

A Method for Preparing Concentrated Nitric Phosphate from Low Grade Rock Phosphate of Patos de Minas

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(Received October 8, 1984)

This study was made with a view to preparing concentrated nitric phosphate from low grade rock phosphate of Patos de Minas containing a large amount of impurities such as SiO_2 , Fe_2O_3 and Al_2O_3 .

A large quantity of water-insoluble gelatinous impurity substance is formed during nitric acidulation of the low grade rock phosphate, resulting in a viscous slurry of about 100 to 200 cp in viscosity and poor filtrability. In the present study, the nitric acidulated slurry was partially ammoniated at pHs ranged from 1.6 to 4.1 to convert the gelatinous phase into crystalline one consisting mostly of relatively large crystals of $\text{NH}_4(\text{Al, Fe})\text{H}_2(\text{PO}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ ("Q"), $\text{NH}_4(\text{Al, Fe})\text{H}_8(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}$ ("R") and $\text{NH}_4(\text{Al, Fe})\text{HF}_2\text{PO}_4$ ("S"), in order to improve the filtrability (1, 2, 3, 4, 5, 6). X-ray diffraction and chemical analysis were made on the precipitates formed during the ammoniation to determine the most desirable pH and to estimate the composition of the filtrate obtained by separation of the precipitates.

Rock Phosphate Used

Chemical composition of rock phosphate used for this study is shown below.

P_2O_5	CaO	Al_2O_3	Fe_2O_3	F	SiO_2
25.8	30.8	5.1	2.6	2.0	29.4

This is a sedimental rock deposited at Patos de Minas in the Central part of Brazil, and very low in grade and high in Al_2O_3 and Fe_2O_3 . The CaO/PO_4 mole ratio is 1.51, which is considerably smaller than 1.78 of Florida rock, 1.72 of Lagamar, 1.69 of Araxá and 1.66 of Catalão. Such low grade rock phosphate has never been used for production of nitric phosphate fertilizer.

Experiment

The rock phosphate (1 kg) was acidulated with 1.6 kg of 64%-nitric acid with retention time of 60 min. at 60°C to make a slurry of about 150 cp in viscosity, which was used for the following tests on the partial ammoniation.

The acidulated material was divided in several parts and 300 ml of it were used for each test of ammoniation. The material was ammoniated to various pHs ranged from 1.6 to 4.1 to convert the gelatinous substance in it into crystalline one, and filtrated by using büchner funnel with suction bottle at reduced pressure of 150 torr to measure the filtration time. The water-insoluble substance on the funnel was washed twice with 300 ml of water, washed twice with about 200 ml of acetone, dried at room temperature overnight, weighed, and then examined by chemical and X-ray diffraction methods of analysis.

The pH of the ammoniated materials was measured by pH meter after diluting 1 ml of the material with 100 ml of water.

Amount and Composition of Water-Insoluble Substance Formed during Ammoniation

The amount and chemical composition of water-insoluble crystalline phase formed during the partial ammoniation are shown in Table I. Also the amounts of citric- and citrate-insoluble phases are shown in the table.

The pH of the nitric acidulated material was 1.6 and the amount of gelatinous substance containing crystalline silica (α -quartz) in the material was 34.5 g/300 ml, before the ammoniation. On ammoniating the material, the amount of water-insoluble precipitated increased considerably with increase in pH, converting some

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Table 1-Amount and chemical composition of water-insoluble phase

Test No.	pH	Water-insoluble substance (g/300 ml)	Chemical composition (%)						Insoluble phase (g/300 ml)	
			N	P ₂ O ₅	Fe ₂ O ₃	Al ₂ O ₃	F	CaO	Citric	Citrate
1	1.6	34.5	0.1	0.0	2.5	0.5	0.5	0.0	34.3	33.9
2	2.7	71.3	0.4	12.5	4.0	5.6	2.0	2.2	44.5	34.1
3	3.1	108.8	1.2	16.1	3.6	5.5	2.1	4.9	64.8	34.3
4	3.7	143.3	3.8	18.4	2.7	4.5	1.7	9.7	63.3	33.9
5	4.1	146.3	1.0	19.1	2.7	4.5	1.9	8.7	61.9	34.0

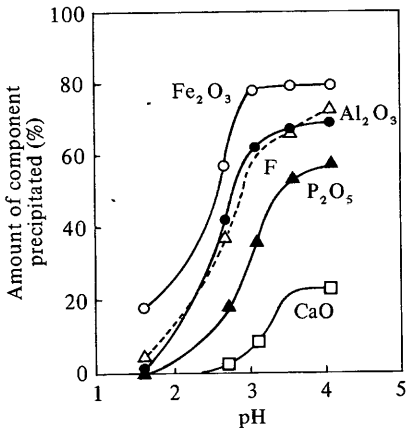


Fig. 1-Effect of pH on amounts of components precipitated during ammoniation

amount of the gelatinous substance into crystalline phase which was supposed to be citric-insoluble and citrate-soluble. It was indicated apparently that mainly iron and aluminum phosphates were precipitated at pH

2.7 to double the amount of the water-insoluble substance; calcium phosphate was precipitated mainly above pH 3.

Amounts of the compositions precipitated by the ammoniation are shown in Fig. 1.

The figure shows that major compound of the gelatinous phase present in the nitric acidulated material of pH 1.6 was not gelatinous iron and aluminum phosphate hydrate as generally had been assumed but another iron compound which was supposed to be derived from the original rock phosphate.

Calcium started to be precipitated at pH about 2.7, combined with phosphate and fluoride ions to form water-insoluble compounds.

Water Insoluble Compounds Formed

The amount of major water-insoluble compounds precipitated were estimated from the results of chemical and X-ray diffraction analyses. The results are shown in Table II.

Table II-Water-insoluble compounds formed (*)

Test	pH	Water-insoluble substance (g/300 ml)	Amount of water-insoluble compound formed (g/300 ml)			
			"Q"	"R"	"S"	CaHPO ₄
1	1.6	34.5	0	0	0	0
2	2.7	71.3	14	1	3	2
3	3.1	108.8	5	0	22	10
4	3.7	143.3	4	0	27	26
5	4.1	146.3	—	0	30	30

(*) Estimated from results of chemical and X-ray diffraction analyses.

"Q": $\text{NH}_4(\text{Al, Fe})\text{H}_2(\text{PO}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$

"R": $\text{NH}_4(\text{Al, Fe})_3\text{H}_8(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}$

"S": $\text{NH}_4(\text{Al, Fe})\text{H}(\text{F, OH})_2\text{PO}_4$

Water-insoluble phase in the nitric acidulated material at pH 1.6 contained a considerable amount of α -quartz and unknown crystalline compound derived from the original rock phosphate, probably a large amount of gelatinous silica and iron silicate hydrate from the original rock, and no phosphate, as described above; it was mostly insoluble in citric and citrate solutions.

A major crystalline iron and aluminum phosphate "Q" was formed mainly at pH 2.7 and its amount decreased with increase in pH, as had been already reported (3, 6). A small amount of "R" was formed at pH 2.7. "S" and dicalcium phosphate anhydride started to be formed at pH 2.7 and their amounts increased with increase in pH.

The formation of dicalcium phosphate is normally accompanied by the formation of colloidal apatite in a small amount (6).

Filtrability

The relation between filtrability of the water-insoluble substance and pH is shown in Fig. 2. The filtrability was determined from the time to filtrate the ammoniated slurry at reduced pressure of 150 torr to separate the water-insoluble substance. The change of the amount of the insoluble substance with pH was shown also in the figure.

It was indicated apparently that the filtrability increased with increase in pH to about 4 in spite of increasing in the amount of water-insoluble substance. This is based clearly upon increasing in amount of crystalline water-insoluble phase with increase with the pH.

Conclusion and Discussion

A test on the partial ammoniation of nitric acidulated material was made with a view to preparing concentrated nitric phosphate from low grade rock phosphate of Patos de Minas. It was found desirable to ammoniate the nitric acidulated material partially to pH about 2.7, where a considerable amount of "Q" consisting of relatively large crystals of about 10 μ m in size was formed to make it easy to filtrate the water-insoluble impurity. The filtrability increased with increase in pH to 4.1, but also the amount of dicalcium phosphate formed increased considerably above pH 2.7. Thus, it is desirable to ammoniate the nitric acidulated material at pH about 2.7 to remove larger amounts of Fe_2O_3 and Al_2O_3 , and smaller amounts of CaO and P_2O_5 . A large quantity of

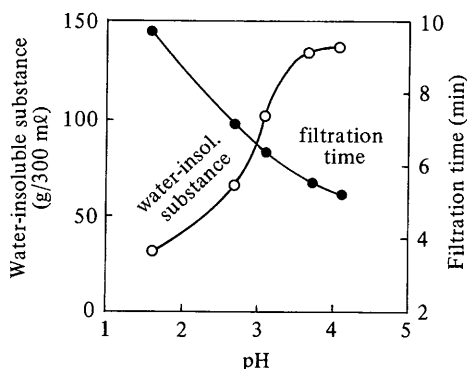


Fig. 2-Relation between filtrability of ammoniated slurry and amount of water-insoluble substance in the slurry and pH.

silica can be also removed together with the iron and aluminum phosphates.

It is calculated that the chemical composition of the filtrate of pH 2.7 is 9.5% P_2O_5 , 13.5% CaO, 1.3% Al_2O_3 , 0.5% Fe_2O_3 , 0.6% F and 45.4% NO_3 . Concentrated nitric phosphate can be prepared by ammoniating the filtrate further above pH 4.5, after removing some amount of CaO from the filtrate as gypsum to give a desirable CaO/ PO_4 mole ratio which prevent the formation of apatite during the neutralization.

On the other hand, the separated impurity phase will be able to be used as another fertilizer material, for instance, such as slow-releasing fertilizer material, because of containing citrate-soluble 12.5% P_2O_5 .

We would like to express our gratitude to Mrs. Queenie Siu Hang Chui Pressinotti and Mr. Glaucio Issao Horita who supported the research in this paper.

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低品位パトスデミナスリン鉱石から高濃度リン硝安の製造法

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(昭和59年10月8日受理)

低品位パトスデミナスリン鉱石の硝酸処理液中の不純物はきわめて微細な粒子からなり、この分離は従来困難であった。今回の研究で、この溶液をpH2.7付近にアンモニア化すると、微細な粒子の多くは10 μ m程度の比較的大きな結晶に変わり、ろ過分離が容易になることを見出した。この際、主としてNH(Al, Fe)H(PO) \cdot 1/2H₂OやNHFeH(PO) \cdot 6H₂Oが生成した。

これらの不純物を分離すると、P₂O₅ 9.5%, CaO 13.5%, Al₂O₃ 1.3%, Fe₂O₃ 0.5%, F 0.6%およびNO₃ 45.4%を含む溶液が得られた。この溶液中のCaO/P₂O₅モル比を1.4付近に調整してからpH4.5に中和することによって、アパタイトを含まない高濃度リン硝安を製造することが可能となる。また、分離された不純物は水と2%クエン酸に難溶で中性クエン酸アンモニウムに可溶のP₂O₅を12.5%含むものであった。