



Solubility of Phosphate Rocks in citric Acid

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Abstract

Taking into account that phosphate rocks can have high solubility regarding the different kinds of solvents used, dissolution of apatite from different places was applied in 2% citric acid solution. Semi analytical, 0,001g resolution scales for quantifying mass were used as well as Stollman bottles attached to Wagner-like agitator where the extraction was carried out. Also, a digital spectrometer for doing the reading which determines the phosphate grades was used. The results consisted of a minimum value of 0,33% and a maximum of 28,2% of P₂O₅ varying according to the origin of the milled samples. The result can be useful for the selection of rocks to be processed.

Keywords: Phosphate rock, Solubility, Citric acid solution

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1. Introduction

Phosphate is an abundant element on Earth and it is crucial for the development of vegetable life. The presence of iron and aluminum cations has a tendency of absorbing phosphate anions which prevents the plants' growth due to the absence of phosphate, essential for animal and vegetable life

The main phosphate source are phosphate rocks. Its trade started in 1847, when about 500 tonnes were extracted. Its consumption has gradually increased over the years. These days, about 93% of the world production is aimed at the fertilizer industry [1].

The main use of the apatite mineral is in phosphoric acid production which, in most cases, is destined to the chemical industry for the production of phosphate fertilizers.

According to Bigarella [2] rocks are aggregates formed by one or more kinds of minerals which can have volcanic origin or be formed by organic material. They can be classified into igneous, metamorphic and sedimentary. Metamorphic rocks undergo transformations under high temperature and pressure conditions which causes them to generate new textures or minerals. Sedimentary rocks are the result of degradation of other kinds of rocks, due to weathering such as rain, wind and temperature variation. Igneous rocks are formed from the magma expelled from volcanoes at high temperature. On the surface of the Earth under lower temperature, this material solidifies and forms the rocks [3]; [2].

The main mineral as a source of phosphate is apatite which can have a wide range of P_2O_5 , likely to vary from 5 to 30%. Apatite can be found both in igneous and metamorphic rocks. This mineral has other denominations such as: fluorine-apatite, chlorine-apatite, hydroxapatite and carbon-apatite [4]. Apatite mineral can be found in several deposits around the world. In Brazil, the most import mines are located in Catalão-GO, Araxá-MG and Tapira-MG. Apatite can have innumerable chemical, physical and chemical-physical variations. It has hardness 5 on Mohs' scale and density 3,1 to 3,2 g.cm⁻³. In its several deposits, it is possible to find complex reserves with impurities which compromise phosphate availability and its disposition to the plants [4]. It can present several colors, varying according to the presence of manganese (Mn) or due to some oxidation with this element [5]. Phosphoric acid can be produced by several processes in which the apatite ore, after going through some stages such as extraction and milling, is eventually destined to the chemical process of phosphoric acid production. The ore is submitted to a premix in continuous stirring reactors, where a dispersion with the chemical reagents takes place so as to maintain its homogeneity and to increase its reaction speed. Phosphoric acid can present grades which range from 28 to 30% P_2O_5 and can reach from 50 to 52% P_2O_5 after the evaporation stage [6].

In the stage of phosphate ore solubilization, the most common is using mineral acids: phosphoric, nitric, sulfuric acids and, in some cases, chloride acid. Acids are used because of the total or partial transformation of tricalcium phosphates contained in some kinds of phosphate rocks. Concentrated acid is added so as to get total acidulation in order to obtain phosphoric acid destined to the chemical industry of fertilizers or other chemical products. One of the main uses of this acid is the production of monoammonium phosphate (MAP) and triple superphosphate [7]. Rocks, apart from being solubilized into mineral acids, are able to solubilize in solutions such as neutral ammonium citrate, citric acid 2% and formic acid 2%. Phosphate rocks can provide P_2O_5 soluble in water, which indicates the presence of monocalcium phosphate or ammonium phosphate. In both forms it can be directly available to the plants [8].

The method for phosphate rock solubilization in 2% citric acid solution was initially proposed by Wagner by the end of IX century and it has been submitted to several modifications.

This method was used to determine P_2O_5 in basic slags in the United States and later on applied in Brazil in order to determine phosphor in slags and phosphate rocks. These days it is used to evaluate phosphor in thermo and natural phosphates [9]. Solubility in the extraction of 2% citric acid is based on citric acid complexation and its ionic species as well as on solution acidity. Citric acid's molecular formula is $C_3H_4(OH)(COOH)_3.H_2O$ and its molecular mass, 210,15 g/mol. Its ionization constants at 25°C are: $K_{ac1} = 8,7 \times 10^{-4}$; $K_{ac2} = 1,8 \times 10^{-5}$; $K_{ac3} = 4,0 \times 10^{-6}$ for a 2% citric acid solution. Molarity in such solution is 0,285 M.

The purpose of this paper is to evaluate the amount of P_2O_5 in phosphate rocks from different regions of the world in order to display phosphate and its solubility in 2% citric acid.

The percentage of phosphate can drastically affect agricultural production, especially at the beginning of the cycle. This is usually associated to the low production of seeds and cereal productivity [10].

The apatite ore can present a variety of representations, described in Table 1.

Table-1. Types of apatite

Apatite	Formula
Fluoride-apatite	$Ca_5(PO_4)_3F$
Chlorine-apatite	$Ca_5(PO_4)_3Cl$
Hydroxyapatite	$Ca_5(PO_4)_3OH$
Carbon-apatite	$Ca_5(PO_4,CO_3,OH)_3(F,OH)$

Source: Deer [5]

Its chrystallography is hexagonal and bi pyramidal; there are often long prismatic chrystals, short or tubular prismatic chrystals may also be found [11].

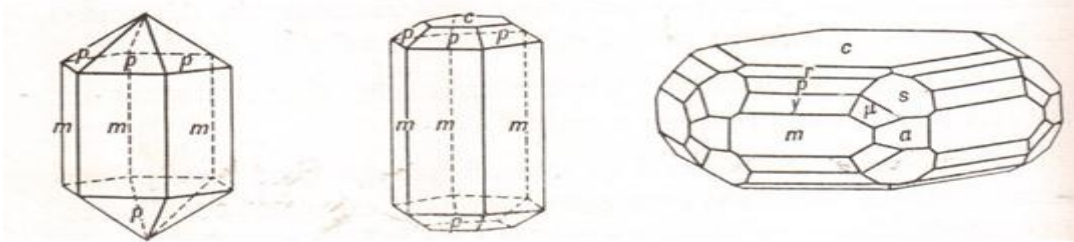


Figure-1. Crystalline Apatite Habits

Source: Dana [11]

In its composition, fluorine, hydroxyl and chlorine, can replace PO_4 , producing carbon-apatite. Manganese can also partially replace calcium [11].

1.1. Physical and Chemical Properties

Apatite present a hexagonal crystallographic system with four crystallographic shafts, where three of the a axis, located on a horizontal plane, have the same length and form angles of 120° among them. The fourth axis c is located on the vertical, perpendicularly to the a axis and it has different length, as it can be observed in Figure 2. Dimensions a and c characterize unitary cells [12].

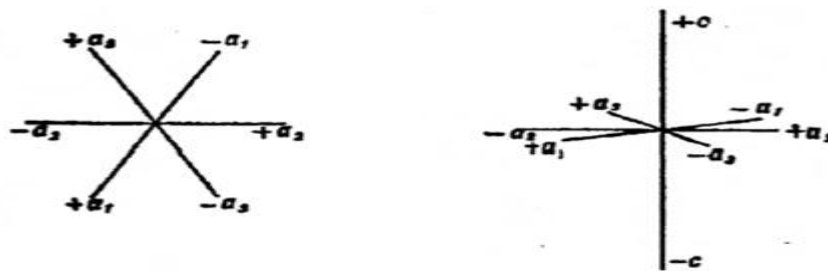


Figure-1. Crystallographic axis in a and c planes

Source: Silva [12]

According to Silva [12] structurally, hydroapatite and chlorine apatite are similar. As for unitary cell dimensions, they are different, affected by different Cl^- , F^- e OH^- ion sizes. Chlorine, fluorine and hydroxyl substitute themselves in the formula $Ca_{10}(PO_4)_6(OH,F,Cl)_2$, forming extremes of isomorphous series.

Table 2 shows the proportion among axis [5] and Figure 3 shows apatite's spatial structure.

Table-2. Network parameters for extreme members of the apatite group

Apatite	$a(\text{\AA})$	$c(\text{\AA})$	c/a
Fluorine-apatite	9,36	6,88	0,735
Chlorine-apatite	9,64	6,78	0,703
Hydroxyl apatite	9,42	6,88	0,730
Carbon-apatite	9,36	6,90	0,740

Source: Deer [5]

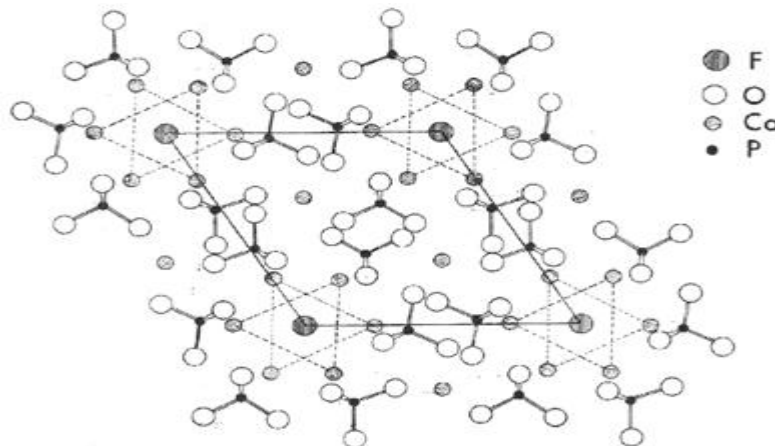


Figure-3. Apatite's structure: atomic arrangement

Source: Silva [12]

1.2. Application to Phosphoric Acid

Apatite, like other phosphate ores, is the main raw material for the production of phosphoric acid. So, it is the main element for the production of phosphate fertilizers. From phosphoric acid, high grade phosphate fertilizers are made, which may range from 18% to 52% P_2O_5 [4].

Phosphoric acid production is based on three kinds of processes: anhydrous, hemihydrate-HH and dihydrate-DH. After extraction, the ore is submitted to milling so that it enables the contact with the reagents, which increase its solubility.

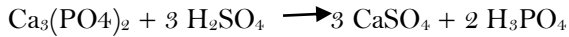
Efficiency in phosphoric acid production can vary due to phosphorus dispersion in each apatite rock. Its solubility in the reaction medium can vary due to impurities which interferes with the reaction kinetics.

The addition of CO_3^{2-} can cause an increase in apatite solubility because it reduces the a axis, which shows a decrease in chemical stability. Therefore, there is an increasing solubility proportional to the molar ratio of CO_3/PO_4 [12]. These details demonstrate that apatite solubility varies according to the rock composition.

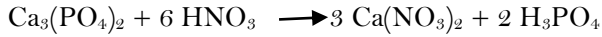
2. Solubility

Global reactions occurred in phosphate rock solubilization using mineral acids such as sulfuric, nitric and phosphoric:

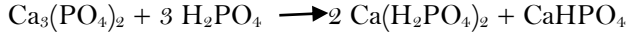
Global reaction to sulfuric acid:



Global reaction to nitric acid:



Global reaction to phosphoric acid



From January 27th, 1961, the Brazilian Ministry of Agriculture, Livestock and Food Supply (MAPA), through decree # 50.146, determined the use of this solution in the extraction proportion of 1:300 (1g in 300 mL), also used in fertilizer blending which contain phosphate rocks [9].

It is obvious that there is an increase in the grade of P_2O_5 in the extraction proportion of 1:300 compared to 1:100 due to the amount of extractor used if there is higher solubility capacity and phosphorus availability [13].

According to Catani [13] the material grain size can influence phosphate solubility. Grain size ratio has the function of increasing the surface contact: the smaller the grain particle, the bigger the contact surface. Therefore, it is possible to increase solubilization and obtain higher P_2O_5 grades.

Solubility in the extraction of 2% citric acid is based on citric acid complexation and its ionic species as well as on solution acidity.

$\text{C}_3\text{H}_4(\text{OH})(\text{COOH})_3$ citric acid is triprotic (three protons). 2% citric acid solution (0,095 M) has pH of about 2,0 and it is represented by the species H_3Cit . It can occur in smaller amount by the species H_2Cit^- . Under the form of H_3Cit , it forms complexes with cations of Ca^{2+} , Fe^{2+} , Mg^{2+} and Mn^{2+} . There are no complex formations with the Al^{3+} cation.

Solubilization in calcium phosphates is expected to be greater than in iron and aluminum phosphates. Likewise, iron phosphates are greater than aluminum phosphate in this kind of extraction.

3. Material and Methods

The materials, apatite samples, used in the tests (Table 3) and the instruments for the analysis were provided by Labfert Análises LTDA, from Uberaba-MG. All the determinations followed the official methodology from the Ministry of Agriculture, Livestock and Food Supply (MAPA), Normative Instruction #3, published in Diário Oficial da União in 2014. The tests were performed in duplicate. Extractions of different apatite proportions were used: citric acid solution, as shown in Table 4. Absorbance was determined by digital spectrophotometer, model Biospectro SP-22, (Figure 4). P_2O_5 mass percentage was calculated by using Equation 1:

Table-3. Rocks identification.

Identification Nr.	Samples	Origin Region
1	Serra do Salitre Rock	Minas Gerais – Brazil
2	Bayóvar Rock	Peru
3	Lagamar Rock	Minas Gerais – Brazil
4	Cajati Rock	São Paulo – Brazil
5	Catalão Rock	Goiás - Brazil
6	Irecê Rock	Bahia - Brazil
7	Rock from Chile	Chile
8	Morocco (Grey)	Morocco
9	Angico Rock	Bahia - Brazil
10	Morocco Rock (White)	Morocco

Source: The author, 2016

$$\text{P}_2\text{O}_5(\%) = \frac{E \cdot C}{A \cdot G} \cdot 0,005 \quad (1)$$

C = P_2O_5 concentration in sample solution, reading in mgL^{-1} .

E = Volume of citric acid in mL.

A = rate volume taken for reading (mL).

G = initial sample mass (g).

Table-4. Mass and volume ratio apatite/citric acid solution

Ration	1:100	1:200	1:300
Sample mass (g)	1,000	1,000	1,000
Citric acid volume 2% (mL)	100	200	300

Source: The author, 2016

4. Results and Discussion

The results from the spectrometric analysis in P_2O_5 are shown in Table 5. In all the rocks there was a considerable variation in P_2O_5 extractions. Rock solubility improved by increasing the solvent amount.

Table-5. Results of %P₂O₅ in different apatite ratios: citric acid solution

Identification	1:100	1:200	1:300
Serra do Salitre rock	2,76	5,31	6,34
Bayóvar rock	7,12	24,16	27,82
Lagamar rock	5,79	9,65	11,78
Cajati rock	0,33	1,06	1,64
Catalão rock	4,09	7,02	9,29
Irecê rock	3,3	6,86	9,35
Chile rock	9,85	15,84	17,92
Morocco Rock – Grey	9,46	15,34	18,55
Angico rock	1,42	1,69	1,94
Morocco rock – White	11,11	19,91	24,9

Source: The author, 2016

5. Conclusion

Cajati and Angico ore samples present mass percentage solubility below 2%, which indicates that these phosphate rocks present low solubility in water and in 2% citric acid solution, probably, due to their physical, chemical, physical-chemical, chrystalline structure, porosity and grain size.

**Figure-4.** Samples prepared for reading in the digital spectrophotometer.

Source: The author, 2016

There is a group of intermediate solubility rocks as well as others which are very soluble:

Bayóvar and Morocco-white, which surpass 25% solubility. Chrystalline structure and particle characterization are useful for assessing the experimental results and can explain the low solubility of some rocks. As for specific applications, Table 5 is useful for industrial applications, especially for the selection of rocks to be processed. Phosphate fertilizers soluble in citric acid are not soluble in water, but they are easily soluble in acid water solutions or in weak acids such as 2% citric acid containing available phosphate. Fertilizers soluble in weak acids are appropriate for acid soils where they can easily dissolve and be available for the plants.

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