Contribution to the study of the distribution of the uranium from the phosphoric acid and gypsum in the presence of cadmium, lanthanum and clay.

D. Chafik, R. Bchitou and A. Bouhaouss.

Chemistry Physics General of materials, Nanomaterials and environment laboratory, department of chemistry, Faculty of sciences, University Mohammed V-Agdal, Rabat, Morocco.

Abstract: This article is devoted to the study of the distribution of uranium from phosphoric acid and gypsum in the presence of several elements in order to determine the amount of uranium that goes into phosphoric acid. To achieve this, we have added a few elements such as CdCl₂, LaCl₂ and clay by varying their contents from 1 to 5 weight percent. The purpose of this research is to minimize the amount of radioactive uranium in the phosphoric acid because the presence of this element is likely to obstruct the further use of phosphoric acid.

Key words: Phosphoric Acid; Phosphogypsum; impurities; radionuclides; Uranium; Clay.

INTRODUCTION

Morocco has three-quarters of the world’s phosphate reserves of minerals and ranks first in the export. Moroccan phosphate sedimentary series contain relatively large amounts of associated minerals (Bilali and al., 2001). The manufacture of wet process phosphoric acid is obtained by a direct attack of the phosphate rock with strong acids such as sulfuric acid, hydrochloric acid or nitric acid (Govere et al., 1995; Bchitou et al., 1996; Bchitou et al., 1998; Boussen, R., 2007). Among these acids sulfuric acid is the most widely used. However, the presence of many metals in trace amounts in the phosphate minerals on the one hand, is a handicap to the purity of industrial acid.

On the other hand, these can lead to the existence of secondary reactions during the production of phosphoric acid generating either complexes or precipitates. Among these impurities, there is the uranium, which is particularly a radioactive element, that when it is associated with phosphate ions, it decreases the value of the phosphoric acid because when the uranium passes into the solution it partially consumes the acid. Thus, the Moroccan phosphate ore contains between 100 and 130 g of uranium per ton of ore (http://ofrir.lcp.cfr/cycle_ap/Lire_article.php, 2013). These radio nuclides can be found in the gypsum as well as in the phosphoric acid (Mazzilli et al., 2000; Habashi et al., 1986; Haridasan et al., 2001; Papastefanou, C., 2001; Rutherford et al., 1995; Rutherford et al., 1996)

Several studies have been carried out show that the radioactivity in the Moroccan phosphates and samples related to these phosphates is similar to what is usually measured in the same samples in the world (Hakam et al., 2005). Several studies have been made by the unit radiochemistry choosing as basic system study the possible reject of phosphate from the phase of the extraction of the mineral rock storage until the phosphogypsum going through the production of various phosphoric acid and fertilizers (Alam et al., 1997; Brevet européen, 1983; Aouazi et al., 2001). In this context, this process has been undertaken to determine the different levels of radio nuclides (239U, 235U, 232Th, 226Ra ...) of the sample of phosphates, or to evaluate the distribution of radio nuclides between phosphoric acid and phosphogypsum. However, the problem of the presence of the uranium in phosphates is directly related to the use of phosphoric acid in the phosphate fertilizers. This phenomenon is due mainly to the accumulation of the uranium in the soil and is considered as an impurity in the phosphoric acid. Note that the uranium is present in phosphoric acid V1 and in V4 state for fresh solutions and especially in the state VI for old solutions (Bessiere et al., 1986). Complexes of the uranium in the phosphoric environment depend on the concentration of \( \text{H}_3\text{PO}_4 \) and can be charged or neutral (Suzuki et al., 1986; Bunus et al., 1994).

We can avoid it if we can move uranium in phosphogypsum during the sulfuric acid decomposition of phosphate rock. And this is the aim of our research, the method is based on the addition of elements such as CdCl₂, LaCl₂ and clay by varying their contents.

MATERIALS AND METHODS

In a three-necked flask is the attack of phosphate rock with sulfuric acid in the presence of industrial phosphoric acid (30% \( \text{P}_2\text{O}_5 \)) prepared from phosphoric acid of 85% purity.

The attack reaction is:

Raw phosphate + 3\( \text{H}_2\text{SO}_4 \) + \( n \) \( \text{H}_2\text{O} \) \( \rightarrow \) 3\( \text{CaSO}_4 \), \( n \text{H}_2\text{O} + 2\text{H}_3\text{PO}_4 \) with \( n = 0; \frac{1}{2} \) or 2.
Processes are classified depending on the form in which the gypsum is crystallized. We observe the processes leading to the formation of anhydrous gypsum ($n = 0$), the gypsum hemihydrate ($n = 1/2$), and gypsum dihydrate ($n = 2$).

The prepared solution was mechanically stirred at a reaction temperature of 80 °C. After 1 hour of maturation, the solution is filtered hot, to retrieve the first filtrate which is phosphoric acid. Then the solid element was washed with hot water double distilled and pure acetone. It is finally dried in an oven overnight at a temperature of 80 °C.

We proceeded by adding some elements such as CdCl$_2$, LaCl$_2$, and clay by varying their contents from 1 to 5 weight percent. Sample analyzes are made by X ray fluorescence spectrometry.

RESULTS AND DISCUSSIONS

The results of the analysis of uranium by X ray fluorescence in the presence of CdCl$_2$ are shown in Figure 1, which shows the spectrum of crude phosphate with addition of 1% and 5% in CdCl$_2$. Analysis of the results of this spectrum shows that the addition of CdCl$_2$ has no affect on the content of uranium in phosphoric acid.

![Fig. 1: X ray fluorescence spectrum of calcium sulfate in the case of adding CdCl$_2$.](image)

Raw phosphate.                                    Adding 1% of CdCl$_2$.
Adding 5% of CdCl$_2$.

The results of the analysis of uranium by X ray fluorescence in the presence of LaCl$_3$ are given in Figure 2, which shows the spectrum of the crude phosphate with addition of 1% and 5% LaCl$_3$. The analysis results of this spectrum show that the increasing of the content of LaCl$_3$ allows the access of the uranium in the phosphoric acid.

![Fig. 2: X ray fluorescence spectrum of calcium sulfate in the case of adding LaCl$_3$.](image)

Raw phosphate.                                    Adding 1% of LaCl$_3$.
Adding 5% of LaCl$_3$. 
The results of the analysis of uranium by the fluorescence X in the presence of clay are shown in Figure 3, which shows the spectrum of crude phosphate, with addition of 3, 5 and 8 grams of clay. The analysis of the results of this spectrum shows that the increase in clay content does not favor the passage of the uranium to the phosphoric acid.

**Table 1: Percentage of uranium in phosphogypsum and phosphoric acid.**

<table>
<thead>
<tr>
<th>element</th>
<th>% Massic</th>
<th>% Uranium in phosphogypsum</th>
<th>% Uranium in phosphoric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdCl₂</td>
<td>1%</td>
<td>40%</td>
<td>60%</td>
</tr>
<tr>
<td></td>
<td>5%</td>
<td>40%</td>
<td>60%</td>
</tr>
<tr>
<td>LaCl₃</td>
<td>1%</td>
<td>50%</td>
<td>50%</td>
</tr>
<tr>
<td></td>
<td>5%</td>
<td>14,28%</td>
<td>85,72%</td>
</tr>
<tr>
<td>clay</td>
<td>3g</td>
<td>20%</td>
<td>80%</td>
</tr>
<tr>
<td></td>
<td>5g</td>
<td>40%</td>
<td>60%</td>
</tr>
<tr>
<td></td>
<td>8g</td>
<td>60%</td>
<td>40%</td>
</tr>
</tbody>
</table>

**Conclusion:**

It has been proved that X ray fluorescence is a quantitative method that has allowed us to determine the percentage of the uranium in the gypsum in order to calculate the amount uranium leakage in the phosphoric acid product. The results show that:

- The addition of cadmium chloride does not affect the distribution of the uranium between the phosphoric acid and gypsum.
- Increasing the amount of lanthanum chloride allows the passage of uranium in the phosphoric acid.
- The increase in the amount of clay blocks the passage of the uranium to the phosphoric acid. Thus, we can conclude that the addition of clay reduces the passage of the radioactive elements especially the uranium in the phosphoric acid.

**REFERENCES**


