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SHORT COMMUNICATION

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Precipitation of monodispersed basic iron(III) sulfate (sodium jarosite) particles

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Abstract Uniform sodium jarosite particles were obtained by forced hydrolysis of ferric salt solutions to which copper sulfate, sodium sulfate, and sodium nitrate were added. It was found that at the same concentrations of ferric and sulfate ions the particle size and yield decreased with the lowering of the concentration of sodium ions, but the morphology remained the same. At a sufficiently small content of sodium in the reacting solution, no precipitation of sodium jarosite particles was observed. Finally, chemical and XRD analyses showed that small amounts of copper ions are incorporated in the crystal lattice which, with the change in the Na^+/H_3O^+ ratio, slightly affected the structure of this mineral, but not its other properties.

Key words Hydrolysis of ferric sulfate solutions · Iron (III) sulfate hydrolysis · Jarosite precipitation · Sodium jarosite · Monodispersed

Introduction

Precipitation of basic iron(III) sulfates (jarosite-type minerals) is widely used in metallurgical processes in order to remove dissolved iron from zinc, copper, and cadmium, and to control the concentration of sulfate and alkali ions in hot acid leach solutions. Norton and coworkers [1] demonstrated technical feasibility of jarosite precipitation as a method for treating acidic waste systems and removing industrial residues. Furthermore, it is well known that rusting is significantly affected by sulfate ions [2–4], and that the latter are present in many corrosion products. Accordingly, systematic studies of the precipitation conditions of iron compounds, as well as of the kinetics and mechanism of their crystal growth, can improve our understanding of corrosion processes of iron and steel, especially as affected by acid rain. Finally, mineralogists have been interested in the formation of jarosite in sulfide ore deposits under acid conditions in the presence of oxygen [5].

Many syntheses of basic iron(III) sulfate sols have been reported [6–14], but only a few describe such particles of uniform size and shape [13, 14]. In an earlier study it appeared that the precipitation of these colloids was strongly affected by the addition of some electrolytes into the reacting solutions [13]. Specifically, it was shown that the size of monodispersed jarosites-type particles, obtained by aging at elevated temperatures (80 °C) solutions containing $Fe(NO_3)_3$ and Na_2SO_4, decreased in the presence of copper and nickel sulfates [14]. Inherently, it was assumed that these metal ions were causing the observed effects. However, no further evidence of the observed phenomenon was offered in the preliminary report in support of that notion.

The purpose of the present investigation was to carry out a systematic study of the effect of cooper and sodium ions on the precipitation of monodispersed basic iron(III) sulfate (jarosite) particles in solutions of ferric nitrate, sodium sulfate, and sodium nitrate, in the presence and in the absence of copper sulfate.

Experimental

Materials

All chemicals were reagent grade and used without further purification. Stock solutions of $Fe(NO_3)_3$, Na_2SO_4, $NaNO_3$, and $CuSO_4$ were freshly prepared and filtered through 0.22-μm

Table 1 Compositions of solutions for the preparations of sodium jarosite particles

Sample	$Fe(NO_3)_3$ (mol dm^{-3})	$CuSO_4$ (mol dm^{-3})	Na_2SO_4 (mol dm^{-3})	$NaNO_3$ (mol dm^{-3})	Particle size (μm)
1	0.18	0	0.27	0	1.8
2	0.18	0.05	0.22	0	1.5
3	0.18	0.09	0.18	0	1.2
4	0.18	0.13	0.14	0	0.9
5	0.18	0.18	0.09	0	0.7
6	0.18	0.23	0.04	0	0.6
7	0.18	0.27	0	0	a
8	0.18	0.18	0.09	0.36	1.7
9	0.18	0.27	0	0.54	1.9

All reacting solutions were aged at 80 °C for 1.5 h. The initial pH was adjusted to 1.37 by the addition of HNO_3 or NaOH as needed
[a] No precipitation observed

Millipore membranes before use. A standard copper solution was employed in atomic absorption chemical analysis.

Preparation of the particles

Jarosite particles were obtained by precipitation in homogeneous solutions following essentially the same procedure as described before [14]. Solutions containing $Fe(NO_3)_3$, Na_2SO_4, $NaNO_3$, and $CuSO_4$ salts were aged at 80 °C for 1.5 h in a preheated forced air convection oven. In all solutions the total content of sulfate ions was kept constant at 0.27 mol dm^{-3} by combining the concentration of $CuSO_4$ and Na_2SO_4, as summarized in Table 1. The initial pH of the reacting solution was adjusted to 1.37.

The obtained particles were separated from the mother liquor by centrifugation and washed four times with 0.05 mol dm^{-3} HNO_3 solution. The purified solids were filtered, dried, and stored in a desiccator before further analyses.

Characterization of the precipitates

The size and the morphology of the particles were examined by scanning electron microscopy (SEM) and by the Voyager X-ray Microanalysis and Digital Imaging System, while their structure was evaluated by X-ray diffraction (XRD). The crystalline phase of jarosite type particles was identified according to the Powder Diffraction File PDF-2 Database Sets 1–41 (International Center for Diffraction Data). The qualitative chemical composition of the solids was assayed by EDAX and the content of copper in the precipitated samples was determined by dissolving the solids, followed by the atomic absorption spectroscopy.

Results

All resulting particles consisted of well-defined uniform pseudocubic crystals as illustrated by scanning electron micrographs in Fig. 1.

The EDAX qualitative chemical analysis of these solids indicated the presence of Fe, Na, and S. Particles precipitated in the presence of 0.18 mol dm^{-3} of $CuSO_4$, contained also a small amount of Cu^{2+} (Fig. 2), the amount of which increased with higher concentrations of $CuSO_4$ in the reacting solution (Fig. 3), although it was less then 1 wt%.

The XRD patterns of the precipitates (Fig. 4) are consistent with that of the mineral sodium jarosite, the composition of which is given as $(Na^+)_{1-x}(H_3O^+)_x Fe_3(SO_4)_2(OH)_6$. The incorporation of Cu^{2+} into these crystals, as well as the change in the Na^+/H_3O^+ ratio, caused by decreasing concentration of sodium sulfate in reacting solutions, affects somewhat the XRD patterns by increasing the lattice constants; i.e., systematic shifts of all peaks towards lower Bragg angles is observed (Fig. 4).

The examples in Fig. 1 show that the average particle size was obviously influenced by the composition of the reacting solution. The reason for this effect can be explained by the inspection of data summarized in Table 1. At constant concentrations of ferric and sulfate ions, the average particle size becomes smaller with the increasing molar ratio of $CuSO_4/Na_2SO_4$ (samples 1–6, Table 1). In order to resolve whether the change in the particle size was due to the increase in copper content or to a decrease in the sodium content, additional experiments were carried out at different ratios of $[CuSO_4]/[Na_2SO_4]$, but the total concentration of sodium ions was adjusted with $NaNO_3$ to 0.54 mol dm^{-3} (samples 8 and 9, Table 1), which is the same as in sample 1. The large particles were again generated despite the presence of copper ions (Fig. 1d). Thus, it is obvious that the observed decrease in the particle size and the yield of the precipitate were due to the depletion of sodium ions in the reacting solutions. Indeed, when the content of the latter falls below a critical concentration, no solid phase formation takes place. These results are summarized in Fig. 5.

Discussion

This study has demonstrated that the precipitation of uniform colloidal sodium jarosite crystals can be achieved by forced hydrolysis. The physical and chemical factors affecting the precipitation of the alkali jarosite have been extensively studied by Dutrizac [7, 15], who showed that the pH of the reacting solution, reaction time, concentration of alkali sulfate, and temperature influenced the amount of jarosite formed. He carried out experiments over longer periods of time (up to 24 h), but did not produce uniform particles. To obtain monodispersed jarosite product, the aging of the solutions at the elevated temperature (80 °C) must be kept short. Indeed, upon prolonged reaction time (>4 h) and higher temperatures (>98 °C) a “secondary growth” becomes dominant, resulting in the formation of irregular particle aggregates.

The precipitation of sodium jarosite is influenced by the concentration of copper and sodium ions in the reacting solution in two different ways. First, the observed systematic change in the lattice parameters, as evidenced by the shifts in the XRD peaks of the obtained precipitates, must be caused by the partial

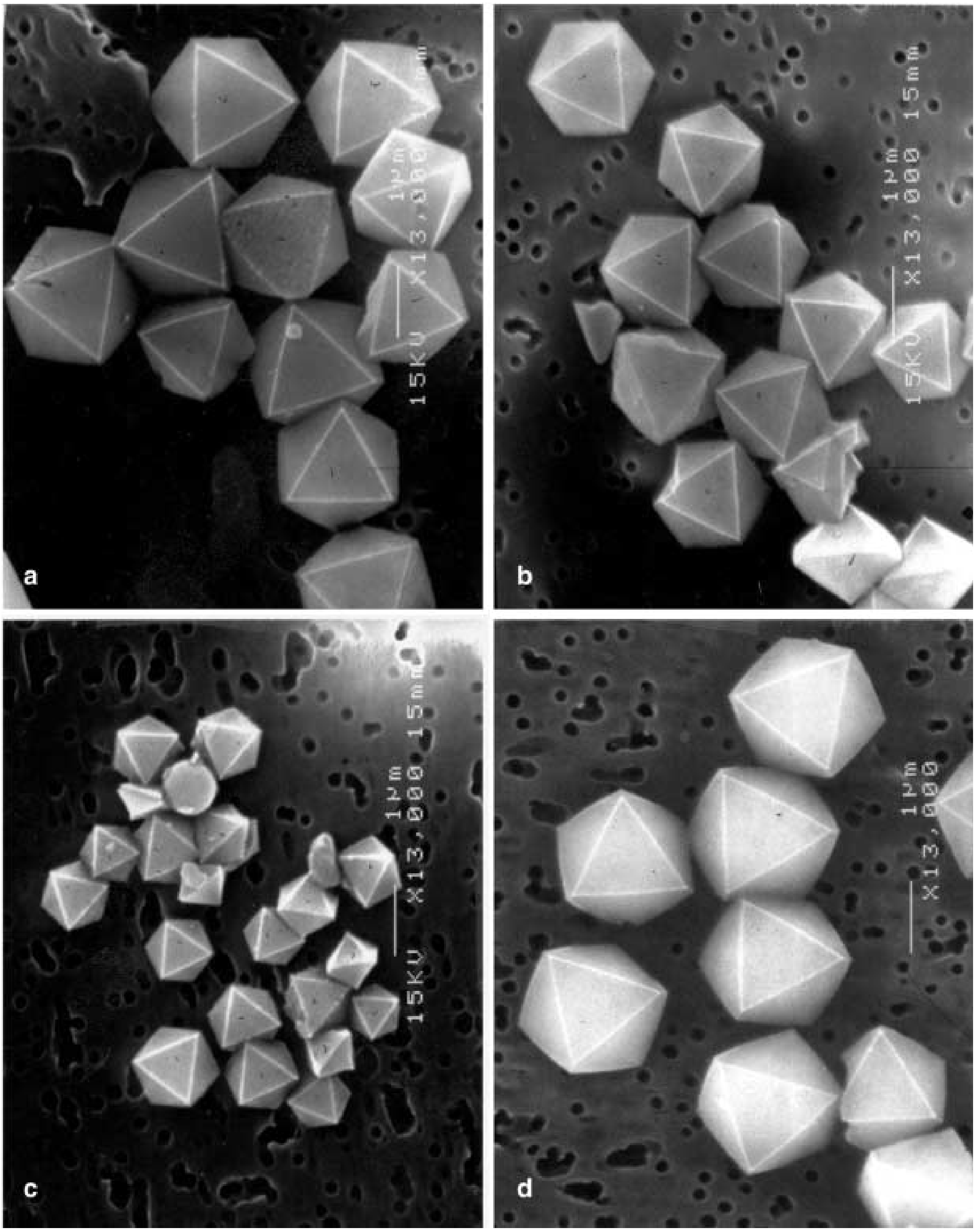

Fig. 1a–d Scanning electron micrographs (SEM) of sodium jarosite particles obtained by aging at 85 °C for 1.5 h solutions containing: **a** 0.18 mol dm^{-3} $Fe(NO_3)_3$, 0.27 mol dm^{-3} Na_2SO_4, (Table 1, sample 1); **b** 0.18 mol dm^{-3} $Fe_2(SO_4)_3$, 0.22 mol dm^{-3} Na_2SO_4, and 0.05 mol dm^{-3} $CuSO_4$ (Table 1, sample 2); **c** 0.18 mol dm^{-3} $Fe_2(SO_4)_3$, 0.14 mol dm^{-3} Na_2SO_4, 0.13 mol dm^{-3} $CuSO_4$, and 0.36 mol dm^{-3} $NaNO_3$ (Table 1, sample 4); **d** 0.18 mol dm^{-3} $Fe_2(SO_4)_3$, 0.27 mol dm^{-3} $CuSO_4$, and 0.54 mol dm^{-3} $NaNO_3$ (Table 1, sample 9). Initial pH of reacting solutions was 1.37

substitution of the smaller Fe^{3+} ions by the larger Cu^{2+} ions in the Fe^{3+}-OH sheet structure and furthermore, by the extent of Na^+/H_3O^+ substitution in the host crystal. Previous investigations [16] have shown that the incorporation of divalent metals, such as Zn, Cd, Co, and Cu, into alkali jarosite is rather small (<3 wt%). The amount of Cu^{2+} in solids prepared under studied conditions did not exceed 0.75 wt%. According to Dutrizac [16], the substitution of divalent metal ions into the Fe^{3+}-OH sheet structure of jarosite causes thermodynamic weaknesses of the crystal lattice and, therefore, these cations are not found in natural and synthetic jarosites. In the present study, this substitution did not cause significant distortion of the crystal lattice.

The second effect is the decrease of the particle size with the increasing substitution of Na_2SO_4 by $CuSO_4$ at a constant content in SO_4^{2-} until, at a sufficiently high value of the $CuSO_4/Na_2SO_4$ molar ratio, no solid phase is formed. It has been demonstrated that with decreasing amount of sodium ions in the reacting solution the fraction of the hydronium ions in the crystal structure increases. Furthermore, it was shown that it is much more difficult to precipitate hydronium-rich jarosite than sodium-rich jarosite [16]. Accordingly, lowering the concentration of sodium ions in the reacting solution significantly decreases the yield of sodium jarosite, resulting in the formation of particles of the same pseudocubic shape but smaller particle size. This inves-

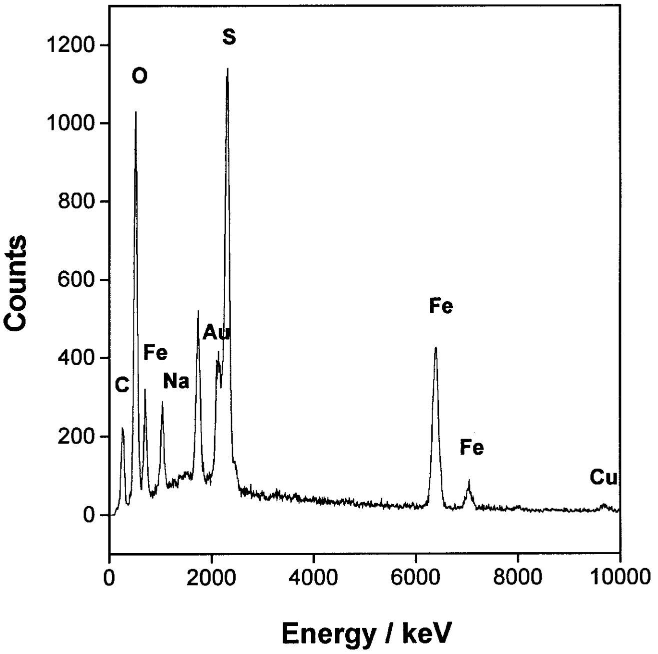

Fig. 2 EDAX spectrum of sodium jarosite prepared at conditions given in Table 1, sample 5

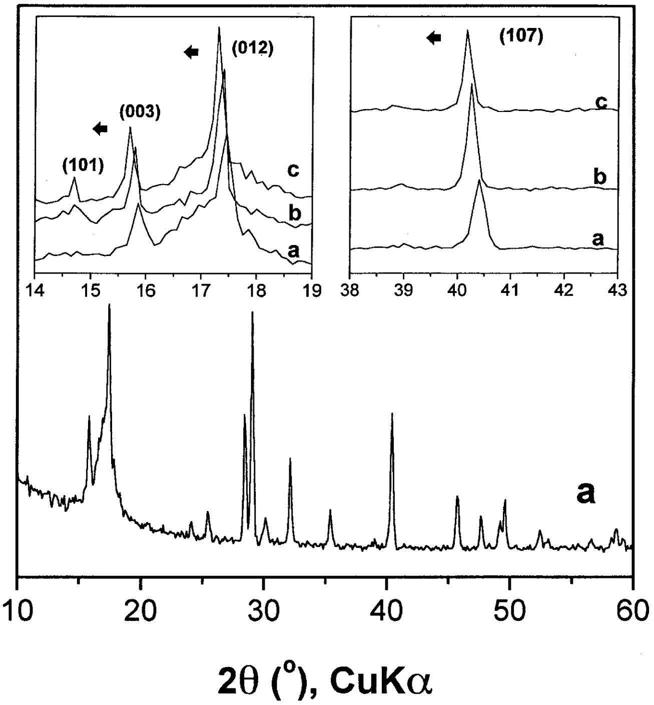

Fig. 4 X-ray diffraction (XRD) patterns of sodium jarosite prepared in the presence of different concentration of Cu^{2+}: (a) none (Table 1, sample 1), (b) 0.09 mol dm^{-3} (Table 1, sample 3), and (c) 0.18 mol dm^{-3} (Table 1, sample 5). Concentration of all other reactants as given in Table 1

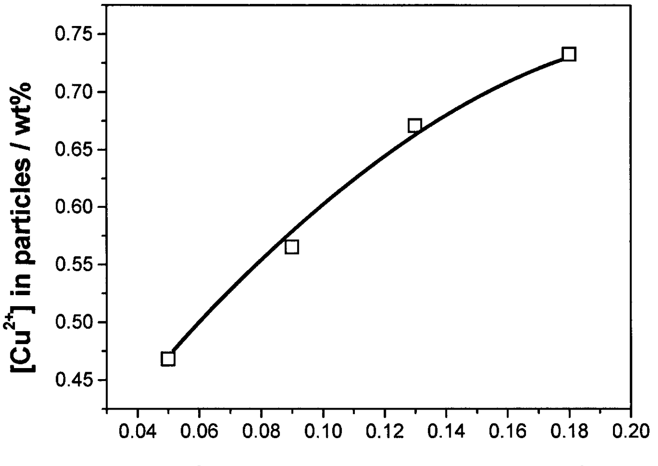

Fig. 3 Content of Cu^{2+} in wt% of sodium jarosite particles prepared at conditions given in Table 1 as a function of the $CuSO_4$ concentration in the reacting solution

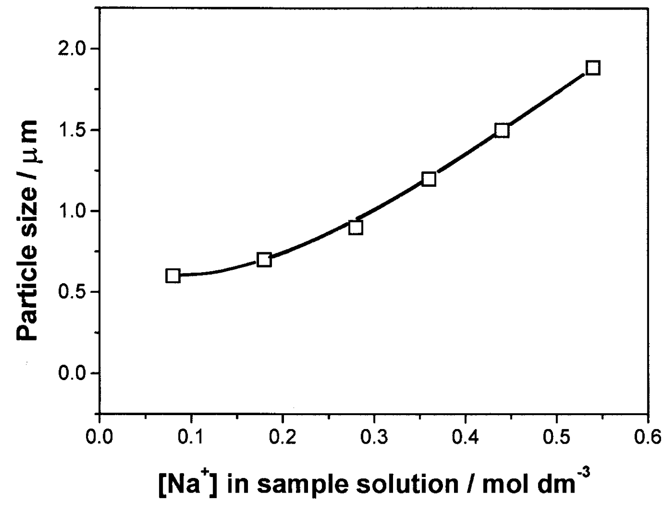

Fig. 5 Particle size of the sodium jarosite particles prepared at conditions given in Table 1 as the function of the concentration of Na^+ ions in the reacting solution

tigation has thus shown that the precipitation of these particles is not affected by the presence of divalent metal ions such as copper, as previously assumed. Instead, the effect is essentially controlled by the concentration of Na^+ ions, which is critical to the precipitation of sodium jarosite, and particularly for the appearance of this compound as uniform colloidal crystals.

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