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Crystallization of jarosite in the presence of amino acids

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ABSTRACT

Jarosite was formed in the presence of five amino acids at two pHs, namely 1.75 and 2.9, to determine what impact amino acids have on its formation. It was found that at the lower pH glycine was the most potent in terms of morphological and yield impacts. XRD analysis showed that incorporation of the amino acid occurs at this low pH for glycine and proline. Dynamic light scattering studies showed that glycine impacts significantly on the jarosite nucleation rate while proline and alanine do not. At the higher pH all of the amino acids had much less impact on morphology or yield. At pH 3 the solids were found to be a 3-phase system consisting of goethite, schwertmannite and jarosite. In this case, alanine appeared to stabilise the presence of schwertmannite more than the other amino acids.

1. Introduction

Jarosite, [$KFe_3(SO_4)_2(OH)_6$], is a mixed iron sulphate mineral commonly found in environments such as acid sulphate soils [1], acid mine wastes [2], saline lakes [3] and hypogene systems [4]. It is also produced in some hydrometallurgical operations (such as zinc processing) to remove unwanted iron and improve metal concentrates [5,6]. Given that jarosite only forms when water is present, the finding of jarosite on Mars in 2004 confirmed that the 'Red planet' had water at some point in its history [7]. The formation of jarosite is, therefore, of wide interest in many fields.

In terrestrial systems, microbes are always present, and this is especially true of acid mine drainage systems where oxidising bacteria often control the iron and sulphur levels of the system (through organisms such as *Thiobacillus ferrooxidans* [4]). The relationship between jarosite and microbes is, however, not fully understood although some research has been conducted in this area [5,6,8–10]. In the case of acid mine drainage, jarosite formation could be extremely beneficial by locking away toxic metals often released by the high acidity, however, this depends on the stability of the jarosite in this environment [11]. Thus, understanding the formation and stability of jarosite in acid environments is of fundamental interest and has many real world applications.

Generally, it is well understood that *T. ferriooxidans*-type microbes will dissolve pyrite and can thereby form jarosite solids [12,13]. For the most part, literature is also agreed that below pH 3 jarosite will form [9,14] while above pH 3 and below pH 5 schwertmannite is the product formed. However, this is temperature dependant [10,14]. From an acid mine drainage point of view we find that the bacteria that grow well in the conditions required for jarosite formation must be acidophiles (pH must be below 3). The pH is however, also linked to the rate of iron (II) which is oxidised to iron (III) [15] in natural systems and to the extent of sulphur-bearing minerals. If jarosites are to be used as repositories of waste materials (in particular, heavy metals) in the remediation of acid mine drainage soils [11], not only their stability in different environments and possible dissolution behaviour must be determined (as already acknowledged) but also the impact microbes have on this process is also vital. Some of this work is already being conducted [16–18] showing the dissolution of different jarosites containing lead or arsenic within the structure but these are in the absence of microbial action. The stability of solids in various environments is, however, also linked to their structure, so one could ask whether the presence of microbes induces the formation of jarosites with different structure and therefore properties. Again, early work is showing that jarosites formed in the presence of microbes may have different features [19] suggesting that there are differences between biogenic jarosite and synthetic jarosites [14,20]. There is also the suggestion that particular microbes promote the presence of different phases [8], however, as stated above pH and temperature are also significant contributors to this. Finally, it should be stressed that microbial action need not form jarosite directly but can be a consequence of the conditions they create; for example, the work of Tazaki et al. [21], show that during the corrosion of a sewer pipe (the microbes present are inferred to have caused the corrosion), the acidic conditions present and maintained by the microbes in the pipe result in jarosite and gypsum formation.

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As high-grade ores diminish, cost effective means of treating low-grade ores must be developed [22]. One such possible method is heap leaching where acid is dripped onto a low-grade ore heap and with the aid of microbes, the desired metals are released, dissolved and thereafter extracted. This process also leads to acid mine drainage. Thus, understanding the interaction between microbe, pH and solids formed is of vital importance for future mining practices.

As a precursor to understanding the impact that microbes (and live organisms in general) have on jarosite formation, we have looked at amino acids. There is very little literature on the effect of amino acids [23], though as discussed above there is some with regard to microbial impacts [5,6,8–10]. From the work of Kotler [23,24], it was hypothesised that glycine might incorporate into the structure, however this was inferred from infrared evidence, which does not actually conclusively give information on incorporation. This is because movements in peak positions can be due to adsorption effects and may not relate to incorporation at all. Even if such small molecules are not incorporated into the jarosite mineral structure, it is probable that they will interact with growing crystallites to modify their growth rate, morphology and particle size. This manuscript, therefore, investigates the formation of jarosite in the presence of 5 amino acids and investigated parameters such as (i) yield (ii) morphology, (iii) the impact of pH and (iv) the possibility of incorporation.

2. Materials and methods

2.1. Materials

Ferric sulphate $Fe_2(SO_4)_3 \cdot xH_2O$ was obtained from Chem Supply and potassium nitrate was AR grade from Ajax Chemicals. To alter pH, concentrated sulphuric acid (H_2SO_4) $>95\%$ from Ajax Chemicals and potassium hydroxide (KOH), AR grade from BDH was used. The amino acids; L-cysteine, D, L-alanine, D, L-aspartic acid, L-proline, D, L-glycine were AR grade from Sigma Aldrich.

2.2. Jarosite formation and determination of yield

Potassium jarosite was prepared according to the method of Dutrizac [4,25]. This involves dissolving $Fe_2(SO_4)_3 \cdot xH_20$ (6.4 g) and KNO_3 (24 g) into 800 g de-ionised water to which 0.8 mL concentrated H_2SO_4 is added to the solution in a clean, glass bottle. The bottle is capped and the resulting clear solution is then heated to 90 °C for 3 or 24 h. The pH measured for more than 3 control samples was 1.75 ± 0.05 and so this was one of the pHs chosen to investigate. A higher pH of 2.9 was also chosen to determine what impact pH had on the system. After the allocated time; any solids formed are collected by filtering, washing with de-ionised water three times and drying in a desiccator. The solids are then weighed to determine the yield of solid formed. On some occasions, smaller 200 mL batches were prepared to collect solids at 3 h to determine the solid phase present only.

When amino acid is present it is added as a solid prior to the addition of water and dissolved along with the other solids. The addition of amino acids normally raises the pH of the system and so the pH is adjusted (using conc H_2SO_4 or KOH) after dissolution of all solids to the same pH as the control system or the desired pH.

2.3. Characterisation of solids

2.3.1. Infrared

Infrared is a well-known method to characterise mineral forms as the technique is phase specific. The solids for Fourier transform infrared (FTIR) were placed onto a diamond ATR accessory of a Nicolet IS50 FTIR Spectrometer. A background spectrum was collected before each new scan. Data were collected from 400 to 4000 cm^{-1} with a spectral resolution of 4 cm^{-1} in transmittance mode. All spectra were uncorrected since the spectra were being used for comparison purposes only.

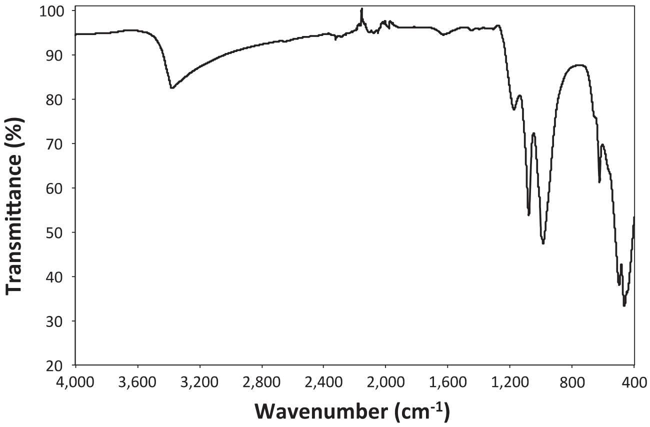

Fig. 1. FTIR spectrum of control jarosite solids.

In Fig. 1 below, the control jarosite infrared is shown. The peaks compare well with literature [26] where the sulphate bands are found between 940 and 1300 cm^{-1} and the water bend and stretch bands can be found at 1600 and $\sim$3350 cm^{-1} respectively. The bands between 1900 and 2400 cm^{-1} are due to the diamond ATR and are not from the solids.

2.3.2. Scanning electron microscopy (SEM)

Morphology of the samples was determined using an Evo Zeiss scanning electron microscope (SEM). The washed and dried solids from crystallization experiments were placed on carbon coated SEM stubs and placed in a dessicator to let the stubs dry. They were then sputter-coated with gold prior to viewing on an Evo Zeiss SEM instrument. The images were usually collected at a working distance of 10 mm and a voltage of 15 kV.

2.3.3. X-ray diffraction (XRD)

Wide angle, powder XRD was performed on the samples containing sufficient solids to pack the XRD holder of a D8 Advance (Bruker) instrument with a 2θ range of 7–70°, step size 0.001, divergence slit of 0.3° while the sample holder was spun at 30 rpm. Cu K_α radiation was used for these samples. In addition, some samples were repeated with a corundum internal standard ($\sim$10%) and run at 5–120° 2θ using Co K_α radiation, step size 0.01 on a D8 Discovery (Bruker) instrument. These XRD patterns were used for Rietveld analysis undertaken with TOPAS® software. Finally, for those samples where insufficient solids were present to pack into the regular holders, these samples were dispersed in ethanol and cast onto low background silicon holders and run as per the other samples on the D8 Advance. The XRD pattern of the control sample confirmed the presence of jarosite (Fig. 2) and was able to be indexed to the PDF file 00-036-0427.

2.3.4. Dynamic light scattering (DLS)

A Malvern Nanosizer ZS was utilised to measure the DLS behaviour of solutions in the absence and presence of amino acids (0.14 M). This instrument can operate at high temperatures and so the particle sizing and particle counts were obtained at 90 °C as per the crystallization experiments. The concentrations of iron sulphate, potassium nitrate and sulphuric acid were as per the crystallization experiments except that the pH of the solutions was