

## The Hydrothermal Microwave Synthesis of Scorodite: Iron(III) Arsenate(V) Dihydrate, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$

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The high yield and rapid precipitation of iron(III) arsenate(V) dihydrate (identical to the mineral scorodite) from aqueous iron(III)–arsenic(V) solutions in the pH range 0.6–1.1 has been achieved using microwave dielectric heating; the results have significant implications for the removal of arsenic from industrial wastes.

Transition metal phosphates and arsenates have important technological applications particularly as paint coatings, insecticides and in electrochromic devices.<sup>1</sup> Furthermore, the fact that some of these compounds have open-channel structures with large pore sizes has attracted interest because of their potential as catalytic microporous solids.<sup>2</sup> In general, these compounds have been made by high temperature solid-state synthetic procedures. Their synthesis in aqueous solutions is problematical because a narrow pH range is required and the kinetics of converting the intermediate mononuclear metal arsenate (or phosphate) complexes into the insoluble infinite solids are extremely slow. For example, at pH 1 an  $\text{Fe}^{\text{III}}$  ( $0.3 \text{ mol dm}^{-3}$ )– $\text{H}_2\text{SO}_4$  ( $0.45 \text{ mol dm}^{-3}$ )– $\text{H}_3\text{AsO}_4$  ( $0.2 \text{ mol dm}^{-3}$ ) aqueous solution at room temperature contains<sup>3</sup> approximately 30%  $[\text{FeHASO}_4]^+$  and 27%  $[\text{FeH}_2\text{AsO}_4]^{2+}$  (the remaining constituents do not contain arsenic). When the solution is heated under reflux conditions for many hours no precipitate is formed. If the pH is raised above 1.8, a gelatinous non-crystalline mixture of uncertain constitution is obtained. These observations are important in the context of the effective and economic treatment of aqueous effluent resulting from the bacterial oxidation of gold-containing concentrates of arsenopyrite.<sup>4</sup> After the liberation of the gold the effluent solution has a pH of 1 and contains  $0.4 \text{ mol dm}^{-3} \text{ Fe}^{\text{III}}$  and  $0.2 \text{ mol dm}^{-3} \text{ As}^{\text{V}}$  and therefore poses a significant environmental threat, and processes which remove the arsenic efficiently are important. The conventional treatment of the effluent solution with calcium hydroxide produces a gelatinous precipitate whose constitution has been the subject of some controversy. There have been suggestions in the literature that the gelatinous solid product from treatment of the effluent with slaked lime contains basic iron(III) arsenate(V) sulfates,<sup>5</sup> iron(III) hydroxide adsorbed onto iron(III) arsenate(V) dihydrate crystals,<sup>6</sup> and compounds<sup>7</sup> related to the mineral, bukovskyite  $\text{Fe}_2\text{AsO}_4\text{SO}_4\text{OH}$ . Therdkiatikul and Dahlstrom<sup>8</sup> have produced crystalline scorodite from iron(III)–arsenate(V) solutions by heating in a conventional autoclave at high temperatures suggesting that microwave dielectric heating may be an effective way of forming scorodite,  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ . In addition, the hydrothermal microwave route has been investigated for the synthesis of electroceramics.<sup>9</sup>

Previously, we have established that this technique provides a convenient and efficient method of superheating solutions<sup>10</sup> and discussed the origins of the superheating phenomenon.<sup>11</sup> In this communication we report that arsenic may be removed effectively from 'model' effluent solutions using microwave dielectric superheating techniques. Here we show that the arsenic may be removed virtually quantitatively as the compound,  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ , which is identical in composition to the mineral scorodite, from solutions which are comparable to those found in the mineral processing of gold-containing arsenopyrite by bacterial oxidation.<sup>4</sup>

Solutions containing  $0.4 \text{ mol dm}^{-3} \text{ Fe}^{\text{III}}$  and  $0.2 \text{ mol dm}^{-3} \text{ As}^{\text{V}}$  in the pH range 0.6–1.2 were exposed to microwaves in a CEM MDS 2000 Microwave Cavity for periods between 10 and 60 min. During these periods the temperatures of the superheated solutions were maintained at preset values and the associated pressures were recorded.

In a typical experiment,  $25 \text{ cm}^3$  of a solution was placed in a  $100 \text{ cm}^3$  Teflon autoclave vessel. The solution was maintained at a temperature of  $130 \text{ }^\circ\text{C}$  and a pressure of 6 atm. The scorodite is obtained as a fine pale yellow–green precipitate and was removed quantitatively by filtration. The scorodite samples were characterized by powder X-ray diffraction,<sup>12</sup> infrared<sup>13</sup> and Raman spectroscopy and shown to be identical to authentic samples of the mineral.

The yields of scorodite as a function of time, temperature and pH are shown in Fig. 1. The data taken collectively suggest that

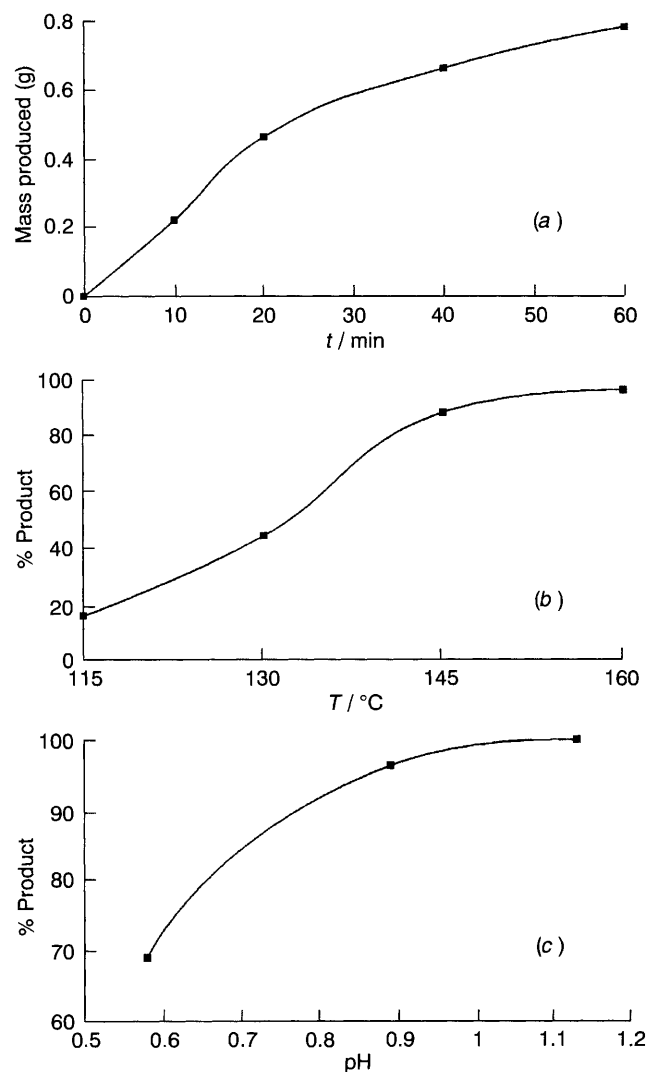


Fig. 1 (a) The mass of scorodite produced after different irradiation times from an  $\text{Fe}^{\text{III}}\text{--As}^{\text{V}}$  solution at a pH of 0.58 at  $160 \text{ }^\circ\text{C}$ . (b) The percentage of scorodite produced by the irradiation of an  $\text{Fe}^{\text{III}}\text{--As}^{\text{V}}$  solution at a pH of 0.89 for 10 min at different temperatures. (c) The percentage of scorodite produced by the irradiation of an  $\text{Fe}^{\text{III}}\text{--As}^{\text{V}}$  solution for 10 min at  $160 \text{ }^\circ\text{C}$  at different pH values.

for the processing of the effluent from the bacterial oxidation of arsenopyrite the optimal conditions are superheating for 20 min at a temperature of 130 °C and at a pH of 1.1.

The powder XRD of the gelatinous product obtained by treating iron(III)–arsenic(V) solution with calcium hydroxide showed that only one crystalline compound was present; calcium sulfate dihydrate identical to natural gypsum. Powder XRD of a sample of natural bukovskyite ( $\text{Fe}_2\text{AsO}_4\text{SO}_4\text{OH}$ ) showed that it was a crystalline material, but there was no evidence for its being a constituent of the gelatinous precipitate.

The research described above and subsequent work has shown that microwave dielectric heating provides an effective and convenient general hydrothermal route into transition metal phosphates and arsenates from aqueous solutions.<sup>14</sup> Clearly, the kinetic barrier for polymerization and precipitation ( $\approx 77 \text{ kJ mol}^{-1}$  at  $\text{pH} = 1.1$ ) is significant and places such reactions outside the range of conditions usually employed for aqueous chemistry. However, the superheating introduced under the microwave conditions accelerates this process sufficiently to obtain the minerals in a convenient and rapid manner. It is noteworthy that the balance between successful and unsuccessful syntheses in this area depends only on a 30 °C difference and the microwave dielectric heating is ideal for introducing the required additional energy input and obviates the need for high-temperature solid-state techniques. The experiments have demonstrated the utility of the technique for removing arsenates from industrial effluents associated with gold extraction in a safe manner. Since the microwave superheating technique may be readily modified to function in a continuous flow manner, large volumes of effluent could be efficiently treated using this technology. Bukovskyite and

similar crystalline substances are not produced in the conventional treatment of the iron(III)–arsenic(V) effluent solutions.

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