



Study the Nature and the Effects of the Impurities of Phosphate Rock in the Plants of Production of Phosphoric Acid

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Abstract

Phosphate rocks from different deposits vary widely in composition, and these variations have important effects in phosphoric acid production. All phosphate rocks contain many impurities. Knowledge of the nature and contents of the various elements in the phosphate is required in the manufacturing process of phosphoric acid. All these chemical characteristics can help the operator to foresee its objectives under the operating conditions and the cost of production in the manufacturing process of phosphoric acid.

Two Tunisian natural phosphates coming from two different deposits were selected. We propose in this work studying the effects of the impurities that depending on their concentration can affect decisively the behavior of these ores in the process of production of phosphoric acid. Study the chemical composition of these ores is carried out according to standard analytical methods used for raw phosphates.

The results obtained show a slight difference in chemical properties between the two types of sedimentary phosphates and their aptitude to be used in the plants of production of phosphoric acid.

Indexing terms/Keywords

Natural phosphate; Chemical characterizations; Effect of the impurities; Process for producing phosphoric acid.

Academic Discipline And Sub-Disciplines

Geochemistry

SUBJECT CLASSIFICATION

Analytical chemistry

TYPE (METHOD/APPROACH)

Chemical Engineering

Council for Innovative Research

Peer Review Research Publishing System

Journal: Journal of Advances in Chemistry

Vol. 7, No. 2

editor@cirworld.com

www.cirworld.com, member.cirworld.com



1. INTRODUCTION

Phosphates exist most commonly in the earth's crust. Phosphorus averages 1180 ppm. The most easily mined phosphate deposits are found in the great sedimentary basins [1]. Phosphates ore are intercalated with sedimentary stratus of other waste materials or similar ores interpenetrated by gangue minerals [1].

Wet process phosphoric acid technology comprises essentially the sulfuric acid attack and the separation of the phosphoric acid produced from the calcium sulfate crystals resulting from the reaction. Both the attack and the separation, which is effected by filtration, are considerably affected by the nature of the ore and its impurities. Besides calcium phosphate, the phosphate ores contain 10-15 major impurities and another 16 or so trace elements. Organic matter, also present in many ores, is not included in this estimation. Each element contained in the ore has its individual transfer coefficient into product acid and waste solids. Phosphoric acid is a major component of many fertilizers. It is mainly produced by digestion of phosphate ore (fluoroapatite) with sulfuric acid. This yields phosphoric acid as a product and hydrated calcium sulphate as a by-product. The ore also contains traces of heavy metal ions, as cadmium and radium are the most worrisome. They can cause serious environmental problems [2].

If phosphate ore is digested by phosphoric acid, the following reactions can take place [3]:



When a mixture of phosphoric acid and sulfuric acid is used for the digestion of the ore, two processes occur more or less simultaneously: digestion of the ore and precipitation of calcium sulfate. Several reactions take place simultaneously and the effective rates of these reactions are very sensitive to the solution composition, agitation, temperature, and rock characteristics. The reaction between phosphate rocks and acids is essentially a surface reaction [4].

According to the phosphate composition, we propose in this work studying the effects of the impurities depending on their contents, they have a decisive effect in the plants of production of phosphoric acid.

2. EXPERIMENTAL

2.1 Atomic absorption

This technique is used to evaluate the free atoms concentration at a temperature of 2000°C. Thus we have a total quantification of each analyzed element. The apparatus used to determine the atomic absorption of phosphates is Perkin-Elmer AA 200.

2.2 Flame spectrophotometry

It is based on measuring the power radiated by the fraction of thermally excited atoms for a given wavelength. In practice, we take measurements of the standards and the unknown solution at the same time in order to be exactly under the same conditions. This method is particularly sensitive for the alkalis. The apparatus used is a type of « RENDHOF ».

3. RESULTS AND DISCUSSION

The principal reaction occurring in a phosphoric acid plant is the reaction between phosphate rock and sulfuric acid to give soluble phosphoric acid and insoluble calcium sulfate. However, phosphate rocks contain many impurities that have important effects in phosphoric acid production. The chemical composition is done according to standard analytical methods used for phosphates and whose results given in weight percentages appear in the following table 1.

Table 1. Chemical Analysis of the Samples of phosphate.

Phosphate	1	2
% P ₂ O ₅	30.79	30.66
% CaO	49.75	49.63
% H ₂ O	1.00	1.40
% CO ₂	6.56	6.47
% C _{org}	0.22	0.24
% SO ₃	3.34	3.39
Cd (ppm)	10	11
% Na ₂ O	1.45	1.42
% K ₂ O	0.04	0.04
Cl (ppm)	947	918



% F	3.14	3.21
% MgO	0.62	0.69
% SiO ₂	3.96	2.51
% Al ₂ O ₃	0.43	0.46
% Fe ₂ O ₃	0.18	0.19

CaO: The calcite content in phosphate rock is determined by the manganometric method. Calcite increases the consumption of sulfuric acid for the attack [2]. A relatively pure acid can be produced from ore containing large quantities of calcite [2]. Calcite causes the formation of foam during the attack, especially nitric. This requires an increased amount of anti-foam, but they improve the reactivity of the ore, particularly appreciated in the production of phosphate fertilizers.

P₂O₅: The strengths of orthophosphoric acid as well as analyses of phosphate rocks and fertilizers are usually expressed in terms of P₂O₅. The P₂O₅ content is determined by the gravimetric method and precipitation of P₂O₅ in a form of quinoline phosphomolybdate. Normally a preferred rock is the one that yields P₂O₅ as phosphoric acid at lowest cost, and primary consideration is usually the delivered price of the rock per unit of P₂O₅ [5]. The ratio of CaO to P₂O₅ eventually determines the amount of H₂SO₄ used per unit of P₂O₅ produced. Since the cost of H₂SO₄ is a major factor in the production cost of phosphoric acid, a low CaO:P₂O₅ ratio is preferred [5]. Many deposits have excess calcium, in compounds not associated with the phosphate that cannot be removed by beneficiation. The resulting high CaO:P₂O₅ ratio causes high H₂SO₄ consumption [5].

CO₂: The CO₂ content is determined by a light hydrochloric attack and measuring the volume of gas released. Carbon dioxide appears with carbonates as important factors in the reactivity. They accentuate the formation of foam if the attack is produced in vacuo in a flash room (as reactor).

Organic matter (% C_{org}): The organic matter content is determined by titration of the organic matter oxidized by potassium dichromate. Organic matter increases the foam formation during the attack and thus increases the use of anti-foaming. They causes the formation of a trouble and a sank solid suspension into the produced acid. There are two types of organic matter present in the phosphate, the soluble and the insoluble organic matter. The soluble organic matter effect essentially on the produced phosphoric acid 26-28 % P₂O₅. And gives merchant phosphoric acid 54% P₂O₅ black in color unwanted by polymers. Its use requires a preliminary clarification especially for the manufacture of technical acid. The insoluble organic matter, its effect is harmful to the filtration; in the tank of attack it inhibits of crystal growth phosphogypsum by changing the morphology of gypsum crystals, which affects the porosity and permeability of the gypsum cake on the filter. Also, the particles clog the pores of the gypsum layer, which do a screen and slowing the passage of liquid through the filter cloths. Therefore, the filtration efficiency is greatly affected.

SO₄: The sulphate content is determined by dosage of sulphate with a solution of barium chloride by the gravimetric method. Sulfates do not significantly alter the conditions of treatment unless they reach very high limits, and maintain the corresponding amount of sulfuric acid during the acidulation.

CdO: The cadmium content is determined by atomic absorption, the dosage of cadmium by photometric measurement of the absorption line in 228.8 nm. Cadmium can be toxic in specific end products (animal food or fertilizers). It is in the form of traces in minerals. To be in global standards, the GCT must reduce the Cd content up to 10 ppm and this is due to the use of a sulfide salt leads to precipitation of Cd and the separation of solid phase is done by filtration. This method generates an exhaust of H₂S and makes the atmosphere of the unit suffocating.

Na and K: The Na₂O and K₂O contents are determined by flame spectrophotometry. This method is applicable to inorganic phosphates which their contents in Na₂O and K₂O are respectively less than 2.7 % and 0.24 %. Na and K react with fluorine and silica to form fluosilicates (Na₂SiF₆ and K₂SiF₆) wich can produce muds in the equipment and whose elimination can raise important problems.

Cl: The chlorine content is determined by precipitation of chloride ions in the form of AgCl. Chlorine is an undesirable impurity because of the danger of corrosion during the production of phosphoric acid and nitric attack. Usually it is dangerous from 0.1 % only at high values because its corrosive action is influenced by interactions with other impurities.

Mg: The magnesium content is determined by atomic absorption, the dosage of magnesium by photometric measurement of the absorption line in 285.2 nm. Magnesium in phosphoric acid has a double effect on the crystallization of gypsum. Combined with fluorine, it enhances crystallization, but over certain limit (2-3 %) it increases the viscosity of the acid which generates a rapid deterioration of the filtration rate.

F: The fluorine content is determined by metering volumetrically of fluorine in form of H₂SiF₆ with a solution of thorium nitrate. The fluorine causes problems of corrosion, mud, slurry formation and atmospheric pollution; moreover, it can decrease the filterability of gypsum due to the formation of complex salts. The fluorine can be a corrosive compound if the reactive silica is present in large quantities. With a high amount of sodium (1% or more) the majority of fluorine will precipitate during the reaction of attack. About half of the remaining part in the acid escapes during the concentration by evaporation [6].



SiO₂: The silica content is determined by the gravimetric method. The silica found in significant quantities leads to greater wear of the grinding apparatus and erodes the agitators and the pumps which handle slurries of attack. It can also negatively affect the filtration of gypsum in the production of phosphoric acid. A lack of silica below the stoichiometric amount necessary will involve the fluoride ion in form SiF₆ and causes difficulties in the phosphoric acid purification for technical use so that the addition of active silica during the attack is necessary.

Al₂O₃ and Fe₂O₃: The aluminum and iron contents are determined by atomic absorption, the dosage by photometric measurement of the absorption line in 309.3 nm for Al and 248,3 nm for Fe. In particular, alumina is undesirable because after dissolution of phosphate by the acid they form insoluble phosphates that decrease water soluble P₂O₅ content in product acid. In addition they reduce the filterability of gypsum. The highest commercial limit to be considered is equal to

the ratio : $\frac{Al_2O_3 + Fe_2O_3}{P_2O_5} = 0.08 \text{ to } 0.1$ [2].

But the phosphates containing a mass content of aluminum less than 1.4 provide better filtration rate with an increasing amount of alumina [7]. Kruger and Fowles [8] showed that for low values of Al₂O₃, aluminum promotes the growth and consequently the formation of uniform crystals of gypsum thus improving the filtration rate, however, for high ratios of (aluminum / fluorine), it increases the viscosity of the acid and its density which has a detrimental effect on the filtration. By studying several sedimentary phosphates, Halaseh and Dukhggan [9] determined a ratio of fluorine complexation, RCF, which is represented as follows:

$$RCF = \frac{\frac{\% F}{19}}{\frac{\% Al_2O_3}{17} + \frac{\% SiO_2}{15}} \quad [9]$$

Halaseh and Dukhggan [9] noticed that for the ratio $0.42 \leq RCF \leq 1.378$, the filterability of phosphoric muds increases with the decrease of this ratio (RCF = 0.571 for raw phosphate 1 and RCF = 0.868 for raw phosphate 2), the mass content of the acid as P₂O₅ of acid increases and corrosion decreases, if this ratio is below 0.42, the filterability decreases due to the presence of undissolved silica salts and a bad crystallization. By referring to RCF report and the filtration rate; phosphate 1 is more favorable to be studied kinetically [10].

4. CONCLUSIONS

From the chemical characterizations performed previously, we can affirm that the two qualities of phosphate can be used in the plants of phosphoric acid. However, phosphate 1 is more appreciated to be operated in the plants of phosphoric acid on the one hand and more favorable to be studied kinetically on the other hand.

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