

Effect of Hydrochloric Acid on Leaching Behavior of Calcareous Phosphorites

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ABSTRACT: *The bulk of the world's phosphate reserves is located in sedimentary horizons that contain appreciable amounts of carbonate. During beneficiation of phosphate rocks, huge amounts of oversize phosphate rocks are rejected from crushers. This reject also mostly contains low tricalcium phosphate and high carbonate content. In this study, experiments have been carried out to reduce/eliminate carbonate content by leaching the ground phosphate rock with dilute hydrochloric acid solution. Effects of hydrochloric acid concentration, reaction time, temperature and liquid/solid ratio (vol./wt. basis) on the process have been studied. Under the reaction conditions, some of the apatite may be dissolved to form soluble monocalcium phosphate during the selective leaching. However, by specifying the pH of the process the lime milk can be used to recover the dissolved apatite. It has been observed that upon treatment of the ground rock with dilute hydrochloric acid, the P₂O₅ percent can be raised up to the industrially acceptable level due to the selective reduction/elimination of calcium carbonate content of the sample, depending on the reaction conditions as well as nature and size of the raw phosphate particles used for analysis.*

KEY WORDS: *Carbonaceous phosphorites, Hydrochloric acid digestion, Carbonate leaching.*

INTRODUCTION

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 primarily composed of the apatite group in association with a wide assortment of accessory minerals, fluorides, carbonates, clays, quartz, silicates,

and metal oxides. Hydroxyapatite, Ca₁₀(PO₄)₆(OH)₂, may be regarded as the parent member of a whole series of structurally related calcium phosphates that can be represented by the formula M₁₀(ZO₄)₆X₂, where M is a metal or H₃O⁺; Z is P, As, Si, Ga, S or Cr; and X is OH, F, Cl, Br, 1/2CO₃, etc. The apatite compounds all exhibit the same type of hexagonal crystal structure. These include a series of naturally occurring minerals, synthetic salts, and precipitated hydroxyapatites. Highly substituted

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apatites such as Francolite, $\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{F}, \text{OH})_{2+x}$, are the principal component of phosphate rock which is generally used for the production of various phosphatic fertilizers (DAP, MAP, TSP, SSP/NSP) as well as wet-process and furnace-process phosphoric acid.

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 phosphatic fertilizers in the world at this time. As the world population continues to increase, so does the demand for phosphate. The low grade calcareous phosphate rocks have no direct use and are rejected all over the world. Such 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 [1]. Some other special beneficiation techniques may also be applied, such as calcination for low-and medium-carbonate phosphate rocks and flotation for both siliceous and high carbonate phosphate rocks [2-5].

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 phosphate rocks usually requires additional acidulent (sulphuric acid) during the manufacture of phosphoric acid and superphosphates by the wet process. In acidulation, the carbon dioxide produced during acidulation causes more foaming and results in production of smaller size gypsum crystals, that may blind the downstream phosphogypsum filters, and a low quality phosphoric acid is produced [6]. The carbon dioxide also contaminates the equipment and pollutes the atmosphere. An antifoam can be added, but if the CO_2 content exceeds a certain limit, it will have negative effects on the economy of the whole process [7].

Much research has been carried out to try to reduce the calcium carbonate content of low grade phosphate rocks by flotation and calcination. Hignett et al. [2] 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. This was the case of the East Mediterranean and North Africa ores where the carbonates crystals are intergrown so that the phosphate is not liberated by crushing until the rock is too fine for

flotation [8, 9].

Siliceous phosphate ores are generally beneficiated by a two stage flotation technique using amine and fatty acids for silica based gangue and phosphates respectively. However, the beneficiation of phosphate ores containing carbonaceous gangue is complicated because of the similarities in the chemical behaviour of the minerals present [10-12]. Flotation of carbonate rich ore poses difficulties because the fatty acids and their derivatives used as flotation collectors have very poor selectivity for carbonates and phosphate minerals [13].

Research efforts to find out the details of mechanism of interaction between ions in the liquid phase and the solid surfaces involved are hindered due to the presence of impurities [11]. A small amount of some impurities present in the ore have marked effect on the surface properties of calcite and apatite as well as the ionic reactions in the liquid phase. It looks like that a $\text{CaO}:\text{P}_2\text{O}_5$ ratio in the flotation product must be less than 1.6 [14].

Calcite and dolomite, both of these carbonate minerals tend to respond in a similar manner to phosphate minerals when exposed to the fatty acid-type collectors that are traditionally used for phosphate flotation. The consequences of dilution of the phosphate concentrate by them are, however, somewhat different: calcite will 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 [15].

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 favourable 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 [16].

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 [17]. 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* [18]. *T. ferrooxidans* uses ferrous iron and reduced sulphur as energy sources and *T. thiooxidans* can only use sulphur compounds [19]. The metabolic activity of these microorganisms 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 [20].

The currently used commercial process of double flotation [21] 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. Moudgil and Chanchani [22, 23] and Ince [24] have conducted some fundamental studies in the development of two processes for the removal of dolomite from apatite. Extension of these fundamental studies to beneficiate the natural ores on a bench scale was also reported [25]. However, a systematic optimization study of the important variables may give guidelines for processing of such complex ores. Zhong et al. [26] have attempted an optimization of some variables using a three stage flotation scheme with various chemicals and flotation reagents. Arafa [27] Judd et al. [28] Alfantazi et al. [29] and Kangnian et al. [30] have also conducted some fundamental studies on flotation using various flotation reagents and it may need further studies regarding optimization and proper guidelines to process complex ores commercially.

Beneficiation by calcination is one of the better known processes. It is based on the dissociation of calcium carbonate gangue materials by thermal energy. Depending on the efficiency of the process, calcination may lead to almost complete disposal of the carbonate materials present in the phosphate rock [31]. In this case, carbon dioxide is removed as a gas from the calcination kiln, while the calcium oxide and most of the magnesium oxide are removed after quenching and desliming of the solids leaving the kiln. By quenching the hot calcined rock in water, the major impurities usually pass into the slime phase, which is then mechanically separated from the coarser high grade 'sand' concentrate fraction [1, 32]. Calcination may tend to decrease the solubility and reactivity of the calcined phosphate rocks in the acidulent

during the manufacture of phosphoric acid by the wet process [33, 34].

Sadeddin et al. [35], Abu-Eishah et al. [36] and Zafar [37] have conducted the studies using dilute acetic acid solutions to leach out the carbonaceous and dolomitic gangue materials from the low grade phosphate rocks. In the acetic acid leaching process, relatively higher liquid/solid ratio and an effective agitation is required to achieve the desired grades of the low grade phosphate rock. Higher liquid/solid ratio may result in a relatively lengthy process including handling, filtration and regeneration of the used acid. The carbon dioxide produced during the leaching process may cause foaming and results in the addition of an antifoam and/or effective agitation causing an extra cost to the process. Formic acid was also tried to leach out calcareous materials from low grade phosphate rock and found to be a relatively promising leaching agent [38]. However, the significant design parameters and economic aspects need further investigations. A number of techniques [39] has been studied to treat the low grade rocks, however, satisfactory beneficiation technology has yet to be developed on commercial scale to deal with the typical indigenous phosphate rocks.

Hydrochloric acid can be used for the manufacture of phosphoric acid. Phosphoric acid manufactured from phosphate rock by this route is much purer than that produced by the sulphuric acid route. However, in addition to the difficulty of recovering phosphoric acid, there are other technical problems that must be overcome in a plant using hydrochloric acid. Plant operation is very sensitive and because of the chloride containing environment special care must be taken to prevent corrosion of equipment [40]. Dilute solutions of hydrochloric acid may be used to selectively leach out the calcareous materials from low grade phosphate rock rather than the dissolution of apatite. In this work, the suitability of dilute hydrochloric acid has been studied to leach out the calcareous and dolomitic gangue materials from the indigenous low grade phosphate rock.

Chemistry of the Leaching Process

The calcareous and/or dolomitic gangue material from a low grade phosphate rock can be removed or reduced by the leaching process using organic or inorganic acids depending on the process parameters as well as nature

and size of the raw material. For the selection of an acid, the following important factors should be taken into consideration:

1- The acid selected for the leaching process should not show any tendency to attack the phosphate element itself or dissolve it.

2- After the leaching process the products should be separable.

3- The acid selected for the leaching process should be cheap.

4- The acid used for the leaching process can be easily and economically recovered for recycle.

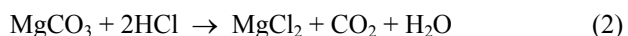
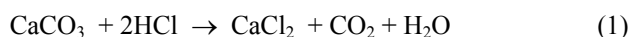
In the present study, on terms of the above parameters dilute hydrochloric acid is expected to be a promising leaching agent for the process. During the reaction between strong acid and phosphate rock, the acid reacts with the main constituents of the phosphate rock such as apatite. In the case of dilute hydrochloric acid the present results show that it may be a promising leaching agent for beneficiation of carbonatic and/or dolomitic phosphates.

1- Hydrochloric acid is a strong acid and a relatively small molecule. This may be expected to have a faster diffusion rate than some other acids in the leaching process.

2- Hydrochloric acid salts are soluble in water. Therefore, after the leaching process they can be separated from the beneficiated phosphate rock by a simple filtration process.

3- The residence time for the leaching process is kept low (15 to 25 minutes), and it ensures that solubility of the phosphate elements is minimal.

The reaction between phosphate rock particles and acids is a surface reaction in which the rate is largely controlled by reaction temperature, hydrogen ion concentration, the diffusion of reactants to the surface and products from the surface, the agitation power and the surface area of the particle available for reaction. For the present case, the reaction between hydrochloric acid and calcium and/or magnesium carbonates may be written as follows:



The calcium and/or magnesium chloride by-products are soluble in the leaching solution, while the CO_2 is evolved as a gas. Reaction (1) and (2) may include the formation of unstable carbonic acid, which

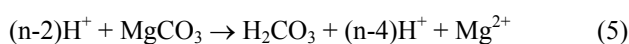
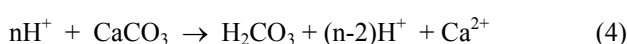
decomposes into CO_2 and H_2O ; any reaction for the other impurities depends on the nature and composition of the raw phosphate. These two main reactions represent a lumping of a larger number of steps. The simplest detailed mechanism necessary for the rational understanding of this system may be given as follows:

a) Ionization of HCl , which is a relatively fast process described by the equation:



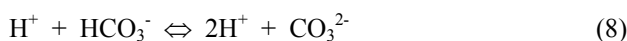
b) Diffusion of H^+ ions through the liquid to the exposed surface of the rock particle.

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



d) Ionization of H_2CO_3

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



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

f) Reaction between Ca^{2+} , Mg^{2+} and Cl^- ions may proceed as:



The formation of calcium and/or magnesium chloride will depend on various parameters, such as the concentration of the acid, reaction time, temperature, nature and grain size of the raw phosphate rock used for the leaching process. For the economic viability of the leaching process the recovery of hydrochloric acid from calcium chloride (formed as a side-product) is important because it will significantly reduce the requirement for fresh leaching agent. Hydrochloric acid may be regenerated from the calcium chloride filtrate for recycle. There are a

number of routes for the recovery of hydrochloric acid from calcium chloride filtrate solution.

EXPERIMENTAL PROCEDURE

Sample Description

The low grade phosphate rock is found in the Northern areas (District Abbotabad) of Pakistan. These deposits mainly contain siliceous and calcareous impurities. The P_2O_5 content of the indigenous phosphate rock generally varies from 15 to 26%. The main deposits are Kakul, Lagarban, Southern Phosphorite, Eastern Phosphorite, Batkanala and Oatkanala. The rock from these areas can't be used directly for the production of high grade phosphatic fertilizers and/or phosphoric acid unless its P_2O_5 contents are increased more than 30-34%. The sample of low grade calcareous phosphate rock was collected from District Abbotabad. It was crushed and screened to collect a fraction of general range size of -65+200# (-0.208 mm + 0.074 mm), using the mesh sieves of U. S. Tyler. The retained material was further crushed using Mortar Grinder to obtain the same size. The test sample, -65+200# (-0.208 mm + 0.074 mm), was analyzed for various constituents of the rock and the results are given in table 1. Total percentage of the determined constituents was found to be less than 100 %. The remaining constituents may be CaO along with small amounts of MgO, moisture, organic matter etc.

Procedure

The samples of the ground phosphate rock were dried in an electric oven at about 105 °C, cooled to room temperature and stored in closed desiccators for analysis before and after leaching with dilute hydrochloric acid. A known amount of the sample was added to a conical flask reactor (500 ml) containing a measured volume of dilute hydrochloric acid solution of a specified concentration. The reaction mixture was then agitated using a magnetic stirrer at moderate speed for a fixed time and temperature. In this case, CO_2 is evolved causing a very little foam of white colour above the mixture. No efficient agitation or antifoam reagent is required to break the foam. After the reaction, the mixture was filtered using a Buchner funnel and Whatman filter paper. The solid material after leaching process was washed with a fixed amount of distilled water to remove any soluble matter. The washing solution was added to the filtrate solution. After washing the solid material was dried at

Table 1: Analysis of low grade phosphate rock before treatment with hydrochloric acid.

P_2O_5 (%)	SiO_2 (%)	Fe_2O_3 (%)	Al_2O_3 (%)	AIR (%)	LOI (CO_2) (%)
22.7	2.6	1.5	2.7	2.5	25.3

105-110 °C to remove the accompanying moisture until the sample weight remained unchanged. Conventional as well as instrumental analysis techniques such as X-Ray Fluorescence (ARL 8410 fully automatic, sequential wavelength dispersive X-ray Fluorescence spectrometer facilitated with 3kW Rhodium target end window X-ray tube (with 70kV accelerating capability from "dry supply" HV generator), Diffraction crystals (LiF220, LiF200, PET, Ge111, A06), Goniometer (Moire Fringe infra-red goniometer control), Detector (solid state scintillation counter and gas flow proportional counter) and Differential Thermal Analysis (DTA -50, Shimadzu, Japan) were used. The type of analysis made in this study and the definitions of some reaction 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- Tricalcium phosphate (TCP) content is usually expressed as TCP, BPL, TPL or P_2O_5 content. The TCP content defines the grade of the phosphate rock (low or high). It also indicates the amount of impurities present in the rock.

4- 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.

5- 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 the leaching process.

6- After the leaching process the recovery percent of P_2O_5 was calculated by the formula:

$$P_2O_5 \text{ Recovery}\% = \frac{(\text{Wt of Concentrate})}{(\text{Wt of Sample})} \times \frac{(P_2O_5 \% \text{ in Concentrate})}{(P_2O_5 \% \text{ in Sample})} \times 100$$

RESULTS AND DISCUSSION

Dilute solution of hydrochloric acid was used to leach out the calcareous material from low grade phosphate rock. A number of experiments were carried out using different concentrations of the leaching acid with various liquid/solid (L/S) ratio. Figs. 1-3 indicate that the dissolution of calcareous material and apatite increases as the leaching agent concentration is increased using different liquid/solid (vol./wt. basis) ratios. Solubility of apatite and calcareous material changes when liquid/solid ratio as well as the leaching agent concentration are changed depending on the nature and type of the low grade calcareous phosphate rock. Fig. 4 indicates that with an increase in liquid/solid ratio, after a certain limit, the amount of the leaching agent increases than the required amount corresponding to be dissolved easily and freely available calcareous material present in the solid sample. It appears that, after a certain limit, the acid causes a relatively higher dissolution of apatite rather than the calcareous material. The results indicate that about 4% concentration of the leaching agent along with 5:1 liquid/solid (vol./wt. basis) ratio is expected to be promising as the degree of dissolution of calcareous material is a relatively higher than that of the apatite (Figs. 1-3).

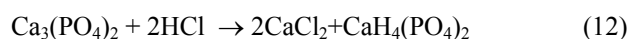
During the reaction the temperature was noted to see the reaction behaviour at different times as shown in Fig. 5. The results indicate that the change in temperature is small and during a sharp rise the reaction took eight minutes to attain the maximum temperature about 28.2 °C. The change in temperature is very small and ignorable after about 11 minutes of time indicating that the reaction is going towards its completion soon. In a separate experiment the complete dissolution behaviour of both of the components was studied as shown in Fig. 6. For complete dissolution of calcareous material and apatite the liquid/solid ratio decreases as the leaching agent concentration is increased. The dissolution trend is almost similar for both of the components, however, the calcareous material shows a higher degree of dissolution at a relatively lower liquid/solid (vol./wt. basis) ratio as compared with apatite.

As Figs. 1,2 and 3 indicate that a considerable amount of apatite is also decomposed during the leaching of calcareous material. Therefore, after the main reaction of the leaching process a required amount of calcium

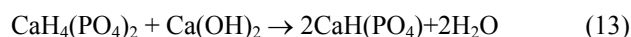
hydroxide, Ca(OH)₂ was used to treat the filtrate and convert the dissolved apatite into insoluble dicalcium phosphate. After the recovery of the dissolved apatite, the filtrate was again analyzed to see the P₂O₅ content. The P₂O₅ content of the filtrate after apatite recovery was found to be very small and ignorable.

Dissolution of Apatite and its Recovery

During the leaching process apatite is also dissolved depending on the concentration of the acid as well as the liquid/solid (vol./wt. basis) ratio. The filtrate was analyzed and a considerable amount of dissolved apatite was found. In fact, monocalcium phosphate (MCP) is produced under the conditions used in superphosphate production (high liquid P₂O₅ concentration), while dicalcium phosphate (DCP) can be produced under the conditions used in nitrophosphate (NP) processing (high-temperature, lower liquid P₂O₅ concentration). Formation of MCP may be reduced/retarded by the use of a relatively diluted acid or by avoiding the drying of the product to keep a lower concentration of the acid in the liquid phase. However, even under the specific and controlled conditions of the leaching process some of the apatite may be dissolved to form soluble monocalcium phosphate (MCP) as follows:



By specifying the pH of the process the lime milk can be used to recover the dissolved apatite as follows:



The above reaction (13) can be completed by controlling the pH parameter of the reaction product. As the pH changes from acidic to basic the relative proportions of the phosphorus containing species (H₃PO₄ to PO₄³⁻) change as well. For values of the pH near one of the pK_a values, two species may be present in substantial amounts, while for values farther away a single species dominates, ranging from H₃PO₄ at low pH through H₂PO₄⁻ and HPO₄²⁻ at intermediate pH, to PO₄³⁻ at high pH. The reaction mixture was filtered to separate dicalcium phosphate (DCP) and the filtrate was again analyzed to see the P₂O₅ content. After the recovery of apatite with lime the P₂O₅ content of the filtrate was found to be very small and ignorable.

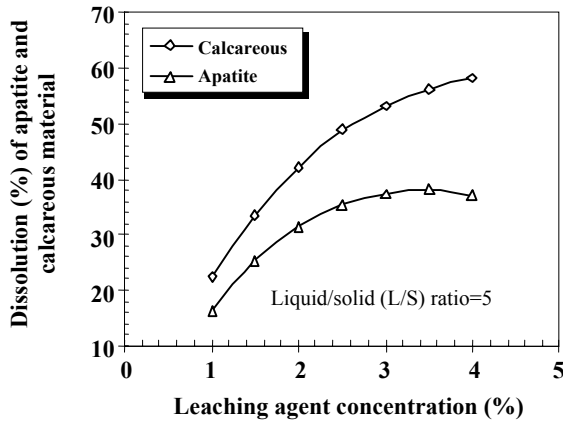


Fig. 1: Effect of leaching agent concentration on calcareous material and apatite for liquid/solid ratio of 5:1 (vol./wt. basis) at ambient temperature.

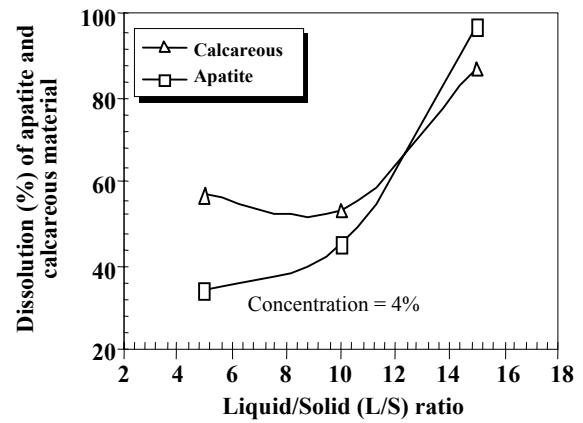


Fig. 4: Effect of liquid/solid ratio (vol./wt. basis) on dissolution of calcareous material and apatite at ambient temperature.

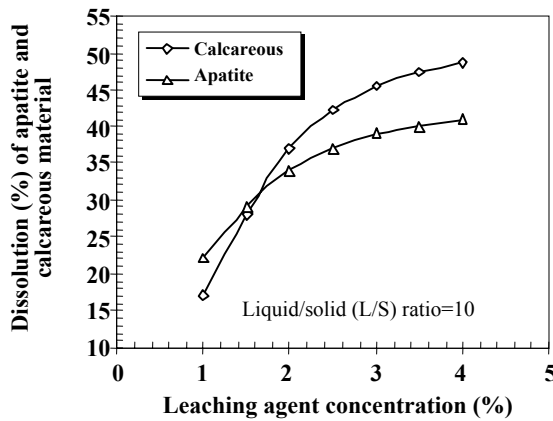


Fig. 2: Effect of leaching agent concentration on calcareous material and apatite for liquid/solid ratio of 10:1 (vol./wt. basis) at ambient temperature.

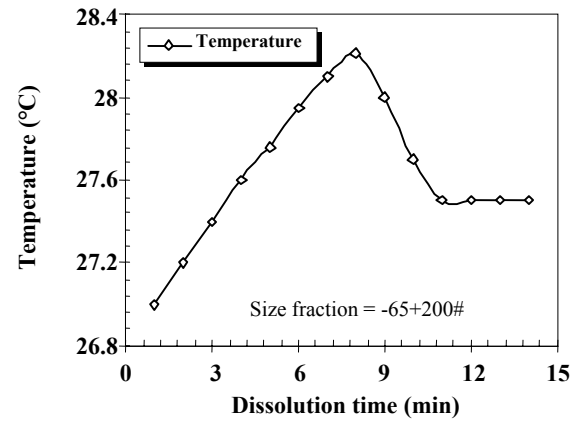


Fig. 5: Temperature rise behavior during leaching/acidulation of low grade phosphate rock with 4% hydrochloric acid.

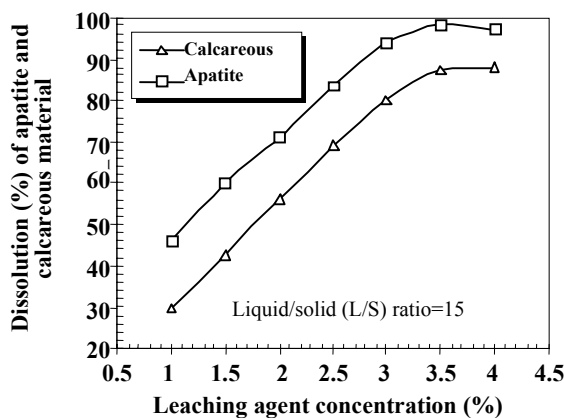


Fig. 3: Effect of leaching agent concentration on calcareous material and apatite for liquid/solid ratio of 15:1 (vol./wt. basis) at ambient temperature.

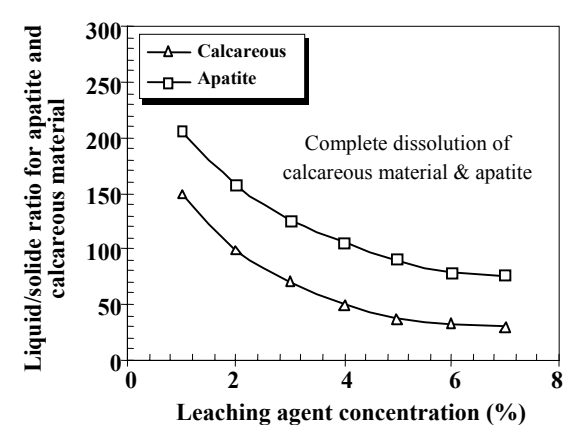
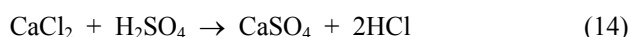


Fig. 6: Effect of leaching agent concentration on liquid/solid ratio (vol./wt. basis) for complete dissolution of calcareous material and apatite at ambient temperature.

Regeneration of the Leaching Agent

Commercial production is always based on the economy of the process. In this leaching process a dilute solution of hydrochloric acid has been used. After the dissolution process the leaching agent is converted into calcium chloride as filtrate. To improve the process economy it is essential to regenerate the leaching agent so that it may be recycled again into the leaching process. Hydrochloric acid may be recovered from the chloride solution by the reaction of the calcium chloride with any strong acid, provided that an insoluble salt is formed in order to separate the recovered hydrochloric acid by simple methods such as filtration.

Sulphuric acid may be potentially the most important for recovering hydrochloric acid from calcium chloride solution. The stoichiometric amount of sulphuric acid can be used to react with calcium chloride solution and convert it back to insoluble calcium sulphate and hydrochloric acid. The regenerated hydrochloric acid can be separated by simple filtration. The regeneration reaction:



The hydrochloric 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 hydrochloric acid from magnesium chloride solution, using sulphuric acid is unlikely since soluble magnesium sulphate may be produced.

A second route for the recovery of hydrochloric acid from the chloride solution is by the use of ion exchange methods. Treatment of the bed and recovery of hydrochloric acid:

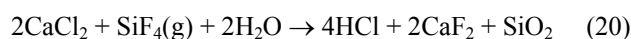


Regeneration of the bed may be carried out by the reversal of reactions (15) and (16):



By the ion exchange method, higher recovery may be achieved. No hydrochloric acid is expected to be lost as long as the chloride solution is recycled to the process for dilution of fresh hydrochloric acid.

A third possible route is by the reaction of the chloride solution with the hydrofluoric acid produced during the manufacture of phosphoric acid or superphosphates from fluorapatite. In the absence of enough active silica in the acidulation, the hydrofluoric acid usually leaves the acidulation reactor and the phosphoric acid concentrator as a gas mixed with silicon tetrafluoride, SiF_4 , gas. These gases may be directly scrubbed with the chloride solution to form hydrochloric acid and insoluble highly valuable calcium and/or magnesium fluorosparas that will be easily separated by filtration. The reactions with calcium chloride, for example, are:



In the presence of enough active silica, silicon tetrafluoride is produced as a gas and fluorosilicic acid is produced in the liquid phase. Again, the silicon tetrafluoride gas may be directly scrubbed with the chloride solution as shown by equation (20). The fluorosilicic acid, after being separated in phosphoric acid plant, may be reacted with the chloride solution to produce hydrochloric acid and soluble calcium and/or magnesium fluorosilicate salts:



The separation of the latter mixture to recover hydrochloric acid needs further investigation. If the amount of fluorine present in any phosphate rock is limited, the above method alone may not be sufficient to recover all of the used hydrochloric acid from the chloride solution. For economical recovery of the used hydrochloric acid, the above method may be combined with the sulphuric acid or ion exchange methods.

A fourth route for the recovery of hydrochloric acid from the chloride solution would be the reversal of reactions (1) and (2) under certain conditions (pH, pressure, temperature, etc.). This route is thermodynamically possible and needs further investigation.

CONCLUSIONS

In this leaching process, some of the significant factors that might affect the increase in $\text{P}_2\text{O}_5\%$ after treatment of low grade calcareous phosphate rock with dilute hydrochloric acid solution have been studied.

The factors that have been considered are the acid concentration and liquid/solid ratio (vol./wt. basis). Using this leaching acid, the P_2O_5 content can be raised by up to more than 30% corresponding to a reduction of up to 60% in the calcium carbonate content along with P_2O_5 weight recovery of more than 70%, depending on reaction conditions as well as the nature and size of the raw phosphate used for the process.

The type and nature of the phosphate rock feed have its direct effect on the speed of attack of the carbonates by the leaching acid. Hard phosphate rocks will tend to be more rigid and less porous than the soft phosphates. Thus more time will be needed for the acid to penetrate through the hard phosphate particles in order to reach the inside carbonates. It would be more beneficial to combine low and medium grade phosphate rocks of the same bed or other beds in order to get the benefits of the ease of raising the tricalcium phosphate (TCP) content to the commercial value, and at the same time to avoid selective mining of the ore, thus increasing savings in the mining process.

The efficiency of the leaching reaction is naturally expected to increase as the particle size of the feed becomes smaller. Fine grinding of the phosphate feed will naturally tend to liberate the carbonates from the pockets of apatite matrix. 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 may cause an extra cost to the process. Adherent materials play an important role in reducing the phosphate content in rocks. The loss on ignition (LOI) and acid insoluble residue (AIR) have been found to be about 23.5 and 2.5% respectively. The amount of combined water and organic matter was found to be not more than about 2.

The acid concentration that gives the promising leaching results has been found to depend on the liquid/solid (vol./wt. basis) ratios used. An acid concentration of about 4%, at a liquid/solid ratio of 5:1 was found to be the most suitable and promising. It has been found that the higher concentrations of the acid favour the dissolution of more apatite rather than that of carbonates in the sample. The temperature rises sharply during the first 8 minutes and then with a rapid fall it becomes almost constant after about 12 minutes of the dissolution time (Fig. 5). The dilute hydrochloric acid may be used to

remove/reduce the calcareous material from low grade phosphate rock as it renders P_2O_5 content to marketable and industrially acceptable level. In case of higher/considerable amount of apatite is dissolved during the leaching of calcareous material, the milk of lime, $Ca(OH)_2$ may be used to easily recover the dissolved apatite by the controlling parameter of a specified pH range of the recovery process.

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Selective leaching kinetics of calcareous material needs to be carried out at various reaction temperatures and the work is in progress. Some of the acid may be consumed in decomposing the impurities present in rock, however, these impurities (such as aluminium, iron, manganese, etc.) may be precipitated for upgrading the final products. Although the significant design parameters, the effect of temperature and reaction kinetics need further investigations, however, the method may be of value to others confronted with the need to use typical indigenous rock phosphates of various countries in the world.

Abbreviations

MCP	Monocalcium Phosphate
DCP	Dicalcium Phosphate
TCP	Tricalcium Phosphate
BPL	Bone Phosphate of Lime
TPL	Total Phosphate of Lime

NP	Nitrophos
DAP	Diammonium Phosphate
MAP	Monoammonium Phosphate
SSP	Single Superphosphate, or
NSP	Normal Superphosphate (also known as super-phosphate)
TSP	Triple Superphosphate (also known as concentrated superphosphate)
AIR	Acid Insoluble Residue
LOI	Loss on Ignition
L/S	Liquid/Solid (vol./wt. basis) ratio; ml of the acid used per unit wt., (1 gm) of the sample

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