ABSTRACT

In present study the crystallization process of ferric sulfate hydrate - Fe$_2$(SO$_4$)$_3$.xH$_2$O from rich in Fe(III) sulfate waste solutions was investigated. These solutions were obtained after autoclave oxidation of pyrite concentrate. They are characterized with high concentrations (> 60 g l$^{-1}$) of ferric ions and sulfuric acid.

Based on the ternary diagram of the Fe$_2$(SO$_4$)$_3$.H$_2$SO$_4$.H$_2$O system and the laboratory tests the necessary compositions and conditions for preparation of saturated solutions for ferric sulfate crystallization process were determined.

It was found that the crystallization process takes place with obtaining of bulky sludge containing following phases: FeH(SO$_4$)$_2$.4H$_2$O (rhomboclase), Fe$_2$(SO$_4$)$_3$.8H$_2$O (ferric sulfate with eight molecules water) and Fe$_{4.67}$(SO$_4$)$_6$(OH)$_2$.20H$_2$O (ferric sulfate hydroxide hydrate). After detention of the sludge for seven days at temperature 373 K two modifications of ferric sulfate hydrate were observed: ferric sulfate hydroxide hydrate (Fe$_{4.67}$(SO$_4$)$_6$(OH)$_2$.8H$_2$O) and paracoquimbite (Fe$_2$(SO$_4$)$_3$.9H$_2$O).

Keywords: waste solutions, crystallization process, ferric sulfate hydrate.

INTRODUCTION

Ferric sulfate is primary used in fresh/drinking water and wastewater treatment. It is also used in pigments, pickling baths for aluminum and steel. Ferric sulfate is effective primary coagulant based on trivalent iron (Fe$^{3+}$), and is excellent for drinking water production, wastewater treatment, phosphorus removal applications, struvite control as well as sludge conditioning [1]. It is also efficient in preventing odor and corrosion by controlling the formation of hydrogen sulfide.

Ferric sulfate can be produced in liquid or in solid form. In patent US7387770 B2 [2] ferric sulfate solution was obtained from finely-divided ferric oxide, sulfuric acid and water in closed reaction vessel at temperatures ranging from about 392 K to about 422 K and pressures from about 172.4 kPa to about 482.6 kPa. It is usually obtained from ferrous sulfate by direct oxidation using strong oxidant such as H$_2$O$_2$ [3], KClO$_3$ [4], NaClO [5], HNO$_3$ [6] or by catalytic oxidation of ferrous sulfate using NaNO$_2$ or NaI as a catalyst in acid media. In Patent US 5766566 A [6] crystals of ferric sulfate are produced by solidification of ferric sulfate slurry by cooling the solution. Also known are processes according to which the ferric sulfate solution is solidified by granulation or by other solidification methods, which always involve evaporation of the water.

In this work we studied the crystallization process of ferric sulfate hydrate from rich of Fe(III) hydrometallurgical waste solutions. Such solutions are obtained from autoclave oxidation of pyrite concentrate. A special feature of these solutions is the high concentration of Fe(III) ions (> 60 g l$^{-1}$) and sulfuric acid (> 61 g l$^{-1}$). From a practical point of view, there is an area for utilization of ferric (III) ions contained in those solutions - for example for crystallization of ferric sulfate hydrate.
The most commonly applied methods for removal of Fe(III) from waste process solutions are iron hydroxide precipitation [7 - 9] and precipitation of jarosite - MeFe₃(SO₄)₂(OH)₆, where Me = Na, K, OH [10 - 14]. In both cases, the generated sludge is a waste product and it is deposited in a special stores. In addition to these methods “Geothite” [10, 15 - 17] and “Hematite” [10, 17 - 19] processes are also applied for removal of ferric ions from waste solutions. Both processes allows purification of the solutions from iron (Fe < 1 g l⁻¹).

There is scarce number of studies in the literature concerning the field of utilization of waste solutions for obtaining ferric sulfate hydrate. A larger part of studies have aimed the production of polyferric sulphate (PFS) [Fe₂(OH)₉(SO₄)₃-n/2]m (n < 2, m > 10) which is used as pre-polymerized inorganic coagulant with high cationic charge [20].

Jiang J.-Q. et al. [21] have studied two methods for preparation of PFS: sodium nitrite catalytic oxidation of waste ferrous sulfate solutions and industrial wastes - TiO₂ by-products (20 % H₂SO₄, 16 % Fe²⁺ and 23 % total iron). The authors found that PFS obtained from industrial wastes could not be applied in the treatment of drinking water because of the low purity of these by-products, but it could be used in the treatment of wastewater. The authors have investigated the coagulation properties of the resulting PFS and did not give a characterization of the obtained compound.

Zhongguo L. et al. [22] have studied a method for disposing sodium-jarosite which can be used to synthesize PFS. The method consists of two-step leaching experimental procedure. First step is pre-leaching process for removal of impurity metals and second step - decomposition of sodium-jarosite to provide enough ferric ions for synthesizing PFS. The second step was carried out at temperature below 332 K and sulfuric acid consumption 0.8 ml g⁻¹ sodium-jarosite. The results showed that the PFS synthesized from sodium-jarosite had a poly-iron complex Fe₄.67(SO₄)₆(OH)₂.20H₂O.

EXPERIMENTS

Materials and methods

Initially the experiments were conducted with synthetic solution. Chemically pure reagents: Fe₃(SO₄)₉·9H₂O, FeSO₄·7H₂O, CuSO₄·5H₂O, concentrated H₂SO₄ (98 %, d = 1.84 g cm⁻³) and distilled water were used for the preparation. The chemical composition of the synthetic solution is given in Table 1. It is characterized by a high concentration of Fe(III) ions and sulfuric acid and is similar in composition to the waste solutions obtained after autoclave pressure oxidation (POX) of pyrite concentrate. The chemical composition of the industrial solution is given in Table 2.

The concentration of Fe(III) and Fe(II) ions in the industrial solution is respectively 58.96 g l⁻¹ and 1.34 g l⁻¹. From all impurities in the solution the copper ions are with the highest concentration (1.47 g l⁻¹). The content of the other impurities is comparatively low and should not affect the crystallization process.

The evaporation was conducted in a water bath without stirring to avoid the formation of poorly soluble basic sulfates. The crystallization process begins only once 70 % of the water from outgoing solution was evaporated.
The crystals obtained after the crystallization process were separated from the mother liquor by filtration with a Buchner funnel and BOECO R300 vacuum pump. The crystals were washed, dried and weighed with analytical scales.

The complexometric method was used for determination of the concentration of \( \text{Fe}^{3+} \) and \( \text{Cu}^{2+} \) ions in the mother liquor. The concentration of \( \text{Fe}^{2+} \) was determined by the bichromate method and the concentration of \( \text{Fe}^{3+} \) ions was determined by the difference in concentrations between \( \text{Fe}^{\text{total}} \) and \( \text{Fe}^{2+} \) ions. For evaluation of the impurities content the AAA and ICP-OES analyzes were used. This involves the use of PERKIN-ELMER 5000 atomic-absorption spectrophotometer and Jeledyne Leeman Lab devices.

The phase composition of the crystals was determined by means of X-ray diffraction (XRD). For this purpose PANalytical Empyrean device, equipped with a multi-channel detector (Pixel 3D) using the (Cu-K\( \alpha \) 45 kV-40mA) radiation in the range of \( 2\theta \) between 20 – 115\( ^{\circ} \), with a step of scanning of 0.01\( ^{\circ} \) for 20 s is used.

The morphology of the resulting crystals was determined microscopically. The stereo microscope Leica 80M with digital color camera was used.

![Ternary diagram of the system Fe\(_2\)(SO\(_4\))\(_3\)-H\(_2\)SO\(_4\)-H\(_2\)O](image)

Fig. 1. Ternary diagram of the system \( \text{Fe}_2(\text{SO}_4)_3-\text{H}_2\text{SO}_4-\text{H}_2\text{O} \) [23].
The concentration of free sulfuric acid was determined by titration with 0.1 N NaOH solution in the presence of an indicator methyl orange after oxidation of Fe(II) ions to Fe(III) ions with hydrogen peroxide.

RESULTS AND DISCUSSION

In our study we have used a ternary diagram of the system Fe_2(SO_4)_3-H_2SO_4-H_2O [23] built at 297 K, as a starting point for the study of the process of crystallization of ferric sulfate hydrate.

The initial composition (by mass) of the synthetic solution was 17.76 % Fe_2(SO_4)_3, 5.04 % H_2SO_4 and 77.2 % H_2O. It is very clearly seen from Fig. 1 that at this composition the crystallization process could not be performed.

In order to fall into the area of compositions where crystallization process is possible, we undertook a series of experiments with evaporation of different amount of water. The composition of the solutions after evaporation is shown in Table 3 and in Fig. 2.

The analysis of the results shows that the process of crystallization starts after evaporation of 70 % water, i.e., at a density of the solutions over 1788 g l\(^{-1}\). In the experiments F8 and F9 all mother liquor is converted to sludge which is extremely undesirable because all the iron present in the solution crystallized along with all solution impurities.

The appearance of the resulting crystals can be seen on Fig. 2. The photographs were made with a stereo microscope Leica 80M equipped with a color digital camera. On the same figure the appearance of the sample, taken from commercial product - ferric sulphate, is shown.

To carry out the process of internal crystallization, the crystalline precipitate is maintained for 7 days in an ampoule at 372.15 K.

In Figs. 3a and 3b diffraction patterns of the crystals obtained from experiment F6 and F9 are presented. They were obtained after 70 % and 75 % evaporation of the water from the solution.

The main phases identified in the sample F6 were: rhombooclase - FeH(SO_4)_2.4H_2O, ferric sulfate with eight molecules water - Fe_2(SO_4)_3.8H_2O and poly ferric sulfate - Fe_{2.67}(SO_4)_{2.67}(OH)_{2.4}20H_2O.

The diffraction patterns in the sample obtained after experiment F9 before heating are: Fe_2(OH)(SO_4)_{2.5}7H_2O, Fe_2(SO_4)_2.H_2SO_4.2H_2O, Fe_2(SO_4)_3.H_2SO_4.8H_2O and Fe_2(SO_4)_3.9H_2O.

It is obvious that the resulting sludge is a mixture of crystalline phases that do not match a commercial product Fe_2(SO_4)_3.9H_2O and require conducting of internal recrystallization.

To determine the conditions of the recrystallization process we performed two parallel experiments with synthetic solution and with solution obtained during autoclave oxidation of pyrite concentrate. After evapora-
tion of 70% of the volume of the solution, it is placed in a bottle weight and left for 2 days at a temperature 389.15 K. After cooling, the resulting crystalline precipitates were weighed on an analytical balance, analyzed for the content of iron, sulfate sulfur and impurities. The results obtained are summarized in Table 4.

The content of impurities in the precipitate obtained from the industrial solution is minimal in respect of heavy non-ferrous metals. From this it can be concluded that it may be used as a coagulant for wastewater treatment.

The appearance of the crystals obtained from industrial solution after recrystallization at 388.15 K and crystals of commercial ferric sulfate are compared on Fig. 4. It is seen that the obtained crystals are bigger than the commercial, but with the same pale purple color.

The diffraction pattern of the crystals obtained from industrial solution is presented in Fig. 5. It can be seen that the main phases after recrystallization at a high temperature are Fe$_2$(SO$_4$)$_3$.H$_2$SO$_4$.8H$_2$O and Fe$_2$(SO$_4$)$_3$.9H$_2$O.

Table 4. Content of impurities in the crystals obtained after recrystallization.

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu, %</th>
<th>Na, %</th>
<th>K, %</th>
<th>Mg, %</th>
<th>Mn, %</th>
<th>Ni, %</th>
<th>Pb, %</th>
<th>Al, %</th>
<th>Ca, %</th>
<th>Cr, %</th>
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<td>0.02</td>
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<td>0.001</td>
<td>0.2</td>
<td>0.06</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

Fig. 3. Diffractogram of the crystals obtained after experiments F6 and F9.

Fig. 4. Appearance of the crystals: a) obtained after recrystallization; b) crystals of commercial ferric sulfate.
CONCLUSIONS

Based on the experimental studies the possibility of crystallization of ferric sulphate (\(\text{Fe}_2\left(\text{SO}_4\right)_3\)) from solution obtained upon pressure oxidation of pyrite concentrate with high concentration of ferric ions (over 60 g l\(^{-1}\)) has been demonstrated. The following conditions for conducting of both the processes of crystallization: 70 \% evaporation of the water, till reaching density of the solution and of recrystallization: temperature 388.15 K, absence of air, process duration 2 days, are determined. The obtained precipitate under these conditions is coarse crystalline, with minimal impurities content and is suitable as a coagulant for industrial wastewaters treatment.

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