Original Article

Comparative study of K$_2$SO$_4$ production by wet conversion from phosphogypsum and synthetic gypsum

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ARTICLE INFO

Article history:
Received 5 July 2018
Accepted 27 February 2019
Available online 25 May 2019

Keywords:
- Wet conversion
- Phosphogypsum
- Potassium sulfate
- Calcite
- Synthetic gypsum
- Syngenite

ABSTRACT

This paper proposes a very attractive process for K$_2$SO$_4$ production via the wet conversion of phosphogypsum (PG) and K$_2$CO$_3$. A parallel study of the conversion of two synthetic types of gypsum by K$_2$SO$_4$ was performed in order to compare their reactivity with that of PG.

We remark that PG is more reactive and yields the desired results while commercial types of gypsum react slowly and generate unwanted secondary products. The factors affecting the PG conversion processes such as the initial concentration of reagents, the reaction time and the reaction temperature was studied to optimize the reaction conditions. X-ray diffraction (XRD) was used to characterize the PG conversion at different conditions while the other techniques (Fourier transform infrared spectroscopy (FTIR), X-ray fluorescence (XRF), scanning electron microscopy (SEM), flame photometer (FP), inductively coupled plasma mass spectrometry (ICP-MS) and thermogravimetric analysis (TGA)) were applied to prove the quality of the final products.

Based on the obtained results, the reaction is carried out with stoichiometric proportions between PG and K$_2$CO$_3$. The maximal conversion of PG is attained at 80 °C; this temperature corresponds to the higher solubility of K$_2$SO$_4$, which is 1.2 mol/l.

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1. Introduction

Potassium sulfate K$_2$SO$_4$ (arcanite) is a type of simple potash fertilizer used especially for high quality cultivation. It allowed bringing to plants two essential nutrients: potassium (up to 54% K$_2$O) and sulfur (18.4% S) [1]. The presence of high chloride content in standard fertilizers, especially potassium chloride, can increase the salinization of soils and accumulate the cadmium in plants [2,3]. For these reasons the use of K$_2$SO$_4$ as a fertilizer is preferred for several advantages such as a good solubility (120g/l at 25 °C), low-to-zero chloride content and low salt index. It also costs half of that of the potassium nitrate [1]. In addition, the agriculture experts often recommend supplemental sulfur to go with nitrogen, phosphorus and potassium (NPK). It is a substance that contributes to increase crop yield by supplying a direct nutritional value

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https://doi.org/10.1016/j.jmrt.2019.02.013
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and by improving the efficiency with which plants use other nutrients elements particularly the nitrogen and the phosphorus [4–6].

The world capacity production of K₂SO₄ is 11 million tons per year of which China produces about 56%. Among the natural sources of K₂SO₄ we quote: Kainite KCl·MgSO₄·3H₂O, Langbeinite K₂SO₄·2MgSO₄, Leonite K₂SO₄·4MgSO₄·4H₂O, Schonite K₂SO₄·MgSO₄·6H₂O, Polyhalite K₂SO₄·MgSO₄·2CaSO₄·2H₂O and Glaserite K₂Na(SO₄)₄. For not to exhaust the magnesium contained in this different ores, several industrial syntheses have been developed for the production of K₂SO₄. Approximately a large part of K₂SO₄ production is based on the Mannheim process according to the reaction of H₂SO₄ acid and KCl at high temperature (800 °C) [7]. In the other hand, the reaction of H₂SO₄ acid and KCl at low temperature allows forming KHSO₄. This latter was desalted with methanol to obtain K₂SO₄ [8,9].

Other processes have been described by numerous researchers to produce K₂SO₄ by thermal decomposition of K-feldspar KAlSi₃O₈ and gypsum [10–12]. Several factors affect on this decomposition such as: the reaction temperature (1000–1400 °C), the mass ratio of CaSO₄/KAlSi₃O₈ and the amount of the additive used (CaCO₃ or CO₂ gas). The final product is a water-soluble solid K₂Ca₂(SO₄)₃, which could dissolve in water to produce K₂SO₄.

It is also possible to produce K₂SO₄ from gypsum and KCl in an aqueous solution containing ammonia. The presence of ammonia induces the reaction between the gypsum and KCl, moves the reaction in the desired direction (selectivity) and prevents the formation of complex salts such as syngenite K₂Ca(SO₄)₂·H₂O or and the pentasulfate K₂SO₄·5CaSO₄·H₂O. The yield of this reaction depends essentially on the nature of gypsum used, KCl purity, ammonia concentration and molar ratios of these reagents [13,14].

Generally, several disadvantages intercept the production of K₂SO₄ by these previous processes such as: high energy consumption, high chloride content in K₂SO₄ salt and the difficulty of separating this salt from the other salts, which requires the addition of other solvents.

In Morocco, the phosphoric acid production is very important for the economic and social area of the country. In fact, this production is mainly realized by wet process attacking the phosphate rock by sulfuric acid according the following chemical reaction:

\[ \text{Ca}_3\text{F}[(\text{PO}_4)_2] + 5\text{H}_2\text{SO}_4 + 10\text{H}_2\text{O} \rightarrow 3\text{H}_3\text{PO}_4 + 5\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{HF} \]  

(1)

The nature and the characteristics of the obtained PG depend strongly on the phosphate ore composition and quality. Although PG is mainly constituted of the CaSO₄·2H₂O dihydrate form, it contains also various impurities such as fluorides, phosphates, clay minerals, organic matter, trace elements and radioelements. Hence, the presence of these impurities at higher than natural levels, would be considered as a source of environmental contamination [15].

The objective of this work is to present a simple process permitting to produce K₂SO₄ via the wet conversion of phosphogypsum (PG) waste generated during the manufacture of phosphoric acid, the Prolabo gypsum (PL) and Riedel the Haën gypsum (RH). The aim to use the two latter commercial types of gypsum is to compare their reactivity with that of PG and to study the factors that affect on this conversion. The basic reaction describing this process is:

\[ \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{K}_2\text{CO}_3 \rightarrow \text{K}_2\text{SO}_4 + \text{CaCO}_3 + 2\text{H}_2\text{O} \]  

(2)

The important factors that influence on the PG conversion studied are: the initial concentration of reagents, the reaction time and the reaction temperature. Thus, the strengths of this process are as follows: the conversion is carried out with easier conditions; the optimal temperature of reaction is 80 °C corresponding to maximum solubility of K₂SO₄; the medium is purely aqueous without additives; the availability of PG; the main product K₂SO₄ is easily recovered by simple filtration while the calcite is interesting in several domains of industry and environment.

2. Experimental

The PG sample was collected from the fertilizer plant Maroc Phosphate (dihydrate processes) settled at Jorf Lasfar near El Jadida city. The PG has undergone a simple wash to remove some of the soluble impurities and suspension materials as organic matter. The synthetic types of gypsum used are chemical reagents type prolabo and Riedel de Haën with purity 98 and 100% respectively. The potassium carbonate (99%, Riedel de Haën) was also utilized as reactant.

To compare the reactivity of PG and commercial types of gypsum, the reactional mixtures were prepared from the washed PG, gypsum PL and gypsum RH dissolved in K₂CO₃ solution at different temperature under constant stirring (500 tr/min). After a sufficient reaction time, the obtained precipitate was separated from the solution and dried in the oven at 100 °C. The transparent salt is recrystallized from the filtrate and introduced in the oven at 40 °C (Fig. 1 and Table 1).

The different analysis carried out on the PG and the compounds produced in this work are accomplished by the following techniques: X-ray powder diffraction (XRD diffractometer BRUKER D8), scanning electron microscopy X-ray analysis (SEM Environmental FEI Quanta 200).
Concentrations of chemical elements were determined by X-ray fluorescence (XRF spectrometer S4 PIONEER BRUKER aXS), flame photometer (FP JENWAY 500-731 Model PFP7) and inductively coupled plasma mass spectrometry (ICP-MS Model HP-4500). Besides that, the sulfate ions in different samples can be measured by the gravimetric method. Infrared spectra were performed by Fourier transform infrared spectroscopy (FTIR 8400s SHIMADZU spectrometer) using potassium bromide (KBr) pellets technique. The thermal behaviors of our samples were examined by thermogravimetric analysis (TGA) (DTG-60 type SHIMADZU).

3. Results and discussion

3.1. Characterization of phosphogypsum

The chemical and mineralogical compositions of the PG show that it is composed mainly of 98% of calcium sulfate dihydrate (JCPDS No. 33-0311). The major impurities are SiO₂, P₂O₅ besides Na₂O, K₂O, Al₂O₃, Fe₂O₃ and MgO with lower contents. PG also contains trace chemical elements such as Ba, Cd, Pb, etc. These latter are absorbed in the PG surface or incorporated in its structure [16].

3.2. Solubility of potassium sulfate in water

The potassium sulfate solubility in water as a function of temperature are representing in Fig. 2 [17]. It is noted that the solubility (S) of potassium sulfate in water increases gradually when the temperature increases. According to the solubility data of potassium sulfate, the predicted concentrations (C = S/Mₚₗₛₒₜ) of the starting reagents K₂CO₃ and PG to obtain the maximum solubility of K₂SO₄ and to avoid the formation of syngenite are 0.6, 0.8, 1 and 1.2 mol/l for room temperature 20, 40, 60 and 80 °C respectively. We have limited the maximum temperature of PG conversion at 80 °C to prevent the transformation of gypsum into plaster, which becomes less reactive.

3.3. Effect of initial concentration

The effect of initial concentration of K₂CO₃ on the conversion of PG to K₂SO₄ during 1.5 h at room temperature was performed by varying its concentration from 0.1 to 0.7 mol/l. The mixture of K₂CO₃ with PG is stoichiometric. The results obtained by DRX analysis reveal that for stoichiometric K₂CO₃ concentration of 0.1 and 0.6 mol/l, the precipitates P1 and P2 (Fig. 3a) and salt crystallized from the filtrates F1 and F2 (Fig. 3b) present a single phase corresponding to the calcite (JCPDS No. 05-0586) for the precipitates and the arcanite (JCPDS No. 44-1414) for the filtrates [18]. However the increase of the K₂CO₃ concentration above 0.6 mol/l allows appearing the syngenite K₂Ca(SO₄)₂·H₂O (JCPDS No. 74-2159) besides the obtained calcite P3 (Fig. 3a). Syngenite is a relatively rare double salt of potassium and calcium sulfate, which is deposited by evaporation in addition to normal inorganic salts such as gypsum, anhydrite and halite [19,20].

According to Abu-Eisah et al. [13], the formation of syngenite beside calcite in this case may be explained by two reactions:

\[
2\text{CaSO}_4 + 2\text{H}_2\text{O} + \text{K}_2\text{CO}_3(\text{aq}) \rightarrow \text{K}_2\text{Ca(SO}_4)_2 \cdot \text{H}_2\text{O} \\
\text{O(s) + CaCO}_3(\text{s}) + 3\text{H}_2\text{O} \tag{3}
\]

\[
\text{CaSO}_4 + 2\text{H}_2\text{O} + \text{K}_2\text{SO}_4(\text{aq}) \rightarrow \text{K}_2\text{Ca(SO}_4)_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O} \tag{4}
\]

From the precedent results, reaction (3) does not explain the absence of syngenite (Kₚₛ = 3.54 × 10⁻⁸ at 25 °C) in the precipitates relative to concentrations lower than 0.6 mol/l.
Fig. 2 – Solubility of potassium sulfate in water and its predicted concentrations as a function of temperature \[16\].

When the concentration of K$_2$SO$_4$ is very high (oversaturation), this salt reacts with PG to form syngenite. Indeed, the filtrate F3 of the K$_2$CO$_3$ concentration equal to 0.7 mol/l (Fig. 3b) reveals that the salt is composed of K$_2$SO$_4$ and K$_2$CO$_3$ (JCPDS No. 87-0730). In this case, there is a consumption of more PG than K$_2$CO$_3$ taking into account the stoichiometry of this reaction. From this result we conclude that reaction (4) is most probable.

The effect of K$_2$CO$_3$ excess on PG conversion to K$_2$SO$_4$ was also examined. Fig. 3a displays that the precipitate P4 obtained for the mixture 0.1 mol/l of PG and 0.2 mol/l of K$_2$CO$_3$ corresponds to the calcite while the relative filtrate F4 (Fig. 3b) contains a mixture of K$_2$SO$_4$ and K$_2$CO$_3$ salts due to the excess of K$_2$CO$_3$. However, when we inverse the concentrations of PG and K$_2$CO$_3$, the decrease of K$_2$CO$_3$ concentration below its stoichiometric value shows that the PG conversion is not yet achieved and we obtained a precipitate P5 containing gypsum and calcite. For the filtrate F5, its salt is composed only of K$_2$SO$_4$.

We conclude that the conversion of PG to K$_2$SO$_4$ with excess of K$_2$CO$_3$ or PG concentration is possible but not gainful.

3.4. Effect of reaction time

The effect of reaction time on the PG conversion to K$_2$SO$_4$ at room temperature was tested by prolonging it to 24 h for stoichiometric K$_2$CO$_3$ concentration equal to 0.6 mol/l.

The results showed well no significant differences in yield and purity of the final precipitates P2, P6 and P7 (Fig. 4a) and filtrates F2, F6 and F7 (Fig. 4b) when we have increased the reaction time up to 24 h, which are always calcite and arcanite respectively. Goerlich \[21\] predicted the formation of syngenite for a longer reaction time, which is not the case of our reaction. This difference can be interpreted by the quality of the
PG used. However, Fernández-Lozano and Wint [14] indicated that the effect of this variable was on the crystal size. According to these authors, crystals produced at shorter reaction time were small and difficult to filter.

3.5. **Effect of temperature**

To increase the limit concentration of K$_2$SO$_4$ in the solution at the end of the reaction, we performed tests at higher temperatures 40, 60 and 80 °C. The effect of temperature on the PG conversion was studied for stoichiometric concentrations equal to the concentrations limit foreseeable. The obtained results for the concentrations of mixtures equal to the concentrations limit 0.8, 1 and 1.2 mol/l at 40, 60 and 80 °C respectively, reveal that the increase of temperature permits obtaining a pure calcite from the precipitate P8, P9 and P10 (Fig. 5a) and concentrated salt in the filtrate F8, F9 and F10 (Fig. 5b). The absence of syngenite in the precipitate for these concentrations limit is explained by the increase of K$_2$SO$_4$ solubility as a function of temperature, which becomes maximal around 80 °C [22]. We conclude that increasing the temperature of PG conversion reaction gives concentrated solution of K$_2$SO$_4$, which allows its rapid recrystallization after cooling. The purity of these products obtained under the optimum conditions at 20, 40, 60 and 80 °C are represented in Table 3. The obtained results show that all precipitates contain calcite with purity of 95%. Also, the purity of the final salts recrystallized from filtrates is 97% of arcanite.

3.6. **Effect of the gypsum purity**

In this part, two types of gypsum PL and RH are used to make a comparison between their reactivity with that of PG generated during the manufacture of phosphoric acid. The conversion of the gypsum PL and the gypsum RH to K$_2$SO$_4$ is performed with stoichiometric mixture between these synthetics types of gypsum and K$_2$CO$_3$. The reaction is carried out for concentrations 0.1 and 0.6 mol/l at room temperature for various reaction times.

3.6.1. **Case of PL gypsum**

The DRX patterns of the precipitates obtained by PL conversion are presented in Fig. 6a. All precipitates P11, P12, P13 and P14 contain two phases: calcite and plaster (effectively the gypsum) (JCPDS No. 33-0310). The increase of the reaction time to 4 h indicates that the gypsum did not totally disappear.
Furthermore, the filtrates F11, F12, F13 and F14 (Fig. 6b) relatives to the same concentrations contain mixture of two phases K$_2$SO$_4$ and K$_2$CO$_3$.

3.6.2. Case of RH gypsum

Fig. 7a represents the XRD patterns of the precipitates obtained by RH conversion to K$_2$SO$_4$. For K$_2$CO$_3$ concentration equal to 0.1 mol/l during a reaction time of 1 h, the formed precipitate P15 is composed of small amount of gypsum beside two varieties of CaCO$_3$ calcite and vaterite (JCDPS No. 24-0030). The increase of the reaction time allows transforming the vaterite into calcite P16 and P17 with reappearance evidently of the gypsum. Generally, the vaterite crystallizes practically only under very particular conditions (neutral medium, pure water, pure reagents). At ambient temperature and in an aqueous medium, the vaterite is very unstable and normally recrystallizes in the form of calcite as a function of time [23].

For K$_2$CO$_3$ concentration equal to 0.6 mol/l during the reaction time of 1.5 h, the obtained precipitates P18 (Fig. 7a) indicate that the major phase corresponds to vaterite with a very minor phase corresponding to syngenite. When we increase the reaction time to 4 h, we observe the presence of vaterite and syngenite with a small amount of calcite P19 (Fig. 7b). In fact, for very pure gypsum and for this concentration, the solution will be saturated with K$_2$SO$_4$. This latter reacts with gypsum to form the syngenite. The same result is attained with PG for the concentrations up to 0.6 mol/l for the reason that PG contains less CaSO$_4$·2H$_2$O than RH gypsum.

The presence of gypsum or syngenite in the precipitates recuperated during RH conversion engenders the existence of K$_2$CO$_3$ and K$_2$SO$_4$ in the filtrates F15, F16, F17, F18 and F19 as shown in Fig. 7b.

From these results, we conclude that the conversion Pl, gypsum and RH gypsum to K$_2$SO$_4$ is not total, which confirms that these types of gypsum are less reactive than PG. This result can be explained by the difference of the purity, the nature of the impurities and the granulometry, which favor the dissolution of PG.
3.7. Physicals and chemical characteristics of final products

In this part, the precipitate P10 and the filtrate F10 recovered after total PG conversion to K₂SO₄ at 80 °C was chosen for all further tests in order to determine the physicals and the chemicals characteristics and the quality of these final products.

The infrared spectrum of the precipitate (Fig. 8b) shows all characteristic bands corresponding to calcite, except for a band observed at 1083 cm⁻¹, which is assigned to Si–O stretching mode [16,24,25]. For the filtrate salt, the infrared spectrum is displayed in Fig. 8c. It illustrates the characteristic bands of pure arcanite [26]. The IR spectra are in good agreement with DRX analysis accomplished on these products.

Table 2 lists the vibration band frequencies and assignments of the PG as well as the obtained calcite and arcanite.

The results of chemical analysis by XRF realized on the obtained calcite and arcanite are represented in Table 3.

Calcium carbonate represents around 95.5% of the precipitate composition. In fact the insoluble impurities incorporated in PG pass totally into calcite. Content of potassium in the precipitate is very high compared to that in PG. This is explained by the presence of K₂SO₄, which is adsorbed in surface of calcite crystals during the filtration. The silica, which is inert during the PG conversion, is detected in the precipitate. It is important to note that the detection of Al, Mg and Fe in the precipitate suggests the presence of clays. These elements can be combined with phosphorus to form insoluble compounds such as AlPO₄, Mg₃(PO₄)₂ and FePO₄·2H₂O. Some elements like as Mg, Sr and Y can react with the carbonate anions during the PG conversion and form insoluble carbonates (MgCO₃, SrCO₃, Y₂(CO₃)₃, etc.). Fluorine exists in PG in soluble and insoluble form. The insoluble complexes (Na₂SiF₆, Na₃AlF₆, K₂AlF₆, MgSiF₆·6H₂O, etc.) remain in the powder. Then, the fluorine in soluble form (HF, H₂SiF₆) passes into the filtrate.

The analysis of the recrystallized salt proves that it is constituted by 97% of K₂SO₄. The presence of impurities such as

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**Table 2 – Infrared frequencies of the PG, calcite P10 and arcanite F10.**

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Wave number ν (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phosphogypsum</td>
</tr>
<tr>
<td>H₂O</td>
<td>ν</td>
</tr>
<tr>
<td></td>
<td>δ</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>ν₁</td>
</tr>
<tr>
<td></td>
<td>ν₂</td>
</tr>
<tr>
<td></td>
<td>ν₃</td>
</tr>
<tr>
<td></td>
<td>ν₄</td>
</tr>
<tr>
<td>HSO₄²⁻</td>
<td>δ₂</td>
</tr>
<tr>
<td>CO₃⁻</td>
<td>ν₁</td>
</tr>
<tr>
<td></td>
<td>ν₂</td>
</tr>
<tr>
<td></td>
<td>ν₃</td>
</tr>
<tr>
<td>HPO₄²⁻</td>
<td>ν</td>
</tr>
<tr>
<td>Si–O</td>
<td>ν</td>
</tr>
</tbody>
</table>
Table 3 – Distribution of chemical elements between PG and reaction products determined by X-ray fluorescence.

<table>
<thead>
<tr>
<th>Major elements (%)</th>
<th>Phosphogypsum</th>
<th>Calcite</th>
<th>Arcanite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P10</td>
<td>P9</td>
<td>P8</td>
</tr>
<tr>
<td>CaO</td>
<td>33.83</td>
<td>53.59</td>
<td>53.86</td>
</tr>
<tr>
<td>SO₃</td>
<td>42.52</td>
<td>0.55</td>
<td>–</td>
</tr>
<tr>
<td>H₂O</td>
<td>21.80</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CO₂</td>
<td>–</td>
<td>41.70</td>
<td>41.68</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.02</td>
<td>1.35</td>
<td>–</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.12</td>
<td>0.01</td>
<td>–</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.67</td>
<td>0.96</td>
<td>–</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.49</td>
<td>0.71</td>
<td>–</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.21</td>
<td>0.19</td>
<td>–</td>
</tr>
<tr>
<td>MgO</td>
<td>0.05</td>
<td>0.18</td>
<td>–</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.02</td>
<td>0.03</td>
<td>–</td>
</tr>
<tr>
<td>SrO</td>
<td>0.08</td>
<td>0.11</td>
<td>–</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>0.02</td>
<td>0.03</td>
<td>–</td>
</tr>
<tr>
<td>Cl</td>
<td>0.02</td>
<td>0.02</td>
<td>–</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.01</td>
<td>0.02</td>
<td>–</td>
</tr>
<tr>
<td>F</td>
<td>0.20</td>
<td>0.32</td>
<td>–</td>
</tr>
<tr>
<td>Purity (%)</td>
<td>98.15</td>
<td>95.29</td>
<td>95.54</td>
</tr>
</tbody>
</table>

a Flame photometer.
b Gravimetric methods.
c Thermal analysis.
d Ionometric method.

Table 4 – Distribution of some trace elements in PG, calcite P10 and arcanite F10.

<table>
<thead>
<tr>
<th>Trace elements (ppm)</th>
<th>Phosphogypsum</th>
<th>Calcite P10</th>
<th>Arcanite F10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba⁶</td>
<td>30.08</td>
<td>49.52</td>
<td>0.00</td>
</tr>
<tr>
<td>Cd</td>
<td>1.34</td>
<td>2.23</td>
<td>0.02</td>
</tr>
<tr>
<td>Hg</td>
<td>0.65</td>
<td>0.57</td>
<td>0.00</td>
</tr>
<tr>
<td>Pb</td>
<td>0.73</td>
<td>3.09</td>
<td>0.00</td>
</tr>
<tr>
<td>Cu⁶</td>
<td>55</td>
<td>68</td>
<td>N.d.</td>
</tr>
<tr>
<td>Zn⁵</td>
<td>45</td>
<td>71</td>
<td>N.d.</td>
</tr>
<tr>
<td>Zr⁶</td>
<td>19</td>
<td>29</td>
<td>N.d.</td>
</tr>
</tbody>
</table>

a Flame photometer.
b X-ray fluorescence.
N.d., not detected.

Fig. 9 – TGA curves of PG (a), calcite P10 (b) and arcanite F10 (c).
Na and Ca is originally reported to the K$_2$CO$_3$ reagent (0.5% of Na$_2$O in K$_2$CO$_3$ reagent) and to the very fine particles of CaCO$_3$ that pass in the filtrate, respectively. The presence of chloride in the salt may be due to chloride existing in initial reagent K$_2$CO$_3$.

According to the results exposed in Table 4, we can conclude that the totality of trace elements is transferred from PG to the resulting calcite. Generally, these elements are adsorbed in the surface of calcite crystals or incorporated into its structure. Several factors favor their presence in the calcite such as: (i) the similar chemical behavior of calcium and these elements; (ii) the presence of these elements in PG under insoluble forms such as (Ba, Ra)SO$_4$, CdSO$_4$, 2H$_2$O; CdHPO$_4$, PbSO$_4$, 2H$_2$O; ZnSO$_4$, 2H$_2$O and CuSO$_4$·2H$_2$O $^{[27,28]}$ that rest insoluble during the conversion of PG; iii) the similarity of the particle size fraction (less than 20 µm) of PG and calcite, which facilitates the presence of these elements in the precipitate.

For radioactivity, the element that can cause toxicity problems by decomposing into radon and lead is radium. The various studies carried out on the radioactivity of PG confirm that radium always precipitates with calcium in the solid phase (PG, calcite and portlandite) $^{[29–31]}$. To avoid this problem, this phase can be simply stored in an open and ventilated environment to dissipate radon into the atmosphere $^{[32]}$. According to these results, we can suppose that the majority of the radionuclides initially present in PG sample pass to calcite. However, potassium sulfates rest uncontaminated from these radionuclides.

K$_2$SO$_4$ recovered from the filtrate is non-toxic and can be utilized directly in the agriculture as fertilizer $^{[33]}$.

The TGA curves of PG, calcite and arcanite are represented in Fig. 9. The TGA curve of PG (Fig. 9a) exhibits a weight loss (21.8%) at 200 °C, which correspond to gypsum dehydration.

The second TGA curve of calcite (Fig. 9b) presents two weight losses: the first at 450 °C is small (~3%) and it is attributed to the elimination of adsorbed or crystalized water of some chemicals impurities (CaHPO$_4$, 2H$_2$O; CaFPO$_4$, 2H$_2$O; MgSiF$_6$, 6H$_2$O, etc.). The second above 800 °C, which is large (41.7%). This is due to the decarbonation of calcite (CaCO$_3$ → CaO + CO$_2$). The minimization of decomposition temperature of the calcite is the goal of the industrial process to use it in cycle CaCO$_3$/CaO. According to our results, the obtained calcite (CaCO$_3$) can be converted to lime (CaO) at temperature below 800 °C while the temperature decomposition of pure calcite is above 900 °C. For this reason, we can conclude that the use of the obtained calcite consumes less energy. Thus this reaction is energetically efficient. In summary, the liberated CO$_2$ may be recuperated for the production of carbonate and used in the Merseberg process for the production of the ammonium carbonate.

For the salt, TGA curve (Fig. 9c) indicates a slight weight loss (0.8%) observed between the temperature 100 and 800 °C, which means that the salt obtained is anhydrous. Anoos et al. $^{[34]}$ have detected a weight loss between 0.5 and 0.8% for K$_2$SO$_4$ prepared by the evaporation method.

The morphology of PG, calcite and arcanite are examined by SEM (Fig. 10). We remark that the crystals form of PG is tabular with a size grading from 5 to 30 µm (Fig. 10a), whereas the calcite morphology (Fig. 10b) displays an agglomerate of super imposed fine scales with a low surface area. The average diameter of scales is 2 µm and thickness is lower than 1 µm $^{[16]}$. Generally, the energy efficiency of synthetic calcite and its low surface area are two favorable parameters for its use in the environment (CaCO$_3$/CaO cycle) as adsorbent of carbon dioxide $^{[35,36]}$. 

![Fig. 10 – SEM images of PG (a), calcite P10 (b) and arcanite F10 (c).](image-url)
For the salt, the photograph (Fig. 10c) indicates the presence of macro-crystals in the form of rods of length between 3 and 5 mm. This permits to recuperate K₃SO₄ easily after recrystallization.

4. Conclusion

During this work, we established a simple and economical process for the production of K₃SO₄ from the conversion of PG with K₂CO₃ in an aqueous medium. Compared to the conversion of synthetic types of gypsum or the use of other processes, this proposed process can be applied industrially on a large scale.

The PG is totally transformed to K₃SO₄ and calcite while the reaction between PL and RH types of gypsum and K₂CO₃ is not total even if we increase the time reaction and engender secondary products as syngenite and vaterite.

The reaction process of PG conversion to K₃SO₄ is optimum at 80 °C with exact stoichiometric proportion of PG and K₂CO₃ for concentration limit of 1.2 mol/l under a time reaction of 1.5 h. Concentrated solution obtained at 80 °C allows rapid recrystallization of K₃SO₄ after cooling.

Under the optimal conditions of PG conversion to K₃SO₄, the different chemical and physical analyses accomplished on the final products show that the totally of solid impurities in PG are transferred into calcite with the recovery of pure K₃SO₄.

The environmental interest of this process is reducing the quantity of PG rejected and obtains a calcite as resource. Also, significant amounts of this obtained calcite could be used by the phosphate industry to remedy of acid mine drainage [30,31]. For a numerical and economical approach, about 1 ton of PG can be treated by 0.803 ton of K₂CO₃ (595 $ per ton [37]) to obtain 0.581 ton of calcite (140 $ per ton [38]) and 1.021 ton of K₃SO₄ (700 $ per ton [38]). In addition, this process does not require any difficult operation for recuperating these valuable products. This economical approach permits to benefit of 312 $ per ton of PG converted, which covers very largely the cost of the transport, the energy and the water used during this process.

The purity of K₃SO₄ tolerates it to be utilized directly in agriculture. While the thermal and morphological characteristic of the obtained calcite allows using it in the environment such as adsorbent for carbon dioxide.

Conflicts of interest

The authors declare no conflicts of interest.

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