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Transactions of Nonferrous Metals Society of China

www.tnmsc.cn



Trans. Nonferrous Met. Soc. China 27(2017) 676-685

# $\varphi$ -pH diagram of As-N-Na-H<sub>2</sub>O system for arsenic removal during alkaline pressure oxidation leaching of lead anode slime

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Received 29 February 2016; accepted 31 August 2016

**Abstract:** In order to illustrate the thermodynamic characteristics of arsenic during alkaline pressure oxidation leaching process of lead anode slime (NaNO<sub>3</sub> as oxidant; NaOH as alkaline reagent), the  $\varphi$ -pH diagrams of As-Na-H<sub>2</sub>O, N-H<sub>2</sub>O, As-N-Na-H<sub>2</sub>O systems at ionic mass concentration of 0.1 mol/kg and temperatures of 298, 373, 423 and 473 K were established according to thermodynamic calculation. The results show that the existence forms of arsenic are associated with pH value, which mainly exists in the forms of H<sub>3</sub>AsO<sub>4</sub>, H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>, HAsO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>AsO<sub>2</sub><sup>-</sup> and As<sub>2</sub>O<sub>3</sub> in lower pH region, while it mainly exists in the form of AsO<sub>4</sub><sup>3-</sup> when pH>11.14. High alkali concentration and high temperature are advantageous to the arsenic leaching. The alkaline pressure oxidation leaching experiments display that the tendency of arsenic leaching rate confirms the thermodynamic analysis results obtained from the  $\varphi$ -pH diagrams of As-N-Na-H<sub>2</sub>O system; lead anode slime; leaching; arsenic reaches 95.85% at 453 K. **Key words:**  $\varphi$ -pH diagram; As-N-Na-H<sub>2</sub>O system; lead anode slime; leaching; arsenic removal

### **1** Introduction

Lead anode slime is an important secondary product from the process of lead electrolytic refining, which is rich in valuable elements such as bismuth, antimony, arsenic, lead, gold and silver [1,2]. As we know, the environmental pollution, low quality of production and complicated process will be caused during the lead anode slime treatment because arsenic is a harmful element. Therefore, the arsenic removal is very essential in pyrometallurgical and hydrometallurgical processes in order to extract other valuable metals from lead anode slime [3]. At present, the treatment process of lead anode slime can be classified in the following two methods as pyrometallurgy and hydrometallurgy: the pyrometallurgy mainly includes reduction roasting [4], volatilization roasting or eliminating arsenic in vacuum [5], and the hydrometallurgy mainly includes oxidizing acid leaching [6], oxidation alkaline leaching [7] or chloridization leaching [8,9]. Pressure leaching is an effective method and widely used for metal extraction from different raw materials [10-13], and alkaline pressure oxidation leaching of lead anode slime is proposed in order to remove arsenic in this research.

The  $\varphi$ -pH diagram (potential-pH diagram) is an useful tool in thermodynamic characteristics analysis during the hydrometallurgy process [14,15]. A rapid and reliable method for intuitive assessment of thermodynamic equilibriums and reaction feasibility can be provided easily according to  $\varphi$ -pH diagram. In addition, it can also be widely used in many other fields such as corrosion and anticorrosion of metal, mineral geology [16–18]. The  $\varphi$ -pH diagram of As-H<sub>2</sub>O system at different temperatures has been investigated [19], but the  $\varphi$ -pH diagrams of As-N-Na-H<sub>2</sub>O system for pressure oxidation alkaline leaching of arsenic-rich lead anode slime have never been reported. This research has done some works in order to explain the thermodynamic characteristics of arsenic in the pressure oxidation leaching progress by means of the construction of the *q*-pH diagrams of As-N-Na-H<sub>2</sub>O system. Based on  $\varphi$ -pH diagrams of As-N-Na-H<sub>2</sub>O system, an originally thermodynamic guidance can be obtained for the arsenic

Foundation item: Project (51564031) supported by the National Natural Science Foundation of China; Project (0201352042) supported by the Cooperation between School and Enterprise of China

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removal during alkaline pressure oxidation leaching of lead anode slime.

#### 2 Thermodynamics

#### 2.1 Thermodynamic calculation method

All the chemical reactions in the hydrometallurgical process can be presented simply as follows:

$$aA+nH^++ze=bB+cH_2O$$
 (1)

where *a*, *n*, *b* and *c* are the stoichiometric coefficients for species A,  $H^+$ , B and  $H_2O$  in the electrochemical reaction, respectively, and *z* is the electron transfer number of the electrode reaction. The Gibbs free energy of Eq. (1) can be shown explicitly as

$$\Delta_{\rm r} G_T = c \Delta_{\rm f} G_{\rm H_2O,T} + b \Delta_{\rm f} G_{\rm B,T} - z \Delta_{\rm f} G_{\rm e,T} - n \Delta_{\rm f} G_{\rm H^+ T} - a \Delta_{\rm f} G_{\rm A,T}$$
<sup>(2)</sup>

Some interrelated equations about Gibbs free energy of Eq. (1) can be shown as follows:

$$\Delta_{\rm r}G_T = \Delta_{\rm r}G_T^{\Theta} + RT \ln[a_{\rm B}^b/(a_{\rm A}^a a_{\rm H^+}^n)] = \Delta_{\rm r}G_T^{\Theta} + RT \ln(a_{\rm B}^b/a_{\rm A}^a) + 2.303nRTpH$$
(3)  
$$\left[\Delta_{\rm r}G_T = -zF\varphi_T\right]$$

$$\begin{cases} \Delta_{\rm r} G_T^{\Theta} = -zF\varphi_T^{\Theta} \end{cases} \tag{4}$$

According to Eqs. (2)-(4), Nernst equation can be deduced as [20]

$$-zF\varphi_{T} = -zF\varphi_{T}^{\Theta} + 2.303RT \lg(a_{\rm B}^{b}/a_{\rm A}^{a}) + 2.303nRT \text{pH}$$
(5)

Equation (5) can be divided into the following three situations and the  $\varphi$ -pH equations in different situations can be shown as follows:

Only electron is involved in the reaction ( $z\neq 0$ , n=0):

$$\varphi_T = \varphi_T^{\Theta} - \frac{2.303RT}{zF} \lg \left( \frac{a_{\rm B}^b}{a_{\rm A}^a} \right) \tag{6}$$

Only H<sup>+</sup> is involved in the reaction (
$$n \neq 0, z=0$$
):  

$$H = \frac{-\Delta_r G_r^{\Theta}}{2 2022 \text{ ptr}} - \frac{1}{2} \log \left(\frac{a_B^b}{a_B^b}\right)$$
(7)

 $pH = \frac{\Delta_{T} \sigma_{T}}{2.303nRT} - \frac{1}{n} lg \left(\frac{\alpha_{B}}{a_{A}^{a}}\right)$ (7) Both electrons and H<sup>+</sup> are involved in the reaction ( $n \neq 0, z \neq 0$ ):

$$\varphi_T = \varphi_T^{\Theta} - \frac{2.303RT}{zF} \lg \left(\frac{a_B^b}{a_A^a}\right) - \frac{2.303RT}{zF} n \text{pH}$$
(8)

where  $\Delta_{\rm f}G_T$  is the formation Gibbs free-energy of a certain specie at temperature *T*;  $\Delta_{\rm r}G_T$  and  $\Delta_{\rm r}G_T^{\Theta}$  are the free energy and standard free energy of reaction at temperature *T*, respectively;  $\varphi_T$  and  $\varphi_T^{\Theta}$  are the electrochemical potential and standard electrochemical potential for the reaction at temperature *T*, respectively; *F* is the Faraday's constant and *R* is the molar gas constant;  $a_{\rm A}$  and  $a_{\rm B}$  are the overall activities of species A and B, respectively. So, the  $\varphi$ -pH diagram based on the Eqs. (6)–(8) can be established in different situations as long as the  $\varphi_{\rm r}$  or  $\varphi_T^{\Theta}$  or  $a_{\rm A}$  and  $a_{\rm B}$  at the certain temperature can be known.

#### 2.2 Species and thermodynamic equilibrium

The leaching process of arsenic from lead anode slime is to make insoluble arsenic turn into dissolvable forms. NaOH and NaNO<sub>3</sub> were employed as leaching agents during the alkaline oxidation leaching, leading to the fact that nitrogen and sodium were involved in the system. Therefore, many elements and species must be involved [21]. The data of the thermodynamic calculation in this research are obtained from Ref. [22] except as otherwise indicated, and the thermodynamic data of the main substances in As–N–Na–H<sub>2</sub>O system are listed in Table 1.

The arsenic leaching is available based on the

Service	$\Delta_{\rm f} G_T^{\Theta} / ({\rm kJ} \cdot {\rm mol}^{-1})$				Species	$\Delta_{\mathrm{f}} G_T^{\Theta} / (\mathrm{kJ} \cdot \mathrm{mol}^{-1})$			
Species	298 K	373 K	423 K	473 K	species	298 K	373 K	423 K	473 K
H <sub>3</sub> AsO <sub>4</sub> (aq)	-799.54	-972.24	-986.36	-1004.97	HNO <sub>3</sub> (aq)	-256.08	-255.77	-264.31	-272.80
$H_2AsO_4^-$	-949.86	-959.85	-966.12	-972.08	HNO <sub>2</sub> (aq)	-164.62	-175.47	-182.09	-188.28
$HAsO_4^{2-}$	-917.35	-916.93	-912.83	-905.69	N <sub>2</sub> (g)	-57.04	-71.65	-81.64	-91.80
HAsO <sub>2</sub> (aq)	-493.12	-501.36	-505.85	-509.94	$\mathrm{NH_4}^+$	-160.01	-167.92	-174.46	-182.03
$AsO_2^-$	-447.02	-448.21	-444.87	-438.97	NH <sub>4</sub> OH(aq)	-419.70	-433.53	-443.34	-454.01
$AsO_4^{3-}$	-857.63	-844.00	-828.10	-806.74	Na <sup>+</sup>	-251.23	-255.44	-259.78	-265.36
As(s)	-10.63	-13.53	15.67	-17.97	NaH (s)	-68.30	-71.63	-74.20	-77.01
$As_2O_3(s)$	-689.30	-699.51	-707.38	-716.05	NaOH(aq)	-483.83	-486.95	-488.38	-489.28
AsH <sub>3</sub> (g)	0.16	-16.87	-28.60	-40.60	e*	-25.68	-31.16	-33.72	-35.39
$NO_3^-$	-257.18	-267.96	-273.18	-276.84	$\mathrm{H}^+$	6.23	6.70	5.79	3.90
$NO_2^-$	-152.48	-162.68	-167.41	-170.47	$H_2(g)$	-38.89	-48.93	-55.87	-62.98
$H_2O(1)$	-306.39	-312.23	-322.15	-321.39	$O_2(g)$	-61.07	-76.69	-87.37	-98.23

Table 1 Thermodynamic data of main substances in As-N-Na-H2O system for lead anode slime leaching process

\*e stands for the electron involved in chemical reaction

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chemical reactions among the species. Nernst equation can be used to illustrate the thermodynamic equilibrium. The  $\varphi$ -pH diagrams for the leaching progress can be established according to the Nernst equation. The relationship expressions between  $\varphi$  and pH value were calculated according to Eqs. (2)–(8). The considered chemical reactions and their  $\varphi$ –pH formulas are listed in Table 2.

<b>Table 2</b> Electrode reaction and standard potential value	in As-N-Na-H2O system for lead anode slin	ne leaching process
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No	Ponotion			$\varphi^{\Theta}_{T}$ or pH			
INO.	Reaction	$\varphi^{-}$ pri equation	298 K	373 K	423 K	473 K	
1	$H_{3}AsO_{4}(aq)+2H^{+}+2e=HAsO_{2}(aq)+2H_{2}O(l)$	$\varphi_T = \varphi_T^{\Theta} - 2.303 \times RT/F \times pH$	0.573	0.542	0.559	0.439	
2	$H_2AsO_4^-+3H^++2e=HAsO_2(aq)+2H_2O(l)$	$\varphi_T = \varphi_T^{\Theta} - 2.303 \times 3 \times RT/(2F) \times pH + 2.303RT/(2F) \lg a(H_2AsO_4^-)$	0.639	0.641	0.694	0.630	
3	HAsO <sub>4</sub> <sup>2-</sup> +4H <sup>+</sup> +2e=HAsO <sub>2</sub> (aq)+2H <sub>2</sub> O(l)	$\varphi_T = \varphi_T^{\Theta} - 2.303 \times 4 \times RT/(2F) \times pH + 2.303RT/(2F) \times \lg a(\text{HAsO}_4^{2-})$	0.84	0.898	1.000	0.994	
4	$HAsO_4^{2-}+3H^++2e=AsO_2^-+2H_2O(1)$	$\varphi_T = \varphi_T^{\Theta} - 2.303 \times 3 \times RT/(2F) \times pH - 2.303 \cdot RT/(2F) \times lg[a (AsO_2^-) / a (HAsO_4^{2^-})]$	0.569	0.588	0.654	0.606	
5	$AsO_4^{3-}+4H^++2e=AsO_2^-+2H_2O(l)$	$\varphi_T = \varphi_T^{\Theta} - 2.303 \times 4 \times RT/(2F) \times pH - 2.303RT/(2F) lg[a (AsO_2^-)/a (AsO_4^{3-})]$	0.911	1.001	1.123	1.139	
6	$H^++AsO_2^-=HAsO_2(aq)$	$pH = -\Delta_r G_T^{\Theta} / (2.303RT) + \lg a (AsO_2^-)$	9.167	8.381	8.241	8.264	
7	$H^+ + H_2 AsO_4^- = H_3 AsO_4(aq)$	$pH = -\Delta_r G_T^{\Theta} / (2.303RT) + lg a (H_2 AsO_4^-)$	2.238	2.672	2.713	3.061	
8	$\mathrm{H}^{+}\mathrm{H}\mathrm{AsO}_{4}^{2-}=\mathrm{H}_{2}\mathrm{AsO}_{4}^{-}$	pH= $-\Delta_r G_T^{\Theta}/(2.303RT)$ + lg a(HAsO <sub>4</sub> <sup>-</sup> )-lg a(H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> )	6.78	6.94	7.29	7.75	
9	$H^+ + AsO_4^{3-} = HAsO_4^{2-}$	pH= $-\Delta_r G_T^{\Theta}/(2.303RT)+$ lg a (AsO <sub>4</sub> <sup>3-</sup> )-lg a (HAsO <sub>4</sub> <sup>2-</sup> )	11.55	11.14	11.17	11.35	
10	$2H_3AsO_4(aq)+4H^++4e=As_2O_3(s)+5H_2O(l)$	$\varphi_T = \varphi_T^{\Theta} - 2.303RT/F \times pH + 2.303RT/(2F) \lg a(H_3AsO_4)$	0.598	0.566	0.605	0.485	
11	$2H_2AsO_4^-+6H^++4e=As_2O_3(s)+5H_2O(l)$	$\varphi_T = \varphi_T^{\Theta} - 2.303RT \times 3/(2F) \times pH + 2.303RT/(2F) \times lg a (H_2AsO_4^-)$	0.664	0.665	0.740	0.675	
12	$2HAsO_4^{2-}+8H^++4e=As_2O_3(s)+5H_2O(l)$	$\varphi_T = \varphi_T^{\Theta} - 2.303RT \times 8/(4F) \times pH + 2.303RT/(2F) \times \lg a(\text{HAsO}_4^-)$	0.865	0.922	1.046	1.040	
13	$2AsO_{2}^{-}+2H^{+}=As_{2}O_{3}(s)+H_{2}O(l)$	$pH = -\Delta_r G_T^{\Theta} / 2.303 / (2RT) + RT / 2 \times \lg a (AsO_2^-)$	9.490	8.852	8.841	8.733	
14	$As_2O_3(s)+6H^++6e=2As(s)+3H_2O(l)$	$\varphi_T = \varphi_T^{\Theta} - 2.303 RT/F \times pH$	0.232	0.203	0.212	0.164	
15	$A_{s}O_{4}^{3-}+8H^{+}+5e=As(s)+4H_{2}O(l)$	$\varphi_T = \varphi_T^{\Theta} - 2.303RT \times 8/(5F) \times pH +$ 2.303RT/(5F)×lg a (AsO <sub>4</sub> <sup>3-</sup> )	0.622	0.655	0.733	0.728	
16	$As(s)+3H^++3e=AsH_3(g)$	$\varphi_T = \varphi_T^{\Theta} - 2.303RT/F \times pH - 2.303RT/(3F) \times \lg p(AsH_3)$	-0.239	-0.242	-0.245	-0.248	
17	$AsO_{2}^{-}+4H^{+}+3e=As(s)+2H_{2}O(1)$	$\varphi_T = \varphi_T^{\Theta} - 2.303RT \times 4/(3F) \times pH + 2.303RT/(3F) \times \lg a (AsO_2^-)$	0.429	0.425	0.474	0.453	
1′	$NO_3^-+3H^++2e =HNO_2(aq)+H_2O(l)$	$\varphi_T = \varphi_T^{\Theta} - 2.303RT \times 3/(2F) \times pH +$ 2.303RT/(2F)lg[a(NO <sub>3</sub> <sup>-</sup> )/a(HNO <sub>2</sub> )]	0.939	0.920	0.938	0.900	
2′	$NO_3^- + 2H^+ + 2e = NO_2^- + H_2O(I)$	$\varphi_T = \varphi_T^{\Theta} - 2.303RT/F \times pH +$ 2.303RT/(2F)lg[a (NO <sub>3</sub> <sup>-</sup> )/a (NO <sub>2</sub> <sup>-</sup> )]	0.844	0.819	0.832	0.788	
3'	$NO_2^- + H^+ = HNO_2(aq)$	$pH = -\Delta_r G_T^{\Theta} / (2.303RT) + \lg a (NO_2^-)$	2.219	2.415	2.588	2.805	
4′	NO <sub>3</sub> <sup>-</sup> +H <sup>+</sup> =HNO <sub>3</sub> (aq)	$pH = -\Delta_r G_T^{\Theta} / (2.303RT) + lg a (NO_3^-)$	-0.101	-1.538	-1.538	1.024	
5'	$HNO_3(aq)+2H^++2e=HNO_2(aq)+H_2O(l)$	$\varphi_T = \varphi_T^{\Theta} - 2.303RT/F \times pH +$ 2.303RT/(2F)lg[a(HNO <sub>3</sub> )/a(HNO <sub>2</sub> )]	0.912	0.948	0.954	0.901	

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No	Ponotion	a-pH equation	$\varphi_T^{\Theta}$ or pH			
INO.	Reaction	$\varphi$ -pri equation	298 K	373 K	423 K	473 K
6'	$HNO_{2}(a_{1})+7H^{+}+6e = NH_{1}^{+}+2H_{2}O(1)$	$\varphi_T = \varphi_T^{\Theta} - 2.303 RT \times 7 \times /(6F) \times pH -$	0.860	1 282	1 285	1 250
0		$2.303RT/(6F)\lg a(NH_4^+)$	0.000	1.202	1.205	1.230
7′	$NO^{-}+8H^{+}+6e = NH^{+}+2H_{-}O(1)$	$\varphi_T = \varphi_T^{\Theta} - 2.303RT \times 8/(6F) \times pH -$	0.801	1 3 1 6	1 3 2 0	1 287
	$100_2 + 011 + 00 = 1011_4 + 211_20(1)$	$2.303RT/(6F)lg[a(NH_4^+)/a(NO_2^-)]$	0.891	1.510	1.320	1.28/
01	$MO^{-} + 7H^{+} + 6a - MH OH(aa) + H O(1)$	$\varphi_T = \varphi_T^{\Theta} - 2.303RT \times 7/(6F) \times pH +$	0 800	0.765	0.754	0.725
0	$\operatorname{NO}_2$ + / $\operatorname{II}$ + $\operatorname{Oe}$ = $\operatorname{NII}_4 \operatorname{OII}(\operatorname{ad})$ + $\operatorname{II}_2 \operatorname{O(I)}$	$2.303 RT/(6F) \lg a(NO_2^-)$	0.800			
0/	$N_{(-)} + 0 \Pi^{+} + C_{-} = 2 N \Pi^{+}$	$\varphi_T = \varphi_T^{\Theta} - 2.303RT \times 8/(6F) \times pH -$	0.274	0.226	0.192	0.157
9'	$N_2(g) + 8H + 6e = 2NH_4$	$2.303 RT/(6F) lg[a (NH_4^+) / a(p_{N_2}/p^{\Theta})]$	0.274			
10/	$\mathbf{N}(\mathbf{r}) + 2\mathbf{H}(\mathbf{O}(\mathbf{r})) + (\mathbf{H}^{+}) + (\mathbf{r} - 2\mathbf{N}\mathbf{H}(\mathbf{O}(\mathbf{r})))$	$\varphi_T = \varphi_T^{\Theta} - 2.303 RT/F \times pH +$	0.001	0.042	-0.012	-0.027
10	$N_2(g) + 2H_2O(1) + 6H + 6e = 2NH_4OH(aq)$	$2.303RT(6F)lg(p_{N_2}/p^{\Theta})$	0.091			
11/	$2 NO^{-} + 12 U^{+} + 10N (-) + (U O(1))$	$\varphi_T = \varphi_T^{\Theta} - 2.303RT \times 12/(10F) \times pH -$	1 0 4 2	1 001	1 244	0.970
11	$2 \text{ NO}_3 + 12 \text{H} + 100 = \text{N}_2(\text{g}) + 6 \text{H}_2 O(1)$	$2.303RT/(10F) \times lg[(p_{N_2}/p^{\Theta})/a(NO_3)]$	1.243	1.221	1.244	0.870
12′	$NH_4OH(aq)+H^+=NH_4^++H_2O(l)$	$pH = -\Delta_r G_T^{\Theta} / (2.303RT) - 2.303RT \times lg a(NH_4^+)$	9.277	7.466	7.287	5.885
Ι	NaOH(aq)+H <sup>+</sup> =Na <sup>+</sup> +H <sub>2</sub> O(l)	$pH = -\Delta_r G_T^{\Theta} / (2.303RT) + \lg a(Na^+)$	14.026	12.240	11.231	11.189
II		$\varphi_T = \varphi_T^{\Theta} - 2.303RT/(2F) \times pH +$	1 1 0 0	-1.240	1 001	1 2 2 2
	Na + H + 2e = NaH(s)	$2.303 RT/(2F) \times \lg a(Na^{+})$	-1.182		-1.281	-1.322
a	$2H^++2e=H_2(g)$	$\varphi_T = \varphi_T^{\Theta} - 2.303 RT/F \times pH$	0	0.0578	0.0848	0.098
b	$O_2(g)+4H^++4e=2H_2O(l)$	$\varphi_T = \varphi_T^{\Theta} - 2.303 RT/F \times pH$	1.228	1.225	1.211	1.186

#### 2.3 φ-pH diagram of As-Na-H<sub>2</sub>O system

The  $\varphi$ -pH diagrams of As-Na-H<sub>2</sub>O system at different temperatures are constructed in Fig. 1 according to equilibrium equations listed in Table 2. The condition parameters are established as the molality of all the species is 0.1 mol/kg and temperatures range from 298 to 473 K.

Arsenic exists as acid radical in the system when  $\varphi$  is positive. H<sub>3</sub>AsO<sub>4</sub>(aq) and H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> exist in the acid region. They exist in the forms of HAsO<sub>4</sub><sup>2-</sup> and HAsO<sub>2</sub> when pH values are between 7 and 11. AsO<sub>4</sub><sup>3-</sup> is stable when pH value is higher than 11. The stable region of H<sub>3</sub>AsO<sub>4</sub>(aq), HAsO<sub>2</sub>(aq), HAsO<sub>4</sub><sup>2-</sup>, As<sub>2</sub>O<sub>3</sub>(s), AsO<sub>4</sub><sup>3-</sup> and As(s) superimposes largely in the stable region of water, which approves the feasibility of acid or alkali leaching of arsenic in the arsenic-rich lead anode slime in water solution [23].

Based on the  $\varphi$ -pH diagrams of As-Na-H<sub>2</sub>O system in Fig. 1, thermodynamics behaviors of arsenic in alkaline pressure oxidation leaching process were discussed. The soluble arsenic ions should be the main research object. The main features of the  $\varphi$ -pH diagrams of As-Na-H<sub>2</sub>O system are summarized as follows.

1) The stability region of NaOH(aq) increases with increasing leaching temperature.

2) The stability region of  $AsO_2^-$  increases with the rise of temperature. More  $AsO_2^-$  will change into  $AsO_4^{3-}$  in the high pH region. Therefore, high leaching

temperature and high pH value or high alkali concentration will be beneficial to the arsenic leaching. Consequently, high temperature and high alkali concentration are very essential at the beginning of the leaching.

3) There is a large area of  $As_2O_3(s)$  containing in the stability region of water. In these superimposed areas, there is a thermodynamic equilibrium region between water and  $As_2O_3(s)$ . The chemical reaction can be written as  $As_2O_3(s)$ +H<sub>2</sub>O(aq)=2HAsO<sub>2</sub>(aq), so,  $As_2O_3(s)$  and HAsO<sub>2</sub>(aq) will coexist in these regions [21].

#### 2.4 *\varphi*-pH diagrams of N-H<sub>2</sub>O system

Dissolved nitrate with several different valences can be involved in many reactions in the solution, and it can be transformed among various forms according to the situation. During the leaching process of arsenic from lead anode slime, NaNO<sub>3</sub> is employed as oxidant, nitrogen atom in  $NO_3^-$  will get electron in the reaction and its valence will decrease. Most insoluble arsenic in the lead anode slime mainly exists as the lower valence state, while  $NO_3^-$  plays an electron acceptor role in the electrochemical reaction, which promotes the dissolution of arsenic during the alkaline oxidation leaching, and solvable arsenic is usually at higher valence state in the solution.

In order to analyze the thermodynamic equilibriums of nitrogenous compounds in the solution, the  $\varphi$ -pH



Fig. 1  $\varphi$ -pH diagrams of As-Na-H<sub>2</sub>O system at different temperatures: (a) 298 K; (b) 373 K; (c) 423 K; (d) 473 K

diagrams of N–H<sub>2</sub>O system are established and shown in Fig. 2. The condition parameters are established when the molality of all the species is 0.1 mol/kg and temperatures range from 298 to 473 K.

The thermodynamic characteristics of  $N-H_2O$  at different temperatures are summarized as follows.

1) The stable regions of  $NH_4OH(aq)$  and  $NO_2^-$  increase apparently with increasing temperature.

2) The stable regions of  $NO_2^-$ ,  $NO_3^-$  and  $N_2$  superimpose with the stable region of water, which indicates the thermodynamic possibility of the redox reactions among nitrogenous compounds in the solution. So, it is reasonable and feasible to use  $NaNO_3$  as the oxidant during the alkaline oxidation leaching of lead anode slime.

3) Large proportion of  $N_2$  stable region superimposes with the stable region of water, which indicates the possibility of  $N_2$  formation during the leaching process.

#### 2.5 *q*-pH diagram of As-N-Na-H<sub>2</sub>O system

The  $\varphi$ -pH diagrams of As-N-Na-H<sub>2</sub>O system are constructed at different temperatures for the leaching of arsenic from lead anode slime, and shown in Fig. 3. It can be seen from Fig. 3 that many stable regions of arsenic compounds and nitrate superimpose with the water stable region, therefore, the occurrence of various reactions among the considered species is possible in the solution.

The main thermodynamic features of As–N–Na– H<sub>2</sub>O system can be summarized as follows.

1) Various forms of arsenic are associated with pH value. It mainly exists as  $H_3AsO_4(aq)$ ,  $H_2AsO_4^-$ ,  $HAsO_4^{2-}$ ,  $H_2AsO_2(aq)$  and  $As_2O_3(s)$  in lower pH value regions, and it mainly exists as  $AsO_4^{3-}$  when pH value is higher than 11.14.

2) In lower pH region, when  $\varphi$  is less than -0.137 V, As<sub>2</sub>O<sub>3</sub> will transform into AsH<sub>3</sub> according to electrode reactions (Eqs. (14) and (16) listed in Table 2).

3) The stable areas of  $AsO_2^-$  and NaOH(aq)increase with the rise of temperature and pH value, which indicates that more  $AsO_2^-$  will generate when temperature and alkali concentration are high, meaning that more soluble trivalent arsenic will be oxidized into high valence states such as  $H_3AsO_4(aq)$ ,  $H_2AsO_4^-$ ,  $AsO_4^{3-}$  or  $HAsO_4^{2-}$ , this transversion complies with the following equations respectively.

$$HAsO_2(aq)+2H_2O(1)-2e=H_3AsO_4(aq)+2H^+$$
 (9)

$$HAsO_2(aq)+2H_2O(l)-2e=H_2AsO_4^-+3H^+$$
 (10)

$$AsO_2^-+2H_2O(1)-2e=AsO_4^{3-}+4H^+$$
 (11)



Fig. 2 φ-pH diagram of N-H<sub>2</sub>O system at different temperatures: (a) 298 K; (b) 373 K; (c) 423 K; (d) 473 K



Fig. 3  $\varphi$ -pH diagrams of As-N-Na-H<sub>2</sub>O system at different temperatures: (a) 298 K; (b) 373 K; (c) 423 K; (d) 473 K

$$AsO_{2}^{-}+2H_{2}O(1)-2e=HAsO_{4}^{2-}+3H^{+}$$
 (12)

$$HAsO_2(aq)+2H_2O(l)-2e=HAsO_4^{2-}+4H^+$$
 (13)

4) More  $As_2O_3(s)$  will dissolve with the rise of temperature and pH value. Main chemical reaction of trioxide arsenic dissolution in alkaline condition is shown as follows:

$$As_2O_3(s) + 2OH^- = 2AsO_2^- + H_2O(1)$$
 (14)

There is a large amount of  $OH^-$  when pH value is high, and  $As_2O_3(s)$  can dissolve more efficiently in the alkaline condition according to the above equation.

5) During the alkaline oxidation leaching of lead anode slime, arsenic will be removed in the form of  $Na_3AsO_4$ . The formation reaction of  $AsO_4^{3-}$  can be shown as follows:

$$10AsO_{2}^{-}+16OH^{-}+4NO_{3}^{-}=10AsO_{4}^{3-}+8H_{2}O(1)+N_{2}(g)(15)$$

The transformation reaction between  $As_2O_3$  (s) and  $Na_3AsO_4(aq)$  in the alkaline leaching system can be written as

$$5As_{2}O_{3}(s)+26NaOH(aq)+4NaNO_{3}(aq) = 10Na_{3}AsO_{4}(aq)+13H_{2}O(l)+2N_{2}(g)$$
(16)

Based on the above description, more  $As_2O_3(s)$  will transform into  $AsO_4^{3-}$  when OH<sup>-</sup> concentration is high. Consequently, alkaline pressure oxidation leaching is feasible to remove arsenic from lead anode slime because  $As_2O_3$  (s) is the main phase. The usage of NaNO<sub>3</sub> (aq) and NaOH (aq) as oxidant and alkaline reagent respectively during the leaching process is reasonable because an advantageous condition for the arsenic leaching can be provided.

AsH<sub>3</sub> is a poisonous substance which is generated easily in the acid environment. It can be seen from Fig. 3 that there are large stable areas of  $AsH_3(g)$  in the low pH region, which demonstrates a high thermodynamic possibility of  $AsH_3$  formation. Therefore, it is not commonly recommendable to remove arsenic by strong acid leaching process in order to avoid the formation of  $AsH_3(g)$ .

## 3 Arsenic removal experiment during alkaline pressure oxidation leaching of lead anode slime

Lead anode slime containing arsenic was employed as the raw materials, and its chemical compositions are shown in Table 3. It can be seen that bismuth (Bi) is the highest content metal and its content is 45.25%, the contents of arsenic (As), antimony (Sb) and lead (Pb) are 10.68%, 11.8% and 11.43%, respectively, the contents of gold (Au) and silver (Ag) are 24.3 and 3408 g/t respectively. In addition, there are slight tin (Sn) and copper (Cu). Arsenic must be removed before extracting bismuth and enriching gold and silver from lead anode slime.

 Table 3 Chemical composition of metallic element in lead anode slime (mass fraction, %)

Bi	As	Sb	Pb	Sn	Cu	$Au^{1)}$	$Ag^{1)}$
45.25	10.68	11.8	11.43	1.08	1.54	24.3	3408
1) g/t							

The anode slime was ground to less than 250  $\mu$ m and then put into the autoclave, the alkaline pressure oxidation leaching process of arsenic was carried out under the following conditions of pressure of 0.8 MPa, liquid to solid ratio of 7:1, leaching time of 180 min, stirring speed of 300 r/min, NaOH concentration of 200 g/L and NaNO<sub>3</sub> concentration of 15% (the mass ratio of NaNO<sub>3</sub> to lead anode slime is 15%). In addition, the temperatures of the alkaline pressure oxidation leaching were controlled from 313 to 493 K. The schematic diagram of the experimental apparatus is shown in Fig. 4.

The effect of temperature on leaching rate of arsenic from lead anode slime is shown in Fig. 5. The result indicates that the arsenic leaching rate increases from 13.86% to 95.55% when the temperature increases from 313 to 433 K, and it reaches the highest value of 95.85% at 453 K. Thereafter, the leaching rate begins to decrease.

The above leaching rate of arsenic confirms the thermodynamic analysis based on the  $\varphi$ -pH diagrams of As-N-Na-H<sub>2</sub>O system at different temperatures. As shown in  $\varphi$ -pH diagrams of As-N-Na-H<sub>2</sub>O from 298 to 473 K, the stabile region of AsO<sub>2</sub><sup>-</sup> gradually increases with the increase of temperature, displaying that more As<sub>2</sub>O<sub>3</sub>(s) will transform into the soluble AsO<sub>2</sub><sup>-</sup> in the high pH region, complying with Eqs. (14) and (17).

$$As_2O_3(s) + H_2O = 2HAsO_2(aq)$$
(17)

Therefore, high temperature and high pH value will be advantageous to the arsenic leaching, and higher leaching rate of arsenic can be obtained during the alkaline pressure oxidation leaching of lead anode slime.

Lixivium was cooled down and crystallized after finishing alkaline pressure oxidation leaching of lead anode slime, and the phase structures of crystals were measured by XRD and the result is shown in Fig. 6. It can be concluded from Fig. 6 that the phase compositions of the crystals obtained from lixivium are Na<sub>3</sub>AsO<sub>4</sub>.10H<sub>2</sub>O. During the course of alkaline pressure oxidation leaching, As<sub>2</sub>O<sub>3</sub> in lead anode slime is dissolved in the form of AsO<sub>2</sub><sup>-</sup> according to Eq. (14). Thereafter, AsO<sub>2</sub><sup>-</sup> will be oxidized to AsO<sub>4</sub><sup>3-</sup> according to Eq. (15) when NaNO<sub>3</sub> is used as oxidant in the alkaline conditions, leading to the fact that large amounts of AsO<sub>4</sub><sup>3-</sup> and Na<sup>+</sup> exist in the system.

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Fig. 4 Schematic diagram of experimental apparatus



Fig. 5 Effect of temperature on leaching rate of arsenic from lead anode slime

Therefore, the main phase composition of arsenic is  $Na_3AsO_4(aq)$  in the lixivium. The transformation reaction between  $As_2O_3(s)$  and  $Na_3AsO_4$  (aq) can be written as Eq. (16). The above research results agree well with the thermodynamic prediction according to  $\varphi$ -pH diagrams of As-N-Na- H<sub>2</sub>O system.

In addition, under the following alkaline pressure oxidation leaching from lead anode slime as NaOH



Fig. 6 XRD pattern of crystals from arsenic lixivium

concentration of 200 g/L, NaNO<sub>3</sub> concentration of 15%, pressure of 0.8 MPa, liquid to solid ratio of 7:1, leaching time of 180 min, leaching temperature of 453 K and stirring speed of 300 r/min, the highest leaching rate of arsenic is obtained and it reaches 95.85%. In addition, the leaching rates of other elements in the lead anode slime are shown in Table 4. As shown in Table 4, the leaching rates of antimony and lead are 72.22% and 73.57%, respectively, and the leaching rate of bismuth is

only 1.83%. The following metals as tin, copper, gold and silver all enter the leaching residue.

 Table 4 Leaching rates of other elements in lead anode slime

 (%)

Bi	Sb	Pb	Sn	Cu	Au	Ag
1.83	72.22	73.57	0	0	0	0

Therefore, the removal of arsenic, antimony and lead by alkaline pressure oxidation leaching method provides the condition for the extracting bismuth and enriching gold and silver from lead anode slime.

#### **4** Conclusions

1) The  $\varphi$ -pH diagrams of As-N-Na-H<sub>2</sub>O systems at different temperatures were established to illustrate the thermodynamic characteristics of arsenic during alkaline oxidation leaching process of lead anode slime.

2) The existing forms of arsenic are associated with pH value. It mainly exists as  $H_3AsO_4(aq)$ ,  $H_2AsO_4^-$ ,  $HAsO_4^{2-}$ ,  $H_2AsO_2(aq)$  and  $As_2O_3(s)$  in lower pH value region; whereas it mainly exists as  $AsO_4^{3-}$  when pH value is higher than 11.14. High alkali concentration and high thermodynamic temperature are advantageous to the arsenic leaching.

3) The tendency of arsenic leaching rate confirms the thermodynamic analysis results obtained from the  $\varphi$ -pH diagrams of As-N-Na-H<sub>2</sub>O system, and the highest leaching rate of arsenic reaches 95.85% at thermodynamic temperature of 453 K during the course of alkaline pressure oxidation leaching.

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# 铅阳极泥碱性加压氧化浸出脱砷过程中 As-N-Na-H<sub>2</sub>O 系的 $\varphi$ -pH 图

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**摘 要:**为阐明砷在铅阳极泥碱性加压氧化浸出过程(NaNO<sub>3</sub>为氧化剂; NaOH 为碱性试剂)中的热力学特性,通过 热力学计算绘制体系离子质量浓度为 0.1 mol/kg,温度为 298、373、423 和 473 K 条件下的 As-Na-H<sub>2</sub>O、N-H<sub>2</sub>O 和 As-N-Na-H<sub>2</sub>O 系的 φ-pH 图。结果表明,砷的存在形态与 pH 值有关。当 pH 值较低时,砷主要以 H<sub>3</sub>AsO<sub>4</sub>、 H<sub>2</sub>AsO<sub>4</sub><sup>2-</sup>、H<sub>2</sub>AsO<sub>2</sub><sup>2</sup>及 As<sub>2</sub>O<sub>3</sub>的形式存在;当 pH>11.14 时,砷主要以 AsO<sub>4</sub><sup>3-</sup>形式存在,高碱浓度及高 温对砷浸出有利。碱性加压氧化浸出实验表明,砷浸出率变化趋势与 As-N-Na-H<sub>2</sub>O 系 φ-pH 图的热力学分析结 果一致,在 453 K 时砷的最佳浸出率为 95.85%。

关键词: φ-pH 图; As-N-Na-H<sub>2</sub>O 系; 铅阳极泥; 浸出; 脱砷

(Edited by Wei-ping CHEN)