Original Article

Potassium alum thermal decomposition study under non-reductive and reductive conditions

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ABSTRACT

Potassium sulfate (K₂SO₄) is a very important compound, mostly used as nutrient for plant growth. Potassium sulfate production can be accomplished through the Mannheim process. For potassium bearing silicate minerals, such as glaukonite, one alternative is acid leaching followed by selective precipitation and thermal decomposition of potassium alum (KAl(SO₄)₂). This chemical process is responsible for the formation of soluble K₂SO₄ and insoluble Al₂O₃, which can be later separated after solubilization in water and filtration. In this pyrometallurgical reaction, the temperature control is very important. Through the addition of a reducing agent, the decomposition temperature could be significantly reduced. In the present work, the thermal behavior of synthetic samples of hydrated potassium alum (KAl(SO₄)₂·12H₂O) is appreciated through thermogravimetric analysis (TGA), both in the absence as well as in the presence of a reducing agent (charcoal) under inert atmosphere (nitrogen) and dynamic analysis. The addition of a stoichiometric amount of the reducing agent stimulated considerably the decomposition, which started at a lower temperature in comparison with the pure alum sample. Based on the XRD characterization of selected samples, it is suggested that the decomposition process should happen in at least two stages, with Al₂(SO₄)₃ as one of the intermediate reagents. After full decomposition, only Al₂O₃ and K₂SO₄ have been identified, as expected based on thermodynamic simulations. Finally, it was demonstrated that the K₂SO₄ formed could be totally transferred to aqueous solution after a solubilization carried out at 363 K for two hours; the remaining solid was characterized as pure aluminum oxide (Al₂O₃).

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1. Introduction

Potassium is an important constituent of essential fertilizers applied in agriculture. Typically, this nutrient is offered on a large scale as a chloride (KCl) or sulfate (K₂SO₄), and the former accounts for the majority share of total market consumption. The latter, however, is mainly applied in specific situations where the crops are sensitive to the presence of chlorides or have the necessity of sulfur ions. Potassium sulfate can be obtained through several processes, like Mannheim process, through catalytic method, neutralization and by solvent extraction [1].

The demand for more efficient fertilizers at the most competitive prices motivates the development of alternative chemical routes to obtain these compounds. Under this perspective, some mining companies have investigated the use of other raw materials for this application such as glauconite bearing ores. A chemical route to obtain K₂SO₄ and Al₂O₃ has been proposed previously through sulfuric acid leaching, water solubilization of the formed sulfates, controlled precipitation of potassium alum (KAl(SO₄)₂) and thermal decomposition under nitrogen atmosphere [2].

The thermal decomposition is one of the most used processes in materials synthesis. Pyska and Glinka [3] have studied the basic aluminum potassium sulfate (K[Al₂(OH)₆][SO₄]₃) thermal decomposition. The results led to the conclusion that the decomposition happens in three stages. The first one considers the partial dehydration at a temperature which varies between 470 and 670 K. After that, between 670 and 870 K it can be observed the completion of dehydration and also, the formation of sulfates which decompose between 870 and 1200 K. One of these sulfates is potassium alum. The study showed that the alum molecule is transformed in potassium and aluminum sulfates. The latter subsequently decomposes in its respective oxide in a parallel reaction. Kucuk and Yildiz [4] have studied the thermal decomposition of alunite ore mechanically activated and non-activated by thermogravimetry using air. The final structure was analyzed by X-ray diffraction after being mechanically worked. Alunite decomposition occurs in two steps: the first through dehydration and the second by desulfurization. From these two steps, the energies of activation were calculated from thermogravimetric. Pacewska et al. [5] have studied the dependence on the degree of conversion over time during the process of potassium and aluminum basic sulfate thermal decomposition in the presence of carbon. The experiment was performed in a tube reactor. The results of this experiment showed that at 903 K after 3.5 h there was only aluminum oxide (Al₂O₃) and potassium sulfate (K₂SO₄). Prost et al. [6] have studied the thermal decomposition of three different alunite compounds, the following: potassium, sodium and ammonium alunite. The work also, indicates that alunites decompose after a series of steps, based in the following processes: dehydration, dehydroxylation and desulfurization. The temperatures applied in the experiment are dependent to the cation in the experiment, in the case of K-alunite it occurs at 957 K.

Within the context of potassium alum thermal decomposition, the present study has its purpose associated with the investigation of potassium alum decomposition under non-reductive and reductive atmospheres. The manuscript covers the thermodynamics of thermal and reductive decomposition reaction systems, their thermogravimetric analysis (TGA) as well as the materials characterization through X-ray diffraction (XRD) of intermediate and final products.

2. Methodology

2.1. Thermodynamics assessment

The thermodynamics calculations were performed using the HSC Chemistry software [7]. For each reaction system (Reactions (1) and (2)), the equilibrium compositions, as a function of temperature, were calculated considering the stoichiometric input of its reagents.

\[ 2\text{KAl(SO}_4\text{)}_2 \rightarrow \text{K}_2\text{SO}_4 + \text{Al}_2\text{O}_3 + 3\text{SO}_2 + 3/2\text{O}_2 \]  

(1)

\[ 2\text{KAl(SO}_4\text{)}_2 + 3\text{C} \rightarrow \text{K}_2\text{SO}_4 + \text{Al}_2\text{O}_3 + 3\text{SO}_2 + 3\text{CO} \]  

(2)

Therefore, for Reaction (1), associated with the non-reductive decomposition, the diagram was obtained for 1 kmol of KAl(SO₄)₂. On the other hand, for Reaction (2), related with the reductive decomposition, the speciation was carried out for 1 kmol of KAl(SO₄)₂ in association with 1 kmol of carbon.

2.2. Experimental procedure

Samples of synthetic hydrate potassium alum (KAl(SO₄)₂·12H₂O) were submitted to thermogravimetric analysis in two conditions: pure (Reaction (3)) and mixed with charcoal (Reaction (4)).

\[ 2\text{KAl(SO}_4\text{)}_2·12\text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 + \text{Al}_2\text{O}_3 + 3\text{SO}_2 + 3/2\text{O}_2 + 24\text{H}_2\text{O} \]  

(3)

\[ 2\text{KAl(SO}_4\text{)}_2·12\text{H}_2\text{O} + 3\text{C} \rightarrow \text{K}_2\text{SO}_4 + \text{Al}_2\text{O}_3 + 3\text{SO}_2 + 3\text{CO} + 24\text{H}_2\text{O} \]  

(4)

For the latter, the fixed carbon content was considered in the mixture preparation in order to attend the stoichiometry of the respective chemical reaction.

Both thermogravimetric analyses were conducted in a pure nitrogen atmosphere applying a heating rate of 20 K min⁻¹ starting at room temperature until 1473 K. In the 12 present study, a Netsch equipment, model STA 449 F3 Jupiter®, has been employed. The remaining materials were then characterized by means of X-ray diffraction through a Bruker equipment, model D8 Discover, and quantitative Rietveld analysis for the identification of the main crystalline phases present, using TOPAS software [8].
2.3. Potassium solubilization

The sample produced after TGA of the pure alum sample (without reducing agent) has been dissolved in distilled water at 363 K for two hours and continuous stirring. After filtration, the remaining solid has been characterized through XRD and Rietveld analysis so as to evaluate the amount of the potassium content, which had been transferred to the solution probably as soluble K$_2$SO$_4$.

3. Thermodynamic assessment

Fig. 1 provides a quantitative picture of the nature of the equilibrium composition associated with 1 kmol of KAl(SO$_4$)$_2$ as function of the temperature.

It can be observed that potassium alum is stable until 773 K. Above that temperature and below 973 K, it is clear that the system tends toward a slight decomposition of this compound in Al$_2$(SO$_4$)$_3$ and K$_2$SO$_4$. For temperatures, higher than that, the equilibrium composition of potassium sulfate increases remarkably and aluminum oxide starts its formation. After 1023 K, there is no more aluminum sulfate in the system and K$_2$SO$_4$ and Al$_2$O$_3$, in the same proportion, have their quantities in equilibrium increased until 1173 K. This temperature, in turn, is associated with the full conversion of potassium alum in the desired reaction products.

It is known, however, that carbon can be used as a reducing agent in order to diminish oxidizing potential of some reaction systems. This specific characteristic could also be responsible for lowering the decomposition temperatures of salts containing oxygen in a polyatomic anion. In order to assess this information, Fig. 2 presents equilibrium composition as function of temperature resulted of the input of 1 kmol of KAl(SO$_4$)$_2$ and 1 kmol of carbon.

It is patent that, under this condition, that potassium alum is not stable in any temperature between 573 and 1273 K. Therefore, it can be said that K$_2$SO$_4$ and Al$_2$O$_3$ are the sole products containing potassium and aluminum which is, of course, associated with lowering the thermal decomposition of KAl(SO$_4$)$_2$ temperature under reductive conditions.

These results, in turn, motivate the development of an experimental study of 28 the thermal behavior of potassium alum as presented next by means of thermogravimetric analysis.

4. Results and discussion

4.1. Thermogravimetric analysis

In the present topic, both TGA results obtained for pure alum and alum plus 2 reducing agent (charcoal) are presented and discussed, together with XRD characterization data, which corroborates some of the facts included in the results discussion.

4.1.1. Potassium alum thermal decomposition under non-reductive conditions

Fig. 3 presents the TGA signal for pure hydrated potassium alum heating in nitrogen atmosphere. The data obtained for the pure alum sample indicated the presence of two main transformations. The first one (373–523 K) can be explained by the water removal from the crystalline structure of the initial compound, and the second one, which happens at much higher temperatures (1023–1303 K), should be associated with the anhydrous salt decomposition.

It is worthwhile to mention that the temperature values associated with these intervals, where each reaction takes place, should be influenced by the applied heating rate. For
instance, for the same mass, the observed starting temperatures of each interval should be displaced to values 30 K lower through a reduction in heating rate to 10 K min\(^{-1}\). Therefore, the precise determination of the initial and final temperatures demand complementary thermal analysis methods, such as DTA or DSC, to be performed in a future study.

The calculated mass losses (absolute and relative) associated with each one of these phenomena based on the compound and global reaction stoichiometry (Reaction (3)) and an initial mass of 280.90 mg are very close to the experimental values (Table 1), and are also consistent with the data obtained through Rietveld analysis applied to the XRD pattern from each one of the produced materials (Figs. 4 and 5). In both cases, the quality of the assessment can be attested by the very low difference between experimental and calculated signals (line in the bottom part of the figure).

Where, \(\Delta m_i\) (%) and \(\Delta m_{exp}\) (%) represent, respectively, the relative theoretical and experimental mass losses for each transformation evidenced, considering as reference the total hydrated alum mass (280.9 mg).

It can be observed that the first material (Fig. 4) is identified as pure anhydrous alum, as expected, because the first TGA steps are associated exclusively to the escape from H\(_2\)O molecules entrapped in the alum crystal structure. In the second case (Fig. 5), the material is composed exclusively of 19 Al\(_2\)O\(_3\) and K\(_2\)SO\(_4\), the only two solid products expected from the thermal decomposition of the dehydrated alum (Reaction (3)). As consequence, for each mole of KAl(SO\(_4\))\(_2\) that decomposes, equal amounts of Al\(_2\)O\(_3\) and K\(_2\)SO\(_4\) are generated.

Therefore, based on the literature values for each molar weight, the final mixture should consist of pure Al\(_2\)O\(_3\) and K\(_2\)SO\(_4\), with mass fractions respectively equal to 36.96% and 63.04%, values which lies closely to the ones obtained through Rietveld refinement of the diffraction pattern of Fig. 5.

A careful observation of each one of the observed TGA steps reveals that both phenomena (water removal and salt decomposition), should happen not in one single step, but it should be comprised of multiple stages. In the case of water removal, at least four steps can be identified in the range between 373 and 523 K, and for the salt decomposition, two well defined steps can be observed. The first observation makes sense, as the water molecules do not occupy the same positions in the crystal lattice [8], and as consequence, the energy required for their removal can vary, and so the temperature necessary to accomplish this. In the case of the salt decomposition, the XRD pattern for the material removed from TGA during the 12 beginning of this step enabled, through Rietveld analysis, the identification of plausible intermediate species, such as Al\(_2\)(SO\(_4\))\(_3\) and K\(_2\)H(SO\(_4\))\(_2\) (Fig. 6), and also a small amount of remaining anhydrous alum. Such evidence suggests that the formation of Al\(_2\)O\(_3\) and K\(_2\)SO\(_4\), the expected decomposition products after full conversion of potassium alum, should also be associated with a non-single

**Table 1 – Theoretical (\(\Delta m_i\)) and experimental (\(\Delta m_{exp}\)) mass losses for thermal decomposition under non-reductive conditions.**

<table>
<thead>
<tr>
<th>Transformation</th>
<th>(\Delta m_i) (mg)</th>
<th>(\Delta m_{exp}) (mg)</th>
<th>(\Delta m_i) (%)</th>
<th>(\Delta m_{exp}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O removal</td>
<td>−128.01</td>
<td>−124.99</td>
<td>−45.57</td>
<td>−44.50</td>
</tr>
<tr>
<td>Salt decomposition</td>
<td>−71.11</td>
<td>−69.78</td>
<td>−25.32</td>
<td>−24.84</td>
</tr>
</tbody>
</table>

*Fig. 4 – XRD pattern of synthesized anhydrous alum.*

*Fig. 5 – XRD pattern for final thermal decomposition product.*
step mechanism. Therefore, Fig. 7 presents a schematic depiction of the thermal decomposition of hydrate potassium alum as well as the theoretical mass balance, detailing the contribution of each step-in weight variation through the chemical processing of this material.

4.1.2. Potassium alum thermal decomposition under reductive conditions
The incorporation of charcoal in the system, as expected from the thermodynamic simulations (Fig. 2), should enhance the driving force for the anhydrous alum thermal decomposition, and as a result, the reaction can be conducted at smaller temperatures. Indeed, the thermogravimetric analysis of the sample under the presence of the mentioned reducing agent (Fig. 8) shows that the decomposition reaction starts at a much lower temperature (853 K), in comparison with the sample of pure alum, whose thermal decomposition should start at 1023 K.

It is interesting to observe that on what touches water removal, no difference among samples (pure alum or alum plus reducing agent) can be detected. This is again expected, as the mass loss associated with the elimination of water molecules occurs without the participation of oxygen. On the other hand, in the case of the thermal decomposition (Reaction (4)), the oxygen produced in the course of salt decomposition combines with carbon, thereby forming CO/CO₂, stimulating, in the end, the process thermodynamic driving force. As observed for the experiment with the pure alum sample, the experimental mass losses (absolute and relative) due to dehydration and decomposition are close to the theoretical values calculated for an initial hydrated alum mass of 188.60 mg, considering 3.65% (w/w) of charcoal (Table 2), and global stoichiometry defined by Reaction (4).

Where, Δm° (%) and Δm°exp (%) represent, respectively, the relative theoretical and experimental mass losses for each transformation evidenced, considering as reference the sample mass of 188.60 mg, containing hydrated alum and charcoal.

4.2. Potassium mass transfer to solution assessment
The sample produced after a complete decomposition of pure potassium alum under non-reductive conditions (topic 4.1.1)
was exposed to a distilled water bath in order to stimulate the solubilization of the K₂SO₄ formed. As Al₂O₃ should be very stable and insoluble at the conditions imposed, it is expected that given sufficient time and sufficient initial hot water, all potassium present would be transported to the final solution. Indeed, after filtering and calcining at 1273 K for four hours, the XRD pattern of the solid indicates the presence of only Al₂O₃ crystals (Fig. 9), in accordance to the expectations. This result corroborates the XRD data obtained for the initial sample (before solubilization), as only Al₂O₃ and K₂SO₄ crystals have been detected (Fig. 5).

Therefore, it can be concluded that the imposed conditions enabled the total transfer of potassium to the aqueous solution. However, it should be pointed out, that the solubilization conditions can still be improved, so as to enhance the solubilization kinetics. To accomplish this task, accurate mass balance data are needed which is a topic that should be covered in a future publication.

5. Final remarks

Thermal behavior of hydrated potassium alum (KAl(SO₄)₂·12H₂O) can be 10 associated with two main stages, which have been identified through TGA experiments. First, water molecules are removed from the alum crystal structure, a phenomenon, which should happen in at least four stages between 373 and 523 K.

Next, through continuous heating, the anhydrous alum decomposes between 1023 and 1303 K, a process, which should also happen in at least two stages, whereas Al₂(SO₄)₃ and K₂H(SO₄)₂ participate as intermediate compounds, as identified through XRD data. Through incorporation of 3.65% (w/w) of charcoal to the initial hydrate potassium alum, the beginning of salt decomposition shifts to a considerable lower temperature range (853–1023 K), in accordance to the expectations built from thermodynamic calculations. Carbon combines with the resulting oxygen molecules (Reactions (3) and (4)), and as a result, enhances the thermodynamic driving force for the decomposition reaction. In addition, the presence of the reducing agent does not affect the alum dehydration.

Finally, solubilization (363 K for two hours) in distilled water of the decomposition product after TGA of potassium alum under non-reductive conditions, resulted in the total transfer of the produced K₂SO₄ to the aqueous media, illustrating the significant driving force for separating aluminium and potassium, when full conversion of the initial anhydrous alum can be performed, thereby resulting in insoluble Al₂O₃ and soluble K₂SO₄.

Conflicts of interest

The authors declare no conflicts of interest.

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