

Phosphoric acid production by attacking phosphate rock with recycled hexafluosilicic acid



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ABSTRACT

During the classical production of phosphoric acid, the reaction between sulfuric acid and phosphate rock generates suspension. The latter is subsequently filtered and concentrated by evaporation process resulting in fluorine or acid gas. In this paper, we present a new procedure of phosphoric acid production by using recycled hexafluosilicic acid instead of sulfuric acid.

Fluorine recycling process involves several steps starting with the bubbling of the resulting acid gas through hexafluosilicic acid solutions followed by a pre-concentration step before attacking the natural phosphate rock. The advantages of such procedure lies in decreasing the sulfuric acid quantities needed for the phosphoric acid production as well as in the environmental benefits from the recycling process of the harmful fluorine gas.

In this work, phosphate rock was attacked by a mixture of hexafluosilicic acid (20% by weight) and recycled phosphoric acid (25% in P_2O_5). The cake obtained by vacuum filtration of the slurry was characterized by X-ray diffraction (XRD), Differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The main peaks obtained by XRD were attributed to chukrovite ($Ca_4AlSiSO_4F_{13} \cdot 12H_2O$), gypsum, and silica quartz. However, the calcium content in the produced phosphoric acid has to be maintained lower than 3.5% in order to avoid the formation of cloudy phosphoric solutions by the formation of CaF_2 which affects the filtration of the mixture.

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1. Introduction

Phosphoric acid is considered as the second mineral acid produced after the sulfuric acid. The major part of phosphoric acid production (90%) is dedicated to chemical fertilizers (Belboom et al., 2015), the rest being used as raw materials for the production of detergents, animals food, additives in toothpastes, ingredients of non-alcoholic drinks like soda or cola (El-Asmy et al., 2007) and in the surface treatment of stainless metals (El-Asmy et al., 2007; Becker, 1989).

Two basic processes for phosphoric acid manufacture were largely discussed in the literature (El-Asmy et al., 2007; Becker, 1989). The first is a pyrometallurgical process, and it was abandoned for economic reasons while the second called wet process is largely profitable than the first one (Becker, 1989; Belboom et al., 2015).

The Wet process consists of mixing phosphate rock e.g. fluorapatite ($Ca_{10}F_2(PO_4)_6$) with sulfuric acid (H_2SO_4) in aqueous media. There

are different types of wet processes depending on the type of by-product, phosphogypsum, and the concentration of phosphoric acid produced.

The nature of the by-product, phosphogypsum, depends on the temperature of the reactor as well as on the concentration of phosphoric acid produced. In conventional operating conditions ($T = 80\text{ }^\circ\text{C}$, 26% P_2O_5), the solid formed is the calcium sulfate di-hydrated (gypsum). At higher temperature, the formation of the hemihydrate or anhydrous form is promoted (Al-Thyabat and Zhang, 2015; Becker, 1989).

In industrial practice, dihydrate is usually used with one or multi-stage reactor producing phosphoric acid between 26 and 28% in P_2O_5 , while hemihydrate is used with one or multi-stage reactor producing phosphoric acid between 40 and 48% in P_2O_5 (Mahmoud et al., 2004; Rashed et al., 2004).

In this study, the work was carried out on a pilot scale with a dihydrate single reactor. The dihydrate wet method is a sequence of three successive stages: attack, filtration and concentration.

The attack of phosphate ore by the sulfuric acid with the presence of recycled phosphoric acid lasts from 2 to 8 min. However, the

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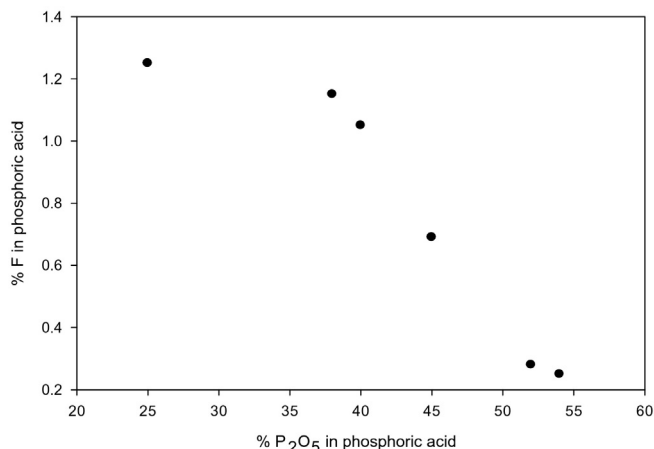


Fig. 1. Content of fluorine (%F) versus the percentage of P₂O₅ in phosphoric acid produced.

proliferation of gypsum crystals takes between 2 and 8 h (Abu-Eishah and Abu-Jabal, 2001; Abdel-Aal et al., 2006).

The filtration is the second stage of the wet process enabling the separation of the solid cake and the produced phosphoric acid. This solid/liquid separation implies a vacuum filtration in which the morphology of crystals plays a major role for a better filterability. This is largely influenced by the nature and elementary composition of the phosphate ore. The content of the produced acid is 25% in P₂O₅ (w/w).

The concentration of phosphoric acid is the last stage in this wet process. During the concentration of phosphoric acid (at 54%) by evaporation, the gaseous fluorine is released in hydrofluoric acid and tetrafluosilicate forms. This fluorine originated from the phosphate which has the fluorapatite (Ca₅(PO₄)₃F) as main constituent (Becker, 1989; Gouider et al., 2009). This hypothesis is confirmed in Fig. 1 which describes the decrease of the fluorine versus the strength of the produced phosphoric acid.

The recovery of the acid gas (fluorine) in aqueous solutions as hexafluosilicic acid (resulting from the reaction of HF + SiF₄/H₂SiF₆) is a potential substitute for the sulfuric acid during the production of the phosphoric acid, hence minimizing certainly the acid rejections in the natural basins (Eyal et al., 1984). The mainly cited techniques for the gaseous fluorine recovery are the adsorption, ion exchange process, precipitation and electrolysis (Eyal et al., 1984; Gouider et al., 2009). These methods are expensive and present application difficulties on the industrial scale. Being the most economic, the absorption method remains the most advantageous (Djololian and Billaud, 1978; Roizard et al., 1997).

The aim of this work is the optimization of a new procedure of phosphoric acid manufacture by using the recycled hexafluosilicic acid. This acid will be used to attack the natural phosphate ore, substituting in part the sulfuric acid (Fig. 2).

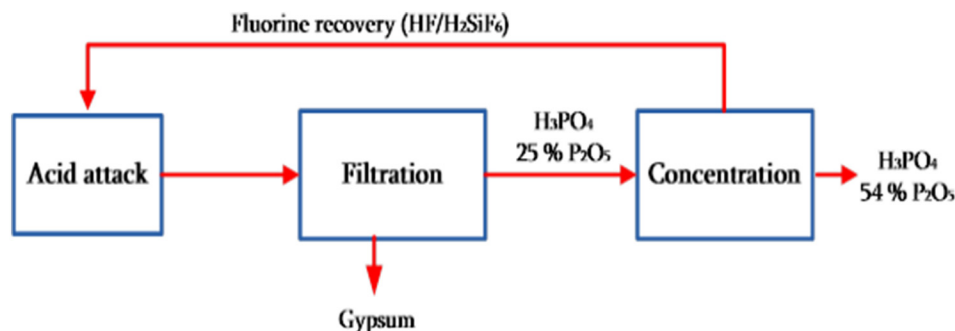


Fig. 2. General process for fluorine recovery.

Table 1

Elemental analysis of the raw materials used during the hexafluosilicic attack.

Component in %	Phosphate	Recycled phosphoric acid	Hexafluosilicic acid
P ₂ O ₅	29.68	25.00	–
SO ₃	1.48	2.23	–
F	2.8	1.25	15.83
Si	4.00	0.23	3.89
Ca	35.79	0.057	–
Al	0.079	0.030	–

2. Experimental procedure

2.1. Characterization of raw materials

The phosphate sample studied is of Syrian origin. Table 1 illustrates the composition of phosphate, the phosphoric acid resulting from the sulfuric attack, and hexafluosilicic acid used as raw material during the attack.

Beside elemental analysis, Fig. 3 presents the analysis by X-ray diffraction (XRD) of the studied phosphate. The main peaks are attributed to Ca₅(PO₄)₃F (ICDD file: 00-015-0876). We note the presence of Ca₃(PO₄)₂ (ICDD file: 00-032-0176). The peaks correspond to CaCO₃ (ICDD file: 01-081-2027) and CaF₂ (ICDD file: 00-048-1298) respectively. We note the presence of the silicon added as standard with its characteristic peaks (ICDD file: 00-005-0565).

The presence of the silica quartz (ICDD file: 01-078-1252) is in good agreement with the elementary analysis of the Syrian phosphate with a rate of SiO₂ of 8,65%. Oxide of iron, aluminum and magnesium, are present in small quantities, and are not detected by DRX even after a long recording duration.

2.2. Apparatus and procedure

Implementation of raw materials for the production of phosphoric acid under hexafluosilicic attack is carried out in our laboratory pilot as shown in Fig. 4. This pilot enables the attack of the natural phosphate at 70 °C by the hexafluosilicic acid at 20% with a diluted solution of phosphoric acid at 25% in P₂O₅ produced from sulfuric attack while maintaining the aluminum in excess (Ninueil, 1986).

We carried out the attack phosphate/hexafluosilicic acid for the different contents in calcium and fluorine in phosphoric acid produced at 24% in P₂O₅. The resulting suspension is filtered at constant pressure. Phosphoric acid and the cake are analyzed in order to determinate their elementary composition. This cake is characterized by X-ray diffraction, DTA (Differential thermal analysis) and optical microscopy and then compared to the ones resulting from the sulfuric attack.

3. Results and discussion

Preliminary tests showed that the phosphoric acid obtained by hexafluosilicic acid attack (FAA) presents a cloudy appearance depending

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