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Separation and Stabilization of Arsenic from Lead Slime by the Combination of Acid Leaching and Forming Scorodite

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Abstract: In this paper, a scheme is proposed for the treatment of arsenic-containing lead slime by the combination of acid pressure oxidation leaching and forming scorodite. On the basis of thermodynamic calculations, the effects of six factors including acid concentration, oxygen partial pressure (pO_2), liquid to solid ratio (L/S), agitating speed, leaching time and temperature for the removal of arsenic were studied in an acid pressure oxidation leaching process, then the optimum leaching conditions were established: L/S of 10 mL/g, leaching time of 2.5 h, pO_2 of 2.0 MPa, leaching temperature of 170 °C, acid concentration of 100 g/L and stirring speed of 300 r/min. Under the optimal conditions, the leaching rate of arsenic from lead slime reached 99.10% and the arsenic content of the leaching residue was about 0.80%. After a decontamination procedure, the total arsenic concentration in the acid solution obtained from leaching experiments was 37.18 g/L, and the initial pH was 0.50. Finally, as high as 98.5% of arsenic extracted from the lead slime was stabilized in the form of scorodite ($FeAsO_4 \cdot 2H_2O$) by the precipitation process under the following conditions: initial pH value of 1.0, Fe(II)/As molar ratio of 1.3, pO_2 of 2.5 MPa, temperature of 160 °C and precipitation time of 2.0 h.

Keywords: arsenic stabilization; acid leaching; lead slime; precipitation; scorodite

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1. Introduction

Arsenic is easily volatilized and transferred in the process of pyrometallurgy, leading to the generation of all kinds of hazardous waste. Smelter ash, as one of the most typical, not only contains arsenic, but also contains a certain amount of lead, antimony, copper, zinc, cadmium and other valuable metals [1–3]. From the perspectives of resource recovery and environmental protection, the resource utilization and harmless disposal of smelter ashes have become urgent [4]. At present, hydrometallurgy, pyrometallurgy and volatilization pre-dearsenization followed by hydrometallurgy methods aiming to extract the valuable metals are usually used for reuse of high arsenic smelter ash [5,6]. Some waste, such as lead slime, will be generated in the reuse treatment of lead smelter ash, and will lead to secondary pollution [7].

Solidification [8], vitrification [9] and chemical stabilization methods [10] are usually used for harmless utilization of such lead slime. The aim of the solidification process is to reduce the chance of the waste coming into contact with the environment by changing its physical properties [11]. This is usually achieved by mechanically mixing the slime with additives to form a solid product [12]. Commonly used additives are divided into two kinds: inorganic additives, mainly including cement, volcanic ash, silicate and other materials, and organic additives such as thermoplastic materials, polymers and organic soil [13]. Solidification technology has shown great advantages in limiting the toxicity of polluting elements, but its applicability is poor due to the complex properties of slime and

the diversity of curing product evaluation methods [14]. In the vitrification method, the slime is mixed with glass matrix and heated to a melt state at high temperature, so that the slime is dissolved and then dispersed; thus, the resulting glass can show excellent chemical and biological inertia [15,16]. The commonly used glass matrixes are oxide glass systems, such as silicate glass, phosphate glass and borate glass [17]. In some research, sodium arsenate was added to silicate glass containing iron, and the research found that Si–O–As and Fe–O–Si/As bonds could be formed and the arsenic toxicity leaching concentration of the resulting glass-cured body was only 1.22 mg/L [18,19]. In other studies, phosphate glass was used to immobilize sodium arsenate at high temperature [20]. The content of free O^{2-} in phosphate has an effect on the arsenic fixation ability and stability of phosphate glass, and it is found that the addition of CaO can significantly improve the arsenic fixation effect while the solidified products formed have good stability. BaO–TiO₂–B₂O₃ glass was analyzed by infrared spectroscopy and raman spectroscopy, and boron anomaly was used to change the properties of glass and improve its arsenic fixation capacity [21]. At the same time, different oxides are added to solve the delamination phenomenon, which opens up a new direction for the study of silicate as arsenic fixation [22]. However, the content of arsenic in borosilicate glass is strictly limited [23]. Even though efficient arsenic fixation was achieved, the vitrification process has a high cost due to its high energy consumption, and does not have the conditions for large-scale market promotion [24]. Chemical stabilization methods forming the chemical stable phase of arsenic by hydrometallurgy have been studied extensively around the world [25,26]. Traditional stabilization methods include the lime neutralization method and sulfide precipitation method [27]. The lime neutralization method refers to adding lime to arsenic-containing wastewater to generate calcium arsenite or calcium arsenate precipitate by adjusting pH value [14,28,29]. Note that calcium arsenate precipitates have high solubility under acidic conditions and will react with CO₂ dissolved in water to convert into calcium carbonate, leading to re-dissolution of arsenic [30,31]. The sulfide precipitation method uses sulfur compounds to react with arsenic in wastewater to produce arsenic sulfide so as to remove arsenic in wastewater [17,32]. The sulfide precipitation method has a good arsenic removal effect, but arsenic sulfide will be oxidized and dissolved under O₂ and bacteria; the generated residues will be unstable and easy to decompose when the pH is less than or equal to 4, and the sulfur ions will exceed the standard [33–35].

With the advantages of low solubility and leaching toxicity of scorodite, the process of converting arsenic into scorodite and then storing it in a rigid landfill has gradually developed into a trend for the treatment of arsenic-containing materials [36,37]. In this method, scorodite (FeAsO₄·2H₂O) was produced and arsenic in the solution was converted into scorodite crystals for storage, thus achieving the purpose of safe disposal. Compared with the lime neutralization method and the sulfide precipitation method, the arsenic fixation method of scorodite has the advantages of high arsenic removal rate, high precipitation stability and decreased chance of causing secondary pollution [38,39]. A technique to form scorodite from arsenic-rich solutions at atmospheric pressure was most widely used [40]. Although the properties of scorodite obtained under atmospheric pressure are similar to the natural mineral scorodite, amorphous ferric arsenate (the precursor of scorodite) will be easily generated under atmospheric pressure. These ferric arsenates need to be transformed into crystal scorodite after aging. The crystallinity of scorodite obtained after aging is often poor, and still contains amorphous ferric arsenate, goethite and other impurities. Although Fujita et al. obtained scorodite with higher arsenic content and good stability by co-precipitation with the systems of oxygen, Fe(II) and As (V), it is necessary to strictly control the supersaturation of Fe(III) in the system during arsenic precipitation [41]. The pressurized oxidation technique has proven to be effective in improving the reaction rate and oxidation efficiency [38].

Inspired by all of these studies, a process scheme was designed to separate and stabilize arsenic from lead slime by the combination of acid pressure leaching and forming scorodite under pressurized conditions. During the acid pressure leaching stage, arsenic

trivalent is oxidized to arsenic pentavalent and selectively extracted from the lead slime, while the lead remains in the leach residue as lead sulfate. Six key parameters including acid concentration, L/S, agitating speed, pO_2 , leaching temperature and time were optimized [42,43]. After a decontamination stage, the arsenic-containing solution is subsequently precipitated for further treatment. In addition, five key parameters including Fe(II) to arsenic ratio, initial pH value, pO_2 , precipitation temperature and time were also studied in the precipitation stage. The whole process is relatively simple and environmentally friendly, providing an alternative method for the treatment of hazardous lead slime.

2. Experimental

2.1. Materials

The lead slime sample used in this study was obtained from a lead smelting plant (Hunan Tengchi Environmental Protection Technology Co., Ltd.) in Hunan province, China, and the slime emerged in a hydrometallurgical circuit of smelter ashes. The chemical compositions of lead slime are shown in Table 1, while the X-ray Diffraction (XRD) pattern and particle size distribution are shown in Figure 1. Table 1 shows that the arsenic content is as high as 33.47%. Figure 1a shows that the particle size is very fine and its distribution ranges from 0.02 μm to 206.50 μm , concentrating around 15.397 μm . According to Figure 1b, As_2O_3 and PbSO_4 are the main phases in the lead slime.

Table 1. The chemical compositions of the lead slime (wt.%).

Elements	Pb	Cd	Sb	In	Zn	As	Sn
Content	15.10	1.44	0.04	0.04	0.25	33.47	2.50

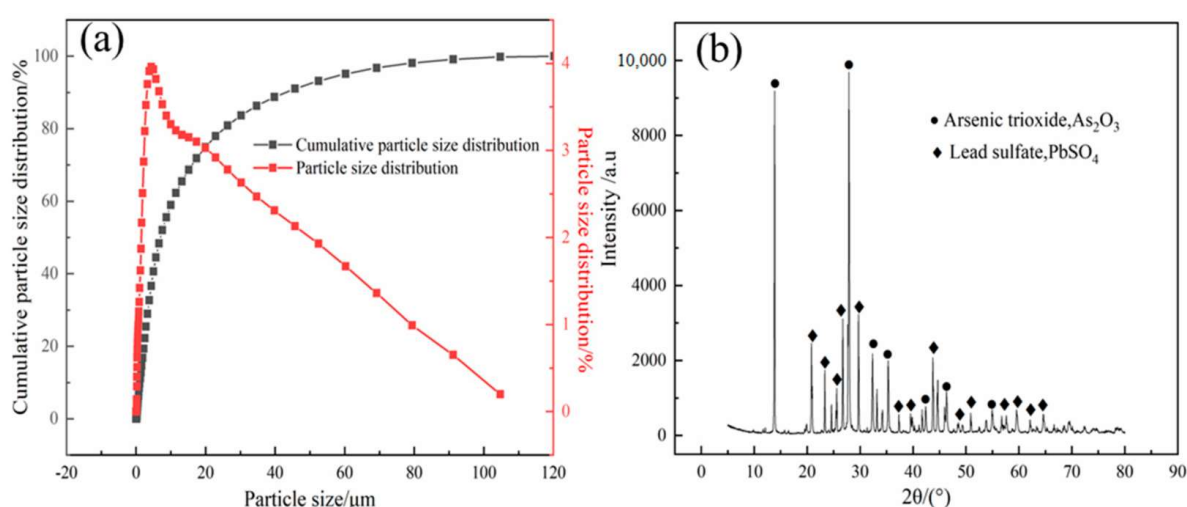


Figure 1. (a) Cumulative particle size distribution and particle size distribution of the lead slime; (b) XRD patterns of the lead slime. a.u: arbitrary unit.

2.2. Experimental Procedure

Both the leaching and precipitation experiments are carried out in the pressurized and stirred leaching equipment provided by Shanghai LABE Instrument Co., Ltd. (<http://www.reactorchina.com/index.html>, accessed date: 14 November 2021), the schematic of which is shown in Figure 2. The process scheme consists of three stages: the first stage is the leaching of lead slime, the second stage is the decontamination of leaching solution, and the third stage is the scorodite precipitation of arsenic in leachate [42]. The flow chart of the process is presented in Figure 3.

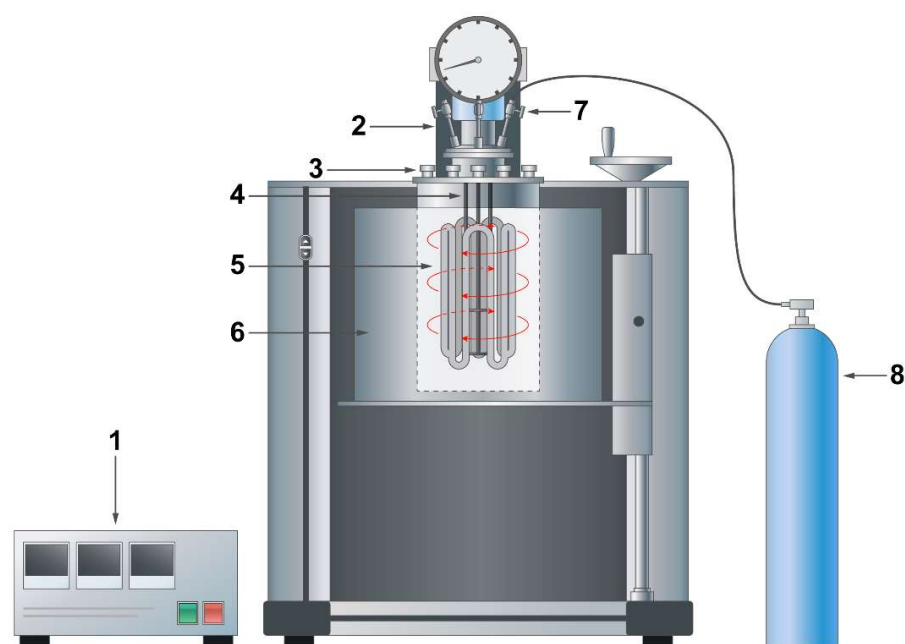


Figure 2. Schematic of the experimental setup for the leaching of lead slime: 1—controller, 2—outlet valve, 3—lid, 4—stirring, 5—container, 6—heating, 7—inlet valve, 8—oxygen.

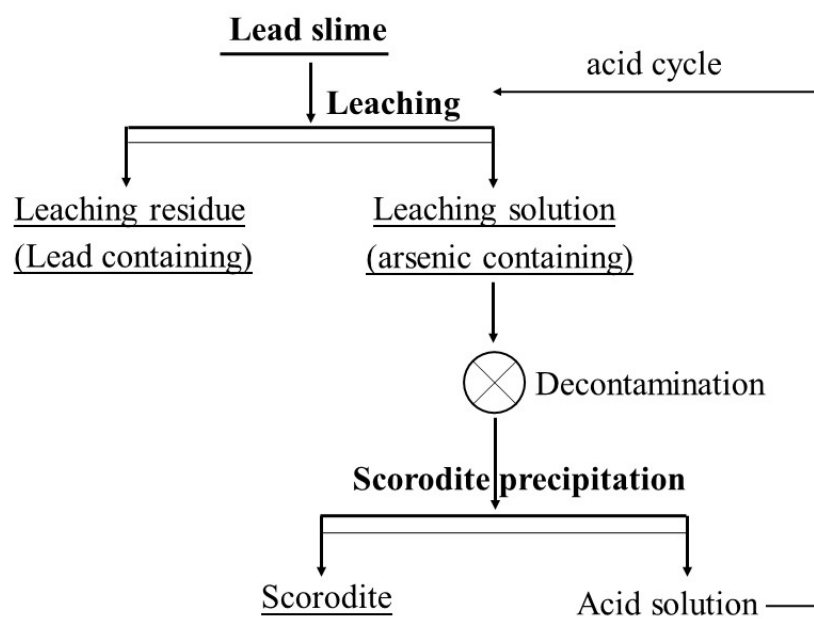


Figure 3. Schematic flowsheet for the treatment of lead slime.

The acid leaching experiments and precipitation experiments all included two parts, namely, the laboratory exploration experiments with a scale of 300 mL and the verification experiments with a larger scale of 600 mL. In the acid leaching experiments, H_2SO_4 solution of certain concentrations ranging from 60 g/L to 120 g/L was first compounded and placed in the container with the lead slime sample. The experiments were carried out at a given pressure ranging from 0.5 Mpa to 2.5 Mpa and temperature ranging from 110 °C to 190 °C. After the experiment, the heating was terminated, then the intake valve was closed and cool water added to cool down the temperature. When the temperature dropped to room temperature, the exhaust valve was opened and the entire facility shut down. Subsequently, the pulp was filtered and the obtained solution proceeded to the next step. In

the scorodite precipitation experiments, ferrous sulphate was used as the iron source. Under the action of oxidation, arsenic in the solution was transformed into iron arsenate precipitation, so as to achieve the role of fixing arsenic [44]. The leaching solution was adjusted with NaOH to a desired pH. After each precipitation experiment, the resulting pulps were filtered and the chemical analysis performed for both solution and solid products.

3. Results and Discussion

3.1. Thermodynamic Calculation

The E-pH diagrams of As-H₂O and As-Fe-H₂O systems at room temperature were calculated by Factsage 8.0 (version 8.0, ThermFact LTD, Quebec, QC, Canada), and the results are shown in Figure 4. Figure 4a illustrates the dominant species within the water line boundaries for the As-H₂O system at room temperature and 101.3 kPa, with redox potential (E) and pH control arsenic speciation. Pentavalent (+5) or arsenate is generally the dominant in an oxidizing environment. H₃AsO₄(aq) dominates at low pH values (less than about 2) in oxidizing conditions. At higher pH values, H₂AsO₄[−], HAsO₄[2−] and AsO₄[3−] are dominant. Trivalent arsenites including H₂AsO₃[−] predominate in moderately reducing anaerobic environments. The results in Figure 4a indicates that an acid system combined with oxidation can effectively leach arsenic into solution, and a decrease in acidity will depress the leaching. Figure 4b illustrates the E-pH diagram for the As-Fe-H₂O system at room temperature and 101.3 kPa. In a low potential solution (<0.19 V), low iron (Fe, Fe²⁺) and low arsenic (As, AsH₃) are relatively stable; on the other hand, high iron (Fe(OH)₃, FeAsO₄) and high arsenic, including AsO₄[3−] and FeAsO₄, are stable in a high-potential solution (>0.19 V). A wide stable region of FeAsO₄ appeared in the pH range of 0.03–5.17, and if the potential decrease gradually, FeAsO₄ would be converted or broken down in the following way: Fe²⁺ + H₃AsO₄ → Fe²⁺ + As₂O₃ → Fe(OH)₃ + As₂O₃. The results in Figure 4b indicate that lower pH value will lead FeAsO₄ to redissolve, and a higher pH value will hydrolyze Fe(III) to Fe(OH)₃.

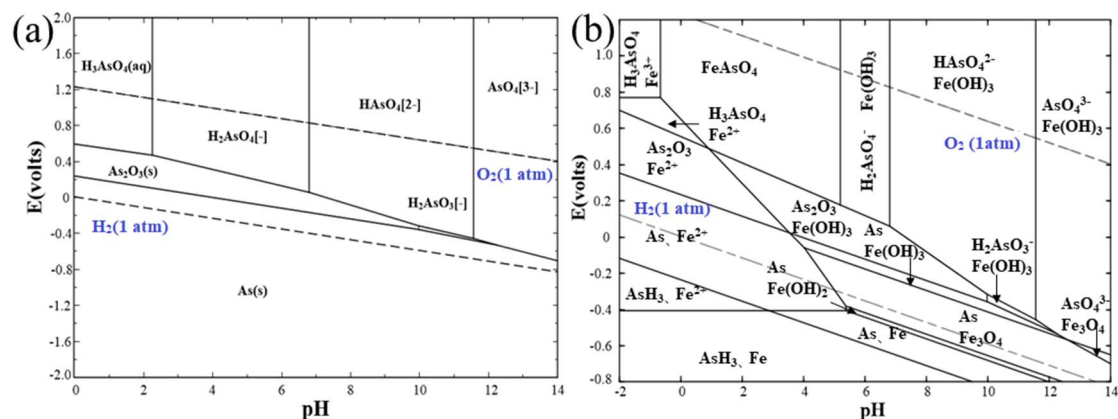


Figure 4. E-pH diagrams of As-H₂O systems and As-Fe-H₂O system at 25 °C. (a) As-H₂O systems (b) As-Fe-H₂O system.

3.2. Acid Pressure Oxidation Leaching

The purpose of acid pressure oxidation leaching is to extract arsenic from the lead slime. Figure 5 summarizes six key parameters affecting the leaching of lead slime, including concentration of H₂SO₄, *p*O₂, L/S, agitating speed, leaching time and temperature. Among these parameters, the first parameter to be determined was the influence of H₂SO₄ concentration on the leaching of lead slime. As shown in Figure 5a, acid concentration had great influence on the leaching of arsenic. When the concentration of H₂SO₄ was set at 60 g/L, the leaching extent of arsenic was 80.25%. When the acid concentration raised from 60 g/L to 100 g/L, the leaching extent of arsenic significantly raised from 80.25% to 97.10%.

In contrast, when the acid concentration continued to increase from 100 g/L to 140 g/L, the leaching extent decreased from 97.10% to 94.44%.

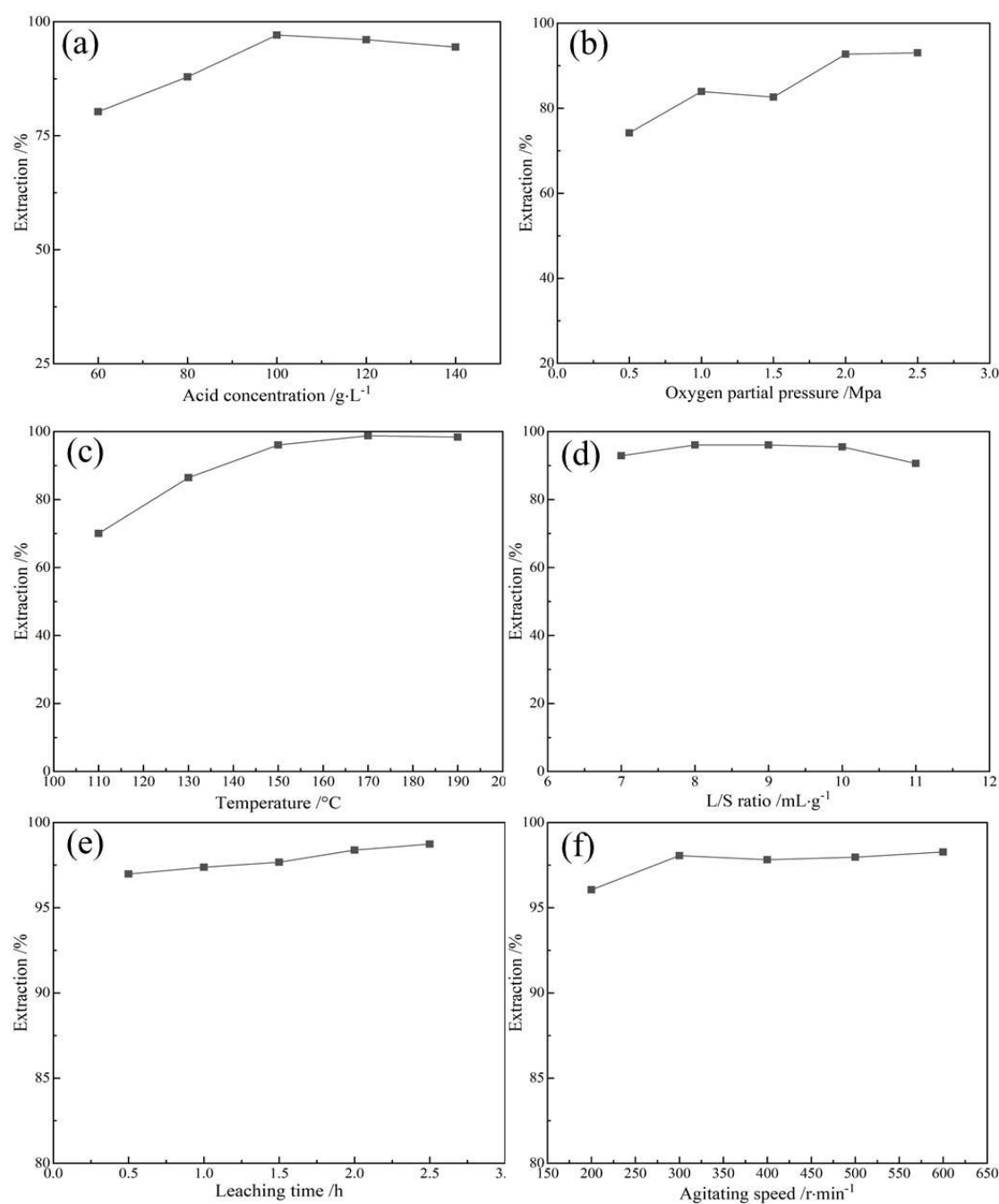


Figure 5. Effects of different acid leaching conditions: (a) acid concentration (150 °C, L/S = 8 mg/L, pO_2 = 2.0 MPa, 2 h, 200 r/min), (b) pO_2 (150 °C, L/S = 8 mg/L, $[H_2SO_4]$ = 100 g/L, 2 h, 200 r/min), (c) temperature (pO_2 = 2.0 MPa, L/S = 8 mg/L, $[H_2SO_4]$ = 100 g/L, 2 h, 200 r/min), (d) L/S ratio (170 °C, $[H_2SO_4]$ = 100 g/L, pO_2 = 2.0 MPa, 2 h, 200 r/min), (e) leaching time (170 °C, L/S = 10 mg/L, pO_2 = 2.0 MPa, $[H_2SO_4]$ = 100 g/L, 200 r/min), (f) agitating speed (170 °C, L/S = 10 mg/L, pO_2 = 2.0 MPa, 2.5 h, 200 r/min).

In order to further understand the reasons for the decrease in leaching rate under high acidity, the leaching residues obtained at 120 g/L and 140 g/L of H_2SO_4 concentration were analyzed by Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) (EV081, Carl Zeiss, Heidenheim, Germany), the results of which are shown in Figure 6. The results in Figure 6c demonstrate that the massive and floccule structure are lead sulfate and arsenic trioxide, respectively. As shown in Figure 6a,b, when the acid

concentrations were 120 g/L and 140 g/L, lead sulfate and arsenic trioxide were tightly wrapped, which prevented the contact of arsenic with leaching agents, and thus preventing the leaching of arsenic. Therefore, in the study, the acid concentration of 100 g/L was selected for the follow-up research.

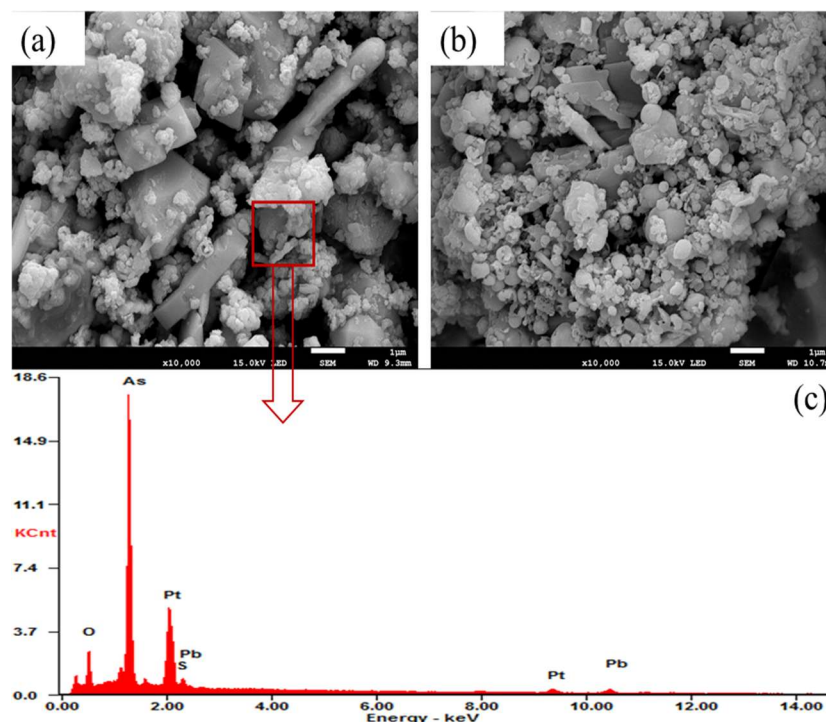


Figure 6. SEM analysis of the leaching residues obtained at different acid concentrations: (a) 120g/L, (b) 140 g/L and (c) EDS analysis of the leaching residue obtained at acid concentration of 120g/L.

Figure 5b depicts the relationship between pO_2 and the leaching extent of arsenic. Obviously, when the pO_2 increased from 0.5 Mpa to 1.0 Mpa, the arsenic leaching rate increased from 74.22% to 83.95%. On the contrary, when the pO_2 increased from 1.0Mpa to 1.5 Mpa, the arsenic leaching rate slightly decreased from 83.95% to 82.63%. However, as the pO_2 continued to increase to 2.0 Mpa, the leaching rate of arsenic increased sharply to 92.73%. When the pO_2 continued to increase to 2.5 Mpa, the increase in the arsenic leaching rate was not obvious. Thus, the pO_2 of 2.0 Mpa was selected.

Figure 5c shows the influence of leaching temperature on the leaching results of lead slime. Obviously, the increase in leaching temperature can significantly promote the leaching rate of arsenic. For the arsenic in the lead slime, the leaching extent sharply increased from 70.00% to 98.79% while the leaching temperature raised from 110 °C to 170 °C. This is perhaps due to the change in the equilibrium constant and rate of the reaction by order of magnitude with the increase in leaching temperature. However, while the leaching temperature rose from 170 °C to 190 °C, the leaching extent did not increase further. A leaching temperature that is too high is conducive to the leaching of arsenic [45]. Note that a high leaching temperature will lead to the generation of highly toxic arsenic-containing steam, but pressure leaching completely avoids this risk; this is because the pressure leaching process takes place in a closed container, which is different from atmospheric leaching. It is also worth noting that a higher leaching temperature means higher energy consumption. Thus, in this study, 170 °C was selected to be the optimal leaching temperature.

Figure 5d reveals the relationship between the liquid to solid ratio and the leaching rate of arsenic in lead slime. When the liquid to solid ratio first increased from 7 mL/g to 8mL/g, the leaching extent of arsenic increased slowly from 92.90% to 96.05%. When the liquid to solid ratio continued to increase from 8 mL/g to 10mL/g, the leaching extent of

arsenic remained stable at about 96%. However, when the liquid to solid ratio further increased from 10 mL/g to 11 mL/g, the leaching rate of arsenic declined sharply from 96% to 90.64%. The results of the extent of leaching change indicated that the liquid to solid ratio had a significant effect on the extraction of arsenic. Some research has investigated the effect of initial arsenic concentration on scorodite formation, and the results indicated that the high initial arsenic concentration was unfavorable for arsenic precipitation [43]. Thus, 10 mL/g of the liquid to solid ratio was selected for the subsequent research.

Figure 5e shows the variation of leaching extent with leaching time, and it is obvious that the leaching time had minimal influence on the leaching of arsenic in lead slime. For the arsenic in the lead slime, the leaching extent gradually increased from 96.99% at 0.5 h to 98.73% at 2.5 h. With the increase in time, the increase in leaching rate is less obvious. Considering that, the longer the period of time, the more energy is consumed. Thus, 2.5 h of leaching time was selected to avoid greater energy consumption.

Figure 5f presents the influence of agitating speed on the leaching extent of arsenic.

When the agitating speed was first raised from 200 r/min to 300 r/min, the leaching extent of arsenic in lead slime slightly increased from 96.05% to 98.06%. However, the leaching extent of arsenic slowly declined to 97.82% when the agitating speed increased to 400 r/min. It is worth pointing out that the leaching extent of arsenic increased from 97.82% to 98.27% when the agitating speed increased from 400 r/min to 600 r/min. Thus, the agitating speed was selected as 300 r/min.

Through a series of laboratory experiments, the optimal acid leaching conditions for the lead slime were determined, that is, 60 g of lead slime, 10 mL/g of L/S, 2.5 h of leaching time, 2.0 MPa of pO_2 , 170 °C of leaching temperature, 100 g/L of acid concentration and 300 r/min of stirring speed. Table 2 demonstrates the leaching results of verification experiments. Under the selected conditions, the leaching extent of arsenic from lead slime was more than 99.1% and the arsenic content of the leaching residue was about 0.80%. The obtained solution of arsenic was subjected to purification and prepared for scorodite precipitation.

Table 2. Results of verification experiments under selected conditions.

No.	Solution		Residue		Leaching Rate /%
	Volume /mL	As Concentration g/L	Mass /g	As Content /%	
I	550	36.17	24.43	0.77	99.06
II	540	36.88	23.52	0.71	99.17

3.3. Scorodite Precipitation

The initial arsenic concentration in the acid solution obtained from leaching experiments was 37.18 g/L, and the initial pH was 0.50. Figures 7 and 8 summarize five key parameters affecting the scorodite precipitation, including initial Fe(II) to arsenic molar ratio (Fe/As ratio), initial pH value, pO_2 and precipitation time and temperature [43,46,47].

3.3.1. Effect of Initial Fe/As Ratio

The precipitation of scorodite is the reaction between Fe and H_3AsO_4 , and thus the first parameter to be determined was the influence of the Fe/As ratio on the scorodite precipitation. Figure 7 presents the influence of the Fe/As ratio within a range from 1.1 to 1.9, and other parameters were fixed as 160 °C temperature, 2 h of reaction time and 2.5 MPa of partial oxygen pressure [48]. As shown in Figure 7a, the Fe/As ratio has a remarkable influence on the arsenic precipitation rate. When the Fe/As ratio was less than 1.3, the arsenic precipitation rate increased dramatically as the Fe/As ratio increased. This is because the dosage of the precipitant increasingly met the stoichiometric ratio of arsenic and iron in $FeAsO_4$. When the Fe/As ratio increased from 1.3 to 1.7, the precipitation extent presented a sharp drop followed by a slow drop. When the Fe/As molar ratio was above

1.7, arsenic precipitation decreased sharply. Furthermore, XRD patterns of the precipitates were observed, and the results in Figure 7b indicate that all the precipitates were only in the form of $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$. The resulting precipitates, as illustrated in Figure 7c, showed the appearance of light green, which was consistent with the appearance of scorodite. Thus, the optimal added amount of Fe(II) is 1.3 times of the theoretical value.

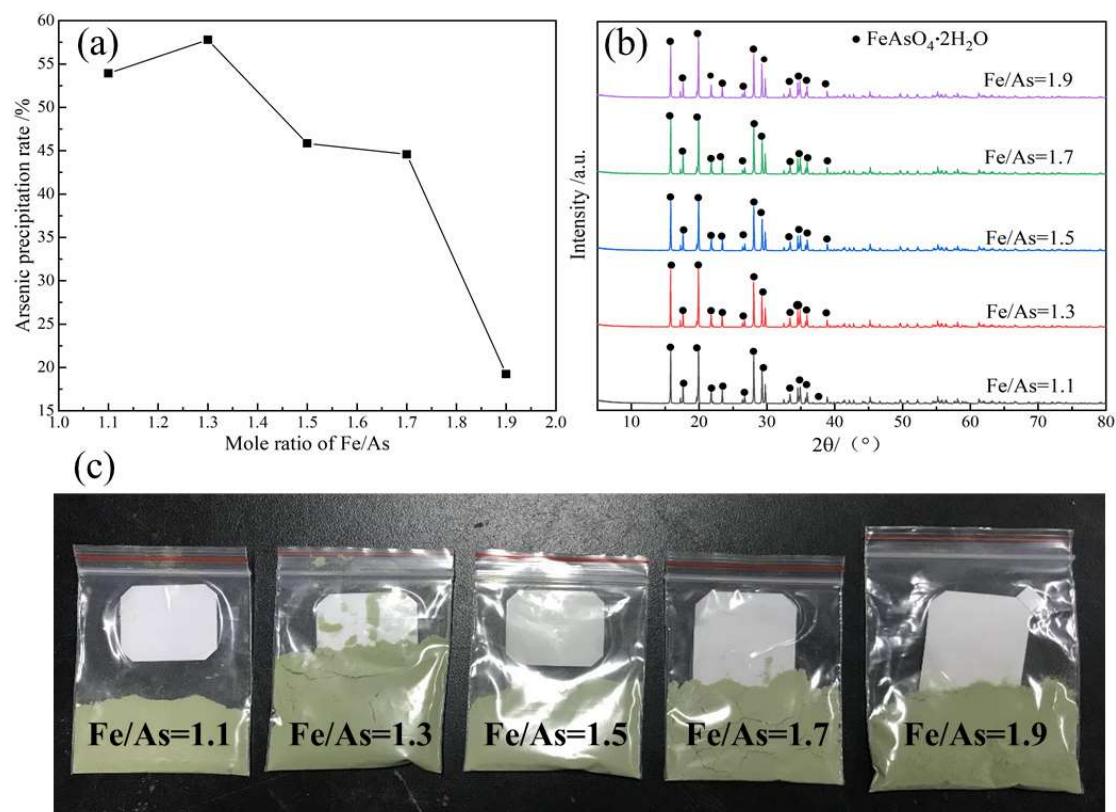


Figure 7. (a) Effect of initial Fe/As ratio on arsenic precipitation rate, (b) XRD patterns of precipitates obtained at different initial Fe/As ratio and (c) the appearance of precipitates obtained at different initial Fe/As ratio.

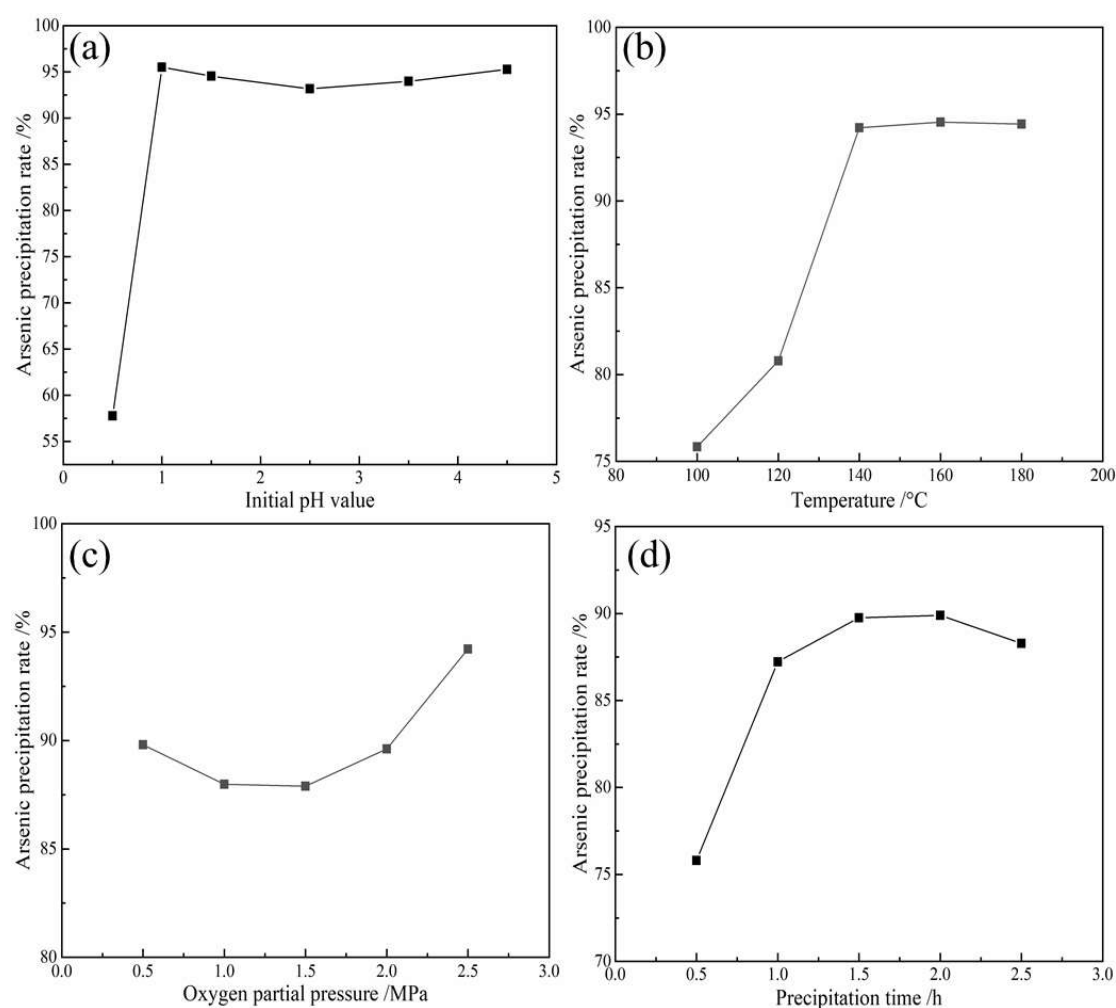


Figure 8. Effects of different precipitation conditions on arsenic precipitation rate: (a) initial pH, (b) temperature, (c) pO_2 , (d) precipitation time.

3.3.2. Effect of Initial pH Value

The pH value also has significant effect on the precipitation process, as presented in the E-pH diagram. Figure 8a presents the influence of pH value within a range from 0.5 to 4.5, and other parameters were fixed as Fe/As molar ratio of 1.3, temperature of 160 °C, precipitation time of 2 h and pO_2 of 2.5 MPa. As shown in Figure 8a, the scorodite precipitation rate increased sharply from 57.66% to 96.13% when the pH value increased from 0.5 to 1.0. Similar results were reported by others [40,43]. They found that the higher the terminal pH value, the higher the arsenic removal rate. In other words, the precipitation rate of arsenic can be improved by increasing the initial pH value appropriately. This may account for the increase in the arsenic leaching rate when the pH value increased from 0.5 to 1.0. When the pH value continued to increase from 1.0 to 2.5, the arsenic precipitation rate decreased slightly. When the pH value increased from 2.5 to 4.5, the arsenic leaching rate started to rise again. XRD analysis was carried out on the precipitates obtained at different pH values, and the results are presented in Figure 9a. As shown in Figure 9a, when the pH value was greater than 1.5, sodium jarosite appeared in the precipitates. The arsenic precipitation process mainly consisted of the adsorption process of arsenic on the surface of hydrated iron oxide, and arsenic was deposited in the form of adsorbed state and iron arsenate [49]. Therefore, sodium jarosite will absorb part of the arsenic, so when the pH value was above 2.5, the arsenic precipitation rate would have also increased.

In addition, the precipitates obtained under different pH values were analyzed by SEM analysis, and the results are presented in Figure 10. As shown in this figure, when

the pH value is 0.5, the precipitate exists in a spherical form of polymerization and the crystal structure has not been expanded, indicating that the precipitate is amorphous. When the pH values were 1.0 and 1.5, the precipitate existed in a crystal structure, and when the pH value was greater than 1.5, the crystal structure of the precipitate increasingly worsened. Therefore, the optimal initial pH value was selected as 1.0 in the experiment of arsenic precipitation.

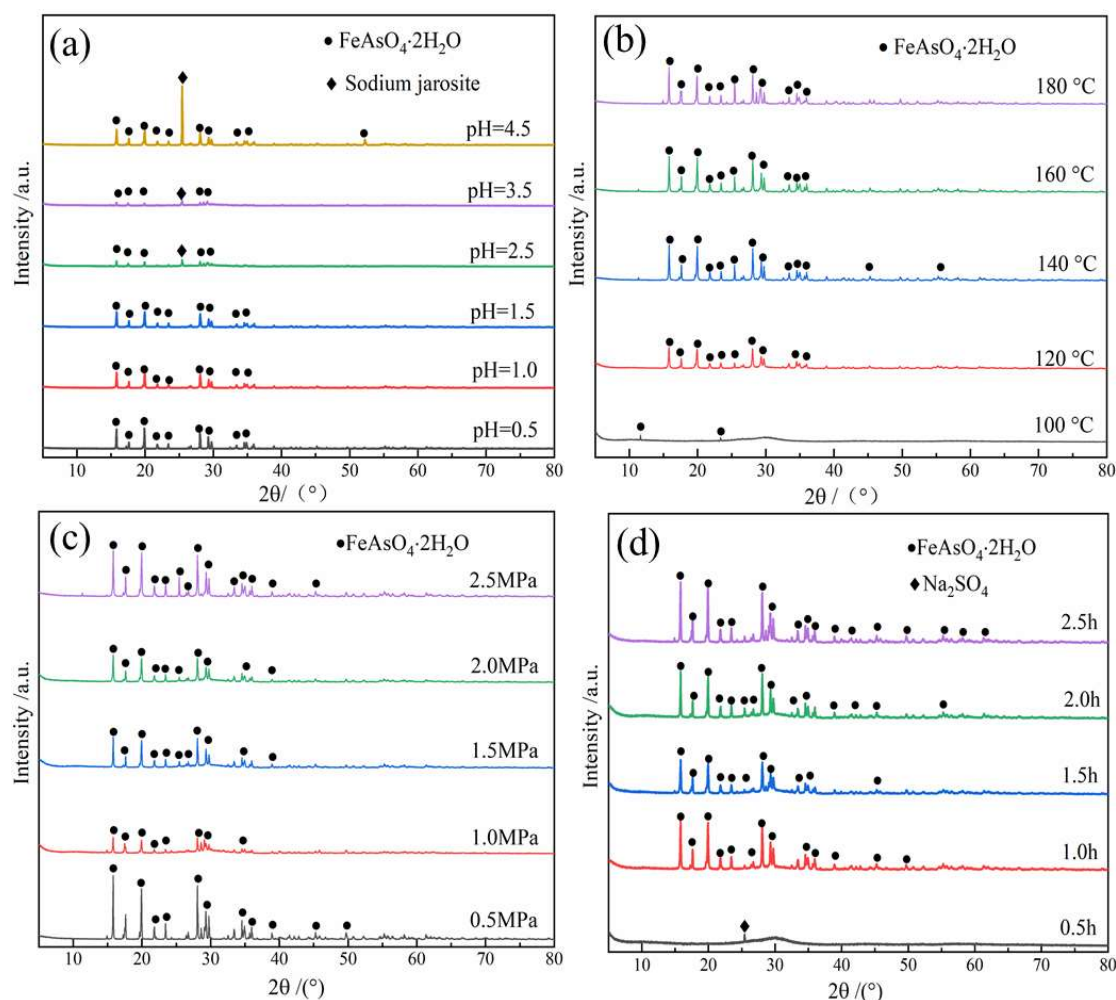


Figure 9. XRD patterns of precipitates at different precipitation conditions: (a) initial pH (Fe/As molar ratio of 1.3, temperature of 160 °C, precipitation time of 2 h and pO_2 of 2.5 MPa), (b) temperature (Fe/As ratio of 1.3, pH value of 1.0, precipitation time of 2 h and pO_2 of 2.5 MPa), (c) pO_2 (Fe/As ratio of 1.3, pH value of 1.0, reaction time of 2 h, temperature of 160 °C), (d) precipitation time (Fe/As ratio of 1.3, pH value of 1.0, pO_2 of 2.5 MPa, temperature of 160 °C).

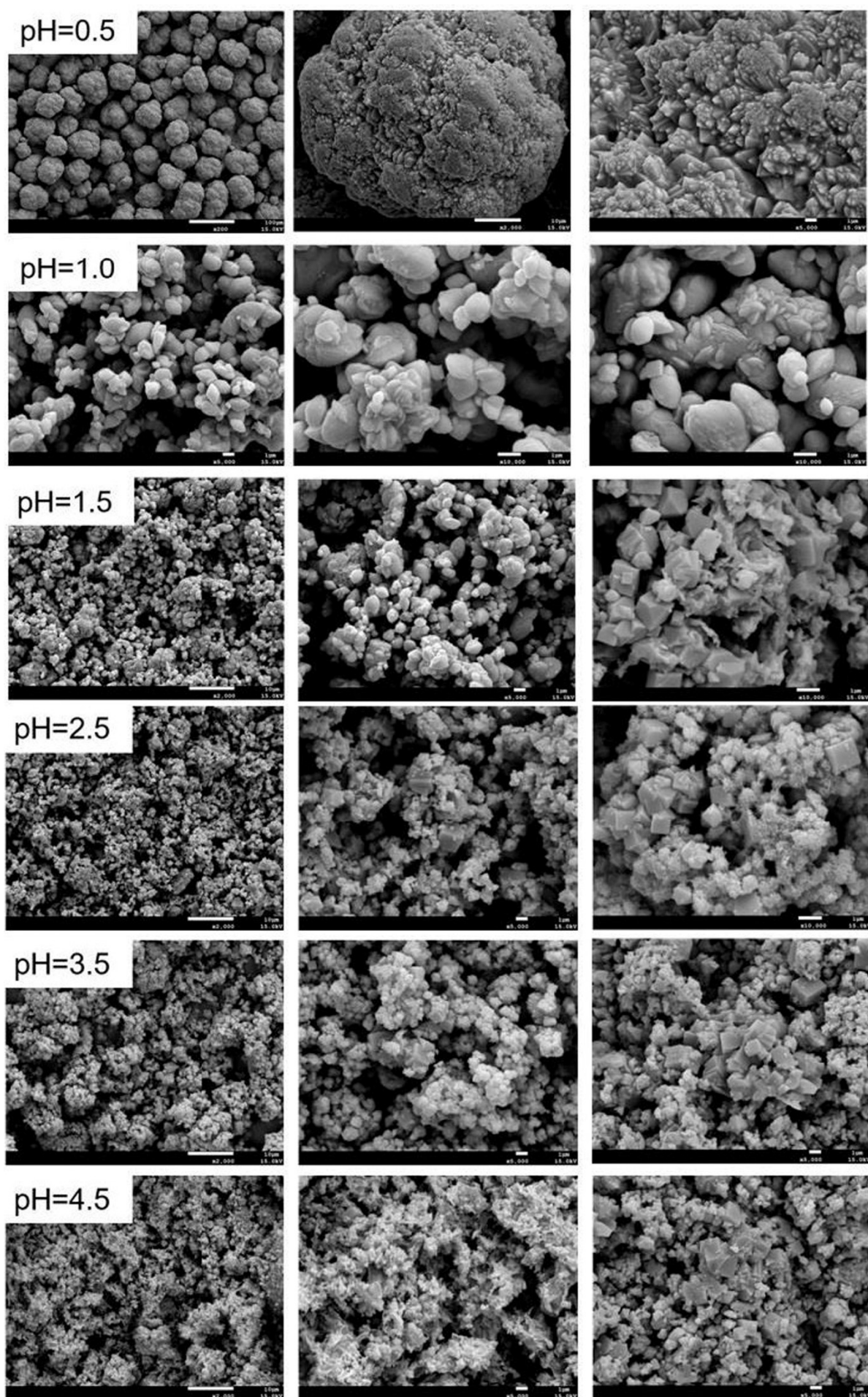


Figure 10. SEM analysis of precipitates obtained at different pH values.

3.3.3. Effect of Temperature

Figure 8b presents the influence of the precipitation temperature on scorodite precipitation within a temperature range from 100 °C to 180 °C, and other parameters were fixed as Fe/As ratio of 1.3, pH value of 1.0, precipitation time of 2 h and pO_2 of 2.5 MPa. As shown in Figure 8b, when the precipitation temperature was lower than 140 °C, the arsenic precipitation rate rose from 75% to about 94% with the increase in temperature. When the temperature was greater than 140 °C, the increasing temperature had little effect on the arsenic precipitation rate, and the arsenic precipitation rate was always maintained at about 95%. Furthermore, the arsenic and iron content of the precipitate obtained at a temperature greater than 140 °C was determined. It was found that the arsenic content of the precipitate obtained at 160 °C was 30.12%, which was closer to the arsenic content in the pure iron arsenate crystal. Figure 9b presents the XRD patterns of the resulting precipitates. The results as shown in Figure 9b indicated that all the precipitates were only in the form of $FeAsO_4 \cdot 2H_2O$. Therefore, the optimal reaction temperature was determined to be 160 °C.

3.3.4. Effect of Oxygen Partial Pressure

The influence of pO_2 on scorodite formation from the leaching solution of lead slime after purification treatment was investigated under the following conditions: Fe/As ratio of 1.3, pH value of 1.0, reaction time of 2 h, temperature of 160 °C. The results are shown in Figure 8c. Figure 8c demonstrates that the partial pressure of oxygen has a significant effect on arsenic precipitation. When the partial pressure of oxygen increased from 0.5 MPa to 1.5 MPa, the arsenic precipitation rate continued to decrease; when it rose from 1.5 MPa to 2.5 MPa, the arsenic precipitation rate continued to increase and the arsenic precipitation rate reached the minimum at 1.5 MPa. Henry's law shows that the concentration of dissolved gas will rise with the increase in gas pressure, and the gas will agitate the solution and product when entering into the container. Therefore, the reaction rate was slow when pO_2 was in a smaller level, and the growth of scorodite crystals was relatively slow. When it was higher, the extent of dissolving oxygen was higher; that is, the oxidation rate of ferrite increases and the arsenic precipitation rate increases. Further, XRD patterns of the precipitates obtained were observed and the results indicated that all the precipitates were only in the form of $FeAsO_4 \cdot 2H_2O$, as shown in Figure 9c. Therefore, the optimal pO_2 was determined to be 2.5 MPa.

3.3.5. Effect of Precipitation Time

The influence of precipitation time on scorodite formation from the leaching solution of lead slime after purification treatment was investigated under the following conditions: Fe/As ratio of 1.3, pH value of 1.0, pO_2 of 2.0 MPa, temperature of 160 °C. The results are shown in Figure 8d. As shown in Figure 8d, when the precipitation time was less than 1.0 h, the precipitation time had a noticeable impact on the scorodite precipitation extent. When the precipitation time increased from 0.5h to 1.0h, the arsenic precipitation rate increased from 75.44% to 87.23%. When the reaction time continued to increase to 1.5 h, the arsenic deposition rate increased to 90.08%. When the reaction time continued to increase to 2.0 h, the arsenic precipitation rate basically remained unchanged. As the precipitation time was further increased to 2.5 h, the arsenic precipitation extent decreased slightly to 87.65%, because excessive extension of the reaction time would cause a small amount of iron arsenate to redissolve. In addition, XRD patterns of the precipitates obtained were observed and the results of Figure 9d indicated that when the reaction time was less than 0.5 h, the ferric arsenate was not formed, and when the reaction time was greater than 1.0 h, the precipitates were in the form of $FeAsO_4 \cdot 2H_2O$. Therefore, the optimal precipitation time was determined to be 2.0 h.

According to the studies of the scorodite precipitation process [50], the optimum conditions for the scorodite precipitation were established as: Fe/As ratio of 1.3, pH value of 1.0, pO_2 of 2.5 MPa, temperature of 160 °C and precipitation time of 2.0 h. Table 3 demonstrates the precipitation results of verification experiments. Under the optimum conditions, the precipitation extent of arsenic in leaching solution reached as high as 98.5%. Figures 11 and 12, respectively, present an XRD pattern and elemental distribution map of the scorodite product resulting from the precipitation process. The results in Figure 11 indicated that $FeAsO_4 \cdot 2H_2O$ was the main form in the resulting products.

Table 3. Results of verification experiments under optimum conditions.

No.	Precipitation Rate/%	Residue Content/%	
		As	Fe
I	99.12	30.12	22.81
II	97.88	30.89	21.76
Mean	98.50	30.51	22.29

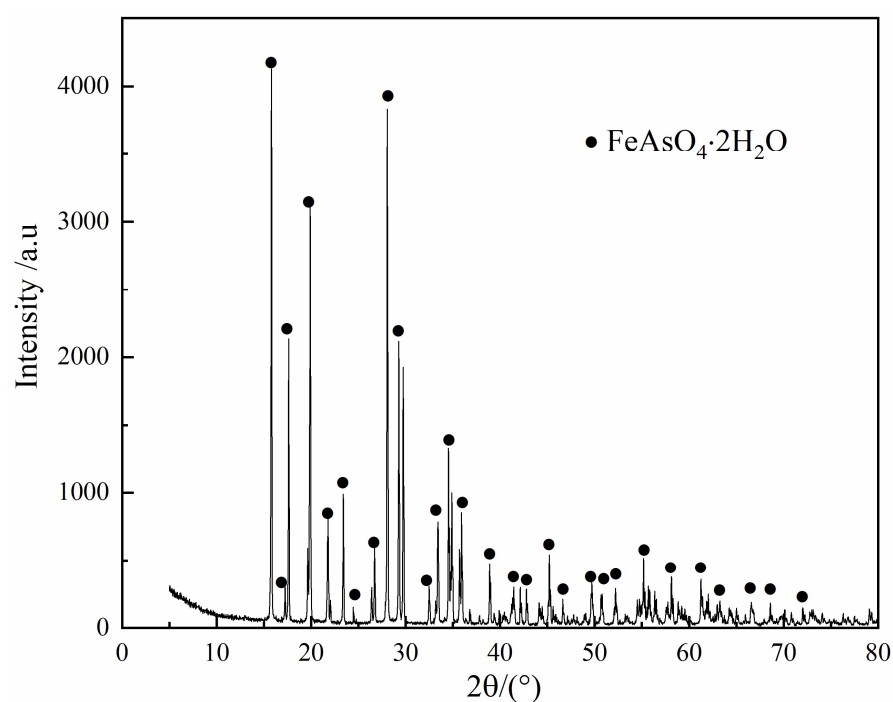


Figure 11. XRD pattern of the precipitation obtained under the optimum conditions.

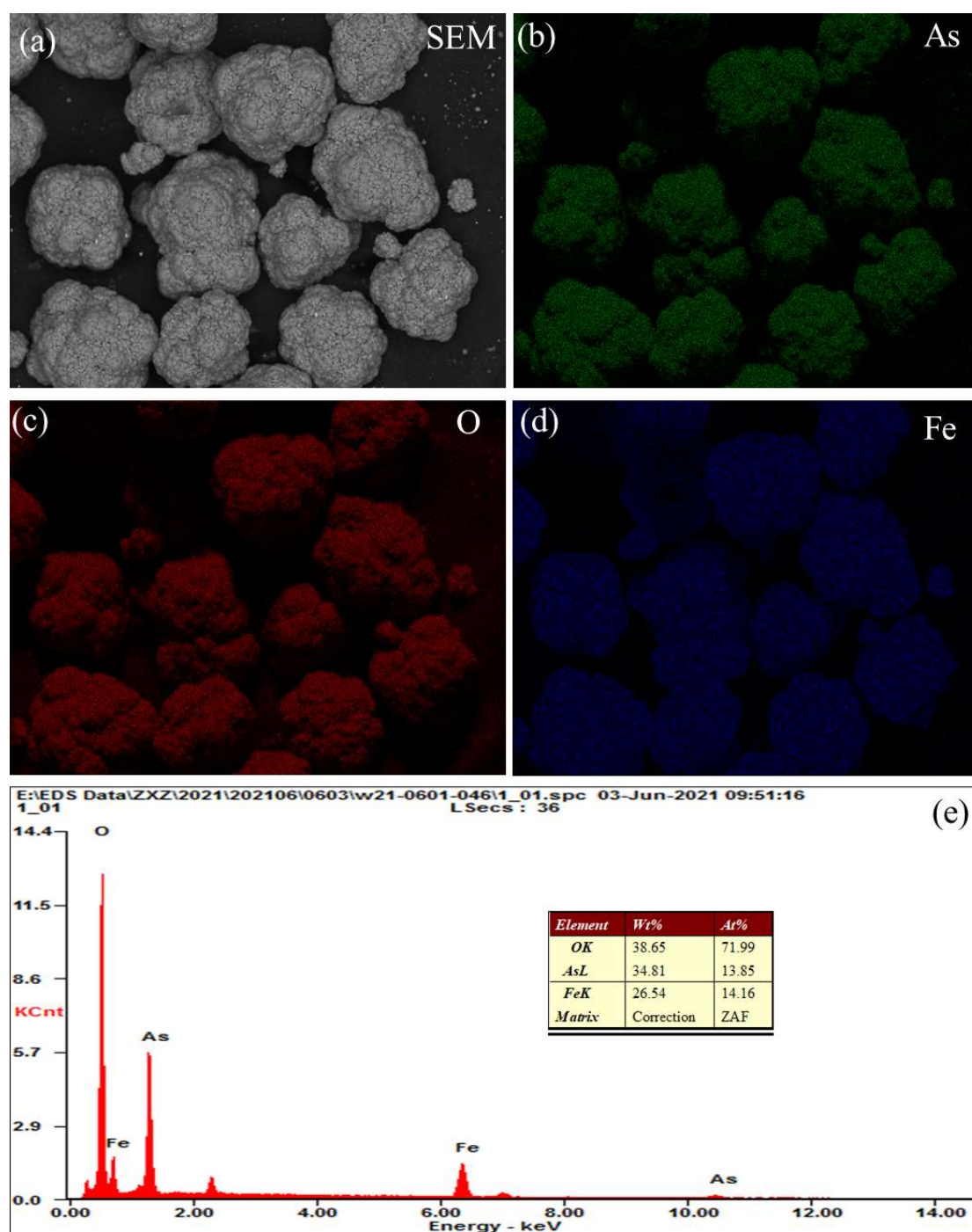


Figure 12. SEM–EDS analysis of the resulting product obtained under the optimum conditions. (a) SEM image of the resulting product, (b) As mapping, (c) O mapping, (d) Fe mapping, (e) EDS analysis of the resulting product; OK: oxygen, AsL: arsenic, FeK: iron, ZAF: a quantitative correction technique and Z means atomic number, A means absorption coefficient, F means fluorescence coefficient.

The results in Figure 12 show that the enrichment areas of main elements including As, Fe and O are overlapped, and the atoms' ratio of Fe to As is close to 1:1, which are good proofs that the product is $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$. A leaching toxicity analysis of the product showed that the leaching concentration of arsenic is far lower than 5 mg/L, indicating that the scorodite formation was a safe and environmentally friendly solution for the stabilization of arsenic from the acid leaching solution.

Herein, we present a method to separate arsenic from lead slime and stabilize arsenic by forming scorodite. The results indicate that initial pH plays an important role. For experiments with initial pH values of 1.0 or above, the scorodite synthesis reaction did not process well. Further, the results indicate that sodium jarosite appeared in the precipitates when the pH value was above 1.5, although arsenic precipitation rates showed a slight increase. On the other hand, in some research [51,52], scorodite was successfully synthesized at pH 2–4.5, which was also favorable for sodium jarosite formation. However, they applied long reaction times of 16 to 400 h to develop scorodite nuclei. They also observed an amorphous phase at 7 h reaction time, and so their observations are not contradictory to our findings. Practical industrial application will favor fast and efficient process design, and the findings obtained from relatively short reaction times are useful as far as our objective is concerned.

4. Conclusions

In this paper, an acid leaching method combined with forming scorodite was proposed to separate and stabilize arsenic from lead slime. The major findings from this study are summarized as follows:

- (1) Under the optimum conditions, namely, leaching temperature of 170 °C, acid concentration of 100 g/L, L/S of 10 mL/g, leaching time of 2.5 h, pO_2 of 2.0 MPa and agitating speed of 300 r/min, the leaching rate of arsenic from lead slime was more than 99.10% and the arsenic content of the leaching residue was about 0.80%.
- (2) The arsenic in the leaching solution (37.18 g/L) was stabilized in the form of scorodite ($FeAsO_4 \cdot 2H_2O$), while the optimum conditions were established as: Fe/As ratio of 1.3, initial pH value of 1.0, pO_2 of 2.5 MPa, temperature of 160 °C and precipitation time of 2.0 h.
- (3) Scorodite ($FeAsO_4 \cdot 2H_2O$) with high purity was obtained by the proposed process, and the arsenic content in the resulting product reached as high as 98.50%.

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