



Redox behavior and chemical species of arsenic in acidic aqueous system

Jin-qin YANG¹, Li-yuan CHAI^{1,2}, Qing-zhu LI^{1,2}, Yu-de SHU^{1,2}

1. School of Metallurgy and Environment, Central South University, Changsha 410083, China;

2. National Engineering Research Centre for Control and Treatment of Heavy Metal Pollution,
Central South University, Changsha 410083, China

Received 16 September 2016; accepted 20 January 2017

Abstract: Arsenic (As) removal from smelting acidic wastewater is an urgent task. The most common method is oxidation of trivalent As(III) to pentavalent As(V) subsequently precipitated by ferric (Fe(III)) salts. Foundations of redox behavior and chemical species are of great importance for understanding As removal. In this work, cyclic voltammetry (CV) and UV–Vis spectroscopy were used for laboratory observation; meanwhile HSC and MINTEQA2 software were employed for theoretical analyses. It is found that As(III) oxidation, a multiple electron transfer reaction, is diffusion-controlled. The oxidation over-potential is very high (about 0.9 V) in sulfuric acid solutions (pH 1.0). In addition, Fe(III)–As(V) complexes are evidenced by UV–Vis spectra and chemical species analyses in series of Fe(III)–As(V)–H₂SO₄–H₂O solutions. Therefore, the Fe(III) and As(V) species distribution against pH values are determined and a new ϕ –pH diagram with inclusion of Fe–As complexes is consequently compiled based on thermodynamic data predicted by other researchers.

Key words: arsenic; ferric-arsenic complexes; ϕ –pH diagram; chemical species; acidic wastewater

1 Introduction

Arsenic (As) is often found in association with nonferrous metal ore [1]. In nonferrous metal smelters, As-containing acidic wastewater was generated from the wet scrubber process of smelting fume [2]. The smelting acidic wastewaters sampled from certain copper smelter and lead-zinc smelter (see Table 1) are very different from common wastewaters, i.e., groundwater, and municipal wastewater [3]. The extremely low pH value, abundant As and complicated composition lead to difficulty in As removal.

One of the potential sources of As is the As₂O₃-bearing flue dust generated by smelting operations [4,5]. Thus, trivalent state As(III) is predominant, e.g., the ratio of As(III)/As(total) is equal to 67% and 85% in lead–zinc and copper smelting acidic wastewaters, respectively (Table 1). A pre-oxidation treatment is significant because As(III) is more mobile and toxic than pentavalent state As(V) [6]. The oxidation of As(III) to As(V) is unlikely to be a problem for the pressure oxidation systems but difficult under atmosphere [7].

Moreover, the on-site oxidation under strong acidic conditions is challenging. Lime neutralization is commonly used for acidic wastewater treatment. However, lime can produce plenty of gypsum and unstable cadmium arsenate [8]. Consequently, the on-site high-effective oxidation is attractive, which can lay foundation for the subsequent ferric arsenate (FeAsO₄) precipitation under strong acidic conditions. As coprecipitation with ferric (Fe(III)) iron has been specified by U.S. EPA as the best demonstrated available technology (BDAT) for the removal of As [9]. Scorodite (FeAsO₄·2H₂O), ferric arsenate and arsenical ferrihydrite are common precipitates formed from As removal in metallurgical industries [10]. Well-crystalline scorodite is more advantageous in lower ferric demand, higher density and greater stability. The production of scorodite is easily conducted under autoclave conditions, i.e., under high temperature and pressure conditions [11].

However, atmospheric scorodite production is of great concern due to lower capital investment [8]. Works done over last decades by DEMOPOULOS and coworkers [5,12,13] achieved the production of scorodite by step-wise lime neutralization at 90 °C. In addition,

Table 1 Compositions of acidic wastewaters from different smelters (mg/L)

Component	#1	#2
S	8182	26435
As(total)	2335.5	9010
As(III)	1557	7660
Na	14371	7038
Ni	0.55	735.6
Si	373.7	674.8
Ca	23.05	537.3
Zn	2.6	369
Bi	–	256.1
Cu	0.85	184.1
Fe	4896.5	124.9
Mg	2.5	108.9
K	15.4	72.5
Cd	12.25	42.8
Al	16.65	27.8
Pb	4.15	4.2
Co	0.25	2.4
P	27.7	1.8
Mn	5.55	1.3
Hg	0.45	0.05

#1: Lead-zinc smelting acidic wastewater (pH=1.88); #2: Copper smelting acidic wastewater (pH=1.21); Trivalent As(III) was determined by HG-AFS and other pollutants by ICP-AES.

scorodite was precipitated from sulfuric acid at pH 2 at temperatures as low as 70 °C, but the long reaction time of 16 h was needed [13]. This is because amorphous ferric arsenate is the initial precipitate, which was formed almost immediately and then transformed into scorodite [14]. Previously, it was found that aqueous Fe(III)–As(V) complexes can convert into colloid ferric arsenate under higher temperature and pH conditions [15]. The conversion of aqueous complexes to amorphous ferric arsenate and subsequently to scorodite is meaningful for the removal of As(V) from acidic effluents by coprecipitation with Fe(III). Therefore, thermodynamic chemistry is needed to be studied to provide an insight into the species distribution and transformation in acidic Fe–As system.

In this work, the redox of As in acidic solutions was studied by the combination of cyclic voltammetry (CV) method and theoretical φ –pH diagram analysis. In addition, the species of As in As–H₂O and As–Fe–H₂SO₄–H₂O systems were discussed. The new φ –pH diagram for As–Fe–H₂SO₄–H₂O system was constructed with the inclusion of aqueous Fe(III)/Fe(II)–As(V) complexes.

2 Calculation and experiment methods

2.1 Calculation methods

The φ –pH diagram was constructed based on the well-known Nernst equation. A half-cell reaction can be written as follows:



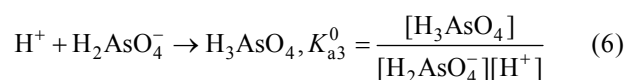
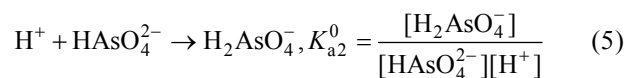
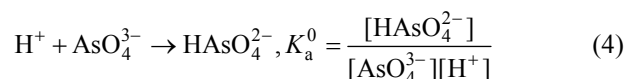
The corresponding Nernst equation was written as Eq. (2). Reversible potential (φ^0) can be derived from the Gibbs free energy of reaction as Eq. (3):

$$\varphi = \varphi^0 + \frac{RT}{nF} \ln \frac{a_X^x a_Y^y}{a_A^c a_D^d} \quad (2)$$

$$\varphi^0 = -\frac{\Delta G_f^0}{nF} \quad (3)$$

where a represents the activity of substances; F is the Faraday's constant. Software HSC 7.1 was used in this work for the construction of φ –pH diagrams. If not specified, the Gibbs free energies in database of HSC 7.1 were adopted.

Visual MINTEQ 3.1 was used to determinate the speciation–pH diagram. The calculation processes were illustrated by taking As(V) (H_xAsO₄^{x–3}) as an example. The formation reaction and corresponding constant equation was shown as Eqs. (4)–(6), where square brackets represent concentration. The sum of H_xAsO₄^{x–3} is equal to the total concentration of As(V) (Eq. (7)). The fractions of As(V) species at various pH values were then solved by MINTEQ 3.1.



$$[As(V)] = [H_3AsO_4] + [H_2AsO_4^-] + [HAsO_4^{2-}] + [AsO_4^{3-}] \quad (7)$$

Same method was used for the determination of As(III) and Fe(III) species distribution against pH value. If not specified, the formation constants in database of MINTEQ 3.1 were adopted. However, the species distribution against pH can be affected by ionic strength (IS). The equilibrium constant at a given ionic strength (K_n^I) is given by the activity coefficients of the species involved in the equilibrium (Eq. (7)):

$$K_n^I = K_n^0 \times \frac{\gamma_{H_xAsO_4^{x-3}}}{\gamma_{H^+} \times \gamma_{H_{x-1}AsO_4^{x-4}}} \quad (8)$$

In MINTEQA software, IS is calculated based on Eq. (9). The activity coefficient at $I < 0.3$ mol/L is calculated from the Davies equation as Eq. (10):

$$I = 0.5 \sum m_i \cdot z_i^2 \quad (9)$$

$$-\lg \gamma_i = A \cdot z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - B \cdot I \right) \quad (10)$$

where γ_i is the activity coefficient of species i , I is the ionic strength, z_i is the charge of the species, A is the Debye–Hückel coefficient, which takes the value of 0.51 at 25 °C, and B is the so-called Davies B parameter, which has a default value of 0.3.

2.2 Experimental methods

1) Cyclic voltammetry (CV) experiments

For the preparation of experimental solutions, pH 1.0 sulfuric acid was prepared in advance as supporting electrolyte. As(III) was incorporated into solutions by NaAsO₂ (Shanghai No. 4 Chemical Reagent Factory, China). Solutions referred to as “blank” contained no As. Cyclic voltammetry (CV) experiments were carried out by a three-electrode test system with a gold working electrode, glassy-carbon counter electrode and saturated calomel reference electrode. The solution was placed in a five-necked electrolysis pool in 25 °C water bath. High purity nitrogen gas was purged into the solutions before applying the potential.

2) UV–Vis spectroscopic experiments

Dilute sulfuric acid solution (50 mmol/L) was prepared using ultrapure water beforehand and used to prepare stock solutions and sample solutions in order to avoid the hydrolysis of Fe(III). The Fe(III) stock solution and As(V) stock solution were prepared by using Fe₂(SO₄)₃ (Xilong, Guangdong Province, China) and Na₃AsO₄·12H₂O (Sinopharm, Shanghai, China), respectively. A series of sample solutions containing 0.5 mmol/L Fe(III) and 0–55 mmol/L As(V) were prepared for UV–Vis tests (Table 2). UV–Vis spectroscopic measurements were performed using a Shimadzu (Japan) UV–2550 double-beam spectrophotometer. A baseline correction was carried out by filling in quartz cells of 1 cm light length with ultrapure water. The spectra were recorded by replacing the ultrapure water with sample solutions in sample cell.

3 Results and discussion

3.1 Redox behavior of As

The ϕ –pH diagram for As–H₂O system was reported in a number of works [16–20], but the stoichiometry of As(III) species was different. HAsO₂ stoichiometry was supported by the mass spectrometry, because mass-to-charge ratios (m/z) of 107 corresponding to AsO₂[−] ion in the gas phase [21]. However, H₃AsO₃, a moiety comprising one As atom coordinated by three OH ligands, was supported by Raman and EXAFS spectroscopy [22–24]. Thus,

Table 2 Solution composition used in UV–Vis experiment and related calculation results

No.	[H ₂ SO ₄] _f /(mmol·L ^{−1})	[Fe ₂ (SO ₄) ₃] _f /(mmol·L ^{−1})	[Na ₃ AsO ₄] _f /(mmol·L ^{−1})	pH ¹	pH ²	IS ²	pH ³	IS ³
1			0	1.35	1.293	0.0791	1.293	0.0791
2			0.5	1.36	1.301	0.0796	1.302	0.0796
3			1	1.41	1.310	0.0800	1.310	0.0800
4			2	1.42	1.327	0.0810	1.328	0.0809
5			4	1.43	1.363	0.0831	1.366	0.0829
6			6	1.44	1.400	0.0853	1.405	0.0850
7			8	1.48	1.440	0.0878	1.448	0.0874
8			10	1.52	1.482	0.0904	1.494	0.0899
9	50	0.25	15	1.63	1.597	0.0980	1.624	0.0971
10			20	1.76	1.730	0.1071	1.786	0.1059
11			25	1.92	1.881	0.1176	1.997	0.1162
12			30	2.10	2.056	0.1292	2.296	0.1281
13			35	2.44	2.261	0.1416	2.714	0.1410
14			40	2.83	2.517	0.1546	3.164	0.1543
15			45	3.75	2.893	0.1678	3.646	0.1678
16			50	6.00	4.123	0.1818	4.730	0.1820
17			55	6.36	5.870	0.2042	5.905	0.2048

1: Measured results; 2: Calculation results with exclusion of Fe(III)–As(V) complexes; 3: Calculation results with inclusion of Fe(III)–As(V) complexes

H_3AsO_3 and its conjugate base were considered here rather than HAsO_2 . As given in Table 3, the Gibbs free energies of As(III) and As(V) species in HSC 7.0 database are in accordance with those in most reports. Consequently, the ϕ -pH diagram for As (0.1 mol/L)- H_2O system was directly constructed by using HSC 7.0 software.

As depicted in Fig. 1, the predominance fields for As(V) species under oxidizing conditions are similar to all published ϕ -pH diagrams. The field boundary for As(III) species was different because of the inclusion of HAsO_3^{2-} and AsO_3^{3-} . Moreover, the critical potentials of As(V)/As(III) couples drop with decreasing pH value, which indicates that the oxidation of As(III) to As(V) is more feasible in alkaline than in acidic solutions. Thus, the redox behavior of As(III) under strong acidic wastewater is challenging. The practice redox behavior of As(III) in sulfuric acid (pH=1.0) was studied by cyclic voltammetry (CV) methods. Figure 2 shows that the voltammogram of a solution contains 0.1 mol/L As(III) and a blank solution. There are six peaks on the CV curve in 0.1 mol/L As(III) solution (blue line). The peaks B and C correspond to the oxygen evolution and the reduction of the oxide layer in comparison with the CV curve in blank solution (red line). The other four peaks A, D, E and F may be related to the redox behavior of As(III). To verify this, a series of CV tests were conducted in As(III)-bearing solutions with different concentrations.

As shown in Fig. 3, the locations of peaks A, D and F all shift to high potential as the concentration of As(III) increases. Moreover, the currents of peak A, D and F increase with As(III) concentration increasing. Peak A obviously splits into three small peaks when As(III) concentration is less than 5 mmol/L. Thus, peak A corresponds to a multiple electron transfer process. Figure 3(b) shows that the current of first electron transfer reaction is linearly correlated with As(III) concentration ($R^2=0.9985$). Peak A is identified as the oxidation of As(III) to As(V). However, the oxidation over-potential of 0.1 mol/L As(III) in sulfuric acid

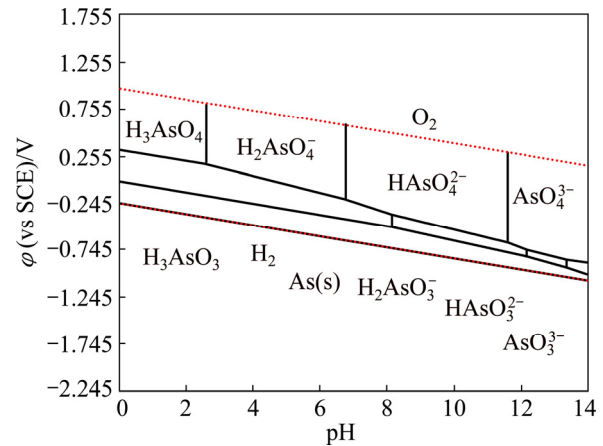


Fig. 1 ϕ (vs SCE)-pH diagram in As (0.1 mol/L)- H_2O system at 25 °C and 10^5 Pa

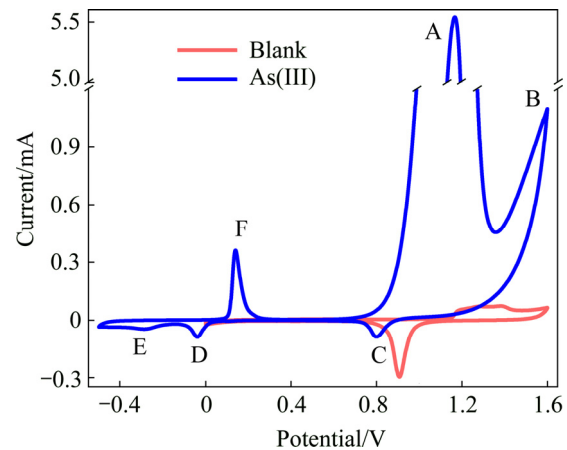


Fig. 2 Voltammogram in 0.1 mol/L As(III) solution (blue line) and blank solution (red line) ($v=50$ mV/s)

solutions (pH 1.0) is about 0.9 V over the theoretical potential (about 0.3 V derived from Fig. 1). Peak D corresponds to the reduction of As(III), because peak current is linearly correlated to As(III) concentration. However, as shown in Fig. 3(c), the slope of fitting line is different in As(III) ranges of 0–1, 1–2 and 2–5 mmol/L. This indicates that multilayer As(s) is electrodeposited from As(III) on gold electrode. As for

Table 3 Gibbs free energies of $\text{H}_x\text{AsO}_3^{x-3}$ and $\text{H}_x\text{AsO}_4^{x-3}$ (kJ/mol)

Species	This work	Ref. [25]	Ref. [26]	Ref. [27,28]	Ref. [29]	Ref. [30]	Ref. [31]
AsO_3^{3-} (a)	-4846.99	—	—	-447.69	—	—	—
AsO_4^{3-} (a)	-647.58	-647.9	-651.87	-647.9	—	-648.39	-648.52
H_3AsO_3 (a)	-638.98	-639.29	-646.01	-639.29	-639.90	-639.85	-639.80
H_3AsO_4 (a)	-767.32	-765.36	-769.86	-765.36	-766.10	-766.09	-766.09
HAsO_3^{2-} (a)	-523.20	—	-524.26	-524.26	—	—	-507.40
HAsO_4^{2-} (a)	-713.74	-714.03	-717.56	-714.03	-714.70	-714.59	-713.73
H_2AsO_3^- (a)	-592.54	-586.66	-593.29	-586.66	—	-587.14	-587.66
H_2AsO_4^- (a)	-752.35	-752.57	-757.56	-752.57	—	-753.16	-753.12

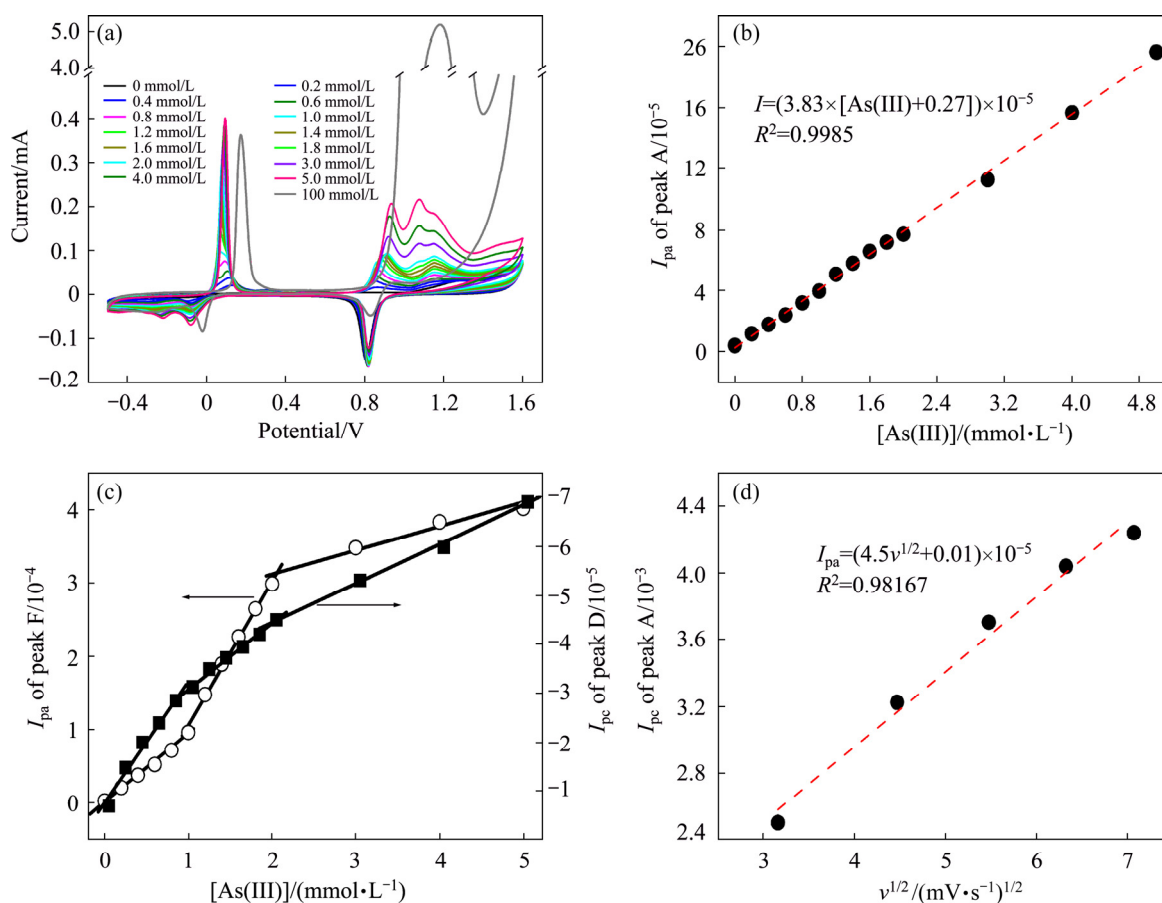


Fig. 3 Voltammograms in As(III) solutions (a), linear calibration plots of peak current against As(III) concentration ($[As(III)] = 0\text{--}5\text{ mmol/L}$, $v = 50\text{ mV/s}$) (b) and (c), and linear calibration plots of peak A current against $v^{1/2}$ ($[As(III)] = 0.1\text{ mol/L}$, $v = 10, 20, 30, 40, 50\text{ mV/s}$) (d)

the weak peak E, it can be explained as outmost As(s) electrodeposited from As(III) or from As(V). The reduction of As(V) to As(s) is thermodynamic sluggish, but the electrogenerated H_2 could chemically reduce As(V) to As(s) [32]. Following peak D and E, the peak F is no doubt the oxidation of As(s) to As(III). Thus, the linear correlation between peak current and As(III) concentration is in accordance with that of peak D. As shown in Fig. 3(c), three lines with different slopes are suitable for fitting in the As(III) concentration ranges of 0–1, 1–2 and 2–5 mmol/L. The consistent trend between peak D and F confirms that As(s) is layeredly electrodeposited on Au electrode. In addition, the oxidation process of As(III) to As(V) was investigated at different scan rates. The good linear relationship between peak current and scan rate ($v^{1/2}$) (Fig. 3(d)) indicates that As(III) oxidation is mainly diffusion-controlled.

3.2 Chemical species of As

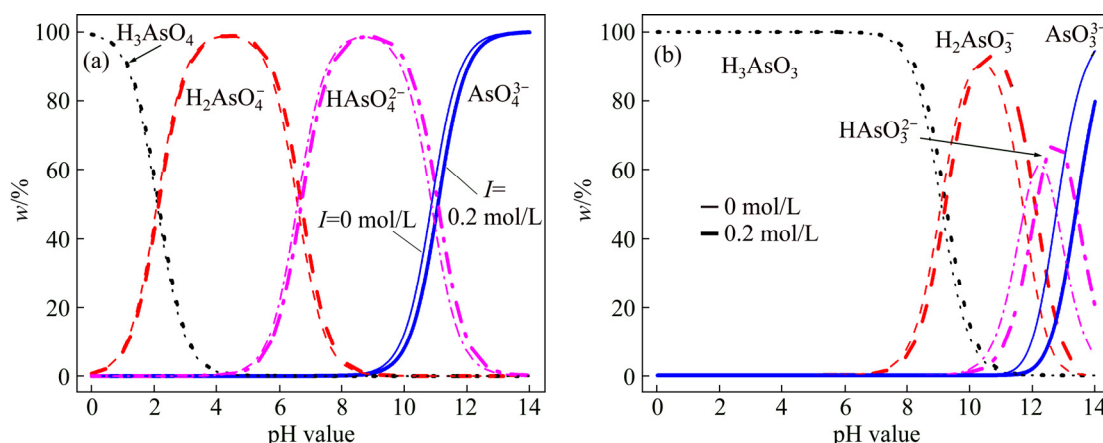
As(III) and As(V) mainly exist as $H_xAsO_3^{x-3}$ and $H_xAsO_4^{x-3}$ ($0 \leq x \leq 3$) in As– H_2O system, respectively. The speciation–pH diagrams for As(III) and As(V) were calculated at ionic strength of 0 based on thermodynamic

formation constants reported by MARINI and ACCORNERO [33]. The thermodynamic constants (K_n^0) for As(III) and As(V) species are reviewed in Table 4. As given in Table 4, there is no significant difference among different reports. As depicted in Fig. 4(a), As(V) predominantly exists as (1) H_3AsO_4 and $H_2AsO_4^-$ at pH 0–4.5, (2) $H_2AsO_4^-$ and $HAsO_4^{2-}$ at pH 4.5–9, and (3) $HAsO_4^{2-}$ and AsO_4^{3-} at pH 9–14. The major form of As(V) is neutral molecules H_3AsO_4 at pH < 2, thus it is hard to be removed by electrostatic adsorption. Figure 4(b) shows that As(III) mainly exists as (1) H_3AsO_3 at pH = 0–7.5, (2) H_3AsO_3 and $H_2AsO_3^-$ at pH = 7.5–10.5, (3) $H_2AsO_3^-$ and $HAsO_3^{2-}$ at pH = 10.5–12 and (4) $H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-} at pH = 12–14. Accordingly, H_3AsO_3 is the only As(III) species under acidic solutions. It is reported that undissociated H_3AsO_3 does not react with H_2O_2 [34]. However, rate constant k for the oxidation reaction between As(III) and H_2O_2 can be determined by pH, temperature and IS at pH = 7.5–10.3 [34]. This is mainly because the molar fraction of $H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-} species can be affected by pH, temperature and

Table 4 Thermodynamic formation constants of $H_xAsO_3^{x-3}$ and $H_xAsO_4^{x-3}$ ($0 \leq x \leq 3$)

Reaction	Ref. [27]	Ref. [26]	Ref. [29]	Ref. [35]	Ref. [31]	Ref. [33]
$H^+ + H_2AsO_4^- \rightarrow H_3AsO_4$	2.24	2.2	2.2	2.2	2.2	2.20
$H^+ + HAsO_4^{2-} \rightarrow H_2AsO_4^-$	6.96	6.96	6.96	6.9	7.08	6.97
$H^+ + AsO_4^{3-} \rightarrow HAsO_4^{2-}$	11.5	11.5	11.5	11.5	11.5	11.53
$H^+ + H_2AsO_3^- \rightarrow H_3AsO_3$	9.2	9.22	9.2	9.2	9.22	9.22
$H^+ + HAsO_3^{2-} \rightarrow H_2AsO_3^-$	12.1	12.10	12.1	12.1	12.3	12.13
$H^+ + AsO_3^{3-} \rightarrow HAsO_3^{2-}$	13.4	13.41	—	13.4	—	13.4

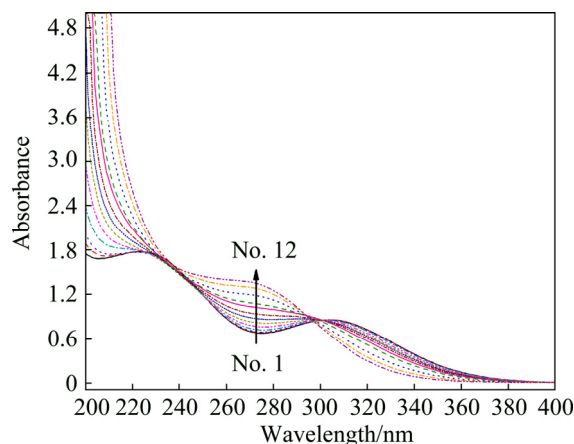
Data in table are $\lg K_n^0$ rather than K_n^0 .

**Fig. 4** Speciation–pH diagrams of As(V) species (a) and As(III) species (b) in As–H₂O system at 25 °C

IS. The speciation–pH diagram at $I=0.2$ mol/L was determined based on the Davies equation (Eq. (8)). As depicted in Fig. 4, high IS facilitates deprotonation reaction. Therefore, negatively-charged species with higher fraction under high IS solutions can be absorbed on the positive-charged surfaces.

In addition, it is predicted that As(V) can complex with metal ion to form aqueous complexes [33]. Fe(III) is usually used as precipitator, thus the complexation between As(V) and Fe(III) is studied here by UV–Vis spectroscopy. The experimental solutions prepared by $Fe_2(SO_4)_3$, H_2SO_4 and Na_3AsO_4 are all acidic solutions. Figure 5 shows that a new peak at about 240–300 nm appears as As(V) concentration increases. The new peak is attributed to Fe(III)–As(V) complexes. The pH value, IS and the fraction of various Fe(III) species were calculated by MINTEQ 3.1 with the consideration of Fe(III)–As(V) complexes or not. The $\lg K$ reported by MARINI and ACCORNERO [36] were adopted here, because they are in accordance with other reports excluding that of $FeAsO_4(a)$ (see Table 5). As displayed in Table 2, the calculated pH values are lower than measured ones, but slightly higher when Fe(III)–As(V) complexes are considered.

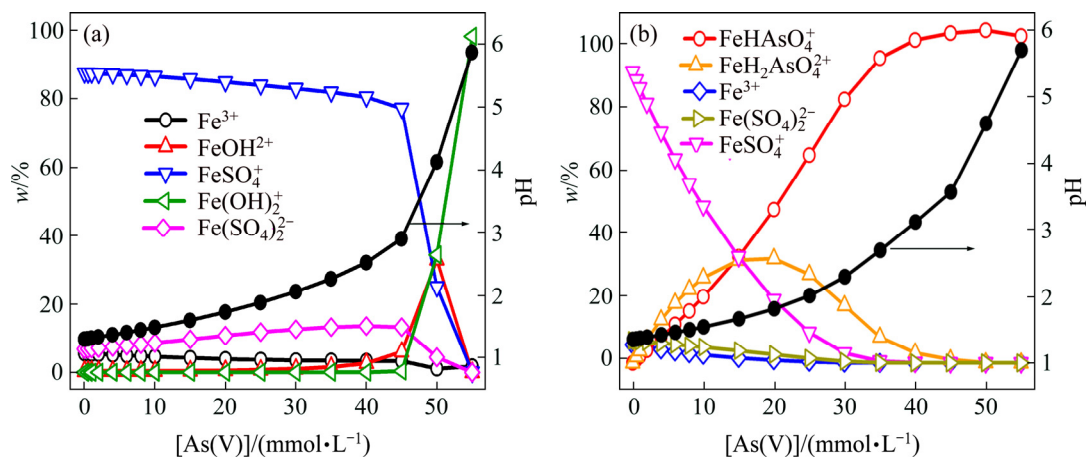
The Fe(III) species in experimental solutions are shown in Fig. 6. Figure 6(a) shows that Fe(III) predominantly exists as $FeSO_4^+$ when As(V)

**Fig. 5** UV–Vis spectra of $Fe_2(SO_4)_3$ – Na_3AsO_4 – H_2SO_4 – H_2O solutions

concentration is less than 45 mmol/L and as $Fe(OH)_2^+$ when As(V) concentration is 45–50 mmol/L. It was reported that the band maxima of $Fe(OH)_2^+$ occur at the wavelength of 300 nm [40]. The new peak at 240–300 nm is indeed not due to $Fe(OH)_2^+$. When Fe(III)–As(V) complexes were considered in the calculations (Fig. 6(b)), $FeH_2AsO_4^{2+}$ and $FeHAsO_4^+$ become the major species in solutions with 15–40 mmol/L As(V) and $FeHAsO_4^+$ is almost the only soluble Fe(III) species when As(V) concentration is 40–50 mmol/L. In addition, the saturation index is higher than 0.577 when $[As(V)]$

Table 5 Reaction equilibrium constants and Gibbs free energies of Fe–As(V) complexes

Complex	$\Delta G/(\text{kJ} \cdot \text{mol}^{-1})$		$\lg K(\text{M}^n + \text{H}_3\text{AsO}_4 = \text{MH}_m\text{AsO}_4^{n+m-3}) + (3-m)\text{H}^+$				
	Ref. [37]	Ref. [36]	Ref. [38]	Ref. [39]	Ref. [37]	Ref. [33]	Ref. [36]
$\text{Fe}^{\text{III}}\text{H}_2\text{AsO}_4^{2+}$	−793.92	−793.97	1.8(1.74)	—	1.74	2.00(1.88)	2.07
$\text{Fe}^{\text{III}}\text{HAsO}_4^+$	−787.24	−786.63	0.66(0.57)	—	0.57	0.71(0.59)	0.77
$\text{Fe}^{\text{III}}\text{AsO}_4$	−771.49	−743.46	−1.8(−2.19)	—	−2.19	−6.86(−6.97)	−6.79
$\text{Fe}^{\text{II}}\text{H}_2\text{AsO}_4^+$	−860.42	−859.8	—	0.44(0.38)	0.38	0.53(0.41)	0.60
$\text{Fe}^{\text{II}}\text{HAsO}_4$	−825.43	−823.30	—	−5.66(−5.75)	−5.75	−5.87(−5.99)	−5.81
$\text{Fe}^{\text{II}}\text{AsO}_4^-$	−778.16	−780.27	—	−13.64(−14.03)	−14.03	−13.41(−13.53)	−13.35

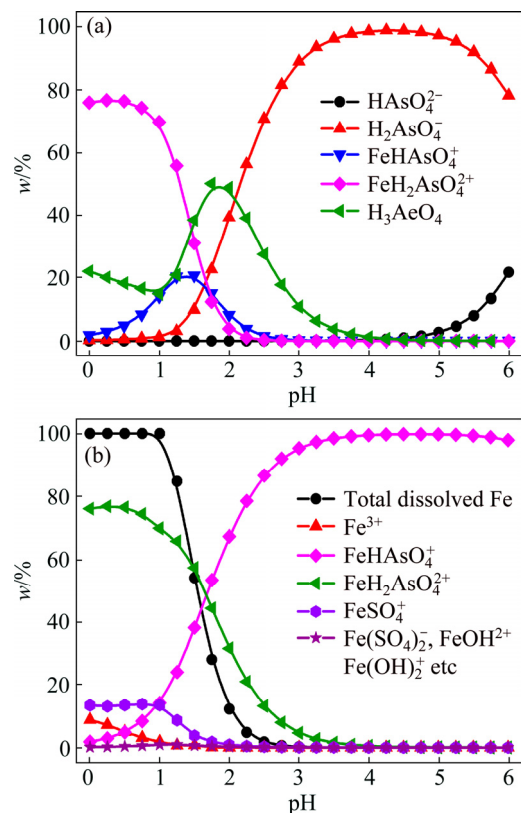
**Fig. 6** Fe(III) species analyses in UV–Vis experiment solutions with exclusion (a) and inclusion (b) of Fe(III)–As(V) complexes

>30 mmol/L. Hematite, goethite, lepidocrocite and $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ etc are oversaturated, which can explain that experimental solutions become turbid when As(III) concentration is more than 30 mmol/L. Accordingly, Fe(III)–As(V) complexes are significant to be considered in Fe(III)–As(V)– H_2SO_4 – H_2O solutions.

As discussed above, Fe(III)–As(V) complexes are important in the species analysis for the system of Fe(III)–As(V)– H_2SO_4 – H_2O , a representative system of As(V) removal from acidic wastewater. Then, the speciation–pH diagrams of Fe(III) and As(V) were calculated for such a system with inclusion of Fe(III)–As(V) complexes. As displayed in Fig. 7(a), As(V) mainly exists as (1) $\text{FeH}_2\text{AsO}_4^{2+}$ and H_3AsO_4 at $\text{pH} < 1$, (2) $\text{FeH}_2\text{AsO}_4^{2+}$, FeHAsO_4^+ , H_3AsO_4 and H_2AsO_4^- at $\text{pH} = 1\text{--}2$, and (3) H_2AsO_4^- at $\text{pH} > 2$. As shown in Fig. 7(b), Fe(III) mainly exists as $\text{FeH}_2\text{AsO}_4^{2+}$ at $\text{pH} < 2$, and FeHAsO_4^+ at $\text{pH} > 2$. However, the total dissolved Fe(III) decreases when pH is higher than 2. Therefore, As(V) mainly exists as $\text{FeH}_2\text{AsO}_4^{2+}$, FeHAsO_4^+ , H_3AsO_4 and H_2AsO_4^- in acidic wastewater treatment system.

3.3 ϕ –pH diagram in Fe–As– H_2O system

As mentioned above, the Fe(III)–As(V) complexes are significant for the speciation of Fe(III) and As(V).

**Fig. 7** Speciation–pH diagrams of As(V) (a) and Fe(III) (b) with inclusion of Fe(III)–As(V) complexes ($[\text{As(V)}] = [\text{Fe(III)}] = [\text{SO}_4] = 0.1 \text{ mol/L}$)

Fe(III)–As(V) complexes should be included in ϕ –pH diagram for As–Fe–H₂O system. According to literatures, Fe(III)–As(III), Fe(II)–As(V) and Fe(II)–As(III) complexes were predicted but there was no experimental evidence. Fe(III)–As(III) and Fe(II)–As(III) complexes are ruled out because of (1) the possible redox reaction between Fe(III) and As(III) and (2) the oxidation of As(III) in parallel to the dark oxidation of Fe(II) by dissolved O₂ [41]. Given the complexation ability of As(V), Fe(II)–As(V) complexes were considered here. Therefore, ϕ –pH diagram for Fe–As–H₂O system was constructed with inclusion of Fe(III)–As(V) and Fe(II)–As(V) complexes, and compared with one with exclusion of these complexes.

The ϕ –pH diagrams are depicted in Fig. 8 for As–Fe–H₂O system at 25 °C and 10⁵ Pa. Figure 8(a) with exclusion of Fe–As complexes shows that FeAsO₄(s) is predominant in the pH range of 1.2–3.4 under oxidizing conditions. It was reported that amorphous ferric arsenate could transform into scorodite [42]. The kinetics of scorodite formation and its transformation from ferric arsenic is strongly controlled by pH, for example, scorodite precipitated after ~384 h at pH 4.5 but ~13 at pH 1 [14]. The pH of

smelting acidic wastewater is usually less than 3, which is suitable for the production of ferric arsenate and scorodite. However, Fe(III)–As(V) complexes (FeH₂AsO₄²⁺, FeHAsO₄⁺ and FeH₂AsO₄⁺) were reported predominant under extremely acidic pH condition [43]. Therefore, the ϕ –pH diagram with inclusion of Fe–As complexes is more meaningful to understand the As geochemistry in Fe–As–H₂O system.

Fe–As complexes were not considered in previous ϕ –pH diagram mainly due to unreliability of thermodynamic data. Recently, MARINI and ACCORNERO [36] estimated the equilibrium constants and Gibbs free energies, which are in good accordance with other reports [37–39]. Accordingly, a new ϕ –pH diagram for Fe–As–H₂O system was constructed based on the estimates. Figure 8(b) shows that Fe(III)–As(V) complexes shrink the stability field of H₃AsO₄ and FeAsO₄(s). Moreover, Fe(II)–As(V) complexes occur in pH range of 0.5–3. The predominant field of Fe₃(AsO₄)₂ is affected by Fe(II)–As(V) complexes. FeH₂AsO₄²⁺, FeHAsO₄⁺ and FeH₂AsO₄⁺ are all restricted at acidic pH conditions. Consequently, Fe–As(V) complexes are considerable in the As removal from smelting acidic wastewaters by coprecipitation with iron salts.

4 Conclusions

1) The cyclic voltammetry curves were tested in As(III)-containing sulfuric acid solutions (pH=1.0). It is shown that the over-potential of As(III) oxidation to As(V) is very high (about 0.9 V). Therefore, on-site peroxidation in acidic wastewater is challenging.

2) The UV–Vis spectra of a series Fe₂(SO₄)₃–Na₃AsO₄–H₂SO₄–H₂O solutions show that a new peak at about 240–300 nm appears as As(V) concentration increases. Corresponding Fe(III) species analyses indicate that Fe(III)–As(V) complexes are formed in the experimental solutions.

3) The ϕ –pH diagram for Fe–As–H₂O system with inclusion of Fe–As(V) complexes were constructed and compared with the one with exclusion of Fe–As(V) complexes. The results illustrate that Fe(III)–As(V) complexes are stable under acidic conditions and shrink the stability field of H₃AsO₄ and FeAsO₄(s).

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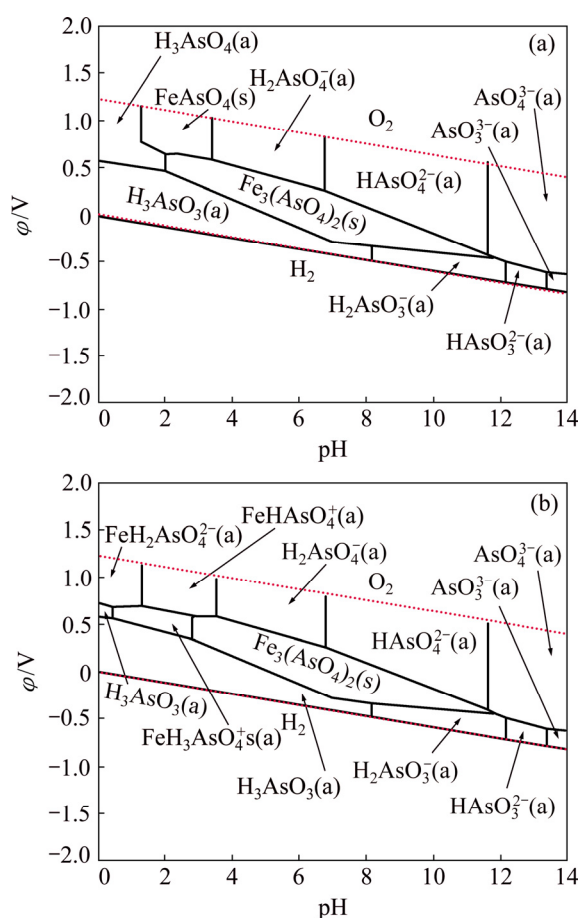


Fig. 8 ϕ –pH diagrams in 0.1 mol/L As–0.1 mol/L Fe–H₂O system with exclusion (a) and inclusion (b) of Fe–As complexes at 25 °C and 10⁵ Pa (ϕ = ϕ (vs SCE) + 0.245)

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砷在酸性溶液体系中的氧化还原行为和化学形态

杨锦琴¹, 柴立元^{1,2}, 李青竹^{1,2}, 舒余德^{1,2}

1. 中南大学 冶金与环境学院, 长沙 410083;

2. 中南大学 国家重金属污染防治工程技术研究中心, 长沙 410083

摘 要: 冶炼酸性废水中砷的去除是一项十分紧迫的工作。目前最常用的方法是先将三价砷氧化为五价砷, 然后再以铁盐进行沉淀去除。砷的氧化还原行为及化学形态基础研究对于砷的去除意义重大。采用循环伏安法和紫外可见分光光度法开展实验室研究, 采用 HSC 和 MINTEQA2 软件进行理论分析。研究发现三价砷的氧化是一个多电子转移反应, 受扩散控制; 在 pH 1.0 的硫酸溶液中, 三价砷的氧化过电位非常高(约 0.9 V)。另外, 针对 Fe(III)–As(V)–H₂SO₄–H₂O 系列溶液的紫外–可见光谱以及物质形态分析均表明 Fe(III)–As(V)配合物的存在。因此, 基于其他研究者预测的热力学数据, 绘制 Fe(III)、As(V)的物质形态随 pH 的分布规律图和包含 Fe–As 配合物的新型电位–pH 图。

关键词: 砷; 铁–砷配合物; 电位–pH 图; 化学形态; 酸性废水

(Edited by Bing YANG)