Research Article

Dissolution, Solubility, and Stability of the Basic Ferric Sulfate-Arsenates $[\text{Fe}(\text{SO}_4)_x(\text{AsO}_4)_y(\text{OH})_z \cdot n\text{H}_2\text{O}]$ at 25–45°C and pH 2–10

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Basic ferric sulfate-arsenates $[\text{FeSAsOH}, \text{Fe}(\text{SO}_4)_x(\text{AsO}_4)_y(\text{OH})_z \cdot n\text{H}_2\text{O}]$ were prepared and characterized to study their potential fixation of arsenic in the oxidizing and acidic environment through a dissolution for 330d. The synthetic solids were well-shaped monoclinic prismatic crystals. For the dissolution of the sample $\text{FeSAsOH}-1$ $[\text{Fe}(\text{SO}_4)_{0.27}(\text{AsO}_4)_{0.73}(\text{OH})_{0.27} \cdot 0.26\text{H}_2\text{O}]$ at 25–45°C and initial pH 2, all constituents preferred to be dissolved in the order of $\text{AsO}_4^{3-} > \text{SO}_4^{2-} > \text{Fe}^{3+}$ in 1–3 h, in the order of $\text{SO}_4^{2-} > \text{AsO}_4^{3-} > \text{Fe}^{3+}$ from 1–3 h to 12–24 h, and finally in the order of $\text{SO}_4^{2-} > \text{Fe}^{3+} > \text{AsO}_4^{3-}$. The released iron, sulfate, and arsenate existed dominantly as $\text{Fe}^{3+}/\text{Fe}(\text{OH})^{2+}/\text{FeSO}_4^+$, $\text{HSO}_4^-/\text{SO}_4^{2-}/\text{FeSO}_4^+$, and $\text{H}_3\text{AsO}_4^0/\text{H}_2\text{AsO}_4^-$, respectively. The higher initial pHs (6 and 10) could obviously inhibit the release of Fe^{3+} from solid into solution, and the solid components were released in the order of $\text{SO}_4^{2-} > \text{AsO}_4^{3-} > \text{Fe}^{3+}$. The crystal tops were first dissolved, and the crystal surfaces were gradually smoothed/rounded until all edges and corners disappeared. The dissociations were restricted by the Fe-O(H) breakdown in the FeO_6 octahedra and obstructed by the OH^- and AsO_4 tetrahedra outliers; the lowest concentration of the dissolved arsenic was 0.045 mg/L. Based on the dissolution experiment at 25°C and pH 2, the solubility products (K_{sp}) for the basic ferric sulfate-arsenate $[\text{Fe}(\text{SO}_4)_{0.27}(\text{AsO}_4)_{0.73}(\text{OH})_{0.27} \cdot 0.26\text{H}_2\text{O}]$, which are equal to the ion activity products ($\log_{\text{IAP}}$) at equilibrium, were calculated to be -23.04 ± 0.01 with the resulting Gibbs free energies of formation (ΔG_f°) of -914.06 ± 0.03 kJ/mol.

1. Introduction

Arsenic is an extremely toxic byproduct of the mining and smelting of precious and nonferrous metals [1–5] and a common metalloid element in mineral feedstocks, which could be mobilized/discharged during the metallurgical operation, and it results in a serious environmental problem [6, 7].

With the pyrite and arsenopyrite destruction in the Au extraction from refractory Au-sulfide ores, large amounts of arsenic would enter into the residues together with ferric ion

and sulfate [8, 9]. The characterization of the different residual solids formed in the autoclave system and their solubilities are related to the environmental and metallurgical problems that have not been finally solved, and their physicochemical properties are still not well understood [10, 11].

The solubility and stability of arsenical solid wastes depend on the type of arsenic-containing phases and their crystallinity [2]. Contrary to the poorly crystalline Fe(III)- AsO_4 compounds coprecipitated during usual neutralization of hydrometallurgical effluents [12], the controlled or

autoclave processing resulted in the formation of well-crystallized precipitates [3]. The basic ferric sulfate-arsenate $[\text{FeSAsOH}, \text{Fe}(\text{SO}_4)_x(\text{AsO}_4)_{1-x}(\text{OH})_x \cdot w\text{H}_2\text{O}]$ [2] was one of the three crystalline ferric sulfate-arsenates, which were detected to crystallize when the arsenic-containing minerals as the raw materials were treated in the autoclave under the hydrothermal condition of the $\text{Fe(III)-SO}_4\text{-AsO}_4$ solution ($150\text{--}230^\circ\text{C}$), on which recent characterizations indicated that arsenic was immobilized in the FeSOH [Basic ferric sulfate]– FeSAsOH solid solution [4].

The crystalline phase “Type 2” $[\text{Fe}_4(\text{SO}_4)_y(\text{AsO}_4)_3(\text{OH})_x]$ was found to precipitate under the autoclave processing condition of Fe/As ratio <1.5 and $200\text{--}225^\circ\text{C}$, which was tetragonal or monoclinic and exhibited a similar leaching behavior of relatively lower solubility ($<0.34\text{ mg/L As}$) with the amorphous mineral scorodite $[\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}]$ ($<0.8\text{ mg/L As}$) and could meet the TCLP leachability criterion ($<5\text{ ppm}$) [13].

The well-crystallized ferric arsenate could be successfully prepared by the hydrothermal precipitation method from the $\text{Fe-SO}_4\text{-AsO}_4\text{-H}_2\text{O}$ solution at $\text{pH} < 2.5$ and $>210^\circ\text{C}$ [10]. The crystalline “Phase 3” $[\text{Fe}_x(\text{SO}_4, \text{AsO}_4)(\text{OH})_y \cdot n\text{H}_2\text{O}]$ was a monoclinic polytype of the basic ferric sulfate and it formed at $175\text{--}225^\circ\text{C}$ through the isomorphic replacement of AsO_4 for SO_4 with the OH decrease to keep the charge balances, for example, the $\text{Fe}(\text{SO}_4)_{0.6}(\text{AsO}_4)_{0.4}(\text{OH})_{0.6} \cdot 0.4\text{H}_2\text{O}$ solid solution [4], although its structure was suggested to be triclinic (pseudoorthorhombic) in the further research. At the Fe/As mole ratios of $3.65\text{--}1.77$, $1.55\text{--}1.20$, and 1.00 , only the “Phase 3”, the mixture of “Phase 3” and minor $\text{FeAsO}_4 \cdot 0.75\text{H}_2\text{O}$ and only the phase $\text{FeAsO}_4 \cdot 0.75\text{H}_2\text{O}$ formed, respectively [11]. The arsenic concentrations leached from “Phase 3” at room temperature for 40 h into the water were steadily $<0.1\text{ mg/L}$, which suggested that “Phase 3” might be a suitable solid phase for arsenic removal [11]. Lately, the crystal structure of the basic ferric sulfate-arsenate $[\text{FeSAsOH}, \text{Fe}(\text{SO}_4)_{0.7-0.2}(\text{AsO}_4)_{0.2-0.7}(\text{OH})_{0.7-0.2}]$ was proposed to be constructed of the FeO_6 octahedral chains that were cross-linked through the SO_4/AsO_4 tetrahedra, which formed alternative layers of SO_4/AsO_4 tetrahedra and FeO_6 octahedra [14]. The “Type 2” $[\text{Fe}_4(\text{SO}_4)_y(\text{AsO}_4)_3(\text{OH})_x]$ was the same as the “Phase 3” $[\text{Fe}_x(\text{SO}_4, \text{AsO}_4)(\text{OH})_y \cdot n\text{H}_2\text{O}]$, although their crystal structure and stability remained unknown [3, 4].

Precise examination of the solubility and stability of the basic ferric sulfate-arsenates (FeSAsOH) is important to promote the risk evaluation on arsenic-polluted sites and to prevent the arsenic to be released back into the environment [15]. But, until now, most researches were carried out mainly on the forming conditions, structural characterization, and leachability of FeSAsOH [2, 4, 13], and little information about the dissolution mechanism, solubility, and stability of the basic ferric sulfate-arsenates is nowadays accessible. Although previous works indicated enormously low reactivity and solubility of these compounds in both acid and alkaline solutions [9, 11, 14], further studies on the arsenic release mechanism and their long-term solubility at various pHs are essential.

In this work, the crystalline FeSAsOH solids from $\text{Fe(III)-SO}_4\text{-AsO}_4$ solutions are prepared by a simple hydrothermal method. The dissolution mechanism, long-term solubility, and stability of the FeSAsOH solids at different solution pHs and temperatures are examined. The structural and morphological variations of the synthetical FeSAsOH phases before and after dissolution are examined using various instruments; besides, the potential for arsenic fixation is discussed.

2. Materials and Methods

2.1. Synthesis. To prepare the starting solutions, the analytic-reagent grade $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ (Shanghai Aladdin Biochemical Technology Co., Ltd.) and As_2O_5 (Hengyang Industrial Corporation, Shuikoushan Mining Administration, Hunan, China) were dissolved in ultrapure water in the chosen mole proportion to give various starting Fe(III)/AsO_4 and SO_4/AsO_4 mole ratios (Table 1). The starting solutions were used at their natural pHs ($0.49\text{--}0.90$). Finally, each resulting mixture was vigorously agitated at 600 r/min for 0.5 h and then moved into a 0.2 L stainless-steel autoclave. After heating at 200°C for 1 day, the resulting slurry was cooled and separated using vacuum filtration. Finally, the precipitate was cleaned 3 times by using ultrapure water and dried at 110°C for 1 day.

2.2. Characterization. To determine the bulk compositions, 50 mg of each basic ferric sulfate-arsenate was digested in 20 mL 6 M hydrochloric acid that was diluted to 50 mL by using HNO_3 solution. The iron, sulfur, and arsenic concentrations were analyzed by a Perkin-Elmer Optima 7000DV inductively coupled plasma-optical emission spectrometer (ICP-OES) with the proper reference standards. The H_2O contents were then estimated by the mass balance based on the thermal analytic results, which were obtained from 30°C to 1135°C in nitrogen gas using a Netzsch STA 409 thermogravimetric analyzer (TGA). All of the prepared solids before and after dissolution were studied by an X'Pert PRO X-ray diffractometer (XRD) with $\text{Cu-K}\alpha$ radiation of $1.540598\text{ \AA}$ (40 mA and 40 kV) in the 2θ range from 5° to 90° at the scan step of 0.0263° and the scan rate of $5.3333^\circ/\text{min}$ and recognized by comparing the recorded XRD spectra to literature references. The functional groups and the morphologies of the basic ferric sulfate-arsenates were analyzed by a Nicolet Nexus 470 Fourier transform infrared spectrophotometer (FT-IR) over the spectral range from 400 to 4000 cm^{-1} and a Jeol JSM-7900F field emission scanning electron microscope (FE-SEM) with an energy dispersive spectrometer (EDS), respectively.

2.3. Dissolution Tests. Five grams of each dried basic ferric sulfate-arsenate was added to 0.1 L of HNO_3 solutions (pH 2 and 6) or NaOH solution (pH 10) in a polypropylene bottle, which was capped and put in the temperature-control water bathes (25°C , 35°C , or 45°C). The pHs of the mixing slurries with no adjustment were recorded periodically. 5 mL of the solution from each bottle was collected at the fixed intervals

TABLE 1: Preparation and component of the synthetical basic ferric sulfate-arsenates.

Sample	Precursor solution (100 mL)				Mole ratio		Solid composition [Fe(SO ₄) _x (AsO ₄) _y (OH) _z ·nH ₂ O]
	Fe(III) + SO ₄ solution Fe ₂ (SO ₄) ₃ ·9H ₂ O (g)	H ₂ O (mL)	H ₃ AsO ₄ solution 1 M H ₃ AsO ₄ (mL)	H ₂ O (mL)	Fe/AsO ₄	SO ₄ /AsO ₄	
FeSAsOH-1	5.6201	50	10	40	2.00	3.00	Fe(SO ₄) _{0.27} (AsO ₄) _{0.73} (OH) _{0.27} ·0.26H ₂ O
FeSAsOH-2	8.4302	50	10	40	3.00	4.50	Fe(SO ₄) _{0.37} (AsO ₄) _{0.59} (OH) _{0.49} ·0.28H ₂ O
FeSAsOH-3	8.4302	50	15	35	2.00	3.00	Fe(SO ₄) _{0.27} (AsO ₄) _{0.72} (OH) _{0.30} ·0.21H ₂ O
FeSAsOH-4	8.4302	50	20	30	1.50	2.25	Fe(SO ₄) _{0.28} (AsO ₄) _{0.74} (OH) _{0.22} ·0.28H ₂ O + FeAsO ₄ ·0.75H ₂ O mixture
FeSAsOH-5	11.2402	50	20	30	2.00	3.00	Fe(SO ₄) _{0.24} (AsO ₄) _{0.70} (OH) _{0.42} ·0.16H ₂ O

from 1 h to 330 days, filtered and immediately stabilized using 0.2% HNO₃ solution, followed by the measurement for iron, sulfur, and arsenic using ICP-OES or an atomic absorption spectrometer (AAS, Perkin-Elmer AAnalyst 700). To hold the starting volume constant, the equivolume HNO₃ or NaOH solutions were supplemented after each sampling. The effect of this volumetric variation on the elemental concentrations was considered in the following thermodynamic simulation. After 330 days (7920 h), the remaining solids were taken out from the bottles and characterized using various instruments, as described formerly. At initial pH 2, the tests were made twice to check the repeatability.

3. Results and Discussion

3.1. Solid Characterization

3.1.1. Solid Composition. The ICP-OES and TGA analysis of the synthetic basic ferric sulfate-arsenates (FeSAsOH) enabled the proportion determination of the main constituents to be described as follows: 41.49 wt% Fe₂O₃, 11.23 wt% SO₃, 43.59 wt% As₂O₅, and 3.68 wt% H₂O for the sample FeSAsOH-1, which corresponded approximately to the values for the chemical compound with the formula of Fe(SO₄)_{0.27}(AsO₄)_{0.73}(OH)_{0.27}·0.26H₂O when it was normalized to Fe = 1.00, and the increase in AsO₄ in the synthetic solids decreased the requirement for OH⁻ to keep the charge balances; i.e., OH⁻ ions were applied to balance the charges (Table 1). These data were also in good agreement with the empirical formulas of the arsenic-containing compound “Type 2” [Fe₄(SO₄)_y(AsO₄)₃(OH)_x] [13], the precipitate “Phase 3” [Fe_x(SO₄, AsO₄)(OH)_y·nH₂O] [11], the arsenical compound “Ba-5” [Fe(SO₄)_x(AsO₄)_{1-x}(OH)_x·(1-x) H₂O] [3, 4], and the FeSAsOH [Fe(SO₄)_{0.7-0.2}(AsO₄)_{0.2-0.7}(OH)_{0.7-0.2}] [9]. Accordingly, the formulas for the samples FeSAsOH-2, FeSAsOH-3, and FeSAsOH-5 were also determined (Table 1). The sample FeSAsOH-4 was a mixture of the FeSAsOH with the formula Fe(SO₄)_{0.28}(AsO₄)_{0.74}(OH)_{0.22}·0.28H₂O and the ferric orthoarsenate subhydrate [FeAsO₄·0.75H₂O] (Table 1).

3.1.2. XRD. The XRD spectra of the basic ferric sulfate-arsenates are shown in Figure 1 and Figure S1 in Supplementary Materials. In the patterns, the major peak positions of the basic ferric sulfate-arsenates “Ba-5” [3], “Phase 3” [11], and “Type 2” [13] were plotted in the higher chart.

The samples FeSAsOH-1 and FeSAsOH-3 agreed well with the arsenical compound “Type 2” [13] in the major peak positions in the XRD spectra (Figure 1) with the strongest lines (*d*_{obs}, *I*_{obs}) of 3.38(100), 3.26(44), 2.64(15), 1.63(11), 2.33(11), and 2.06(10).

The samples FeSAsOH-2 and FeSAsOH-5 were also in agreement with the arsenical compounds “Type 2” [13] in the major peak positions (Figure 1, Figure S1 in Supplementary Materials). The major XRD peaks showed that the sample FeSAsOH-4 was identified as a mixture of the basic ferric arsenate sulfate [13] and ferric orthoarsenate subhydrate [FeAsO₄·0.75H₂O] (Figure 1, Figure S1 in Supplementary Materials), which was related to its forming condition [3, 16]. It was also reported previously that some of the ferric sulfate-arsenate (FAS) samples contained trace-to-minor amount of the basic ferric sulfate (BFS), as indicated by the presence of overlapping peaks at 2θ values of -26.5° and 27.5°, which occurred as the asymmetric and broadened peaks. The acicular crystals of the ferric orthoarsenate subhydrate (FeAsO₄·0.75H₂O) occurred in trace amounts in the samples [9]. No obvious variations were recognized in the XRD spectra after dissolution (Figure 1, Figure S1 in Supplementary Materials).

3.1.3. FT-IR. The FT-IR spectra for the basic ferric sulfate-arsenates before and after dissolution for 330 d were recorded (Figure 2, Figure S2 in Supplementary Materials) and assigned with reference to the literature [2–4, 17, 18]. No significant variations could be viewed in the spectra after dissolution. It could serve as a simple method to identify the functional groups on the precipitate surface. All spectra showed the vibrations of SO₄²⁻, AsO₄³⁻, OH⁻, and M-O [19, 20]. No split was observed for the stretching vibrations of the FeO₆ octahedra [17].

The OH stretching regions from 2800 cm⁻¹ to 3800 cm⁻¹ were characterized by the bands at 3537–3552, 3448–3471, and 3408–3415 cm⁻¹ for the sample FeSAsOH-1. The OH stretching bands at 3408–3415 cm⁻¹ indicated the existence of the strong H-bonds. The higher wavenumber vibration is regularly assigned to the weak H-bonding. The H₂O bending (1626–1639 cm⁻¹) vibration is unrecognized in the vibrational structure when the hydration degree is insignificant [2–4]. The 1626–1639 cm⁻¹ bands were readily ascribed to be bending of adsorbed water, i.e., the framework deformation vibrations of H-bonded H₂O molecules [15].

FIGURE 1: XRD spectra of the synthetic basic ferric sulfate-arsenates before and after dissolution for 330 days.

The free SO_4^{2-} ions have the same tetrahedral symmetry as the free AsO_4^{3-} ions, and both show four fundamental vibrations, i.e., ν_1 , ν_2 , ν_3 , and ν_4 at 983, 450, 1105, and 611 cm^{-1} for SO_4^{2-} and at 818, 350, 786, and 405 cm^{-1} for AsO_4^{3-} , respectively [2–4]. In the present work, the structural SO_4^{2-} exhibited the ν_1 , ν_2 , ν_3 , and ν_4 vibrations at 1032–1034, 434–438, 1130–1134, and 640 cm^{-1} , respectively [19]. The 849–852 and 785–791 cm^{-1} bands were the ν_1 and ν_3 vibrations of AsO_4^{3-} , respectively [2–4]. The 582–584 cm^{-1} bands were possibly the OH bending vibrations or the stretching vibrations of Fe–OH₂ [2]. The 501–505 cm^{-1} vibrations were ascribed to Fe–O–As.

The FT-IR spectra of FeSAsOH-1, FeSAsOH-3, and FeSAsOH-5 were very similar. The FT-IR spectra of FeSAsOH-2 showed a stronger $\nu_1(\text{SO}_4)$ vibration at 1032–1034 cm^{-1} , a weaker $\nu_4(\text{SO}_4)$ vibration at 640 cm^{-1} , and a weaker Fe–OH₂ stretching vibration at 582–584. The FT-IR spectra of FeSAsOH-4 showed a weaker $\nu_3(\text{SO}_4)$ vibration at 1128–1136 cm^{-1} and stronger $\nu_2(\text{SO}_4)$ vibration

FIGURE 2: FT-IR spectra of the basic ferric sulfate-arsenate [FeSAsOH-1] before and after dissolution for 330 days.

at 442–457 cm^{-1} in comparison to the sample FeSAsOH-1. The weak $\nu_1(\text{AsO}_4)$ vibration at 804–808 cm^{-1} and strong $\nu_1(\text{AsO}_4)$ vibration at 858 cm^{-1} in the FT-IR spectra of FeSAsOH-4 were considered as the contributions of the ferric orthoarsenate subhydrate and FeSAsOH, respectively (Figure 2, Figure S2 in Supplementary Materials).

3.1.4. FE-SEM. It was suggested that the crystal structure of the basic ferric sulfate-arsenates could be related to monoclinic polytypes [4, 11] and orthorhombic-monoclinic [2] and triclinic (pseudo-orthorhombic) crystal systems [9]. The morphologies of the synthetic basic ferric sulfate-arsenates before and after dissolution for 330 days, which were evaluated by X-ray diffraction, were also examined by FE-SEM with EDS (Figures 3–5, Figure S3 in Supplementary Materials).

For the synthetic solid FeSAsOH-1, the particles consisted of aggregates and the individual crystallites were generally the well-shaped monoclinic prismatic crystals with the size of <5 μm (Figure 3). The EDS analysis showed that the surface had a relatively higher As/(As + S) molar ratio (0.77–0.85) than that of the bulk solid (0.73). After the dissolution at different temperatures and pHs for 330 d, almost all tops of the crystals and some edges and corners were corroded, and finally, the crystals became smoothed/rounded (Figures 3 and 4).

For the synthetic solid FeSAsOH-4, the basic ferric sulfate-arsenate particles appeared in two shapes: the well-shaped monoclinic prismatic crystals and the rounded type particles (Figure 5). The EDS results confirmed that the two shapes were identical, with one grown to its full monoclinic

FIGURE 3: FE-SEM-EDS results of the basic ferric sulfate-arsenate [FeSAsOH-1] showing the (a) well-shaped monoclinic crystals and the crystals (b) before and (c) after dissolution.

FIGURE 4: FE-SEM images of the basic ferric sulfate-arsenate [FeSAsOH-1] before and after dissolution for 330 days.

FIGURE 5: FE-SEM-EDS results of (a) basic ferric sulfate-arsenate [FeSAsOH-4 , $\text{Fe}(\text{SO}_4)_{0.28}(\text{AsO}_4)_{0.74}(\text{OH})_{0.22} \cdot 0.28\text{H}_2\text{O}$] and (b) ferric orthoarsenate subhydrate [$\text{FeAsO}_4 \cdot 0.75\text{H}_2\text{O}$].

crystal and the other redissolved and/or recrystallized to form its rounded shape having the $\text{As}/(\text{As} + \text{S})$ molar ratios of 0.85–0.89 and 0.85–0.87, respectively (Figure 5). Furthermore, the ferric orthoarsenate subhydrate [$\text{FeAsO}_4 \cdot 0.75\text{H}_2\text{O}$] aggregates appeared in the well-shaped triclinic prismatic crystals without terminations having the $\text{As}/(\text{As} + \text{S})$ mole ratios of 0.98–1.00 and with terminations having the $\text{As}/(\text{As} + \text{S})$ mole ratios of 0.94–0.97 (Figure 5), which was well in accordance with the XRD analysis (Figure 1).

Similar to FeSAsOH-1 , almost all tops of the crystals and some edges and corners were dissolved, and the crystals became smoothed/rounded after the dissolution at different temperatures and pHs for 330 d (Figure S3, Supplementary material).

3.2. Solution Evolution during Dissolution

3.2.1. FeSAsOH-1 . For the dissolution of the sample FeSAsOH-1 [$\text{Fe}(\text{SO}_4)_{0.27}(\text{AsO}_4)_{0.73}(\text{OH})_{0.27} \cdot 0.26\text{H}_2\text{O}$] at 25°C and initial pH 2 (Figure 6), the aqueous pHs fluctuated between 1.88 and 2.09 and attained a steady state of 1.98 after

5760 h. At initial pH 6, the pHs decreased gradually to 3.51 within 48 h and then increased steadily to 3.68 after 5040 h. At initial pH 10, the pHs decreased gradually to 3.77 within 2880 h and then increased steadily to 4.04 after 5040 h.

The released Fe^{3+} concentrations rose gradually to 0.122–0.123 mmol/L after 5760 h. The final Fe^{3+} concentrations declined from 0.122 to 0.123 mmol/L to 0.000203–0.000217 mmol/L as the initial pH was increased from 2 to 10 for the dissolution at 25°C (Figure 6).

The dissolved SO_4^{2-} concentrations rose quickly to 0.073130 mmol/L within 12 h and then declined/increased with a slight fluctuation to 0.096832–0.099170 mmol/L after 5760 h for the dissolution at 25°C and pH 2. The final SO_4^{2-} concentrations declined from 0.096832 to 0.099170 mmol/L to 0.072195–0.072663 mmol/L as the initial pH was increased from 2 to 10 for the dissolution at 25°C and rose obviously to 0.244496–0.247302 mmol/L as the temperature was increased from 25°C to 45°C .

The dissolved AsO_4^{3-} concentrations rose quickly to 0.091229 mmol/L after 12 h and then slightly declined to 0.019954–0.026161 mmol/L over 12–120 h, and after that, it increased/decreased once again steadily to 0.059796–0.060330 mmol/L after 5760 h for the dissolution at 25°C and pH 2 (Figure 6). The final dissolved AsO_4^{3-} concentrations at 25°C and pH 6 were found to be the lowest of 0.006838–0.006851 mmol/L, and it declined from 0.019954 to 0.026161 to 0.035103–0.036772 mmol/L as the temperature was increased from 25 to 45°C .

3.2.2. $\text{FeSAsOH-2-FeSAsOH-5}$. For the dissolution of the FeSAsOH-3 [$\text{Fe}_{1.00}(\text{SO}_4)_{0.27}(\text{AsO}_4)_{0.72}(\text{OH})_{0.30} \cdot 0.21\text{H}_2\text{O}$] and FeSAsOH-5 [$\text{Fe}_{1.00}(\text{SO}_4)_{0.24}(\text{AsO}_4)_{0.70}(\text{OH})_{0.42} \cdot 0.16\text{H}_2\text{O}$] samples at different initial pHs and temperatures (Figure S4 in Supplementary Materials), the aqueous pHs and the elemental concentrations of iron, arsenate, and sulfate showed almost the same evolution trends as in the sample FeSAsOH-1 [$\text{Fe}_{1.00}(\text{SO}_4)_{0.27}(\text{AsO}_4)_{0.73}(\text{OH})_{0.27} \cdot 0.26\text{H}_2\text{O}$], because the three samples had almost the same components.

For the dissolution of the FeSAsOH-2 [$\text{Fe}_{1.00}(\text{SO}_4)_{0.37}(\text{AsO}_4)_{0.59}(\text{OH})_{0.49} \cdot 0.28\text{H}_2\text{O}$] sample at different initial pHs and temperatures (Figure S4 in Supplementary Materials), the aqueous pHs and the elemental concentrations of iron, arsenate, and sulfate showed almost the same evolution trends as in the FeSAsOH-1 , FeSAsOH-3 , and FeSAsOH-5 samples, but with higher concentrations of the final dissolved Fe^{3+} and SO_4^{2-} and lower concentration of the final dissolved AsO_4^{3-} . As assumed, it could be related to the fact that the sample FeSAsOH-2 had a lower AsO_4/SO_4 mole ratio in comparison to the FeSAsOH-1 , FeSAsOH-3 , and FeSAsOH-5 samples.

For the dissolution of the sample FeSAsOH-4 [$\text{Fe}_{1.00}(\text{SO}_4)_{0.28}(\text{AsO}_4)_{0.74}(\text{OH})_{0.22} \cdot 0.28\text{H}_2\text{O} + \text{FeAsO}_4 \cdot 0.75\text{H}_2\text{O}$ mixture] at 25°C and initial pH 2 (Figure S4 in Supplementary Materials), the aqueous pHs and elemental concentrations of iron, sulfate, and arsenate showed almost the similar evolution trends as in the samples FeSAsOH-1 , FeSAsOH-2 , FeSAsOH-3 , and FeSAsOH-5 , although the

FIGURE 6: Solution evolution during the dissolution of the basic ferric sulfate-arsenate $[\text{FeSAsOH-1}, \text{Fe}(\text{SO}_4)_{0.27}(\text{AsO}_4)_{0.73}(\text{OH})_{0.27} \cdot 0.26\text{H}_2\text{O}]$ at 25–45°C and initial pH 2–10 for 330 days.

sample FeSAsOH-4 contained trace amount of $\text{FeAsO}_4 \cdot 0.75\text{H}_2\text{O}$.

The concentrations of the released arsenate showed the lowest value of 0.006837–0.006851 mmol/L (~ 0.51 mg/L As), 0.000604–0.000608 mmol/L (~ 0.045 mg/L As), 0.009817–0.010044 mmol/L (~ 0.75 mg/L As), 0.005991–0.006026 mmol/L (~ 0.45 mg/L As), and 0.001844–0.001853 mmol/L (~ 0.139 mg/L As) for the dissolution of FeSAsOH-1–FeSAsOH-5 at different temperatures and pHs, respectively (Figure 6, Figure S4 in Supplementary Materials). In the previous studies, it was shown that, during short-term environmental stability tests, pure basic ferric sulfate-arsenates release less than 5 mg/L of arsenic into solution [3]. The “Type 2” with an X_{As} mole fraction of 0.75 produced a similar As concentration (i.e., 0.8 mg/L) in the TCLP leaching [13].

3.3. Dissolution Mechanism

3.3.1. *FeSAsOH-1*. The dissolution of the FeSAsOH-1 sample $[\text{Fe}(\text{SO}_4)_{0.27}(\text{AsO}_4)_{0.73}(\text{OH})_{0.27} \cdot 0.26\text{H}_2\text{O}]$ is expressed by

Accordingly, one mole of the FeSAsOH-1 sample would release 0.27 mol OH^- . Thus, this dissolution in stronger acidic solution could deplete H^+ ions causing an increase in solution pH, while the dissolution in alkaline medium could deplete OH^- ions causing a decrease of solution pH. The complexations would control the speciations of all released constituents (equation (2)–equation (4)).

For the dissolution of the sample FeSAsOH-1 at initial pH 2 (Figure 6), the aqueous AsO_4/Fe molar ratios attained 1.53–22.64 within 1 h and then declined to the solid stoichiometric AsO_4/Fe molar ratio of 0.73 in 12–24 h and finally to 0.49–0.52 (25°C), 0.24–0.28 (35°C), and 0.13–0.14 (45°C) after 5760 h of dissolution. This means that, at the beginning, AsO_4^{3-} was favorably released from solid into solution with respect to Fe^{3+} .

The solution SO_4/Fe molar ratios varied between 0.50 and 3.46 and approached continuously to 0.59–0.60 (25°C), 0.89–0.90 (35°C), and 0.91 (45°C) after 5760 h (240 d) of dissolution. The ratio was always higher than 0.27, the stoichiometric SO_4/Fe molar ratio of the solid; i.e., SO_4^{2-} was also preferentially released into solution with respect to Fe^{3+} .

The solution AsO_4/SO_4 molar ratios attained 3.92–8.15 within 1 h and afterward decreased to the solid stoichiometric ratio of 2.70 in 1–3 h and finally to 0.86–0.87 (25°C), 0.30–0.31 (35°C), and 0.14–0.15 (45°C) after 5760 h. AsO_4^{3-} ions were preferentially dissolved into solution in comparison with SO_4^{2-} at the beginning of dissolution.

All constituents were preferentially dissolved in the order of $\text{AsO}_4^{3-} > \text{SO}_4^{2-} > \text{Fe}^{3+}$ within 1–3 h, in the order of $\text{SO}_4^{2-} > \text{AsO}_4^{3-} > \text{Fe}^{3+}$ from 1–3 h to 12–24 h, and finally in the order of $\text{SO}_4^{2-} > \text{Fe}^{3+} > \text{AsO}_4^{3-}$, indicating a nonstoichiometric dissolution of the basic ferric sulfate-arsenate FeSAsOH-1 and/or formation of $\text{AsO}_4^{3-}/\text{Fe}$ -rich residuals at initial pH 2. Additionally, the higher initial pHs (6 and 10) could obviously inhibit the release of Fe^{3+} from solid into solution and prefer to form iron-rich residuals, and the solid components were released in the order of $\text{SO}_4^{2-} > \text{AsO}_4^{3-} > \text{Fe}^{3+}$.

The speciation of toxic metals and metalloids is an important factor for their mobility in the environment [1]. During the dissolution of the basic ferric sulfate-arsenate FeSAsOH-1 at initial pH 2, the released components existed mainly as $\text{Fe}^{3+}/\text{Fe}(\text{OH})^{2+}/\text{FeSO}_4^+$, $\text{H}_3\text{AsO}_4^0/\text{H}_2\text{AsO}_4^-$, and $\text{HSO}_4^-/\text{SO}_4^{2-}/\text{FeSO}_4^+$ for iron, arsenate, and sulfate, respectively. For the dissolution of FeSAsOH-1 at different temperatures and pHs (Figure 6), all solutions were undersaturated with respect to $\text{Fe}_2(\text{SO}_4)_3$, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$, maghemite, ferrihydrite, and H-jarosite, suggesting that the formation of all these ferric sulfates/arsenates was thermodynamically unfavorable. By contrast, all solutions were very closely saturated or oversaturated in respect to lepidocrocite ($\text{SI} = -1.90$ – 2.46), goethite ($\text{SI} = -0.36$ – 3.34), and hematite ($\text{SI} = 1.77$ – 9.07), suggesting that the formation of these iron-rich precipitates was thermodynamically favorable. Even though the XRD measurement indicated that no

other phases than the basic ferric sulfate-arsenates existed, their presence in a small amount under the detection limit could not be excluded (Figure 1).

The FeSAsOH structure is constructed from layered FeO_6 octahedra that are cross-linked by AsO_4 and SO_4 tetrahedra (Figure 7) [4, 9, 18]. For the dissolution of the basic ferric sulfate-arsenate [FeSAsOH-1] at $\text{pH} \geq 2$, the gradual decrease in solution pH indicated an OH^- depleting. The reaction was expressed by the favorable release of AsO_4^{3-} , followed by SO_4^{2-} and Fe^{3+} from solid into solution, whereas Fe^{3+} was preferentially left behind to form a residual octahedral outlier (Figure 7). The components at the tops of the crystals were first dissolved and the crystal surfaces were gradually smoothed/rounded until all edges and corners disappeared (Figure 7). In the subsequent recrystallization, the arsenate ions and Fe^{3+} cations were also preferentially removed from the aqueous solution, while sulfate ions were preferentially left in the aqueous solution. The dissolution was finally restricted by the Fe-O(H) breakdown in the FeO_6 octahedra and obstructed by the OH^- and AsO_4 tetrahedra outliers.

This could be also verified by comparing the FE-SEM-EDS measurements on the FeSAsOH-1 surface before and after dissolution at 25°C and initial pH 2 for 7920 h, which showed that the $(\text{AsO}_4 + \text{SO}_4)/\text{Fe}$, AsO_4/Fe , and SO_4/Fe molar ratios increased from 1.06, 0.85, and 0.20 to 0.99, 0.80, and 0.19 after 330 days of dissolution, respectively. The $\text{AsO}_4/(\text{AsO}_4 + \text{SO}_4)$ mole ratios on the solid surface showed no obvious variation after dissolution. In consideration of the crystal structure of $\text{FeSO}_4(\text{OH})$, the nonstoichiometric dissolution behavior can be explained by the precipitation of a ferric oxyhydroxide phase or by the preferential release of SO_4 leaving behind chains of FeO_6 octahedra [9].

3.3.2. FeSAsOH-2–FeSAsOH-5. For the dissolution of the basic ferric sulfate-arsenates FeSAsOH-2, FeSAsOH-3, and FeSAsOH-5, all components preferred to be released in the order of $\text{AsO}_4^{3-} > \text{SO}_4^{2-} > \text{Fe}^{3+}$ within 1–3 h, in the order of $\text{SO}_4^{2-} > \text{AsO}_4^{3-} > \text{Fe}^{3+}$ from 1 to 3 h to ~24 h, and finally, in the order of $\text{SO}_4^{2-} > \text{Fe}^{3+} > \text{AsO}_4^{3-}$, suggesting a nonstoichiometric dissolution and/or formation of $\text{AsO}_4^{3-}/\text{Fe}$ -rich residuals at initial pH 2 (Figure S4 in Supplementary Materials). Additionally, the higher initial pHs (6.00 and 10.00) could obviously inhibit the release of Fe^{3+} from solid into solution and prefer to form iron-rich residual, and the solid components were released in the order of $\text{SO}_4^{2-} > \text{AsO}_4^{3-} > \text{Fe}^{3+}$.

For the dissolution of FeSAsOH-4, all components were preferentially released in the order of $\text{AsO}_4^{3-} > \text{SO}_4^{2-} > \text{Fe}^{3+}$ in ~1 h, in the order of $\text{SO}_4^{2-} > \text{AsO}_4^{3-} > \text{Fe}^{3+}$ from ~1 h to ~45 d, and finally, in the order of $\text{SO}_4^{2-} > \text{Fe}^{3+} > \text{AsO}_4^{3-}$ after ~45 d, suggesting a nonstoichiometric dissolution and/or formation of $\text{AsO}_4^{3-}/\text{Fe}$ -rich residuals at initial pH 2 (Figure S4 in Supplementary Materials). Additionally, the higher initial pHs (6.00 and 10.00) could obviously inhibit the release of Fe^{3+} from solid into solution and prefer to form iron-rich residual, and the solid components were released in the order of $\text{SO}_4^{2-} > \text{AsO}_4^{3-} > \text{Fe}^{3+}$. However, it was also observed that the aqueous solutions for the

FIGURE 7: Dissolution mechanism of the basic ferric sulfate-arsenates in aqueous solution.

FeSAsOH-4 sample showed a slower evolution than those for FeSAsOH-1 and FeSAsOH-3, which was related to the higher H_2O mole ratio in FeSAsOH-4.

3.4. Solubility Calculation. Based on the batch dissolution results of the synthetic basic ferric sulfate-arsenates, the computing of the aqueous Fe^{3+} , SO_4^{2-} , AsO_4^{3-} , and OH^- activities in the final steady state (5760 h, 6480 h, 7200 h, and 7920 h) was achieved by the PHREEQC program [21] with the minteq.v4.dat database [22] and the thermodynamic properties for aqueous metal-arsenate species [23, 24]. The ion activity products ($\log_{\text{IAP}}$) for the basic ferric sulfate-arsenates were calculated, which were equal to their solubility products ($\log_{K_{\text{sp}}}$) at the dissolution equilibrium. The key speciations are summarized in Table S1 in Supplementary Materials.

The dissolution of the basic ferric sulfate-arsenates $[\text{Fe}(\text{SO}_4)_x(\text{AsO}_4)_y(\text{OH})_z \cdot n\text{H}_2\text{O}]$ is described by

The ion activity product (IAP) is expressed according to

$$\text{IAP} = \{\text{Fe}^{3+}\}^{1.00} \{\text{SO}_4^{2-}\}^x \{\text{AsO}_4^{3-}\}^y \{\text{OH}^-\}^z, \quad (7)$$

where $\{\}$ is the aqueous activity of Fe^{3+} , SO_4^{2-} , AsO_4^{3-} , or OH^- .

By using the Gibbs free energies of formation (ΔG_f°), $\Delta G_f^\circ[\text{Fe}^{3+}] = -4.6 \text{ kJ/mol}$, $\Delta G_f^\circ[\text{SO}_4^{2-}] = -744.6 \text{ kJ/mol}$, $\Delta G_f^\circ[\text{AsO}_4^{3-}] = -647.618 \text{ kJ/mol}$, $\Delta G_f^\circ[\text{OH}^-] = -157.3 \text{ kJ/mol}$, and $\Delta G_f^\circ[\text{H}_2\text{O}] = -237.18 \text{ kJ/mol}$ [24, 25], the ΔG_f° values for the synthetic basic ferric sulfate-arsenates $[\text{Fe}(\text{SO}_4)_x(\text{AsO}_4)_y(\text{OH})_z \cdot n\text{H}_2\text{O}]$ were calculated, suggesting that the IAPs to the end of dissolution (5760–7920 h) were equal to the K_{sp} values for the basic ferric sulfate-arsenates. At the thermodynamic standard state, the standard free energy of reaction (ΔG_r°) is estimated according to

$$\Delta G_r^\circ = -5.708 \log_{\text{IAP}}. \quad (8)$$

For equation (6),

$$\begin{aligned} \Delta G_r^\circ &= 1.00\Delta G_f^\circ[\text{Fe}^{3+}] + x\Delta G_f^\circ[\text{SO}_4^{2-}] + y\Delta G_f^\circ[\text{AsO}_4^{3-}] \\ &\quad + z\Delta G_f^\circ[\text{OH}^-] + \\ &\quad n\Delta G_f^\circ[\text{H}_2\text{O}] - \Delta G_f^\circ[\text{Fe}(\text{SO}_4)_x(\text{AsO}_4)_y(\text{OH})_z \cdot n\text{H}_2\text{O}]. \end{aligned} \quad (9)$$

Rearranging,

$$\begin{aligned} \Delta G_f^\circ[\text{Fe}(\text{SO}_4)_x(\text{AsO}_4)_y(\text{OH})_z \cdot n\text{H}_2\text{O}] &= 1.00\Delta G_f^\circ[\text{Fe}^{3+}] + \\ &\quad x\Delta G_f^\circ[\text{SO}_4^{2-}] + y\Delta G_f^\circ[\text{AsO}_4^{3-}] + z\Delta G_f^\circ[\text{OH}^-] \\ &\quad + n\Delta G_f^\circ[\text{H}_2\text{O}] - \Delta G_r^\circ. \end{aligned} \quad (10)$$

TABLE 2: Experimental data and solubility determination for the basic ferric sulfate-arsenate FeSAsOH-1 $[\text{Fe}(\text{SO}_4)_{0.27}(\text{AsO}_4)_{0.73}(\text{OH})_{0.27-0.26}\text{H}_2\text{O}]$.

Temp (°C)	Initial pH	Time (h)	Dissolution data (mmol/L)				log_IAP	Mean log_IAP	ΔG_f° (kJ/mol)	Mean ΔG_f° (kJ/mol)
			pH	Fe	SO ₄	AsO ₄				
25 ^a	2	5760	1.98	0.122388	0.099170	0.060330	-23.04	-23.04	-914.05	-914.06
		6480	1.98	0.122030	0.096832	0.059796	-23.05	±0.01	-914.09	±0.03
		7200	1.98	0.123373	0.099482	0.059996	-23.04		-914.04	
		7920	1.98	0.122746	0.099170	0.059863	-23.04		-914.06	
25	6	5760	3.68	0.000252	0.069076	0.007664	-25.19	-25.22	-926.33	-926.47
		6480	3.68	0.000253	0.068764	0.006838	-25.23	±0.03	-926.53	±0.14
		7200	3.68	0.000257	0.069232	0.006851	-25.22		-926.49	
		7920	3.68	0.000254	0.068453	0.006837	-25.22		-926.52	
25	10	5760	4.03	0.000217	0.072195	0.010698	-25.22	-25.24	-926.50	-926.59
		6480	4.04	0.000203	0.072195	0.010925	-25.25	±0.02	-926.64	±0.09
		7200	4.04	0.000207	0.072663	0.010887	-25.24		-926.59	
		7920	4.04	0.000203	0.072351	0.010961	-25.24		-926.63	
25 ^b	2	5760	1.98	0.130983	0.079056	0.068739	-22.99	-22.97	-913.76	-913.64
		6480	1.99	0.132236	0.078588	0.069339	-22.96	±0.02	-913.60	±0.12
		7200	1.99	0.132594	0.079991	0.068538	-22.96		-913.61	
		7920	1.99	0.133669	0.079523	0.068605	-22.96		-913.59	
35	2	5760	1.94	0.152202	0.135814	0.041910	-23.06	-23.04		
		6480	1.95	0.153634	0.138153	0.042044	-23.03	±0.02		
		7200	1.95	0.153813	0.136593	0.041510	-23.04			
		7920	1.95	0.153545	0.136749	0.041910	-23.04			
45	2	5760	1.91	0.267427	0.244496	0.036772	-22.86	-22.86		
		6480	1.92	0.272351	0.246679	0.035837	-22.84	±0.02		
		7200	1.91	0.270829	0.247302	0.035103	-22.87			
		7920	1.91	0.271187	0.246211	0.035771	-22.86			

^{a,b}Dissolution tests in duplicate.TABLE 3: Experimental data and solubility determination for the basic ferric sulfate-arsenate FeSAsOH-2 $[\text{Fe}(\text{SO}_4)_{0.37}(\text{AsO}_4)_{0.59}(\text{OH})_{0.49} \cdot 0.28\text{H}_2\text{O}]$.

Temp (°C)	Initial pH	Time (h)	Dissolution data (mmol/L)				log_IAP	Mean log_IAP	ΔG_f° (kJ/mol)	Mean ΔG_f° (kJ/mol)
			pH	Fe	SO ₄	AsO ₄				
25 ^a	2	5760	2.08	1.466507	1.233705	0.077881	-22.03	-22.01	-931.40	-931.31
		6480	2.09	1.469193	1.222011	0.078749	-22.00	±0.02	-931.28	±0.09
		7200	2.09	1.468476	1.222011	0.078682	-22.00		-931.28	
		7920	2.09	1.469551	1.220452	0.078349	-22.00		-931.29	
25	6	5760	3.00	0.065984	0.634473	0.000728	-23.46	-23.45	-939.59	-939.56
		6480	3.00	0.066342	0.642113	0.000745	-23.45	±0.01	-939.54	±0.03
		7200	3.00	0.066432	0.641022	0.000730	-23.46		-939.57	
		7920	3.00	0.066342	0.646479	0.000735	-23.45		-939.55	
25	10	5760	3.05	0.052823	0.601104	0.000611	-23.59	-23.59	-940.35	-940.33
		6480	3.04	0.053987	0.604534	0.000604	-23.59	±0.00	-940.33	±0.02
		7200	3.04	0.054076	0.602195	0.000606	-23.59		-940.32	
		7920	3.04	0.054041	0.601572	0.000608	-23.59		-940.32	
25 ^b	2	5760	2.06	1.463821	1.244932	0.073477	-22.08	-22.06	-931.70	-931.62
		6480	2.07	1.462030	1.235109	0.074745	-22.06	±0.02	-931.58	±0.08
		7200	2.07	1.461672	1.226377	0.074011	-22.06		-931.59	
		7920	2.07	1.462925	1.228872	0.073677	-22.06		-931.60	
35	2	5760	2.02	1.420846	1.403979	0.060930	-22.11	-22.10		
		6480	2.02	1.423532	1.405071	0.060797	-22.11	±0.01		
		7200	2.03	1.426218	1.396495	0.060130	-22.09			
		7920	2.02	1.425144	1.401173	0.060730	-22.11			
45	2	5760	1.97	1.292818	1.598266	0.057994	-22.17	-22.19		
		6480	1.96	1.283865	1.626333	0.058461	-22.19	±0.02		
		7200	1.96	1.277598	1.615886	0.058261	-22.19			
		7920	1.96	1.282970	1.611676	0.058394	-22.19			

^{a,b} Dissolution tests in duplicate.

TABLE 4: Experimental data and solubility determination for the basic ferric sulfate-arsenate FeSAsOH-3 [$\text{Fe}(\text{SO}_4)_{0.27}(\text{AsO}_4)_{0.72}(\text{OH})_{0.30} \cdot 0.21\text{H}_2\text{O}$].

Temp (°C)	Initial pH	Time (h)	Dissolution data (mmol/L)				log_IAP	Mean log_IAP	ΔG_f° (kJ/mol)	Mean ΔG_f° (kJ/mol)
			pH	Fe	SO_4	AsO_4				
25 ^a	2	5760	1.97	0.144323	0.103381	0.059262	-23.16	-23.14	-901.14	-901.02
		6480	1.98	0.145487	0.104004	0.059462	-23.14	± 0.02	-900.99	± 0.12
		7200	1.98	0.145755	0.104160	0.059329	-23.14		-900.99	
		7920	1.98	0.145666	0.104472	0.059596	-23.14		-900.98	
25	6	5760	3.91	0.000420	0.068764	0.010056	-25.07	-25.08	-912.05	-912.08
		6480	3.90	0.000417	0.067517	0.009817	-25.08	± 0.01	-912.11	± 0.03
		7200	3.90	0.000414	0.067049	0.010044	-25.08		-912.09	
		7920	3.90	0.000416	0.067829	0.010053	-25.08		-912.07	
25	10	5760	4.22	0.000375	0.083110	0.012148	-25.12	-25.13	-912.28	-912.35
		6480	4.21	0.000367	0.084045	0.011985	-25.13	± 0.01	-912.34	± 0.07
		7200	4.21	0.000363	0.084825	0.011878	-25.13		-912.38	
		7920	4.21	0.000358	0.085293	0.011962	-25.14		-912.40	
25 ^b	2	5760	1.97	0.143249	0.111801	0.057060	-23.17	-23.18	-901.19	-901.21
		6480	1.97	0.145755	0.111489	0.055992	-23.17	± 0.01	-901.19	± 0.11
		7200	1.96	0.144144	0.110163	0.056659	-23.19		-901.32	
		7920	1.97	0.145308	0.111333	0.056793	-23.17		-901.16	
35	2	5760	1.95	0.213082	0.201304	0.041310	-23.04	-23.05		
		6480	1.95	0.216395	0.203642	0.039374	-23.05	± 0.01		
		7200	1.95	0.217290	0.201459	0.039641	-23.04			
		7920	1.95	0.217648	0.201771	0.039308	-23.05			
45	2	5760	1.93	0.314430	0.285037	0.035971	-22.90	-22.89		
		6480	1.93	0.322936	0.287064	0.036238	-22.89	± 0.01		
		7200	1.93	0.322846	0.286596	0.036572	-22.89			
		7920	1.93	0.322936	0.288156	0.036638	-22.89			

^{a,b}Dissolution tests in duplicate.TABLE 5: Experimental data and solubility determination for the basic ferric sulfate-arsenate FeSAsOH-4 [$\text{Fe}(\text{SO}_4)_{0.28}(\text{AsO}_4)_{0.74}(\text{OH})_{0.22} \cdot 0.28\text{H}_2\text{O}$ and $\text{FeAsO}_4 \cdot 0.75\text{H}_2\text{O}$ mixture].

Temp (°C)	Initial pH	Time (h)	Dissolution data (mmol/L)				$\text{Fe}(\text{SO}_4)_{0.28}(\text{AsO}_4)_{0.74}(\text{OH})_{0.22} \cdot 0.28\text{H}_2\text{O}$		$\text{FeAsO}_4 \cdot 0.75\text{H}_2\text{O}$	
			pH	Fe	SO_4	AsO_4	log_IAP	Mean log_IAP	log_IAP	Mean log_IAP
25 ^a	2	5760	1.96	0.131878	0.282386	0.054991	-22.66	-22.64	-23.89	-23.87
		6480	1.97	0.133490	0.271627	0.054323	-22.64	± 0.02	-23.86	± 0.02
		7200	1.97	0.133937	0.276617	0.054857	-22.63		-23.86	
		7920	1.97	0.133848	0.275370	0.054257	-22.63		-23.86	
25	6	5760	3.20	0.000566	0.340704	0.005979	-24.39	-24.40	-25.53	-25.54
		6480	3.20	0.000548	0.337897	0.005991	-24.40	± 0.01	-25.54	± 0.01
		7200	3.20	0.000536	0.338832	0.006026	-24.41		-25.55	
		7920	3.20	0.000539	0.337585	0.006021	-24.41		-25.55	
25	10	5760	3.20	0.000468	0.317314	0.006248	-24.47	-24.48	-25.59	-25.61
		6480	3.20	0.000457	0.313884	0.006032	-24.49	± 0.01	-25.62	± 0.02
		7200	3.20	0.000461	0.313416	0.006066	-24.48		-25.61	
		7920	3.20	0.000458	0.312325	0.006059	-24.49		-25.61	
25 ^b	2	5760	1.95	0.132953	0.281919	0.055792	-22.67	-22.66	-23.91	-23.90
		6480	1.95	0.139488	0.283790	0.055591	-22.65	± 0.01	-23.89	± 0.01
		7200	1.94	0.141100	0.280047	0.055925	-22.66		-23.90	
		7920	1.94	0.140025	0.283322	0.055391	-22.67		-23.91	
35	2	5760	1.94	0.195266	0.389509	0.031099	-22.66	-22.66	-24.03	-24.03
		6480	1.95	0.201264	0.383896	0.030899	-22.63	± 0.03	-24.00	± 0.03
		7200	1.93	0.199742	0.382181	0.030565	-22.68		-24.05	
		7920	1.93	0.200369	0.382492	0.030565	-22.68		-24.05	
45	2	5760	1.89	0.275127	0.484937	0.024692	-22.67	-22.64	-24.12	-24.09
		6480	1.90	0.288914	0.487276	0.024359	-22.63	± 0.03	-24.09	± 0.03
		7200	1.90	0.291511	0.484625	0.024359	-22.63		-24.08	
		7920	1.90	0.289989	0.488680	0.024626	-22.62		-24.08	

^{a,b} Dissolution tests in duplicate.

TABLE 6: Experimental data and solubility determination for the basic ferric sulfate-arsenate FeSAsOH-5 [Fe(SO₄)_{0.24}(AsO₄)_{0.70}(OH)_{0.42}·0.16H₂O].

Temp (°C)	Initial pH	Time (h)	Dissolution data (mmol/L)				log _{IAP}	Mean log _{IAP}	ΔG_f° (kJ/mol)	Mean ΔG_f° (kJ/mol)
			pH	Fe	SO ₄	AsO ₄				
25 ^a	2	5760	1.96	0.156678	0.120377	0.028163	-24.29	-24.27	-879.30	-879.20
		6480	1.97	0.157752	0.121780	0.028096	-24.27	±0.02	-879.16	±0.10
		7200	1.97	0.157842	0.122092	0.027896	-24.27		-879.17	
		7920	1.97	0.157484	0.123651	0.028163	-24.27		-879.16	
25	6	5760	3.90	0.000913	0.079679	0.001860	-26.01	-26.01	-889.09	-889.12
		6480	3.89	0.000902	0.081083	0.001853	-26.01	±0.00	-889.11	±0.03
		7200	3.89	0.000894	0.081083	0.001844	-26.01		-889.14	
		7920	3.89	0.000897	0.081239	0.001849	-26.01		-889.12	
25	10	5760	4.16	0.000584	0.093557	0.002324	-26.16	-26.17	-889.95	-890.05
		6480	4.15	0.000573	0.090750	0.002227	-26.18	±0.01	-890.08	±0.10
		7200	4.15	0.000570	0.090594	0.002232	-26.18		-890.09	
		7920	4.15	0.000572	0.091374	0.002228	-26.18		-890.08	
25 ^b	2	5760	1.96	0.160080	0.125211	0.027562	-24.29	-24.26	-879.28	-879.15
		6480	1.97	0.163393	0.127238	0.027095	-24.26	±0.03	-879.13	±0.13
		7200	1.97	0.163751	0.125834	0.027762	-24.25		-879.08	
		7920	1.97	0.163482	0.127082	0.027562	-24.25		-879.10	
35	2	5760	1.94	0.240299	0.208788	0.006020	-24.49	-24.48		
		6480	1.94	0.247909	0.212998	0.005877	-24.48	±0.01		
		7200	1.94	0.246925	0.208320	0.005908	-24.48			
		7920	1.94	0.247014	0.212842	0.005897	-24.48			
45	2	5760	1.88	0.373162	0.342887	0.004635	-24.42	-24.40		
		6480	1.89	0.373700	0.345070	0.004664	-24.39	±0.02		
		7200	1.89	0.373521	0.344290	0.004661	-24.39			
		7920	1.89	0.374147	0.345849	0.004678	-24.39			

^{a,b}Dissolution tests in duplicate.

The experimental data of the dissolution for 240 d (5760 h), 270 d (6480 h), 7200 h (300 d), and 7920 h (330 d) and the calculated thermodynamic properties for the basic ferric sulfate-arsenates are presented in Tables 2–6. The log_{IAP} and ΔG_f° values were -23.04 ± 0.01 and -914.06 ± 0.03 kJ/mol for the basic ferric sulfate-arsenate FeSAsOH-1 [Fe(SO₄)_{0.27}(AsO₄)_{0.73}(OH)_{0.27}·0.26H₂O], respectively (Table 2). For all the five synthetic basic ferric sulfate-arsenates, the ion activity products (log_{IAP}s) varied between -26.17 ± 0.01 and -22.01 ± 0.02 . The solubilities decreased slightly with the increasing initial pH and were not obviously affected by the system temperature. The experimental results on dissolution were highly reproducible (Table 2–Table 6).

Using the result of the solubility experiments at initial pH 2 for 240 d (5760 h), 270 d (6480 h), 7200 h (300 d), and 7920 h (330 d), the log_{IAP} for FeAsO₄·0.75H₂O is determined after the following reaction:

The calculated log_{IAP} of -23.87 ± 0.02 (Table 5) is in good agreement with the log_{K_{sp}} of -26.54 ± 0.35 [26].

4. Conclusions

The basic ferric sulfate-arsenates [FeSAsOH, Fe(SO₄)_x(AsO₄)_y(OH)_z·nH₂O] were prepared and

characterized to investigate their potential fixation of arsenic in the oxidizing and acidic environment through a dissolution for days. The synthetic solids were generally the well-shaped prismatic crystals of the monoclinic polytypes. In the dissolution of the FeSAsOH-1 [Fe(SO₄)_{0.27}(AsO₄)_{0.73}(OH)_{0.27}·0.26H₂O] sample at 25–45°C and pH 2–10, the constituents were released in the order of AsO₄ > SO₄ > Fe within 1–3 h, in the order of SO₄ > AsO₄ > Fe from 1–3 h to 12–24 h, and finally, in the order of SO₄ > Fe > AsO₄. The released iron, sulfate, and arsenate existed dominantly as Fe³⁺/Fe(OH)²⁺/FeSO₄⁺, HSO₄⁻/SO₄²⁻/FeSO₄⁺, and H₃AsO₄⁰/H₂AsO₄⁻, respectively. The higher initial pHs (6 and 10) could obviously inhibit the release of Fe(III) from solid into solution, and the solid components were released in the order of SO₄ > AsO₄ > Fe. The detaching was restricted by the Fe-O(H) breakdown in the FeO₆ octahedra and obstructed by the OH⁻ and AsO₄ tetrahedra outliers; the lowest concentration of the dissolved arsenic was 0.045 mg/L. The components at the tops of the crystals were first dissolved, and the crystal surfaces were gradually smoothed/rounded until all edges and corners disappeared.

Based on the dissolution experiment at 25°C and pH 2 for 330 d, the solubility products (K_{sp}) for Fe(SO₄)_{0.27}(AsO₄)_{0.73}(OH)_{0.27}·0.26H₂O, which are equal to the ion activity products (log_{IAP}) at equilibrium, were calculated to be -23.04 ± 0.01 with the resulting Gibbs free energies of formation (ΔG_f°) of -914.06 ± 0.03 kJ/mol. For all

the five synthetic basic ferric sulfate-arsenates, the log IAPs varied between -26.17 ± 0.01 and -22.01 ± 0.02 . The log IAP for $\text{FeAsO}_4 \cdot 0.75\text{H}_2\text{O}$ was estimated to be -23.87 ± 0.02 from the result of the solubility experiments at initial pH 2 for 240–330 d.

Data Availability

The powder XRD data in XML format, the FT-IR data in XLSX format, and all solution analytical data in XLSX format used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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Supplementary Materials

Additional details regarding XRD, FT-IR, and FE-SEM characterization of the basic ferric sulfate-arsenates [$\text{FeSAsOH-1-FeSAsOH-5}$] before and after dissolution for 330d; plotting of the solution evolution during the dissolution of $\text{FeSAsOH-2-FeSAsOH-5}$ at 25–45°C and initial pH 2–10 for 330 d; major speciation reactions involved in the PHREEQC calculation (PDF). (*Supplementary Materials*)

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