Impurities in Eppawala Rock Phosphate and Removal Methods

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Abstract

Apatite mined from Eppawala (Eppawala Rock Phosphate - ERP) cannot be directly used as a fertilizer for annual crops such as paddy and vegetables because of its low water solubility. It is difficult to manufacture water soluble phosphate fertilizers from ERP due to its stable chemical formation and impurities in ERP. This study focuses on impurities in ERP and methods of their removal. Removing the impurities in ERP will help to produce water soluble phosphate fertilizers for annual crops. Literature shows high contents of Fe_2O_3, Al_2O_3 and chlorine as impurities in ERP. This investigation helped us to reduce combined Fe_2O_3 and Al_2O_3 content from 12.36% to 6.42% in test 1 of this study and to 4.61% in test 2 by using froth floatation technique. Acceptable level of combined Fe_2O_3 and Al_2O_3 content for the production of water soluble phosphate fertilizer is less than 5%. Therefore, the concentrate of test 2 is suitable for the production process, but high chlorine content in the concentrate will create difficulties in the formation of water soluble phosphate fertilizers.

Keywords: Apatite, Eppawala Rock Phosphate, Solubility, Water soluble phosphate fertilizers

1. Introduction

Eppawala Rock Phospahe deposit is one of the major mineral deposits in Sri Lanka used for low soluble phosphate fertilizer manufacturing. This ERP deposit consists of primary apatite crystals and secondary phosphate matrix (fine matrix) formed due to weathering of the primary apatite crystals [1].

The primary apatite crystals can easily be separated from the groundmass and it contains high P_2O_5 (around 40%) and low combined Fe_2O_3 and Al_2O_3 (less than 1%) contents [2]. Eppawala fine matrix contains relatively low P_2O_5 (around 30%) and high combined Fe_2O_3 and Al_2O_3 (around 12%) contents [2]. Both primary apatite crystals and Eppawala fine matrix contain high chlorine contents around 1.5% [2].

Finely ground products from run-off of quarry material are used as straight fertilizers for tea, coconut and rubber in Sri Lanka. These fertilizers cannot be used for annual crops because of its low water solubility.

Phosphoric acid is used as an intermediate product in the production of water soluble phosphate fertilizers for annual crops such as paddy and vegetables. Industry standards for phosphate rock in phosphoric acid production by the wet process are 0.05% Chloride and 5% R_2O_3 (Fe_2O_3+Al_2O_3) [3].

High Chloride content increases the corrosion in the filtration plant and reduces the rate of slurry filtration [3]. High amounts of R_2O_3 will decrease plant capacity and small amounts are beneficial in reducing corrosiveness by complexing with fluoride [3].

Chloride is held in the crystal lattice of the Apatite rock as chlorapatite. Therefore, chloride cannot be removed from ERP by any physical beneficiation method [4]. Iron (Fe) presents in ERP as gothite ($Fe_2O_3.H_2O$), hemetite (Fe_2O_3) and illmanite ($FeTiO_3$) minerals and aluminium (Al) presents as crandallite ($CaAl_3(PO_4)_2(OH)_5.H_2O$) and wavellite ($Al_3(OH)_3(PO_4)_2.5H_2O$) minerals [4-5]. Therefore, high R_2O_3 content in ERP can be reduced by removing minerals containing Fe and Al.

2. Previous Study

Hanna and Anazia, 1990 upgraded the phosphate rock to get a concentration of 29.5 - 30.6% P_2O_5, 0.7-1.0% MgO, and 2.8 - 8% Insol. The recoveries from the concentration ranged from 65% to 88%. The optimum conditions for Carbonate flotation using a feed from 105μm to 420μ (16%), were found 0.4 g H_2SO_4 g/ kg of feed as pH modifier, and three step addition of 0.3 g Oleic acid/ kg of feed with 0.1 g pine oil /kg of feed mixture for each step [6-7]. Oleic acid was used as the phosphate collector and pine oil was used as the frother.

3. Methodology

3.1 Materials

An ERP finely ground product (ERP Fertilizer from rock phosphate milling plant) was taken as the initial samples in this study

3.2 Particle Size Distribution Analysis

Particle size distribution of the initial samples were analyzed by using laser particle size analyzer, HMK-CD2 designed according to international standards ISO 13320. It has broad size range from 0.02 to 2000 μm with higher accuracy.

3.3 Wet Chemical Analysis

A Thermo-iCE3500 Atomic Absorption Spectrometer equipped with deuterium background correction was used with iron and aluminum hollow-cathode lamps as radiation sources. The optimum conditions were those recommended by the manufacturer and a minimum of three standard solutions were used for the calibration in each analysis. Acetylene flow rate, nitrous oxide flow rate, air and the burner height were adjusted in order to obtain the maximum absorbance signal, while aspirating the analyte solutions. Iron and aluminum concentrations were determined in ppm range by software using the calibration graph. Concentration of each element in reagent blank and the digested SRM were also determined and these values were used for the calculation of the accuracy of the results. Then amount of each element present in the samples were calculated as oxide percentages [8].

3.4 Reducing R_2O_3 Content in ERP by Floatation

2 kg sample by weight from ERP was treated to three-stage carbonate floatation as given by Hanna and Anazia in 1990. Solid/water ratio of the feed was 0.25. Conditioning time period was 10 minutes and the total time for the process was 60 minutes.

4. Results and Discussion

4.1 Particle Size Distribution of Eppawala Rock Phosphate (ERP) Fertilizer

Particle size distribution of Eppawala Rock Phosphate (ERP) fertilizer was analyzed by using the laser particle size analyzer and results are shown in Figure 1. From the results, it can be observed that the maximum particle size of ERP fertilizer is less than 100 µm. In three stage carbonate floatation, Hanna and Anazia have obtained optimum recovery using a feed from 105 µm to 420 µm (16%) and remaining 84% of the feed is less than 105 µm.

In this study, recoveries from the concentration ranged from 55% to 60% and that will not be the optimum recovery, because particle size distribution of the feed affects the recovery.

When particles are getting too small they tend to float on the slurry surface. That causes to increase the impurity levels in the concentrate. Therefore, small particles should be removed before the floatation process, but in this study we could not remove the smaller size particles from the feed.

4.2 Collecting Mechanism of Oleic Acid

In this study, oleic acid was used as the phosphate collector. Oleic acid is a complex molecule which is asymmetric in structure and hetoropolar. Heteropolar means that oleic acid consists of polar (hydrophilic) group and non-polar (hydrophobic) hydrocarbon group as shown in Figure 2.

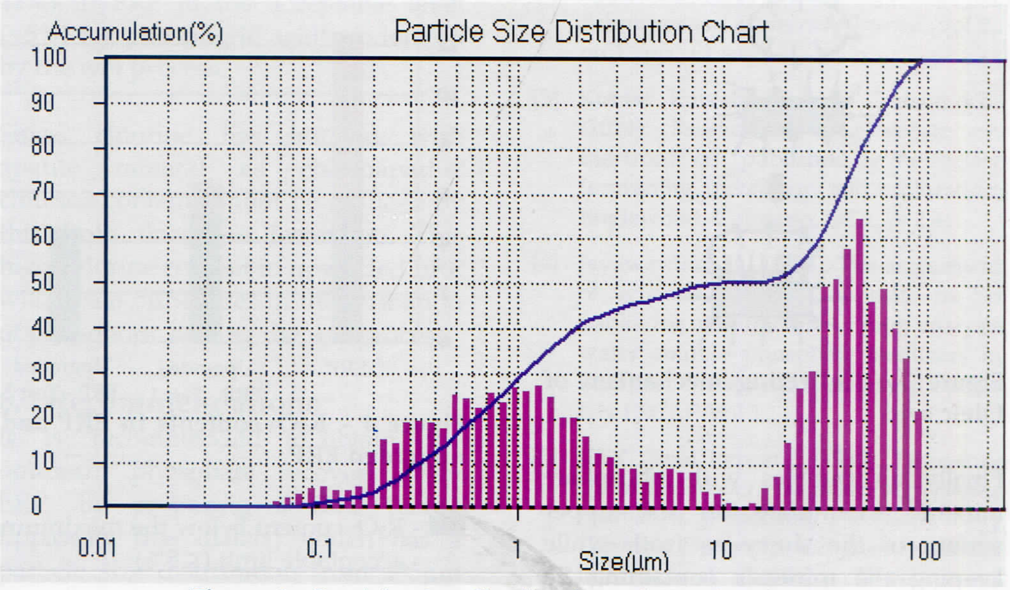

Figure 1 - Particle size distribution of ERP fertilizer

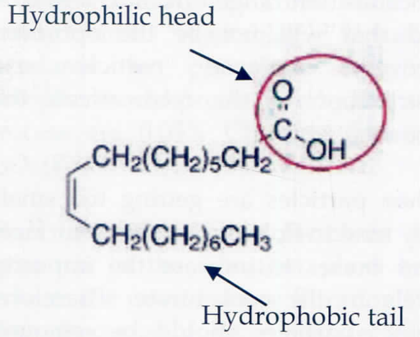

Figure 2 – Oleic acid

Oleic acid dissociates into carboxylate ions (R-CO_3^-) and H^+ ions in water. Then hydrophobic group of the carboxylate ions goes into the air bubbles and the hydrophilic group of the carboxylate ions adsorbs on the apatite mineral. This mechanism is shown in Figure 3.

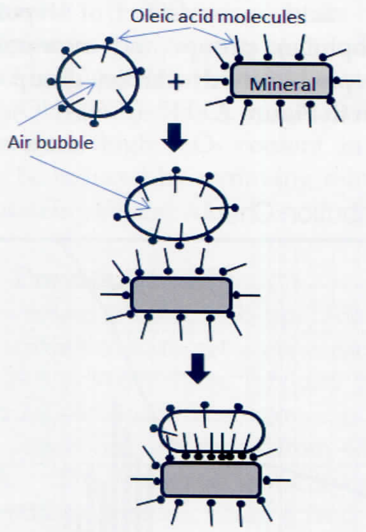

Figure 3 - Collecting mechanism of Oleic acid

Finally air bubbles with phosphate mineral accumulate on the upper surface of the slurry as froth while keeping the minerals containing Fe and Al at the bottom of the slurry.

4.3 Reduction of Fe_2O_3, Al_2O_3 and Chlorine Contents in Upgraded Eppawala Rock Phosphate (ERP)

Following table shows contents of Fe_2O_3, Al_2O_3 and R_2O_3 (Fe_2O_3 + Al_2O_3) in the initial ERP and upgraded ERP.

Table 1 - Fe_2O_3, Al_2O_3 and R_2O_3 contents in ERP and upgraded ERP

	ERP	Upgraded ERP - Test 1	Upgraded ERP - Test 2
Fe_2O_3	9.35%	4.71%	2.92%
Al_2O_3	4.01%	1.71%	1.69%
R_2O_3	12.36%	6.42%	4.61%

High R_2O_3 content in ERP was reduced from 12.36% to 6.42% in Test 1 and it (12.36% of R_2O_3) was reduced to 4.61% in Test 2. The maximum acceptable limit of R_2O_3 for phosphoric acid production by the wet process is 5%. Therefore, upgraded ERP - Test 2 is suitable for phosphoric acid formation by the wet process. Above results are shown in Figure 4.

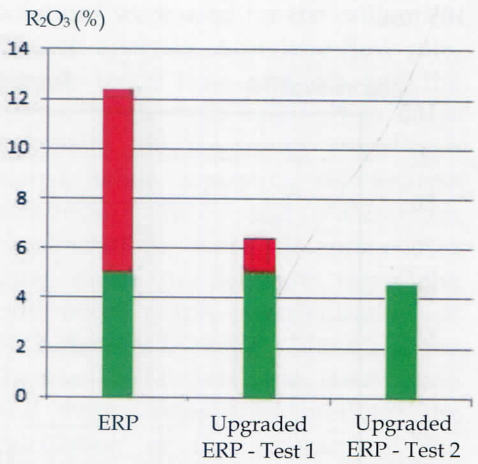

Figure 4 – R_2O_3 contents in ERP and upgraded ERP

- R_2O_3 content below the maximum acceptable limit (< 5%)

- R_2O_3 content above the maximum acceptable limit (> 5%)

Since, chlorine has bonded with apatite mineral as chloroapatite, chlorine content cannot be reduced by this froth floatation technique. Therefore, chlorine content in upgraded ERP will not change and that will remain around 1.5% [2]. This high chlorine levels can increase corrosion in the filtration plant and reduces the rate of slurry filtration in the formation of phosphoric acid by the wet process [3].

Chlorine concentration above 0.03% increase corrosion of stainless steel Higher quality alloys can handle concentrations around 0.1% [3].

5. Conclusions

Chlorine, Fe_2O_3 and Al_2O_3 are impurities in Eppawala fine matrix and Chlorine is the only impurity in Eppawala primary apatite crystals.

According to the above results carbonate floatation given by Hanna and Anazia in 1990, can be used to reduce high R_2O_3 content (around 12%) in ERP to the acceptable level (<5%) for phosphoric acid production by the wet process.

Since, chlorine has bonded with apatite mineral as chloroapatite, chlorine content cannot be reduced by this froth floatation technique. This high chlorine content in upgraded ERP will create difficulties in the formation of phosphoric acid by the wet process.

6. Recommendations

It is recommended to obtain the optimum phosphate recovery from ERP, by preparing a feed (using Eppawala fine matrix) which has a particle size distribution from 105μm to 420μm (16%).

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