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Non hygroscopic superphosphate fertilizer from apatite and hydrochloric acid

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Abstract. A method is described for the production of a nonhygroscopic fertilizer from apatite by treatment with hydrochloric acid .

Apatite is acidulated with HCl to the stoichiometric level needed for generating dicalcium phosphate. The reaction product when mixed with ammonium sulphate sufficient to double-decompose calcium chloride and dicalcium phosphate yields a nonhygroscopic product containing almost all phosphorus in the water-soluble form. Results of laboratory experiments conducted to determine the optimum conditions for the process, chemical properties of the material and its agronomic effectiveness are described. The studies were carried out with the intention of utilizing the reserve of apatite at Eppawala in Sri Lanka using indegenous raw materials.

Introduction

The beneficiation of rock phosphate is heavily dependent upon the use of sulphuric acid [1–4). In fact the largest consumer of this acid is the phosphate fertilizer industry. Sulphur is becoming an expensive commodity in the world market. Sulphur and sulphide ores that could be used for the manufacture of sulphuric acid are not as widely distributed as the rock phosphate. Unless alternative routes are devised for the beneficiation of apatite, the superphosphate industry would be limited by the shortage of sulphur. Several countries possessing reserves of rock phosphate are finding it difficult to develop superphosphate industries mainly because of the cost of sulphur. The established alternative methods for the production of superphosphates are the furnace process for direct conversion of apatite into phosphoric acid and the nitric-phosphate process. The furnace process is capital-intensive and not sufficiently developed to supersede the wet process based on sulphuric acid. The chief factor that restricts the production of nitric-phosphates is the cost of nitric acid. Almost all commercial nitric acid is made by the oxidation of ammonia. Ammonia synthesis is energy expensive and depends on fossel fuels for the hydrogen requirements. It is unlikely that any developing nation not having an established ammonia industry could economically utilize the phosphate reserve for manufacturing nitric-phosphates. The other avenue available for solublization of apatitite is the use of hydrochloric acid. Hydrogen chloride as an alternative to sulphuric or nitric acids has attractive features. This acid is an under-utilized by-product of the sodium hydroxide industry. Provided the energy requirements are met, the raw material (NaCl) needed for its production is inexhaustible. In the conventional method for production of HCl, hydrogen and chlorine generated in the electrolysis of brine are burnt together. The possibility remains that hydrogen is saved for ammonia manufacture and that chlorine is photochemically reacted with water to obtain HCl and oxygen. From laboratory experiments it is known that this reaction can be carried out using sunlight and a semiconductor photocatalyst [5].

Unfortunately, calcium chloride resulting from °°acidulation apatite°° with HCl makes the fertilizer hygroscopic and unsuitable for storage and handling in the field. Although methods have been devised for the removal of phosphoric acid from calcium chloride, the complicated separation technique becomes the cost-determining factor. In a method developed by the Israel Mining Industries, H_3PO_4 is separated from $CaCl_2$ by solvent extraction with butyl or isoamyl alcohol which is recycled [6].

We have studied a simpler method where the calcium chloride is rendered insoluble by double decomposition with ammonium sulpate. The method has the following advantages. (1) Phosphate fertilizers are generally used in conjunction with nitrogeneous sources. Although ammonium nitrate and urea are becoming more popular nitrogeneous fertilizers, substantial quantities of ammonium sulphate are still used. Several industries yield this salt as a by-product. (2) Ammonium sulphate can be manufactured independently of sulphuric acid using gypsum. The world reserve of gypsum is far in excess of sulphur or sulphide ores available for the manufacture of sulphuric acid. (3) Most high analysis nitrogen and/or phosphate fertilizers do not contain sulphur which is an essential plant nutrient [7–8]. Fertilizer made by this method contains sulphur in addition to phosphorus and nitrogen.

This study was motivated by the necessity of finding a method for beneficiation of apatite mined at Eppawala in Sri Lanka, using local raw materials [9–12]. At present the only mineral acid that is manufactured in Sri Lanka is HCl. The apatite reserve at Eppawala in Sri Lanka is estimated to be 25,000,000 tonnes and at the present demand rate in Sri Lanka, the deposit could provide phosphate fertilizers for 3–4 centuries. To this date Eppawala apatite is exploited only as a fertilizer for direct application to long-term crops, ie, tea and rubber [13]. As the citric acid solubility of Eppawala is low, for other requirements the country still depends on imported rock phosphate and superphosphate.

Experiment

Eppawala deposit in Sri Lanka is mainly a fluor-chlorapatite with little admixture of hydroxyapatite and carbonatoapatite. The exact composition and the impurity levels are variable. In this investigation the highest and poorest quality ores were studied to represent the possible extremes. The highest quality ore which is designated as grade A is rock from the enriched primary deposit. The poorest quality ore designated as grade Z containing high levels of iron and aliminium is found in the leached zones. The compositions of the two grades of ores used in the experiments are given in Tables 1 and 2

In all experiments pulverized apatite sieved through mesh BS200 was used. The total and 2% citric-acid soluble P_2O_5 in the samples were esti-

Table 1. Composition of grade A apatite

Constituent	Percentage
CaO	55.5
P_2O_5 (citric acid)	4.4
P_2O_5 (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. Composition of grade 2 apatite.

Constituent	Percentage
CAO	48.1
P_2O_5 (citric acid)	1.2
P_2O_5 (insoluble	32.0
SiO_2	2.0
Fe^2O_3	6.1
Al^2O_3	3.2
Cl	3.1
F	2.2

mated by the vandomolybdate method (for the estimation of total P_2O_5 the powder was dissolved in aqua regia). Aliminium and iron were determined by atomic absorption spectroscopy (Hitachi 170–30). The fluorine contents were estimated using a ion-selective electrode.

20 g of powder mixed with different amounts of commercial HCl (35%) were aged in 250 ml beakers covered with a polyethylene membrane. Samples taken from the beakers at different intervals of time were analysed for citric acid soluble, water soluble and total P_2O_5. Figure 1 shows the variation of the fraction (F = water-or citric acid-soluble P_2O_5/total P_2O_5) with time. It is seen that in each case an equilibrium is reached and time taken to approach the saturation is longer in the case of the grade Z material. Once the saturation is reached, different amounts of finely ground ammonium sulphate were mixed and the resulting paste aged for one day to complete the double decomposition reaction. The product was dried in a ventilated oven at 70°C. During drying citric acid-and water-soluble P_2O_5 content were continuously monitered. The same procedure was repeated at 100°C, 150°C to study the stability, chemical changes and possible reversions

The hygroscopic character of the material dried at 70°C was assessed by storing samples in a atmosphere (desiccator containing $H_2O + H_2SO_4$) of relative humidity 75%.

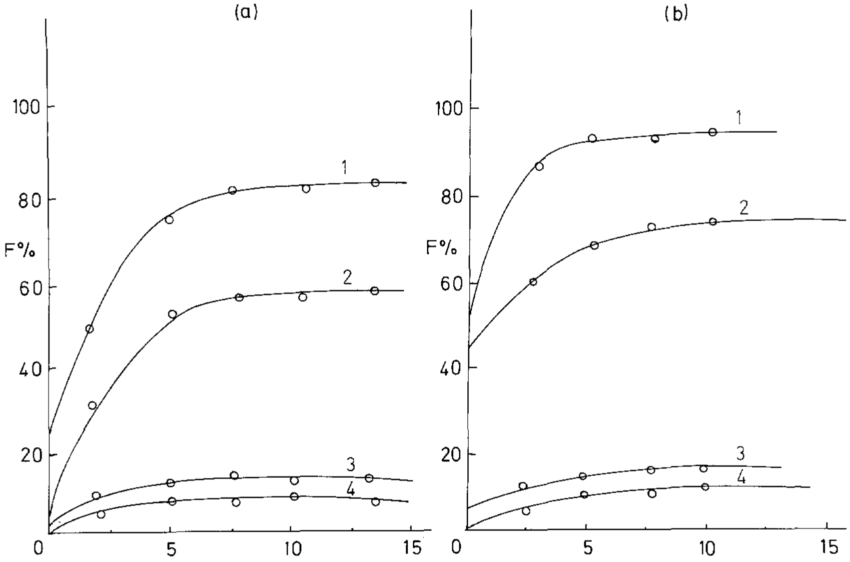

Fig. 1. Time variation of water (curve 1 = grade A, curve 2 = grade Z) and citric acid (curve 3 = grade A, curve 4 = grade Z) soluble P_2O_5 in apatite treated with HCl (a) apatite: HCl = 1: 1 (b) apatite:HCl = 1:0.5 (F is defined in the text).

Results and discussion

The action of HCl on apatite can be represented by the following equations,

$$2Ca_5(PO_4)_3.X + 8HCl \rightarrow \underset{\substack{\downarrow \\ \text{dicalcium phosphate}}}{3Ca_2(HPO_4)_2} + 4CaCL_2 + 2HX, \qquad (1)$$

$$2Ca_5(PO_4)_3.X + 14HCl \rightarrow \underset{\substack{\downarrow \\ \text{monocalcium phosphate}}}{3Ca(H_2PO_4)_2} + 7CaCl_2 + 2HX, \qquad (2)$$

$$2Ca_5(PO_4)_3.X + 20HCl \rightarrow 6H_3PO_4 + 10CaCl_2 + 2HX, \qquad (3)$$

In addition, The HCl treatment also assists breaking of the apatite lattice into tricalcium phosphate, i.e.,

$$2Ca_5(PO_4)_3.X \rightarrow 3Ca_3(PO_4)_2 + CaX_2 \qquad (4)$$

The determination of the water, 2% citric acid and neutral ammonium citrate soslubilities of HCl treated apatite shows that depending on the amount of acid used, temperature and degree of ageing, varying quantities of mono-, di- and tricalcium phosphate are produced (Fig. 1). The double decomposition reactions of calcium salts produced with ammonium sulphate are,

$$CaCl_2 + (NH_4)_2SO_4 \rightarrow CaSO_4 + 2NH_4Cl \qquad (5)$$

$$Ca(HPO_4) + (NH_4)_2SO_4 \rightarrow \underset{\substack{\downarrow \\ \text{diammonium phosphate}}}{(NH_4)_2(HPO_4)} + CaSO_4 \qquad (6)$$

$$Ca(H_2PO_4)_2 + (NH_4)_2SO_4 \rightarrow CaSO_4 + \underset{\substack{\downarrow \\ \text{monoammonium phosphate}}}{2NH_4(H_2PO_4)} \qquad (7)$$

The experiments with the grade A ore show that, when apatite is aged after addition of HCl stoichiometrically sufficient to yield dicalcium phosphate (Equation 1), mixing with ammonium sulphate in the proportion needed to convert all calcium chloride and dicalcium phosphate into calcium sulphate generates a product (drying temperature 70%) containing almost all phosphate in the water soluble form. Simple calculation based on Equations. (1), (2), (5), and (6) shows that to convert 1 kg of apatite (grade A) containing x% by weight of P_2O_5, the weights of commercial HCl (35% and ammonium sulphate required are

$$HC = 1.96x \times 10^2 \, kg \tag{8}$$

$$(NH_4)_2SO_4 = 2.17x \text{ x } 10_2 \, kg \tag{9}$$

It is interesting to note that unlike the conventional H_2SO_4 process for making single superphosphate, a product containing nearly 100% water soluble P_2O_5 can be achieved by acidulation up to the stoichiometric level of dicalcium phosphate. Calcium phosphate formed in the double decomposition remains as dihydrate at the drying temperature. Taking this into the account, the theoretical composition calculated from equations (1), (2), (5) and (6) can be expressed in the form

$$P_2O_5\% = \frac{100x}{100 + 4.7x}, \tag{10}$$

$$N\% = \frac{75.7x}{100 + 4.7x} \tag{11}$$

$$S\% = \frac{85.7x}{100 + 4.7x} \tag{12}$$

$$Cl\% = \frac{66x}{100 + 4.7x} \tag{13}$$

Table 3 compares the experimental and theoretical values for the two grades of the ore tested (x $\simeq$ 39, 32 for A and Z grade ores, corresponding

Table 1. Experimental and theoretical values for the analysis of the fertilizer at the optimum mixing ratio.

Constituent	Grade A		Grade B	
	Exp %	Th %	Exp %	Th %
P_2O_5 (water)	13.0	13.7	5.2	10.6
P_2O_5 (citric)	1.5	0	4.4	0
N (NH_4)	9.8	10.4	8.0	8.1
S (SO_4)	12.0	11.8	9.5	9.6
Cl	9.1	9.0	10.1	7.1

amounts of HCl and $NH_4)_2SO_4$ obtained from (8) and (9) are 0.78, 0.63 Kg and 0.85, 0.70 Kg respectively). In the case of the grade A material the agreement is reasonably good. Impurities present in the grade Z material inhibit complete conversion

For practical purposes, it is probably unnessary to acidulate to the above optimum level. Partial acidulation and addition of the requisite amount of ammonium sulphate to suppress the hygroscopic character could give good agronomic effectiveness. Table 4 gives water and citric acid solubilities of products of different compositions.

The fertilizer does not show signs of reversion when stored at room temperature. However, at elevated temperatures (above 100°C) changes in citric acid and water soluble phosphates are noticed. These changes become more pronounced, when the ammonium sulphate blended is less than the quantity needed to double-decompose all calcium chloride and dicalcium phosphate (Fig 2). This can be easily understood, the factor responsible for reversion being dicalcium phosphate. When less ammonium sulphate is added, the dicalcium phosphate concentration increases. Drying at temperatures slightly above 100°C converts calcium sulphate dihydrate into the hemihydrate. The P_2O_5/N ratio can be adjusted within reasonably wide limits while maintaining room temperature stability and the non-hygroscopic character. Another advantage of the process is the extreme ease with which the fertilizer can be granulated. Calcium sulphate assists the formation of granules.

Stable and non-hygroscopic fertilizers made by this method using grade Z material contain relatively lower levels of available phosphate (Table 3 and Table 4). Conversion percentages comparable to the grade A material can be obtained if the pulverized rock is heated with 5% conc. HCl in a closed container to 250°C. Because of the volatility of HCl, the apatite lattice is broken during this process.

To test the effectiveness of the fertilizer a pot experiment was carried out

Table 4. Water and citric acid acid soluble P_2O_5 in samples of different composition (conversion % = (water + citric) P_2O_5 × 100/total P_2O_5, all samples of apatite were grade A exept the one marked Z).

Apatite Wt/Kg	HCl (35%) Wt/Kg	$(NH_4)_2SO_4$ Wt/Kg	P_2O_5 (water) %	P_2O_5 (citric) %	P_2O_5 (total)	Conversion %
1.0	2.0	1.0	15.1	0.7	15.8	100
1.0	1.0	1.0	13.3	1.0	16.2	88.3
1.0	0.8	1.4	13.0	0.5	13.7	98.5
1.0	1.0	0.5	12.6	2.6	18.0	84.4
1.0	0.3	0.7	4.5	2.0	22.2	29.3
1.0(Z)	0.7	1.0	5.2	4.4	13.6	70.5

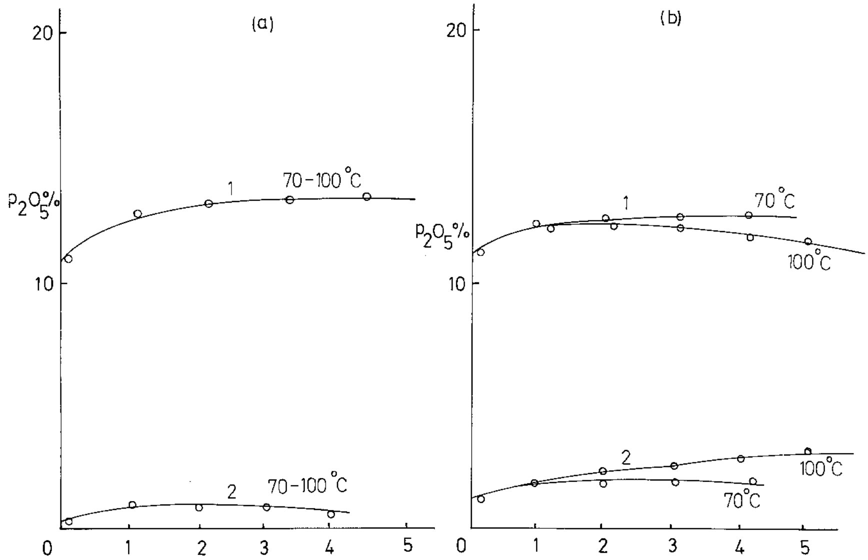

Fig. 2. The variation of water (curve 1) and citric acid (curve 2) solubilities of the fertilizer. The mixing ratio apatite (grade A):HCl (35%):$(NH_4)_2SO_4$ (a) 1:1:1 (b) 1:1:0.5.

with rice plants (variety BG 11) as follows. The top 5 cm of pots (cross-sectional area = 225 cm^2, height = 18 cm) were mixed with ingredients whose compositions are given below. Four pots were used to test each sample and five seedlings were planted on each pot, five days after the application of fertilizer.

Set 1 10 g of fertilizer of composition given in the third row of the Table 4.

Set 2 The same quantity of apatite (grade A) and ammonium sulphate as in the pots of set 1 (i.e., no HCl treatment).

Set 3 The fertilizer of composition given in the fifth row of the Table 4 and additional ammonium sulphate so that the total amount of apatite and ammonium sulphite per pot is the same as in the set 1.

Set 4 Single superphosphate made from grade A apatite + ammonium sulphate. The amount of apatite and ammonium sulphite per pot maintained as in the Set 1.

All pots were supplemented with 4 g potassium sulphate. Results of the experiment which gives the average of the four measurements are given in Table 5. It is clear that HCl-treated fertilizer is superior in terms of the yield of grain, total biomass and the growth rate. Fully acidulated product (ie,

Table 5. Results of the pot experiment.

Pots	Grain/g	Table Biomass/g	Ripening age/days
Set. 1	22	102	80
Set. 2	12	70	100
Set. 3	20	90	90
Set. 4	20	98	80

HCl sufficient to convert apatite into dicalcium phosphate) seems to be comparable or slightly better than single superphosphate. It is also interesting to note that although the amount of HCl used to process the fertilizer applied to the pots of the set 3 is much less, the effectiveness is not very different from the fully acidulated material

Conclusion

The above investigation demonstrates the feasibility of adopting hydrochloric acid to solubilize apatite. A problem that needs further study is the corrosion involved in handling large quantities of hydrochloric acid. In some plants excessive chloride is known to have unfavourable effects. It is unlikely that for most crops this problem would arise even if the fertilizer is used in conjunction with potassium chloride. Instead of ammonium sulphate, potassium sulphate can be used to immobilize calcium chloride in the HCl treated apatite.

Note

A patent covering the process described in this paper for making nonhygroscopic fertilizer from apatite and hydrochloric acid has been granted (Sri Lanka Patent No. 9772).

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