Treatment of strongly acidic wastewater with high arsenic concentrations by ferrous sulfide (FeS): Inhibitive effects of S(0)-enriched surfaces

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HIGHLIGHTS

- FeS shows higher removal efficiency towards As(III) than As(V).
- In acidic solution FeS dissolve to S(-II) for As(V) reduction and As₂S₃ formation.
- S(-II) react with As(V) to form S(0)-rich surface on FeS and inhibit As removal.
- S(II)-rich surface inhibit FeS dissolution and arsenic removal.
- As(V) reduction to As(III) by dosing Na₂S prior to FeS improve As(V) removal.

GRAPHICAL ABSTRACT

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ABSTRACT

The utilization of arsenopyrite (FeAsS), the As ore mineral, produces strongly acidic wastewater with extremely high arsenic (As) concentrations. This study investigates the feasibility of using ferrous sulfide (FeS) as a sulfide [S(-II)] source to treat strongly acidic wastewater with high concentrations of arsenite [As(III)] and arsenate [As(V)]. The removal of As(III) by FeS was nearly 30% higher than that of As(V), and higher acidity and elevated FeS doses benefited their removal. At extremely high acidity of above 7 mol/L as H₂SO₄, the consumption of S(-II) by H₂SO₄ inhibited As removal. At lower acidity of below 2 mol/L as H₂SO₄, elevated FeS doses up to 4 times the theoretical dose could achieve good As removal. SEM/EDS and XPS analysis indicated the formation of As₂S₃ precipitates, and sulfur [S(0)] also formed in the As(V)-removing system. The tiny and negatively-charged S(0) particles tend to coat the FeS surface. The S(0)-enriched surface acts as a barrier to inhibit S(-II) detachment and As(V) penetration and inhibits As(V) removal thereafter. The reduction of As(V) to As(III) by Na₂S, prior to dosing with FeS, is preferred to achieve rapid and favorable As(V) removal. The low-cost FeS provides available Fe(II) and S(-II) for As removal, and is practically valuable to treat acidic high-As wastewater.

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1. Introduction

Arsenic (As) is widely distributed and occurs in more than 200 minerals [1]. Arsenopyrite, FeAsS, is the most abundant As ore mineral in the Earth's crust, and is frequently associated with

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the minerals pyrite and arsenian ('arsenic-rich') pyrite ($\text{Fe}(\text{S,As})_2$). Pyrite, with the associated FeAsS , has been widely used as a raw material for the sulfuric acid manufacturing industry, and the As content of above 0.05% within raw material may exert arsenic pollution problems involve in. The mining and smelting industries using As ore minerals sometimes produce wastewater with extremely high As concentrations, from several thousand to tens of thousands mg/L. Additionally, these wastewaters are usually strongly acidic and named as acidic mining drainage (AMD), and they are usually continuously reclaimed and recirculated due to the difficulty to achieve the discharging standard. This strategy concentrates the acid greatly and the percentage concentrations of acid may be even as high as 1–30 percent. The AMD with extremely high acid concentrations of over 10% may be relatively uncommon; however, it does occur in some factories. The discharge of these AMD creates great risks to the environment and is strictly prohibited, and the permitted As concentration for discharge is below 0.5 mg/L in China [2]. To avoid As pollution in the environment, the As-related industries must be well monitored to avoid either deliberate or unexpected discharge of point and non-point AMD. The development of highly-efficient, relatively low cost, and easy-to-handle technologies to treat these AMD is crucial for the control of arsenic pollution in the environment.

The abundant association of As with the mineral pyrite in Earth's crust suggests the feasibility of using pyrite and ferrous sulfide (FeS) for As removal. Zouboulis et al. (1993) first proposed the use of pyrite fines as an adsorbents for the removal of arsenite [$\text{As}(\text{III})$] and arsenate [$\text{As}(\text{V})$] [3]. In the uptake of $\text{As}(\text{V})$ by pristine pyrite, $\text{As}(\text{V})$ is first reduced to $\text{As}(\text{III})$ and then is incorporated into the solid phase; however, on surface-oxidized pyrite, $\text{As}(\text{V})$ reduction rarely occurs [4]. The products formed on pyrite surfaces are complicated. The formation of As_2S_3 or As_4S_4 surface phases has been demonstrated in the uptake of $\text{As}(\text{III})$ and $\text{As}(\text{V})$ by synthetic pyrite [5], and the formation of outer-sphere surface complexes between $\text{As}(\text{V})/\text{As}(\text{III})$ and mackinawite and pyrite is also reported [6]. Additionally, pH impacts the species of products formed between $\text{As}(\text{III})$ and nano- FeS_m and the removal efficiency of $\text{As}(\text{III})$ thereafter [7]. Furthermore, FeS may be coated on quartz sand and be used as a adsorbent for flow-through reactors such as permeable reactive barriers [8]. The *in situ* coating of Fe -sulfide onto quartz sand by alternative injection of $\text{Fe}(\text{II})$, O_2 -free water and S^{2-} achieves good arsenic removal efficiency, and beside its direct uptake by Fe -sulfide coating, the surface complexation between $\text{As}(\text{III})$ and Fe oxides/hydroxides and the $\text{As}(\text{III})$ precipitation also involves in [9]. These studies mainly focus on the adsorption of arsenic; however, studies focusing on the treatment of AMD by precipitation are rare, to the best of our knowledge.

In strongly acidic solution, FeS may dissolve into Fe^{2+} and sulfide (S^{2-}) (Eq. (1)), and S^{2-} tends to transform into HS^- and H_2S in acidic solution (Eqs. (2) and (3)). In case of sufficient alkalinity, the formed $\text{Fe}(\text{II})$ can be further oxidized to $\text{Fe}(\text{III})$ by dissolved oxygen and other chemical oxidants, and $\text{Fe}(\text{III})$ (hydro)oxides can also be used for arsenic removal [10,11]. Sulfide acts as a reductant to convert $\text{As}(\text{V})$ to $\text{As}(\text{III})$ [12] and to form soluble and insoluble arsenic-sulfide complexes, e.g., di- and tri-thioarsenite monomers, dimeric and trimeric arsenic-sulfur complexes [13,14]. The precipitation of $\text{As}_2\text{S}_3(\text{am})$ occurs, and the dominant dissolved As species is dependent on sulfide levels, pH, and temperature [15]. In the treatment of these AMD, the dominant factors affecting the removal of arsenic is far from being well understood.

This study aims to: 1) evaluate the removal efficiency of $\text{As}(\text{III})$ and $\text{As}(\text{V})$ by FeS over wide ranges of FeS doses and acidity; 2) indicate the dominant reactions involved in and the inhibiting effects in regarding to arsenic removal by FeS ; 3) propose the strategy to optimize the utilization of FeS to treat high-As AMD.

2. Materials and methods

2.1. Materials and reagents

All the reagents used in this study were analytical grade. FeS powder was carefully ground and sieved, and the particle size was in the range from 200 to 300 mesh. The stock solutions of sodium arsenite (NaAsO_2) and sodium arsenate ($\text{NaHAsO}_4 \cdot 7\text{H}_2\text{O}$) at 10 g/L as As were prepared in de-ionized water every 10 days whereas that of sodium sulfide ($\text{Na}_2\text{S} \cdot 12\text{H}_2\text{O}$) was prepared just prior to use. As-containing water was prepared through spiking As stock solution into de-ionized water, and H_2SO_4 solution was added to provide the desired acidity. No background electrolyte was provided. The species distribution of $\text{As}(\text{III})$ and $\text{As}(\text{V})$ over wide pH ranges from -0.30 to -1.15 , i.e., the H_2SO_4 concentrations in the range from 1 to 7 mol/L, were calculated by the Visual MINTEQ software (Version 3.0, beta), and H_3AsO_3 and H_3AsO_4 are determined to be the dominant species of $\text{As}(\text{III})$ and $\text{As}(\text{V})$, respectively.

2.2. Experimental Methods

FeS doses were expressed by the molar ratios of FeS to $\text{As}(\text{III})$ and $\text{As}(\text{V})$, i.e., $R_{\text{FeS:As}(\text{III})}$ and $R_{\text{FeS:As}(\text{V})}$. The theoretical equivalent molar ratios of FeS to $\text{As}(\text{III})$ and $\text{As}(\text{V})$ were 1.5:1 and 2.5:1, as expressed in Eqs. (4) and (5). It was noted that the arsenic chemistry in sulfidic waters is rather complicate [15,16], and the species distribution of As thioanion, mainly from As_2S_3 dissolution, can be well predicted [16]. However, in this strongly-acidic wastewaters involve in this study, As_2S_3 dissolution is greatly inhibited [15] and it is indicated as the dominant product in this study.

When investigating the effects of acidity on the removal of $\text{As}(\text{III})$ and $\text{As}(\text{V})$ by FeS , $R_{\text{FeS:As}(\text{III})}$ and $R_{\text{FeS:As}(\text{V})}$ were 3:1 and 5:1 at two initial As concentration (i.e., $[\text{As}]_0$) of 1000 and 3000 mg/L. Batch experiments were conducted with magnetic stirring in capped 250-mL flasks at room temperature. Soon after adding FeS powder at the desired amount into 100-mL As solutions of pre-determined concentrations in the flasks, the flasks were quickly capped and Vaseline was carefully smeared onto the bottle cork to ensure leak tightness and to avoid the dissipation of hydrogen sulfide (H_2S) gas. After 1-h stirring, the suspension was filtered by a 0.45- μm membrane filter to analyze the concentrations of soluble $\text{As}(\text{III})$, $\text{As}(\text{V})$, total arsenic [$\text{As}(\text{tot})$, $\text{As}(\text{III}) + \text{As}(\text{V})$], and iron in the filtrate. While investigating the effect of FeS doses on arsenic removal at $[\text{As}]_0$ of 1000 and 3000 mg/L, FeS doses over a wide range from 1:1 to 9:1 were investigated. In relatively low acidity ranges of 0.5 to 3 mol/L as H_2SO_4 , the elevated FeS doses of 8:1 as $R_{\text{FeS:As}(\text{III})}$ and 15:1 as $R_{\text{FeS:As}(\text{V})}$ were investigated. Similar procedures were followed when investigating the removal kinetics of arsenic by FeS except that sampling was carried out at intervals, and the FeS doses were 2.5:1 for $R_{\text{FeS:As}(\text{III})}$ and 5:1 for $R_{\text{FeS:As}(\text{V})}$.

To evaluate the removal behaviors of Na_2S towards $\text{As}(\text{III})$ and $\text{As}(\text{V})$, the Na_2S doses as expressed by the molar ratios of Na_2S to As, i.e., $R_{\text{S:As}}$, ranged from 0.125:1 to 3:1, and the initial concentrations of $\text{As}(\text{III})$ and $\text{As}(\text{V})$ were 1000 mg/L. The abovementioned procedures were followed.

2.3. Analysis and characterization

The concentrations of As(tot) and Fe were determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Optima 2000, PerkinElmer Co.). The concentrations of As(III) and As(V) were measured with Hydride Generation Atomic Fluorescence Spectroscopy (HG-AFS), following the methods described in our previous study [17]. Soluble As(V) concentrations were calculated from the difference between the As(tot) and As(III) concentrations.

Electrokinetic potential (ζ potential) was estimated from electrophoretic mobility using the Smoluchowski equation measured by a Zetasizer 2000 Zeta Potential Analyzer (Malvern Co., U.K.), and each sample was measured at least three times. The average volumetric particle diameter [AVPD, $d(0.5)$] and particle size distribution (PSD) were determined with a Mastersizer 2000 Laser Particle Size Analyzer (Malvern Co., U.K.). The ζ potential and PSD were directly measured without sample pretreatment, and it was noted that the precipitates were not analyzed at high acidity levels above 0.5 mol/L as H_2SO_4 .

The particle shapes and the elemental compositions were observed using a scanning electron microscope (SEM) with an EDAX KEVEX level 4 (Hitachi S-3500 N). The X-ray photoelectron spectroscopy (XPS) spectra were determined by an ESCA-Lab-220i-XL spectrometer (Axis Ultra, UK) with monochromatic Al K α radiation (1486.6 eV). The XPS results were collected in binding energy form and fit using the software of Vision (PR2.1.3) and CasaXPS (2.3.12Dev7). After reactions, suspensions were filtered through 0.45- μm membrane filters, and the residues were washed with ultra pure water several times and then freeze-dried. The obtained powders were kept in an air-tight container for use.

3. Results and discussion

3.1. Removal behaviors of FeS towards As(III) and As(V) in strong acidity

3.1.1. Effects of acidity on the removal of As(III) and As(V)

The theoretical equivalent molar ratios between FeS and arsenic are 1.5:1 for As(III) and 2.5:1 for As(V), as indicated in Eqs. (4) and (5). Fig. 1 illustrates the removal efficiency of As(III) and As(V) by

FeS over a wide acidity range from 0.5 to 9 mol/L as H_2SO_4 . The FeS doses as expressed by $R_{\text{FeS:As(III)}}$ and $R_{\text{FeS:As(V)}}$ were 3:1 and 5:1, respectively. At initial As concentration (i.e., $[\text{As}]_0$) of 1000 mg/L, As(III) and As(V) showed little difference in removal efficiency (Fig. 1a), and the maximum removal achieved was as high as 99.8% for As(III) and 98.5% for As(V). At $[\text{As}]_0 = 3000$ mg/L, the removal efficiency of As(III) was generally 30% higher than that of As(V) (Fig. 1b), and the maximum removal was achieved at acidity of 6 mol/L as H_2SO_4 , and was determined to be 99.5% and 50.3% for As(III) and As(V), respectively.

The elevated acidity benefited the removal of these two As species; however, at extremely high acidity, above 6 mol/L as H_2SO_4 , both As(III) and As(V) showed decreased removal efficiency to a large extent. The increase of acidity to 8 mol/L as H_2SO_4 decreased the removal efficiency to 55.6% for As(III) and to 2.3% for As(V) ($[\text{As}]_0 = 3000$ mg/L). At $[\text{As}]_0$ of 1000 mg/L similar trends were also observed, and the removal efficiency decreased to 78.2% for As(III) and to 62.5% for As(V) accordingly. This was attributed to the oxidation of S(-II) to elemental S(0) by strong H_2SO_4 (Eq. (6)).

3.1.2. Effects of FeS doses on the removal of As(III) and As(V)

Fig. 2 indicates the positive effects of elevated $R_{\text{FeS:As}}$ on the removal of As(III) and As(V) at two $[\text{As}]_0$ of 1000 and 3000 mg/L. Quantitatively, at $[\text{As}]_0$ of 3000 mg/L the removal efficiency of As(III) increased from 29.0% to as high as nearly 100% with $R_{\text{FeS:As(III)}}$ increasing from 1:1 to 2.5:1, and that of As(V) increased from 1.2% to 86.7% with elevated $R_{\text{FeS:As(V)}}$ from 2:1 to 6:1. At lowered $[\text{As}]_0$ of 1000 mg/L, the elevated $R_{\text{FeS:As}}$ also improved As removal. Comparatively, the removal efficiency of As(V) was lower than that of As(III) at the same $R_{\text{FeS:As}}$. The dissolution of FeS was dependent on acidity, and the effects of acidity on the removal of As(III) and As(V) by FeS ought to be similar. Interestingly, the required FeS dose as expressed by $R_{\text{FeS:As(V)}}$ was much higher than the stoichiometric value. Comparatively, the gap between the required $R_{\text{FeS:As(III)}}$ and the theoretical dose was much lower in the As(III)-removing system.

Results in Figs. 1 and 2 indicated the significance of the acidity and FeS doses on the removal of arsenic by FeS, and the elevated acidity and FeS doses were beneficial to the removal of arsenic.

Fig. 1. Effects of acidity as H_2SO_4 on the removal of As(III) and As(V) by FeS (a: $[\text{As}]_0 = 1000$ mg/L, b: $[\text{As}]_0 = 3000$ mg/L; $R_{\text{FeS:As(III)}} = 3:1$, $R_{\text{FeS:As(V)}} = 5:1$).

Fig. 2. Effects of FeS doses as expressed by $R_{\text{FeS:As}}$ on the removal of As(III) and As(V) by FeS (a: $[\text{As}]_0 = 1000$ mg/L, acidity = 4 mol/L as H_2SO_4 ; b: $[\text{As}]_0 = 3000$ mg/L, acidity = 5 mol/L as H_2SO_4).

Fig. 3. Removal of As(III) and As(V) by FeS in relatively low acidity ranges (a: [As(III)]₀ = 3000 mg/L, b: [As(V)]₀ = 3000 mg/L).

In cases where the acidity in raw wastewater was relatively low, the addition of excessive acid was not feasible whereas the increase of FeS dose worked well. As indicated in Fig. 3, the elevation of R_{FeS:As(III)} from 3:1 to 5:1 contributed to the increase of As(III) removal efficiency from 42.3% to 99.6% (acidity = 1 mol/L as H₂SO₄). At low acidity of 2 mol/L as H₂SO₄, the removal efficiency of As(V) was as low as 5.5% at R_{FeS:As(V)} = 5:1. R_{FeS:As(V)} at 10:1 and 15:1 significantly increased As(V) removal to 92.1% and to 94.1% accordingly.

3.1.3. Removal kinetics of As(III) and As(V) by FeS

Fig. 4 illustrates the removal kinetics of As(III) and As(V) by FeS at different R_{FeS:As} with prolonged contact time. The removal of As(III) by FeS was remarkably faster than that of As(V). After 5-min contact time the removal efficiency of As(III) was 52.8% whereas that of As(V) was as low as 11.7% ([As]₀ = 1000 mg/L). After 60 min, the removal efficiency of As(III) was 99.5% and 75.7% at [As]₀ of 1000 and 5000 mg/L, respectively. The removal of As(V) by FeS was much slower, and after 210 min the removal of As(V) was as low as 69.9% ([As]₀ = 1000 mg/L).

The formation of As₂S₃ precipitates upon acidification of samples containing arsenic and sulfide has also been demonstrated

Fig. 4. The removal kinetics of As(III) and As(V) by FeS at different R_{FeS:As} (■—3 mol/L as H₂SO₄, R_{FeS:As(III)} = 2.5:1; ●—4 mol/L as H₂SO₄, R_{FeS:As(III)} = 5:1; ▲—4 mol/L as H₂SO₄, R_{FeS:As(V)} = 2.5:1).

before [18], and the rapid As(III) removal may be attributed to the rapid formation of As₂S₃ precipitate formed by As(III) and the dissolved S(-II) (Eq. (7)). The removal of As(V) by FeS was more complicated (Eq. (8)). Prior to the formation of As₂S₃ precipitates, the reduction of As(V) to As(III) occurred first (Eq. (9)). This redox reaction may be the rate-limiting step in As(V) removal.

3.2. Reduction of As(V) to As(III) in the removal of As(V) by FeS

SEM/EDS analysis indicated the presence of low Fe ratios below 3% on the surfaces of the formed precipitates. It was inferred that the dissolved Fe²⁺ played little role, whereas the sulfur [S(-II), i.e., S²⁻, HS⁻, H₂S] dominated in the removal of arsenic by FeS. To confirm this, the removal of As(III) and As(V) by Na₂S with elevated R_{S:As} was investigated, and the elevated R_{S:As} was related to more significant removal of both As species (Fig. 5). At R_{S:As} of below 1.5:1, i.e., the equivalent molar ratio of S(-II) to As(III) to form As₂S₃ (Eq. (7)), As(III) showed much higher removal efficiency than As(V) did. At elevated R_{S:As} of 2.5:1, i.e., the equivalent molar ratio of S(-II) to As(V) (Eq. (8)), the removal efficiency of As(V) was nearly 100%. FeS may act as a sulfur source to provide S(-II) available for the reduction of As(V) to As(III) and the formation of As₂S₃ thereafter. However, the required FeS doses to achieve high As(V) removal as expressed by R_{FeS:As(V)} in Fig. 2 were much higher than R_{S:As(V)}. By comparison, much less difference between R_{S:As(III)} and R_{FeS:As(III)} was observed to achieve the same As(III) removal.

The analysis of As(III) concentrations indicated the reduction of As(V) to As(III) by FeS in the As(V)-removing system (Fig. S1). However, As(V) was the dominant species over a wide R_{FeS:As(V)} range, as indicated by the high ratios of As(V) to As(tot), i.e., R_{As(V):As(tot)}. Upon the reduction of As(V) to As(III), As(III) was inferred to rapidly form As₂S₃ precipitates. The consumption of As(III) was observed to be dependent on acidity. At extremely high acidity of 8 mol/L, the formed sulfide (i.e., H₂S) was oxidized by H₂SO₄ to S(0) (Eq. (10)). This effect greatly inhibited the formation of As₂S₃, and R_{As(V):As(tot)} was observed to be near to 0.

XPS analysis further confirmed the dominant reactions involved in the removal of As(III) and As(V) by FeS. The observed elemental ratios of S to As (R_{S:As}), as indicated from Table 1, were near the theoretical stoichiometric ratios as calculated from Eqs. (4) and

Fig. 5. The removal of As(III) and As(V) by Na₂S with elevated R_{Na₂S:As} ([As]₀ = 1000 mg/L, acidity = 0.5 mol/L as H₂SO₄).

Table 1

Surface atomic compositions derived from the peak areas of As(3d) and S(2p) components in survey XPS spectra and SEM/EDS analysis.

Elements	SEM/EDS (Atomic ratios)		XPS (Atomic ratios)		XPS (Binding energy)	
	As(III) removing system (%)	As(V) removing system (%)	As(III) removing system (%)	As(V) removing system (%)	As(III) removing system (eV)	As(V) removing system (eV)
As	44.25	35.74	14.27	8.60	43.7	43.3
S	53.14	61.90	22.55	19.36	162.6	163.2
R _{S:As}	1.20:1	1.73:1	1.58:1	2.25:1	/	/

(5). SEM/EDS analysis, on the basis of at least three randomly selected locations, also indicated the presence of a sulfur-enriched surface in the As(V)-removing system. The reduction of As(V) to As(III) and the formation of As_2S_3 precipitates was inferred to dominate in the removal of As(V) by FeS. It should be noted that the formation of other products such as disulfide (S_2^{2-}), polysulfide (S_n^{2-}) and thioarsenate (e.g., $\text{AsO}_3\text{S}^{3-}$, $\text{AsO}_2\text{S}^{3-}$) may also occur [7,19].

XPS survey scans indicated the presence of S, As, O, and C. Adventitious carbon [C(1s)] was observed in both samples, and the atomic ratios of O(1s) were as low as below 2%. Fig. 6 illustrates the narrow As(3d) XPS spectra for these two precipitates, and the sharp peaks indicate the existence of one prominent species. The As(3d) binding energy, as determined at 43.7 and 43.3 eV, may be attributed to the As(+III) within As_2S_3 . Han et al. (2011) investigated the XPS spectra of As 3d peaks for several As-related model components, and indicated that the position of the As 3d_{5/2} peak for arsenic(III) sulfide (i.e., As_2S_3) was 43.2 eV [20]. Corkhill et al. (2006) investigated the charge-corrected binding energies for the photoelectrons emitted from a natural orpiment crystal (As_2S_3), which was collected from Twin Creeks Mine, Nevada and was fractured along the [010] cleavage plane, and the binding energies of As(3d) and S(2p) were reported to be 43.5 and 162.3 eV [21]. The observed slight shift in the binding energies may be attributed to several effects such as surface charging involved in X-ray photoemission [22]. The precipitates formed in the As(III)-removing system showed the S(2p) binding energy of 162.6 eV, which was assigned to the sulfide ion [S(-II)] [23]. In the As(V)-removing system, the S(2p) binding energy showed a 0.9 eV shift to higher energy at 163.2 eV, and indicated the existence of elemental sulfur [S(0)] at higher binding energy [24].

3.3. The formation of S(0) and its effect on As(V) removal by FeS

The removal of arsenic by Na_2S was slightly dependent on acidity over a wide acidity range, and the low acidity condition of

0.02 mol/L as H_2SO_4 was sufficient to achieve the reduction of As(V) to As(III) and the formation of As_2S_3 (Fig. S2). After the dissolution of FeS to soluble S(-II), the homogeneous reactions between soluble S(-II) and arsenic, as indicated in Eqs. (7) and (8), may be easily achieved. Consequently, the dissolution of FeS was the rate-limiting step for the removal of arsenic by FeS.

Additionally, FeS showed remarkably different removal behaviors towards As(III) and As(V), and this may be attributed to the inhibitive effects of formed S(0). First, the formation of S(0) may inhibit FeS dissolution. Fig. S3 illustrates the dissolved Fe concentrations (Fe_{dis}) with elevated acidity for the As(III)- and As(V)-removing systems, and the calculated Fe_{dis} values equivalent to the removed arsenic are also indicated. Compared to the As(V)-removing system, the As(III)-removing system showed much higher Fe_{dis} , i.e., more significant FeS dissolution, and a more remarkable difference between the observed and calculated Fe_{dis} was also observed. The formation of S(0) in the As(V)-removing system may dominate in inhibiting FeS dissolution. This was supported by the obviously decreased Fe_{dis} at the extremely high acidity level of 7 mol/L as H_2SO_4 in the As(III)-removing system. In this case the heterogeneous oxidation of S(-II) within FeS by H_2SO_4 occurred to form S(0) on the FeS surface, and S(0) acted as a barrier to inhibit FeS dissolution and the release of Fe^{2+} or S(-II) thereafter.

The formed S(0) may tend to coat onto the FeS surface to inhibit further FeS dissolution. Unfortunately, this assumption cannot be demonstrated by characterizing FeS surfaces because FeS particles cannot be precisely separated from the As_2S_3 precipitates to analyze their surfaces. To give more information to support this assumption, we prepared two precipitates from the reactions between Na_2S and these two As species and then analyzed their particle size distribution (PSD) and ζ -potential. Note that the acidity used, as indicated by equilibrium pH, was higher than pH 1 to avoid detrimental effects on these instruments at extremely high acidity. The obtained results of PSD and ζ -potential may be different from those in strongly-acidic pH conditions; however, these results are expected to benefit the optimization of pH adjustment

Fig. 6. XPS spectra of As(3d) peaks for the precipitates formed in the removal of (a) As(III) and (b) As(V) by FeS.

Fig. 7. The particles size distribution of the formed precipitates in the removal of (a) As(III) and (b) As(V) by Na_2S over a wide pH range ($[\text{As}]_0 = 1000 \text{ mg/L}$; $R_{\text{Na}_2\text{S}:\text{As}} = 1:1$).

and precipitates separation in considering that pH neutralization is inevitable to treat these acidic wastewaters. Fig. 7 indicates that the precipitates formed in the As(III)-removal system showed much higher particle diameter than those formed in the As(V)-removal system over a wide equilibrium pH range from 1 to 8. The precipitate formed in the As(III)-removing system appeared to be loose and large flocs, and its volume average diameter as expressed by $d(0.5)$ showed slight variation in the equilibrium pH range from 1 to 2.5 (Fig. S4). Additionally, only one peak in the plot of volume percentage vs. particle diameter was observed (Fig. 7a), and this indicated that this precipitate was uniform in particle diameter. By comparison, the precipitate formed in the As(V)-removing system appeared to consist of compact and tiny particles with much lower $d(0.5)$ values. These precipitates were unevenly distributed with two main peaks (Fig. 7b), possibly owing to the coexisting precipitates of As_2S_3 and $\text{S}(0)$.

These two precipitates also showed critically different ζ -potential variation trends. In the As(III)-removing system, the ζ -potential of the precipitate decreased from -14.6 mV to -34.1 mV with pH increasing from 1.8 to 7.5. In comparison, much lower ζ -potentials were observed in the As(V)-removing system, determined to be -47.7 mV at pH 1.9 and -56.7 mV at pH 6.7. The lower ζ -potential inhibited aggregation and formation of larger particles, as indicated by the positive correlation between ζ -potential and $d(0.5)$ values. The $d(0.5)$ values decreased from 132.5 to $30.9 \mu\text{m}$ with pH increasing from 1.8 to 7.5 in the As(III)-removing system. In the As(V)-removing system, $d(0.5)$ also decreased from $95.5 \mu\text{m}$ at pH 1.9 to $29.5 \mu\text{m}$ at pH 6.7. The tiny precipitates with low ζ -potential, as formed in the As(V)-removing system, were assumed to coat onto FeS surfaces.

The dominant reactions involved in the removal of As(III) and As(V) by FeS and the inhibitive effects of $\text{S}(0)$ are proposed and illustrated in Fig. 8. In strong acidity, FeS dissolved into Fe^{2+} and $\text{S}(-\text{II})$, and the formation of As_2S_3 between $\text{S}(-\text{II})$ and As(III) directly occurred without redox reactions. Additionally, a heterogeneous

Fig. 8. Proposed schematic on the inhibitive effects of $\text{S}(0)$ on the removal of As(III) and As(V) by FeS.

reaction between As(III) and FeS also occurred to form loose and large As_2S_3 flocs. These flocs rapidly detached from the FeS surface and showed little inhibition of either FeS dissolution or As_2S_3 formation. In the presence of As(V), however, the tiny $\text{S}(0)$ particles tended to coat onto the FeS surface to inhibit its dissolution thereafter. At extremely high acidity, H_2SO_4 showed strong activity to oxidize $\text{S}(-\text{II})$ to $\text{S}(0)$ with standard electrode potential of 0.479 V (Eq. (11)), and the formation of $\text{S}(0)$ coating on FeS surfaces inhibited the removal of either arsenic species thereafter.

3.4. Implication for the treatment of high-As AMD by FeS

The abovementioned results indicate the feasibility of using FeS powder as the sources of $\text{Fe}(\text{II})$ and $\text{S}(-\text{II})$ for the treatment of AMD. As for the economic evaluation, the initial arsenic concentration is assumed to be 3000 mg/L and the ratio of As(III) to As(V) to be 1:1, and the acidity is assumed to be sufficient. The cost of the industrial FeS powder is $700 \text{ \$/ton}$. The theoretical FeS doses as indicated by stoichiometric calculation are 80 mmol/L ($\sim 7 \text{ g/L} = 7 \text{ kg/m}^3$). In practice, FeS should be overdosed to achieve good As removal efficiency, and the optimized FeS doses ($R_{\text{FeS}:\text{As}}$) are 2:1 for As(III) and 6:1 for As(V) (Fig. 2). The total FeS dose is determined to be 160 mmol/L ($\sim 14 \text{ g/L} = 14 \text{ kg/m}^3$), and the cost for FeS is calculated to be $9.8 \text{ \$/m}^3$. It is noted that in the continuous process, the extra FeS powder could be easily separated and then circulated into the raw water for reclamation. This would decrease the cost by half to be $4.9 \text{ \$/m}^3$. The economic evaluation indicates the priority of using FeS powder in terms of treatment cost.

FeS cannot achieve the permitted discharging concentrations of the Chinese Industrial Wastewater Discharge Standard ($<0.5 \text{ mg/L}$), and further treatment processes are required and the dissolved $\text{Fe}(\text{II})$ may be used. Fig. 9 illustrates the strategy for the treatment of high-As AMD by FeS and the dominant reactions involved therein. First, the dissolution of FeS consumes acidity, and stoichiometric calculation indicates that the removal of 3000 mg/L As(III) and As(V) consumes 0.16 and 0.28 mol/L as H^+ , respectively. Additionally, FeS dissolves into Fe^{2+} and $\text{S}(-\text{II})$, and these two species are valuable for arsenic removal. The homogeneous reactions between arsenic and soluble $\text{S}(-\text{II})$ achieve the rapid removal of both As(III) and As(V) with As_2S_3 as the dominant species, although the formation of other arsenic-sulfur intermediates such as thioarsenite monomers occurs and is rather complicated [7,13,14,19]. Additionally, heterogeneous reactions between As(III) and the FeS surface also play an important role. The prompt detachment of

Fig. 9. The dominant reactions involve in the treatment of acidic high-As wastewater with by FeS and the proposed strategy for FeS application.

As_2S_3 maintains fresh FeS surfaces, and this benefits FeS dissolution and As_2S_3 formation (Fig. 8). In the presence of As(V), unfortunately, the coating of S(0) on FeS surfaces acts as a barrier to isolate FeS and inhibits the removal of arsenic. The elevated FeS doses may alleviate this adverse effect to some extent; however, the conversion of As(V) to As(III) by Na_2S prior to dosing FeS may be more cost-effective and practically valuable. At extremely high acidity, the oxidation of S(-II) to S(0) by strong H_2SO_4 also inhibits arsenic removal, and sufficient alkalinity is required to avoid this side effect. After the formation of As_2S_3 and S(0) precipitates, particulate As may be removed by solid-liquid separation. Furthermore, the addition of oxidants such as O_2 and chorine and pH adjustment by increasing alkalinity can be carefully managed to achieve the oxidation of Fe(II) to Fe(III), the formation of Fe-As precipitates, and the adsorption of arsenic onto $Fe(OH)_3$. The addition of extra Fe(III) and chemical oxidants may be preferred to achieve better removal efficiency.

4. Conclusion

FeS acts as a source of Fe(II) and S(-II) and is feasible and cost-effective to treat high-arsenic AMD. The formation of As_2S_3 precipitates between S(-II) and As(III) rapidly occurs to achieve good As(III) removal. In the As(V)-removing system, the formation of S(0) and S(0)-rich surfaces greatly inhibits the removal of As(V) by FeS. The conversion of As(V) to As(III) prior to dosing with FeS is recommended to avoid the coating of S(0) onto the FeS surface. The adverse effect of S(0) also occurs at extremely high acidity above 7 mol/L as H_2SO_4 , and this can be avoided by increasing alkalinity to the preferred acidity range of 6–7 mol/L to favor FeS dissolution. It is noted that the obtained sludge mainly includes As_2S_3 precipitate and S(0) and the As content is extremely high. This sludge must be safely disposed of by cheap and convenient means such as solidification in roadbed or encapsulation in cement-lime mixture to avoid secondary pollution to environments.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2016.05.109>.

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