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# Removal and stabilization of arsenic from anode slime by forming crystal scorodite

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**Abstract:** A process was proposed for removing and stabilizing arsenic (As) from anode slime. The anode slime with high arsenic concentration was pretreated by circular alkaline leaching process. Then, the arsenic in the leaching solution can be further precipitated as a form of scorodite crystalline (FeAsO<sub>4</sub>·2H<sub>2</sub>O). In the precipitating arsenic reaction, in which ferrous ions were oxidized by air gas, the effects of acidity (pH), reaction temperature, air flow rate, initial concentration of arsenic and initial molar ratio of Fe(II) to As(V) on arsenic precipitation were investigated. The results showed that sufficiently stable crystal scorodite could be achieved under the condition of initial arsenic concentration of 10 g/L, pH 3.0–4.0, Fe/As molar ratio of 1.5, the temperature of 80–95 °C, and the air flow rate higher than 120 L/h. Under the optimal condition, more than 78% of arsenic could be precipitated as a form of scorodite crystalline. The As leaching concentration of the precipitates was less than 2.0 mg/L and the precipitates may be considered to be safe for disposal.

Key words: scorodite; anode slime; arsenic; ferric arsenate; arsenic stabilization

# **1** Introduction

During the metallurgical process of lead, copper, zinc, gold and silver, considerable amounts of anode slime with high arsenic (As) concentration can be generated [1]. Due to its high toxicity, environmental regulations are becoming increasingly more rigorous regarding the utilization and disposal of As compounds [2]. Long-term exposure to arsenic can cause serious disease and various cancers including skin, liver, bladder, kidney, and lung cancer [3]. Therefore, arsenic removal and immobilization remain an important environmental issue for metallurgical and mining industry.

The conventional processes for treatment of anode slimes can be classified into pyrometallurgical and hydrometallurgical groups. As these processes dissolve most of the elements present in anode slimes, treatment of the leaching solutions becomes complex. The general method of removing and immobilization from contaminated water sources and industrial waste streams chemical stabilization. Chemical stabilization methodologies for controlling arsenic pollution have been studied and implemented [4]. A common method for removing arsenic from waste streams is precipitation. Typical precipitates are arsenic sulphides, calcium arsenates or ferric arsenates [5]. However, arsenic sulphide residue is not stable at pH≤4. Meanwhile, calcium arsenate is not effective to completely remove arsenic, easily releasing arsenic with decreasing pH [6]. So, the disposal and storage of these compounds are not entirely safe as they easily undergo physical and chemical changes with time, resulting in arsenic releasing to the environment [7]. Ferric arsenate has been also identified as an effective method of arsenic removal in industrial waste [8]. Ferric arsenate exists either in amorphous or crystalline form. The solubility of crystal scorodite (FeAsO<sub>4</sub>·2H<sub>2</sub>O) was about two orders of

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magnitude lower than amorphous ferric arsenates [9,10]. Amorphous ferric arsenate compounds are very unstable, and dissolved arsenic levels have been reported to reach 20 mg/L [11]. Conversely, crystalline ferric arsenate or scorodite, which has very low solubility and high stability under acidic to neutral pH conditions, is suitable for arsenic stabilization and storage [12].

Conventional As precipitation processes have disadvantages because the crystal scorodite particles are agglomerated by nano-sized particles. Such properties affect long-term stability for the storage of scorodite. Several factors including pH, the molar ratio of iron to arsenic and temperature affect the formation of scorodite precipitation. Controlling pH in scorodite precipitation is very important. A rapid pH change results in the formation of poor crystalline phases and amorphous precipitate [13]. The initial molar ratio of iron to arsenic can affect the rate of arsenic removal and the stability of the precipitate. It has been reported that, a well crystallized precipitate with As leachability of 0.5 mg/L was obtained by increasing the initial molar ratio of Fe(III) to As(V) to 3:1 [14]. Scorodite is readily produced under hydrothermal conditions (temperature of 100 °C or higher) [15]. In the last decade, scorodite synthesis at temperatures below 100°C has been a matter of great concern. The particle size decreases with high crystallinity, so it is difficult to get the large scorodite particles and high crystallinity at temperature below 100 °C [16].

In this study, a new technology was proposed for removing and stabilizing arsenic from anode slime. The anode slime with high arsenic concentration was pretreated to remove arsenic by circular alkaline leaching process. Then, the arsenic in the leaching solution can be further precipitated as a form of crystal scorodite by using ferrous ion and air oxidation. The objective of this research was to investigate the effects of acidity (pH), reaction temperature, air flow rate, initial concentration of arsenic and molar ratio of Fe(II) to As(V) on scorodite precipitation in high arsenic concentration, and to optimize scorodite formation in a practical process.

# 2 Experimental

#### 2.1 Materials

The anode slime was supplied from a lead and zinc smeltery in Chenzhou city, China. The anode slime with high arsenic concentration was pretreated by circular leaching process using sodium hydroxide solution. Then, the arsenic in the leaching solution can be further treated by precipitation experiments. The experimental procedure for removal and stabilizing arsenic is shown in Fig. 1. The physicochemical properties and chemical composition of the leaching solution are shown in Table 1.



Fig. 1 Procedure for removing and stabilizing arsenic

#### 2.2 Experimental procedure and apparatus

Ferrous sulphate was used as the iron source to remove arsenic through the crystal scorodite precipitation. The ferrous ion was oxidized into ferric ion by the use of air oxidation. The apparatus used in our experiments is illustrated in Fig. 2. A three-necked round-bottomed flask (1 L) was used as a reaction vessel which was equipped with mechanical stirrer. The leaching solution containing arsenic was indirectly heated by thermostatic water bath and stirred at 200 r/min until the pre-determined temperature was achieved. A ferrous solution was then injected into the reaction vessel. Meanwhile, the preheated air was blown into the reaction vessel to oxidize the ferrous ion. The temperature of reaction was measured with a thermometer. The pH of the mixture was adjusted with H<sub>2</sub>SO<sub>4</sub> to a desired pH. Another three-necked roundbottomed flask as the buffer bottle was employed to preheat air stream.

#### 2.3 Analytical methods

When the precipitation reaction ceased, the mixture was cooled down and passed through a 3  $\mu$ m pore membrane filter to separate the solid and liquid. Arsenic and iron content in the filtrate was determined by an inductive coupled plasma-atomic emission spectrophotometry (ICP-AES). The precipitate was washed with distilled water, and then filtrated to separate the solid

Table 1 Physical-chemical properties of leaching solution

pН	$ ho(Na)/(g\cdot L^{-1})$	$ ho(As(V)/(g\cdot L^{-1}))$	ho(S)/ (mg·L <sup>-1</sup> )	$ ho({ m Sb})/({ m mg}\cdot{ m L}^{-1})$	$ ho({ m Fe})/$ (mg·L <sup>-1</sup> )	ho(Si)/ (mg·L <sup>-1</sup> )	$ ho(Ca)/(mg\cdot L^{-1})$	ho(Mg)/ (mg·L <sup>-1</sup> )	$ ho(\mathrm{K})/(\mathrm{mg}\cdot\mathrm{L}^{-1})$
11.2	1.75	16.4	942.36	261.25	62.15	542.19	685.73	129.65	83.24



**Fig. 2** Experimental apparatus for precipitating arsenic: 1—Air blower; 2—Glass-tube rotameter; 3—Thermostat water bath; 4—Mechanical stirrer; 5—Thermometer; 6—Glass reactor

which was subsequently dried at 60 °C. The dried solid was pulverized in a mortar and used for analysis and characteristics by a scanning electron microscope (SEM) and an X-ray diffraction (XRD). Leaching tests were carried out to examine the leachability of the precipitates, according to the toxicity characterization leaching procedure (TCLP) [17].

#### **3 Results and discussion**

#### 3.1 Effect of pH value

The effect of the pH value on scorodite formation from the leaching solution of anode slime after pre-treatment was investigated within a pH range from 1.0 to 11.0 under the initial arsenic concentration of 10 g/L, Fe(II)/As(V) molar ratio of 1.5, the temperature of 95 °C and the air flow rate of 120 L/h. The composition and characteristic of scorodite precipitates produced at different initial pH values were summarized in Table 2. As shown in Table 2, the final pH value in the solution gradually increased from 0.99 to 3.59 as the initial pH increased from 1.0 to 11.0. The only exception was a slight decrease at the initial pH 4.0. This was also reflected in the rate of arsenic precipitation. Arsenic precipitation rate at pH 4.0 was 84.6%, which was higher than that at pH 3.0 (73.57%) and pH 5.0 (77.59%). The precipitates were of pale green color at the initial pH lower than 6.0, which was characteristic of scorodite. The chemical analysis of those precipitates was close to the scorodite stoichiometry with Fe/As molar ratio of 1:1.

The XRD and SEM patterns of scorodite precipitate produced at different initial pH values are shown in Figs. 3 and 4. The XRD pattern demonstrated that the precipitates consisted of crystal scorodite. The spherical grains were observed under initial pH value of 1.0 and the XRD pattern of the above spherical grains indicated the formation of crystal scorodite particles with moderate crystallinity. Similar results were reported by others [18], and they found that large spherical grains were formed by agglomeration of fine primary particles at lower pH values. The SEM images showed that the individual dipyramidal octahedron crystals were formed at the initial pH 2.0. In contrast, when the initial reaction pH values were 3 and 4, the size of crystal increased, and the growth of secondary small crystals on the surface of large crystals was observed. It was the secondary nucleation phenomenon. The XRD pattern also showed an increase in crystallinity at the initial pH range from 2.0 to 4.0, and the peaks on the diffractogram became sharper and higher. However, a decrease in crystallinity at the initial pH of 5.0 and 6.0 was observed. The average particle size significantly decreased at the initial pH of 6.0, although the XRD pattern confirmed that the precipitates were almost scorodite.

When the initial pH was higher than 6, dark green precipitates were changed to reddish brown and flocculent ones. The precipitates were characteristic of non-crystal substance. Probably, it was amorphous ferric arsenate, FeOOH or Fe(OH)<sub>3</sub> rather than stable scorodite [19]. At the initial pH of 9.0, 99.91% of arsenic was precipitated, mainly adsorbed onto ferric oxyhydroxide or precipitation as amorphous ferric arsenate.

Table 2 Composition and characteristic of precipitates produced at different initial pH values

Initial Final		Filtrate	Filtrate re	esidue	Descipitation rate of A s/0/
pH value	lue pH value $\rho(As)/(g \cdot L^{-1})$		Color	n(Fe)/n(As)	Precipitation rate of AS/%
1	0.99	6.36	Light green	1.15	6.38
2	1.72	2.74	Light green	1.21	50.51
3	1.81	1.41	Pale green	1.22	73.57
4	1.73	0.91	Pale green	1.18	84.60
5	2.12	1.15	Gray green	1.18	77.59
6	2.15	0.59	Gray green	1.24	88.48
7	2.65	0.07	Dark green	1.28	98.78
9	3.15	0.01	Olivine	1.40	99.91
11	3.59	0.01	Reddish brown	1.74	99.81



**Fig. 3** XRD patterns of precipitates produced at different initial pH values

As discussed above, the pH plays an important role in scorodite formation from the leaching solution of anode slime. A higher crystallinity scorodite precipitation and rate of arsenic precipitation were obtained at the initial reaction pH of 4.0 than other pH. Thus, the optimal pH for generating stable scorodite and stabilizing arsenic from anode slime was 4.0.

# **3.2 Effect of reaction temperature**

The effect of the reaction temperature on scorodite formation in the leaching of anode slime was investigated at temperature of 30-95 °C. The experiment was conducted at initial arsenic concentration of 10 g/L, Fe(II)/As(V) molar ratio of 1.5, the air flow rate of 120 L/h, pH of 3.0-4.0. The composition and characteristics



Fig. 4 SEM images of precipitates obtained at different initial pH values: (a) pH=2; (b) pH=4; (c) pH=5; (d) pH=6

Torrestore /9C	Filtrate	F	TCLP		
Temperature/ *C	$\rho(As)/(g \cdot L^{-1})$	Color	Dry mass/g	n(Fe)/n(As)	$\rho(As)/(mg \cdot L^{-1})$
30	4.19	Dark gray-green	3.81	1.12	4.0
50	3.13	Gray-green	7.28	1.10	5.9
70	1.96	Pale green	10.23	1.10	1.0
80	1.87	Pale green	10.93	1.08	2.0
95	1.54	Pale green	11.34	1.08	1.0

**Table 3** Composition and characteristics of product obtained at different reaction temperature

of precipitates obtained at different reaction temperatures are summarized in Table 3. The dry mass of precipitation gradually increased from 3.81 to 11.34 g as the reaction temperature increased from 30 to 95 °C. Thus, the reaction temperature has a positive impact on the arsenic precipitation.

When the reaction temperature was 30 °C, dark green and flocculent precipitates were observed. From the XRD pattern, the precipitates revealed the characteristic of amorphous substance, indicating that amorphous ferric arsenate was produced (Fig. 5). Thus, a reaction temperature of 30 °C for scorodite formation was not sufficient. The TCLP result showed that arsenic concentration of the precipitates produced at 50 °C was 5.9 mg/L, exceeding its permitted limit (5 mg/L), and being not suitable for direct disposal. The XRD patterns revealed that a weak crystallinity of scorodite generated at 50 °C, whilst poorly-crystalline ferric arsenate was scorodite precursor (FeAsO<sub>4</sub>·(2+x)H<sub>2</sub>O (0<x<1)) [20]. When the reaction temperature was higher than 70 °C, the precipitate was the usual pale green colour, indicating that crystal scorodite was generated (Table 3). The XRD analysis also confirmed that the precipitates were almost crystal scorodite. The results implied that the scorodite precipitate with high crystallinity can be obtained at the higher reaction temperature. The scorodite grains produced at 70 °C were less agglomerated. The results also showed that greater crystal scorodite particles were synthesized at 80 °C. Similar result was also found at 95 °C except for the growth of secondary small crystals observed on the surface of large crystals. It obviously reflected the fact that the high temperature can promote the crystal growth and secondary nucleation [21].



Fig. 5 XRD patterns of precipitates obtained at different temperatures

The TCLP tests showed that As leaching concentration of the precipitates obtained at 70 to 95 °C was below 5 mg/L. Therefore, the precipitates may be

considered to be safe for disposal. However, compared with the experiments carried out at 70 °C, those crystals formed at 80 °C and 95 °C were more stable according to the TCLP test. The minimum temperature for scorodite synthesis was 80 °C.

#### 3.3 Effect of air flow rate

The key point of the scorodite formation from the leaching solution of anode slime is the oxidation of ferrous ions. The air flow rate directly affects the oxidation rate of Fe(II) to Fe(III). Table 4 shows the composition and characteristic of products obtained at different air flow rates. It can be seen that As concentration in the filtrate decreased from 1.99 to 0.99 g/L as the air flow rate increased from 40 to 200 L/h. The rate of arsenic precipitation was 80% at the air flow rate of 40 L/h, 85% at 40 L/h, and 90% at 160 L/h and 200 L/h. These results indicated that the high air flow rate was favorable for arsenic precipitation.

**Table 4** Composition and characteristic of product obtained at different air flow rates

Air flow	Filtrate	Filtra	TCLP	
rate/ $(L \cdot h^{-1})$	$\rho(As)/(g\cdot L^{-1})$	Dry mass/g	n(Fe)/n(As)	ho(As)/ (mg·L <sup>-1</sup> )
40	1.99	9.24	1.06	2.0
80	1.80	12.56	1.06	1.3
120	1.54	10.56	1.06	1.0
160	1.08	10.65	1.01	0.5
200	0.99	10.94	1.09	0.4

The precipitate was identified as a crystal scorodite according to the XRD patterns (Fig. 6). The result of TCLP test showed that As leaching concentration of precipitate produced at 40 L/h of air flow rate was less than 2.0 mg/L. By increasing the air flow rate to 160 L/h,



Fig. 6 XRD patterns of precipitates obtained at different air flow rates

a very stable precipitate can be obtained, with As leaching concentration of 0.5 mg/L. The crystallinity of precipitates obtained at 40 L/h and 80 L/h of air flow rate was lower than that at 120–200 L/h because irregular scorodite particles and flocculent aggregate substance were observed at the air flow rates of 40 L/h and 80 L/h. The results indicated that higher air flow rate was favorable for the formation of crystal scorodite. At least 120 L/h of air flow rate would be required to form well-developed crystals scorodite.

Generally, scorodite was formed by co-precipitation of ferrous and arsenic ions in an air oxidation process. The main reaction mechanism included two steps of oxidation and crystallization precipitation. The reaction can be expressed as

$$Fe^{2+} + H^+ + \frac{1}{4}O_2 = Fe^{3+} + \frac{1}{2}H_2O$$
  
 $Fe^{3+} + AsO_4^{3-} + 2H_2O = FeAsO_4 \cdot 2H_2O$ 

The oxidation rate was critical for obtaining a crystal scorodite. In this study, 90% of arsenic in the solution was precipitated at the air flow rate of 200 L/h. The fact that the precipitation was not 100% was due to the presence of ferrous hydroxide stemming from the hydrolysis of ferrous which was unfavorable for scorodite formation [22]. A high air flow rate increased the dissolved oxygen content, reduced rates of Fe(II) hydrolysis and promoted the crystal nucleus formation. The dissolved oxygen in the vicinity of the crystal nucleus boundary plays a key role in the crystal growth. A high dissolved oxygen concentration is favorable for the crystal growth.

One possible method for controlling Fe(II) oxidation rate was to change the air flow rate. It should be noted that air oxidation used in the scorodite synthesis may cause significant heat loss due to the large amount of remaining nitrogen gas in the system. The potential heat loss will be largely influenced on the reaction temperature and reaction time. In order to reduce the heat loss, preheated air was required. Using air as oxidant for the scorodite formation is cost-efficient.

## 3.4 Effect of initial arsenic concentration

The effect of the initial arsenic concentration on scorodite formation in the leaching solution of anode slime was investigated within a range from 10 to 50 g/L. The experiment was conducted at Fe(II)/As(V) molar ratio of 1.5, the air flow rate of 120 L/h, pH of 3.0-4.0, and the temperature of 95 °C. As shown in Table 5, As concentrations in the filtrate was 1.64 g/L at the initial arsenic concentration of 10 g/L, and 4.67 g/L at 20 g/L, 14.19 g/L at 50 g/L, respectively. These results indicated that the high initial arsenic concentration was unfavorable for arsenic precipitation.

 Table 5 Composition and characteristic of product obtained at different initial As concentrations

Initial As	Filtrate	Filtra	TCLP	
concentration/ $(g \cdot L^{-1})$	$\rho(As)/(g\cdot L^{-1})$	Dry mass/g	n(Fe)/n(As)	$\rho(As)/(mg\cdot L^{-1})$
10	1.64	11.34	1.08	1.2
20	4.67	18.41	1.15	0.9
30	5.94	25.24	1.26	0.6
50	14.19	49.72	1.39	0.4

The precipitate amount increased with the increase of initial arsenic concentration. For instance, the amount of precipitate gradually increased from 11.34 to 49.72 g as the initial arsenic concentration increased from 10 to 50 g/L. The arsenic leaching concentration of the TCLP tests in the precipitates produced at the initial arsenic concentration of 10 g/L was 1.2 mg/L, which was lower than toxicity limits established. However, XRD pattern revealed the pure scorodite crystalline presented only at the reaction with 10 g/L initial arsenic concentration, and the chemical analysis of the precipitates also showed that the molar ratio of Fe to As of the precipitate was close to the scorodite stoichiometric value (Fig. 7). The chemical analysis of the precipitates showed that the molar ratio of Fe to As in the precipitate increased from 1.15 to 1.39 as the initial arsenic concentration increased from 20 to 50 g/L. The results of the chemical analysis indicated that the Fe(II) to As(V) molar ratio in the precipitate produced at high initial arsenic concentration obviously was higher than the scorodite stoichiometric value. The result of XRD confirmed that the precipitates obtained at 20 g/L of initial arsenic concentration contained amorphous FeAsO<sub>4</sub> and scorodite precursor  $FeAsO_4 \cdot (2+x)H_2O$  (0<x<1) [19], and a small amount of FeOOH. When the initial arsenic concentration was



Fig. 7 XRD patterns of precipitates obtained at different As concentrations

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higher than 30 g/L, the precipitates mainly contained FeAsO<sub>4</sub> and FeOOH (Fig. 7). The results indicated that the high initial arsenic concentration was unfavorable for the formation and growth of crystal scorodite. Thus, initial arsenic concentration of 10 g/L was available for the formation of stable scorodite crystalline.

### 3.5 Effect of initial Fe(II) to As(V) molar ratio

The effect of the initial Fe(II) to As(V) molar ratio on scorodite formation from the leaching solution of anode slime was investigated within a range from 0.8 to 3.0 under the conditions of initial arsenic concentration of 10 g/L, the temperature of 95 °C, pH 4.0, the air flow rate of 120 L/h. The composition and characteristic of precipitates and collected filtrate are shown in Table 6. It can be seen that the arsenic concentration of the filtrate increased from 2.02 to 2.55 g/L as the initial Fe(II) to As(V) molar ratio increased from 0.8 to 1.2. The rate of arsenic precipitation slightly decreased as the initial Fe(II) to As(V) molar ratio increased. The retardation of arsenic precipitation by increasing the Fe to As molar ratio was also observed by DROPPERT et al [23], who found that the yield of precipitation was only 24% with an initial Fe to As molar ratio of 5. The precipitates obtained had the characteristic of pale green scorodite. The chemical analysis showed that the precipitates had a composition very close to the scorodite stoichiometry in terms of As and Fe. The XRD patterns also demonstrated that the precipitates consisted of crystal scorodite, and the crystallinity was increased with the increase of initial Fe(II) to As(V) molar ratio (Fig. 8). The TCLP tests showed that As leaching concentration of the precipitates obviously decreased from 6.3 to 0.9 mg/L with the increase of Fe(II) to As(V) molar ratio. This obviously reflected the fact that the high Fe(II) to As(V) molar ratio within the range from 0.8 to 1.2 had a positive effect on crystallinity of scorodite. The SEM images of the

 Table 6 Composition and characteristic of product obtained at different initial As concentrations

Initial Fe(II)	Filtrate		Filtra	TCLP	
to As(V) molar ratio	ho(As)/ (g·L <sup>-1</sup> )	$ ho(Fe)/(g\cdot L^{-1})$	Dry mass/g	n(Fe)/n(As)	$\rho(As)/(mg\cdot L^{-1})$
0.8	2.02	1.89	9.17	1.02	6.3
1.0	2.49	3.03	8.96	1.07	1.6
1.2	2.55	4.12	9.81	1.08	0.9
1.5	2.06	5.56	11.45	1.19	1.0
2.0	2.67	8.99	10.44	1.27	0.6
3.0	2.13	14.19	12.24	1.37	0.7



**Fig. 8** XRD patterns of precipitates obtained at different initial Fe(II) to As(V) molar ratios

precipitates revealed that the shape of scorodite produced with initial Fe(II) to As(V) molar ratio varying between 0.8 and 1.2 was extremely irregular (Fig. 9).

With increasing Fe(II) to As(V) molar ratio from 1.5 to 3.0, Fe concentration in filtrate obviously increased from 5.56 to 14.19 g/L. Because the excess of ferrous remained in solution, the light green filtrate was observed at Fe(II) to As(V) molar ratio higher than 2.0. The results of chemical analysis indicated that the Fe(II) to As(V) molar ratio in the precipitate increased from 1.19 to 1.37, which was higher than the scorodite stoichiometric value. Although the XRD pattern showed that precipitates were crystal scorodite, an obvious decrease in crystallinity was obtained as the initial Fe(II) to As(V) molar ratio increased from 1.5 to 3.0. This change was possibly attributed to the incorporation of excess ferrous in the crystal lattice of scorodite. The SEM images revealed that amorphous materials on the surface of large crystals was present with Fe(II) to As(V) molar ratio higher than 2.0 (Fig. 9).

Moreover, the highly crystallized scorodite was produced at initial Fe(II) to As(V) molar ratios of 1.2 and 1.5. The TCLP tests also showed that As leaching concentration of the precipitates was about 1.0 mg/L, and the precipitates were considered to be safe for disposal. However, arsenic concentration in the filtrate indicated that 75.5% and 79.4% of arsenic removal at Fe(II) to As(V) molar ratios of 1.2 and 1.5, respectively (Table 6). The SEM images revealed that individual octahedron scorodite grains were only observed with Fe(II) to As(V) molar ratio of 1.5 (Fig. 9). Therefore, an initial Fe(II) to As(V) molar ratio of 1.5 was favorable for the formation of stable scorodite crystalline and arsenic removal from leaching solution of anode slime.



Fig. 9 SEM images of precipitates obtained at different initial Fe(II) to As(V) molar ratios: (a) n=0.8; (b) n=1.2; (c) n=1.5, (d) n=3.0

#### **4** Conclusions

1) pH plays an important role in scorodite formation in arsenic leaching solution of anode slime. Scorodite can be produced at pH lower than 5.0. High-crystalline scorodite can be obtained in the initial pH range from 2.0 to 4.0. The rate of arsenic precipitation reaches 84.6% at initial pH 4.0.

2) The high temperature can promote the crystal scorodite growth and secondary nucleation. When temperature is controlled at 80-95 °C, sufficiently stable scorodite precipitates are obtained, and leaching concentration of As in scorodite is less than 2.0 mg/L.

3) The high air flow rate is favorable for scorodite formation. When the air flow rate is higher than 120 L/h, the regular octahedron scorodite with high crystallinity and good particle dispersion is produced.

4) The amorphous  $FeAsO_4$  rather than scorodite is obtained at the initial arsenic concentration higher than 20 g/L. In contrast, at the initial arsenic concentration of 10 g/L, regular scorodite precipitates with As leaching concentration of 1.2 mg/L can be obtained.

5) By increasing the initial Fe(II) to As(V) molar ratio to 1.5, 79.4% arsenic was precipitated as a form of highly crystallized scorodite grains with As leaching concentration lower than 1.0 mg/L.

#### References

- XIANG Ping, FENG Qi-ming, ZHU Yang-ge, DENG Jie, LONG Tao, NIU Yin-jian. Occurrence of lead and silver minerals and their interaction with xanthate in slurry of zinc electrolysis anode slime [J]. Transactions of Nonferrous Metals Society of China, 2012, 22(7): 1794–1800.
- [2] CAETANO M L, CIMINELLI V S T, ROCHA S D F, SPITALE M C, CALDEIRA C L. Batch and continuous precipitation of scorodite from dilute industrial solutions [J]. Hydrometallurgy, 2009, 95(1–2): 44–52.
- [3] CAMACHO J, WEE H Y, KRAMER T A, AUTENRIETH R. Arsenic stabilization on water treatment residuals by calcium addition [J]. Journal of Hazardous Materials, 2009, 165(1–3): 599–603.
- [4] HARRIS B. The removal of arsenic from process solutions: Theory and industrial practice [J]. Electrometallurgy and Environmental Hydrometallurgy, 2003, 2: 1889–1902.
- [5] TIWARI S K, PANDEY V K. Removal of arsenic from drinking water by precipitation and adsorption or cementation: An environmental prospective [J]. Recent Research in Science & Technology, 2013, 5(5): 88–91.
- [6] NISHIMURA T, ROBINS R G. A re-evaluation of the solubility and stability regions of calcium arsenites and calcium arsenates in aqueous solution at 25 °C [J]. Mineral Processing and Extractive Metallurgy Review, 1998, 18(3–4): 283–308.
- [7] GONZALEZ C P, WEIJMA J, WEIJDEN R V D, BUISMAN C J N. Biogenic scorodite crystallization by acidianus sulfidivorans for arsenic removal [J]. Environmental Science & Technology, 2010, 44(2): 675–680.
- [8] KLERKA R J, JIA Y, DAENZERA R, GOMEZA M A, DEMOPOULOSA G P. Continuous circuit coprecipitation of arsenic

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(V) with ferric iron by lime neutralization: Process parameter effects on arsenic removal and precipitate quality [J]. Hydrometallurgy, 2012, 111–112: 65–72.

- [9] KRAUSE E, ETTEL V A. Solubility and stability of scorodite, FeAsO<sub>4</sub>·2H<sub>2</sub>O: New data and further discussion [J]. The American Mineralogist, 1988, 73(7–8): 850–854.
- [10] MARIA E, TABOADA M A, HERNANDEZ P C, FLORES E K, GALLEGUILLOS H R, GRABER T A. Equilibria of aqueous system phases containing arsenic + iron and arsenic + calcium at (323.15 and 343.15) K [J]. Journal of Chemical & Engineering Data, 2009, 54(11): 3059–3068.
- [11] KRAUSE E, ETTEL V A. Solubilities and stabilities of ferric arsenate compounds [J]. Hydrometallurgy, 1989, 22(3): 311–337.
- [12] FUJITA T, TAGUCHI R, ABUMIYA M, MATSUMOTO M, SHIBATA E, NAKAMURA T. Novel atmospheric scorodite synthesis by oxidation of ferrous sulfate solution. Part I [J]. Hydrometallurgy, 2008, 90(2–4): 92–102.
- [13] DIRKSEN J A, RING T A. Fundamentals of crystallization: Kinetic effects on particle size distributions and morphology [J]. Chemical Engineering Science, 1991, 46(10): 2389–2427.
- [14] SINGHANIA S, WANG Q, FILIPPOU D, DEMOPOULOS G P. Acidity, valency and third-ion effects on the precipitation of scorodite from mixed sulfate solutions under atmospheric-pressure conditions [J]. Metallurgical and Materials Transactions B, 2006, 37(2): 189–197.
- [15] MONHEMIUS A J, SWASH P M. Removing and stabilizing as from copper refining circuits by hydrothermal processing [J]. The Journal of the Minerals, Metals & Materials Society (JOM), 1999, 51(9): 30–33.

- [16] FUJITA T, TAGUCHI R, ABUMIYA M, MATSUMOTO M, SHIBATA E, NAKAMURA T. Novel atmospheric scorodite synthesis by oxidation of ferrous sulfate solution. Part II: Effect of temperature and air [J]. Hydrometallurgy, 2008, 90(2–4): 85–91.
- [17] USEPA Office of Solid Waste And Emergency. Method 1311 [M]// Toxicity characteristic leaching procedure, methods for envaluating solid waste [M]. Washington DC: U.S. Environmental Protection Agency, 1992.
- [18] FUJITA T, TAGUCHI R, ABUMIYA M, MATSUMOTO M, SHIBATA E, NAKAMURA T. Effect of pH on atmospheric scorodite synthesis by oxidation of ferrous ions: Physical properties and stability of the scorodite [J]. Hydrometallurgy, 2009, 96(3): 189–198.
- [19] FUJITA T, FUJIEDA S, SHINODA K, SUZUK S. Environmental leaching characteristics of scorodite synthesized with Fe(II) ions [J]. Hydrometallurgy, 2012, 111–112: 87–102.
- [20] LE BERRE J F, GAUVIN R, DEMOPOULOS G P. Characterization of poorly-crystalline ferric arsenate precipitated from equimolar Fe(III)-As(V) solutions in the pH range 2 to 8 [J]. Metallurgical and Materials Transactions B, 2007, 38(5): 751–762.
- [21] THOMPSON C V. Grain growth in thin films [J]. Annual Review of Materials Science, 1990, 20: 245–268.
- [22] DAENZER R, XU Li-ying, DOERFELT C, JIA Yong-feng, DEMOPOULOS G P. Precipitation behaviour of As(V) during neutralization of acidic Fe(II)–As(V) solutions in batch and continuous modes [J]. Hydrometallurgy, 2014, 146: 40–47.
- [23] DROPPERT D J, DEMOPOULOS G P, HARRIS G B. Ambient pressure production of crystalline scorodite from arsenic-rich metallurgical effluent solutions [C]//EPD Congress, San Francisco, CA, 1996: 227–239.

# 臭葱石沉淀法脱除和固定阳极泥中的砷

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摘 要:利用循环碱浸方法预处理脱除和固定高砷阳极泥中的砷,然后通过臭葱石沉淀阳极泥浸出液中的砷。采 用亚铁盐空气氧化法沉砷,并考察 pH、温度、空气流量、砷离子浓度以及铁砷摩尔比对臭葱石形成的影响。结 果表明:当阳极泥浸出液中砷离子浓度达到 10 g/L, pH 为 3.0~4.0,反应温度在 80~95 ℃,空气流量≥120 L/h 的 条件下能形成稳定的晶形臭葱石,且其砷沉淀率达到 78%以上。沉淀的砷浸出毒性低于 2.0 mg/L,适宜堆存处理。 关键词: 臭葱石;阳极泥;砷;砷酸铁;砷稳定化

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