



Redox behavior and chemical species of arsenic in acidic aqueous system



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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:



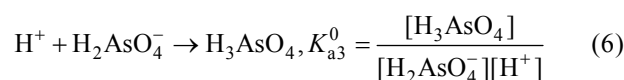
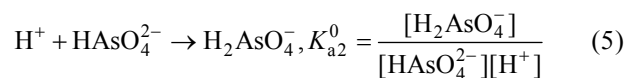
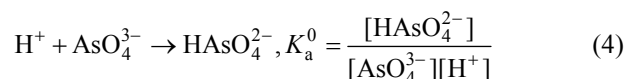
The corresponding Nernst equation was written as Eq. (2). Reversible potential (φ^0) can be derived from the Gibbs free energy of reaction as Eq. (3):

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

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

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)):

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

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