Phosphate Rock Conversion into Phosphoric Acid: Chemistry, Chemical Engineering and Corrosion Control

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Abstract: Phosphate rock (PR) and phosphoric acid (PA) are the central subjects of a worldwide economic sector supplying chemicals for the fertilizer, metal, food, medicine and dentistry sectors. PA is a triprotic acid that ionizes in three steps:

$$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^- \leftrightarrow 2\,H^+ + HPO_4^{2-} \leftrightarrow 3\,H^+ + PO_4^{-3}. \quad [1]$$

It is produced by chemical reactions of PR with mineral acids: sulfuric (H_2SO_4) or hydrochloric (HCl) and posterior separation by filtration and evaporation or solvent extraction. The corrosivity of the reaction system depends on two main chemical factors: the chloride and fluoride content of the PR and the chemical interaction between the HF formed during the acid leaching and the SiO_2, Al_2O_3 and MgO present in the PR. Therefore, it is a common industrial practice to add SiO_2 and Al_2O_3 containing clays, or acid-soluble silicates to reduce the corrosion effects. The PR and PA industry is spread out in countries of four continents: Asia, Africa, America and Europe, which operate PR mines, PA production plants and produce phosphatic fertilizers. The chemical reactions, the corrosion problems and the solutions implemented are illustrated and discussed, based on the authors experience and knowledge

Introduction

PA is an important industrial chemical, used as an intermediate in the fertilizer industry [1,2], for metal surface treatment in the metallurgical industry [3,4], water purification and as an additive in the food industry [5]. Cola-type beverages and fruit juices contain food-grade PA to impart acid taste and to avoid sedimentation of iron hydroxides. Corrosion protection of steel infrastructure assets and industrial equipment is achieved applying a phosphatization process, based on PA [6]. A singular application is the manufacture of artificial apatite for coating stainless steel orthopedic implants in the human body.

Table 1 presents the chemical composition of different PRs from several countries, showing the great diversity and, consequently, their chemical behavior during conversion into PA.

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Constituent	Florida, U.S.A.	North Carolina, U.S.A.	Palfos, RSA	Pesca, Colombia	Hazara, Pakistan	Monte Fresca, Venezuela	Araxa, Brazil	Hidalgo, Mexico	Sahara, Morocco	Safi, Morocco	Ruseifa, Jordan	Oron, Israel
P_2O_5	31.2	29.7	39.9	20.5	28.5	34.18	35.5	43.3	34.2	32.4	33.4	29.8
CaO	45.0	47.4	-	29.0	41.9	42.30	47.3	46.3	50.3	49.9	51.0	51.0
Cl	0.05	0.015	-	0.001	0.03	-	0.001	0.02	0.02	0.02	4.2	0.03
F	3.60	3.53	2.35	2.0	2.92	2.94	2.54	-	3.8	4.1	4.9	3.8
SiO_2	9.48	1.73	1.0	39.2	23.2	10.29	0.41	2.8	-	2.85	0.2	0.68
Fe_2O_3	1.33	0.79	-	0.8	1.85	0.66	2.42	-	0.22	0.70	0.3	0.2
Al_2O_3	1.76	0.53	0.35	1.1	1.0	1.15	0.32	1.11	0.48	0.40	-	0.3
MgO	-	0.79	0.51	0.09	0.13	0.21	0.07	2.17	0.12	0.70	-	-
Na_2O	0.89	0.98	-	0.14	0.16	1.30	0.03	0.05	-	0.90	-	-
K_2O	0.11	0.17	-	0.14	0.31	0.18	0.10	-	-	0.10	4.5	-
CO_2	3.48	4.18	1.0	3.0	1.1	-	1.7	0.02	2.7	4.1	-	7.8
Organic C	2.18	1.38	-	0.3	0.18	-	<0.1	-	0.06	-	-	0.6
Total S	1.05	1.1	-	0.1	0.18	-	1.52	-	-	0.20	-	-

Table 1: Chemical composition of phosphate rocks

The corrosivity of phosphate ores, used in the production of PA depends on two main chemical factors: the chloride content and the interaction between HF formed in the PA reaction slurry with SiO_2, Al_2O_3, and MgO present in the ore [7,8]. Corrosion events occur mainly in the reaction system, taking place under severe hydrodynamic operating conditions, which include agitation of an erosive slurry and high temperature, 70-80 C. To prevent these pernicious events, industrial plant equipment is fabricated from corrosion-resistant alloys (CRA) plastics and elastomers [9].

Phosphoric acid production

Two main processes are used to produce PA: the wet process (WPA) by attack with H_2SO_4 and a novel process by attack with HCl followed by separation of PA applying solvent extraction (SX) technology. The composition and purity of the PA obtained by these processes depend upon the mineral and chemical composition of the PR and the acid used.

The wet process consists of three main stages:
1. Acidulation of PR by H_2SO_4; the overall reaction with fluoroapatite is usually expressed as:

$$Ca_{10}(PO_4)_6F_2 + 10\ H_2SO_4 \leftrightarrows 10CaSO_4 + 6H_3PO_4 + 2HF. \quad [2]$$

2. The hydrogen fluoride reacts with any active silica present to form silicon tetrafluoride:

$$4\ HF + SiO_2 \rightarrow SiF_4 + 2\ H_2O, \quad [3]$$

3. which volatilizes as such or hydrolyzes to fluorosilicic acid, forming silica deposits:

$$3\ SiF_4 + 2\ H_2O \rightarrow 2\ H_2SiF_6 + SiO_2. \quad [4]$$

During the acidulation, a thick slurry is formed containing 30% of solid particles, mainly gypsum ($CaSO_4$) and unreacted PR components.
2. Filtration, to separate the solid particles from the filter acid, 30% P_2O_5 (50% PA).
3. Concentration, by evaporation of the filter acid to merchant-

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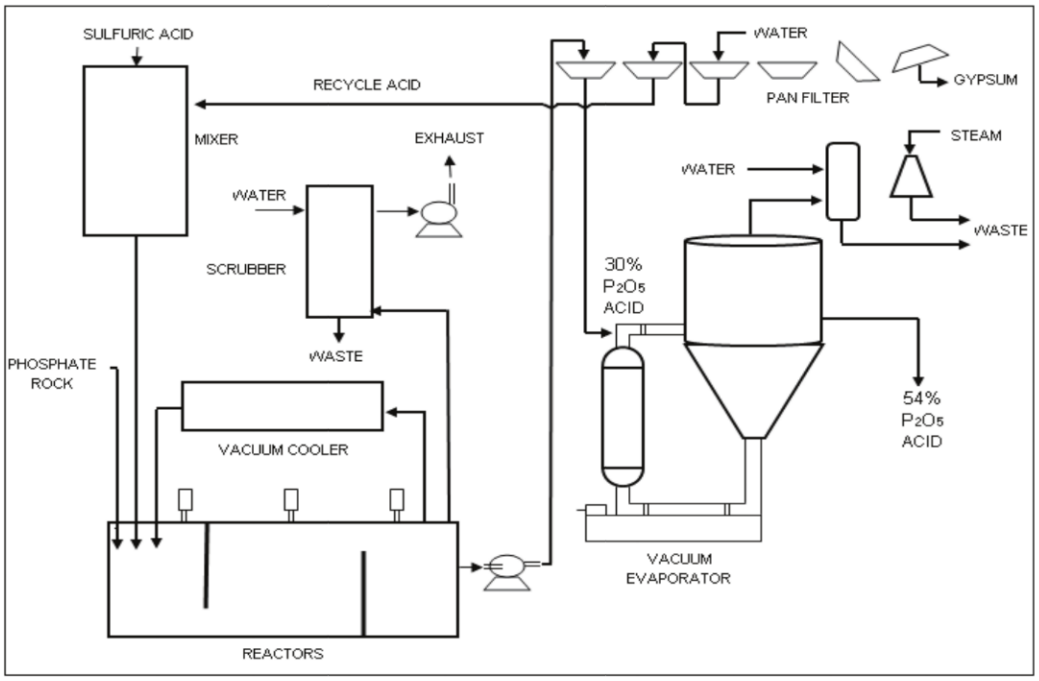

Figure 1: Typical wet process acid plant, showing three stages and industrial equipment.

grade PA, 54 % P_2O_5 (70% PA).

A schematic diagram of a typical WPA plant presents the process three stages and the diverse plant equipment and the products (Figure 1).

The solvent extraction process (SX)

PR is reacted with HCl to form an aqueous reaction mixture comprising PA and $CaCl_2$:

$$Ca_3(PO_4)_2 + 6\,HCl \rightarrow 2\,H_3PO_4 + 3\,CaCl_2\,. \qquad [5]$$

PA is extracted by contacting the mixture with a lower aliphatic alcohol (RCH_2OH). The aqueous extract is separated from the solvent extract, it is washed with water to release PA which is concentrated by distillation to produce food grade, pure PA. Sometimes, the wet process (PR reacted with H_2SO_4) is integrated into the SX process (Figure 2). In this version, the slurries obtained by treatment with H_2SO_4 (wet process) and with HCl (SX process) are mixed, and subsequently, the PA is extracted with an aliphatic alcohol [10,11]. The HCl is generated as a byproduct at adjacent chemicals plants.

Chemistry of phosphate rock impurities

PR is the principal source of dissolved and suspended impurities in WPA. Other impurities such as Cl^- may be introduced in process water, particularly brackish water [12]. Sometimes contaminated H_2SO_4 obtained from the hydrometallurgical industry introduces additional impurities. Cl^- and F^- are particularly corrosive, other impurities that affect production are SiO_2, Al_2O_3, MgO, alkali metal salts, SO_4^{2-}, S^{2-}, organic matter, and oxidizing agents.

The Cl^- ion is adsorbed on metal surfaces and replaces adsorbed oxygen or water molecules. During attack on stainless steel, chlorides of iron, nickel, and chromium are formed; these are highly soluble in PA because of its complexing of cations of the transition group elements. The corrosivity of the halogen acids: HCl and HF, and of the halide ions Cl^- and F^-, that dissolve in strong mineral oxygen-acid, such as H_3PO_4 and H_2SO_4, is related to the physicochemical properties of the halogens, their electronegativity, ion size, and ionic character of the HX molecule that indicates their high chemical reactivity [13].

The interaction of HF with SiO_2, Al_2O_3 and MgO

The CaF_2 constituent of the fluorapatite reacts with H_2SO_4 during acidulation to produce HF which may form HF^{2-}, and F^- ions, depending on the hydrogen ion activity of the solution. HF reacts with any active silica, alumina and magnesia compounds in the rock to form acid-soluble silicon fluoride and aluminum fluoride complexes and salts, e.g., $(SiF_6)^{-2}$, $(AlF_6)^{-3}$, and $MgSiF_6$. Other reactions that decrease

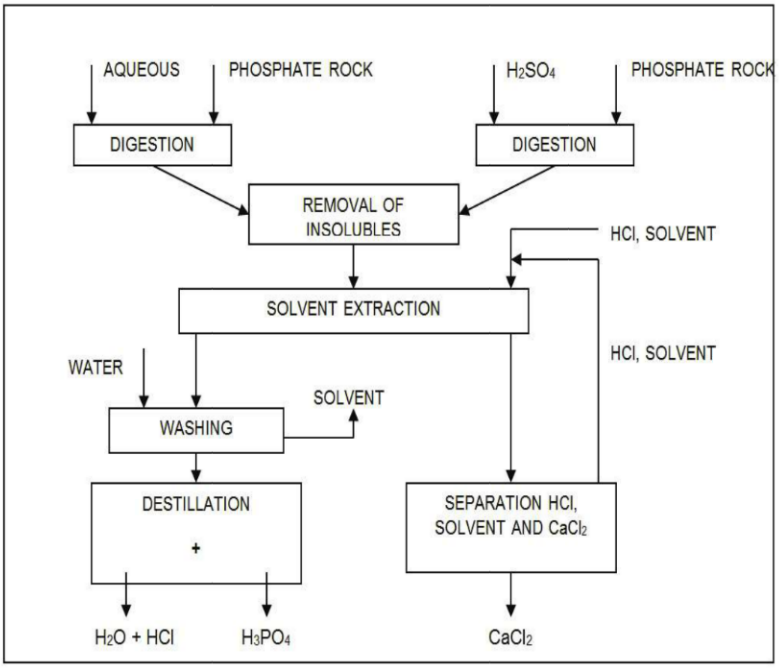

Figure 2: Diagram of the phosphoric acid solvent extraction process.

corrosion include formation of partially soluble metal fluoride complexes with Fe^{+3}, Ca^{+2}, K^{+} and Na^{+}, and formation of insoluble fluoraluminates and fluorosilicates that settle on equipment surfaces [14,15].

Becker [7] states that, according to his personal experience, acceptable corrosion rates are obtained when F/SiO_2(% weight ratio) in the phosphate ore is held below the threshold value of 1.4. A more accurate and complete calculation of the complexing ratio is based on the stoichiometry of the complex-forming reaction between F^- and equivalent SiO_2, Al_2O_3, MgO:

$$24\ HF + 2\ SiO_2 + Al_2O_3 + MgO \rightarrow H_2SiF_6 + 2\ H_3AlF_6 + MgSiF_6 + 8H_2O. \quad [6]$$

The chemical equivalent ratio is:

$$\frac{\frac{\%F}{19}}{\left(\frac{\%SiO_2}{15}+\frac{\%Al_2O_3}{17}+\frac{\%MgO}{20.2}\right)}. \quad [7]$$

An equivalent ratio, $F/(SiO_2+Al_2O_3+MgO) > 1$, indicates the presence of non-complexed fluoride and, consequently, enhanced corrosivity during production of WPA. When the equivalent ratio is < 1, the ore contains enough SiO_2, Al_2O_3 and MgO to ensure the formation of non-corrosive fluoride complexes.

Corrosivity of phosphoric acid

The PA plants, both implementing the wet and the SX processes, have a high level of corrosion risk resulting from several corrosion common characteristics: they handle and process aggressive mineral acids such as H_3PO_4, H_2SO_4, HF and HCl; operate under severe hydrodynamic conditions that include mineral leaching, chemical reaction, agitation, circulation at high flow velocities and distillation. Furthermore, they operate at relatively elevated temperatures to accelerate the chemical reactions[16].

Many forms of corrosion, mainly localized, are encountered in PA production plants and facilities. The most common type is erosion-corrosion (EC), generated by the joint, simultaneous action of mechanical erosion and electrochemical corrosion [17,18]. Testers for the study and measurement of EC were developed and built by the corrosion and materials section of IMI-TAMI Institute for Research and Development Ltd, Haifa, now a part of Israel Chemicals Ltd. (ICL)[19]. The electronic part of these testers was designed by Ch. Yarnitzky, Technion-Israel Institute of Technology [20].

The addition of fluoride complexants

The addition to the phosphate ore or to the WPA reaction system, of fluoride complexants: clays, amorphous silica or acid-soluble silicates improves the system chemical reactions.

The addition of such minerals has other positive influences, e.g., increased plant capacity by improving filtration rate, higher filter acid strength, control of HF emission and F^- content in the final product. Based on their influence during the production of WPA, clays are considered as chemical modifiers of the PR, since its chemical behavior changes as a result of clay addition [14,15].

The selection of a suitable clay and the amount to be added must be based on a thorough analysis of the PR, the clay components, their chemical and physical nature (amorphous or crystalline) and their reactivity with different acids present in the reaction slurry: H_3PO_4, H_2SO_4, HF, H_2SiF_6, and HCl. Several properties are required from a suitable clay to improve the chemical performance during WPA production, namely:

- A high degree of chemical reactivity of the SiO_2 and Al_2O_3 components. In general, amorphous minerals are more reactive than crystalline ones. For instance, quartzite (sand) does not react quickly with HF. In that case, HF in the liquid phase and SiO_2 as a solid suspension will coexist in the slurry and enhance the erosion-corrosion effects. On the other hand, porcelanite is more reactive due to its amorphous state.
- A very low content of impurities, to avoid contamination of the PA product, e.g. iron, copper and heavy metals such as Cd, Pb, Ti, Sr; radionuclides and organic matter.
- A low content of crystallization and bounded water, which may rise to 25%, to save in transportation, storage and handling expenses.
- Low price and easy, local availability.

Conclusions

PA is an important chemical used in many industries; its composition, purity and applications depend upon the composition of the PR. The interaction between HF and SiO_2, Al_2O_3 and MgO in the WPA reaction system is quantitatively expressed by a chemical equivalent ratio: $F/(SiO_2 + Al_2O_3 + MgO)$. Mineral modifiers such as clays and silicates are added to the PR or the WPA reaction system to modify the PR concentration, to amend their behavior, to reduce corrosion and overcome problems in WPA production.

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