

Any change in crystallizing phase in the temperature range from 0° C. to the estimated crystallization temperature. This is a serious source of error in the range below 0° C. for a solution from which diammonium phosphate crystallizes above 0° C. The equation should not be used in this case. Other phase changes are shown in Table I. Estimation of solubility in regions near a phase change is generally not as accurate as in regions remote from the boundary of two phases.

Although the equation gives only an approximation, it should be useful in practice as a rough guide for predicting salting out temperature.

Acknowledgment

The assistance of A. D. Jones, Owen W. Livingston, James E. Tackett, and Gail Barclay Colley in various aspects of the laboratory work is gratefully acknowledged.

Literature Cited

(1) Aronova, S. I., Lunskeya, Z. N., *Kalii (U.S.S.R.)* 1933, No. 2, 24-8.

- (2) Askenasy, Paul, Nessler, F., *Z. anorg. u. allgem. Chem.* **189**, 305-28 (1930).
 (3) Bergman, A. G., *Bull. acad. sci. (U.R.S.S.) Classe Sci. math. nat., Sér. chim.* **1938**, No. 1, 203-16.
 (4) Bergman, A. G., Bochkarev, P. F., *J. Applied Chem. (U.S.S.R.)* **10**, 1531-6 (1937).
 (5) Bergman, A. G., Bochkarev, P. F., *Bull. acad. sci. (U.R.S.S.) Classe math. nat., Sér. chim.* **1938**, No. 1, 237-65.
 (6) Blidin, V. P., *J. Gen. Chem. (U.S.S.R.)* **11**, 887-90 (1941).
 (7) Bochkarev, P. F., *Trudy Vostochno-Sibirskogo Gosudarst. Inst.* **1937**, No. 3, 3-22; *Khim. Referat. Zhur.* **1**, No. 8-9, 11-12 (1938).
 (8) Bokhovkin, I. M., Bokhovina, J. I., *J. Gen. Chem. U.S.S.R.* **17**, 621-4 (1947).
 (9) Brosheer, J. C., Anderson, J. F., *J. Am. Chem. Soc.* **68**, 902 (1946).
 (10) Flatt, R., Brunisholz, G., Blumer, O., *Helv. Chim. Acta* **38**, 3753-69 (1955).
 (11) Howells, W. J., *J. Chem. Soc.* **1929**, 910-15.
 (12) Janecke, E. Z., *Angew. Chem.* **41**, 916-24 (1928); **42**, 318 (1929).
 (13) Kapusta, E. C., *Com. Fertilizer and*

- Plant Food Ind.* **97**, 24-9 (1958).
 (14) Kuznetsov, D. I., Kozhukhovskii, A. A., Borovaya, F. E., *J. Appl. Chem. (U.S.S.R.)* **21**, 1278-81 (1948).
 (15) Langguth, R. P., Payne, J. H., Arvan, P. G., Sisler, C. C., Brautigam, G. F., *J. AGR. FOOD CHEM.* **3**, 656-62 (1955).
 (16) Polosin, V. A., Ozolin, R. F., *J. Gen. Chem. U.S.S.R.* **17**, 403-10 (1947).
 (17) Polosin, V. A., Shakhparonov, M. I., *J. Phys. Chem. (U.S.S.R.)* **21**, 119-23 (1947).
 (18) Polosin, V. A., Treshchov, A. G., *Izvest. Timiryazev. Sel'skokhoz. Akad. No. 2 (3)*, 203-20 (1953).
 (19) Ravich, M. I., Popova, Z. V., *Ann. secteur anal. physico-chim. Inst. chim. gen. (U.S.S.R.)* **14**, 373-86 (1941).
 (20) Slack, A. V., *Coml. Fertilizer and Plant Food Ind.* **95**, 28 (August 1957).
 (21) Slack, A. V., *J. AGR. FOOD CHEM.* **3**, 568 (1955).
 (22) Sokolov, V. A., *J. Gen. Chem. (U.S.S.R.)* **9**, 753-8 (1939).

Received for review December 12, 1958.
 Accepted March 2, 1959.

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			
	Phosphate Rock		Gypsum	
	A	B	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.

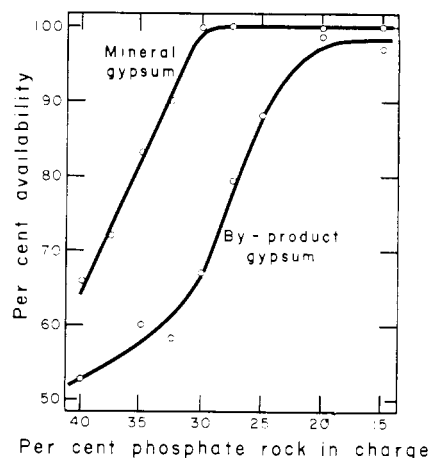


Figure 1. Effect of charge composition on P₂O₅ availability in fused gypsum phosphate

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
	2375	12.1	7.9	65
72.5	2385	11.1	8.8	79
	2365	9.0	8.3	92
75	2400	(lost)		
	2390	10.7	9.0	84
80	2425	8.5	8.3	98
	2435	8.1	8.1	100
85	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.

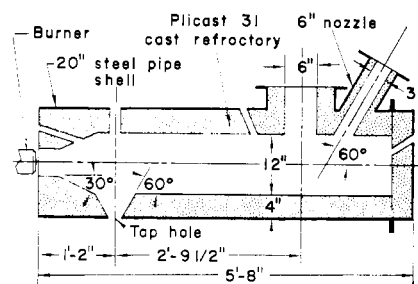


Figure 2. Pilot plant fusion furnace

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, %							Available P ₂ O ₅	P ₂ O ₅ availability
Phosphate rock	Gypsum ^a	CaO	SO ₃	F	SiO ₂	R ₂ O ₃	P ₂ O ₅			
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 ^c	48.1	18.8	0.80	20.0	3.0	10.1	9.4	93	
30 ^b	70 ^e	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.

Literature Cited

- (1) Boylan, D. R., Larson, M. A., J. AGR. FOOD CHEM. 5, 104 (1957).
- (2) Bridger, G. L., Boylan, D. R., *Ind. Eng. Chem.* 45, 646 (1953).
- (3) Bridger, G. L., Boylan, D. R., Markey, J. W., *Anal. Chem.* 25, 386 (1953).
- (4) Davy, W. C., unpublished M.S. thesis, Iowa State College Library, Ames, Iowa, 1953.
- (5) Greaves, S. G., unpublished M.S. thesis, University of Washington Library, Seattle, Wash., 1947.
- (6) Hebner, P. G., unpublished M.S. thesis, University of Washington Library, Seattle, Wash., 1948.
- (7) Moulton, R. W., *Chem. Eng.* 56, 102-4 (1949).
- (8) Stinson, J. M., Munna, C. E., *Ind. Eng. Chem.* 46, 453 (1954).
- (9) Walthall, J. H., Bridger, G. L., *Ibid.*, 35, 774-7 (1943).

Received for review October 13, 1958. Accepted March 6, 1959. Division of Fertilizer Chemistry, 134th Meeting, ACS, Chicago, Ill., September 1958. Research supported by Iowa Engineering Experiment Station.

FERTILIZER TECHNOLOGY

High-Analysis Phosphate Fertilizers from Normal Superphosphate

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Normal superphosphate can be converted into dicalcium phosphate, monocalcium phosphate, and phosphoric acid by washing with water, and concentrating the water extract. Dicalcium and monocalcium phosphates are formed in the solid phase as concentration proceeds, and can be separated. Some of these solids have a low F/P₂O₅ ratio as is required for feed supplements. A crude acid can be obtained. Triple superphosphates with from good to excellent physical properties can be prepared by solubilizing phosphate rocks with this crude acid. Concentrated normal superphosphate water extract can also react with phosphate rock at 150° to 200° C. to produce a high-analysis phosphate fertilizer. Other process modifications are possible.

NORMAL SUPERPHOSPHATE is used primarily for direct application as such and for the preparation of fertilizer mixtures. Limited quantities have been used in South Africa as a source of low-fluorine, water-soluble feed supplement (20). More recently, Bridger, Horzella, and Lin have shown that it can react with phosphate rock to produce a dicalcium phosphate fertilizer (3). It has found few other commercial applications.

A process is proposed, by which normal superphosphate can be converted into several high-analysis phosphate ferti-

lizers. The reactions involved are well known (2-4, 8, 14, 17-20, 24-26). The process suggests a number of possibilities, some of which appear commercially feasible.

Figure 1 indicates the products which can be prepared from normal superphosphate.

Materials and Analytical Methods

Three phosphate rock samples with the analysis shown in Table I were used.

Total, water-soluble, and citrate-insoluble phosphorus pentoxide contents were determined by volumetric titration,

and the Association of Official Agricultural Chemists' (AOAC) procedures were closely followed (7). Free acid was determined by extraction with 95% alcohol according to an unofficial procedure based on the work of Hill and Beeson, and Ross (13, 22), and adopted in the control laboratories of the Taiwan Fertilizer Co. A Florida phosphate rock sample from the National Bureau of Standards was used in checking the results of phosphorus pentoxide determinations.

Calcium oxide was determined by the