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Optimising P_2O_5 availability for fertilizer use, by direct treatment of apatite with hydrochloric or nitric acids

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Abstract

Hydrochloric and nitric acid treated apatite is not directly used as a fertilizer because of the hygroscopic character of the products. Another problem arises from the volatility of these acids and that acidulated product undergo reversions during drying with loss of the acid. We have found that apatite beneficiated with hydrochloric and nitric acids dried at an optimum temperature ~120°C has high available phosphorous. The products can be stored in the solid form in sealed polythene bags.

Introduction

The manufacture of phosphate fertilizers is largely dependent upon sulphuric acid [1–7]. Most extensively used phosphate fertilizers, e.g. single superphosphate, triple superphosphate and ammonium phosphate production needs large quantities of this acid [1–7] made from elemental sulphur. Sulphur deposits in the world are confined to few areas and the cost of sulphur is continuing to increase. Developing countries possessing reserves of apatite are finding it difficult to utilize it for the manufacture of soluble fertilizer because of the cost of imported sulphur. An alternative is nitric and hydrochloric acids. The chief objection for use of these acids has been the hygroscopic character of the beneficiated product. Both calcium chloride and nitrate are highly hygroscopic. Nonhygroscopic materials can be made by treating the acidulated apatite with ammonia [3] or ammonium sulphate [8]. As cheap moisture-proof methods of packing are now available, it is necessary to re-examine the possibility of adopting hydrochloric or nitric acid treated apatite directly as a fertilizer.

Another problem associated with hydrochloric and nitric acids is that the commercial concentrated acids contain large quantities of water (Commercial hydrochloric and nitric acids contain approximately 65 and 35% respectively of water. The acid treated product has to be dried to remove excess water. We have studied the possibility of direct beneficiation of Eppawala apatite in Sri Lanka with hydrochloric and nitric acids and found that storeable fertilizers can be produced.

Experimental

In all experiments, the good quality Eppawala ore of composition given in Table 1 was used. Ground apatite powder sieved through mesh BS200 was mixed with commercial hydrochloric (35% HCl) and nitric (70% HNO_3) in different proportions starting from the stoichiometric level of monocalcium phosphate to levels below the stoichiometry of dicalcium phosphate. Product is dried at different temperatures and water/citric acid soluble P_2O_5 was determined colormetrically by the vanadomolybdate methods. Results were

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Table 1. Composition of the ore use in the experiments

Constituent	Percentage
CaO	55.5
P_2O_5 (citric acid soluble)	4.4
P_2O_5 (citric acid insoluble)	34.8
SiO_2	0.3
Fe_2O_3	0.3
Al_2O_3	0.3
Cl	2.0
F	1.5

Table 2. Water and citric acid soluble P_2O_5 in apatite treated with varying proportions of HCl and dried at different temperatures

T/°C	P_2O_5%(H_2O)	P_2O_5%(Citric)	Conversion%
Acidulation HCl: Level of monocalcium phosphate			
80	23.6	24.6	84.8
100	25.4	29.0	100
110	22.4	29.0	100
120	23.0	29.0	100
130	19.4	29.0	100
140	17.1	29.0	100
150	17.0	27.8	95.9
Acidulation HCL: 77% of the level of monocalcium phosphate			
80	25.7	27.4	88.1
100	24.4	26.9	86.5
110	23.4	28.3	90.9
120	16.0	29.4	95.0
130	13.6	29.6	95.2
140	12.1	25.1	80.7
150	12.1	25.1	82.6
Acidulation HCL: level of dicalcium phosphate			
80	17.1	18.9	57.1
100	11.7	17.1	51.7
110	10.5	19.8	59.8
120	7.5	19.8	59.8
130	4.8	21.7	65.5
140	6.3	17.8	53.7
150	6.7	13.6	41.2
Acidulation HCl: 50% of the level of dicalcium phosphate			
80	10.8	12.4	33.3
100	10.2	12.7	34.1
110	10.7	13.5	36.3
120	9.3	12.4	33.3
130	6.5	12.2	32.7
140	5.6	11.7	31.5
150	5.2	11.7	31.5

methods. Results were also confirmed by the gravimetric ammonium molybdate method.

Results and discussion

The action of HY ($Y = Cl, NO_3$) can be represented by the following equations,

$$2Ca_5(PO_4)_3.X + 8HY \rightarrow 3Ca_2(HPO_4)_2 + 4CaY_2 + 2HX \qquad (1)$$

$$\downarrow$$

dicalcium phosphate

$$2Ca_5(PO_4)_3.X + 14HY \rightarrow 3Ca(H_2PO_4)_2 + 7CaY_2 + 2HX \qquad (2)$$

$$\downarrow$$

monocalcium phosphate

$$2Ca_5(PO_4)_3.X + 20HY \rightarrow 6H_3PO_4 + 10CaY_2 + 2HX \qquad (3)$$

$$\downarrow$$

orthophosphoric acid

Acid treatment also assists breaking of the apatite lattice, ie

$$2Ca_5(PO_4)_3.X \rightarrow 3Ca_3(PO_4)_2 + CaX_2$$

At any level of acidulation all the four reactions occur to some extent. This is confirmed by X-ray diffraction analysis and determinations of water, 2% citric acid and neutral ammonium citrate solubilities of the acid treated apatite. Tables 1 and 2 show water and 2% citric acid soluble P_2O_5 in apatite treated with HCl and HNO_3 in varying proportions dried at different temperatures for $1\frac{1}{2}$ h ($1\frac{1}{2}$ h is approximately the minimum time needed to dry the samples to yield a dry solid mass. Drying to a constant weight, at each temperature is not possible as drying removes some HCl or HNO_3 in addition to water). A glance at Tables 2 and 3 reveal the following features.

1. Water soluble P_2O_5 decreases with the increase of the drying temperature. This results from the occurrence of following reversion reactions.

$$CaY_2 + Ca_2(HPO_4)_2 \rightarrow (Ca_3(PO_4)_2 + 2HY \qquad (4)$$