

# Bench-Scale Studies of Sulfate Recycle Nitric Phosphate Process

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Laboratory studies were made of operating conditions for the sulfate recycle nitric phosphate process. Gypsum-slurry filtering rates were high when the acid-rock acidulate was aged for 2 hours before addition of ammonium sulfate and the gypsum crystallization temperature and retention time were 140° F. and 30 minutes, respectively. A novel procedure was developed for ammonium sulfate regeneration; high filtering rates of the resulting

calcium carbonate slurry were obtained through use of a single-stage converter operated at 125° to 140° F. with 2-hour retention time and a minimum of agitation. Ammoniation and concentration of the filtrate from the gypsum separation step resulted in a product having an N-P-K grade of 28-6-0 (N-P<sub>2</sub>O<sub>5</sub>-K<sub>2</sub>O grade, 28-14-0). A method to recover the fertilizer values as multiple products of other grades is being studied.

Fertilizer production methods involving the acidulation of phosphate rock with nitric acid (Beveridge, 1968; Hignett, 1966; Mitchell, 1968) are of interest since they offer an opportunity to reduce or eliminate the need for sulfur, which is required for the usual phosphatic fertilizer processes. Interest in nitric phosphates has cycled somewhat in relation to the supply and demand of sulfur (Slack *et al.*, 1967).

When nitric acid alone is used in the acidulation of phosphate rock, a solution of calcium nitrate in phosphoric acid is obtained. Removal of calcium from the acidulate prior to ammoniation decreases hygroscopicity and increases the grade of the product. The sulfate recycle nitric phosphate process has been proposed (Liljenroth, 1930; Strelzoff and Roberts, 1954; and Segar, 1966) as a method for calcium removal; however, little information on the effects of the process variables has been published. The basic steps of the process shown in Figure 1 are: ammonium sulfate solution is added to the acid-rock acidulate and the resulting calcium sulfate precipitate is filtered off and washed with ammonium sulfate solution; the ammonium sulfate solution is regenerated by treating the calcium sulfate with ammonia and carbon dioxide and filtering off the resultant calcium carbonate. The filtrate from the calcium removal step is ammoniated and dried to give an N-P-K grade of 28-6-0 (N-P<sub>2</sub>O<sub>5</sub>-K<sub>2</sub>O grade, 28-14-0) ammonium phosphate nitrate product of high water solubility.

The purpose of the bench-scale tests of the sulfate recycle process made at TVA was to determine the effects of operating conditions on the various steps of the process. In the course of this study, it was determined that Florida rock as well as several other domestic or foreign rocks were adaptable to the process. A single-stage continuous reactor was developed which greatly improved filterability of calcium carbonate-ammonium sulfate slurry over that reported (Gopinath, 1963; Higson, 1951) for slurries made in conventional multi-stage equipment.

## EXPERIMENTAL

The bench-scale studies were carried out in two parts: acidulation of phosphate rock with nitric acid and crystallization of the calcium as calcium sulfate dihydrate, CaSO<sub>4</sub>·2H<sub>2</sub>O (gypsum), by addition of ammonium sulfate, and regeneration of the ammonium sulfate by treating the gypsum with ammonium carbonate.

### Acidulation of Rock and Crystallization of Gypsum. EQUIP-

MENT AND PROCEDURE. Phosphate rock usually was acidulated in continuous-flow apparatus, although filtration of the gypsum was batchwise. Phosphate rock (Florida flotation concentrate: 32.7% P<sub>2</sub>O<sub>5</sub>; 47.2% CaO) and nitric acid (55 to 65% HNO<sub>3</sub>) were fed continuously to the first of three small stainless steel tanks in series, and the acidulate was fed from the third tank, together with ammonium sulfate solution (38 to 40%), to the gypsum crystallizer, a stainless steel tank 6 inches in diameter by 12 inches high. The feed rate of rock was about 12 grams per minute. An antifoam agent was used in the acidulation step to help control foaming, and heat was added externally to maintain the desired temperature. The gypsum crystallizer was equipped with baffles and a low-speed agitator. The temperature in the crystallizer was maintained by external heating. The ammonium sulfate solution was fed with a pulse-type feeder from a constant-level vessel through an orifice; the solution was produced in the conversion step or was made up from reagent-grade ammonium sulfate. The acidulate and ammonium sulfate solution generally were fed at the top of the crystallizer onto the surface of the liquid. The gypsum slurry was withdrawn intermittently from the bottom.

Gypsum was filtered with a Büchner-type filter (10.1-sq. inch area) at a vacuum of 15 inches of Hg. Batches of slurry were of size to yield filter cakes about 1.5 inches thick. A coarse monofilament polyethylene cloth (105 × 40 thread count) was used. The gypsum was washed with about 1.8 grams of recycle ammonium sulfate solution (40%) per gram of dry cake. Two-stage countercurrent washing was used. The cake was washed first with the second wash filtrate from the previous batch and then with fresh recycle ammonium sulfate solution.

Variables found to have significant effects on precipitation and filterability of gypsum were acidulation retention time and temperature, crystallization temperature, and SO<sub>4</sub>:CaO mole ratio.

EFFECT OF ACIDULATION CONDITIONS. The effects of temperature in the acidulation step on the subsequent gypsum filtration were studied with 65% nitric acid (HNO<sub>3</sub>:CaO mole ratio of 2.0) and a retention time of 2 hours. Conditions of gypsum crystallization were: SO<sub>4</sub>:CaO mole ratio of 1.0; crystallization temperature, 140° F.; retention time, 30 minutes.

Results in Table I show that filtration rate increased from about 185 to 430 gal./(hr.)(sq. ft.) as the temperature was increased from 130° to 180° F. The autogenous acidulation temperature is expected to be 150° F. in large-scale equipment.

The average wash rate was about half the product filtering rate. This was presumed to be due to the relatively high

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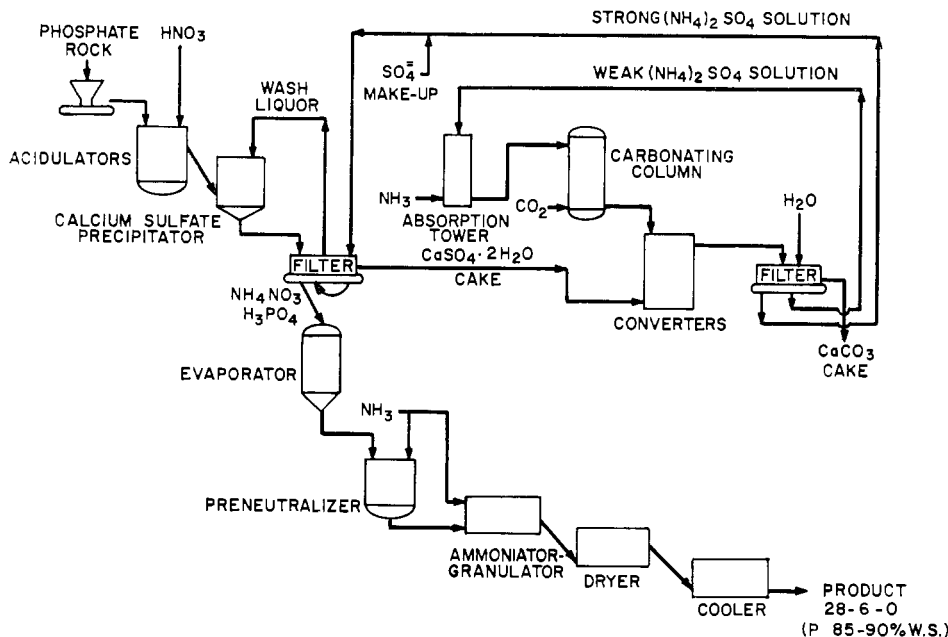


Figure 1. Flow diagram of ammonium sulfate recycle process

viscosity of the ammonium sulfate wash solution and to a reaction between the wash solution and the solubilized CaO in the mother liquor in the gypsum cake, which caused precipitation of small gypsum crystals that slowed washing. However, all the filtering rates, which include washing, were considered satisfactory. The gypsum was in the form of agglomerates ranging in size from about 50 to 200 microns. The good filtering properties were attributed to formation of agglomerates. More nearly uniform particles were obtained through the use of a low-speed agitator with little shearing action. Decreasing the acidulate retention time from 2 hours to 0.5 hour decreased the filtration rate substantially; increasing it to 3.5 hours had little effect. Recovery of  $P_2O_5$  was about 96%; calcium removal was 94 to 96%. The product filtrate contained about 8.5%  $P_2O_5$  and 36% ammonium nitrate.

When the acidulation ratio (moles  $HNO_3$ :mole CaO in the rock) was decreased from 2.0 to 1.8, the acidulate was viscous and difficult to handle. The gypsum slurry filtering rate was substantially lower and recovery of  $P_2O_5$  was slightly decreased; the only benefit was an increase of 1 to 2 percentage points (96 *vs.* 94%) in lime removal. An acidulation ratio of 2.2 did not increase filtering rate and the degree of lime removal decreased, probably because of the increased solubility of gypsum in the excess acid. The use of 55% instead of 65% nitric acid in stoichiometric quantities did not increase filtering rate on a  $P_2O_5$  basis.

EFFECT OF GYPSUM CRYSTALLIZATION TEMPERATURE AND  $SO_4$ :CaO MOLE RATIO. The effects of temperature of gyp-

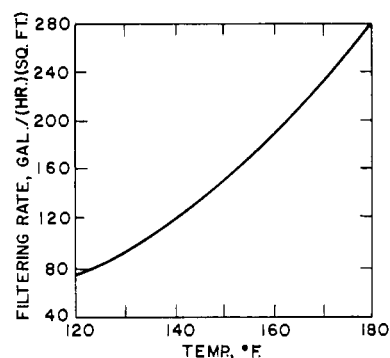


Figure 2. Effect of crystallization temperature on gypsum filtering rate

( $SO_4$ :CaO mole ratio = 1.0, retention time = 0.6 hr.)

sum crystallization and  $SO_4$ :CaO ratio were studied with an acidulate retention time of 3.5 hours at 130° F.,  $HNO_3$ :CaO mole ratio of 2.0, and gypsum crystallization time of 0.6 hour. The effect of temperature of crystallization was tested with an  $SO_4$ :CaO mole ratio of 1.0. These tests were made before the benefits of higher acidulation temperature were recognized; however, it is likely that the same general effects would result at higher temperatures.

Figure 2 shows that the filtration rate increased from about 80 to 280 gal./(hr.)(sq. ft.) as the temperature was increased from 120° to 180° F., presumably because of decreased viscosity of the gypsum slurry and increase in gypsum agglomerate size. Recovery of  $P_2O_5$  in the filtrate was about 96%. Lime removal decreased somewhat (91 *vs.* 94%) and sulfate losses (in the filtrate) increased (6 to 8.5%) with increase in temperature, probably caused by greater gypsum solubility at the higher temperatures.

The effect of varying the  $SO_4$ :CaO mole ratio from 0.9 to 1.2 during gypsum crystallization at 140° or 160° F. is shown in Figure 3. The highest filtering rate [317 gal./(hr.)(sq. ft.)] was obtained at 160° F. and an  $SO_4$ :CaO mole ratio of about 1.1. The highest rate [240 gal./(hr.)(sq. ft.)] at 140° F. also

Table I. Effect of Temperature on Filtration Rate

Acidulate Temperature, °F.	CaO Removal, %	$P_2O_5$ Recovery, %	Gypsum Filtering Rate, gal./(hr.)(sq. ft.) <sup>a</sup>
130	94.2	96.0	185
140	93.7	95.8	265
160	93.7	96.6	317
180	96.4	96.0	432

<sup>a</sup> Includes washing.

**Table II. Analyses of Solid Products**

Test No.	Per cent							
	N		P			H <sub>2</sub> O	CaO	SO <sub>4</sub>
	Total	NH <sub>3</sub>	Total	Available <sup>a</sup>	Water-soluble			
1	27.9	16.6	6.8	6.7	6.0	0.9	1.1	2.4
2	26.5	19.1	6.5	6.5	5.7	1.0	2.6	4.0
3	28.0	16.8	6.6	6.6	5.8	0.9	2.1	2.5

<sup>a</sup> Water-soluble plus neutral ammonium citrate-soluble (AOAC).

**Table III. Analyses of Products**

Product	Per cent					
	N		P			H <sub>2</sub> O
	Total	NH <sub>3</sub>	Total	Available <sup>a</sup>	Water-soluble	
Dried precipitate	21.6	16.7	15.1	15.1	13.4	1.0
Evaporated filtrate	33.9	17.5	0.09	...	...	0.4

<sup>a</sup> Water-soluble plus neutral ammonium citrate-soluble (AOAC).

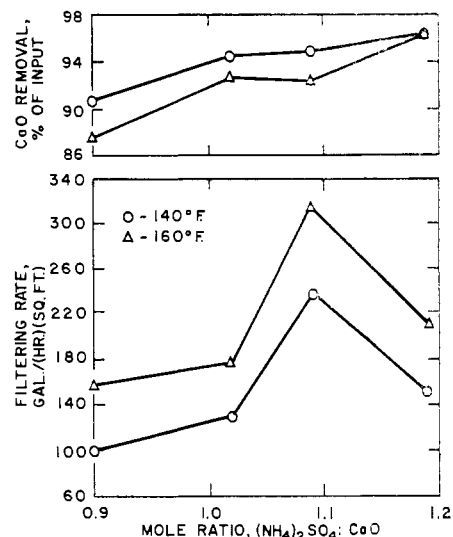
was obtained at a mole ratio of 1.1. Lime removal (88 to 96%) increased with the increase in SO<sub>4</sub>:CaO mole ratio but decreased as the crystallizer temperature was increased. P<sub>2</sub>O<sub>5</sub> recovery averaged 96% and could not be related to reaction conditions. Sulfate loss in the filtrate (5 to 14%) increased with temperature and with the amount added.

**PHOSPHATE LOSSES.** Analyses of the washed gypsum cake indicated that only about 1% of the input P<sub>2</sub>O<sub>5</sub> was water-soluble and potentially recoverable. Essentially all the remaining P<sub>2</sub>O<sub>5</sub> (3% of input) was soluble in alkaline ammonium citrate solution and was assumed to be coprecipitated in the gypsum and not recoverable. Any loss occurring as unreacted rock was so small as to be undetectable. Two-stage countercurrent washing was only slightly more effective than single-stage washing. Analysis of gypsum cakes indicated that essentially all nitrate nitrogen was recovered from the cakes by washing.

**COMPOSITION OF PRODUCT.** Typical product filtrates were concentrated by evaporation to a P content of about 5% and then ammoniated to a pH of 5.5 and dried at 140° F. Analyses of three of these solid products are given in Table II. The proportion of P in water-soluble form was 87 to 89%. Essentially all the P was available. The products were mixtures of ammonium phosphates, ammonium nitrate, and small amounts of calcium phosphates.

Because many producers probably would object to the 4.7:1 weight ratio of N-P in the product (28-6-0) normally obtained in this process, separation of ammonium nitrate from ammonium phosphate was investigated. In the present study, triammonium phosphate trihydrate was crystallized for separation from the solution. Others have effected this separation by crystallization of ammonium nitrate (McFarlin and Brown, 1968) or monoammonium phosphate (Strelzoff and Dell, 1968).

A portion of the filtrate from the gypsum precipitation step (product filtrate) used in test 2 was ammoniated to a pH of about 9 with anhydrous ammonia. The resulting precipitates of triammonium phosphate trihydrate (TAP) and impurities were filtered off and heated to evolve NH<sub>3</sub> and H<sub>2</sub>O so that a stable ammonium phosphate would result. In practice, the NH<sub>3</sub> released from unstable triammonium phosphate would be recovered by scrubbing the off-gases with the incoming product filtrate. The filtrate from the TAP filtration



**Figure 3. Effect of proportion of ammonium sulfate to CaO on gypsum filtering rate and CaO removal**

(Retention time = 0.6 hr., mole ratio, HNO<sub>3</sub>:CaO = 2.0)

step was evaporated to a solid. Analyses of these products are shown in Table III.

The dried precipitate (ammonium phosphate nitrate) contained 21.6% N and 15.1% P; ammonium nitrate was present because the precipitate was not washed. Evaporation of the filtrate resulted in ammonium nitrate essentially free of phosphate.

Some difficulty was encountered in filtering the precipitated solids due to the formation of very fine complex iron, aluminum, and calcium phosphates during ammoniation. Tests are being made to form crystalline compounds or agglomerates of these impurities with better filtering characteristics.

**EFFECT OF TYPE OF PHOSPHATE ROCK.** Gypsum crystallization tests with acidulates from several different phosphate rocks were made for comparison with Florida rock (flotation concentrate). Analyses of the rocks are given in Table IV.

In the first tests, all the rocks were acidulated with 65% nitric acid at 140° F. and the acidulate retention time was 2 hours. Gypsum was crystallized at 140° F. with 38% ammonium sulfate solution (SO<sub>4</sub>:CaO mole ratio = 1.0). Under these conditions, high filtering rates [200 to 360 gal./ (hr.)(sq. ft.)] were obtained with calcined North Carolina and Oron rocks; the gypsum formed into 50- to 600-micron agglomerates. These filtration rates compared favorably with those experienced with Florida rock acidulates [250 to 430

**Table IV. Analyses of Rocks**

Type of Rock	Analysis, Wt. %						
	CaO	P <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	F	CO <sub>2</sub>	SiO <sub>2</sub>
Uncalcined							
Florida, flotation concentrate	47.2	32.7	1.5	1.4	3.7	3.4	3.6
Morocco	53.5	36.9	0.12	0.30	4.3	2.5	0.80
Arad (Israel)	50.6	28.1	0.28	0.41	3.1	8.9	0.60
Calcined							
North Carolina	50.7	31.3	0.72	0.46	3.8	...	...
Oron (Israel)	56.0	33.6	0.16	0.36	3.6	2.9	0.80

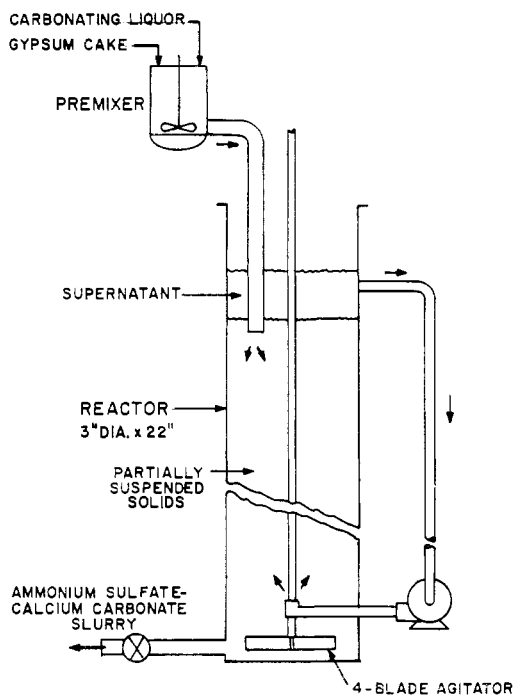


Figure 4. Continuous single-stage gypsum conversion vessel

gal./hr.)(sq. ft.]. Lime removal was 95% and  $P_2O_5$  recovery 97%. However, gypsum slurries made from the uncalcined Morocco and Arad rocks formed into viscous suspensions and could not be filtered. The crystals were extremely small ( $1 \times 15$  micron) and did not agglomerate.

In other tests with acidulate from the uncalcined Morocco rock (additional Arad rock was not available), large gypsum crystals ( $15 \times 80$  micron; no agglomeration) formed and filtering rates of about 180 gal./hr.)(sq. ft.) were obtained at  $140^\circ F.$  through use of a high temperature procedure, which consisted in heating the acidulate to about  $230^\circ F.$  before the addition of the ammonium sulfate solution at  $230^\circ F.$  The resultant slurry was held at this temperature with moderate stirring for 30 minutes and then cooled slowly (1.5 hours) to  $140^\circ F.$  in passage through two crystallizers in series. During cooling, the slurry was agitated only mildly to maintain flowability.

**Conversion of Gypsum to Ammonium Sulfate.** The initial conversion studies were carried out with filter cake from the gypsum crystallization and filtration tests described previously. Prior to reaction with ammonium carbonate solution, the cakes had been washed only with ammonium sulfate solution (40%) and, therefore, contained residual ammonium sulfate solution in addition to impurities such as phosphate, iron, aluminum, silica, and some antifoam agent. Analyses of a typical gypsum cake and ammonium carbonate solution used in the conversion studies are given in Table V.

The calcium carbonate from the conversion of laboratory-prepared gypsum was filtered in a Büchner-type filter at a vacuum of 15 inches of Hg with a fine Orlon cloth as the filtering medium. As in the tests of filtration of gypsum, the proportions of slurry filtered resulted in cakes about 1.5 inches thick, and filtering rates reported include washing. The calcium carbonate cake was washed in two stages; 1 gram of water per gram of dry cake was used in each stage.

The first conversion tests were made by a continuous, multistage procedure, since Gopinath (1963) and Kasturirangan (1965) reported that such procedures were used in the conversion of gypsum from phosphoric acid production. Proportion of ammonium carbonate used in these tests was 110 to 125% of that stoichiometrically required for reacting with the gypsum. The temperature was varied from  $80^\circ$  to  $140^\circ F.$  and the retention time was 4 hours. Because of the tendency for the solids in the converter tanks to settle out, agitation was fairly vigorous. The results were unsatisfactory because of low calcium carbonate filtering rates, of the order of 45 gal./hr.)(sq. ft.). The calcium carbonate was in the form of small agglomerates 2 to 15 microns in size.

When conversion tests were made batchwise under essentially the same conditions but with only mild agitation, the calcium carbonate agglomerates were larger (15 to 30 microns) and higher filtration rates, of the order of 140 gal./hr.)(sq. ft.), were obtained. These tests eventually resulted in the development of a continuous single-stage process for the conversion of gypsum to ammonium sulfate.

**SINGLE-STAGE GYPSUM CONVERTER.** Figure 4 is a flow sheet of the single-stage conversion step. The equipment consisted of a gypsum-ammonium carbonate premixing vessel and a 3-inch-diameter by 22-inch externally heated reaction vessel equipped with a slow-speed paddle-type mixer and a liquor recycling pump. The reactor was designed to provide very mild agitation during the conversion reaction of gypsum to ammonium sulfate. Relatively large agglomerates of calcium carbonate (10 to 500 microns; average, 75 microns) were formed and good filtering rates were obtained without a decrease in conversion efficiency.

The procedure was as follows. Gypsum cake (700 grams per hour) and ammonium carbonate solution (750 grams per hour) were premixed at room temperature ( $75^\circ$  to  $80^\circ F.$ ) and fed by gravity to a point about 5 inches below the liquid level in the reactor. This proportion of ammonium carbonate is 110% of stoichiometric. Product slurry of calcium carbonate-ammonium sulfate solution was withdrawn from the bottom of the vessel. The paddle-type mixer was operated at a low speed (tip speed, 20 feet per minute) to aid in slurry discharge. Relatively clear liquor from the top of the reactor was recycled to a point near the bottom of the reactor at 10 to 20 times the gypsum-ammonium carbonate slurry feed rate. The gypsum moved downward countercurrent to the upward flow of liquid and was converted to calcium carbonate in the process. This mild agitation resulted in the formation of large agglomerates of calcium carbonate.

Table V. Analyses of Typical Gypsum Cake and Ammonium Carbonate Solution

	Analysis, wt. %							Av. Particle Size, Microns
	CaO	SO <sub>4</sub>	N		P <sub>2</sub> O <sub>5</sub>	Free H <sub>2</sub> O	CO <sub>2</sub>	
Gypsum <sup>a</sup>	23.6	48.0	Total	NH <sub>3</sub>	0.7	12.6	...	70
Ammonium carbonate solution <sup>b</sup>	...	...	12.1	12.1	...	...	18.8	...

<sup>a</sup> Gypsum derived from Florida rock. <sup>b</sup> Made from reagent-grade ammonium carbonate, ammonium hydroxide, and water.

**Table VI. Conversion of Gypsum to Ammonium Sulfate<sup>a</sup>**

Source	Gypsum						Av. particle size, microns	Results			
	Analysis, %							Conversion, % <sup>b</sup>	Type <sup>d</sup> cloth	Filtering rate <sup>e</sup>	
	CaO	SO <sub>4</sub>	NH <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> O	CO <sub>2</sub>				Gal./(hr.)-(sq. ft.)	Lb. dry solids/(hr.)-(sq. ft.)
Laboratory <sup>e</sup>	21.9	44.1	3.2	1.1	18.0	...	35	94	Orlon	294	560
Wet-process acid <sup>f</sup>	23.3	38.0	...	0.6	22.8	...	125	93	Orlon	146	312
									Orlon	96	146
Pilot plant <sup>g</sup>	21.0	44.0	3.5	0.9	17.7	<0.1	60	97	Poly-ethylene	431	769

<sup>a</sup> Conditions of operation: temperature, 125° F.; retention time, 3 hr.; ammonium carbonate: rate, 110% stoichiometric; pH, 9.2; NH<sub>3</sub>:CO<sub>2</sub> sulfate-free mole ratio, 2.09. <sup>b</sup> SO<sub>4</sub> basis. <sup>c</sup> Includes two cake washes. <sup>d</sup> Orlon: fine, Eimco No. OR-595; polyethylene: coarse, Eimco No. PO-801RF. <sup>e</sup> Washed with neutral ammonium sulfate solution. <sup>f</sup> Washed with water. <sup>g</sup> Washed with alkaline (pH 8) ammonium sulfate solution.

This single-stage ammonium sulfate regeneration procedure was used in tests with gypsum filter cakes produced in the laboratory and in TVA's ammonium sulfate recycle nitric phosphate pilot plant, which came into initial operation at the time. Florida phosphate was used in both the laboratory and pilot-plant work. The process also was tested with phosphogypsum from a commercial wet-process phosphoric acid plant in which Florida rock was used.

**EFFECT OF GYPSUM SOURCE.** Table VI shows the effect of gypsum source on conversion to ammonium sulfate and filtering rates of the ammonium sulfate-calcium carbonate slurry. The pilot-plant gypsum had been washed with recycle ammonium sulfate solution from the gypsum conversion step; this solution was alkaline (pH 7 to 8) because it contained unreacted ammonium carbonate. The other two gypsums were washed with a neutral ammonium sulfate solution and with water, respectively. The temperature was 125° F. and the retention time was 3 hours.

With both the laboratory gypsum (precipitated from nitric acid acidulation) and the phosphogypsum (from production of wet-process acid), conversion was about 93%; it was about 97% with the pilot-plant gypsum. The ammonium sulfate content of the filtrates was between 35 and 40%. Filtering rates of calcium carbonate from the first two gypsums were 150 to 300 gal./(hr.)(sq. ft.) through a fine Orlon cloth. However, with the same filter cloth, the filtering rate of the slurry obtained from conversion of the pilot-plant gypsum was only 100 gal./(hr.)(sq. ft.). Changing to a coarse filter cloth increased rates of the order of 400 gal./(hr.)(sq. ft.) without passage of calcium carbonate into the filtrate. The difference was due to the presence of a very small amount of finely divided precipitated phosphates (calcium plus some iron and aluminum) in the calcium carbonate slurry; these fines blinded the fine cloth but passed through the coarse cloth into the filtrate.

These precipitated fines probably originated where the alkaline ammonium sulfate wash reacted with the acidic mother liquor occluded in the gypsum cake, precipitating insoluble calcium, iron, and aluminum phosphates.

It is not known if these impurities tend to build up in the closed conversion loop. This is being studied in the pilot plant. The substitution of a water wash for the gypsum cake should prevent the buildup. The solid impurities in the ammonium sulfate solution would be dissolved in the gypsum precipitator system, which is acidic. As an alternative, neutralization of the ammonium sulfate wash liquor with part of the feed nitric acid or with make-up sulfuric acid would minimize the problem by preventing impurity precipitation in the gypsum wash step.

**Table VII. Effect of Temperature and Retention Time on Gypsum Conversion<sup>a</sup> and Calcium Carbonate Filtration**

Retention Time, Hr.	Gypsum Conversion, %	Filtering Rate	
		Gal./(hr.)-(sq. ft.)	Lb. dry solids/(hr.)(sq. ft.)
125° F.			
0.5	95	160	280
1.0	96	500	710
3.0	97	660	770
140° F.			
0.5	97	275	390
1.0	96	390	490
3.0	97	640	1035

<sup>a</sup> Gypsum from Florida flotation concentrate (see Table VI); % conversion on SO<sub>4</sub> basis.

**EFFECTS OF RETENTION TIME AND TEMPERATURE.** The effects of temperature from 125° to 140° F. and retention time from 0.5 to 3.0 hours were studied with pilot-plant gypsum of the composition described earlier (Table VI). The proportion of ammonium carbonate solution was 10% in excess of stoichiometric, and a coarse filter cloth was used. Table VII shows that the degree of conversion of gypsum to ammonium sulfate was about 96 to 97% under all conditions. The filtering rate was increased two- to fourfold, to as high as 650 gal./(hr.)(sq. ft.), by increasing the retention time from 0.5 to 3.0 hours. Temperature did not appear to be an important factor.

Equally satisfactory results were obtained in tests in which the gypsum had been prepared by acidulating calcined North Carolina and Orlon rocks with nitric acid and adding ammonium sulfate.

#### SUMMARY

No difficulties were encountered in removal of calcium as gypsum from nitric acid acidulates of Florida rock and calcined North Carolina and Orlon rocks; filtering rates were of the order of 300 gal./(hr.)(sq. ft.) when operation was such that crystals of gypsum formed into agglomerates. To obtain satisfactory filtering rates with gypsum slurry from uncalcined Morocco rock, it was necessary to use multistage crystallization and high temperatures (230° F.) in the acidulation and early phase of the crystallization step.

High filtering rates for the calcium carbonate slurry from the regeneration step were obtained by use of a single-stage converter in which only mild agitation was provided by recirculation of liquor through the reaction zone. The calcium carbonate formed into large agglomerates in the single-stage unit.

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