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The solubility behavior of sodium arsenate in NaOH solution based on the Pitzer model

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ABSTRACT

Alkaline leaching is an effective method for dealing with arsenic-containing resources. Arsenic is dissolved in an alkaline solution in the form of arsenate, but the lack of relevant basic data has caused difficulties in the theoretical analysis during production and research. The dissolution behavior of arsenic in the solution was systematically studied in this paper. The solubility behavior of the self-made sodium arsenate in water and NaOH solution were measured. The research on sodium arsenate solution was carried out to obtain the quasi-solubility product using the Pitzer model, and the effect of temperature and NaOH concentration on the solubility and quasi-solubility product of sodium arsenate was clarified.

1. Introduction

Arsenic is a ubiquitous element in nature, and its content in the earth's crust is 1.5^{-3} mg/kg [1,2]. Arsenic is usually enriched in lead, zinc, copper, and other nonferrous metal ores in the form of minerals, such as arsenopyrite (FeAsS), sulfur arsenic (Cu₃AsS₄), and realgar (As₂S₂) [3,4]. Arsenic compounds are protoplasmic poisons with metal-like properties and have been identified as the first category of carcinogens by the International Anticancer Agency [5,6]. It is harmful to the human body, especially for workers in factories dealing with arsenic-containing materials and personnel engaged in arsenic research [7,8].

The general beneficiation method cannot completely remove the arsenic in the minerals [9,10]. Therefore, partial arsenic will be in different forms during the processes of smelting [11,12], such as smelting residue, smelting fume, and wastewater. Many arsenic-containing materials are produced in the metallurgical process of nonferrous metals every year [13,14]. To avoid secondary pollution of arsenic-containing materials during storage or landfilling, harmless treatment is necessary [15]. Arsenic removal can be divided into pyrometallurgical processes [16,17], hydrometallurgical processes [18,19], and hybrid processes [11,20]. Arsenic removal by pyrometallurgical processes involves separating and enriching arsenic by volatilization at high temperatures [18]. Arsenic removal by hydrometallurgy mainly refers to the extraction of arsenic in suitable systems [21–23]. Compared with the pyrometallurgical processes, the hydrometallurgical ones have the advantages of high removal efficiency, wide application range, and low energy consumption. The alkaline leaching of arsenic-containing materials is a widely used process for removing arsenic [24]. Alkaline systems mainly include NaOH, NaOH–NaHS, and NaOH–Na₂S [25,26]. Arsenic is often leached in the form of sodium arsenate [27,28] in an aqueous system, which involves the solubility of sodium arsenate. The solubility of sodium arsenate is valuable and needed in arsenic-related industries, especially in a nonideal state [29]. The solubility of sodium arsenate under different conditions can provide

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a theoretical basis for the purification of arsenic-containing materials and disposal of arsenic-related dust and ashes. Solubility refers to the maximum amount of a substance dissolved in a certain amount of solvent at a certain temperature. The solubility can be measured using some methods, such as dynamic and static methods [30,31]. The advantage of static method is simple and accurate, but the disadvantage is that it takes longer [32].

The activities of the components participating in the chemical reactions are adopted for thermodynamic equilibrium calculations [33]. In practice, the molecules and ions making up the solution interact in various ways [34]. The most intuitive point is that the numerical value of the activity is not equal to that of the substance. Therefore, when studying and analyzing the system, the activity coefficient is always needed. It is difficult to determine the activity coefficients of electrolyte solutions in complex systems. Kenneth S. Pitzer proposed a model for estimating the activity coefficients of complex systems based on the data of simple ones, namely the Pitzer model [35,36]. The Pitzer model is a semi-empirical statistical mechanics model [37,38]. The activity coefficients and permeability coefficients derived from the Pitzer model can be effectively applied to the thermodynamic analysis of complex systems.

In this paper, the static method is adopted to detect the solubility of sodium arsenate in the NaOH solution, and the Pitzer model is used to obtain the quasi-solubility product.

2. Experimental

2.1. Materials

The sodium arsenate used in the study was self-made in our laboratory. High arsenic dust is used as raw material to prepare crude sodium arsenate through alkaline leaching, purification, and crystallization method. Then crude sodium arsenate solution was further purified by multiple dissolution-crystallization. The XRD pattern and chemical analysis of sodium arsenate are shown in Fig. 1 and Table 1.

The purity of $Na_3AsO_4 \cdot 10H_2O$ is calculated based on the arsenic content, which is 98.58%. Besides, it also contains a total of 0.078% of impurity elements such as Sb, Sn, Pb, and Zn. The agent used in this study were listed in Table 2.

2.2. Measurement process

A supersaturated sodium arsenate solution was prepared and put in a water bath for a certain time to reach a solid-liquid equilibrium. Then the supernatant was taken and detected using atomic fluorescence spectrometry (AFS) regularly. When the concentration of sodium arsenate in the solution is almost unchanged (<2%), the concentration would be used to calculate the solubility. The uncertainty of the measurement results is also controlled here. The solubility of sodium arsenate at different temperatures was studied and measurements are performed at 101.3 kPa. The influence of equilibrium time, system temperature, and sodium hydroxide concentration on the solubility of sodium arsenate was studied.

2.3. Pitzer model

When the electrolyte Na₃AsO₄·10H₂O reaches the dissolution-crystallization equilibrium in the solution, the dissolution reaction is shown in Equation (1). The solubility product constant of Na₃AsO₄·10H₂O is expressed by Equation (2) using K_{sp} .

$$Na_3AsO_4 \cdot 10H_2O \rightarrow 3Na^+ + AsO_4^{3-} + 10H_2O$$

Fig. 1. XRD pattern of sodium arsenate.

(1)

Table 1

Composition of self-made sodium arsenate.

Element	Na	As	Sb	Sn	Pb	Zn	Other insoluble materials
Content (wt%)	18.04	19.04	0.046	0.017	0.009	0.006	1.342

Table 2	
Chemical compounds and models.	

Chemical name	chemical formula	CAS No.	Suppliers	Fraction	method
Water	H ₂ O	7732-18-5	Jinan Aquaken Environmental Technology Co., Ltd. Xilong Scientific Co., Ltd $^{\rm c}$	a	AFS ^b
Sodium hydroxide	NaOH	1310-73-2		≥98% (GR)	AFS ^b
Sodium arsenate	Na ₃ AsO ₄	c		98.58%	AFS ^b

 a Deionized water, conductivity less than 0.1 $\mu S/cm,$ resistance greater than 15 M $\Omega/cm.$

^b Atomic fluorescence spectroscopy.

^c Self-made materials, XRD pattern indicated that the corresponding pdf card number is 00-027-1207.

$$K_{sp} = a_{Na^+}^3 \times a_{AsO_4^{3-}} \times a_{H_2O}^{10} = (m_{Na^+} \times \gamma_{Na^+})^3 \times \left(m_{AsO_4^{3-}} \times \gamma_{AsO_4^{3-}}\right) \times a_{H_2O}^{10}$$
(2)

a is the activity of the ion, *m* is the ion concentration, mol/Kg; γ is the activity coefficient of the ion. The activity coefficient of the ions in the solution can be calculated by the Pitzer model, and the solubility of the electrolyte in the water can be obtained using the systems of equations joined.

Since the sodium arsenate in the system is in a quasi-saturated state, the model satisfies semi-equal Equation (3).

$$K_{sp}^* = a_{Na^+}^3 \times a_{AsO_4^{3-}} = (m_{Na^+} \times \gamma_{Na^+})^3 \times (m_{AsO_4^{3-}} \times \gamma_{AsO_4^{3-}}) \le K_{sp(Na_3AsO_4)}$$
(3)

The activity coefficients of the cation M and the anion X in the system can be expressed by Equation (4) -(5).

$$\ln \gamma_{M} = \frac{1}{2} z_{M}^{2} \times f'(I) + 2 \sum_{a} m_{a} \Big[B_{Ma} + \Big(\sum mz \Big) C_{Ma} \Big] + \sum_{c} \sum_{a} m_{c} m_{a} \times \big(z_{M}^{2} B_{ac}' + z_{M} C_{ac} \big)$$
(4)

$$\ln \gamma_{X} = \frac{1}{2} z_{X}^{2} \times f'(I) + 2 \sum_{c} m_{c} \left[B_{Xc} + \left(\sum mz \right) C_{Xc} \right] + \sum_{a} \sum_{c} m_{a} m_{c} \times \left(z_{X}^{2} B_{ac}^{'} + z_{X} C_{ac} \right)$$
(5)

where f(I) and f'(I) are functions of ionic strength, as shown in Equation (6) -(7).

$$f(I) = -2A_{\phi}\frac{2I}{b}\ln\left(1 + b\sqrt{I}\right)$$
(6)

$$f'(I) = \frac{df(I)}{dI} = -2A_{\varnothing} \left[\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b} \ln\left(1 + b\sqrt{I}\right) \right]$$
(7)

 A_{Φ} is the Debye-Hückel parameter of water, Kg^{0.5}/mol^{0.5}, which only changes with the temperature. At 298.13 K, A_{Φ} is 0.3915 and b is the Pitzer constant, which is 1.2 kg^{1/2} mol^{-1/2}. *I* is the ionic strength, mol/Kg, and its expression is shown.

$$I = \frac{1}{2} \sum_{i} m_i z_i^2 \tag{8}$$

 B_{ca} represents a function of ion intensity, and C_{ca} is an ion function, their equations and mz in equation (5) are listed in Eequations (9)-(12)

$$B_{ca} = \beta_{ca}^{(0)} + \frac{2\beta_{ca}^{(1)}}{\alpha^2 I} \left[1 - \left(1 + \alpha \sqrt{I} \right) \exp\left(-\alpha \sqrt{I} \right) \right]$$
(9)

$$B_{ca}^{\prime} = \frac{\partial B_{ca}}{\partial I} = \frac{2\beta_{ca}^{(1)}}{\alpha^2 I^2} \left[-1 + \left(1 + \alpha\sqrt{I} + \frac{1}{2}\alpha^2 I\right) exp\left(-\alpha\sqrt{I}\right) \right]$$
(10)

$$C_{ca} = \frac{C_{ca}^{\emptyset}}{2\sqrt{|Z_c Z_a|}} \tag{11}$$

$$\sum mz = \sum_{a} m_a |z_a| = \sum_{c} m_c |z_c|$$
(12)

 α is the Pitzer constant, kg^{1/2} mol^{-1/2}, for 3:1, 2:1, and 1:1 electrolyte solution, α is 2.0 kg^{1/2} mol^{-1/2}.

Pitzer parameter of electrolyte in the system.	Table 3
	Pitzer parameter of electrolyte in the system.

Material	$eta_{ ext{ca}}^{(0)}$	$\beta_{\rm ca}^{(1)}$	C^{Φ}
NaOH	0.0864	0.253	0.0044
Na ₃ AsO ₄	0.2388	3.93	-0.004772762
Na ₂ HAsO ₄	0.030525	1.62975	0.000901561

$$\gamma_{+-ca} = (\gamma_{+}\gamma_{-})^{(1/\nu)}$$
(13)

 γ_{+-ca} is the average activity coefficient in equation (13), and ν is the sum of the number of anions and cations in the electrolyte. The expression of water activity is shown in Equation (14).

$$\ln a_{H_2O} = \frac{-(\sum_i m_i) M_w}{1000} \emptyset$$
(14)

 Φ is the permeability coefficient, m/s, as shown in Equation (15).

$$\emptyset - 1 = \frac{1}{\sum_{i} m_{i}} \left\{ \begin{array}{c} [If'(I) - f(I)] \\ + 2\sum_{c} \sum_{a} m_{c} m_{a} \left[B_{ca} + IB'_{ca} + 2\left(\sum mz\right) C_{ca} \right] \end{array} \right\}$$
(15)

Pitzer parameters of related substances are listed in Table 3.

A tertiary ionization reaction of arsenate will undergo in solution [1], as shown in Equations (16-18)). Therefore, arsenic exists in different forms, as shown in Fig. 2. Fig. 2(a) shows the distribution of arsenic under different pH, and Fig. 2(b) shows the distribution of arsenic under higher alkalinity

$$H_3AsO_4 \to H^+ + H_2AsO_4^-pK_{a1} = 2.24$$
 (16)

$$H_2AsO_4^- \to H^+ + HAsO_4^{2-}pK_{a2} = 6.96$$
 (17)

$$HAsO_4^2 \to H^+ + AsO_4^3 - pK_{a3} = 11.50$$
 (18)

The hydrogen ion participating in complexation reactions with arsenate comes from the ionization of water. The concentration of OH^- generated in the ionization is equal to that of H^+ , as shown in equation (19).

$$\mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{H}^{+} + \mathrm{O}\mathrm{H}^{-} \tag{19}$$

Based on the law of conservation of mass, Equation (20) could be established.

$$[HAsO_4^{2-}] + 2 * [H_2AsO_4^{-}] + 3 * [H_3AsO_4] = [OH^{-}]$$
(20)

The relationship between the equilibrium concentration of H^+ in the solution and OH^- , $HAsO_4^{2-}$, $H_2AsO_4^-$, and H_3AsO_4 are shown in Equation (21) -(24).

$$[OH^{-}] = K_w / [H^{+}]$$
²¹

$$\left[\mathrm{HAsO}_{4}^{2-}\right] = \left[\mathrm{AsO}_{4}^{3-}\right] * \left[\mathrm{H}^{+}\right] / K_{\mathrm{a}3}$$
(22)

$$\left[H_{2}AsO_{4}^{-}\right] = \left[AsO_{4}^{3-}\right] * \left[H^{+}\right]^{2} / \left(K_{a2} * K_{a3}\right)$$
(23)

$$[H_3AsO_4] = [AsO_4^{3-}] * [H^+]^3 / (K_{a1} * K_{a2} * K_{a3})$$
(24)

Equation (25) is obtained by substituting the above equations into Equation (20).

$$\left[\operatorname{AsO}_{4}^{3-}\right]\left(\left[\operatorname{H}^{+}\right]/K_{a3}+2*\left[\operatorname{H}^{+}\right]^{2}/(K_{a2}*K_{a3})+3*\left[\operatorname{H}^{+}\right]^{3}/(K_{a1}*K_{a2}*K_{a3})\right)=K_{w}/\left[\operatorname{H}^{+}\right]$$
(25)

The concentration of arsenic in the solution is calculated in Equation (26).

$$[As]_{T} = [AsO_{4}^{3-}] + [HAsO_{4}^{2-}] + [H_{2}AsO_{4}^{-}] + [H_{3}AsO_{4}] = [AsO_{4}^{3-}](1 + [H^{+}]/K_{a3} + [H^{+}]^{2}/(K_{a2} * K_{a3}) + [H^{+}]^{3}/(K_{a1} * K_{a2} * K_{a3}))$$
(26)



Fig. 2. Relationship between the occurrence of As(V) in solution and pH value(a) and alkalinity(b).

[As] $_{\rm T}$ is a known quantity. The equilibrium H⁺ concentration can be obtained by combining Equations (25) and (26), as shown in Equation (27).

$$1 + [H^{+}] / K_{a3} + [H^{+}]^{2} (1 / (K_{a3} * K_{a2}) - [As]_{T} / (K_{a3} * K_{w})) + [H^{+}]^{3} (1 / (K_{a3} * K_{a2} * K_{a1}) - 2 * [As]_{T} / (K_{a3} * K_{a2} * K_{w})) - 3 * [H^{+}]^{4} [As]_{T} / (K_{a3} * K_{a2} * K_{a1} * K_{w})) = 0$$
(27)

It is assumed here the ionization constant of arsenate remains unchanged in this temperature range, the occurrence of arsenic can be obtained and used for the calculation of the data in the Pitzer model.

3. Results and discussion

3.1. Solubility of sodium arsenate in pure water

The solubility of sodium arsenate in pure water at different temperatures was studied. The experimental results are shown in Fig. 3. When the difference between the measured values is small (less than 2%), the dissolution of sodium arsenate is considered to be in balance, and the average of these latest measured values was chosen as the solubility.

It can be seen from Fig. 3, that the solubility increases with the increase in temperature. Substituting the total arsenic concentration into Equation (26), the equilibrium pH value of the system can be obtained by calculation, and the occurrence of arsenic can be obtained based on Fig. 2. At the same time, the hydroxide concentration generated by the ionization reaction could be obtained, as shown in Table 4.

The concentration of the $HASO_4^{--}$ and AsO_4^{--} increase with the increase in temperature, and the equilibrium pH value decreases with the increase in temperature. As the temperature increases, the hydrogen bonding force between water molecules decreases, and the water activity increases, which is conducive to the dissolution of sodium arsenate. The $HAsO_4^{--}$ is derived from the complexation reaction of AsO_4^{--} and H^+ , which will produce a certain number of OH⁻⁻. At the same time, the ion product constant of water increases when the temperature increases. Therefore, the concentration of OH⁻⁻ in the solution increases as the temperature increases. The main



Fig. 3. Solubility curve of the experimental value.

Table 4Related data of pure water system.

Temperature	Endpoint pH	Tested pH	[As] _T mol/Kg	[HAsO ₄ ^{2–}] mol/Kg	[AsO ₄ ³⁻] mol/Kg	[OH ⁻] mol/Kg
298.15 K	12.68	12.65	0.0503	0.0189	0.0314	0.0542
308.15 K	12.60	12.31	0.0610	0.0229	0.0381	0.0710
318.15 K	12.50	12.54	0.0769	0.0289	0.0480	0.1030
328.15 K	12.39	12.44	0.0904	0.0340	0.0564	0.1461
338.15 K	12.28	12.30	0.0988	0.0372	0.0616	0.1935
348.15 K	12.18	12.20	0.1037	0.0390	0.0647	0.2502
358.15 K	12.11	12.10	0.1236	0.0465	0.0771	0.3153

anions in the solution are AsO_4^{3-} , $HAsO_4^{2-}$, and OH^- , and the cation is Na^+ . Due to the low concentration of H^+ , it is not considered here. The interaction of the three anions is not considered here, only the interaction between the two is considered. The related data, such as activity coefficients, permeability coefficient, and quasi-solubility product (K^*_{sp}) at different temperatures, are obtained by calculation using Equation (4) -(11), as shown in Fig. 4.

The activity coefficient of Na⁺ increases with the increase of solubility and temperature and the activity coefficient is greater than 1.0. Na⁺ is the only cation in the solution, which interacts with other anions, so the activity coefficient is high. The three anions in the solution have different trends. The activity coefficient of the OH⁻ remains stable. The activity coefficients of the HAsO₄²⁻ and AsO₄³⁻ increase with the increase in temperature and concentration. The permeability coefficient of the solution increases as the temperature increases, indicating the interaction between water molecules and the electrolyte increases, for example, hydration and ionization. Consistent with the arsenic solubility, the quasi-solubility product constant increases with the increase in temperature.

3.2. Solubility of sodium arsenate under different alkalinity

The solubility of sodium arsenate in NaOH solution at different temperatures was measured. The method is the same as that of solubility in pure water. The NaOH concentrations after calibration at 298.15 K are listed in Table 5 and the solubility of sodium arsenate at different temperatures and alkalinities are listed in Table 6 and demonstrated in Fig. 5.

The trend of solubility can be more visually represented in Fig. 5(a), because of the co-ion effect [39,40], the solubility of sodium arsenate decreases as the NaOH concentration increases. According to the solubility product equation, it is clear that the effect of the co-ion Na⁺ on the solubility of Na₃AsO₄ is greater than its effect on the solubility of NaOH. At the same time, the solubility of sodium arsenate increases with the increase in temperature. When the alkalinity is low, there is a large increase with the increase in temperature, and when the alkalinity is high, there is only a small increase with the increase in temperature. Since no complex salt of sodium hydroxide and sodium arsenate was found, while the solubility of NaOH is high, the location of the triple phase point is on the NaOH–H₂O line due to the co-ion effect, so a simple aqueous salt phase diagram of the NaOH–Na₃AsO₄–H₂O system can be obtained, as shown in Fig. 5(b). According to Fig. 2, there is almost no complexation reaction of arsenate in the alkaline system. Therefore, the anions in the solution are mainly OH⁻ and AsO₄³⁻, and the cation is Na⁺. The H⁺ concentration is low and would not be considered. The activity coefficients of related ions can be obtained by calculation using Equation (4) -(11), and then the quasi-solubility products were calculated and are demonstrated in Fig. 6.

At a certain temperature, the K^*_{sp} increases with increasing alkalinity, and since the sodium ion increases, the solubility of sodium arsenate decreases. At certain alkalinity, when the NaOH concentration is not greater than 4.43 mol/kg, the K^*_{sp} decreases with the increase of temperature, which is because the activity coefficients of sodium and arsenate ions decrease with the increase of temperature, as shown in Fig. 4. When the NaOH concentration was greater than 4.43 mol/kg, the K^*_{sp} of sodium arsenate showed a trend of first increasing and then decreasing, which was the change exhibited by the dual effect of increasing sodium ion concentration and



Fig. 4. Substance quasi-solubility product (a) and ion activity coefficient, permeability coefficient (b) at different temperatures.

Table 5

NaOH concentration.

$mol \cdot L^{-1}$	1.07	2.09	3.17	4.28	5.39	6.43	8.33	10.47
$mol \cdot Kg^{-1}$	1.03	1.93	2.81	3.65	4.43	5.11	6.25	7.38

Table 6		
Solubility of sodium arse	nate at different temperature	s and alkalinities (mol/Kg).

Alkalinity Temperature	1.03 mol/Kg	1.93 mol/Kg	2.81 mol/Kg	3.65 mol/Kg	4.43 mol/Kg	5.11 mol/Kg	6.25 mol/Kg	7.38 mol/Kg
298.15 K	0.268	0.127	0.071	0.043	0.028	0.020	0.011	0.007
308.15 K	0.322	0.154	0.088	0.054	0.033	0.023	0.016	0.012
318.15 K	0.460	0.234	0.133	0.086	0.050	0.038	0.030	0.021
328.15 K	0.609	0.308	0.186	0.117	0.075	0.06	0.045	0.035
338.15 K	0.822	0.439	0.271	0.185	0.134	0.105	0.078	0.064
348.15 K	1.111	0.662	0.434	0.294	0.227	0.190	0.134	0.112
358.15 K	1.254	0.840	0.553	0.435	0.300	0.244	0.223	0.185



Fig. 5. (a) Solubility of arsenic at different temperatures and alkalinity and (b) Na₃AsO₄–NaOH–H₂O system ternary phase at 298.15 K.

decreasing activity coefficient. It should be noted that since the results of this study were obtained in the NaOH–Na₃AsO₄–H₂O system, the applicability of the obtained results is somewhat limited, and the results can be applied if the system ion types and quantities are not larger than the present study system. The results of this study can only be used as a reference if the system ion type or quantity is larger than the present system and the interaction relationship between ions cannot be ignored. For example, if there are other cations in the system, Ca^{2+} , Zn^{2+} , etc., or other acids that can form polyoxometalates with arsenate, such as molybdate, tungstate, etc., the research of this study is not applicable.

Based on the results, the relationship equation of solubility with temperature and alkalinity was obtained by regression calculation with temperature and alkalinity as dependent variables. Equations (28) and (29) can be obtained by fitting a binary multiple regression equation assuming a temperature of T, an alkalinity concentration of A, a solubility of S, and a quasi-solubility product of C.

$$S = 19.621 - 0.153T + 3.487 * 10^{-4} * T^{2} - 1.701 * 10^{-7} * T^{3} - 0.259A - 0.036A^{2} - 2.277 * 10^{-3} * A^{3} + 3.737 * 10^{-3} * T * A - 1.247 * 10^{-5} * T^{2} * A + 2.675 * 10^{-4} * T * A^{2}R^{2} = 0.980$$
(28)
$$C = -0.306 + 2.889 * 10^{-3} * T - 9.155 * 10^{-6} * T^{2} + 9.709 * 10^{-9} * T^{3} - 0.012A - 4.464 * 10^{-4} * A^{2} - 6.163 * 10^{-6} * A^{3} + 9.530 * 10^{-5} * T * A - 1.782 * 10^{-7} * T^{2} * A + 1.637 * 10^{-6} * T * A^{2}R^{2} = 0.988$$
(29)

Furthermore, the correlation of temperature and alkalinity with solubility and K^*_{sp} was analyzed using the Pearson model to obtain the results in Table 7.



Fig. 6. Solubility of sodium arsenate at different conditions (a: Three dimensions, b: K*sp vs. Temperature, c: K*sp vs. NaOH).

Table 7	
Correlation of temperature and alkalinity on solubility and K	*sp

		Temperature	NaOH
Solubility	Pearson Correlation	.539 ^a	614 ^a
	Sig. (2-tailed)	.000	.000
K^*_{sp}	Pearson Correlation	416 ^a	.840 ^a
	Sig. (2-tailed)	.001	.000

^a Correlation is significant at the 0.01 level (2-tailed).

As can be seen from Table 7, solubility has a significant correlation with temperature and alkalinity, with solubility positively correlated with temperature and negatively correlated with alkalinity. Therefore, the solubility of sodium arsenate can be increased by reducing the alkalinity and lowering the temperature. K^*_{sp} also has a significant correlation with temperature and alkalinity, negatively correlated with temperature, and positively correlated with alkalinity. Due to the co-ion effect, the solubility product of sodium arsenate can be increased by increasing the alkalinity. The results of the Pearson model are consistent with the experimental phenomena and theoretical calculations.

4. Conclusion

In metallurgical and chemical production, alkaline leaching is used as a common method to extract or separate arsenic, so it is necessary to study the solution behavior of sodium arsenate in an alkaline solution to provide a theoretical basis for the relevant process. In this paper, the solubility of self-made sodium arsenate decahydrate was studied by static method at different temperatures and alkalinity, and its solubility product was investigated in combination with the Pitzer model.

- (1) The solubility of self-made sodium arsenate increased with the increase of temperature and decrease of NaOH concentration owing to the co-ion effect. The activity coefficients of ions in the ternary system were calculated using the Pitzer model, and the quasi-solubility products were calculated for different conditions.
- (2) The ternary aqueous salt phase diagram of the NaOH–Na₃AsO₄–H₂O system at 298.15 K temperature was plotted based on the solubility test results.
- (3) Solubility and solubility products had a significant correlation with temperature and alkalinity, with solubility positively correlated with temperature and negatively correlated with alkalinity. While the solubility product was negatively correlated with temperature, and positively correlated with alkalinity.

Ethical approval

There existed no human or animal studies in this study.

Author contribution

Yuntao Xin - Conceived and designed the experiments; Xiaodong Lv and Kun Song - Performed the experiments; Yu Yi - Analyzed and interpreted the data; Jing Shi - Contributed reagents, materials, analysis tools or data; Kun Song - Wrote the paper.

Availability of data and materials

The data are available upon request to the authors. Supporting data for this study can be obtained from the corresponding author upon reasonable request.

Declaratio of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] Kevin R. Henke, Aaron Hutchison, Arsenic Chemistry, John Wiley & Sons, Ltd), 2009, https://doi.org/10.1002/9780470741122.ch1.
- [2] Badal Kumar Mandal, Kazuo T. Suzuki, Arsenic round the world: a review, Talanta 58 (2002) 201–235, https://doi.org/10.1016/S0039-9140(02)00268-0.
 [3] O'Day, A. Peggy, 'Chemistry and mineralogy of arsenic, Elements 2 (2006) 77–83, https://doi.org/10.2113/gselements.2.2.77.
- [4] D. Avramidis, G. Panagiotaras, D. Panagopulos, P. Papoulis, Arsenic geochemistry in groundwater system, in: geochemistry-Earth's System Processes, InTech, 2012, https://doi.org/10.5772/39384.
- [5] H. Vasken Aposhian, Mary M. Aposhian, Arsenic toxicology: five questions, Chem. Res. Toxicol. 19 (2006) 1–15, https://doi.org/10.1021/tx050106d.
- [6] Shuhui Wei, Hong Zhang, Shasha Tao, A review of arsenic exposure and lung cancer, Toxicol. Res. 8 (2019) 319–327, https://doi.org/10.1039/C8TX00298C.
- [7] Hemda Garelick, Huw Jones, Agnieszka Dybowska, Eugenia Valsami-Jones, Arsenic pollution sources, Rev. Environ. Contam. Toxicol. 197 (2009) 17–60, https://doi.org/10.1007/978-0-387-79284-2.
- [8] Wilson H. Miller, Hyman M. Schipper, Janet S. Lee, Jack Singer, Samuel Waxman, 'Mechanisms of action of arsenic trioxide, Cancer Res. 62 (2002) 3893–3903.
- [9] X. Ma, W.J. Bruckard, 'Rejection of arsenic minerals in sulfide flotation a literature review, Int. J. Miner. Process. 93 (2009) 89–94, https://doi.org/10.1016/ j.minpro.2009.07.003.
- [10] Al-Abed, R. Souhail, G. Jegadeesan, J. Purandare, D. Allen, 'Arsenic release from iron rich mineral processing waste: influence of pH and redox potential, Chemosphere 66 (2007) 775–782, https://doi.org/10.1016/j.chemosphere.2006.07.045.
- [11] Amir Mohammad Nazari, Rebecca Radzinski, Ghahreman Ahmad, 'Review of arsenic metallurgy: treatment of arsenical minerals and the immobilization of arsenic, Hydrometallurgy (2016) 258-281, https://doi.org/10.1016/j.hydromet.2016.10.011.
- [12] John S. Carpenter, Chenguang Bai, Jiann Yang Hwang, Shadia Ikhmayies, Bowen Li, Sergio Neves Monteiro, Zhiwei Peng, Mingming Zhang, Characterization of High-Arsenic Sludge in Copper Metallurgy Plant, John Wiley & Sons, Inc., 2014, https://doi.org/10.1002/9781118888056.ch21.
- [13] Tara M. Clancy, Kim F. Hayes, Lutgarde Raskin, Arsenic waste management: a critical review of testing and disposal of arsenic-bearing solid wastes generated during arsenic removal from drinking water, Environ. Sci. Technol. 47 (2013) 10799–10812, https://doi.org/10.1021/es401749b.
- [14] Guo-Iin Yu, Ying Zhang, Shi-li Zheng, Xing Zou, Xiao-hui Wang, Yi Zhang, 'Extraction of arsenic from arsenic-containing cobalt and nickel slag and preparation of arsenic-bearing compounds, Trans. Nonferrous Metals Soc. China 24 (2014) 1918–1927, https://doi.org/10.1016/S1003-6326(14)63272-6.
- [15] Ramesh Narasimhan, Joseph D. Chwirka, Glenda Rousseau, Nelline Scheurer, Hazardous waste regulatory applicability for arsenic residuals, Proc. Water Environ. Federat. 2001 (2001) 1097–1113, https://doi.org/10.2175/193864701784993074.
- [16] Safarzadeh, M. Sadegh, Jan D. Miller, 'The pyrometallurgy of enargite: a literature update, Int. J. Miner. Process. (2016) 103–110, https://doi.org/10.1016/j. minpro.2016.09.008.
- [17] C.B. Alcock, Principles of Pyrometallurgy, Academic Press, 1976, https://doi.org/10.1002/ange.19770890739.
- [18] F. Dalewski, 'Removing arsenic from copper smelter gases, Jom-J. Min. Metals Mater. Soc. 51 (1999) 24–26, https://doi.org/10.1007/s11837-999-0153-0.
- [19] Dimitrios Filippou, Pascale St-Germain, Tassos Grammatikopoulos, 'RECOVERY of metal values from copper—arsenic minerals and other related resources, Miner. Process. Extr. Metall. Rev. 28 (2007) 247–298, https://doi.org/10.1080/08827500601013009.
- [20] Dimitrios Filippou, George P. Demopoulos, 'Arsenic immobilization by controlled scorodite precipitation, JOM 49 (1997) 52–55.
- [21] R. Padilla, D. Girón, M.C. Ruiz, 'Leaching of enargite in H2SO4-NaCl-O2 media, Hydrometallurgy 80 (2005) 272–279, https://doi.org/10.1016/j. hydromet.2005.08.006.
- [22] Safarzadeh, M. Sadegh, Michael S. Moats, Jan D. Miller, An update to "recent trends in the processing of enargite concentrates, Miner. Process. Extr. Metall. Rev. 35 (2014) 390–422, https://doi.org/10.1080/08827508.2012.725683.
- [23] Maria C. Ruiz, Felipe Daroch, Padilla Rafael, 'Digestion kinetics of arsenic removal from enargite-tennantite concentrates, Miner. Eng. 79 (2015) 47–53, https://doi.org/10.1016/j.mineng.2015.05.004.
- [24] William Tongamp, Yasushi Takasaki, Atsushi Shibayama, 'Arsenic removal from copper ores and concentrates through alkaline leaching in NaHS media, Hydrometallurgy 98 (2009) 213–218, https://doi.org/10.1016/j.hydromet.2009.04.020.
- [25] M.C. Ruiz, L. Grandon, R. Padilla, 'Selective arsenic removal from enargite by alkaline digestion and water leaching, Hydrometallurgy 150 (2014) 20–26, https://doi.org/10.1016/j.hydromet.2014.09.004.
- [26] Xue Yi Guo, Yi Yu, Jing Shi, Qing Hua Tian, 'Leaching behavior of metals from high-arsenic dust by NaOH–Na2S alkaline leaching, Trans. Nonferrous Metals Soc. China 26 (2016) 575–580, https://doi.org/10.1016/s1003-6326(16)64118-3.
- [27] B.W. Vink, 'Stability relations of antimony and arsenic compounds in the light of revised and extended Eh-pH diagrams, Chem. Geol. 130 (1996) 21–30, https:// doi.org/10.1016/0009-2541(95)00183-2.
- [28] Marcel Pourbaix, Jeanne Burbank, 'Atlas D-equilibres electrochimiques, J. Electrochem. Soc. 111 (1964) 14C, https://doi.org/10.1149/1.2426051.
- [29] F. Albertcotton, GeoffreyWilkinsonWrited, Advanced Inorganic Chemistry: a Comprehensive Text, third ed., Interscience Publishers, 1972.
- [30] Hiroyuki Matsuda, Sho Matsumoto, Kenta Kaguragi, Kiyofumi Kurihara, Katsumi Tochigi, Kazuo Tomono, 'Determination and correlation of solubilities of famotidine in water + co-solvent mixed solvents, Fluid Phase Equil. 302 (2011) 115–122, https://doi.org/10.1016/j.fluid.2010.09.029.
- [31] Zhao Guo Chen, Wen Ge Yang, Yong Hong Hu, Zi Yu Lei, Yao Han Wang, Wen Qian Wan, Measurement and correlation for the solubility of dimethyl 1,4-Cyclohexanedione-2,5-dicarboxylate in different solvents at temperatures from (278.15 to 323.15) K, J. Chem. Eng. Data 56 (2011) 2726–2729, https://doi.org/ 10.1021/je2000292.

- [32] Ai-liang Chen, Xu Dong, Xing-yu Chen, Wen-yong Zhang, Xu-heng Liu, 'Measurements of zinc oxide solubility in sodium hydroxide solution from 25 to 100 °C, Trans. Nonferrous Metals Soc. China 22 (2012) 1513–1516, https://doi.org/10.1016/S1003-6326(11)61349-6.
- [33] Teh Fu Yen, Chemical Equilibrium, 2014.
- [34] Hardy, Amanda, Advanced Chemistry, second ed., Biologist, 2014.
- [35] Kenneth S. Pitzer, Activity Coefficients in Electrolyte Solutions, 2018, https://doi.org/10.1201/9781351069472-3.
- [36] Nazanin Zahra Norouzi, Mohammad Ali Bagherinia, 'Mean activity coefficients measurements and thermodynamic modeling of the ternary mixed electrolyte KCl + lactose + water system at T = 298.15 K, Physical Chemistry Research 5 (2017) 783–794, https://doi.org/10.22036/pcr.2017.88607.1387.
- [37] Ji Min Yang, Jing Peng, Yu Xia Duan, Chong Tian, Ping Mei, The phase diagrams and Pitzer model representations for the system KCl + MgCl2 + H2O at 50 and 75°C, Russ. J. Phys. Chem. A 86 (2012) 1930–1935, https://doi.org/10.1134/S0036024412130146.
- [38] Hossein Safari, Shokrollahi Amin, Mohammad Jamialahmadi, Mohammad Hossein Ghazanfari, Sohrab Zendehboudi, 'Prediction of the aqueous solubility of BaSO4 using pitzer ion interaction model and LSSVM algorithm, Fluid Phase Equil. 374 (2014) 48–62, https://doi.org/10.1016/j.fluid.2014.04.010.
- [39] Abu T.M. Serajuddin, Pai Chang Sheen, Matthew A. Augustine, 'Common ion effect on solubility and dissolution rate of the sodium salt of an organic acid, J. Pharm. Pharmacol. 39 (2011) 587–591, https://doi.org/10.1111/j.2042-7158.1987.tb03434.x.
- [40] X. Wang, Q. Ge, 'Separation and recovery of NaF from fluorine containing solution by the common ion effect of Na(), Heliyon 4 (2018), e01029, https://doi. org/10.1016/j.heliyon.2018.e01029.