustion chamber was connected to the reactor and the reducing gas mixture required for the reaction was generated here by burning natural gas and air. These gases were metered with orifice meters and their flow rates were controlled manually. The air to natural gas ratio was adjusted to give the desired concentrations of hydrogen and carbon monoxide in the gas entering the reactor. The carbon monoxide concentration was checked periodically with an Orsat apparatus and according to a study of the American Gas Association¹ the concentration of hydrogen should have been equal to the carbon monoxide concentration.

The bed temperature was controlled by regulating the amount of cooling which the reducing gas received

Table 4
AVERAGE OPERATING CONDITIONS AND RESULTS FOR FINAL 7 HOURS OF THE DEMONSTRATION RUN

| | |
|---|-------|
| Gypsum feed rate, lb./hr. | 12 |
| Natural gas flow rate, std. cu. ft./min. | 1.22 |
| Air flow rate, std. cu. ft./min. | 11.7 |
| Hot spot temperature, ° C. | 1,215 |
| Bed depth, in. | 12 |
| Bed pressure drop, cm. of water | 2 |
| CO in gas entering reactor (dry basis), % | 2 |
| CaS in solids, % | 3.1 |
| Desulphurization, % | 89 |
| <i>Composition of reactor off-gas:—</i> | |
| SO ₂ , mol % | 2.9 |
| CO ₂ , mol % | 9.5 |
| H ₂ O, mol % | 17.5 |
| N ₂ , mol % | 70.1 |
| | 100.0 |

in flowing from the combustion chamber to the reactor. For control purposes the temperature of the hottest spot in the reactor was determined by probing the bed with a protected chromel-alumel thermocouple. Incidentally, the temperature of the bed varied greatly with both radial and longitudinal position. Porcelain, cermet and stainless steel thermocouple protection tubes were tried. The first withstood the attack of the corrosive atmosphere but it was somewhat fragile and not too resistant to thermal shock. The second performed satisfactorily but was expensive and not available in sizes smaller than $\frac{7}{8}$ in. diameter. Stainless steel (Type 304) was generally used because it was more readily available, but it withstood only a few hours of service.

Initially an attempt was made to burn natural gas and air in the lower part of the bed. It proved impossible to control adequately both the temperature and composition of the reducing gas, so a combustion chamber was added. This introduced the problem of conducting the gas from the combustion chamber to the reacting solids. Uninsulated stainless steel pipe satisfactorily carried the gas to the reactor wall but the portion of the pipe projecting into the bed of solids rapidly disintegrated. The gas had to be introduced near the shaft centreline to obtain satisfactory distribution. Ultimately a cermet tube was found to withstand the service.

An operating technique had to be developed for keeping the solids movable. When solids were discharged from the bottom of the reactor, the bed would seldom flow freely. Some rodding was needed but it was easy to crush the soft, dehydrated gypsum and to compact the bed to the point where the shaft would be solidly plugged.

For a 50-hour demonstration run the conditions shown in Table 4 were selected. The gypsum feed rate was chosen on the basis of previous operating experience, while the gas rate was designed to

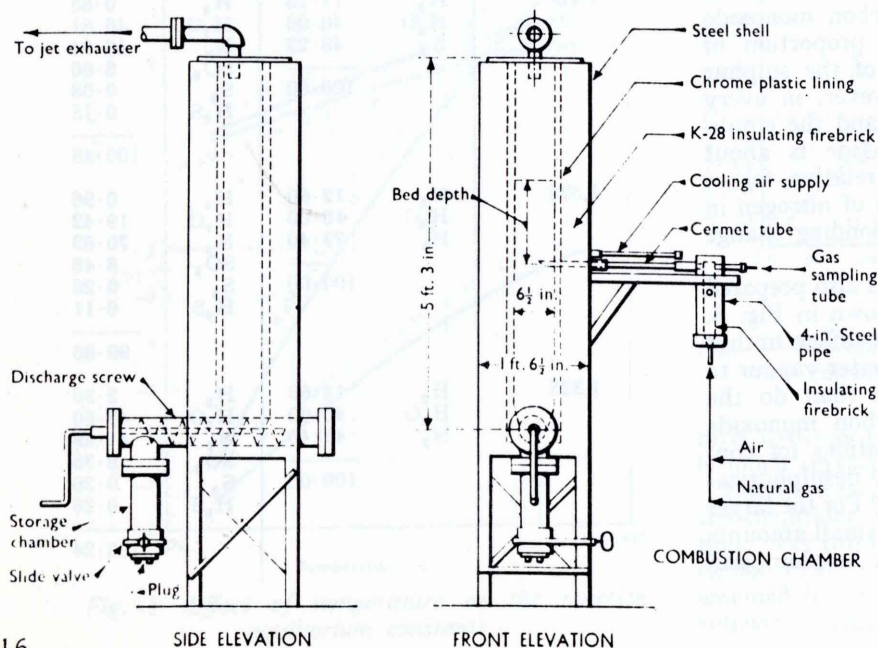


Fig. 4—Pilot plant scale moving bed reactor

provide corresponding stoichiometric amounts of the reducing agents. The choices of temperature and carbon monoxide concentration were based on the results of the earlier laboratory investigation. The choice of bed depth was purely arbitrary.

The demonstration proceeded smoothly and without difficulty. During the operation the bed was rodded and an increment of gypsum was added at 15-minute intervals. More frequently the discharge screw was given a turn, the turns being regulated to keep the bed depth constant. After every 10th revolution the solids were withdrawn from the storage chamber and sampled for chemical analysis.

The best results were obtained during the final 7 hours of the demonstration, when the gypsum was 89 per cent. desulphurized and the remaining solids contained 3.1 per cent. calcium sulphide. The concentration of sulphur dioxide in the gas from the reactor was somewhat low for supplying a sulphuric acid plant and the calcium sulphide content of the solids was probably too high to consider the lime of marketable quality. Hence, the results do not indicate immediate technical feasibility of the process. However, the results are encouraging in light of the large temperature gradients observed in the reactor and the unsteady nature of the operation.

Future Development Programme

To supply the heat absorbed by the reactions and the heat for dehydrating the gypsum and for

increasing the temperature of the solids, the hot gas must give up a large amount of sensible heat. In a moving-bed reactor or in a rotary kiln this will result in large temperature gradients in both the gas and solids. Since the reacting gypsum should be kept within a temperature range of about 30° C., it seems doubtful that a moving-bed reactor or rotary kiln through which the gas makes a single pass will ever prove satisfactory. Recycling a large portion of the gas could provide a more uniform temperature in the reactor, but the build-up of reduction products in the gas might present additional problems.

An alternative type of reactor which seems to offer more promise is the fluidized-bed reactor, for this type can provide a very uniform temperature and the temperature is readily controlled. We are now assembling such a reactor and the process will be given a thorough test with it.

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Table 1. Comparison of Solid Determination by the Present Method and the Gravimetric Method

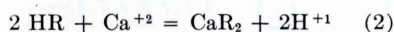
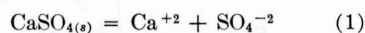
| Sample No. | Present Method | | Gravimetric Method | |
|------------|----------------|-------|--------------------|-------|
| | wt.-% | wt.-% | wt.-% | wt.-% |
| 1 | 8.10 | 8.10 | 8.10 | 8.10 |
| 2 | 8.10 | 8.10 | 8.10 | 8.10 |
| 3 | 8.10 | 8.10 | 8.10 | 8.10 |
| 4 | 8.10 | 8.10 | 8.10 | 8.10 |
| 5 | 8.10 | 8.10 | 8.10 | 8.10 |
| 6 | 8.10 | 8.10 | 8.10 | 8.10 |
| 7 | 8.10 | 8.10 | 8.10 | 8.10 |
| 8 | 8.10 | 8.10 | 8.10 | 8.10 |
| 9 | 8.10 | 8.10 | 8.10 | 8.10 |
| 10 | 8.10 | 8.10 | 8.10 | 8.10 |
| 11 | 8.10 | 8.10 | 8.10 | 8.10 |
| 12 | 8.10 | 8.10 | 8.10 | 8.10 |
| 13 | 8.10 | 8.10 | 8.10 | 8.10 |
| 14 | 8.10 | 8.10 | 8.10 | 8.10 |
| 15 | 8.10 | 8.10 | 8.10 | 8.10 |
| 16 | 8.10 | 8.10 | 8.10 | 8.10 |
| 17 | 8.10 | 8.10 | 8.10 | 8.10 |
| 18 | 8.10 | 8.10 | 8.10 | 8.10 |
| 19 | 8.10 | 8.10 | 8.10 | 8.10 |
| 20 | 8.10 | 8.10 | 8.10 | 8.10 |

Rapid Titrimetric Determination of Sulfate in Mixtures of Gypsum, Anhydrite, Calcium Oxide, and Calcium Sulfide Using Ion Exchange

SIR: The conventional sulfate determination by gravimetrically precipitating barium sulfate is very tedious and time consuming. The present technique uses an ion exchanger so the sulfate can be titrimetrically determined as sulfuric acid. An analysis can be completed in 30 minutes. This method is being used for the routine analysis of sulfate in mixtures of gypsum, anhydrite, calcium oxide, and calcium sulfide. The mixtures are produced from laboratory and pilot plant investigations on the reductive decomposition of gypsum.

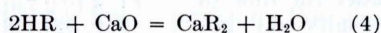
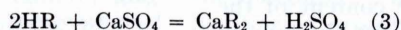
Ion exchangers have been used to some extent for analysis of solutions (3), but the present technique uses an ion exchanger for the analysis of a slightly soluble solid. The method is similar to procedures developed by Kniestedt and Wahle (1) for determining sulfate in naturally occurring anhydrite and by Perry (2) for determining the sulfate content of gypsum, anhydrite, and hemihydrate. The main step uses a cation exchange resin in the hydrogen form so that all the cations in solution will be replaced by hydrogen ions. The resin used can be either Dowex 50 or Amberlite IR 120. Both resins have a high capacity and high thermal stability.

The sulfate exists in the solid samples mostly as calcium sulfate. When the solids are suspended with an excess of exchange resin in hot water, all of the calcium sulfate will eventually dissolve (1). The main reactions that occur are as follows:



where HR = hydrogen-form cation exchange resin.

With a mixture of solids the overall reactions are as follows:



All of the calcium is replaced by hydrogen ions. Calcium oxide gives no net change of hydrogen ions in solution and calcium sulfide gives hydrogen sulfide which can be liberated by heating. The calcium sulfate equivalent remains as sulfuric acid. Other insoluble sulfates such as those of barium and strontium will behave similarly (2).

exchange column is a 65-ml. cylindrical separatory funnel with a stopcock drain.

Procedure. For analyses the ion exchange column is completely filled with moist hydrogen-form resin and the mixing chamber is partially filled with approximately 25 grams of resin. A 0.2- to 0.3-gm. sample of finely pulverized solids is stirred with the resin and 50 ml. of hot distilled water for 15 minutes in the mixing chamber. The hot solution is then drawn out of the mixing chamber through the ion exchange column by vacuum. Finally, the system is rinsed twice with additional hot water.

Most of the cations are replaced by hydrogen ions in the mixing chamber but the ones remaining are replaced in the ion exchange column. With this arrangement several samples can be analyzed before the resin needs to be replenished. To ensure an excess of resin at all times the mixing chamber is replenished with fresh resin after every five determinations and the ion ex-

EXPERIMENTAL

Apparatus. The apparatus consists of a mixing chamber, an ion exchange column, a 500-ml. vacuum flask, and a source of hot, 90° C. distilled water. The mixing chamber is a 75-ml. Buechner funnel with a coarse grain sintered glass bottom, and the ion

Table I. Comparison of Sulfate Determinations by the Present Method and the Gravimetric Method

| Other main components present | | SO ₃ , % | | | | | |
|-------------------------------|--------|---------------------|-------|-------|----------------|-------|-------|
| CaO, % | CaS, % | Gravimetric Method | | | Present Method | | |
| | | 1st | 2nd | Av. | 1st | 2nd | Av. |
| 74.0 | 5.6 | 6.00 | 5.95 | 5.97 | 5.74 | 6.16 | 5.95 |
| 69.1 | 10.4 | 4.50 | 4.82 | 4.66 | 4.89 | 4.46 | 4.67 |
| 56.8 | 13.7 | 11.03 | 10.79 | 10.91 | 10.79 | 10.42 | 10.61 |
| 62.9 | 11.9 | 9.79 | 9.70 | 9.75 | 10.60 | 10.72 | 10.66 |
| 60.2 | 11.7 | 9.57 | 9.80 | 9.68 | 9.56 | 7.63 | 8.59 |
| 45.9 | 35.1 | 5.01 | 4.91 | 4.96 | 5.12 | 4.79 | 4.95 |
| 38.8 | 36.9 | 8.44 | 8.48 | 8.46 | 8.56 | 8.73 | 8.64 |
| 34.4 | 43.5 | 7.87 | 7.96 | 7.91 | 8.26 | 8.50 | 8.38 |
| 28.4 | 49.5 | 7.63 | 7.70 | 7.66 | 7.77 | 7.60 | 7.68 |
| 25.9 | 52.8 | 6.43 | 7.46 | 6.94 | 6.44 | 6.67 | 6.55 |
| 22.3 | 54.9 | 6.33 | 5.93 | 6.13 | 7.14 | 7.08 | 7.11 |
| 29.6 | 49.7 | 7.87 | 7.67 | 7.77 | 7.88 | 7.87 | 7.87 |
| 33.4 | 47.3 | 6.42 | 6.24 | 6.33 | 6.71 | 6.43 | 6.57 |
| 31.3 | 50.9 | 5.26 | 5.13 | 5.19 | 5.48 | 5.21 | 5.34 |

change column is replenished after every ten determinations.

Most of the sulfide present in the sample is vaporized from the hot mixing chamber as hydrogen sulfide but positive removal of hydrogen sulfide is assured by heating the filtrate to boiling and then subjecting the solution to an aspirator-produced vacuum. The remaining solution is titrated with 0.1N sodium hydroxide to a pink end point using phenolphthalein indicator.

RESULTS AND DISCUSSION

When this method was adopted for routine analysis some of the pilot plant samples were analyzed by both the present method and the gravimetric method for comparison. The results for a series of fourteen samples are shown in Table I. The oxide and sulfide contents of these samples varied over a wide range while the sulfate content varied between 5 and 11% expressed as SO_3 . The mean sulfate content of all samples found by the present method was 7.40% as compared to 7.31% by the gravimetric method. An analysis of variance for each method showed the standard deviation between determinations within samples for the present

method to be 0.41% and for the gravimetric method to be 0.24%. The corresponding relative standard deviations were 5.5 and 3.2%.

If it is assumed that tests of significance are valid and applicable to this situation, it can be shown that there is no significant difference between the means found by the two analytical methods. However, the difference in the standard deviations is significant. The accuracy of the two methods appears to be the same but the present method does not have as great a precision.

For this series of samples the precision of either method was not great and this is probably due to the relative inexperience of the analyst who was a freshman college student with very little formal training in quantitative analysis. Possibly better results would have been obtained with methyl orange indicator since it would not have permitted any unvaporized sulfide to be titrated. Hence, it appears likely that better results can be obtained with the present method than are reported here.

Nonvolatile anions, where present, can interfere with the determination.

These would have to be determined separately and corrections applied for them. With the samples analyzed here, the chloride ion content required less than 0.1 ml. of sodium hydroxide, so no correction was made.

ACKNOWLEDGMENT

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FERTILIZER RAW MATERIALS

Use of Wet Process By-Product Gypsum in Fertilizer Manufacture

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By-product gypsum from the manufacture of wet process phosphoric acid was fused with phosphate rock. Products having phosphorus pentoxide contents greater than 90% were obtained from mixtures of three parts of dehydrated gypsum and one part of phosphate rock produced in a gas-fired laboratory fusion furnace. A 1-ton-per-day pilot plant fusion furnace produced products having from 10.1 to 13.6% total phosphorus pentoxide. Phosphorus pentoxide availability ranged from 88 to 93% based on solubility in 2% citric acid and 80 to 90% based on solubility in neutral ammonium citrate. This process provides a possible method for the utilization of wet process by-product gypsum in a granular, nonhygroscopic, nonacidic phosphate fertilizer.

PHOSPHATE ROCK can be fused with certain addition agents to produce available phosphorus pentoxide. The fused mass is generally quenched in a high velocity stream of water and the resulting products are usually granular, nonacidic, nonhygroscopic, and easily ground. No attention is given to the removal of fluorine and the phosphorus pentoxide is soluble in neutral ammonium citrate or 2% citric acid.

This type process has been studied using olivine as the addition agent in an electric furnace (5, 6, 9). Moulton (7) described a commercial plant using the olivine process and Davy (4) demonstrated its feasibility in a gas fired furnace. Bridger and Boylan (2) developed a process using langbeinite as

the addition agent and a gas-fired furnace. The authors (7) studied a process using mineral gypsum as an addition agent and produced an 0-10-0 fertilizer material in the laboratory. Stinson and Munna (8) produced a phosphate slag as a by-product of a process designed to recover sulfur dioxide from by-product gypsum obtained in the manufacture of phosphoric acid.

The present study was a direct attempt to produce a phosphate fertilizer from phosphate rock and by-product gypsum obtained from wet process phosphoric acid, without the addition of any other material. Such a process would have the advantage of a no-cost raw material at the site of supplies of the other raw material.

Raw Materials and Analysis

Phosphate rock (Davison Chemical Corp.) was used in these studies (Table I). Ground rock A was dried at 212° F. for 5 hours before using. The ground rock, as well as the unground, non-dried rock B, was used in the pilot plant.

The by-product gypsum (Davison Chemical Corp., Joplin, Mo.) was received wet and was dehydrated at 500° F. before use. A portion of the gypsum was reduced to the hemihydrate before agglomeration for use in the pilot plant. It was not ground in either case.

The mineral gypsum (U. S. Gypsum Corp., Fort Dodge, Iowa) was treated similarly as the by-product gypsum before use. The chemical and the Tyler Standard screen analyses of these raw materials are given in Table I.

The total phosphorus pentoxide was determined by the Association of Official Agricultural Chemists method and the available phosphorus pentoxide was determined by its solubility in 2% citric acid. The final determination of phosphorus pentoxide was done colorimetrically as described by Bridger, Boylan, and Markey (3).

Procedure

Laboratory fusions were made in Coors porcelain crucibles, in a small gas fired refractory furnace, as previously described (7). One of the bricks in the front was cut, so that a portion could be removed, for placement and removal of crucibles. A laboratory blast burner provided a maximum temperature of 2800° F.

Thirty-gram charges of various mixtures of phosphate rock A and dehydrated by-product gypsum were prepared, fused, and quenched. The charges were difficult to keep in the crucible during fusions, because of the vigorous boiling and foaming. A considerable amount of sulfur dioxide was given off, much more than was observed by the authors (7) when mineral gypsum was used, making it difficult to ascertain when fusion was complete. The residence time of the sample in the furnace was 8 minutes. The resulting melt was highly viscous and difficult to quench properly. The total phosphorus pentoxide and the citric acid-soluble phosphorus pentoxide contents are given in Table II. The phosphorus pentoxide availability is plotted against charge composition in Figure 1. For comparison, the availability of mineral gypsum fused phosphates is also plotted in Figure 1. The data indicate that the mineral gypsum is superior to by-product gypsum as an addition agent in the fusion process. However, the data show that high phosphorus pentoxide availability can be obtained using 25% of phosphate rock and 75% of dehydrated by-product gypsum.

The fact that mineral gypsum gives better results than by-product gypsum is probably due to the greater silicon dioxide content of the by-product gypsum. The addition of small quantities of silicon dioxide to mineral gypsum fusions produced results similar to those resulting from the use of by-product gypsum. This effect is probably due to two things: the dilution effect, in that less calcium sulfate is present per unit of addition agent and the decomposition effect of the silicon dioxide on calcium sulfate. This decomposition would result in higher melting points and poor fluxing action making it necessary to add larger quantities of addition agent to get sufficient attack on the apatite.

Table I. Raw Material Analysis

| Constituents | Sample, % Dry Basis ^a | | Gypsum | |
|-------------------------------|----------------------------------|---------|------------|------|
| | Phosphate Rock | Mineral | By-product | |
| Chemical Analysis | | | | |
| H ₂ O, combined | ... | 19.9 | 20.1 | |
| P ₂ O ₅ | 33.8 | 30.5 | 0.7 | |
| CaO | 47.8 | 45.7 | 32.1 | 32.1 |
| SO ₃ | ... | 44.8 | 33.8 | |
| SiO ₂ | 9.1 | 11.6 | 2.5 | 9.4 |
| R ₂ O ₃ | 2.4 | 2.5 | 0.4 | 0.3 |
| F | 4.6 | 3.4 | ... | ... |
| Screen Analysis | | | | |
| +3 | ... | 8.1 | ... | ... |
| -3 +8 | ... | 19.5 | 2.6 | ... |
| -8 +14 | ... | 34.1 | 19.4 | ... |
| -14 +28 | ... | 18.1 | 14.5 | 0.4 |
| -28 +48 | ... | 7.2 | 15.0 | 2.8 |
| -48 +100 | 10.6 | 6.8 | 18.5 | 17.0 |
| -100 +200 | 34.2 | 2.7 | 12.0 | 47.6 |
| -200 | 55.2 | 3.5 | 18.0 | 32.2 |

^a Phosphate rock dried for 5 hours at 212° F. Gypsum dried for 2 hours at 113° F.

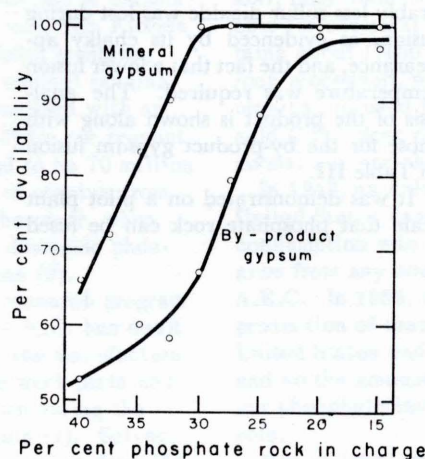


Figure 1. Effect of charge composition on P₂O₅ availability in fused gypsum phosphate

Pilot Plant

A pilot plant fusion furnace (Figure 2) was constructed to demonstrate this process on a larger scale. It consisted of a gas-fired horizontal shell provided with a feed preheater and a heat recuperator to preheat the combustion gases. Furnace temperatures were measured with an optical pyrometer and exhaust gas, primary air, and shell temperatures were measured with Chromel-Alumel thermocouples. The exhaust stack was provided with a steam ejector, so that the draft on the furnace could be regulated. The furnace was also provided with a high velocity water quench.

The furnace feed was composed of a mixture of phosphate rock, by-product gypsum as received, and by-product gypsum reduced to the hemihydrate. The mixture was agglomerated in a cement mixer and particles ranging from

Table II. Compositions of Products of Fusions Using Mixtures of Rock Phosphate and By-Product Gypsum

| Dehydrated Gypsum ^a , % | Temp., ° F. | Product Compn. % | | P ₂ O ₅ Availability, % |
|------------------------------------|-------------|-------------------------------------|---|---|
| | | Total P ₂ O ₅ | Available P ₂ O ₅ | |
| 60 | 2490 | 16.1 | 8.4 | 52 |
| | 2520 | 15.9 | 8.5 | 54 |
| 65 | 2415 | 13.5 | 8.4 | 62 |
| | 2445 | 13.7 | 8.0 | 58 |
| 67.5 | 2350 | 12.6 | 6.6 | 52 |
| | 2375 | 12.8 | 8.2 | 64 |
| 70 | 2385 | 12.2 | 8.5 | 70 |
| | 2405 | 12.1 | 8.0 | 66 |
| 72.5 | 2375 | 12.1 | 7.9 | 65 |
| | 2385 | 11.1 | 8.8 | 79 |
| 75 | 2365 | 9.0 | 8.3 | 92 |
| | 2400 | (lost) | | |
| 80 | 2390 | 10.7 | 9.0 | 84 |
| | 2425 | 8.5 | 8.3 | 98 |
| 85 | 2435 | 8.1 | 8.1 | 100 |
| | 2400 | 6.8 | 6.4 | 94 |
| | 2400 | 6.0 | 6.0 | 100 |

^a By-product from H₂PO₄ manufacture, (Davison Chemical Corp.) dried at 500° F. before fusion.

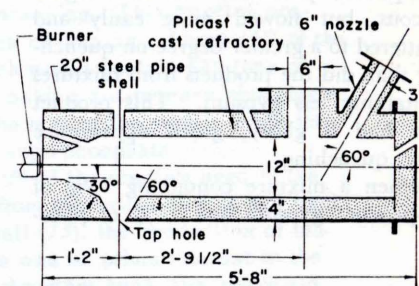


Figure 2. Pilot plant fusion furnace

0.5 to 2 inches were produced and used for furnace feed. These particles were very firm and required little drying because of rehydration of the hemihydrate. Molten product from the furnace was quenched and collected in the settling basin. Rates up to 75 pounds per hour were attained. Feed was added when needed. Product was tapped continuously.

The product was dried and analyzed for total and citric acid soluble phosphorus pentoxide.

Results

The results of fusions of by-product gypsum are presented in Table III. The feed compositions are given on an anhydrous basis, because the agglomeration mixture contained both the dihydrate and the hemihydrate of calcium sulfate. The mixture containing 67% by-product gypsum on an anhydrous basis did not give satisfactory availability. The melt was very viscous and it was necessary to rake it from the furnace. Because of its high viscosity it did not shatter on quenching, and consequently the actual cooling was not as rapid as desired. The product showed a high loss of sulfur dioxide

Table III. Analysis of Pilot Plant Products

| Feed Composition, % | | Product Composition, % | | | | | | | |
|---------------------|---------------------|------------------------|-----------------|------|------------------|-------------------------------|-------------------------------|---|--|
| Phosphate rock | Gypsum ^a | CaO | SO ₃ | F | SiO ₂ | R ₂ O ₃ | P ₂ O ₅ | Available P ₂ O ₅ | P ₂ O ₅ availability |
| 33 ^b | 67 ^c | 51.1 | 17.2 | 1.19 | 13.8 | 1.8 | 14.5 | 10.2 | 70 |
| 30 ^b | 70 ^c | 51.1 | 20.4 | 0.78 | 15.2 | 1.3 | 13.6 | 12.0 | 88 |
| 25 ^d | 75 ^e | 48.1 | 18.8 | 0.80 | 20.0 | 3.0 | 10.1 | 9.4 | 93 |
| 30 ^b | 70 ^c | 47.7 | 33.0 | 0.97 | 5.2 | 1.0 | 11.6 | 11.0 | 95 |

^a Anhydrous basis. ^b Phosphate rock A. ^c By-product gypsum. ^d Phosphate rock B. ^e Mineral gypsum.

during fusion and it appeared as a glassy, dark green slag. Approximately 47% of the sulfur present was lost as sulfur dioxide in the flue gas. It was not feasible to determine the sulfur dioxide content in the flue gas in this or subsequent runs.

The mixture containing 70% of by-product gypsum gave a product which was satisfactory. It had a phosphorus pentoxide availability of 88% and contained 12.0% of citric acid soluble phosphorus pentoxide. It was highly viscous, but flowed more easily and shattered to a greater degree on quenching than did the products from mixtures containing less gypsum. This product also had a glassy, green appearance after quenching.

When a mixture containing 75% of by-product gypsum and 25% of phos-

phate rock was used, the melt flowed easily from the furnace, shattered very well on quenching, and gave a granular product with a 93% phosphorus pentoxide availability. The availability based on solubility in neutral ammonium citrate varied from 80 to 90%.

Mineral gypsum, in the proportion found to be optimum in previous work, was used for control fusions (7). The product was chalky white, granular, and had a 2% citric acid-soluble phosphorus pentoxide content of 11.0%. Considerably less sulfur dioxide was lost during fusion, as evidenced by its chalky appearance, and the fact that a lower fusion temperature was required. The analysis of the product is shown along with those for the by-product gypsum fusion in Table III.

It was demonstrated on a pilot plant scale that phosphate rock can be fused

with by-product gypsum to give a product suitable as a fertilizer. The product has the advantage of nonacidity, is nonhygroscopic, and does not need to be ground after quenching. Inasmuch as wet process gypsum is an undesirable by-product, the fusion process provides a use as well as a method for its disposal.

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RECOVERY OF URANIUM IN THE MANUFACTURE OF WET-PROCESS PHOSPHORIC ACID

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and
George Burnet

A uranium balance was completed across each of two recently constructed wet-process phosphoric acid plants of different design. Seventy-five to eighty per cent of the uranium entering in the phosphate rock and other raw materials was found in a recoverable form in the product acid at both plants. Most of the remainder was accounted for in plant waste streams. Basic engineering design data were developed for recovery of the uranium from one of the plant acids through either solvent extraction or ion exchange.

It is generally recognized today that the uranium in phosphate rock cannot be recovered economically except as a by-product in the manufacture of certain commercial fertilizers. Phosphate rock from Florida and the phosphoria formations of Idaho, Montana, Utah, and Wyoming have a uranium content ranging from 0.01 to 0.02%. This is low compared with an average uranium content of 0.23% (7) for our present uranium ore reserves, now estimated to be 70 million tons (8). The long-range potential of uranium from phosphate rock becomes apparent, however, when the latter figure is compared to our domestic phosphate rock reserves of 13 billion tons (9).

Over a period of several years a research program at the Ames Laboratory of the U.S.A.E.C. has dealt with the recovery of uranium during the manufacture of commercial fertilizers. Previous work pertained principally to the recovery of uranium during the manufacture of normal superphosphate (1). Solvent extraction was used to recover the uranium from the solid acid-digested product, but serious difficulties were encountered in separating the extract from the solid phase; solvent losses were high and uranium recovery was correspondingly low.

In the manufacture of wet-process phosphoric acid, on the other hand, 70 to 80% of the uranium goes into solution in the product acid, from which it is readily recovered by solvent extraction or ion exchange. Hence recovery of uranium from phosphate rock is limited, principally by process considerations, to the manufacture of wet-process phosphoric acid, which is used in the manufacture of triple superphosphate or the ammonium phosphates.

AVAILABILITY

The total phosphate rock mined annually in the United States is about 13.5 million tons. If an average uranium content of 0.015% is assumed, this rep-

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resents approximately 2,000 tons of uranium. Because much of the rock is applied directly to the soil, only about 70% of the total rock mined is available for chemical processing. This fraction contains about 1,400 tons of uranium. About 45% of the rock processed, which would contain 630 tons of uranium, is used for making wet-process phosphoric acid (15). Most of the rest of the rock is made into normal and enriched superphosphate (11).

In 1948, as only 10% of the uranium used in the United States came from domestic sources and total consumption was small (13), the production of uranium from any source was of prime interest to the A.E.C. In 1959, on the other hand, the free-world production of uranium was 34,000 tons, with the United States and Canada producing 75% of this (8), and so the amount available as a by-product from our phosphate industry assumed a less important role.

For national security, however, the A.E.C. has maintained an interest in all significant domestic sources of uranium. Also the current trend in the fertilizer industry is toward production of high-analysis fertilizers, many of which require wet-process acid in their manufacture. To companies in this expanding field, uranium recovered from the acid represents a valuable by-product from an already existing industry and hence may justify continued interest on their part.

SOURCE OF DATA

Until recently (6, 10) information on the commercial recovery of uranium during the manufacture of wet-process acid was treated confidentially by those companies doing work in this field. Consequently, little has been known about what happens to the uranium entering in the rock other than the fact that a large portion of it is found in the product acid. It was the purpose of this investigation to complete a uranium balance across each of two recently constructed wet-process plants of different design.

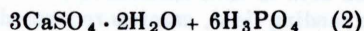
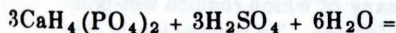
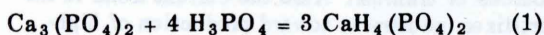
NADIG and BURNET

From the resulting data, it is possible to determine, among other things, whether acid-process variables affect uranium distribution and whether process streams other than the product acid are significant sources of economically recoverable uranium. The two plants visited were the Farmers Chemical Company plant in Joplin, Missouri, which was designed and erected by the Dorr-Oliver Company, and the Smith-Douglass plant at Streator, Illinois, which was designed by Singmaster and Breyer and uses the Belgian Prayon process. At present neither of these plants is recovering uranium.

At the plants every attempt was made to obtain representative samples. Flow rates were based on actual measurements when possible or were estimated from long-term production records where an accurate measurement could not be made. Over-all and internal material balances were made to help spot any readings that were out of line and required verification.

THE BASIC PROCESS

To appreciate the significance of the data to be presented, one must have at least a basic knowledge of the processes used in these plants. In each case, the fundamental chemistry is the same (2). Briefly, finely divided phosphate rock and a slight excess of sulfuric acid are reacted to produce a slurry of gypsum in phosphoric acid. The reaction actually takes place in two stages. The tricalcium phosphate (used to represent the various apatite minerals actually in the rock) is first converted into soluble monocalcium phosphate, which then reacts with sulfuric acid to form phosphoric acid and a gypsum precipitate:



The resulting slurry is fed to a continuous vacuum filter where the gypsum is separated from the approximately 32% P_2O_5 product acid. The principal waste streams produced are the gypsum, which is usually reslurried and pumped to a waste pond, and scrub water from some device used to scrub the corrosive fumes produced during the acid digestion of the rock.

URANIUM DISTRIBUTION

Figure 1 shows a greatly simplified flowsheet for the Joplin plant of the Farmers Chemical Company and the results of the uranium balance across it. The heavy lines are the main process flow streams. Digestion of the rock is carried out in a series of

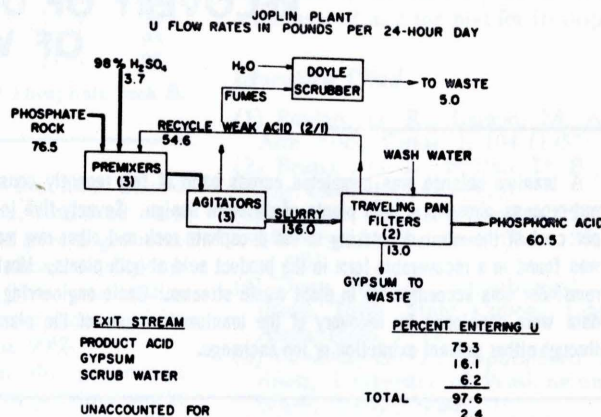


Fig. 1. Flowsheet and uranium balance for the Farmers Chemical Company plant.

premixers and agitators. The filtration is carried out with traveling pan filters. Weak acid (17% P_2O_5) from the first wash of the cake is recycled to the premixers. The cake is given a final wash with water prior to discharge, and the very weak acid thus produced becomes the wash solution for the first wash. The fumes from the digestion vessels are scrubbed with a patented wet impingement type of scrubber (3).

The uranium content of the various streams is shown on the flow sheet as pounds of uranium per 24-hr. day. Uranium was determined fluorimetrically (14). Because of the interference of phosphoric acid a standard addition technique was used. As was anticipated, most (75.3%) of the uranium entering was found in the product acid. The gypsum contained 16.1%, and the scrub water 6.2%. The balance came within 2.4% of closing, which testifies well to the accuracy of the flow measurements and the analyses for uranium. This conclusion was supported by a number of internal balances completed

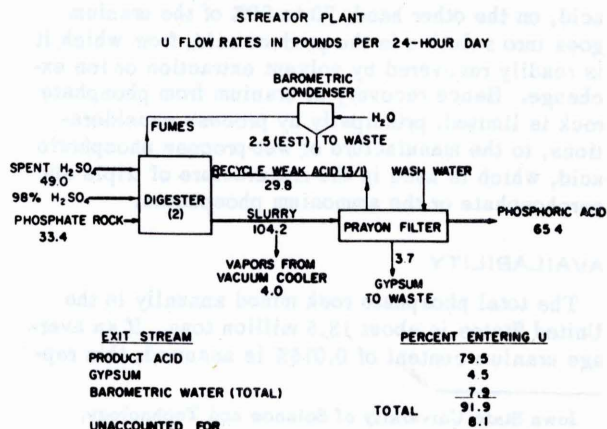


Fig. 2. Flowsheet and uranium balance for the Smith-Douglass plant.

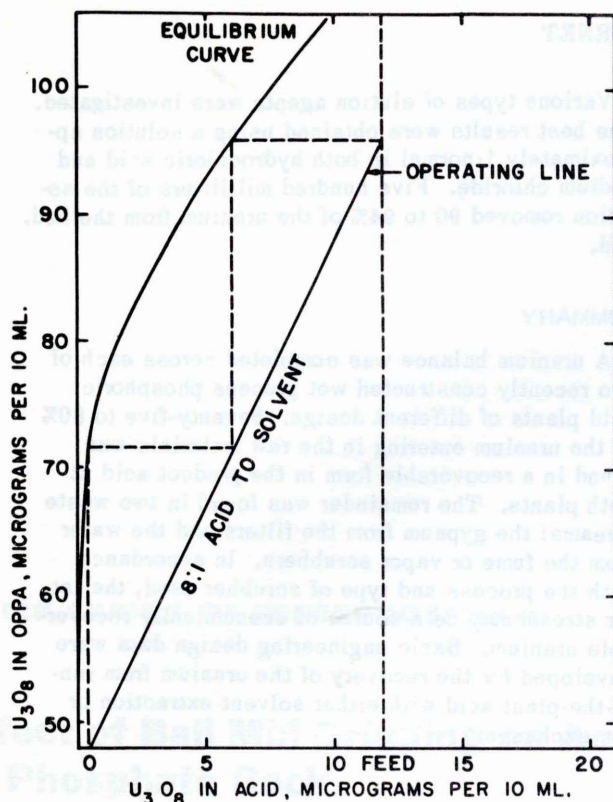


Fig. 3. Stage-by-stage extraction diagram with 5% octyl pyrophosphoric acid (OPPA) in kerosene as the solvent.

over sections of the process, such as the digestion section and filtration section.

Figure 2 shows a similar flowsheet for the Streator plant of the Smith-Douglass Company, Inc. The digestion is carried out in two tanks each divided into four compartments. The digestion slurry flows through the compartments in series. The first six act as a six-stage digester, and the last two as hold-up tanks used to assure a uniform flow to the filter. Fumes from the digesters and from a vacuum slurry cooler (not shown on the flowsheet but installed in the line to the filter) are scrubbed in a conventional barometric condenser.

The outstanding piece of equipment in this plant is the filter. The single unit used is a horizontal, rotary, tilting tray, vacuum filter, 28 ft. in diameter, with fifteen individual trays. On the filter the cake is given a two-stage countercurrent wash, and the weak acid (22% P_2O_5) thus produced is recycled to the digesters. The gypsum filter cake is reslurried and pumped to a waste pond.

The uranium balance data obtained were somewhat atypical. This is due principally to the fact that approximately one-fourth of the sulfuric acid required in the digestion is added as spent acid. The

acid is a waste stream from the acid digestion of monazite sand carried out in a thorium recovery process. The acid as received contains 0.027 to 0.030% uranium which greatly increases the amount of uranium present per ton of rock processed.

Again, as shown in Figure 2, a large percentage (79.5%) of the total uranium entering (in spent acid plus rock) was found in the product acid. The gypsum contained 4.5% and the water from the barometric condensers 7.9%. If the latter two percentages are based only on that uranium entering in the rock, they become 11.1% and 19.4%, respectively. This assumes all the uranium entering in the spent acid simply passes through the process and ends up in the product acid.

It should be noted that 8.1% of the uranium entering is unaccounted for. A similar figure resulted from two independent balances made by Smith-Douglass (12). Failure to complete a balance is probably due to errors in measuring the flow rate of one or more process streams. The errors are not thought to be large enough to affect the conclusions.

The uranium balance data for the two plants show that:

1. The product acid can be expected to contain 75 to 80% of the uranium entering with the raw materials.
2. The use of a vacuum cooler to reduce the slurry temperature between the digestion and filtration steps tends to increase the uranium lost in vapors and fumes. This is apparent when one compares the losses for the Streator plant, where a flash is used,

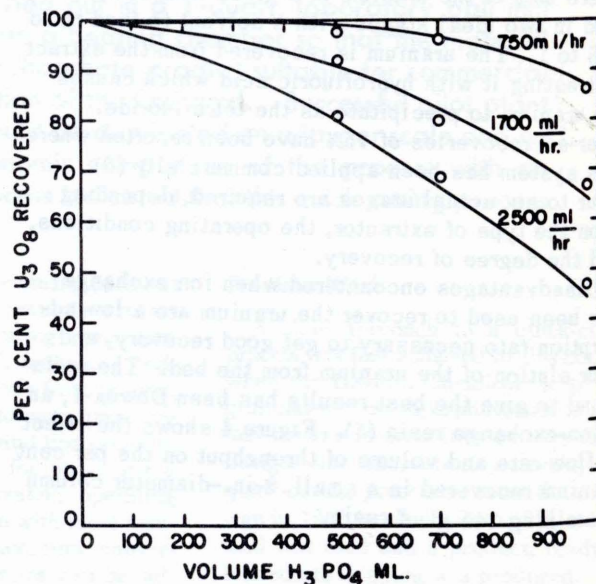


Fig. 4. Effect of flow rate and volume of throughput on uranium recovery with Dowex-1 in a laboratory column.

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with those for the Joplin plant where slurry cooling is not employed. Depending upon the volume of water used and whether or not it is recycled, uranium recovery from this waste stream may be justified.

3. The amount of uranium lost in the gypsum can vary significantly between plants but does not appear to be large enough to warrant recovery.

RECOVERY OF URANIUM FROM PRODUCT ACID

In order to ascertain the difficulty and degree of recovery from one of the run-of-the plant acids, solvent extraction and ion exchange were investigated with acid (30.2% P_2O_5) from the Joplin plant. The work was limited to that necessary to provide basic engineering design data.

A large number of extraction solvents for the recovery of uranium has been tried and the results reported in the literature (4). Low concentrations (3 to 5%) of the alkyl pyrophosphoric acids in a solvent, such as kerosene, have given the most favorable extraction coefficients when the uranium is in the tetravalent state. Figure 3 shows an equilibrium curve giving the distribution of U_3O_8 between the plant acid and an extraction solvent consisting of 5% octyl pyrophosphoric acid (OPPA) in kerosene.

From the equilibrium diagram the number of ideal stages required to recover a given percentage of uranium can be determined. Figure 3 shows an example where 95% of the uranium in a given feed is recovered in two ideal stages with a solvent-to-feed ratio of 8 to 1. The uranium is recovered from the extract by treating it with hydrofluoric acid which causes the uranium to precipitate as the tetrafluoride. Over-all recoveries of 75% have been reported where this system has been applied commercially (6). Four to six actual stages are required, depending upon the type of extractor, the operating conditions, and the degree of recovery.

Disadvantages encountered when ion exchange has been used to recover the uranium are a low adsorption rate necessary to get good recovery, and poor elution of the uranium from the bed. The resin found to give the best results has been Dowex-1, an anion-exchange resin (5). Figure 4 shows the effect of flow rate and volume of throughput on the per cent uranium recovered in a small, 2-in.-diameter column containing 145 g. of resin.

Various types of elution agents were investigated. The best results were obtained using a solution approximately 1-normal in both hydrochloric acid and sodium chloride. Five hundred milliliters of the solution removed 90 to 94% of the uranium from the bed.

SUMMARY

A uranium balance was completed across each of two recently constructed wet process phosphoric acid plants of different design. Seventy-five to 80% of the uranium entering in the raw materials was found in a recoverable form in the product acid at both plants. The remainder was found in two waste streams: the gypsum from the filters and the water from the fume or vapor scrubbers. In accordance with the process and type of scrubber used, the latter stream may be a source of economically recoverable uranium. Basic engineering design data were developed for the recovery of the uranium from run-of-the-plant acid with either solvent extraction or ion exchange.

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QUICK CURING OF SUPERPHOSPHATE

Effect of Ball Mill Grinding on Acidulation of Phosphate Rock

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An investigation was undertaken to determine the effect of grinding during the acidulation of phosphate rock. Bench-scale work was carried out in a 1-quart, laboratory ball mill made of stainless steel, which was equipped with a heating chamber so that the material could also be dried in the mill. A normal superphosphate product suitable for commercial use was obtained within an hour after the addition of the first acid. Successful pilot plant operation showed that the bench-scale results could be duplicated on a larger scale and on a continuous or semicontinuous basis. An economic comparison of the process with an equivalent standard normal superphosphate process indicated that this quick-curing process was competitive, if not favored.

IN THE USUAL MANUFACTURE of normal superphosphate, the required amounts of sulfuric acid and phosphate rock are mixed and allowed to "set up" in some kind of closure. The resulting porous solid is mechanically disintegrated and transferred to piles for curing while the chemical reactions are allowed to go to completion. During this curing period of from 4 to 6 weeks, the free acid and free moisture contents are reduced and the available phosphorus content is increased.

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Processes in which the curing period is reduced or eliminated entirely are referred to as quick-curing processes. Their advantages (3, 5) include: product can be shipped directly from process, thus reducing bulk storage space required and working capital tied up in inventory; opportunities for producing a granular product are greater; operating conditions can be chosen with more flexibility for attaining maximum conversion; and production rates can be adjusted to meet an almost instantaneous demand because the final product can be produced in a matter of hours.

Previous Work

A close approach to a quick-curing process was first achieved in this country when the Davison Chemical Corp. (19) granulated fresh superphosphate in a rotary drum and dried it in a rotary dryer. Bridger and Kapusta (5) developed a quick-curing process at Iowa State College in 1952 in which 50 to 65% sulfuric acid was used and a product, ready for immediate shipping was produced.

In 1953, a process was announced in Japan (15) in which the reaction between sulfuric acid and rock was promoted by

Table I. Screen Analysis of Florida Pebble Phosphate Rock

| Screen Mesh | Weight % of Sample |
|-------------|--------------------|
| + 65 | 7.1 |
| - 65 +100 | 15.1 |
| -100 +150 | 7.5 |
| -150 +200 | 27.2 |
| -200 | 43.1 |

passing an alternating electric current through the mixture for 2½ hours. An exceptionally high acidulation ratio was used to achieve the quick-curing effect.

In January 1957, the Tennessee Valley Authority announced a process (6) for a quick-curing normal superphosphate. In this process ultrafinely ground rock was acidulated with an excess of dilute acid. The acidulated material was subsequently dried.

Although the use of excess acid in the last two processes makes the economics somewhat questionable, the advantage of overacidulated material in ammoniated and mixed goods may justify the expense.

Process Variables

Several factors are known to affect the reaction between sulfuric acid and phosphate rock. Perhaps the most important is acid concentration. The initial reaction rate increases as more dilute acid is employed. Under the usual acidulation conditions, 70% sulfuric acid appears to give the best results (17). Use of higher acid concentrations results in poor mixing, while the calcium sulfate formed as a by-product tends to coat the particles (17). On the other hand, use of too dilute acid results in a product with a high moisture content and poor physical characteristics. The reaction is slow or incomplete because of resulting low temperature.

Acid temperature is also of some importance. Temperatures of 35° to 65° C.

Table II. Chemical Composition of Florida Pebble Phosphate Rock (7) (Dry Basis)

| Component | % |
|--------------------------------|------|
| CaO | 47.8 |
| MgO | 0.4 |
| F | 4.6 |
| P ₂ O ₅ | 33.4 |
| B.P.L. ^a | 72.8 |
| SO ₃ ^b | 0.2 |
| Fe ₂ O ₃ | 1.05 |
| Al ₂ O ₃ | 1.35 |
| SiO ₂ | 9.07 |
| Moisture | 0.51 |

^a Represents bone phosphate of lime or equivalent per cent of Ca₃(PO₄)₂.

^b Not determined.

are generally used (12). With lower acid temperature, the reaction is sluggish. With higher acid temperature, the mixture of acid and rock thickens too rapidly (18).

The particle size of the rock has a marked effect (8, 13, 17). Grinding before acidulation is beneficial; however, the effect of particle size is small in the size range of 20 to 95% through 100 mesh. Extremely fine grinding results in greatly increased rate of reaction (17).

The calcium sulfate formed during acidulation is thought to coat the rock particles and to prevent further reaction. Grinding during the acidulation should prevent such coating and provide a clean surface on the rock particles for the reaction to proceed. No evidence of this ever having been done appears in the literature, and the present work was undertaken to determine the effect of grinding during acidulation.

Laboratory Procedure

Materials and Methods. The phosphate rock used in these studies was Florida pebble obtained from the Davison Chemical Corp. plant at Perry, Iowa. Although the rock was transported and stored in covered 55-gallon

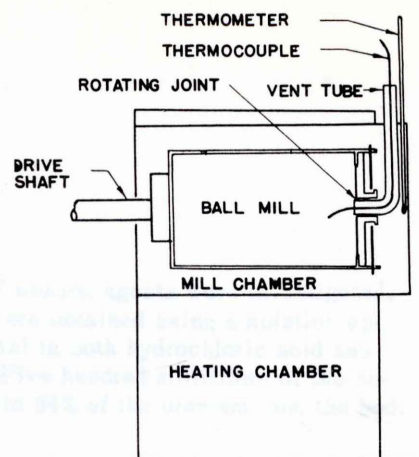


Figure 1. Cross section of ball mill and heating unit

steel drums, sufficient moisture was present or adsorbed to cause agglomeration. The rock was passed through a gyratory crusher and rolls to break up the lumps. Little, if any, actual grinding took place. Screen analyses are given in Table I.

Free moisture and free acid analyses of the product were carried out according to the procedure of the Association of Official Agricultural Chemists (2). The colorimetric procedure of Bridger, Boylan, and Markey (4) was used in the determination of phosphorus pentoxide. A typical chemical analysis of the rock used is given in Table II.

Bench-scale tests were made in a 1-quart, stainless steel, laboratory ball mill. The mill contained 4.5 pounds of 0.75-inch diameter stainless steel balls. A cover was used with a vent tube in a rotating joint to permit refluxing of the vapor or drying at atmospheric pressure. The ball mill was enclosed in a chamber which could be heated indirectly as shown in Figure 1. This heating shell was constructed of 18-gage galvanized iron and provision was made to measure

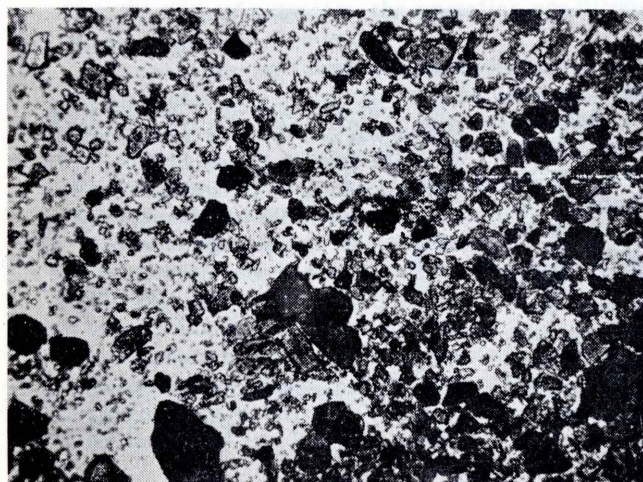


Figure 2. Photomicrograph of raw phosphate rock, 100X magnification



Figure 3. Photomicrograph of freshly acidulated phosphate rock, 100X magnification

the temperature of the gas within the mill chamber.

The mill was equipped with two condensers; a vertical condenser to reflux any escaping vapors when drying was not desired and an inclined condenser to condense the vapors coming from the mill during the drying operation. Measurement of the amount of condensate gave a good indication of the progress of drying.

In the test procedure, the desired quantities of 72% sulfuric acid and rock were first mixed in a beaker, the mixture was emptied into the mill, and the last traces of rock and acid were washed from the beaker into the mill with the required amount of dilution water.

After the mill was assembled, grinding was started, and the reflux condenser was attached. Heated grinding was accomplished by maintaining the mill chamber temperature between 110° and 115°C. Actual product temperature at this point was about 103°C., measured by means of a thermocouple inserted through the vent tube into the mill.

When grinding action with reflux had continued for the desired length of time, drying was started. The reflux condenser was removed, the inclined condenser connected and the heat input increased to maintain the required mill chamber temperature. As in earlier runs, a white crystalline precipitate formed in the condenser at a product-free moisture content of about 3 or 4%. This occurred after a drying time of 30 to 60 minutes. The precipitate formation was used as a criterion for stopping the drying operation in many of the runs.

At the end of the drying step, the product was removed from the mill and either immediately analyzed, diluted with water, or extracted with acid to stop the reaction.

Laboratory Results. Quick-cured normal superphosphate was made in the laboratory ball mill using batches of 50 to 100 grams of rock. The variables studied were grinding temperature, grinding time, drying temperature, acidulation ratio, and acid concentration. The results of these studies are given in Table III. The data indicate, in general, that there is little effect of acid concentration below 60% or of drying temperatures between 125° and 150° C., as determined by the appearance of the white precipitate in the condenser tube.

A microscopic examination of the rock before and after acidulation showed that the primary effect of acidulation is the production of a large amount of fines. Figures 2 and 3 are photomicrographs showing this. The sample of superphosphate for Figure 3 was taken after about 1 minute of mixing in a beaker and was washed to remove the soluble products. The fines shown do not contribute heavily to the total weight.

Table III. Results of Quick-Curing Normal Superphosphate in a Laboratory Ball Mill

| Run No. | Acidul. Ratio | Acid Conc., % | Prelim. Grind | Drying Temp., °C. | Product Analysis, % | | | | | |
|---------|---------------|---------------|---------------|-------------------|-------------------------------------|------------------------------------|--------------------------------------|-------|-------------|-----------|
| | | | | | Total P ₂ O ₅ | C.I. P ₂ O ₅ | Avail. P ₂ O ₅ | Conv. | Free moist. | Free acid |
| 54-6 | 1.45 | 39.1 | Hot | 125 | 22.0 | 4.2 | 17.9 | 81.0 | 2.43 | ... |
| 61 | 1.80 | 39.1 | Cold | 150 | 20.3 | 0.9 | 19.3 | 95.4 | 2.97 | 1.80 |
| 62 | 1.80 | 39.1 | Cold | 125 | 19.8 | 0.6 | 19.1 | 97.0 | 4.55 | 1.53 |
| 63 | 1.80 | 39.1 | Cold | 125 | 20.4 | 0.8 | 19.6 | 96.0 | 3.39 | 1.91 |
| 64 | 1.80 | 39.1 | Cold | 150 | 21.5 | 1.3 | 20.1 | 94.5 | 3.61 | 2.71 |
| 65 | 1.80 | 39.1 | Cold | 125 | 21.2 | 1.0 | 20.2 | 95.5 | 3.25 | 1.14 |
| 69 | 1.80 | 39.1 | Cold | 135 | 20.3 | 0.8 | 19.5 | 95.9 | 3.78 | 0.87 |
| 70 | 1.80 | 39.1 | Hot | 135 | 20.6 | 0.8 | 19.8 | 96.1 | 3.98 | 0.60 |
| 71 | 1.80 | 39.1 | Hot | 125 | 20.9 | 0.7 | 20.2 | 96.6 | 4.66 | 2.34 |
| 72 | 1.80 | 44.6 | Cold | 125 | 21.8 | 0.7 | 21.1 | 96.9 | 2.60 | 3.42 |
| 73 | 1.80 | 39.1 | Hot | 125 | 21.6 | 1.1 | 20.5 | 94.9 | 4.90 | 0.74 |
| 74 | 1.58 | 37.4 | Hot | 125 | 22.1 | 2.6 | 19.5 | 88.1 | 2.66 | 2.08 |
| 75 | 1.80 | 39.1 | Hot | 150 | 20.3 | 1.0 | 19.3 | 95.0 | 3.53 | 2.36 |
| 76 | 1.80 | 39.1 | Hot | 125 | 20.7 | 0.6 | 20.1 | 97.1 | 3.43 | 0.56 |
| 77 | 1.80 | 55.5 | Cold | 125 | 22.5 | 1.2 | 21.3 | 94.6 | 3.46 | 1.81 |
| 78 | 1.80 | 72.2 | Cold | 125 | 22.6 | 4.3 | 18.3 | 80.9 | 2.56 | 2.62 |
| 79 | 1.80 | 39.1 | Hot | 135 | 20.7 | 0.8 | 19.9 | 96.0 | 2.78 | 2.55 |
| 80-I | 1.80 | 39.1 | Hot | 150 | 20.8 | 0.7 | 20.1 | 96.6 | 3.07 | 1.88 |
| 81 | 1.80 | 39.1 | Cold | 135 | 20.7 | 1.0 | 19.7 | 95.2 | 3.40 | 1.21 |
| 82 | 1.58 | 37.4 | Hot | 125 | 21.6 | 2.1 | 19.5 | 90.3 | 3.17 | 0.13 |
| 87 | 1.80 | 39.1 | Cold | 165 | 20.4 | 0.6 | 19.8 | 97.1 | 3.46 | 0.94 |
| 89 | 1.80 | 55.5 | None | 125 | 20.3 | 0.5 | 19.8 | 97.5 | 5.81 | 1.79 |
| 90 | 1.80 | 39.1 | Cold | 135 | 21.7 | 0.9 | 20.8 | 95.8 | 2.73 | 2.51 |
| 91 | 1.80 | 55.5 | None | 135 | 25.5 | 1.5 | 24.0 | 94.2 | 4.06 | 3.24 |
| 92-I | 1.80 | 39.1 | a | b | 14.2 | 3.6 | 10.6 | 74.6 | ... | 9.05 |
| 92-II | 1.80 | 39.1 | c | 135 | 21.0 | 1.1 | 19.9 | 94.7 | 2.58 | 3.04 |
| 93 | 1.80 | 39.1 | Cold | 185 | 20.6 | 0.5 | 20.1 | 97.6 | 4.69 | 1.67 |
| 94 | 1.80 | 61.1 | Cold | 125 | 21.7 | 1.1 | 20.7 | 95.2 | 3.28 | 2.54 |
| 96-II | 1.80 | 39.1 | Cold | 125 | 21.4 | 0.7 | 20.7 | 96.7 | 3.18 | 1.50 |
| 97 | 1.80 | 39.1 | Cold | 200 | 19.9 | 0.6 | 19.3 | 97.0 | 4.32 | 2.14 |
| 104 | 1.80 | 39.1 | Cold | 125 | 20.4 | 0.5 | 19.9 | 97.5 | 3.31 | 1.54 |
| 115 | 1.80 | 39.1 | 45 min. | b | 13.9 | 1.2 | 12.7 | 86.3 | ... | ... |
| 120 | 1.80 | 55.5 | None | 135 | 21.0 | 0.6 | 20.4 | 97.2 | 1.94 | 1.59 |
| 121-I | 1.80 | 39.1 | 15 min. | b | 13.4 | 2.8 | 11.6 | 86.5 | ... | ... |
| 121-II | 1.80 | 39.1 | 30 min. | b | 19.2 | 2.6 | 16.6 | 86.5 | ... | ... |
| 121-III | 1.80 | 39.1 | 60 min. | b | 13.9 | 2.0 | 11.9 | 85.6 | ... | ... |
| 122-I | 1.80 | 39.1 | None | b | 18.8 | 7.8 | 11.0 | 58.5 | ... | ... |
| 122-II | 1.80 | 39.1 | 5 min. | b | 13.0 | 2.0 | 11.0 | 84.6 | ... | ... |
| 132-4 | 1.80 | 72.0 | Cold | 125 | 20.7 | 1.8 | 19.0 | 91.6 | 1.85 | ... |
| 150 | 1.02 | 50.0 | Cold | 125 | 25.2 | 10.7 | 14.5 | 57.5 | 2.63 | 1.32 |

a Material mixed in Mixmaster rather than mill.

b Analysis of wet material ground cold, no drying used.

c Material from 92-I placed in mill for drying.

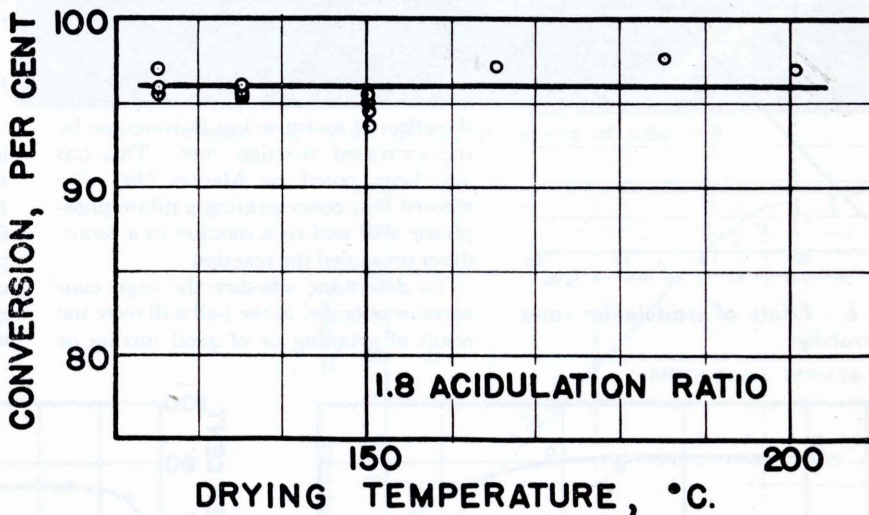


Figure 4. Effect of drying temperature on conversion preground at 30° C.

The effect of mill chamber drying temperature on the conversion of normal superphosphate is shown in Figures 4 and 5. Acidulated samples were preground either hot or cold for 45 minutes before

starting the drying operation. According to these data, the mill drying temperature had little or no effect on the final conversion of the product, and there was no significant difference between pre-

grinding the sample with or without heating.

Actual measurements of the product temperature were made when a mill chamber drying temperature of 185° C. was used. Although the product temperature measurements were made about 5 minutes after the free moisture had dropped to 3%, as indicated by the precipitate formation in the condenser, the product temperature was still below 147° C. After 5 more minutes, the product temperature increased another 10° C. This indicated that conditions approximating constant rate drying existed as long as the free moisture content of the product was above 3%.

Drying proceeded rapidly in the ball mill even at temperatures as low as 125° C. in the mill chamber. Recently, Hatch and Regen (10) investigated drying under similar conditions with equally rapid drying rates.

No consistent correlation between final free acid and free moisture content was indicated and little variation was found in their actual values. Free moisture content varied between 2.5 and 4.9% while the free acid content ranged from 0.5 to 3.5%. These values compare favorably with common commercial superphosphate (20).

Decrease in the acidulation ratio below the recommended 1.8 caused a rapid drop in the conversion of the product as shown in Figure 6. This same effect was reported by Bridger and Kapusta (5).

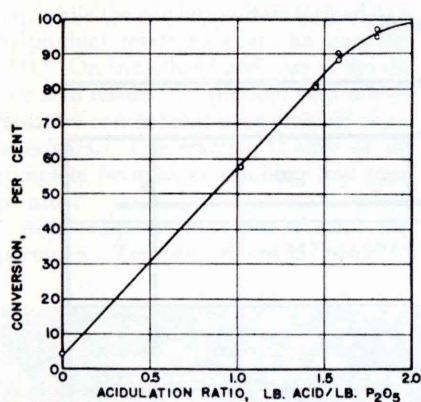


Figure 6. Effect of acidulation ratio on conversion

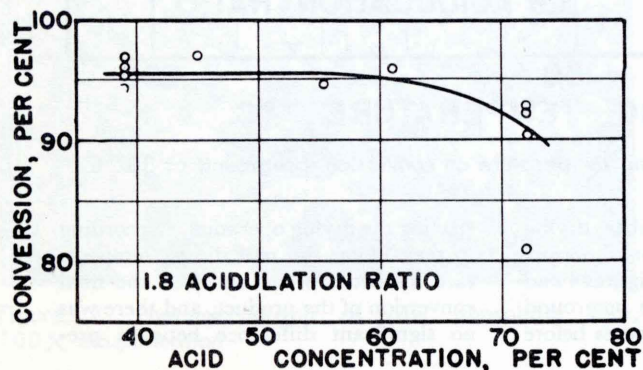


Figure 7. Effect of acid/LB. concentration on conversion

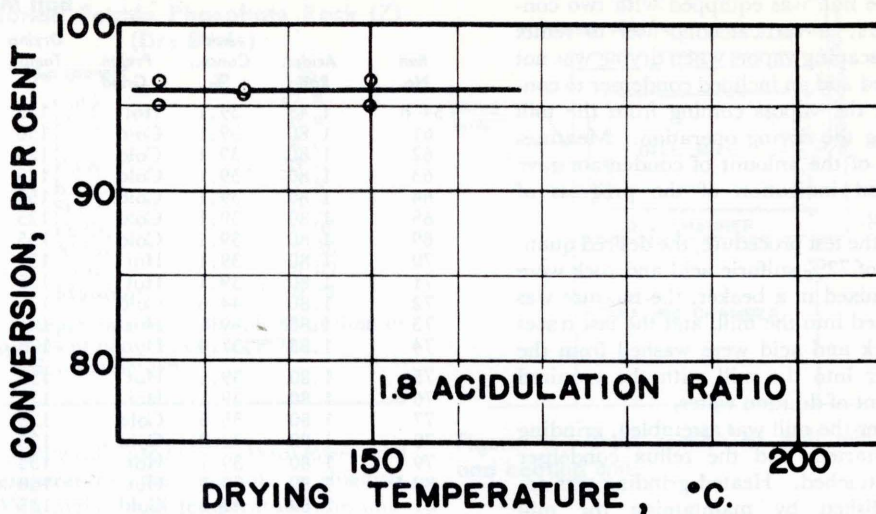


Figure 5. Effect of drying temperature on conversion, preground at 103° C.

Figure 7 shows that the effect of acid concentration used in the acidulation was small as long as the acid strength was below 60%. Above this concentration conversion dropped off rapidly. The data of Bridger and Kapusta for Roto-Louvre quick curing show the same effect, indicating that the initial free moisture content is significant. At these high acid concentrations, the balls did not move freely in the mixture.

The results of runs 89, 91, and 120 in Table III indicate that high conversion (about 95%) could be obtained if the drying were started immediately, without preliminary grinding. To check this, samples were taken "wet" from the mill during the grinding period and analyzed. Figure 8 shows the effect of grinding time on the availability, which indicates that long grinding is unnecessary. However, conversions higher than 86% were not obtained.

The drying step does, therefore, seem to increase the conversion. Apparently the effect of moisture loss is overcome by the increased reaction rate. This has also been noted by Meyers (14) who showed that concentrating a dilute phosphoric acid and rock mixture in a rotary dryer promoted the reaction.

To determine whether the high conversions obtained in the ball mill were the result of grinding or of good mixing or

drying technique, acidulations were made using a Sunbeam Mixmaster Model 9 and the laboratory ball mill as a control. Analyses were made immediately after 10 minutes mixing, after 45 minutes in the Mixmaster and after 45 minutes in the ball mill. The results are given in Table IV. The ball mill is superior. Furthermore, this represents an improvement in conversion over the laboratory ball mill data of Bridger and Kapusta (5) in which the basis was drying technique alone.

The results of the bench-scale work showed that a quick-curing process was possible using a laboratory ball mill. To demonstrate the process on a larger scale, a pilot plant for producing 50 to 100 pounds per hour was constructed. The pilot plant was expected to assist in solving the related problems in materials handling, grinding, and heat transfer.

Pilot Plant Work

A flow sheet for the pilot plant is given in Figure 9. The pilot plant was essentially a heated tube mill, lined with 16-gage stainless steel, with provision for feeding acid and rock and removing product continuously. Flint balls were used. The acid was introduced into the mill from a rotameter; the rock was fed with a vibrating feeder. The acid and

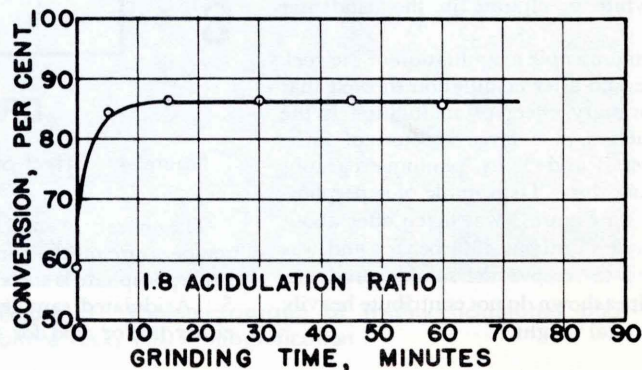


Figure 8. Effect of grinding time in ball mill on conversion

Table IV. Comparison of Conversion with and without Grinding

| Run | Sample | Free Acid, % | Conv., % |
|------|--------------------------------|--------------|----------|
| 84-I | Freshly mixed rock (10 min.) | ... | 65.0 |
| 92-I | 45 minutes in Mixer-master | 9.05 | 74.6 |
| 76-I | 45 minutes in ball mill (cold) | 7.60 | 82.5 |

rock were mixed, ground, and dried in the mill where the action of the balls and the addition of heat promoted the reaction. The product was discharged from the opposite end of the mill in a powdered or granular form.

The mill was heated indirectly, a portion of the hot air being recycled. Exhaust vapors from the mill, containing various gases produced by side reactions, were removed at the feed end of the mill, scrubbed to remove the fluorides, and separated in a cyclone to remove water droplets. The scrubbed gas was discharged from the building (Figure 10).

The acid used in the pilot plant was diluted and cooled in batches of about 35 pounds to a concentration of 50%. The rock used was the same as that used in the laboratory work. The diluted, cooled acid was then pumped to a storage tank where it was fed into the mill by gravity.

Although the rock feeder was calibrated, its calibration changed with the humidity of the air. This change in calibration affected the acidulation ratio. To evaluate the acidulation ratio properly, an analysis for sulfate was made on the product. As the only significant source of sulfate was the sulfuric acid and the rock was the only source of phosphate, the initial acidulation ratio could be evaluated.

Pilot Plant Results. Because the first four runs with the pilot plant were made for the purpose of evaluating operating technique and eliminating mechanical trouble, little data were collected for these runs. The data for the preliminary and steady-state runs are given in Table V.

The conversion of all samples taken during operation of the pilot plant is plotted in Figure 11 as a function of the acidulation ratio. The solid line represents the data from the bench-scale work taken from Figure 6. The data of Figure 11 clearly show that the results from the pilot plant are equivalent to those of the bench-scale ball mill.

The most important aspect of the pilot plant work, not shown in the data, was that the normal superphosphate could be handled adequately on a continuous basis.

At a product moisture content of approximately 5%, a granular product was obtained. At lower moisture content, the product was fine powder.

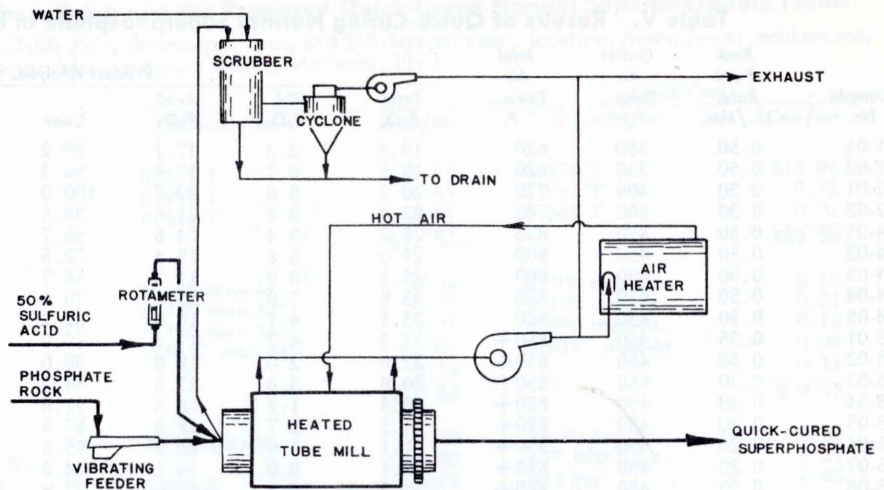


Figure 9. Flow sheet of a quick-curing pilot plant for normal superphosphate

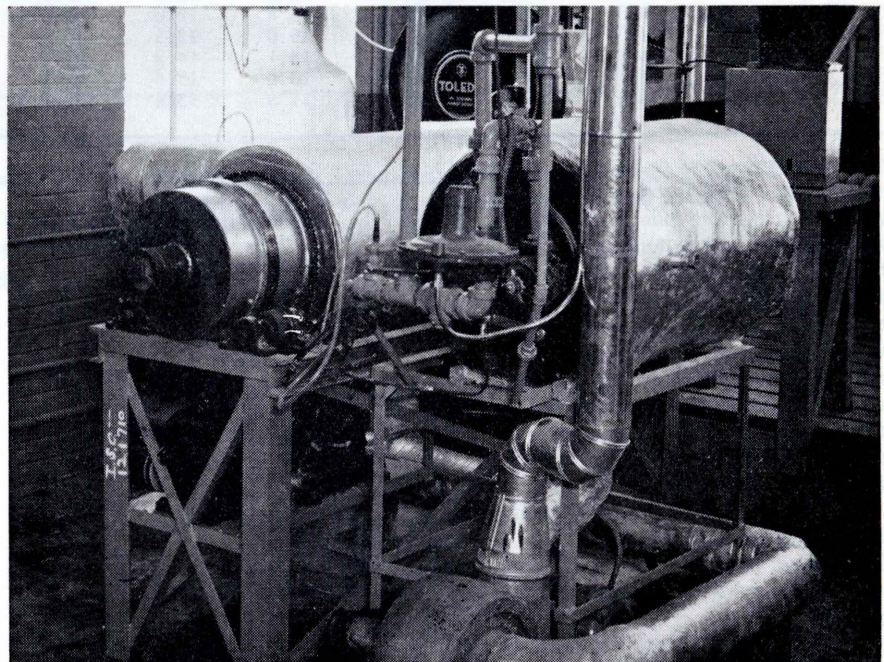


Figure 10. View of discharge end of tube mill

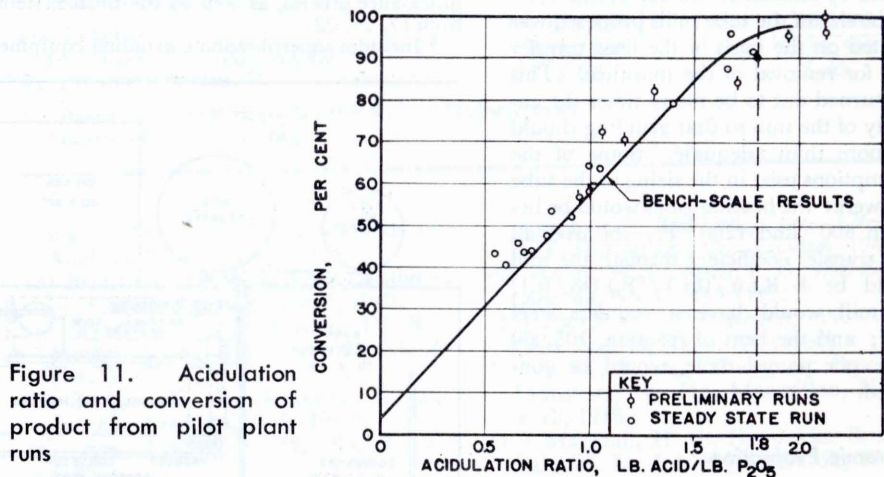


Figure 11. Acidulation ratio and conversion of product from pilot plant runs

Evaluation of the Process

Proposed Process. A proposed layout for a 480-ton-per-day, quick-cured,

normal superphosphate plant is shown in Figure 12. In the proposed layout, the rock and acid would be brought in by

Table V. Results of Quick-Curing Normal Superphosphate in Pilot Plant Tube Mill

| Sample No. | Rock Feed Rate, Lb./Min. | Outlet Air Temp., ° F. | Inlet Air Temp., ° F. | Product Analysis, % | | | | | | | |
|------------|--------------------------|------------------------|-----------------------|-------------------------------------|------------------------------------|--------------------------------------|-------|-------|-----------|-----------------|---------------|
| | | | | Total P ₂ O ₅ | C.I. P ₂ O ₅ | Avail. P ₂ O ₅ | Conv. | Moist | Free acid | SO ₃ | Acidul. Ratio |
| 1-01 | 0.50 | 350 | 620 | 19.4 | 2.3 | 17.1 | 88.2 | 11.0 | 5.0 | 27.6 | 1.71 |
| 1-02 | 0.50 | 350 | 620 | 18.5 | 0.7 | 17.8 | 96.2 | 8.2 | 8.5 | 32.6 | 2.13 |
| 2-01 | 0.30 | 400 | 770 | 20.7 | 0.0 | 20.7 | 100.0 | 1.66 | ... | 36.1 | 2.13 |
| 2-02 | 0.30 | 400 | 768 | 22.4 | 0.8 | 21.6 | 96.5 | 0.37 | 2.46 | 38.1 | 1.95 |
| 4-01 | 0.50 | 450 | 825 | 25.2 | 10.4 | 14.8 | 58.7 | 2.72 | 1.76 | 21.3 | 1.00 |
| 4-02 | 0.50 | 450 | 800 | 24.0 | 6.6 | 17.4 | 72.5 | 3.74 | 1.07 | 23.3 | 1.06 |
| 4-03 | 0.50 | 450 | 800 | 25.1 | 10.9 | 14.2 | 56.7 | 2.94 | 1.20 | 20.2 | 0.95 |
| 4-04 | 0.50 | 450 | 800 | 23.8 | 7.0 | 16.8 | 70.6 | 3.60 | 0.91 | 23.2 | 1.17 |
| 4-05 | 0.50 | 450 | 800 | 23.1 | 4.1 | 19.0 | 82.2 | 4.09 | 1.13 | 25.1 | 1.31 |
| 5-01 | 0.35 | 450 | 850+ | 22.3 | 4.7 | 17.6 | 79.0 | 4.03 | 2.07 | 26.0 | 1.41 |
| 5-02 | 0.30 | 450 | 850+ | 22.0 | 2.0 | 18.0 | 90.0 | 4.78 | 2.25 | 29.9 | 1.80 |
| 5-03 | 0.30 | 450 | 850+ | 20.8 | 3.3 | 17.5 | 84.2 | 3.70 | 3.43 | 29.4 | 1.71 |
| 5-04 | 0.30 | 450 | 850+ | 20.3 | 1.7 | 18.6 | 91.6 | 4.76 | 2.02 | 29.8 | 1.78 |
| 5-05 | 0.20 | 450 | 850+ | 21.5 | 2.7 | 18.8 | 87.5 | 3.86 | 3.31 | 29.5 | 1.66 |
| 5-06 | 0.20 | 450 | 850+ | 21.1 | 0.9 | 20.2 | 95.8 | 6.98 | 1.89 | 29.2 | 1.67 |
| 5-07 | 0.20 | 450 | 850+ | 25.1 | 9.0 | 16.1 | 64.2 | 3.79 | 0.47 | 21.0 | 1.00 |
| 5-08 | 0.20 | 450 | 850+ | 27.2 | 14.2 | 13.0 | 47.8 | 2.67 | 0.76 | 18.3 | 0.80 |
| 5-09 | 0.20 | 450 | 850+ | 27.0 | 15.1 | 11.9 | 48.0 | 2.66 | 0.36 | 16.0 | 0.70 |
| 5-10 | 0.20 | 450 | 850+ | 27.7 | 16.5 | 11.2 | 40.5 | 2.42 | 0.28 | 14.2 | 0.60 |
| 5-11 | 0.20 | 450 | 850+ | 26.8 | 15.2 | 11.6 | 43.3 | 1.88 | 0.25 | 12.7 | 0.55 |
| 5-12 | 0.20 | 450 | 850+ | 25.3 | 9.2 | 16.1 | 63.6 | 2.13 | 0.32 | 22.2 | 1.05 |
| 5-13 | 0.20 | 450 | 850+ | 28.9 | 16.3 | 12.6 | 43.6 | 1.41 | 0.06 | 16.8 | 0.69 |
| 5-14 | 0.20 | 450 | 950+ | 27.4 | 15.4 | 12.0 | 43.8 | 1.76 | 0.00 | 16.8 | 0.72 |
| 5-15 | 0.20 | 450 | 850+ | 27.5 | 15.0 | 12.5 | 45.5 | 0.62 | 0.00 | 15.4 | 0.66 |
| 5-16 | 0.20 | 450 | 850+ | 27.3 | 13.1 | 14.2 | 52.0 | 0.46 | 0.00 | 21.0 | 0.92 |
| 5-17 | 0.20 | 450 | 850+ | 26.4 | 10.8 | 15.6 | 59.1 | 2.07 | 0.50 | 22.5 | 1.02 |
| 5-18 | 0.20 | 450 | 850+ | 25.2 | 11.8 | 13.4 | 53.2 | 5.80 | 0.26 | 17.4 | 0.82 |

railroad cars. The rock would be conveyed to a storage pile of 2 weeks' capacity and the acid pumped to a tank holding 10 days' supply. The rock would be moved by conveyor from the storage pile to overhead hoppers which would discharge into each of the five tube mills. The acid and water for dilution would be pumped to the mills and automatically metered in proportion to the rock. As a ball or tube mill is capable of handling the grinding of phosphate rock (76, 78), no preliminary rock grinding equipment has been proposed.

The product from the mills would be moved by belt conveyor to storage or bagging.

An exhaust system for the mills would also be provided with a scrubber to remove the fluorides. The mills would be heated by oil burners for each unit.

The size of the tube mills proposed was selected on the basis of the heat transfer area for removal of the moisture. This size turned out to be many times the capacity of the mill so that grinding should be more than adequate. Some of the assumptions used in the sizing of the tube mill were: the heating gases would be between 600° and 1200° F.; the over-all heat transfer coefficient through the mill would be 8 B.t.u./(hr.) (°F.) (sq. ft.); the mill would have a stainless steel liner; and the heat of reaction, 105,000 B.t.u. per pound mole, would be conserved.

Economic Evaluation

An estimate of the total fixed capital cost for a conventional normal superphosphate plant and for the proposed

Table VI. Fixed Capital Cost Estimates for a Batch and the Proposed Quick-Curing Superphosphate Plants

(Basis: product, normal superphosphate, 20% available P₂O₅; capacity, 120,000 short tons per year; location, Ames, Iowa; and period, December 1956 costs)

| Item | Installed Cost, Dollars ^a | |
|---|--------------------------------------|-------------|
| | Batch | Quick-cure |
| Land and railroad siding | 18,500 | 18,500 |
| Process building | 91,500 | 87,900 |
| Materials handling and storage facilities | 400,000 | 233,100 |
| Major grinding equipment | 60,000 | 243,700 |
| Acid mixing and dilution equipment dens | 65,000 | ... |
| Heating equipment | ... | 15,100 |
| Instrumentation and controls | ... | 20,500 |
| Bagging equipment | 50,000 ^b | 50,000 |
| Contingencies, 20% | 137,000 | 133,800 |
| Total installed equipment | \$ 822,000 | \$ 802,600 |
| Insurance and taxes, 2% | 16,400 | 16,100 |
| Contractor profit, 10% | 83,800 | 81,900 |
| Construction overhead, 15% | 138,300 | 135,100 |
| Total fixed capital investment | \$1,060,500 | \$1,035,700 |

^a Equipment costs for the batch process are taken from (9). Comparable costs for the quick-cure process, as well as the burden items for both processes, have been estimated from (7, 27, 22).

^b Includes superphosphate grinding equipment.

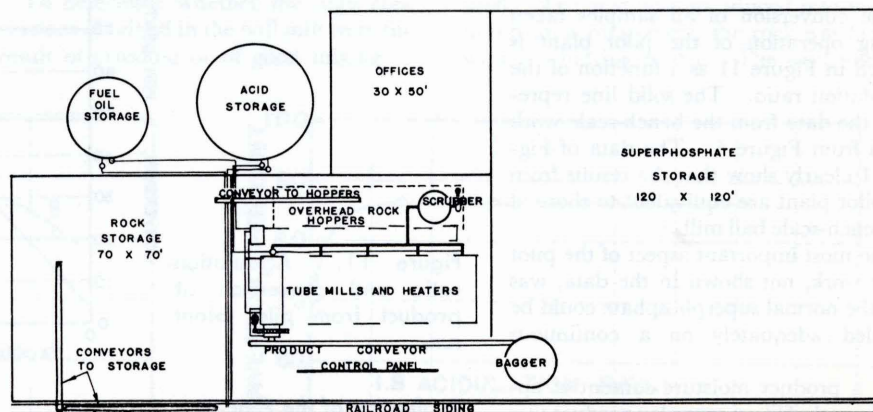


Figure 12. General layout of proposed siding quick-cured superphosphate plant

Table VII. Production Cost Estimates for a Batch and the Proposed Quick-Cured Normal Superphosphate Plants(Basis: 1 ton of normal superphosphate, 20% available P₂O₅, 20 tons per hour, and 250 days per year; location, Ames, Iowa; acid source, St. Louis, Mo.; and rock source, Mulberry, Fla.)

| Item | Unit Cost | Batch | | Quick-Cure | |
|-----------------------|--------------------------|----------------|----------|----------------|----------|
| | | Quantity/ton | Cost/ton | Quantity/ton | Cost/ton |
| Raw materials | | | | | |
| Acid | \$35.15/T | 0.371 T | \$13.04 | 0.371 T | \$13.04 |
| Rock | 15.0904/T | 0.594 T | 9.45 | 0.594 T | 9.45 |
| Water | 0.04/T | 0.341 T | 0.01 | 0.341 T | 0.01 |
| | | | \$22.50 | | \$22.50 |
| Labor | | | | | |
| Unskilled | 1.60/hr. | 0.150 man-hr. | 0.24 | 0.100 man-hr. | 0.16 |
| Semiskilled | 2.10/hr. | 0.150 man-hr. | 0.32 | 0.100 man-hr. | 0.21 |
| Skilled | 2.50/hr. | 0.100 man-hr. | 0.25 | 0.050 man-hr. | 0.12 |
| Supervision | 3.00/hr. | 0.0167 man-hr. | 0.05 | 0.0167 man-hr. | 0.05 |
| Reserve | 20% of above | | 0.16 | | 0.11 |
| | | | \$ 1.02 | | \$ 0.65 |
| Services | | | | | |
| Power | 0.02/kw.-hr. | 20.83 kw.-hr. | 0.42 | 16.67 kw.-hr. | 0.33 |
| Heat | 0.000467/100 B.t.u. | | 0.00 | 577,000 B.t.u. | 0.27 |
| Water | 0.03/1000 gal. | 208 gal. | 0.01 | 833 gal. | 0.03 |
| Maintenance | | | | | |
| Including labor | 20%/yr. of fixed capital | | 0.44 | | 0.43 |
| Packaging | 0.15/bag | | 3.60 | | 3.60 |
| Indirect costs | | | | | |
| Depreciation | 10%/yr. of fixed capital | | 0.88 | | 0.86 |
| Taxes and insurance | 3%/yr. of fixed capital | | 0.27 | | 0.26 |
| Overhead | 50% of labor | | 0.51 | | 0.33 |
| Total production cost | | | \$29.65 | | \$29.26 |

quick-curing plant is presented in Table VI. Although the total cost for the two processes are about the same, individual items in the cost estimate vary greatly. As the batch normal superphosphate plant requires storage facilities for curing for 30 days, the handling and storage equipment for the plant is the biggest item. For the quick-curing process the grinding equipment, which includes the stainless steel-lined tube mills, is the biggest item. Although \$50,000 is listed for both processes for bagging equipment, the author who compiled the costs for the batch process (9) included superphosphate grinding equipment in this figure.

The manufacturing costs for the two processes are compiled in Table VII. Because the proposed quick-curing process is well adapted to automatic control, considerable saving in labor is affected. Part of the saving, however, is cancelled by the cost of heat in the quick-curing process.

The working capital, net profit, and return on investment are compared in Table VIII for the batch and quick-curing plant. The principal advantage for the quick-curing process is the reduction of working capital. The batch process requires curing of the product for 30 days with a resulting large inventory; the quick-curing process requires no curing.

According to these estimates, the quick-curing process may be economically favorable in comparison with the normal superphosphate process.

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Table VIII. Comparison of Estimated Return on Investment for a Batch and the Proposed Quick-Cured Superphosphate Plants(Basis: product, normal superphosphate and 20% available P₂O₅; capacity, 20 tons per hour, 250 days per year; and location, Ames, Iowa)

| Item | Batch | | Quick-Cure | |
|---|--------------|----------------------|--------------|------------|
| | Cost, \$/ton | Amount, \$ | Cost, \$/ton | Amount, \$ |
| Annual sales ^a | 32.34 | 3,880,800 | 32.34 | 3,880,800 |
| Manufacturing cost | | 3,558,000 | | 3,511,200 |
| Gross profit | | 322,800 | | 369,600 |
| Administration and selling cost at 3% of annual sales | | 116,400 | | 116,400 |
| Net profit, before taxes | | 206,400 | | 253,200 |
| Taxes, 50% | | 103,200 | | 126,600 |
| Net profit, after taxes | | 103,200 | | 126,600 |
| Working capital | | | | |
| Raw materials inventory | | | | |
| Acid, 10 days | 35.15 | 62,500 | 35.15 | 62,500 |
| Rock, 2 weeks | 15.09 | 60,300 | 15.09 | 60,300 |
| In process inventory | 29.65 | 427,000 ^b | 29.26 | 1,500 |
| Product inventory | 29.65 | 199,200 | 29.26 | 199,000 |
| Production for 30 days | 29.65 | 427,000 | 29.26 | 421,000 |
| Credit, 30 days | 32.34 | 465,500 | 32.34 | 465,500 |
| Total working capital | | 1,641,500 | | 1,209,800 |
| Fixed capital | | 1,060,500 | | 1,035,700 |
| Total fixed + working capital | | 2,702,000 | | 2,245,500 |
| Return on investment, % | | 3.82 | | 5.63 |

^a Based on current dealer's price in Des Moines, Iowa.^b Based on 30 days' storage.

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FERTILIZER TECHNOLOGY

A One-Step Continuous Quick-Curing Triple Superphosphate Process Employing Rod Mill Grinding

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An investigation was undertaken to determine the feasibility of a one-step quick-curing continuous process for the manufacture of triple superphosphate. Bench-scale work was carried out in a 1-quart, laboratory ball mill made of stainless steel. The results from this preliminary work indicated that quick-curing triple superphosphate of high conversion could be produced. The process was investigated on pilot-plant scale with successful operation. Completely cured powdered triple superphosphate was obtained within 1 hour.

THE ADVANTAGES of a quick-curing continuous superphosphate process include the following: the product can be shipped directly, thus reducing the required storage facilities and process inventory; operating conditions in the mixing step can be chosen with more flexibility; control of the process can be essentially automatic; uncertainty as to production rates can be eliminated to some extent because a finished product can be produced in a matter of hours, instead of weeks as required by the storage curing process; and there is a possibility of lower operating labor and maintenance requirements and elimination of a final crushing and screening step since finely ground products can be obtained directly.

Previous Work

Many processes (3, 5, 9, 12) have been tried for quick-curing of triple superphosphate. None of these processes has been able to eliminate curing time entirely without loss of phosphorus availability. In some processes, both drying and storage curing are employed to shorten the period of curing. A quick-curing process is therefore desirable in which a minimum amount of phosphoric acid is needed to convert a maximum amount of rock into available form without curing. The present paper

discusses an investigation of such a process.

The development of a quick-curing, one-step process for normal superphosphate was carried out by Rounsley and Boylan (74) and Martinez (8), by grinding and drying in a single piece of equipment. This process was extended to the manufacture of triple superphosphate. Essentially the same laboratory and pilot plant equipment were used.

Process Variables

The important process variables which effect the reaction stage and curing stage of the process are acid concentration, temperature, acidulation ratio (acidulation ratio as used here is the weight ratio of acid P_2O_5 to rock P_2O_5), and time. The effects of these variables using grinding in a laboratory ball mill and a pilot-plant rod mill were investigated.

The effect of acid concentration is the most important process variable. An acid concentration of about 70% H_3PO_4 has been found most suitable, considering the physical properties of the mixture during the process and the degree of completion of reaction. Higher acid concentrations result in poor conversion, probably due to excessive side reactions. Very low acid concentrations result in

slow reaction and incomplete curing with a resulting product of high moisture and free acid content.

Temperature is also an important process variable. Its effect interferes with acid concentration because the reaction is exothermic. Acid concentrations above 75% H_3PO_4 increase the rate of reaction, and an excessive amount of heat is liberated within a short time in the first stage of the reaction. Temperatures above 284° F. may decompose the monocalcium phosphate into unavailable pyrophosphate (17). Rapid rise in temperature of the freshly acidulated mass tends to drive off water, increasing the concentration of the acid. The increased concentration means further increase in reaction rate, and hence higher temperature of the mixture. Thus a balance is required between the temperature and the acid concentration such that optimum conditions are obtained in the first stage of the reaction. Various workers (2-4, 6, 15) have suggested limiting temperatures in the range of 150° to 302° F.

Acidulation ratio is less important as a process variable than as an economic factor. An acidulation ratio of 2.0 is the theoretical minimum based on stoichiometry. Generally, it is necessary to use an acidulation ratio greater than theoretical due to the loss of acid consumed by impurities and side reactions.

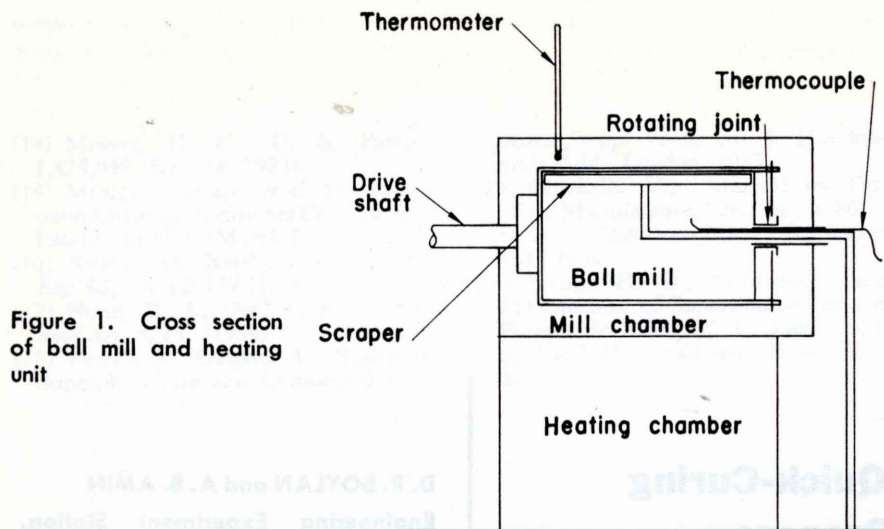


Figure 1. Cross section of ball mill and heating unit

Table I. Typical Analyses of Florida Phosphate Rock

| | | Type Sieve Size | | | |
|-------------------------------|----------|-----------------|-------|------|--|
| Screen mesh | +20 | +48 | +65 | +100 | |
| | | -20 | -48 | -65 | |
| Weight % | 0.10 | 3.03 | 9.37 | 3.09 | |
| Screen mesh | +150 | +200 | -200 | | |
| | | -100 | -150 | | |
| Weight % | 23.79 | 5.95 | 54.67 | | |
| | | Composition | | | |
| Component | Weight % | | | | |
| CaO | 47.20 | | | | |
| F | 2.90 | | | | |
| P ₂ O ₅ | 34.17 | | | | |
| P | 14.91 | | | | |
| SO ₃ | 0.30 | | | | |
| R ₂ O ₃ | 2.90 | | | | |
| SiO ₂ | 9.40 | | | | |
| Moisture | 0.42 | | | | |

Grinding during reaction is a new process variable introduced in this investigation. The effect of grinding the rock before acidulation has been shown to be beneficial (7, 10, 11), and rocks of porous structure can be benefited by preacidulation grinding. Rounsley (13) studied the effect of grinding during and after the acidulation of rock phosphate with sulfuric acid. The results showed considerable increase in the conversion. The process of curing is assumed to take place by the diffusion of the free acid into the pores of the unreacted rock particles. The grinding action continuously makes available new unreacted rock particle surfaces.

Time is a process variable closely associated with other variables such as acid concentration, acidulation ratio, and temperature. Higher acidulation ratios and lower concentrations introduce large amounts of excess water and require more curing time for specified final moisture and free acid contents in the product. Use of lower temperatures would mean lower drying rates, slower reaction, and longer process time. Thus selection of acid concentration, temperature, acidulation ratio, drying rate, and final product specifications, in effect, sets the time of reac-

tion. Lower drying rates are preferable to avoid side reactions and achieve complete curing.

Bench-Scale Investigation

Bench-scale experiments were carried out in a setup similar to that used by Rounsley and Boylan (14). Initial difficulties were experienced as a result of stickiness of the freshly acidulated mass. Larger steel balls, 1.5 inches in diameter, and a continuous scraper were employed to eliminate this problem.

The phosphate rock used was Florida pebble rock of the composition and size analyses given in Table I. Analytical grade phosphoric acid was used for the bench-scale work.

Phosphate rock and phosphoric acid for the desired acidulation ratio were mixed and introduced into the ball mill (Figure 1). The ball mill was heated by a gas burner below the outer shell, and the temperature of the shell was maintained constant throughout each run. A sample was taken at the end of each run for analysis.

Total water-soluble, and citrate-insoluble phosphorus were determined

by the official methods of Association of Official Agricultural Chemists (7). Moisture was determined by heating the samples at 105° C. for 5 hours in an oven. Calcium was determined using a flame photometer.

Bench-Scale Results

Experiments were carried out to study the effect of temperature, time, acid concentration, and acidulation ratio in the quick-curing process with grinding. The results are presented in Table II. Figure 2 shows that optimum acid concentration, under the process conditions employed, was about 65% H₃PO₄. The lower conversion at acid concentrations below 65% is probably due to slow reaction rate and incomplete curing. At acid concentrations above 65% the reaction rate was very fast, causing an excessive temperature rise and side reactions and thus driving off much of the water and resulting in a poor mix with high acid concentration. This condition caused a longer curing, since diffusion of highly viscous free acid is slow.

Figure 3 shows the effect of acidulation

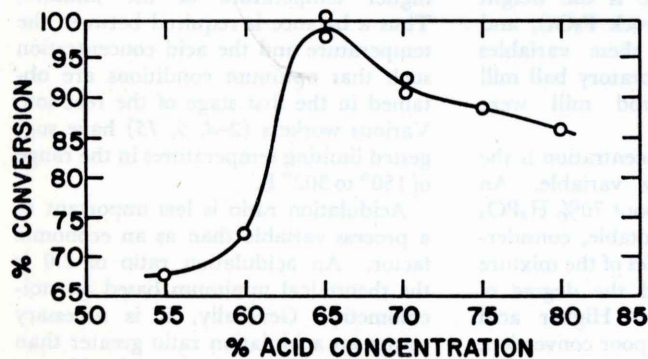


Figure 2. Effect of acid concentration on conversion
Temperature, 230° F.; time, 2 hours; acidulation ratio, 2.4

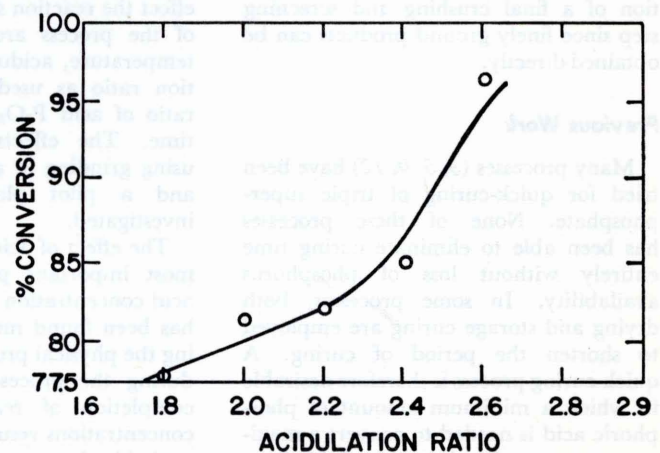


Figure 3. Effect of acidulation ratio on conversion
Acid concentration, 65%; time, 1.5 hours; temperature, 220° F.

Table II. Typical Analysis of Laboratory Ball Mill Acidulation (Dry Basis)

| Run No. | Total Time (Hr.) | Temp., ° F. | Acid Conc., % | Acid Ratio | Phosphorus, % | | | | | | | | Moist., % | Conv., % |
|---------|------------------|-------------|---------------|------------|---------------|----------------------------------|-------------------|----------------------------------|---------------|----------------------------------|-----------|----------------------------------|-----------|----------|
| | | | | | Total | | Citrate-insoluble | | Water-soluble | | Available | | | |
| | | | | | P | (P ₂ O ₅) | P | (P ₂ O ₅) | P | (P ₂ O ₅) | P | (P ₂ O ₅) | | |
| A-27 | 0.33 | 230 | 75 | 2.4 | 22.41 | (51.30) | 0.09 | (0.22) | 21.70 | (49.70) | 22.32 | (51.08) | 7.14 | 98.6 |
| A-21 | 1.25 | 280 | 70 | 2.4 | 23.60 | (54.00) | 1.25 | (2.86) | 19.71 | (45.10) | 22.33 | (51.10) | 4.43 | 82.0 |
| A-17 | 1.50 | 220 | 65 | 2.0 | 22.40 | (51.27) | 1.43 | (3.24) | 17.05 | (39.06) | 21.00 | (48.00) | 0.92 | 81.4 |
| A-19 | 1.50 | 220 | 65 | 2.4 | 21.93 | (50.20) | 0.97 | (2.23) | 15.52 | (36.58) | 21.00 | (48.00) | 5.36 | 84.9 |
| A-2 | 2.00 | 220 | 70 | 2.4 | 20.82 | (47.70) | ... | ... | 18.32 | (41.97) | 20.82 | (47.70) | 7.07 | 100.0 |
| B-3 | 2.00 | 230 | 65 | 2.4 | 23.79 | (54.45) | ... | ... | 19.70 | (45.05) | 23.79 | (54.45) | 1.45 | 100.0 |
| B-5 | 2.00 | 230 | 70 | 2.4 | 23.32 | (53.40) | 0.63 | (1.44) | 20.71 | (47.44) | 22.70 | (51.96) | 8.30 | 91.0 |
| A-4 | 4.00 | 220 | 70 | 2.4 | 22.31 | (51.10) | ... | (...) | 20.82 | (47.70) | 22.31 | (51.10) | 2.96 | 100.0 |

Table III. Typical Pilot-Plant Operating Conditions

| Run No. | Acid Conc., % | Approx. Rock Feed Rate G./Min. | Approx. Acid Feed Rate G./Min. | Outlet Heating Gas Temp., ° F. | Drying Air Temp., ° F. | | | Product Temp., ° F. | Acid Temp., ° F. | Heating Chamber Gas Temp., ° F. | Drying Air Rate, Cu. Ft./Min. |
|---------|-------------------|--------------------------------|--------------------------------|--------------------------------|------------------------|--------------|-------------|---------------------|------------------|---------------------------------|-------------------------------|
| | | | | | Inlet, D.B. | Outlet, D.B. | Inlet, W.B. | | | | |
| 3 | 71.6 | 100 | 161 | 375 | 225 | 215 | ... | ... | 65 | 650 | 0.350 |
| 4 | 70.6 | 100 | 161 | 350 | 200 | 194 | ... | ... | 68 | 575 | 0.350 |
| 5 | 70.6 | 100 | 161 | 300 | 135 | 170 | ... | ... | 68 | 450 | 0.370 |
| 6 | 71.0 | 100 | 161 | 250 ^a | ... | ... | ... | ... | ... | ... | ... |
| 7 | 72.4 | 100 | 174 | 350 | 150 | 190 | ... | 198 | 66 | 550 | 0.365 |
| 8 | 71.6 | 100 | 148 | 350 | 156 | 180 | 85 | 162 | 68 | 575 | 0.365 |
| 9 | 66.0 | 50 | 87 | 350 | 177 | 195 | 100 | 180 | 71 | 550 | 0.365 |
| 10 | 61.0 | 50 | 94 | 350 | 160 | 185 | ... | 175 | 72 | 530 | 0.342 |
| 11 | 72.8 ^b | 100 | 174 | 325 | 73 | 175 | 48 | 170 | 66 | 450 | 0.512 |

^a The low heating gas temperature was insufficient for adequate curing and drying.

^b Acid concentration of 71.7% was used for the first 4 hours.

ratio on the conversion. Conversion increases with increasing acidulation ratio. The curing was incomplete as sufficient time was not allowed for the completion of reactions.

Figure 4 shows the effect of heating shell temperature. An optimum temperature of about 230° F. is indicated. Higher temperatures probably result in excessive side reactions and decomposition of monocalcium phosphate to pyrophosphate. At lower temperatures, the reaction is too slow. Processing time in these runs was insufficient for the completion of curing, and low conversions were obtained.

Figure 5 indicates the effect of time on conversion. A minimum time of about 2 hours is indicated for the completion of curing. Grinding and heating the product for a period of more than 2 hours had no detrimental effects on the

conversion under the conditions employed.

No consistent relationship between final moisture content and other process variables was indicated. Drying took place inside the ball mill, and the gases evolved escaped through the small central opening.

The results of the bench-scale work suggested that a quick-curing process based on grinding and drying was possible.

Pilot-Plant Work

Investigation of the quick curing process on a pilot-plant scale was undertaken using essentially the same equipment as used by Rounsley (13).

The pilot plant consisted of a 6-foot long, 1-foot diameter, stainless steel-lined rod mill with an external heating

jacket (Figure 6). Hot gases from the jacket were introduced into the mill to increase the drying rate. Phosphoric acid and rock were fed continuously at one end of the mill. Product was collected at the other end. The rod mill contained 10 stainless steel rods, 1 inch diameter and 6 feet long, each weighing 16 pounds. The temperature in the outside heating jacket was kept constant by a controller. The reaction gases evolved in the mill were passed through a scrubber and exhausted to the atmosphere by a blower.

The rod mill was first heated for 2 hours before each run, then rock and acid feed were started. No samples were taken during the unsteady state period. Four samples were taken every hour thereafter in the first seven runs, three per hour in run 8, and two samples per hour in the rest of the runs. The product samples were collected for 5-

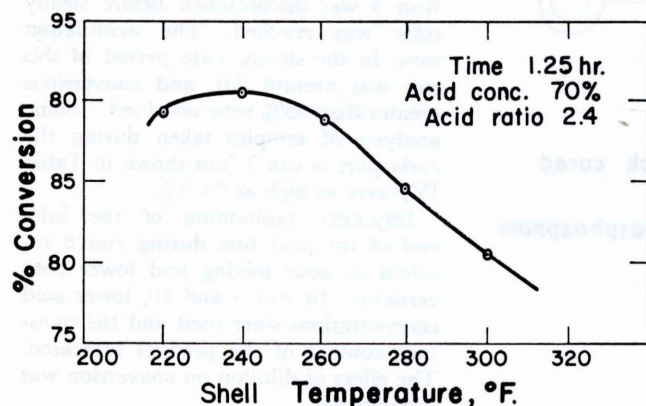


Figure 4. Effect of temperature on conversion
Time, 1.25 hours; acid concentration, 70%; acidulation ratio, 2.4

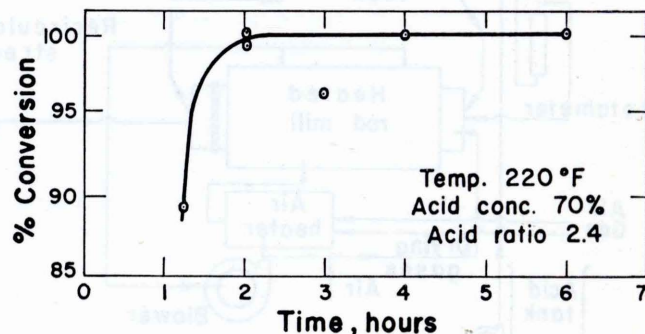


Figure 5. Effect of time on conversion
Temperature, 220° F.; acid concentration, 70%; acidulation ratio, 2.4

Table IV. Typical Analysis of Pilot-Plant Product (Wet Basis)

| Sample No. | Phosphorus, % | | | | | | Moist., % | CaO, % | Calcd. Acid Ratio | Free Acid P, % | Free Acid P ₂ O ₅ , % | Conv., % | | |
|------------|---------------|----------------------------------|-------------------|----------------------------------|-----------------|----------------------------------|-----------|---------|-------------------|----------------|---|----------|-----------|----------------------------------|
| | Total | | Citrate-insoluble | | Water-insoluble | | | | | | | | Available | |
| | P | (P ₂ O ₅) | P | (P ₂ O ₅) | P | (P ₂ O ₅) | | | | | | | P | (P ₂ O ₅) |
| 4-23 | 23.22 | (53.17) | 0.43 | (0.99) | 20.80 | (47.63) | 22.80 | (52.18) | 4.40 | 24.10 | 2.00 | 0.62 | 1.41 | 94.42 |
| 4-24 | 22.80 | (52.17) | 0.76 | (1.74) | 20.20 | (46.26) | 22.00 | (50.43) | 2.90 | 23.50 | 2.02 | 0.39 | 0.90 | 89.95 |
| 4-25 | 22.81 | (52.20) | 0.85 | (1.94) | 20.20 | (46.26) | 21.96 | (50.26) | 3.01 | 23.40 | 2.07 | 0.33 | 0.76 | 88.60 |
| 5-34 | 22.88 | (52.37) | 0.59 | (1.36) | 19.74 | (45.19) | 22.30 | (51.01) | 2.39 | 22.40 | 2.04 | 0.57 | 1.30 | 92.12 |
| 5-35 | 22.83 | (52.26) | 0.71 | (1.62) | 20.52 | (46.98) | 22.12 | (50.64) | 4.03 | 22.14 | 2.21 | 0.37 | 0.86 | 90.06 |
| 5-36 | 22.90 | (52.41) | 0.60 | (1.38) | 20.88 | (47.75) | 22.32 | (51.03) | 4.42 | 23.50 | 2.03 | 0.79 | 1.82 | 92.04 |
| 7-56 | 22.70 | (51.98) | 0.33 | (0.75) | 21.21 | (48.55) | 22.40 | (51.23) | 5.84 | 22.43 | 2.15 | ... | ... | 96.46 |
| 7-57 | 22.33 | (51.55) | 0.26 | (0.60) | 21.35 | (48.85) | 22.25 | (50.95) | 5.30 | 22.80 | 2.08 | 0.77 | 1.76 | 96.44 |
| 7-58 | 22.99 | (52.63) | 0.29 | (0.68) | 20.15 | (46.12) | 22.70 | (51.95) | 3.17 | 23.19 | 2.09 | ... | ... | 96.04 |
| 9-79 | 23.60 | (53.97) | 0.14 | (0.32) | 23.15 | (52.97) | 23.43 | (53.65) | 4.55 | 20.90 | 2.51 | ... | ... | 97.89 |
| 9-80 | 24.02 | (55.00) | 0.14 | (0.33) | 23.00 | (52.66) | 23.90 | (54.68) | 4.09 | 21.52 | 2.48 | ... | ... | 97.95 |
| 9-81 | 23.61 | (54.05) | 0.11 | (0.26) | 22.70 | (51.97) | 23.52 | (53.79) | 3.81 | 21.63 | 2.40 | ... | ... | 98.40 |
| 10-88 | 23.23 | (53.20) | 0.33 | (0.74) | 21.98 | (50.26) | 22.92 | (52.46) | 4.98 | 22.76 | 2.19 | ... | ... | 95.55 |
| 10-89 | 23.63 | (54.15) | 0.37 | (0.84) | 22.05 | (50.50) | 23.30 | (53.31) | 3.41 | 23.00 | 2.20 | ... | ... | 95.00 |
| 10-90 | 23.61 | (54.02) | 0.29 | (0.66) | 22.18 | (50.71) | 23.32 | (53.36) | 1.69 | 22.00 | 2.34 | ... | ... | 95.94 |
| 11-99 | 22.35 | (51.13) | 0.41 | (0.93) | 21.63 | (49.53) | 21.95 | (50.20) | 4.54 | 22.15 | 2.14 | ... | ... | 93.31 |
| 11-100 | 22.54 | (51.58) | 0.39 | (0.90) | 21.58 | (49.41) | 22.15 | (50.68) | 4.07 | 23.20 | 2.02 | 0.96 | 2.19 | 94.71 |
| 11-101 | 22.82 | (52.24) | 0.42 | (0.95) | 21.60 | (49.49) | 22.42 | (51.29) | ... | 22.35 | 2.18 | 1.47 | 3.37 | 94.19 |

Table V. Pilot-Plant Size Analyses

| Run No. | Tyler Sieve Size | | | | | | | | | | Remarks |
|-------------|------------------|------|------|------|------|------|------|------|------|-----------------|---------|
| | +20 | +28 | +48 | +65 | +100 | +115 | +150 | +200 | -200 | -28 | |
| 3 | 4.0 | 4.6 | 28.5 | 19.1 | 11.9 | 11.7 | 3.3 | 6.1 | 10.8 | Screens clogged | |
| 4 | 4.5 | 4.1 | 33.9 | 33.0 | 8.5 | 4.6 | 4.4 | 4.3 | 2.9 | Screens clogged | |
| 5 | 9.9 | 5.2 | 23.3 | 13.5 | 14.4 | 5.5 | 4.2 | 5.9 | 18.3 | ... | |
| 7 | 30.3 | 9.4 | 26.2 | 25.7 | 3.3 | 1.4 | 0.7 | 0.7 | 2.4 | Screens clogged | |
| 9 | 5.0 | 11.0 | 27.0 | 15.9 | 8.0 | 6.0 | 4.1 | 8.6 | 14.4 | Predried | |
| 10 | 7.5 | 13.6 | 27.1 | 10.3 | 10.2 | 4.6 | 2.4 | 6.8 | 17.5 | Predried | |
| 11 | 12.1 | 8.4 | 23.6 | 11.7 | 10.9 | 4.2 | 2.6 | 5.7 | 20.8 | Predried | |
| Rock sample | 0.1 | 0.2 | 2.8 | 9.4 | 3.1 | 23.2 | 0.6 | 6.0 | 54.7 | As received | |

and 10-minute periods for rock feeding rates of 50 and 100 grams per minute, respectively.

The inside of the mill was examined under steady state conditions. A wet crust extending about 1 to 2 feet was observed at the inlet end of the mill where the first stage of reaction took place. Operating conditions of the different runs are given in Table III. Materials used were the same as those used for the laboratory studies.

Pilot-Plant Results

The results of the pilot-plant runs are given in Tables IV and V. The analyses of the samples of the first six runs were made after a few days, and analyses of the samples for the rest of the runs were made immediately to give zero day results.

The effect of acidulation ratio, acid concentration, feed rate, and temperature on the product was investigated. Other parameters for the process, such as the

source and particle size of the rock, rod mill diameter, speed, slope, and length, and the size and number of rods were kept constant, except for run 11 when the number of rods were reduced to six. This last run was carried out to examine the possible variation of operating variables.

Evaluation of Pilot-Plant Results

The results obtained in the laboratory-scale ball mill were to a large extent confirmed in the pilot-plant scale equipment (Table IV).

Analytical results of run 4 show poor consistency and reflect the poor control of the acid and rock feed rates in this run. Also, sufficient time was not allowed to reach steady state conditions. Run 5 was discontinued before steady state was reached. The acidulation ratio in the steady state period of this run was around 2.0, and conversions greater than 95% were obtained. Some analyses of samples taken during the early part of run 7 (not shown in Table IV) were as high as 99.3%.

Improper positioning of the inlet end of the acid line during run 8 resulted in poor mixing and lower conversions. In run 9 and 10, lower acid concentrations were used and the moisture content of the product increased. The effect of dilution on conversion was insignificant.

Operating conditions were changed in run 11 to test their flexibility. Only

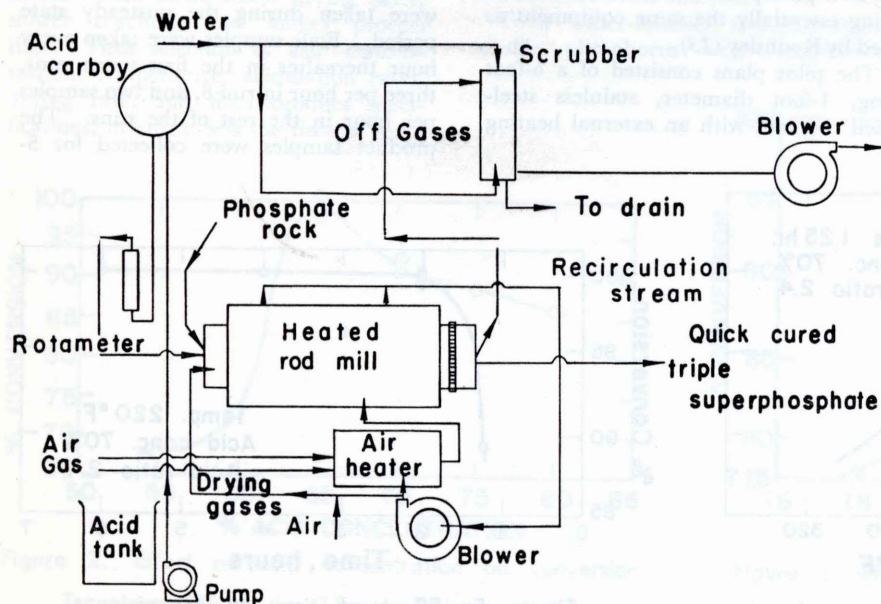


Figure 6. Flow sheet of the pilot plant for quick cured triple superphosphate

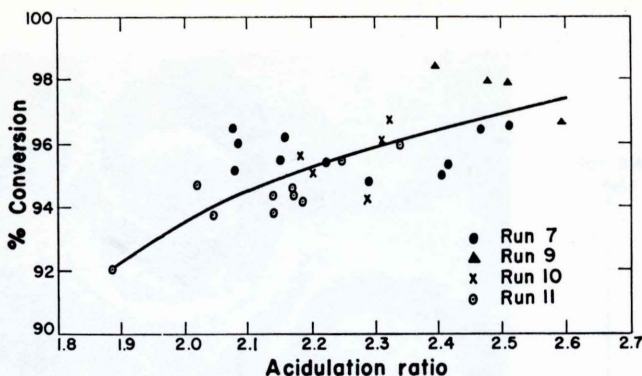


Figure 7. Effect of acidulation ratio on conversion

six rods were used instead of the 10 rods used in previous runs. A lower heating jacket temperature of 325° F. was used instead of 350° F. The drying air rate was increased from 0.365 cu. ft. per minute to 0.512 cu. ft. per minute, and the drying air temperature was decreased from about 160° to 73° F. The opposing effects of changes in these operating variables resulted in no distinguishable changes in the product, except for higher moisture and free acid content. This could be corrected either by increasing the temperature, increasing the residence time, increasing the amount of drying air or its temperature, or by decreasing the acid and rock feeding rates. Moisture content between 3 and 4% gave optimum results and satisfactory free acid contents.

Figure 7 indicates the effect of the

variation of the acidulation ratio on the conversion obtained in various runs. The particle size analysis of the rock used and the product triple superphosphate are given in Table V. Agglomeration of fine particles in the product of these runs prevented correct indication of the degree of grinding.

A residence time in the mill of about 45 minutes was indicated during run 10 by introducing ground charcoal with the rock feed and subsequent examination of the product for color.

The product was examined for storage characteristics after one month and two months. It was found free flowing and had excellent physical condition.

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FERTILIZER TECHNOLOGY

Granulation Characteristics of a 5-4-12 (5-10-15) Fertilizer Containing Potassium Nitrate

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Factors influencing the granulation of a mixed fertilizer containing potassium nitrate have been studied. Kilogram batches of a 5-4-12 (5-10-15) mixed fertilizer containing potassium nitrate were granulated at different feed moisture levels and at inlet gas temperatures ranging from 405° to 575° F. Optimum conditions of moisture in the feed and inlet gas temperature were determined for maximum yield of the granular product and uniform distribution of the three major nutrient elements (N, P, K) in the various product size fractions. Similar experiments were performed with a 2-4-12 (2-10-15) mixed fertilizer containing potassium chloride. This grade represents a simple substitution of KCl for KNO₃ so physical changes due to KNO₃ could be more closely compared. A comparative study has been made of the results obtained with the two mixtures. The experiments were based on a statistical central composite rotatable design, and the results were statistically analyzed. An attempt has been made to relate mathematically the yield and total absolute deviation in nutrient analysis between product and feed with moisture in a feed and temperature of granulation.

POTASSIUM nitrate has a high agronomic value as a source of both nitrogen and potash, but high cost has been the chief reason for its limited use as fertilizer. The new production facilities of Southwest Potash Corp. for fertilizer-grade potassium nitrate, 13% N, 36.5% K (44% K₂O), may make this material economically attractive. This has stimulated considerable interest in the properties of potassium nitrate with respect to its behavior in mixed fertilizers during processing and its effect on the physical quality of the resulting products.

Previous Work

During the past few years, much work has been done on the granulation char-

acteristics of mixed fertilizers. Pilot plant studies conducted at TVA (3) showed that in production of very low nitrogen grades [e.g., 3-5-9 (3-12-12) or 4-6-13 (4-16-16)] the amount of moisture required for granulation of the charge material was high (14 to 16%), and the products were rather wet. Smith (4), in the study of temperature and moisture relationships in granulation, noted that the utilization of ammonia as anhydrous or nitrogen solutions reduced not only the cost of nitrogen but also the free water content. A high salt solution phase contributed to rapid crystallization and therefore aided formulation of granules during agglomeration. These grades contained potassium nitrate as the source of potassium.

Recently, Hardesty and his coworkers, working with grades containing potassium nitrate, noted that slightly less moisture was required for agglomeration with potassium nitrate mixtures (2), but they produced a "popped-corn" shape of granules which effloresced on drying. Comparison of the yield and homogeneity of the product with mixtures that contained potassium nitrate and potassium chloride was not reported.

Experimental Work

Experiments were performed to study the effect of moisture in the feed and inlet gas temperature on the yield and the distribution of plant nutrients in the various product size fractions. Two

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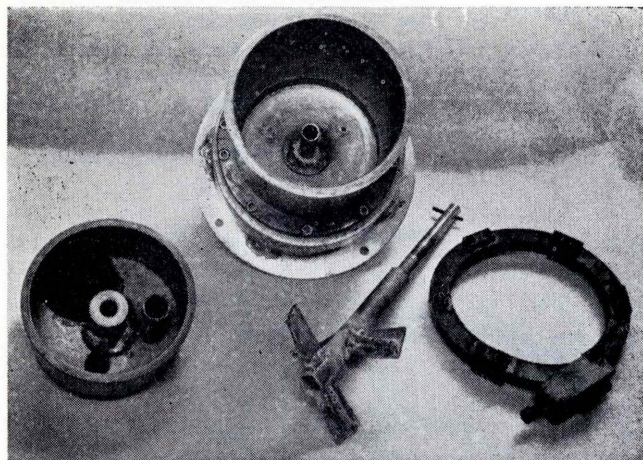


Figure 1. Photograph of the ammoniator-mixer disassembled

grades were prepared—5-4-12 (5-10-15) tobacco fertilizer with potassium nitrate as the major source of potassium, and 2-4-12 (2-10-15) mixed fertilizer with potassium chloride as the major source of potassium (Table I). The solid raw materials (all crushed to -20 mesh) were mixed in a batch reactor, and then reacted with sulfuric acid and ammonia. The required moisture content was obtained by addition of predetermined amounts of water to the feed mixtures.

The batch reactor was constructed from a section of 5-inch o.d., type 304, stainless steel tube with a wall thickness of $\frac{3}{32}$ inch (see Figures 1 and 2). A stainless steel stirrer, with a hollow shaft and four paddles, was used to mix the ingredients and to distribute ammonia.

The feed materials were screened and stored in individual bins. As needed, the required quantities were removed from the bins and dry mixed in the mixer. The water, sulfuric acid, and anhydrous ammonia were added one at a time to the mixture and mixing was continued for a predetermined time. Before transferring the mixture to the granulator dryer, duplicate samples were removed for analysis.

The mixtures were granulated in a bench-scale Roto-Louvre dryer 13 inches in diameter and $3\frac{1}{8}$ inches long (Figure

3). The dryer speed was 7.4 r.p.m. The product was dried, screened, and analyzed for nitrogen, phosphorus, and potassium.

Experiments on both grades were statistically designed (1). The two major factors, per cent moisture in the feed and average inlet gas temperature, were varied over a reasonable range. Preliminary experiments showed that even a variation of 0.5% moisture in the feed affected the yield of granules appreciably with the 5-4-12 (5-10-15) grade, while 1.5% moisture variation was necessary to get an approximately equivalent effect on the yield of granules with the 2-4-12 (2-10-15) mixture. The experiments with the 5-4-12 (5-10-15) grade were performed randomly according to the design in Figure 4, and those with the 2-4-12 (2-10-15) according to the design in Figure 5.

Table I. Formulation of 5-4-12 (5-10-15) and 2-4-12 (2-10-15) Mixed Fertilizers

| Material | Analysis | | | | Formula, Lb. / Ton | |
|--------------------|----------|-----------------------------------|---------------------|----------|---------------------|---------------------|
| | N | P(P ₂ O ₅) | K(K ₂ O) | Mg(MgO) | 5-4-12 (5-10-15) | 2-4-12 (2-10-15) |
| Superphosphate | 0 | 8.95(20.5) | 0 | 0 | 1020 | 1020 |
| Anhydrous ammonia | 82.2 | 0 | 0 | 0 | 52 | 52 |
| Sul-Po-mag | 0 | 0 | 18.1(21.7) | 10.8(18) | 222 | 222 |
| Potassium nitrate | 13.2 | 0 | 36.1(43.4) | 0 | 460 | 0 |
| Potassium chloride | 0 | 0 | 50.0(60.2) | 0 | 75 | 425 |
| Sulfuric acid | 0 | 0 | 0 | 0 | 50 | 50 |
| Filler (Sand) | 0 | 0 | 0 | 0 | 171 | 281 |
| | | | | Total | 2050 | 2050 |

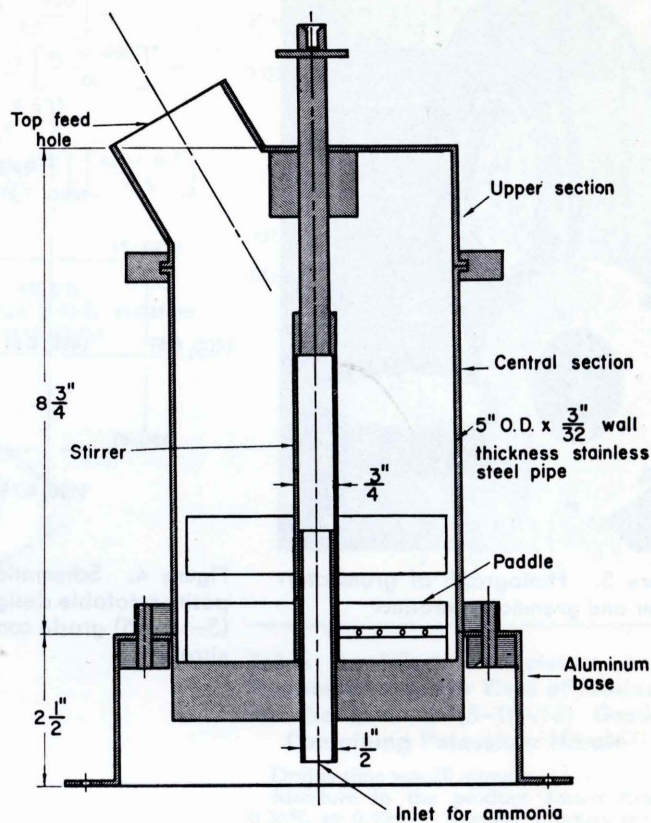


Figure 2. Sectional drawing of ammoniator-mixer

Two mathematical models were set up—model I, relating the per cent yield with per cent moisture in the feed and temperature of the inlet gas, and model II, relating the total absolute deviation of the three nutrients N, P, and K in the product from that in feed with per cent moisture in feed and temperature of the inlet gas. The total absolute deviation was the statistic which expressed the variation of the plant nutrients between the feed and the granular product. It was estimated for every experimental run by summing up the individual absolute differences for N, P, and K between feed and -6 + 20 granular product.

$$Y = b_0 + b_1x_1 + b_2x_2 + b_{11}x_1^2 + b_{22}x_2^2 + b_{12}x_1x_2$$

Model I:

$$Y = \% \text{ Yield } (-6+20 \text{ mesh granules})$$

$$x_1 = \text{Average inlet gas temperature, } ^\circ \text{F.}$$

$$x_2 = \% \text{ Moisture in feed (dry basis).}$$

Model II:

$$Y = \text{Total absolute deviation of N-P-K in product from that in feed.}$$

$$x_1 = \text{Average inlet gas temperature, } ^\circ \text{F.}$$

$$x_2 = \% \text{ Moisture in feed (dry basis)}$$

The regression coefficients b_0 , b_1 , b_2 , b_{11} , b_{22} , b_{12} of these models were determined from the experimental results.

Discussion

The experimental results with both the grades are shown in Tables II, III, IV,

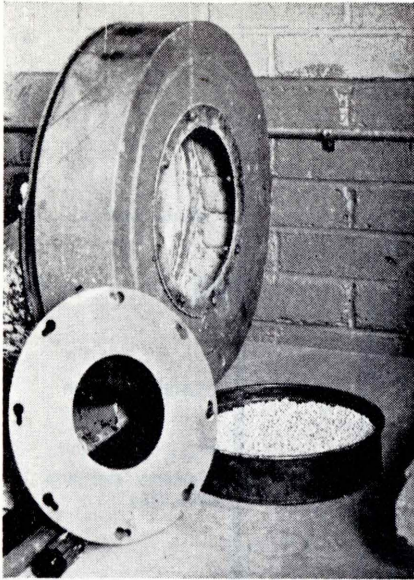


Figure 3. Photograph of granulator-dryer and granulated product

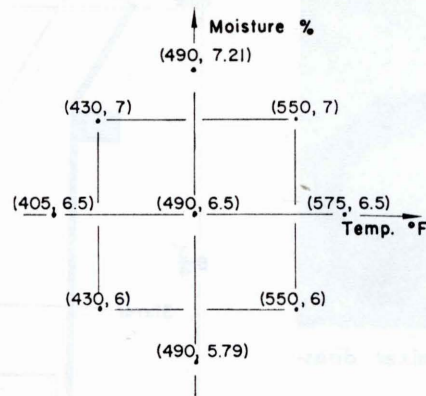


Figure 4. Schematic of central composite rotatable design for the 5-4-12 (5-10-15) grade containing potassium nitrate

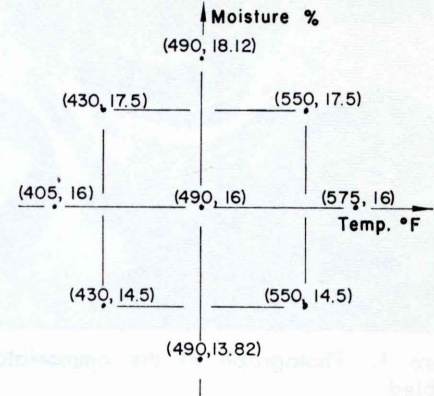


Figure 5. Schematic of central composite rotatable design for the 2-4-12 (2-10-15) grade containing potassium chloride

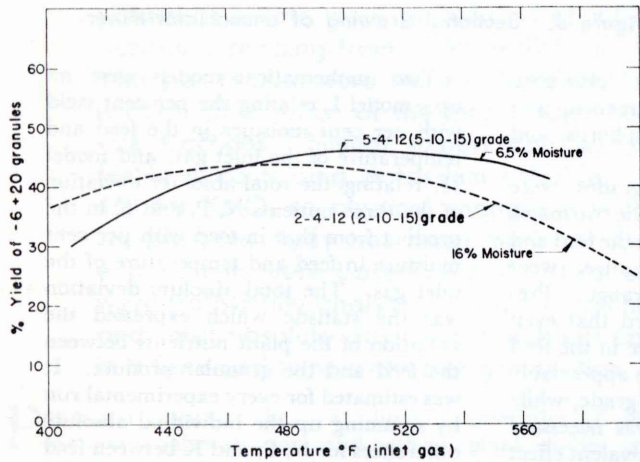


Figure 6. Effect of temperature on the yield of -6+20 product size fraction for both fertilizer grades at their central moisture levels

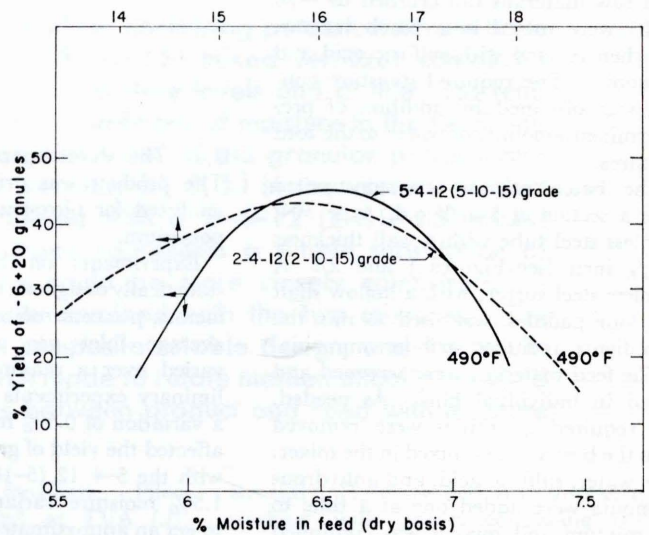


Figure 7. Effect of moisture on the yield of -6+20 product size fraction for both fertilizer grades at their central temperature level

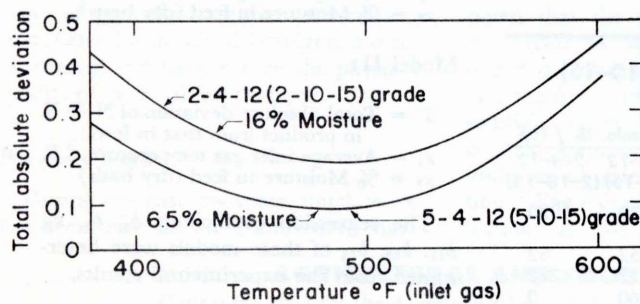


Figure 8. Effect of temperature on the total absolute deviation for both fertilizer grades at their central moisture levels

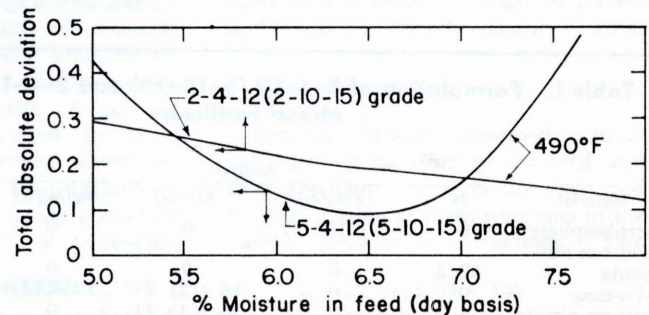


Figure 9. Effect of moisture on the total absolute deviation for both fertilizer grades at their central temperature level

and V. Tables II and III show the effect of moisture and temperature on the yield of granules, and Tables IV and V present the effect of moisture and temperature on the total absolute deviation in the product. The statistical analysis of these results gave the following quadratic relationships:

Model I:

$$Y = 45.40 + 3.36 \left[\frac{x_1 - 490}{60} \right] + 1.8 \left[\frac{x_2 - 6.5}{0.5} \right] - 5.17 \left[\frac{x_1 - 490}{60} \right]^2 - 13.37 \left[\frac{x_2 - 6.5}{0.5} \right]^2 - 1.92 \left[\frac{x_1 - 490}{60} \right] \left[\frac{x_2 - 6.5}{0.5} \right]$$

with the 5-4-12 (5-10-15) grade.

$$Y = 43.36 - 2.10 \left[\frac{x_1 - 490}{60} \right] - 3.05 \left[\frac{x_2 - 16.0}{1.5} \right] - 4.46 \left[\frac{x_1 - 490}{60} \right]^2 - 8.04 \left[\frac{x_2 - 16.0}{1.5} \right]^2 - 0.20 \left[\frac{x_1 - 490}{60} \right] \left[\frac{x_2 - 16.0}{1.5} \right]$$

with the 2-4-12 (2-10-15) grade.

Model II:

$$Y = 0.0960 + 0.0175 \left[\frac{x_1 - 490}{60} \right] + 0.0125 \left[\frac{x_2 - 6.5}{0.5} \right] + 0.0664 \left[\frac{x_1 - 490}{60} \right]^2 + 0.0464 \left[\frac{x_2 - 6.5}{0.5} \right]^2 - 0.0575 \left[\frac{x_1 - 490}{60} \right] \left[\frac{x_2 - 6.5}{0.5} \right]$$

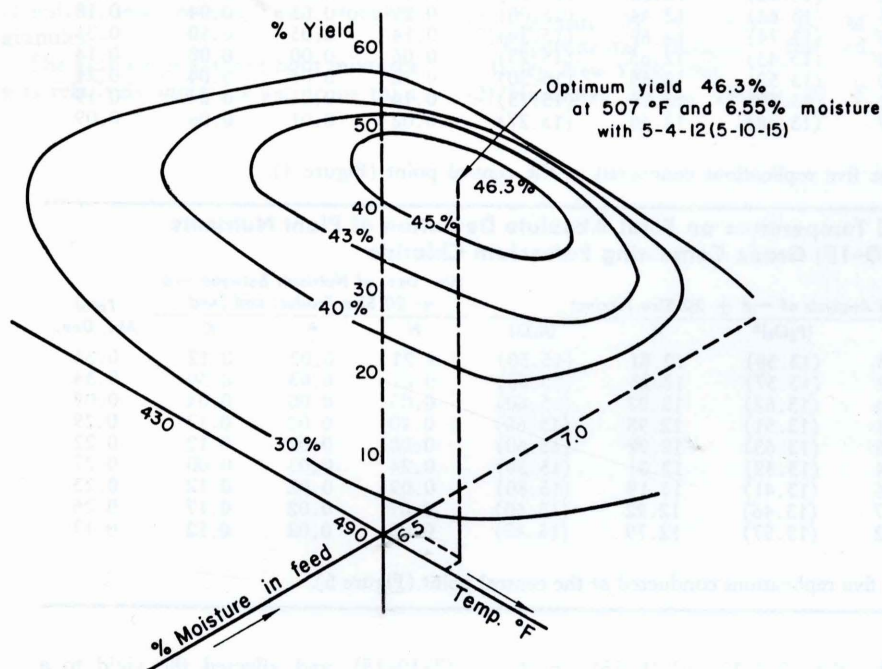


Figure 10. Response surface showing contours of constant yield for the 5-4-12 (5-10-15) grade containing potassium nitrate

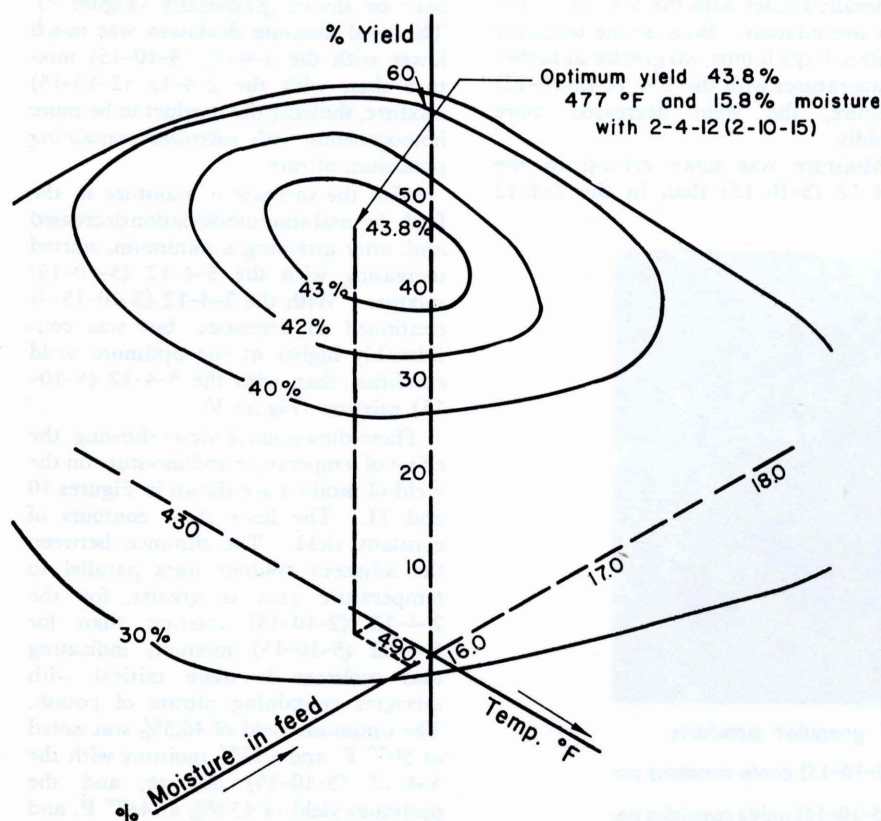


Figure 11. Response surface showing contours of constant yield for the 2-4-12 (2-10-15) grade containing potash chloride

Table II. Effect of Moisture and Temperature on the Yield of Product for the 5-4-12 (5-10-15) Grade Containing Potassium Nitrate

Drying time was 20 minutes. Moisture in the product varied from 0.38% to 0.92%. Average product temperature varied from 203° to 256° F.

| Run No. | Temp. of Gas, ° F. | Moisture in Feed, % | Yield -6+20 % |
|-------------------|--------------------|---------------------|---------------|
| K-10 | 492 | 5.75 | 13.8 |
| K-11 | 552 | 6.99 | 27.8 |
| K-12 | 432 | 6.98 | 27.1 |
| K-13 | 492 | 7.23 | 23.1 |
| K-16 | 550 | 5.98 | 31.0 |
| K-18 | 429 | 6.01 | 22.6 |
| K-21 | 574 | 6.50 | 36.2 |
| K-27 | 406 | 6.51 | 33.4 |
| K-29 ^a | 490 | 6.50 | 45.4 |

^a K-29 readings were estimated by averaging the 5 replications conducted at the central point (Figure 4).

Table III. Effect of Moisture and Temperature on the Yield of Product for the 2-4-12 (2-10-15) Grade Containing Potassium Chloride

Drying time was 45 minutes. Moisture in the product varied from 0.29% to 0.92%. Average product temperature varied from 194° to 249° F.

| Run No. | Temp. of Gas, ° F. | Moisture in Feed, % | Yield -6+20 % |
|-------------------|--------------------|---------------------|---------------|
| K-32 | 575 | 16.05 | 41.4 |
| K-33 | 406 | 15.87 | 30.9 |
| K-34 | 495 | 18.15 | 33.9 |
| K-35 | 491 | 13.94 | 24.1 |
| K-36 | 552 | 17.49 | 32.1 |
| K-38 | 553 | 14.62 | 27.2 |
| K-42 | 430 | 14.53 | 25.8 |
| K-46 | 432 | 17.54 | 31.5 |
| K-47 ^a | 494 | 16.08 | 43.4 |

^a K-47 readings were estimated by averaging the 5 replications conducted at the central point (Figure 5).

Table IV. Effect of Moisture and Temperature on Total Absolute Deviation of Plant Nutrients for 5-4-12 (5-10-15) Grade Containing Potassium Nitrate

| Run No. | Temp. of Gas, °F. | Moisture in Feed, % | Nutrient Analysis of -6 + 20 Size Product | | | | | Abs. Dev. of Nutrients between -6 + 20 Size Product and Feed | | | Total Abs. Dev. |
|-------------------|-------------------|---------------------|---|----------------|---|-------|--------------------|--|------|------|-----------------|
| | | | N | P ^a | (P ₂ O ₅) ^a | K | (K ₂ O) | N | P | K | |
| K-10 | 492 | 5.75 | 5.31 | 5.92 | (13.57) | 12.58 | (15.15) | 0.08 | 0.01 | 0.08 | 0.17 |
| K-11 | 552 | 6.99 | 5.45 | 5.98 | (13.71) | 12.79 | (15.40) | 0.10 | 0.04 | 0.08 | 0.22 |
| K-12 | 432 | 6.98 | 5.79 | 5.92 | (13.58) | 12.65 | (15.25) | 0.15 | 0.05 | 0.08 | 0.28 |
| K-13 | 492 | 7.23 | 5.59 | 5.95 | (13.64) | 12.44 | (15.00) | 0.11 | 0.03 | 0.04 | 0.18 |
| K-16 | 550 | 5.98 | 5.38 | 6.00 | (13.74) | 12.69 | (15.30) | 0.14 | 0.05 | 0.10 | 0.31 |
| K-18 | 629 | 6.01 | 5.51 | 5.86 | (13.43) | 12.65 | (15.25) | 0.06 | 0.00 | 0.08 | 0.14 |
| K-21 | 574 | 6.50 | 5.23 | 5.90 | (13.52) | 12.69 | (15.30) | 0.12 | 0.05 | 0.04 | 0.21 |
| K-27 | 406 | 6.51 | 5.60 | 5.92 | (13.69) | 12.58 | (15.15) | 0.14 | 0.01 | 0.04 | 0.19 |
| K-29 ^b | 490 | 6.50 | 5.53 | 5.87 | (13.48) | 12.68 | (15.27) | 0.02 | 0.01 | 0.06 | 0.09 |

^a Total.

^b K-29 readings were estimated by averaging the five replications conducted at the central point (Figure 4).

Table V. Effect of Moisture and Temperature on Total Absolute Deviation of Plant Nutrients for 2-4-12 (2-10-15) Grade Containing Potassium Chloride

| Run No. | Temp. of Gas, °F. | Moisture in Feed, % | Nutrient Analysis of -6 + 20 Size Product | | | | | Abs. Dev. of Nutrients Between -6 + 20 Size Product and Feed | | | Total Abs. Dev. |
|-------------------|-------------------|---------------------|---|----------------|---|-------|--------------------|--|------|------|-----------------|
| | | | N | P ^a | (P ₂ O ₅) ^a | K | (K ₂ O) | N | P | K | |
| K-32 | 575 | 16.05 | 2.26 | 5.83 | (13.38) | 12.81 | (15.50) | 0.21 | 0.03 | 0.12 | 0.36 |
| K-33 | 406 | 15.87 | 2.48 | 5.82 | (13.37) | 13.23 | (15.85) | 0.01 | 0.03 | 0.30 | 0.34 |
| K-34 | 495 | 18.15 | 2.32 | 5.94 | (13.62) | 12.92 | (15.60) | 0.05 | 0.00 | 0.04 | 0.09 |
| K-35 | 491 | 13.94 | 2.41 | 5.91 | (13.51) | 12.98 | (15.65) | 0.10 | 0.02 | 0.17 | 0.29 |
| K-36 | 552 | 17.49 | 2.36 | 5.96 | (13.63) | 12.92 | (15.60) | 0.08 | 0.02 | 0.12 | 0.22 |
| K-38 | 553 | 16.62 | 2.39 | 5.84 | (13.39) | 12.81 | (15.50) | 0.24 | 0.03 | 0.00 | 0.27 |
| K-42 | 430 | 16.53 | 2.39 | 5.86 | (13.41) | 13.19 | (15.80) | 0.09 | 0.02 | 0.12 | 0.23 |
| K-46 | 432 | 17.54 | 2.47 | 5.87 | (13.46) | 12.92 | (15.60) | 0.07 | 0.02 | 0.17 | 0.26 |
| K-47 ^b | 494 | 16.08 | 2.45 | 5.92 | (13.57) | 12.79 | (15.45) | 0.05 | 0.02 | 0.12 | 0.19 |

^a Total.

^b K-47 readings were estimated by averaging the five replications conducted at the central point (Figure 5).

with the 5-4-12 (5-10-15) grade.

$$Y = 0.1900 + 0.0038 \left[\frac{x_1 - 490}{60} \right] - 0.0380 \left[\frac{x_2 - 16.0}{1.5} \right] + 0.0737 \left[\frac{x_1 - 490}{60} \right] + 0.0063 \left[\frac{x_2 - 16.0}{1.5} \right]^2 - 0.0200 \left[\frac{x_1 - 490}{60} \right] \left[\frac{x_2 - 16.0}{1.5} \right]$$

with the 2-4-12 (2-10-15) grade.

The effect of temperature on the yield with the two mixtures may be shown graphically (Figure 6). The yield was generally higher with the 5-4-12 (5-10-15) formulation. Because the tendency to form large lumps was greater at higher temperatures with the 2-4-12 (2-10-15) mixture, the yield decreased more rapidly.

Moisture was more critical in the 5-4-12 (5-10-15) than in the 2-4-12

(2-10-15), and affected the yield to a greater extent (Figure 7).

The effect of temperature on the total absolute deviation with the two mixtures may be shown graphically (Figure 8). The total absolute deviation was much lower with the 5-4-12 (5-10-15) mixture than with the 2-4-12 (2-10-15) mixture, showing the product to be more homogeneous with mixtures containing potassium nitrate.

With the increase of moisture in the feed, the total absolute deviation decreased and, after attaining a minimum, started increasing with the 5-4-12 (5-10-15) mixture. With the 2-4-12 (2-10-15) it continued to decrease; but was considerably higher at the optimum yield condition than with the 5-4-12 (5-10-15) mixture (Figure 9).

Three-dimensional views showing the effect of temperature and moisture on the yield of product are shown in Figures 10 and 11. The lines show contours of constant yield. The distance between the adjacent contour lines parallel to temperature axis is greater for the 2-4-12 (2-10-15) mixture than for 5-4-12 (5-10-15) mixture, indicating that moisture is more critical with mixtures containing nitrate of potash. The optimum yield of 46.3% was noted at 507° F. and 6.55% moisture with the 5-4-12 (5-10-15) mixture, and the optimum yield of 43.8% at 447° F. and 15.8% moisture with the 2-4-12 (2-10-15) formulation.

The granules obtained with the 5-4-12 (5-10-15) mixed fertilizer containing

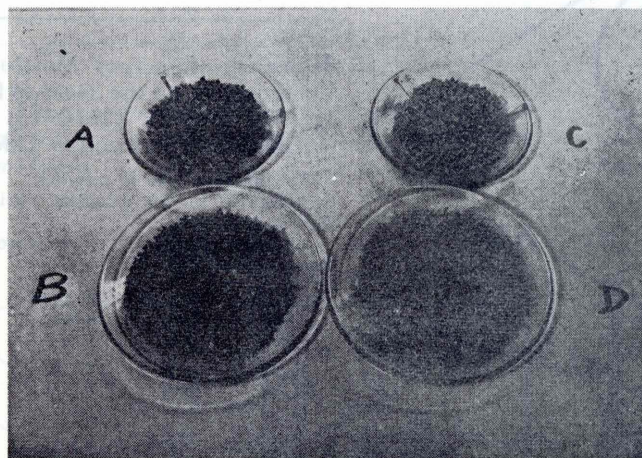


Figure 12. Photographs of granular products

- A: -6+8 size fraction of the 5-4-12 (5-10-15) grade containing potassium nitrate
- B: -8+16 size fraction of the 5-4-12 (5-10-15) grade containing potassium nitrate
- C: -6+8 size fraction of the 2-4-12 (2-10-15) grade containing potassium chloride
- D: -8+16 size fraction of the 2-4-12 (2-10-15) grade containing potassium chloride

potassium nitrate were more spherical and uniformly shaped than those obtained with the 2-4-12 (2-10-15) mixed fertilizer containing potassium chloride (Figure 12). The 5-4-12 (5-10-15) mixed fertilizer also gave more cohesive, less porous, and tougher granules.

The granule product in both mixtures was relatively more homogeneous than

reported in the literature since the raw materials used in this study were of finer mesh size.

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Potassium Nitrate as an Aid to Fertilizer Granulation

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Because of the availability of potassium nitrate as a new raw material, its effect as an aid to granulation was studied. Small batches of an 8-6.98-13.28 (8-16-16) grade mixed fertilizer containing potassium nitrate were granulated at different moisture and temperature levels in a laboratory Roto-Louvre dryer. The optimum moisture in the feed and inlet gas temperature were 9.6% and 450° F., respectively, for a maximum yield of - 6+20-mesh granules. The distribution of the three primary nutrients, nitrogen, phosphorus, and potassium, was determined in the various product size fractions. Similar experiments were made on an 8-6.98-13.28 (8-16-16) grade mixed fertilizer containing only potassium chloride. The optimum moisture in the feed, inlet gas temperature levels, yield, and nutrient distribution were also determined. At least 12.2% moisture was required for maximum yield, and the variation in nutrient distribution was greater.

POTASSIUM nitrate has a high agronomic value as a source of both nitrogen and potassium, but high cost has been a major limitation to its use in fertilizer formulations. The new production facilities of the Southwest Potash Corp. in Vicksburg, Miss., for a fertilizer grade potassium nitrate may make this material economically attractive. This has stimulated considerable interest in the granulation characteristics of mixed fertilizer formulations containing potassium nitrate and also in the physical properties of the resulting products. Studies (1-5) have shown that potassium nitrate is an aid to granulation. This paper presents results of laboratory studies using potassium nitrate in a vegetable grade fertilizer.

Granulation experiments in a laboratory Roto-Louvre dryer were made on an 8-6.98-13.28 (8-16-16) grade vegetable fertilizer to study the effects of moisture in the feed and of inlet gas temperature on the yield and distribution of plant nutrients in the various sized fractions. Two formulations were prepared (Table

I): Formulation I contained potassium nitrate which contributed 27% of the total potassium and 16% of the total nitrogen, and Formulation II contained potassium chloride as the only source of potassium. The solid raw materials (sieved through a 20-mesh Tyler screen) were mixed in a batch reactor and made to react with phosphoric acid and anhydrous ammonia. The moisture content was varied by adding predetermined amounts of water to fertilizer mixture.

The experimental equipment is shown in Figures 1 and 2. Details of the reactor-mixer have been reported (7). The batch reactor, in the center of Figure 1, was constructed from a section of 5-

inch O.D. Type 304 stainless steel tube with a 3/32-inch wall thickness. A stainless steel stirrer, consisting of a hollow shaft and four paddles, was used to mix the ingredients and to distribute the ammonia.

The bench scale Roto-Louvre dryer on the right in Figure 2 was 13 inches in diameter and 3 1/8 inches long, and operated at 7.4 r. p. m. The product was dried, screened, and analyzed for nitrogen, phosphorus, and potassium.

The time in the Roto-Louvre dryer was 30 and 45 minutes, respectively, for Formulations I and II. Final product temperature ranged from 196° to 280° F. To keep the number of variables at a minimum, inlet gas temperature was varied while residence time in the dryer

Table I. Formulations for 8-16-16 Grade Fertilizer

| Material | Analysis Basis, % N-P ₂ O ₅ -K ₂ O | Formulation No. | |
|------------------------------|--|-----------------|------|
| | | I | II |
| Triple superphosphate | 0-41.0-0 | 248 | 330 |
| Normal superphosphate | 0-20.6-0 | 492 | 339 |
| Phosphoric acid | 0-62.9-0 | 200 | 200 |
| Anhydrous ammonia | 82.2-0-0 | 90 | 90 |
| Ammonium sulfate | 20.5-0-0 | 313 | 438 |
| Potassium nitrate | 13.4-0-44.6 | 200 | — |
| Potassium chloride | 0-0-58.4 | 397 | 543 |
| Magnesium limestone | — — — | 100 | 100 |
| Borax | — — — | 10 | 10 |
| (Evaporation loss 50 pounds) | | Total 2050 | 2050 |



Figure 1. Mixer-reactor assembly

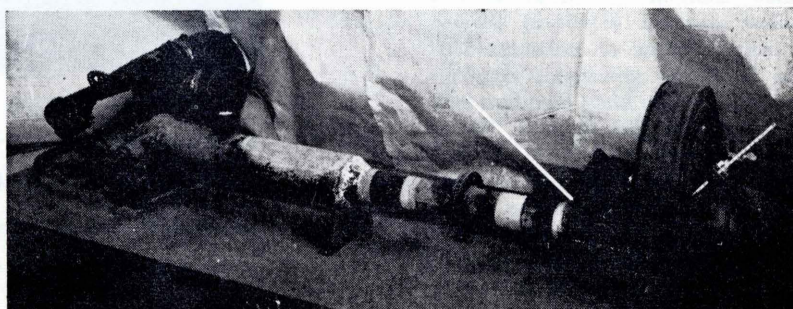


Figure 2. Granulator-dryer assembly

Table II. Relationship between Temperature and Moisture on Yield of -6 +20-Mesh Granules

| Run No. | Temp. of Inlet Gas, °F. | Moisture in Feed, % | Yield of -6 +20-Mesh Granules, % |
|---|-------------------------|---------------------|----------------------------------|
| Formulation I Containing Potassium Nitrate | | | |
| R-4 | 425 | 9.43 | 79.70 |
| R-5 | 425 | 9.08 | 47.56 |
| R-6 | 425 | 10.24 | 64.13 |
| R-10 | 425 | 9.02 | 64.13 |
| R-11 | 425 | 9.48 | 56.79 |
| R-12 | 425 | 10.53 | 69.80 |
| R-13 | 425 | 8.53 | 51.40 |
| R-14 | 425 | 9.37 | 39.04 |
| R-15 | 500 | 9.58 | 58.85 |
| R-17 | 350 | 9.80 | 69.33 |
| R-18 | 475 | 9.47 | 62.56 |
| R-19 | 375 | 9.26 | 43.65 |
| R-20 | 475 | 9.11 | 72.40 |
| R-21 | 375 | 9.50 | 63.24 |
| Formulation II Containing Only Potassium Chloride | | | |
| R-100 | 475 | 12.85 | 60.17 |
| R-101 | 475 | 11.78 | 67.51 |
| R-103 | 475 | 12.35 | 55.47 |
| R-104 | 475 | 12.32 | 48.96 |
| R-105 | 475 | 10.94 | 58.41 |
| R-106 | 475 | 12.28 | 58.88 |
| R-107 | 550 | 12.26 | 72.51 |
| R-108 | 400 | 12.69 | 52.86 |
| R-109 | 475 | 13.26 | 66.36 |
| R-110 | 475 | 11.43 | 56.36 |
| R-111 | 525 | 11.39 | 69.25 |
| R-112 | 525 | 12.90 | 71.41 |
| R-113 | 425 | 12.92 | 54.15 |
| R-114 | 425 | 10.94 | 67.14 |

was held constant. If product temperature had been the variable, it would have been necessary also to vary residence time.

Discussion

The experimental work followed the central composite rotatable design used by Boylan and Kamat (7). The central point was established by averaging four of six runs. The results of granulation experiments using each formulation are shown in Table II. The data in Table II were analyzed by the composite design and plotted in Figures 3 and 4. Runs 5, 14, 103, and 104 were rejected statistically.

Figure 3 shows the relationship between temperature and yield for both formulations. Formulation I, containing potassium nitrate, shows a maximum yield of approximately 70% at an inlet gas temperature of 455° F. Formulation II, without potassium nitrate, shows no maximum within the inlet gas temperature range investigated, although a maximum might be obtained at a higher temperature level.

Figure 4 shows the relationship between moisture and yield for both formulations. Formulation I shows a maximum yield of approximately 68% at 9.6% moisture. Formulation II shows

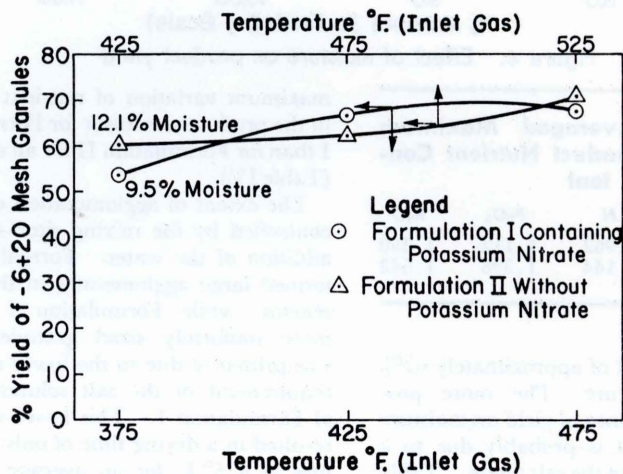


Figure 3. Effect of temperature on product yield

Table III. Nutrient Distribution in Various Sized Fractions

| Run No. | +6-Mesh Granules | | | -6 +14-Mesh Granules | | | -14 +20-Mesh Granules | | | -20-Mesh Granules | | |
|---|------------------|--|---------------------|----------------------|--|---------------------|-----------------------|--|---------------------|-------------------|--|---------------------|
| | N, % | P ₂ O ₅ , ^a % | K ₂ O, % | N, % | P ₂ O ₅ , ^a % | K ₂ O, % | N, % | P ₂ O ₅ , ^a % | K ₂ O, % | N, % | P ₂ O ₅ , ^a % | K ₂ O, % |
| Formulation I Containing Potassium Nitrate | | | | | | | | | | | | |
| R-4 | 9.04 | 17.72 | 16.18 | 8.83 | 17.62 | 16.13 | 7.69 | 18.63 | 16.26 | 7.24 | 17.76 | 17.32 |
| R-5 | 8.52 | 18.05 | 16.11 | 8.64 | 18.32 | 15.80 | 8.23 | 18.80 | 15.78 | 7.70 | 17.41 | 17.30 |
| R-6 | 7.73 | 17.88 | 16.48 | 7.55 | 18.45 | 16.70 | 6.94 | 18.39 | 17.71 | 7.23 | 18.29 | 17.21 |
| R-10 | 8.24 | 18.16 | 15.76 | 8.18 | 18.29 | 16.03 | 7.46 | 17.68 | 18.08 | 7.82 | 17.77 | 16.54 |
| R-11 | 8.56 | 17.77 | 16.53 | 8.56 | 18.06 | 16.03 | 7.80 | 19.15 | 16.09 | 7.49 | 18.13 | 17.51 |
| R-12 | 8.42 | 17.30 | 16.62 | 8.64 | 17.93 | 16.06 | 7.64 | 19.20 | 16.52 | 7.46 | 18.36 | 17.50 |
| R-13 | 8.61 | 18.13 | 16.11 | 8.64 | 18.12 | 15.59 | 8.00 | 19.00 | 15.80 | 7.56 | 17.50 | 17.96 |
| R-14 | 8.02 | 18.23 | 16.91 | 8.28 | 17.96 | 15.80 | 7.34 | 18.51 | 17.36 | 7.56 | 18.18 | 17.24 |
| R-15 | 7.78 | 18.24 | 16.94 | 7.72 | 18.52 | 16.77 | 7.26 | 19.02 | 17.56 | 7.36 | 18.81 | 17.05 |
| R-17 | 8.22 | 17.95 | 16.60 | 8.30 | 18.52 | 16.09 | 7.78 | 19.24 | 16.31 | 7.66 | 18.47 | 17.32 |
| R-18 | 8.28 | 18.09 | 16.31 | 7.89 | 18.73 | 16.41 | 7.21 | 19.66 | 16.88 | 7.36 | 18.66 | 16.98 |
| R-19 | 8.04 | 18.75 | 16.65 | 7.68 | 18.85 | 16.80 | 7.79 | 19.27 | 16.13 | 8.04 | 18.66 | 17.58 |
| R-20 | 8.60 | 17.84 | 16.64 | 8.20 | 18.38 | 16.00 | 7.38 | 19.62 | 16.02 | 7.09 | 17.72 | 16.86 |
| R-21 | 7.94 | 18.37 | 16.67 | 7.87 | 18.79 | 16.19 | 7.48 | 18.87 | 17.12 | 7.38 | 18.80 | 17.09 |
| Formulation II Containing Only Potassium Chloride | | | | | | | | | | | | |
| R-100 | 7.78 | 17.16 | 16.74 | 7.98 | 17.43 | 16.42 | 7.28 | 18.20 | 17.68 | 7.44 | 18.24 | 16.98 |
| R-101 | 8.01 | 18.01 | 16.74 | 7.96 | 18.81 | 16.53 | 7.08 | 19.28 | 17.42 | 7.18 | 19.30 | 17.15 |
| R-103 | 8.04 | 18.63 | 16.24 | 8.36 | 17.91 | 16.49 | 7.96 | 19.42 | 16.02 | 7.36 | 19.26 | 16.53 |
| R-104 | 7.70 | 18.62 | 16.53 | 7.55 | 19.41 | 16.21 | 7.06 | 19.85 | 16.50 | 6.91 | 19.00 | 17.44 |
| R-105 | 8.13 | 18.53 | 16.45 | 8.35 | 18.48 | 16.09 | 7.44 | 18.46 | 17.82 | 7.31 | 18.71 | 17.00 |
| R-106 | 8.38 | 18.37 | 16.35 | 7.98 | 18.66 | 16.50 | 7.20 | 18.62 | 18.36 | 7.36 | 18.80 | 17.24 |
| R-107 | 8.18 | 18.52 | 16.52 | 8.12 | 18.20 | 16.78 | 7.36 | 19.16 | 17.77 | 6.98 | 20.01 | 16.25 |
| R-108 | 8.80 | 18.25 | 16.00 | 8.90 | 16.95 | 16.27 | 8.16 | 18.52 | 16.10 | 7.56 | 18.91 | 17.13 |
| R-109 | 8.33 | 17.85 | 16.06 | 8.04 | 18.16 | 16.30 | 7.00 | 18.74 | 18.07 | 6.83 | 19.66 | 16.41 |
| R-110 | 8.55 | 19.41 | 15.20 | 8.60 | 18.10 | 15.27 | 7.52 | 17.25 | 18.91 | 7.38 | 18.26 | 18.08 |
| R-111 | 8.18 | 18.28 | 16.60 | 8.52 | 16.90 | 16.21 | 7.44 | 18.75 | 17.45 | 7.02 | 19.16 | 17.51 |
| R-112 | 8.18 | 18.23 | 16.83 | 8.18 | 18.41 | 16.27 | 7.44 | 19.50 | 17.14 | 6.96 | 19.17 | 17.76 |
| R-113 | 7.96 | 18.13 | 16.60 | 7.92 | 18.52 | 16.86 | 7.14 | 19.24 | 17.50 | 6.82 | 19.59 | 17.16 |
| R-114 | 8.27 | 18.40 | 16.10 | 8.66 | 18.60 | 15.78 | 7.40 | 17.58 | 19.08 | 7.48 | 18.50 | 17.79 |

^a Total.

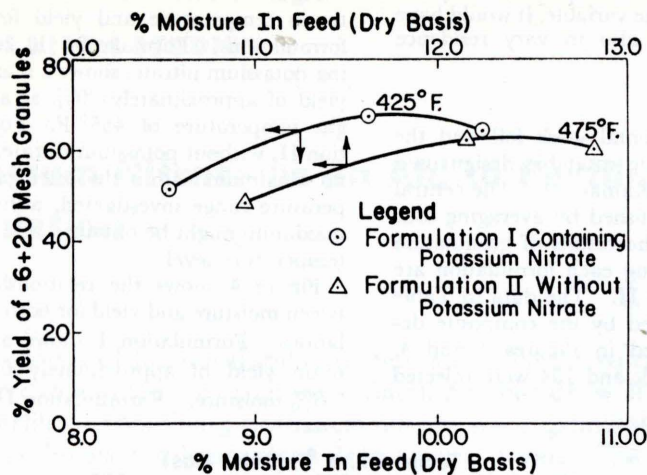


Figure 4. Effect of moisture on product yield

Table IV. Averaged Maximum Variation in Product Nutrient Content

| Formulation | N | P ₂ O ₅ | K ₂ O |
|-------------|-------|-------------------------------|------------------|
| I | 0.962 | 1.112 | 1.360 |
| II | 1.144 | 1.396 | 1.642 |

a maximum yield of approximately 62% at 12.2% moisture. The more pronounced dependence of yield on moisture in Formulation I is probably due to a higher solubility of the salt phase. Table III shows the nutrient distribution of both formulations in the various sized fractions of the granules. The averaged

maximum variation of nutrient content in the product was lower for Formulation I than for Formulation II for all nutrients (Table IV).

The extent of agglomeration could be controlled by the mixing time after the addition of the water. Formulation II formed large agglomerates in the batch reactor, while Formulation I formed more uniformly sized granules. This was primarily due to the lower moisture requirement of the salt solution phase of Formulation I. This lower moisture resulted in a drying time of only 30 minutes at 425° F. for an average product moisture content of less than 1%; Formulation II required 45 minutes drying at 475° F.

Conclusions

Because of the high solubility of potassium nitrate at the elevated temperatures of granulation, Formulation I, containing potassium nitrate, required only 9.6% moisture for a maximum yield of 67.6% in the -6 +20-mesh size fraction. Formulation II, without potassium nitrate, required 12.2% moisture for a maximum yield of 62.3%. This yield was considered good, since no recycle was employed.

For a product with an average moisture content of less than 1%, Formulation I required a drying time of 30 minutes at an inlet gas temperature of 425° F; Formulation II required 45 minutes at 475° F.

Literature Cited

- (1) Boylan, D. R., Kamat, D. V., J. AGR. FOOD CHEM. **12**, 423 (1964).
- (2) Hardesty, J. O., unpublished data.
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- (4) Jacob, K. D., *Comm. Fertilizer* **107**, No. 5, 23 (1963).
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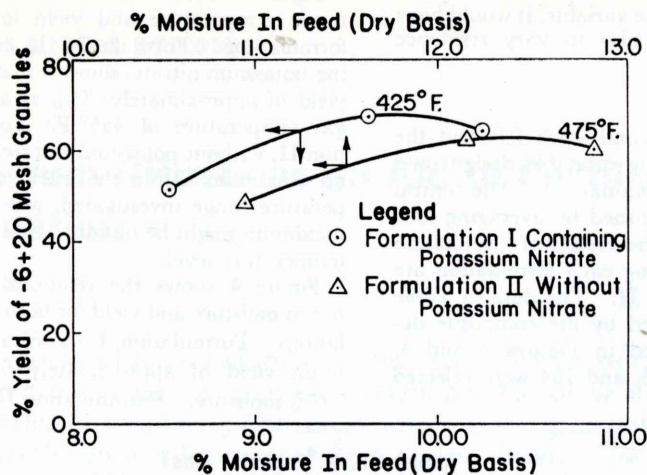


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FERTILIZER STABILITY

Decomposition of Mixed Fertilizers during Drying

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LARGE scale continuous processes and the use of high proportions of ammoniating solutions containing heat-sensitive salts have led to considerable difficulty in maintaining nitrogen guarantees during the manufacture of high analysis mixed fertilizers. A survey conducted by TVA (6) showed that the nitrogen content of 10-10-10 (10-4.37-8.30 NPK) and 12-12-12 (12-5.24-

9.96) grade fertilizers was consistently low. About half of the samples were deficient in nitrogen to an extent that exceeded the tolerances set by state laws. In these cases the manufacturers gave assurances that the nitrogen input was at least equal to and usually more than that guaranteed.

As part of the same investigation, a pilot plant study on the manufacture of 12-12-12 (12-5.24-9.96) grade fertilizers disclosed that the loss of nitrogen, in a form that would explain why the losses

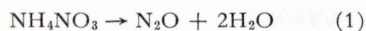
could not be detected by scrubbing samples of exhaust gas, resulted from the decomposition of ammonium nitrate to form N_2O or N_2 . Near the distributors of the pilot plant ammoniator there were localized areas of high acidity and observed temperatures as high as 260° F. Such conditions favor serious loss of nitrogen by decomposition of ammonium nitrate.

Stability of pure ammonium nitrate has been studied extensively (3-5, 7), and in the temperature range 210° to

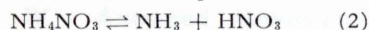
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Rate of decomposition of fertilizer mixtures prepared from reagent grade materials increased rapidly with temperature from 85° to 180° C. and as the pH changed from 3.9 to 2.8. In the absence of chloride ion there was no significant decomposition but addition of only 0.05 weight % chloride caused substantial loss of nitrogen. When either the nitrate or ammonium ion was missing no nitrogen loss occurred. Decomposition was found to result from the hydrolysis of monocalcium phosphate to give dicalcium phosphate and phosphoric acid; the latter reacted with ammonium nitrate or chloride to release nitrous oxide, elemental nitrogen, and chlorine. Addition of ammonium or potassium sulfate to the mixtures inhibited decomposition by preventing hydrolysis and the formation of phosphoric acid.

500° F. 98% of the decomposition has been found to occur as follows:



A reversible and endothermic dissociation reaction also takes place.



The presence of impurities has a significant influence on the decomposition of ammonium nitrate. Relatively small amounts of chloride and free acid may cause spontaneous decomposition at temperatures as low as 140° C.

Stability of ammonium nitrate in the presence of the salts commonly associated with it in commercial fertilizers and some of the factors influencing this stability were investigated by Borland and Schall (2), who gave particular attention to the effect of chloride, hydrogen, ammonium, and nitrate ions on stability. Decomposition was found to be extremely sensitive to the presence of chloride and free acid, but the presence of both ammonium and nitrate ions was required for significant nitrogen losses to occur. The stability of the fertilizer mixture was increased when sulfate-containing salts were present. Losses dropped markedly with increasing sulfate concentration and reached a minimum when the mole ratio of sulfate ion to ammonium nitrate approached 1 to 1. The fact that equimolar quantities of sulfate ion to ammonium nitrate were required was interpreted as evidence that the $\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$ double salt may have been involved, but no data were obtained to support this.

The present investigation deals with stability problems encountered primarily during the drying and subsequent operations in the manufacture of mixed fertilizers. The effects of composition, pH, and temperature have been studied. A series of reactions has been proposed which accounts for nitrogen and chloride losses and explains the stabilizing effect of ammonium sulfate and potassium sulfate in fertilizer mixtures.

Experimental Method

Fertilizer mixtures made from reagent grade materials were prepared batchwise as needed. One hundred-

gram portions were ground in a large mortar to ensure thorough mixing of the samples. The weighed samples were placed in a tared flask, stoppered with a vented cork, and held in a constant temperature bath at the desired temperature. Periodically the flask was withdrawn, allowed to cool, and after the adhering oil was removed, weighed and returned to the bath for another heating period. The loss in weight was recorded each time the sample was withdrawn, and the loss in weight of each constituent was determined from the initial and final analysis of the samples.

In a number of runs, the gaseous products were collected and analyzed to determine the amount of Cl_2 , N_2 ,

and N_2O produced. A schematic drawing of the apparatus is shown in Figure 1. The 500-ml. round-bottomed flask, which was used as the reactor, was connected to a series of absorbers fitted with fritted glass bubblers. The first absorber was charged with a 10% potassium iodide solution and the second was filled with potassium hydroxide pellets. From the absorbers, the gas passed through a U-tube, which was immersed in a dry ice-acetone bath, and then into the gas collector, a calibrated glass cylinder with a small opening at one end which was sealed with a serum cap. Gas samples were withdrawn from the collector through the serum cap with a hypodermic syringe and analyzed chromatographically.

Table I. Composition of 12-12-12 (12-5.24-9.96) Grade Fertilizer Control Mixtures

| Ingredients | Mixture, G. | | | | | |
|---|-------------|-------|-------|-------|-------|-------|
| | A | B | C | D | E | F |
| NH_4NO_3 | 12.40 | 12.40 | 12.40 | ... | ... | ... |
| NH_4Cl | 29.50 | ... | 29.50 | 45.90 | ... | 37.80 |
| $(\text{NH}_4)_2\text{SO}_4$ | ... | 36.00 | ... | ... | ... | ... |
| NaNO_3 | ... | ... | ... | ... | 59.70 | 13.20 |
| $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ | 21.30 | 21.30 | ... | 21.30 | 21.30 | 21.30 |
| CaHPO_4 | ... | ... | 23.00 | ... | ... | ... |
| KCl | 19.00 | ... | 19.00 | 19.00 | 3.40 | 19.00 |
| K_2SO_4 | ... | 22.20 | ... | ... | ... | ... |
| KNO_3 | ... | ... | ... | ... | 15.60 | ... |
| Sand | 17.80 | 8.10 | 16.10 | 13.80 | ... | 8.70 |

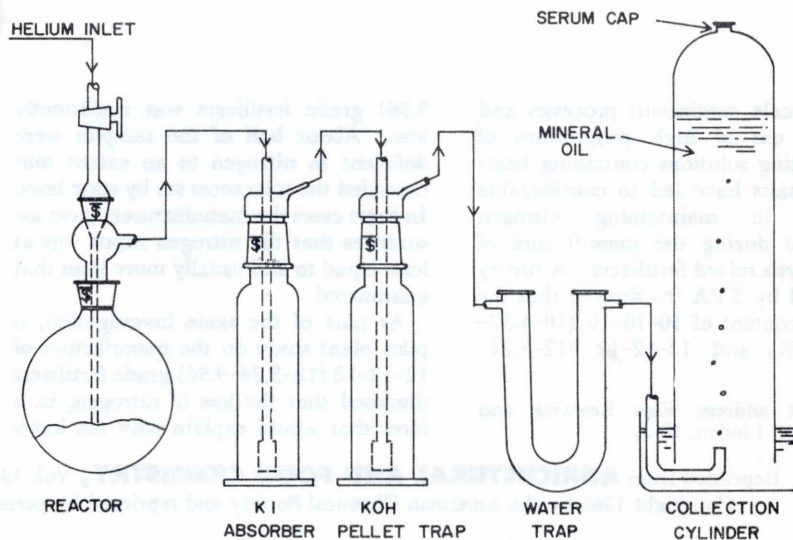


Figure 1. Gas collection apparatus

In the first absorber, Cl₂ was removed from the gas by reaction with the potassium iodide to liberate free iodine. The second absorber removed all acid-forming gases such as HCl, NOCl, and NO₂ which may have been present in small quantities. Any water vapor in the gas was condensed as it passed through the U-tube to the collector. Only N₂ and N₂O were present in the gas collected in the cylinder.

At the beginning of a run a 25-gram fertilizer sample was transferred to the reactor and the system was purged with helium for 15 minutes to ensure complete removal of air. The delivery tube was then inserted into the collection cylinder, which was filled with light mineral oil, and the reactor was placed in the constant temperature bath. After heating for the desired time, the system was again flushed with helium to ensure complete transfer of the gaseous reaction products through the absorbers and into the collector. The reactor containing the sample was then weighed to determine the total weight loss. By chemical analysis, the amounts of chloride, ammoniacal nitrogen, and nitrate nitrogen lost were determined. From the gas analysis, it was possible to determine the amount of chloride recovered as Cl₂ and the amount of nitrogen recovered as N₂ and N₂O.

The chromatographic determination of N₂ and N₂O was carried out on an F & M Scientific Corp. Model 500-A linear - programmed temperature gas chromatograph. A 1/4-inch o.d. copper tube, 2 meters long, and packed with Alcoa F-1 activated alumina, -30+60 U. S. standard mesh, was used to separate the two gases. Helium served as the carrier gas, and a flow rate of 30 ml. per minute was maintained through the column, which was kept at a temperature of 100° C. Under these conditions, the retention times were 5.8 and 12.3 minutes for N₂ and N₂O, respectively. Samples of the gas to be analyzed were injected into the column, and the amounts of N₂ and N₂O were determined by relating peak area and volume to the values obtained with known amounts of each gas under identical conditions.

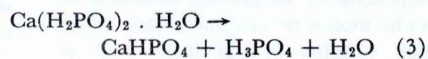
The compositions of the 12-12-12 (12-5.24-9.96) grade fertilizer control mixtures are presented in Table I. Mixtures B to F are similar to control mixture A, except that from each formulation one of the four ions—Cl⁻, H⁺, NH₄⁺, or NO₃⁻—was eliminated in order to determine the effect of each ion on the stability of the fertilizer. Modifications of the control mixtures were prepared in which the concentrations of the chloride, hydrogen, and sulfate ions were varied, to gain some idea of the effect of concentration of these ions on the stability of the fertilizer samples.

Effect of Temperature

Samples of mixture A were heated in the constant temperature bath for up to

8 hours. Losses were determined at 85°, 100°, 120°, 130°, 140°, and 180° C. The results, shown in Figure 2, indicate that the losses increase rapidly as the temperature is increased. At 85° C. there was no loss other than moisture, but at 100° C. there was some loss of nitrogen and chloride, indicating that decomposition had occurred at this temperature. At 180° C. the losses leveled off at 16.80 grams after only 1 hour of heating. The losses included 90% of the nitrate nitrogen originally present. Chloride and ammoniacal nitrogen losses were substantial, but potash and total P₂O₅ content remained unchanged.

In addition to total P₂O₅, analyses were made to check the extent of reversion of the water-soluble monocalcium phosphate to citrate-soluble dicalcium phosphate. At 85° C. there was no reversion of the monocalcium phosphate, but at the higher temperature levels significant amounts of dicalcium phosphate were formed during heating. Almost 50% of the water-soluble P₂O₅ had reverted to the citrate-soluble P₂O₅ at 180° C. The reversion reaction is as follows:

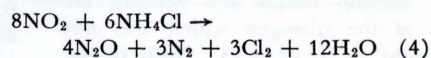


Equation 3 is important because the free acid formed enhances the decomposition of ammonium nitrate, particularly in the presence of chloride.

Experimental runs were made with mixture A in which the gas products were collected and analyzed. The studies were carried out at three temperature levels: 120°, 130°, and 140° C. The principal products were Cl₂, N₂, and N₂O. Table II shows that an average of 82.70% of the chloride lost from the samples was recovered as Cl₂. Material balances for nitrogen are presented in

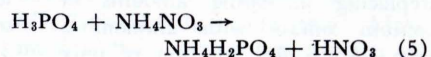
Table III. An average of 86.78% of the total nitrogen lost was recovered as N₂ and N₂O. The weight ratio of N₂O to N₂ was constant at about 2.13 to 1.00 over the temperature range investigated. Although temperature effects the rate of decomposition, it does not alter the course of the reactions taking place.

The nature of the gas products indicates that the principal reaction involved in the nitrogen and chloride loss is between ammonium nitrate and ammonium chloride. Besson and Rosset (7) found that what actually occurs is a reaction between nitrogen dioxide, an intermediate in ammonium nitrate decomposition, and ammonium chloride as follows:

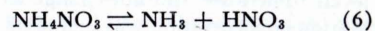


According to this equation, the weight ratio of N₂O to N₂ should be 2.09 to 1.00, very close to the weight ratio of 2.13 to 1.00 which was observed. In addition, Equation 4 indicates that the nitrate nitrogen loss should be slightly greater than the ammoniacal nitrogen loss, a fact which was also confirmed experimentally.

The nitrogen dioxide involved in Equation 4 is a product of nitric acid decomposition. Nitric acid can be produced in the fertilizer in several ways. The most important is probably the reaction of the free phosphoric acid formed by Equation 3 and ammonium nitrate.



Another possibility is the dissociation of ammonium nitrate:



However, at the temperatures used in

Table II. Recovery of Chloride from 25-Gram Samples of Mixture A, Heated 8 Hours

| Run | Temp., °C. | Cl ⁻ Lost | | Cl ⁻ Recovered as Cl ₂ | |
|---------|------------|----------------------|-------|--|-------|
| | | G. | % | G. | % |
| A-3-R-5 | 120 | 0.4428 | 6.21 | 0.3614 | 81.62 |
| A-3-R-6 | | 0.3493 | 4.96 | 0.2887 | 82.65 |
| A-4-R-5 | 130 | 0.7223 | 10.14 | 0.5753 | 79.65 |
| A-4-R-6 | | 0.7003 | 9.89 | 0.5902 | 84.28 |
| A-5-R-4 | 140 | 1.0583 | 14.76 | 0.9029 | 85.32 |

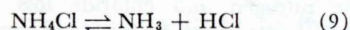
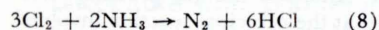
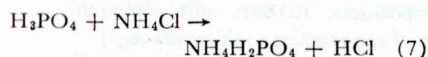
Table III. Recovery of Nitrogen from 25-Gram Samples of Mixture A, Heated 8 Hours

| Run | Temp., °C. | N ₂ Lost | | N ₂ Recovered, G. | | Recovery, % | Weight ^a Ratio, N ₂ O:N ₂ |
|---------|------------|---------------------|-------|------------------------------|------------------|-------------|--|
| | | G. | % | N ₂ | N ₂ O | | |
| A-3-R-5 | 120 | 0.3324 | 11.15 | 0.1195 | 0.1595 | 83.94 | 2.10 |
| A-3-R-6 | | 0.2619 | 8.68 | 0.1000 | 0.1280 | 87.06 | 2.01 |
| A-4-R-5 | 130 | 0.6606 | 22.09 | 0.2570 | 0.3465 | 91.36 | 2.12 |
| A-4-R-6 | | 0.6541 | 21.78 | 0.2204 | 0.3168 | 82.13 | 2.26 |
| A-5-R-4 | 140 | 0.8814 | 29.26 | 0.3294 | 0.4588 | 89.42 | 2.19 |

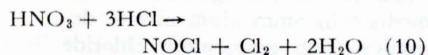
^a N₂ recovered as N₂O is converted to equivalent grams N₂O to calculate weight ratio.

this work, the dissociation may not be significant.

It is likely that most of the chloride not recovered as Cl_2 was lost as HCl . Several side reactions which would result in formation of HCl are:



Since the fertilizer is distinctly acidic, the following reaction may also occur:



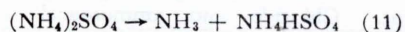
This reaction would also account for some of the nitrogen which was not recovered as N_2 or N_2O . Most of the nitrogen which was not recovered was probably lost as NH_3 , HNO_3 , or NO_2 . No attempt was made to isolate these gases.

Effect of Chloride Ion

One hundred-gram samples of mixture B which contained no chloride were heated in the constant temperature bath at 130°C . for 16 hours. An observed loss of only 2.10 grams indicated that the presence of chloride was necessary for significant decomposition to occur. Modifications of control mixture B were prepared in which the chloride concentration was varied from 0.05 to 10% by replacing increasing amounts of ammonium sulfate with ammonium chloride. With the addition of only 0.05% chloride, the losses increased markedly and reached a plateau at the 0.50 level. The losses did not change as the chloride concentration was increased beyond 0.50% (Figure 3).

In the mixture which contained no

chloride, the nitrogen lost was almost all ammoniacal nitrogen. This is in contrast to the results obtained with mixture A, where the nitrate nitrogen loss was always somewhat greater than the ammoniacal nitrogen loss. It is evident that when chloride is not present, the reactions involved in the decomposition are not the same. The nitrogen loss in the absence of chloride in mixture B may be due to the decomposition of ammonium sulfate which is present in high concentration.



The addition of chloride even in trace amounts increases the nitrate nitrogen loss. At a chloride concentration of 0.50%, the total nitrogen loss is again divided between ammoniacal nitrogen and nitrate nitrogen in the same manner as in mixture A.

Effect of Acidity

The acidity of mixture C was varied by preparing 100-gram samples in which the relatively neutral dicalcium phosphate was replaced by increasing amounts of the acidic monocalcium phosphate. The samples, ranging in pH from 2.80 to 6.30, were heated in the constant temperature bath at 130°C . for 16 hours. The pH was determined by suspending a 1-gram sample in 10 ml. of water adjusted to pH 7.00.

A sharp drop in weight loss from 15.68 to approximately 1.00 gram was observed as the pH increased from 2.80 to 3.90. In the sample of pH 2.80, the weight loss included 89.63% of the nitrate nitrogen, 15.83% of the ammoniacal nitrogen, and 13.24% of the chloride present in the preheated sample. In samples of pH greater than 3.90, no losses were observed other than moisture.

Effect of Ammonium and Nitrate Ions

Samples (100-gram) of mixture D from which the nitrate ion was absent and mixture E which contained no ammonium ion were heated in the constant temperature bath at 130°C . for 16 hours. The losses in weight were 1.54 and 1.49 grams, respectively. Analyses showed that these losses were moisture only. Mixture F, in which the nitrate ion was supplied by sodium nitrate and the ammonium ion by ammonium chloride, lost 15.31 grams upon heating at 130°C . for 16 hours. Thus, the presence of both ions is required for decomposition to occur. They need not be supplied by ammonium nitrate, since equivalent losses occurred when the ions were supplied by other ammonium and nitrate salts.

Effect of Sulfate Ion

Since the experiments with mixture B indicated that the sulfate ion tended to stabilize the mixture, this effect was further investigated. A series of samples containing increasing amounts of sulfate ion was prepared from a sulfate-free mixture G. The basic formula of this mixture was: 12.40 grams of NH_4NO_3 , 29.40 grams of NH_4Cl , 21.40 grams of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, and 36.80 grams of sand. The sulfate content was varied from 0.0% to a maximum of 35.0% by replacing sand with increasing amounts of $(\text{NH}_4)_2\text{SO}_4$, K_2SO_4 , or CaSO_4 . One hundred-gram samples of the mixtures were heated in the constant temperature bath for 16 hours at 130°C .

Losses from the mixtures in which the sulfate was added as $(\text{NH}_4)_2\text{SO}_4$ or K_2SO_4 dropped sharply as the concentration of sulfate ion increased and reached a minimum of approximately

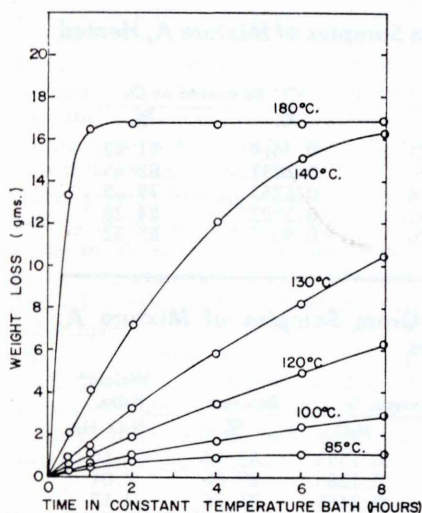


Figure 2. Effect of temperature on decomposition of 100-gram samples of mixture A

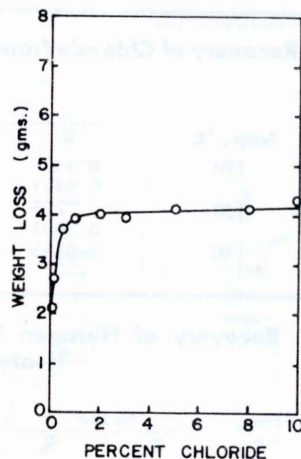


Figure 3. Effect of chloride concentration on decomposition of 100-gram samples of mixture B, heated 16 hours at 130°C .

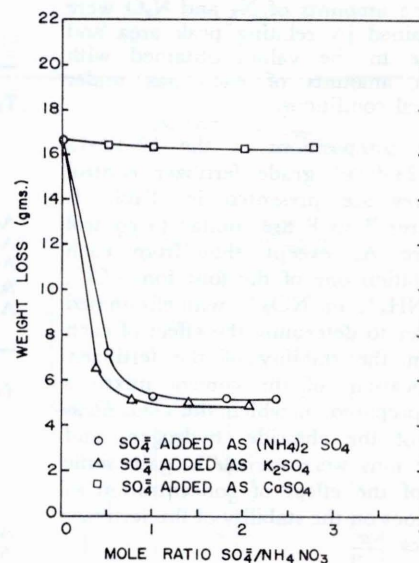


Figure 4. Effect of sulfate ion on stability of 100-gram samples of mixture G, heated 16 hours at 130°C .

Table IV. Effect of Sulfate Ion on Reversion of Water-Soluble P₂O₅ in 100-Gram Samples of Mixture G, Heated 16 Hours at 130° C.

| Sulfate Salt Added | % SO ₄ ⁻² | Water-Soluble P ₂ O ₅ , G. | | Citrate-Soluble P ₂ O ₅ after Heating, G. |
|---|---------------------------------|--|-------|---|
| | | Before | After | |
| (NH ₄) ₂ SO ₄ | 0.00 | 11.92 | 7.24 | 4.68 |
| | 7.21 | 11.98 | 8.67 | 2.31 |
| | 14.58 | 12.02 | 11.89 | 0.13 |
| | 26.76 | 12.16 | 12.07 | 0.09 |
| | 34.98 | 12.07 | 11.96 | 0.11 |
| K ₂ SO ₄ | 5.52 | 11.87 | 9.04 | 2.83 |
| | 11.02 | 11.97 | 11.80 | 0.17 |
| | 20.28 | 12.04 | 11.94 | 0.10 |
| | 28.43 | 12.01 | 11.87 | 0.14 |

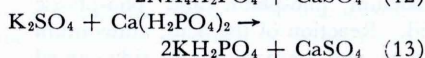
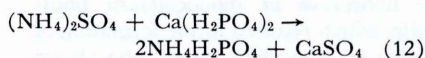
5.0 grams at a sulfate content of 11%. Whether the sulfate was supplied by the ammonium salt or the potassium salt, the 5.0-gram level was approached as the mole ratio of sulfate ion to ammonium nitrate approached 1 to 1. As can be seen from Figure 4, the addition of sulfate as CaSO₄ did not have the same stabilizing effect.

Results of the P₂O₅ analyses in Table IV show that the reversion of water-soluble P₂O₅ to citrate-soluble P₂O₅ is reduced by the addition of sulfate as (NH₄)₂SO₄ or K₂SO₄. At a sulfate concentration of 11% almost all of the P₂O₅ remained in the water-soluble form. Nitrogen and chloride losses were also reduced considerably as the sulfate concentration increased (Table V).

X-ray diffraction studies were made on two of the heated samples: in one the sulfate was supplied by the ammonium salt and in the other, by the potassium salt. Because of the complexity of the mixtures, it was difficult to identify the compounds. In the mixture where the

sulfate was added as ammonium sulfate, NH₄H₂PO₄, NH₄Cl, CaSO₄, and (NH₄)₂SO₄ were identified. Compounds identified from the mixture in which the sulfate was added as potassium sulfate were KH₂PO₄, NH₄Cl, CaSO₄, and K₂SO₄.

The results of the P₂O₅ analyses and the x-ray diffraction studies indicate that the following reactions probably occur:



These reactions explain why the P₂O₅ remains water-soluble if sufficient ammonium sulfate or potassium sulfate is present in the mixture. Reactions 12 and 13 are also important in inhibiting the decomposition of the fertilizer because with the removal of calcium as insoluble, thermostable calcium sulfate, the reversion of the phosphate to citrate-soluble dicalcium phosphate cannot occur. This prevents the formation of free phosphoric acid according to Equa-

Table V. Nitrogen and Chloride Losses from 100-Gram Samples of Mixture G, Heated 16 Hours at 130° C.

| Sulfate Salt Added | % SO ₄ ⁻² | Total N Lost, G. | Cl ⁻ Lost, G. |
|---|---------------------------------|------------------|--------------------------|
| (NH ₄) ₂ SO ₄ | 0.00 | 4.24 | 3.97 |
| | 7.21 | 4.11 | 3.84 |
| | 14.58 | 1.13 | 0.92 |
| | 26.76 | 0.47 | 0.33 |
| | 34.98 | 0.44 | 0.39 |
| K ₂ SO ₄ | 5.52 | 0.43 | 0.31 |
| | 11.02 | 1.85 | 1.78 |
| | 20.28 | 0.67 | 0.39 |
| | 28.43 | 0.46 | 0.32 |

tion 3. With the control of the free acid in the mixture Reactions 4, 5, and 7 cannot proceed and the decomposition is effectively stopped. It is evident from Equations 12 and 13 that addition of the sulfate to the fertilizer as calcium sulfate would not stabilize the mixture. This was confirmed experimentally.

The maximum stability of the fertilizer was obtained as the mole ratio of sulfate ion to ammonium nitrate approached 1 to 1. However, considering Reactions 12 and 13, it would appear that the maximum stability should be obtained when the mole ratio of sulfate ion to monocalcium phosphate approaches 1 to 1. In Figure 5, the weight loss from mixture G has been plotted against the SO₄⁻²/Ca(H₂PO₄)₂ mole ratio. Maximum stability was obtained when the ratio was slightly more than 1 to 1, and to confirm the significance of this ratio, mixture H was prepared in which the ammonium nitrate concentration was

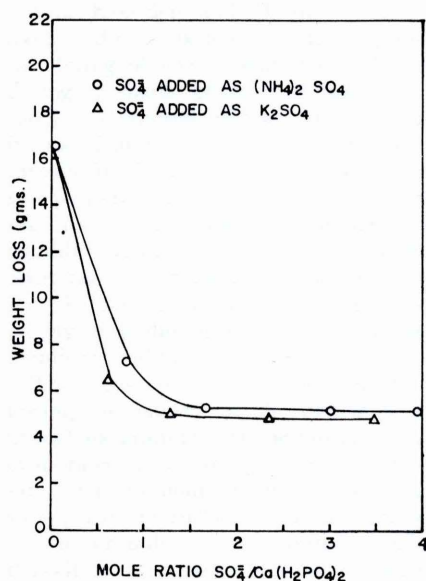


Figure 5. Effect of sulfate ion on stability of 100-gram samples of mixture G, heated 16 hours at 130° C.

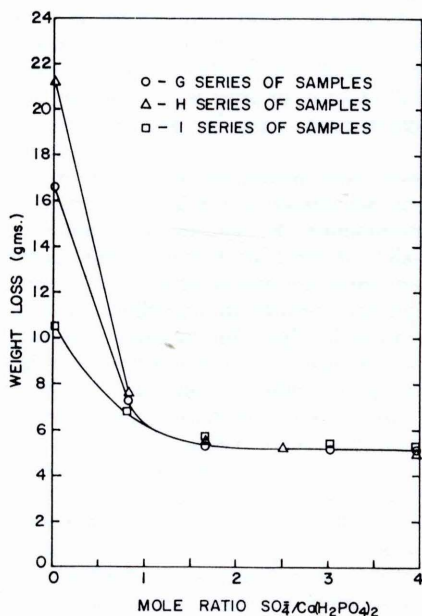


Figure 6. Weight loss data for G, H, and I series of mixtures, plotted against SO₄⁻²/Ca(H₂PO₄)₂ mole ratio

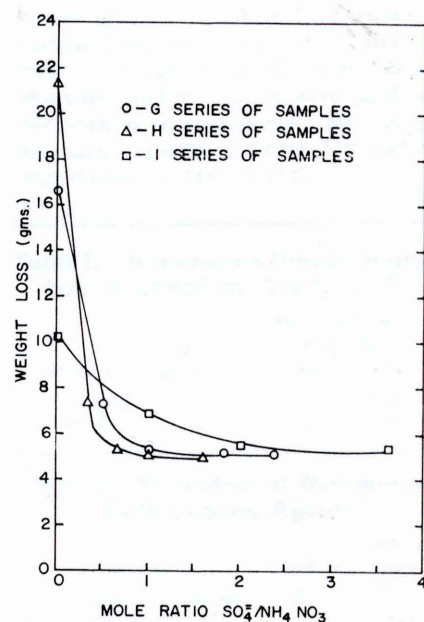


Figure 7. Weight loss data for G, H, and I series of mixtures, plotted against SO₄⁻²/NH₄NO₃ mole ratio

50% greater than in mixture G. The sulfate concentration was varied in the same manner as with mixture G. Weight loss was greater in mixture H than in mixture G, but dropped sharply as the sulfate concentration increased and approached a minimum of 5.0 grams as the mole ratio approached 1 to 1.

Mixture I, which contained 50% less ammonium nitrate than mixture G, did not lose so much weight as mixture G, as was expected. The losses again reached a minimum at about the same mole ratio of sulfate ion to monocalcium phosphate as in mixture G and H. For comparison of the results of the runs made with the G, H, and I series of samples, the weight loss data for all runs were plotted against the $\text{SO}_4^{-2}/\text{Ca}(\text{H}_2\text{PO}_4)_2$ mole ratio in Figure 6 and the $\text{SO}_4^{-2}/\text{NH}_4\text{NO}_3$ mole ratio in Figure 7. Maximum stability is obtained in all three mixtures as the $\text{SO}_4^{-2}/\text{Ca}(\text{H}_2\text{PO}_4)_2$ mole ratio reaches 1 to 1. This is not true as the $\text{SO}_4^{-2}/\text{NH}_4\text{NO}_3$ mole ratio approaches 1 to 1 in the fertilizer mixtures. In mixture H, maximum stability is reached at a $\text{SO}_4^{-2}/\text{NH}_4\text{NO}_3$ mole ratio of 0.5 to 1, and in mixture I, at a 2 to 1 mole ratio.

These results indicate that an important factor in inhibiting the decomposition is to prevent the formation of free acid in the mixture. This can be accomplished by adding either ammonium sulfate or potassium sulfate to the fertilizer.

Conclusions

The stability of laboratory fertilizer mixtures was found to be dependent upon temperature, acidity, concentration of chloride and sulfates, and the presence of both ammonium and nitrate ions. Under certain conditions decomposition of the samples was initiated at temperatures as low as 100° C. and the rate of decomposition increased rapidly with temperature. Nitrogen, nitrous oxide, and chlorine were identified as the principal gaseous reaction products.

A key reaction in decomposition was the hydrolysis of monocalcium phosphate, which resulted in the formation of dicalcium phosphate and phosphoric acid. Reaction of the acid, ammonium nitrate, and ammonium chloride caused substantial losses of nitrogen and chloride

from the fertilizer mixtures. The effects obtained in these tests are those which would be observed during the commercial manufacture of fertilizer blends where unammoniated superphosphate is used. The stabilizing effect of ammonium sulfate or potassium sulfate in the fertilizer blends was conclusively demonstrated.

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Use of Diatomaceous Earth to Accelerate Drying of Ammonium Nitrate

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The drying characteristics of ammonium nitrate prills coated with diatomaceous earth were compared to those of noncoated material using both a tray and small rotary dryer. Nitrate with 3 to 4% coating agent dried from 2.5 or 3.0% to 0.2% moisture, dry basis, in about one third the time required for noncoated material. This amount of coating agent gave the greatest increase in drying rate. The relative difference in drying rate between coated and uncoated material increased as the moisture content decreased. Air velocity had no significant effect. In the rotary dryer less fines were formed during the drying of coated material. A mechanism to account for the phenomena observed is postulated and supported by photomicrographs of individual prill cross sections.

AMMONIUM NITRATE is widely used in this country in fertilizers and as an explosive. The Stengel and conventional prilling processes are generally used in its manufacture. In the conventional prilling process the solid prills are formed from a solution containing 3 to 5% water and the resulting product is dried. If the moisture content is not reduced to a few tenths of 1% or if the ammonium nitrate later picks up water from the atmosphere, the particles cake and become unmanageable.

Removal of moisture from solid ammonium nitrate is difficult and the operation requires a series of large rotary dryers frequently supplied with specially conditioned air. Consequently the drying operation represents a significant part of the cost of manufacturing ammonium nitrate.

Van Krevelen and Hoftijzer (4, 5) have studied bulk and individual granule drying of several materials. When drying a single granule of nitrochalk (60% ammonium nitrate, 40% marl) it was found that the granule dried rapidly for the first 5 minutes (a falling rate period) and then at a lower constant rate for 4 hours before attaining the equilibrium moisture content. The constant rate of drying for nitrochalk was only 1/1500 of that for a similar completely insoluble granule dried under identical conditions.

These investigators assumed the following mechanism for the drying of a nitrochalk granule: At the outset water evaporates at a constant rate from a saturated ammonium nitrate solution supplied to the surface from the interior of the granule; next nitrate crystals deposit at the surface, gradually closing the pores through which the solution

has been flowing to the surface and thus decreasing the drying rate; finally all the pores are closed and the flow of solution to the surface is stopped. Soon the entire granule reaches the temperature of the drying air and drying at a constant but greatly reduced rate takes place by vaporization within the pores of the granule, followed by diffusion of the water vapor through the crystal "shell" at the surface.

Studying the problem of drying nitrochalk in a rotary dryer using grain sizes from about 25- to 32-mesh, the same investigators found the over-all coefficient of mass transfer for the final constant rate period to be nearly the same as that for a single granule. The reason suggested for this was that in both cases the rate-determining process was the diffusion of water vapor through the thin layer of ammonium nitrate which obstructed the pores of the granules. There is every reason to believe that these same conclusions can be used to account for the slow drying of pure ammonium nitrate.

The purpose of the present work was to learn more about a means for accelerating the drying of ammonium nitrate first reported in 1956 by Giachino (2). His invention consisted essentially of mixing a moisture-containing granular material of high moisture-diffusion resistance which was to be dried, with a water-insoluble, inorganic material—e.g., diatomaceous earth—having a large surface area, and then drying the mixture in a stream of air. This, it was reported, greatly increased the drying rate of high moisture diffusion resistance material. Results obtained by Giachino in a small rotary dryer using 3% coating agent on ammonium nitrate are shown in Table I. No work has been done by the consignee beyond that which led to the original discovery (3).

Fertilizer grade nitrate particles are normally conditioned prior to shipment or storage, by either coating or dusting with a parting agent (diatomaceous earth is most commonly used) to retard adsorption of water and reduce the effects of water which may be present. Hence incorporation of the Giachino discovery into the ammonium nitrate manufacturing process could call for no more than adding the parting agent before instead of after drying.

Diatomaceous earth is a hydrous opaline form of silica composed of innumerable skeletons of microscopic aquatic plants. Impurities include small amounts of sand, clay, calcium carbonate, magnesium carbonate, volcanic ash, and organic matter. Chemically combined water varies from 2 to 10%. The material is usually mined from a quarry or open pit, then dried, pulverized, and sometimes calcined. Table II gives the properties of the two Johns-Manville products which were used in this work as coating agents; the run of the mine material is Celite 379 and a refined product, Micro Cel E.

Table I. Ammonium Nitrate Drying Data Reported by Giachino (2)

| Material | Drying Time, Min. | Moisture Content, Wt. % | |
|----------|-------------------|-------------------------|-------|
| | | Initial | Final |
| Uncoated | 20 | 1.6 | 1.10 |
| Coated | 20 | 1.5 | 0.34 |

Table II. Properties of Diatomaceous Earth Coating Agents (1)

| Properties | Micro Cel E | |
|-----------------------------|-------------|----------|
| | Celite 379 | Celite E |
| Bulk density, lb./cu. ft. | 8.2 | 5.4 |
| Water absorption, wt. % | 195 | 560 |
| Surface area, sq. meters/g. | 10-15 | 95 |
| Av. particle size, microns | 0.5-1.5 | 2.1 |

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Tray Dryer Tests

A schematic drawing of the tray dryer is shown in Figure 1. Air was partially recirculated past steam-heated coils and over the drying tray. A needle valve was used to regulate steam flow to the coils and consequently the air temperature. Pans of water were placed in the dryer to maintain a constant humidity. The drying tray was suspended by a rod from one arm of a pan balance mounted on top of the dryer. The rod passed through a small hole in the top of the dryer.

The drying tray was insulated to reduce heat transfer through the bottom and sides and sheet metal cowlings were fitted to the ends to minimize air turbulence. A wet- and dry-bulb thermometer set was used to measure the humidity in the dryer and an anemometer the air velocity over the tray.

The ammonium nitrate used was a conventional prilled product (-6+14 mesh) obtained from the Spencer Chemical Co. The material was dried prior to shipping but was not coated. To prepare test samples, moisture in the form of a saturated solution was added to dry ammonium nitrate in a small twin-shell blender. This resulted in a uniform product that gave drying curves typical of run of the plant prills and to which the coating agent was added while the moist fertilizer was still in the blender. The Karl Fischer reagent was used to determine moisture in the fertilizer both before and after drying.

To carry out a drying test the dryer was turned on and allowed to come to equilibrium. The moisturized and coated prills were placed in the tray and the tray was hung from the balance. As drying progressed, total tray weight was recorded as a function of time. For all tests the dry bulb temperature was maintained at 160° F., the wet bulb at 64° F., and the air velocity at 12.4 feet per second.

The drying rate of ammonium nitrate as a function of the amount of Celite 379 coating added was first studied. Figure 2 shows the effect of weight per cent coating on drying time, expressed as the fraction of time required to dry uncoated material under identical conditions. Data were taken for three different final moisture contents.

From these curves it can be seen that the least drying time is required (when drying from 2.5% initial moisture) for a coating level of about 3.5% by weight Celite 379. The greatest increase in drying rate occurs at the lower moisture levels. The fraction of time required to dry material from 2.5 to 0.4 or 0.5% moisture is greater than that required to dry from 2.5 to 0.2% moisture for the same amount of coating. Figure 3 shows that the increase in drying rate varies inversely with moisture content.

Similar tests were carried out using Micro Cel E, which has greater adsorptive capacity than Celite 379 and a higher surface area per gram. While

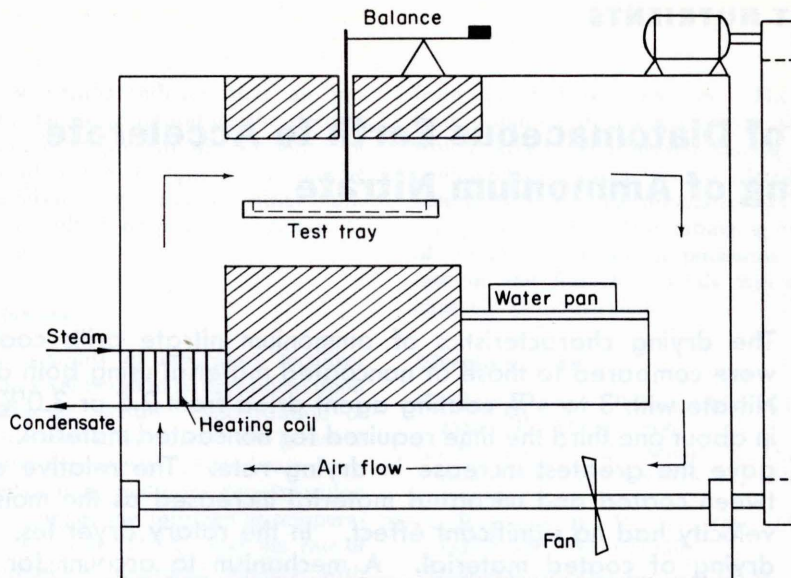


Figure 1. Schematic diagram of tray dryer

the data are not as complete for Micro Cel E as for Celite 379, Micro Cel E is the more effective agent for increasing the drying rate of ammonium nitrate (Figure 4). At 3.0% coating agent, the drying time fraction when going from 2.5 to 0.2% moisture was 0.33 for Celite 379 and 0.19 for Micro Cel E. Similar results were obtained for other moisture ranges.

In other tests the air velocity over the tray was varied while all other conditions were held constant. No change in drying time was observed, which indicated that the drying mechanism was not simply a case of surface evaporation.

Rotary Dryer Tests

The dryer used was a Bartlett-Snow-Pacific Model T-9091 (Figure 5). It was operated in a countercurrent manner with finned steam coils used to preheat the entering air. Steam inlet valves to each of three banks of coils made possible control of the inlet air temperature for any one run to within $\pm 0.5^\circ$ F. Two dampers controlled the air velocity from 0 to a maximum of 27 feet per second.

The dryer shell measured approximately 6 inches in i.d. by 3 feet in length. The feed end had a 1-inch retainer ring to prevent loss during charging. There were six evenly spaced flights parallel to the axis of rotation and extending halfway down the shell at the feed end, and six identical flights at the product end, the two sets of flights being offset by 30°.

Wet- and dry-bulb mercury thermometer sets were used to measure inlet and outlet air temperatures.

Tests were conducted using moisturized and coated prills prepared in the same manner as those used in the tray dryer tests. All runs were made with an initial moisture content of approximately 3%, a linear air velocity of 12.3 feet per second, and a rate of rotation of 10 r.p.m.

One hour prior to a run the blower and steam to the dryer were turned on to

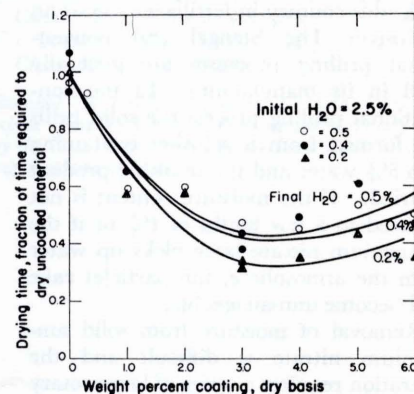


Figure 2. Time required to dry ammonium nitrate from 2.5% water for various amounts of Celite 379 coating and different final moisture contents

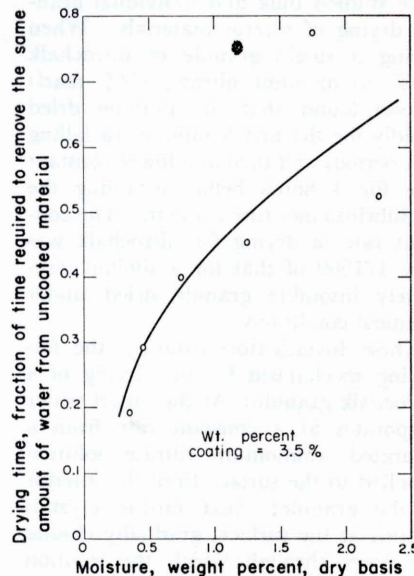


Figure 3. Incremental drying times for ammonium nitrate coated with 3.5% Celite 379 at various moisture levels

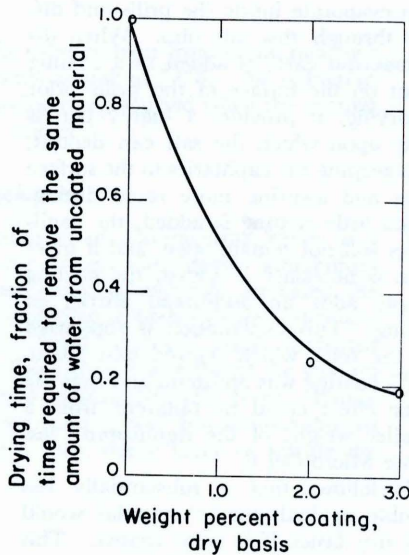


Figure 4. Time required to dry ammonium nitrate from 2.5 to 0.2% water for various amounts of Micro Cel E coating

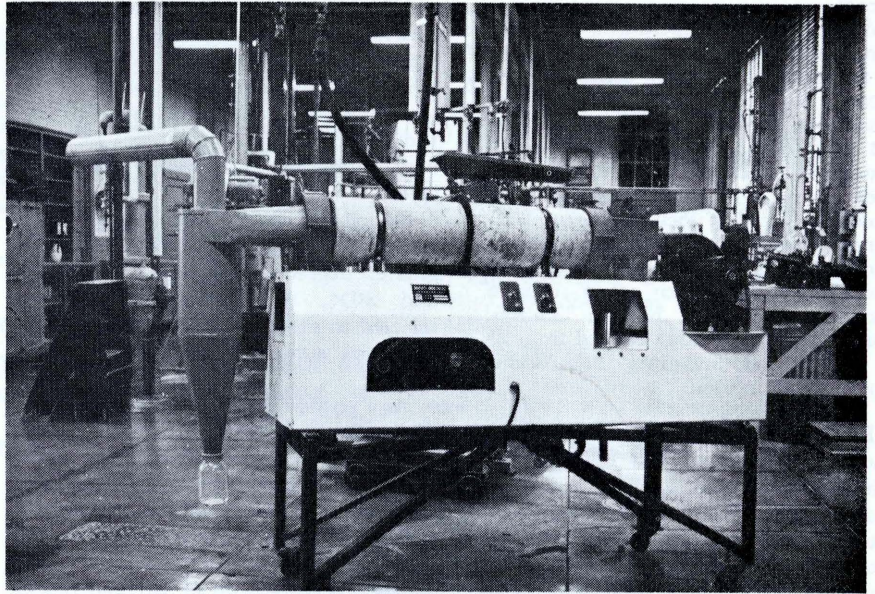


Figure 5. Steam direct-heated, countercurrent, rotary dryer

allow time to reach equilibrium and adjust the inlet air temperature. Preliminary tests were conducted in a batch manner by rapidly charging 1200 grams of prepared prills (7% of the dryer volume) to the dryer and then removing 6- to 8-gram samples periodically until the run was terminated. In no run did the total amount of material removed exceed 50 grams. The inlet and outlet air temperatures were held constant to $\pm 1^\circ$ F.

Moisture content as a function of inlet air temperature and drying time is shown in Figure 6. From the results of these tests 190° F. was selected as a standard temperature at which to determine the optimum per cent coating agent. This temperature closely corresponds to that used industrially to dry ammonium nitrate prills.

Figure 7 shows the effect of per cent coating agent on moisture content. As can be seen, a 4.0% coating reduced the moisture content from 3.0 to 0.38 in 60 minutes. In the same period a 3.0% coating gave a final moisture content of

0.24%, while 2.5% coating gave 0.33%. These data indicate that approximately 3.0% coating is optimum from the standpoint of drying time required to reach a given final moisture content.

During the above rotary dryer tests it was observed that uncoated prills produced more fines during drying than did the coated material, time in the dryer being the same (60 minutes). This effect was confirmed by screen analyses of the dryer product from runs made with no coating and with 3.0% coating. Fines (-14-mesh) in the uncoated product comprised 12% by weight; for the coated material only 4%. Although "dusting" from suspended solids in the exit air stream was very slight in all tests, it was noticeably greater with the uncoated material.

This phase of work culminated in a continuous run on the rotary dryer in which the drying conditions were the same as in the batch tests. Prills were fed to the dryer at a rate that gave a residence time of 70 minutes, during

which the moisture content was reduced from 3.0 to 0.2%. Inlet air temperature was 190° F. and level of coating 3.0%.

Photomicrographs

To determine changes occurring during drying, thin sections of individual prills were prepared. Two clear glass slides, A and B, were placed in an oven at about 140° F. After they had reached oven temperature, a drop of thermoplastic resin was placed on each slide. Then on slide A, 15 or 20 prills were placed in the resin and that slide was removed from the oven and placed in a desiccator.

When the resin had set, the slide was removed from the desiccator and the prills were ground off to approximately their horizontal axial plane, using a rough glass plate and kerosine as a lubricating agent. Slide A was then placed back in the desiccator for a short time to allow the adhering traces of kerosine to evaporate. It was then placed face down on slide B, which was still in the oven, and pressed firmly to obtain tight adhesion. Both slides were

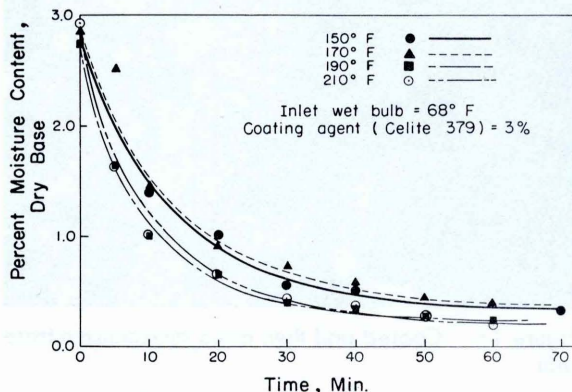


Figure 6. Effect of inlet air temperature on drying time

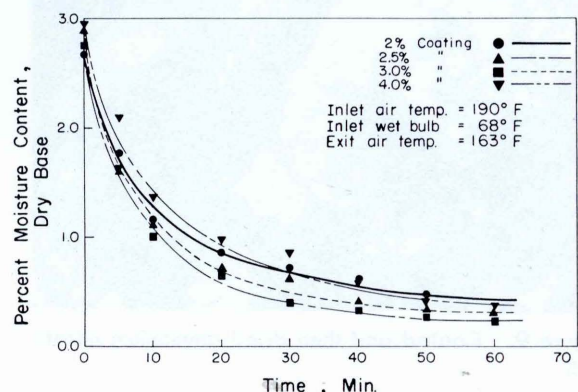


Figure 7. Effect of amount of coating added on drying time

then removed from the oven and allowed to cool.

When at room temperature, the slides were placed back in the oven with slide A on the bottom resting on a metal plate. Because A was heated faster because of conduction from the plate, it could be slid away from B with the prill "halves" remaining attached to B with their flat sides down. This slide could then be cooled and a thin section prepared by grinding the prills to a wafer with a thickness of about 30 microns. Photomicrographs were then taken using a microscope with a built-in 35-mm. camera. Magnification ranged from 25 to 600 \times and fine-grain Pan-Atomic Kodak film was used.

Figures 8 through 11 are selected photomicrographs typical of those obtained from the thin sections. Figure 8 shows an uncoated, nondried prill which was hollow in the center, a condition already generally known to exist in conventional prills. A coated and dried prill is shown at somewhat greater magni-

fication (100 \times in place of 50 \times) in Figure 9. The layer of coating agent is clearly discernible, as are crystals of nitrate which were deposited on the outside of the layer from solution diffusing to the surface and then evaporating. Individual nitrate crystals can be seen both within the prill and in the outer layer.

Figures 10 and 11 are of a different coated and dried prill and are at a greater degree of magnification, 160 \times and 400 \times , respectively. These were selected to show the dense nature of the deposited surface layer of ammonium nitrate.

As a possible explanation of the results observed, the following is proposed. It is known that uncoated ammonium nitrate prills have a very low drying rate. Apparently moisture initially leaves the individual prills by evaporation at the surface from a saturated solution which deposits a dense film of salt and blocks the limited number of capillaries to the

surface. The remaining moisture must then evaporate inside the prills and diffuse through this salt film. When diatomaceous earth is added as a coating agent on the surface of the prills prior to drying, it provides a highly porous layer upon which the salt can deposit, thus keeping the capillaries to the surface open and assuring more rapid drying. If too little coating is added, the capillaries will not remain open, and if more than is necessary is added, the coating simply adds an additional barrier to drying. This explanation is supported by the tests, which showed that 3.0 to 3.5% coating was optimum and that the same effect could be obtained from a smaller weight of the significantly less dense Micro Cel E.

It follows that a substantially less soluble or hygroscopic material would not dry faster if it were coated. This conclusion was supported by tests performed using 16-20-0 granular fertilizer, during which samples were dried

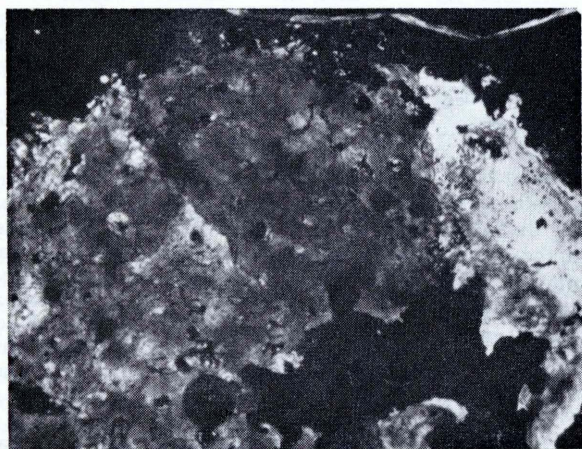


Figure 8. Photomicrograph of uncoated ammonium nitrate prill, showing hole in center of prill

50 \times

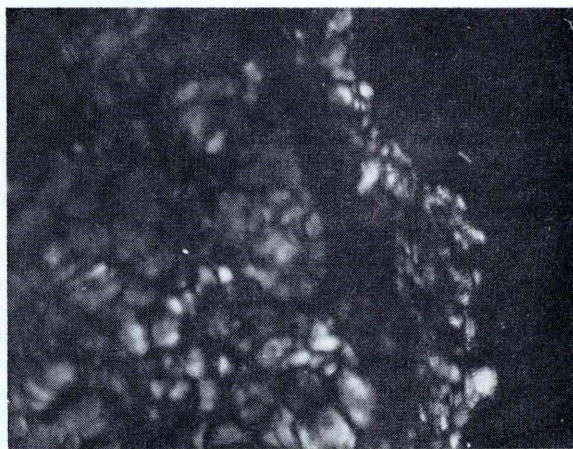


Figure 10. Coated prill showing ammonium nitrate diffused through diatomaceous earth coating during drying

160 \times

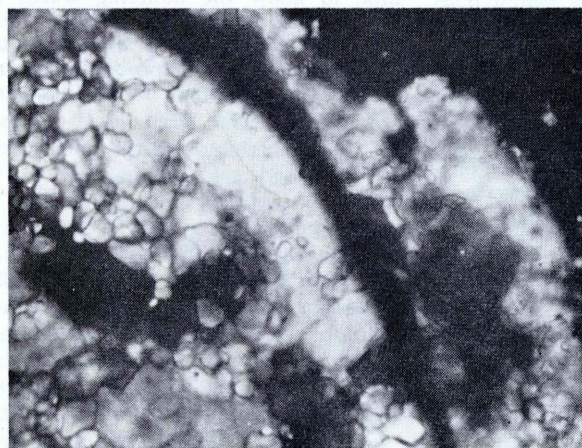


Figure 9. Coated and then dried ammonium nitrate prill

100 \times . Dark curving line is layer of Celite 379 originally on outside of wet prill.



Figure 11. Coated and then dried ammonium nitrate prill

400 \times . Note more dense crystalline nature of diffused ammonium nitrate at right

in the cabinet dryer from initial moisture contents as high as 5.0%. No reduction in drying rate occurred when the coating was added.

Conclusions

Addition of diatomaceous earth as a coating agent to moist ammonium nitrate prills significantly increased the rate of drying in both cabinet and rotary dryer tests. Limited data indicated that the coating also reduced the amount of fines produced in the dryer. Photomicrographs of prill thin sections showed that a thin, dense layer of nitrate de-

posited during drying on the outside of the coating. Without the coating the deposited salts would have quickly blocked the capillaries which bring moisture to the surface. At optimum thickness, the layer of coating probably keeps the capillaries to the surface of the prill open, resulting in a shorter drying time.

Acknowledgment

The prilled ammonium nitrate was donated by the Spencer Chemical Co. and the diatomaceous earth by Johns-Manville.

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