▼ Journal of Research (Science), Bahauddin Zakariya University, Multan, Pakistan.
Vol. 18, No. 2, April 2007, pp. 145-157 ISSN 1021-1012

SELECTIVE LEACHING OF LOW GRADE CALCAREOUS PHOSPHATE ROCK IN SUCCINIC ACID

Mohammad Ashraf, Zafar Iqbal Zafar*, Tariq Mahmood Ansari
Department of Chemistry, Bahauddin Zakariya University,
Multan 60800, Pakistan.
***email:** drzafarbzu@hotmail.com

Abstract

In this work, a number of experiments have been carried out to reduce the carbonate content by leaching the ground phosphate rock with dilute succinic acid solution in order to get marketable and industrially acceptable phosphate grades. By using this technique, the effect of acid concentration, reaction time, process temperature and liquid/solid ratio (v/w basis) have been studied. Depending on the reaction conditions as well as nature and size of the particles, it was found that the P_2O_5 percent can be raised more than 30% along with the corresponding reduction of more than 70% in the calcareous material of the sample.

Keywords: Calcareous material, carbonate dissolution, selective leaching, succinic acid.

INTRODUCTION

Phosphates are essential ingredient in the fertilizers used to supply food and feed for mankind and animals. There is no substitute for phosphate rock as a raw material in the production of phosphate fertilizers in the world at this time. As the world population continues to increase, so does the demand for phosphate. Phosphate rocks are complex raw materials and are mainly used in the manufacture of phosphate fertilizers. The composition of these rocks varies from one deposit to another. Therefore, phosphate rocks from different sources are expected to behave differently in acidulation processes. Most of the world's phosphate rocks are of sedimentary origin and are primarily composed of the apatite group in association with a wide assortment of accessory minerals, fluorides, carbonates, clays, quartz, silicates, metal oxides, etc.

Commercial phosphate rocks should not contain more than 8% carbonates (about 3.5% CO_2) in order to be economical. The presence of free carbonates in the phosphate rocks usually requires additional acidulent during the manufacture of phosphoric acid and phosphatic fertilizers. Therefore, low grade phosphate rocks are not usually suitable for direct use in acidulation plants unless their tricalcium phosphate content is increased to 70% or more, using conventional methods such as crushing, screening and drying, or some other physical separation process which include washing and desliming [Good 1976]. A number of other beneficiation techniques [Ray and Roberts 1969, Hignett *et al.* 1977, Lawver *et al.* 1978, Lodha *et al.* 1984, Hsieh 1988, Zafar *et al.* 1996] may also be applied. These techniques are:

BENEFICIATION TECHNIQUES

Flotation

Separating technique for silica based gangue and phosphates by using different types of floating reagents (amine and fatty acids) are called flotation. Hignett *et al*. [1977] claimed that flotation seems to work best on ores containing well-crystallized carbonates. When the ore contains soft and chalky carbonates the flotation results were less satisfactory. The beneficiation of phosphate ores containing carbonaceous gangue is complicated because of the similarities in the chemical behavior of the minerals present [Robinson 1978, Mew 1980, Baudet 1988]. Calcite may consume part of the sulphuric acid used for superphosphate manufacture, but dolomite is more objectionable since magnesium in quantity renders the phosphoric acid unacceptably viscous [Hignett 1980]. The currently used commercial process of double flotation [Crago 1940] is not adequate for reducing the dolomitic impurity level to less than 1.0 weight percent MgO in the concentrate, as stipulated by the phosphate industry. A number of chemicals are used in flotation which may increase the overall process cost.

Calcination

Beneficiation by calcination is one of the better known processes. It is based on the dissociation of the calcium carbonate gangue materials by thermal energy. The high cost of energy required for calcination has always acted against the implementation of such proposals. The calcination may tend to decrease the solubility and reactivity of the calcined phosphate rocks during the manufacture of phosphoric acid by the wet process. In other words, the calcined phosphate will need more retention time in order to get the same solubility as that of non-calcined phosphate of the same grade. The calcination and desliming processes usually result in concentration of silica in the final concentrate product to more than the 3-4% desired for wet process phosphoric acid. The removal of this silica is essential and may add an extra cost to the process. Upon hot quenching, the magnesium oxide may be transformed into an insoluble magnesium hydroxide. Higher amount of thermal energy is required for complete removal of calcareous and dolomitic materials [Zafar *et al.* 1995]. Calcination requires complete decomposition and removal of the calcite and dolomite present in the phosphate rock; otherwise, the hard particles of calcite and dolomite remaining will cause serious problems during the acidulation and also increase the acid consumption for fertilizer manufacture.

Bioleaching

In the bioleaching process for low grade phosphate rocks, several microbial species can grow at extreme conditions, including high acidity and low organic matter concentrations [Brierley 1982]. This environment, through its high selectivity, presents various microbial species. The predominating species found in these environments are those from the genus *Thiobacillus*, specially *T. ferrooxidans* and *T. thiooxidans* [Harrison 1984]. *T. ferrooxidans* uses ferrous iron and reduced sulphur as energy sources and *T. thiooxidans* can only use sulphur compounds [Hutchins and Davison 1986]. The metabolic activity of these micro-organisms is regulated by a series of factors that must be controlled to achieve maximum biological action. Control of temperature, pH and oxygen levels, is required for the maintenance of ideal leaching process conditions; otherwise the acid production is not enough to solubilize the high phosphate content and neutralize the carbonaceous material [Costa *et al.* 1992].

Selective Magnetic Coating

The principal of the process is the selective adsorption of fine grained magnetic material on to mineral surfaces in a mixed pulp, which renders the coated grains amenable to recover the conventional high intensity magnetic separation. High intensity magnetic separation is reported to be successful in upgrading Egyptian ores containing dolomite, silica, significant amounts of pyrite, organic and water soluble alkali. After careful dry size reduction, the ore is wetted and classified to eliminate fines and reduce the alkali content.

Electrostatic Upgrading

Electrostatic upgrading of phosphate ores has also been tried. The process is based upon selective turbo charging of the various mineral components followed by separation in a free-fall chamber. Results show that the concentrates can be obtained with fairly good recoveries especially for the ore having favorable liberation characteristics; and unfortunately the electrostatic separation of pyrite from the phosphate phase is quite inefficient, and thus the concentrate is polluted to a significant extent.

Partial Acidulation

A fully acidulated phosphate rock is treated with the stoichiometric quantity of acid required to convert the insoluble phosphate mineral (apatite) to the water-soluble form, monocalcium phosphate monohydrate. In contrast, a partially acidulated phosphate rock (PAPR) is generally treated with only a portion of the stoichiometric quantity of acid (expressed as a percentage, for example 60% PAPR). Partially acidulated phosphate rock can show a favorable response to the soil having acidic nature. Sulphuric and phosphoric acids can be used for partial acidulation. For economic reasons, however, the use of sulphuric acid for acidulation is the more usual choice. The presence of iron and aluminium give rise to reaction products and decrease phosphate availability. Because of the unpredictable nature of the acidulation of phosphate rock, mainly due to the complexity of the reaction and the influence of associated compounds in the rock, it is necessary to conduct thorough test work on a rock if it is being considered for partial acidulation, particularly since altering the process variables may significantly alter the nature of the product.

Direct Application

Direct application represents one of the simplest uses of phosphate rock. In direct applications, after grinding and screening the rock can be directly applied to the acidic soils without any further treatment. The rock may be finely ground up to 100-200 meshes (Tyler) to increase the agronomical effect on the soil. To control the problems associated with handling and distribution, granulation may be carried out. The International Fertilizer Development Centre (IFDC) has developed a method of granulating ground phosphate rock using various soluble salt binders. There is still scope to further improve the process in order to achieve a product with good mechanical properties without losing its agronomic effectiveness. A variety of binders have been used, including soluble salts (such as urea, potassium chloride, and magnesium sulfate and magnesium chloride), mineral acids (such as sulfuric acid or phosphoric acid) and some organic materials. The choice of the binder may be important if micro nutrients must also be added to the soil. Granules made with a soluble-salt binder break down and disperse in soil to give a performance almost as effective as finely ground rock.

Selective Leaching

A few researchers used some reagents regarding selective leaching of calcareous material from low grade phosphate rocks. The type and nature of impurities in low grade phosphate rock varies form deposit to deposit in the world. Sometimes the type and level of certain impurities may vary even within the same deposit as well. Therefore, each and every rock may be considered as a special case regarding beneficiation technique and technology. The present work aimed to study the selective leaching of calcareous phosphate rock. Apatite reserves located in the North East of the country, Hazara Administrative Division of Pakistan, categorized, Kakul, Lagarban, Oatkanala, Batkanala, East and South phosphorites. The rock phosphate of all these areas is generally grey to dark grey, hard and compact. Some of these deposits contain a considerable amount of calcareous materials and the rock from these areas can’t be used directly for phosphate fertilizers as well as phosphorous containing compounds. That is why; Pakistan has to import phosphate rock as a raw material for the production of phosphate fertilizers from different countries of the world, e.g. Jordan and Morocco. The P_2O_5 content of the indigenous phosphate rock varies form deposit to deposit; however, the average content is about 25%. On the other hand, a number of deposits of the world need commercial exploitation regarding improvements in mining as well as beneficiation technology. About two-thirds of known resources are composed of carbonate-rich phosphate rock for which satisfactory beneficiation technology has yet to be developed on a commercial scale.

CHEMISTRY OF THE LEACHING PROCESS

The dissolution study of various ores in inorganic acids has been investigated in detail [Ekmekyapar *et al.* 1993, Biskupski and Borowik 1996, Economou *et al.* 2002, Morse and Arvidson 2002, Liang *et al.* 2005]. However, the studies concerning the solubility in organic acids are quite limited [Fredd and Fogler 1998, Sarda *et al.* 2002]. Only a few workers [Sadeddin and Abu-Eishah 1990, Abu-Eishah *et al.* 1991, Zafar *et al.* 1996] used dilute organic acids for the leaching of carbonaceous and dolomite gangue materials in low-grade phosphate rocks. The dissolving ability of organic acids is relatively weak, however, these weak acids show high selectivity and may be used as leaching agents for low-grade calcareous and/or dolomite phosphate rocks. In scale-up studies with inorganic acid, high CO_2 pressure and froth forming owing to fast dissolution can lead to some risks and the organic acids may be an attractive extracting agent as the extraction is carried out at moderately acidic conditions (pH 3-5) and their degradation is biologically easy [Veeken and Hamelers 1999].

Calcareous and dolomite gangue materials may be reduced by leaching the low grade phosphate rocks by dilute organic acids such as citric acid, acetic acid, formic acid, succinic acid, etc., depending on various parameters of leaching process as well as nature and size of the samples. There are some limitations in the selection of an organic acid that should be taken into consideration:

a. The selected acid and its concentration should not have the tendency to attack the phosphate itself, or dissolve it in the solution.
b. The products of leaching should be easily separated from the phosphate product.
c. The organic acid should be either very cheap (which is not always possible), or can be recovered easily and economically for further use.

On this basis, dilute succinic acid is found to be one of the promising leaching agents for this purpose. Any strong acid when mixed with ground phosphate rocks, will react with the main constituents of the phosphate and change them to other compounds. In this case, dilute succinic acid has been used to selectively leach the carbonatic and/or dolomitic phosphate rock. The salts of succinic acid are, depending on temperature, soluble in water and may be separated easily from the leached solid phosphate product by filtration.

Highly concentrated succinic acid solution may not react, for example, with pure calcium carbonate due to the large polarity of the succinic acid O-H bond. In dilute solutions, water molecules tend to decrease the effect of polarity of the succinic acid O-H bond. These characteristics allow the acid molecules to react with calcium and/or magnesium carbonates, but not with the tricalcium phosphate itself appreciably. The dilute acid may be less destructive if some of the produced solution is added to the reaction solution, or recycled to the process. No physical or chemical changes in the phosphate rock, or considerable losses of its tricalcium phosphate content, are observed under lower concentrations of succinic acid about up to 6-9 %.

The reaction between succinic acid and calcium and/or magnesium carbonates can be written as follows:

$$CaCO_3 + C_4H_6O_4 \rightarrow Ca(C_4H_4O_4) + CO_2 + H_2O \qquad (1)$$

$$MgCO_3 + C_4H_6O_4 \rightarrow Mg(C_4H_4O_4) + CO_2 + H_2O \qquad (2)$$

The CO_2 is evolved as a gas, while the calcium and magnesium succinate by-products are soluble in the leaching solution. Reactions (1) and (2) may include the formation of instable carbonic acid and then decomposition into CO_2 and H_2O; and reaction for the other impurities depending on the nature and composition of the raw phosphate. These two main reactions represent in fact a lumping of a larger number of steps. The simplest detailed mechanism necessary for the rational understanding of this system may be given as follows:

(a) Ionization process of $HOOCCH_2CH_2COOH$ may be described by the equation:

$$C_4H_6O_4 \rightarrow 2H^+ + C_4H_4O_4^{2-} \qquad (3)$$

(b) Diffusion of H^+ ions through liquid to the exposed surface of rock particles.

(c) H^+ ions attack on the particles of the calcareous and dolomitic gangue material in the rock.

$nH^{+} + CaCO_3 \rightarrow H_2CO_3 + (n\text{-}2)H^{+} + Ca^{2+}$ (4)

$(n\text{-}2)H^{+} + MgCO_3 \rightarrow H_2CO_3 + (n\text{-}4)H^{+} + Mg^{2+}$ (5)

The H^{+} ions participating in these reactions may ' belong ' to the succinic acid as well as to the carbonic acid in the slurry.

(d) Ionization of H_2CO_3: When carbon dioxide dissolves in water, most of it is present as CO_2 molecules rather than H_2CO_3 molecules. However, if a small amount of carbonic acid is formed, the ionization which is fast process and can be described by the equations:

$CO_2 + H_2O \rightarrow H_2CO_3$ (6)

$H_2CO_3 \rightarrow H^{+} + HCO_3^{-}$ (7)

$H^{+} + HCO_3^{-} \rightarrow 2H^{+} + CO_3^{2-}$ (8)

$2H^{+} + CO_3^{2-} \rightarrow CO_2 + H_2O$ (9)

(e) Diffusion of products from the reaction sites to the bulk of the liquid.

(f) Reaction between Ca^{2+}, Mg^{2+} and $C_4H_4O_4^{2-}$

$Ca^{2+} + C_4H_4O_4^{2-} \rightarrow Ca(C_4H_4O_4)$ (10)

$Mg^{2+} + C_4H_4O_4^{2-} \rightarrow Mg(C_4H_4O_4)$ (11)

The formation of calcium and magnesium succinate will depend on the various parameters, such as concentration of the acid, reaction time, temperature, nature and grain size of the raw phosphate rock used for the leaching process.

MATERIALS AND METHODS

SAMPLE PREPARATION AND ANALYSIS

The low grade phosphate rock sample was crushed and sieved using U. S. Tyler standard sieves to collect various size fractions for analysis. The +9# (+1.981mm) fraction was further crushed using Mortar Grinder to obtain the desired size fractions. All the sieved samples were dried in an electric oven at about 105 °C, cooled to room temperature and stored in closed desiccators. These sample fractions were analyzed for the main conditions, namely, combined water and organic matter, P_2O_5 content, CO_2 content or loss on ignition (LOI), and acid insoluble residue (AIR) as shown in Table 1. Conventional [Furmann 1963] as well as instrumental analysis techniques such as Atomic Absorption Spectrophotometer were used for analysis. For the determination of calcareous material in the samples calcination method was also used at 950 °C.

Table 1: Analysis of Rock Samples.

Sample size (mesh)	P_2O_5%	AIR%	LOI%	CO_2%
-9+16# (-1.981+0.991 mm)	15.43	2.23	29.6	27.3
-16+32# (-0.991+0.495 mm)	16.21	2.59	28.1	25.9
-32+60# (-0.495+0.246 mm)	17.13	2.71	26.2	24.4
-60+115# (-0.246+0.125 mm)	18.23	2.73	24.9	23.1
-115+250# (-0.125+0.061 mm)	19.12	2.74	23.4	21.7

The type of analysis made in this study and discussion of the effect of process parameters are as summarized below:

1. Moisture content is the loss in weight of the original sample after being dried at 105-110 °C.
2. Combined water + organic matter is the loss in weight of the dried sample after being heated from 110 to 550 °C.
3. Acid insoluble Residue (AIR) is defined as the amount of the residue that remained unreacted in the sample, after being treated with a standard HNO_3/HCl solution and ignited at 950 °C.
4. Loss on ignition (LOI) is defined as the decrease in weight of the sample after being ignited from 550 to 950 °C. It refers to the amount of CO_2 in the sample, either before or after beneficiation.
5. The recovery percent of P_2O_5 was calculated by the formula:

$$P_2O_5 \text{ recovery } \% = \frac{\text{Wt. of Conc. x } P_2O_5 \text{ \% in Conc.}}{\text{Wt. of Rock x } P_2O_5 \text{ \% in Rock}} \text{x}100$$

EXPERIMENTAL PROCEDURE

For selective leaching studies -115+250# (-0.125+0.061mm) fraction was used in a well mixed spherical glass batch reactor (500 mL) heated by a constant temperature bath and equipped with a mechanical stirrer having a digital controller unit. A known amount of succinic acid, 8% with liquid/solid (L/S) ratio of 9:1 was slowly pipetted into the reactor vessel containing 5.0g of the sample for each run. At the end of each reaction, the reaction vessel was immediately placed in an ice bath to stop the reaction before the separation of the leach slurry by filtration. The resulting phases were then weighed and analyzed. The Ca^{2+} content in the leach solution was determined by Atomic Absorption Spectrophotometer, A-1800, Hitachi. To confirm the results for calcareous material and degree of beneficiation the solid phase after the leaching process was also analyzed by calcination method at 950 °C.

RESULTS AND DISCUSSION

EFFECT OF ACID CONCENTRATION

The effect of acid concentration on P_2O_5 and CO_2 contents after leaching with liquid/solid ratio of 8:1 at 60 °C was found as shown in Figs. 1 and 2 respectively. Depending on the leaching conditions as well as type and nature of the rock, the acid concentration of 8% was observed to be promising. The results indicated that the effect of acid concentration on P_2O_5 and corresponding reduction in CO_2 contents depended on reaction time, temperature, liquid-solid ratio and particle size used in the leaching process. For example, after 45 min the P_2O_5 content raised up to about 30.9% corresponding to a reduction of more than 70% in the calcareous material of the leached slurry at the reaction conditions. After the acid concentration of 8% the efficiency of the selective leaching process was slowed down.

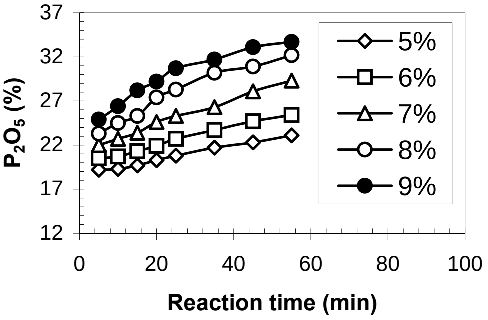

Fig. 1: Effect of Acid Concentration on P_2O_5 Content using Liquid/solid ratio of 8:1 at 60°C

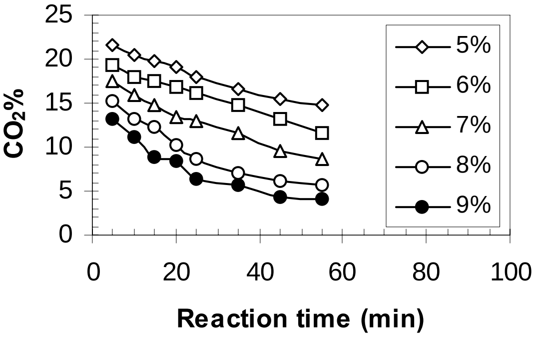

Fig. 2: Effect of Acid Concentration on CO_2 Content using Liquid/solid ratio of 8:1 at 60°C.

In the treatment of magnesite ore with higher concentrations of acetic acid, Oral et al. [Bunuyamin and Fatih 2005] observed that the intensity of negative effect of water (the solvent) decrease, after a certain value of acid concentration, was more dominant than that of positive effect of increase of acid concentration. Also, when the acid concentration exceeds a certain value, the number of hydrogen ions in the medium may decrease due to decrease of water amount more and more. This behavior was also explained by the fact that as the acid concentration in the medium increases, the appearance rate of product may increase by attaining the saturation value near the solid particle along with the formation of a difficult soluble solid film layer around the particle and this may result into a decrease in dissolution process [Ozmetin *et al.* 1996]. However, the acid concentration in the present case of selective leaching should not be increased more than 7-9% as it was found that by increasing the acid concentration up to about 10% and above, the acid started to dissolve the phosphate element itself that appeared as losses in the filtrate solution.

EFFECT OF LIQUID/SOLID RATIO

The effect of liquid/solid ratio (vol./wt. basis), on P_2O_5 and CO_2 contents using the acid concentration of 8% at 60 °C was shown in Figs. 3 and 4 respectively.

Depending on the leaching conditions as well as type and nature of the rock, the liquid/solid ratio of about 9:1 was found to be promising with a relatively higher reduction of calcareous material in the rock. The results indicated that the effect of liquid/solid ratio on P_2O_5 and corresponding reduction in CO_2 contents depended on reaction time, temperature, acid concentration, and particle size used in the leaching process. For example, after 45 min the P_2O_5 content raised up to about 32% resulting in a reduction down to about 6% in the CO_2 content of the leached slurry at the reaction conditions.

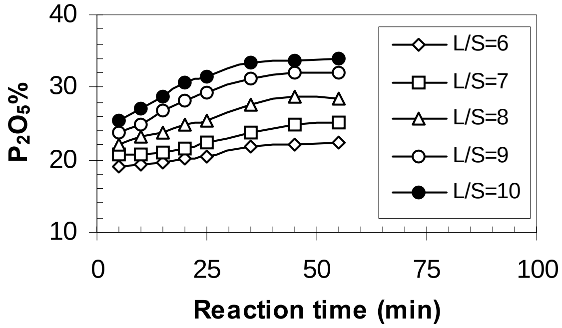

Fig. 3: Effect of Liquid/solid ratio on P_2O_5 Content using the Acid Concentration of 8% at 60 °C.

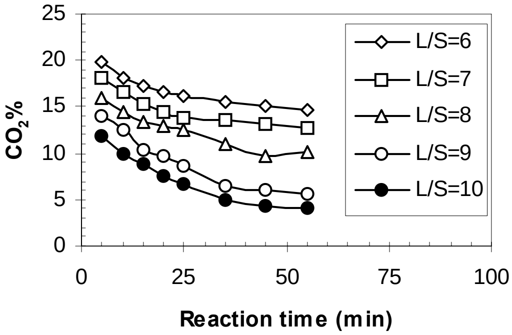

Fig. 4: Effect of Liquid/solid ratio on CO_2 Content using the Acid Concentration of 8% at 60 °C.

EFFECT OF REACTION TEMPERATURE

At known reaction parameters a number of experiments were carried out to see the effect of temperature on the selective dissolution of calcareous material using stirring speed of 350 rpm. Typical rate curves are shown in Fig. 5. The results indicate that the selective leaching process was sensitive to reaction temperature depending on the reaction parameters as well as type and the nature of raw phosphate. At relatively lower temperatures the selective leaching appreciably increased as shown in Fig. 5. After 65 °C the rate of increase in P_2O_5 and corresponding reduction in CO_2contents was slowed down. This indicated that higher temperatures, after certain limits, tended to decrease the solubility of the succinate product along with the contamination of CO_2 gas stream with water and succinic acid vapors.

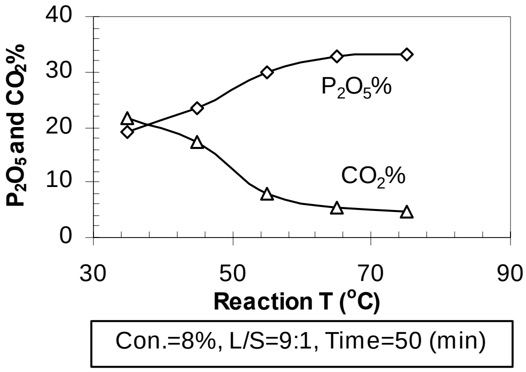

Fig. 5: Effect of Temperature on P_2O_5 and CO_2 Contents at the Given Conditions.

SUCCINIC ACID RECOVERY AND LEACHING PROCESS

The economy of the leaching process depends on the price of succinic acid and the cost of its recovery. Succinic acid may be recovered from the succinate solution by the reaction of the calcium succinate with any strong acid, provided that an insoluble salt is formed in order to separate the recovered succinic acid by simple methods such as filtration. Sulphuric acid is potentially most important for recovering succinic acid from calcium succinate solution. It is found that the reaction of sulphuric acid with the calcium succinate solution produced calcium sulphate that was insoluble in succinic acid solution and could easily be separated by filtration. In this case, 98 parts of H_2SO_4 were needed per 44 parts of CO_2 removed from the rock.

The succinic acid recovered by this method should be absolutely free from sulphuric acid in order to avoid any attack of the phosphate element by the latter acid and formation of gypsum at this stage. However, the recovery of succinic acid from magnesium succinate solution, using sulphuric acid is unlikely since soluble magnesium sulphate may be produced. Various other routes for the recovery of succinic acid from the succinate solution may be employed and the work is in progress.

CONCLUSIONS

For selective leaching of low grade calcareous phosphate rock with succinic acid the factors, that may affect the process, acid concentration, liquid/solid ratio (vol./wt. basis), reaction time and temperature have been studied. Depending on experimental results the following conclusions may be drawn:

Succinic acid may be used to eliminate/reduce calcium carbonate from low grade calcareous phosphate rocks as it improves the P_2O_5 content of the rock and may make it viable as a feed to an acidulation plant. An acid concentration of about 8% with liquid/solid ratio of 9:1 is found to be promising for the selective leaching of calcareous material in the rock. The acid concentration that gives the best leaching results is found to be depending on the liquid/solid ratio and it has been observed that the higher concentration of the acid (about 10% and above) starts to dissolve the phosphate element itself that appears as losses in the filtrate solution.

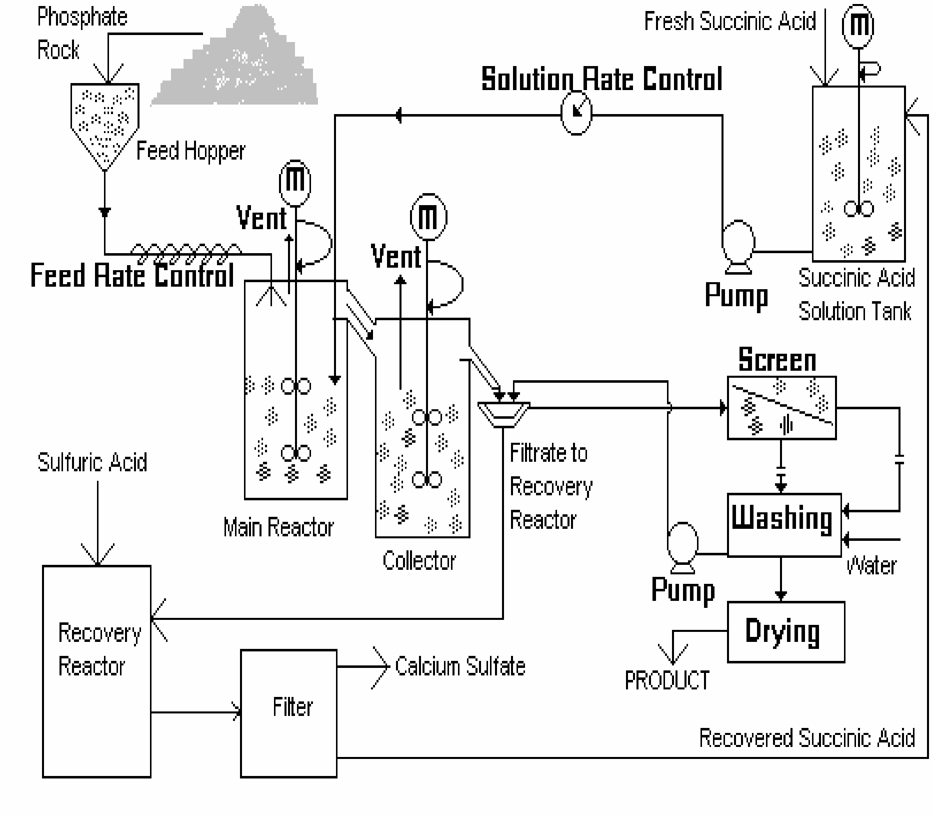

Fig. 6: Selective Leaching Flow Sheet Diagram.

It is observed that the leaching process is sensitive to reaction temperature. At a relatively lower temperature the efficiency of selective leaching process appreciably increases as shown in Fig. 5. However, after 65 °C the increase in P_2O_5 and corresponding reduction in CO_2contents is slowed down. This indicates that higher temperatures tend to decrease the solubility of the succinate product along with the contamination of CO_2 gas stream with water and succinic acid vapors. The important aspect observed in the present study is the limitation of solubility of succinic acid depending on temperature and its concentration. It is observed that succinic acid may not be considered as a successful leaching agent below about 37 ^oC.

The time required to minimize the carbonate content of phosphate rocks is naturally expected to depend on the size of particles and the nature of raw phosphate. The efficiency of leaching process increases as the reaction time is increased. However, after about 50 min the rate of increase in the dissolution process is small which indicates that most of the freely available calcareous material in the rock gets dissolved within this time. The loss on ignition (LOI) and acid insoluble residue (AIR) in the test sample are found to be 23.4% and 2.74% respectively. The amount of combined water and organic matter is found to be not more than about 3%. The separation of excess silica (above 4%) by flotation prior to the leaching may make rock as well as the process more beneficial.

The efficiency of the leaching process is naturally expected to increase with a decrease in the particle size as this may tend to liberate more calcareous material from the apatite matrix. In soft rocks the phosphate grains are already free and need not to be liberated from the pockets of the raw phosphate matrix. Fine grinding of the phosphate feed can increase the efficiency of the leaching process but the problems related to handling, filtration and marketing of fine phosphates, may not allow grinding to exceed a certain limit. On the other hand, higher energy for grinding would cause an extra cost to the process.

The type and nature of phosphate rock will have its direct effect on the speed of attack of the carbonates by the leaching acid. Hard phosphate rocks may tend to be more rigid and less porous than the soft phosphates and if the calcareous material is not free in the apatite matrix, the diffusion of ionic species through the aqueous phase to the reaction sites may affect the efficiency of leaching process. The economic aspects may need further investigations at different reaction parameters; however, the studies may be of some value to others confronted with the need to use typical indigenous rock phosphates of various countries in the world.

Acknowledgments

The authors would like to thank the Department of Chemistry, B. Z. University, Multan for providing the facilities, the Institute of Chemical Engineering and Technology, NFC, Multan, Institute of Chemical Engineering and Technology, Faisalabad for helping to complete this work.

References

Abu-Eishah, S.I., El-Jallad, I.S., Muthaker, M., Touqan, M. and Sadeddin, W. (**1991**) *Internat. J. Miner. Proc.* **31,** 115.

Baudet, G. (**1988**) “The Processing of Phosphate Ores”, *Chron. Rech. Min.,* **67.**

Biskupski, A. and Borowik, M. (**1996)** *Przemysl Chemiczny*, **75**, 59.

Brierley, C. (**1982**) *Pour la Science,* **60**, 38.

Bunyamin, L., Oral, D. and Fatih, D. (**2005**) *Internat. J. Miner. Proc.*, **75,** 91.

Costa, A.C.A., Medronho, R.A. and Pecanha, R.P. (**1992)** *Biotechnol. Lett.,* **14,** 233.

Crago (**1940**) “Process of Concentrating Phosphate Minerals”, US Patent No. **2,** 293.

Economou, E.D., Vaimakis, T.C. and Papamichael, E.M. (**2002**) *J. Coll. Interf. Sci.,* **245***,* 133.

Ekmekyapar, A., Ersahan, H. and Donmez, B. (**1993**) *J. Doga Turkish,* **17**, 197.

Fredd, C.N. and Fogler H.S. (**1998**) *Chem. Engg. Sci.,* **53**, 3863.

Furmann, N.H. (**1963**) “Standard Methods of Chemical Analysis”, 6th ed., D. Van Nostrand Company, New Jersey, USA.

Good, P.C. (**1976**) Report No 815*,* US Bureau of Mines: Washington.

Harrison, J.R. (**1984**) *Annu. Rev. Microbiol.,* **38**, 265.

Hignett, T.P. (**1980**) In: *Proc. 2nd Internat. Cong. Phosphorus Compounds,* 401.

Hignett, T.P., Doll, E.C., Livingston, O.H. and Raistrick, B. (**1977**) In: L.J. Carpentier (Ed.), *New Developments in Phosphate Fertilizer Technology*, Elsevier, Amsterdam, p. 273.

Hsieh, S.S. (**1988**) *Ind. and Eng. Chem. Res*., **27**, 594.

Hutchins, S.R. and Davison, M.S. (**1986**) *Annu. Rev. Microbiol.*, **40,** 311.

Lawver, J.E., Mcclintock, W.O. and Snow, R.E. (**1978**) *Miner. Sci. Eng*., **10**, 278.

Liang, B., Zhang, C.L.C. and Zhang. Y. (**2005**) *Hydrometall.,* **76**, 173

Lodha, T.R., Sinha, N.K. and Srivastava, A.C. (**1984**) *Chemic Age of India,* **35**, 15.

Mew, M.C. (**1980**) “World Survey of Phosphate Deposits”, The British Sulfur Corp. Ltd., London, p. 2.

Morse, J.W. and Arvidson, R.S. (**2002**) *Earth-Sci. Rev.,* **58,** 51.

Ozmetin, C., Kocakerim, M.M., Yapici, S. and Yartasi, A. (**1996**) *J. Ind. and Engg. Chem. Res.,* **35,** 2355.

Ray, H. and Robert, J.P. (**1969)** *Miner. Proc.*, **10**, 13**.**

Robinson, N. (**1978**) *ISMA (IFA),* Orlando.

Sadeddin, W. and Abu-Eishah, S.I. (**1990**) *Internat. J. Miner. Proc.,* **30,** 113.

Sarda, S.E., Fernandez, M., Nilsson, M., Balcells, L. and Planell, A. (**2002**) *J. Biomed. Mater. Res.,* **61**, 653.

Veeken, A.H.M. and Hamelers, H.V.M. (**1999**) *Water Sci. Technol.,* **400**, 129.

Zafar, Z.I., Anwar, M.M. and Pritchard, D.W. (**1995**) *Internat. J. Miner. Proc.,* **43**, 123.

Zafar, Z.I., Anwar, M.M. and Pritchard, D.W. (**1996**) *J. Fert. Research,* **44,** 133.

Zafar, Z.I., Anwar, M.M. and Pritchard, D.W. (**1996**) *J. Nutrient Cycling in Agroecosystems*, **46,** 135.

View publication stats