



Process and mechanism of hydrothermal stabilization for arsenic sulfide sludge containing elemental sulfur

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Abstract: An optimized hydrothermal treatment was employed to stabilize the arsenic sulfide sludge (ASS). Under the optimal conditions (160 °C, 2 h, liquid-to-solid (L/S) ratio of 1:1, and initial pH of 2), the leaching concentrations of As and Cd decreased from 504.0 and 12.0 mg/L to 1.23 and 0.03 mg/L of the treated ASS, respectively. The results indicate that the stabilization of the ASS was achieved through structure transformation from the particles into a bulk and the speciation transformation of As and Cd. Besides, sulfur in the ASS could significantly improve the stabilization property due to its melting and polymerization.

Key words: hydrothermal stabilization; arsenic sulfide sludge; elemental sulfur; structure transformation

1 Introduction

Arsenic as an extremely toxic element, which is mainly associated with non-ferrous metal (Cu, Pb, Zn, etc) ores in nature, is usually mobilized through the nonferrous metal extraction processes [1–3]. It has been reported that 80000–90000 t of arsenic concentrate are transported into smelters annually in China. Moreover, arsenic could distribute in flue gas, wastewater, sludge, and further threat the environment to some extent [4–6]. In fact, As is nontoxic, and arsenic compounds are highly toxic with the toxic order of arsenic hydride > arsenious oxide > arsenite > arsenate. At present, arsenic pollution has attracted worldwide attention.

A large amount of arsenic-containing acidic wastewater is discharged when flue gas is spray washed with the dilute acid in the smelting process

of Cu, Pb, and Zn [7]. Arsenic removal from the wastewater is usually achieved by coagulation, precipitation, membrane separation, and adsorption [8,9]. Among them, sulfide precipitation has been widely used due to the simple process and high efficiency via employing sodium sulfide (Na₂S), sodium hydrosulfide (NaHS) or hydrogen sulfide (H₂S) as reagent. Nevertheless, a huge quantity of arsenic sulfide sludge (ASS) has been discharged [10–12]. As a typical hazardous solid waste, it is of great significance to treat and dispose ASS properly.

Generally, stabilization/solidification has been employed to prevent arsenic pollution of the solid waste [13–15]. However, stabilization/solidification conducted with binders inevitably causes a high ratio of compatibilization [16]. In terms of hydrothermal treatment, this method has been widely used to dry and/or densify the waste [17].

Our preliminary results indicated that hydrothermal process could achieve dehydration, volume reduction and stabilization for several kinds of ASS, while the process and specific parameters have not been investigated in detail [18]. Besides, it has been found that the sludge which consists of sulfur was easier to be stabilized, although the related mechanism was unclear.

In this work, hydrothermal stabilization process of the ASS contained elemental sulfur from a copper smelter has been systematically studied. More importantly, to reveal the reaction mechanism of the hydrothermal process, the phase and structure transformation of the sludge in the process have been characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). This study provides a novel treatment avenue for the stabilization of the arsenic sulfide via the utilization of sulfur.

2 Experimental

2.1 Materials

The ASS was obtained from the sulfurization process of high arsenic-containing acidic wastewater by Na_2S in a copper smelter of Hubei province, China. The ASS with a moisture content of 62.9% was acidic (pH 1.41), and predominant elements were 35.10% As and 60.20% S (Table 1). The XRD pattern of the ASS (Fig. 1) presents that it contained S_8 and amorphous As_2S_3 [19]. The SEM/EDS results shown in Fig. 2 indicate that the ASS was composed of the irregular and flocculent tiny particles of As–S compounds.

Table 1 Composition of arsenic sulfide sludge (wt.%)

As	S	Na	Pb	Zn	Cd	Sb	Cu
35.10	60.20	1.53	0.26	0.08	0.07	0.06	0.05

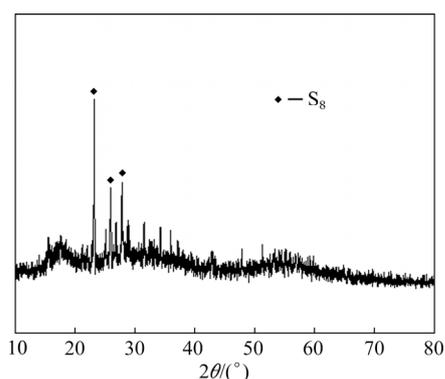


Fig. 1 XRD pattern of arsenic sulfide sludge

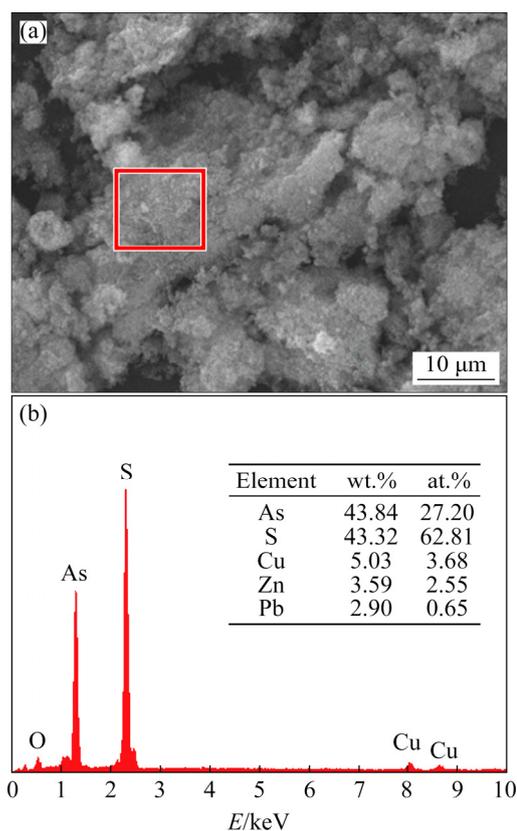


Fig. 2 SEM image (a) and EDS analysis result (b) of arsenic sulfide sludge

Toxicity characteristics leaching procedure (TCLP) has been performed to investigate the concentrations of As, Cd, Pb, Cr, and Zn in the leachate. The concentrations of As and Cd in leachate were 504.0 and 12.0 mg/L, which were far more than the specified values set by United States Environmental Protection Agency (USEPA) ($\text{As} \leq 5$ mg/L and $\text{Cd} \leq 1$ mg/L). The concentrations of Pb, Cr and Zn were 3.0, 0.13 and 20.0 mg/L, which were all less than the specified values ($\text{Pb} \leq 5$ mg/L, $\text{Cr} \leq 5$ mg/L, and it is not specified for Zn) [20].

Combined with the above analysis, the ASS contained sulfur could be identified as the hazardous solid waste due to its corrosivity and high leaching toxicity of As and Cd. Thereafter, the ASS should be stabilized and/or solidified properly.

2.2 Hydrothermal treatment

As described in our previous study, the ASS and the ultra-pure water were mixed with a certain ratio in a 25 mL stainless-steel autoclave [21]. Then, the hydrothermal treatment was carried out in the oven at the desired temperature for a given time.

The different liquid-to-solid ratio was achieved by adjusting the amount of ultra-pure water, and the different initial pH was obtained by adding the dilute H₂SO₄ or NaOH solution. Afterward, the stainless-steel autoclave was cooled naturally for collecting the as-treated sludge. At last, it was placed into a vacuum oven at 60 °C to dry.

2.3 Stability evaluation

To evaluate the stability of the original and the treated sludge, the TCLP method was employed according to USEPA Method 1311. The extract was diluted with glacial acetic acid with deionized water, and the pH of the extract was adjusted to 2.88±0.05 with 1 mol/L HNO₃ and 1 mol/L NaOH. And for assessing the environmental activity and potential mobility, an improved BCR three-stage sequential extraction procedure was performed [22,23].

2.4 Characterization

To determine elemental composition in the ASS and treated ASS, the samples dried in a vacuum oven at 60 °C were digested using a mixture of concentrated HCl and HNO₃ (3:1, volume ratio). The solution was filtrated with filter paper (1 μm pore), and then elemental concentrations in filtrate were analyzed with inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent 5100). The phases of the original and the treated sludge were analyzed by XRD (D/max 2500 VB+18 kW). The surface compositions were characterized by XPS with Thermo Fisher Scientific K-Alpha 1063 using Al K_α radiation. The microstructural observation and elemental compositions were performed by SEM/EDS (Nova Nano SEM 230). The concentrations of As, Cd, Pb, Cr, and Zn in leachate were identified by ICP-OES.

3 Results and discussion

3.1 Hydrothermal conditions

3.1.1 Effect of temperature

Temperature acts as a critical role in the hydrothermal process because it could have a certain effect on the substance dissolution and recrystallization. Figure 3 reveals that the ASS could be well stabilized when the temperature increased. The concentration of As in leachate obviously decreased from 34.62 to 7.4 mg/L with

the temperature increasing from 120 to 130 °C. However, this concentration was still higher than that of the specified values (5 mg/L). With the temperature rising further to 160 °C, concentration of As decreased to 1.24 mg/L, which indicated that temperature could significantly influence the hydrothermal process. In terms of Cd, the tendency of the concentration was similar to that of As. In addition, it could be controlled below 1 mg/L over 120 °C.

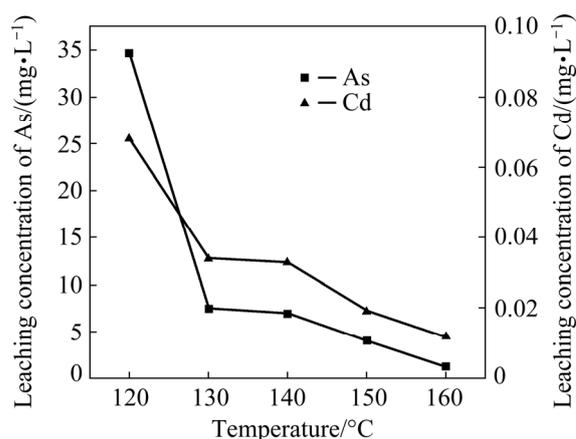


Fig. 3 Concentrations of As and Cd in leachate at different temperatures (2 h, L/S ratio of 1:1, and initial pH of 2)

Compared with the original sludge, the morphology of ASS obtained at 120 °C expressed a denser structure (Fig. 4(a)), which was in a good agreement with other results. According to the previous studies, polymerization and densification of the ASS may be attributed to the presence of S₈ [24,25]. With the temperature increasing to 150 °C, the sludge gradually fused into a bulk structure and was covered with a few flocculent particles (Fig. 4(b)). When the temperature reached 160 °C, the flocculent sludge aggregated into a smooth bulk, which suggested that densification occurred through the hydro-thermal process. This densification may contribute to the decrease of As and Cd concentrations in leachate (Fig. 4(c)). The increased temperature is beneficial to stabilizing the ASS during the hydrothermal process.

3.1.2 Effect of reaction time

To investigate the effect of the reaction time, the experiments were performed at 160 °C for 0–10 h with the L/S ratio of 1:1 and initial pH of 2. As shown in Fig. 5, the concentration of As in leachate decreased rapidly within the initial 2 h,

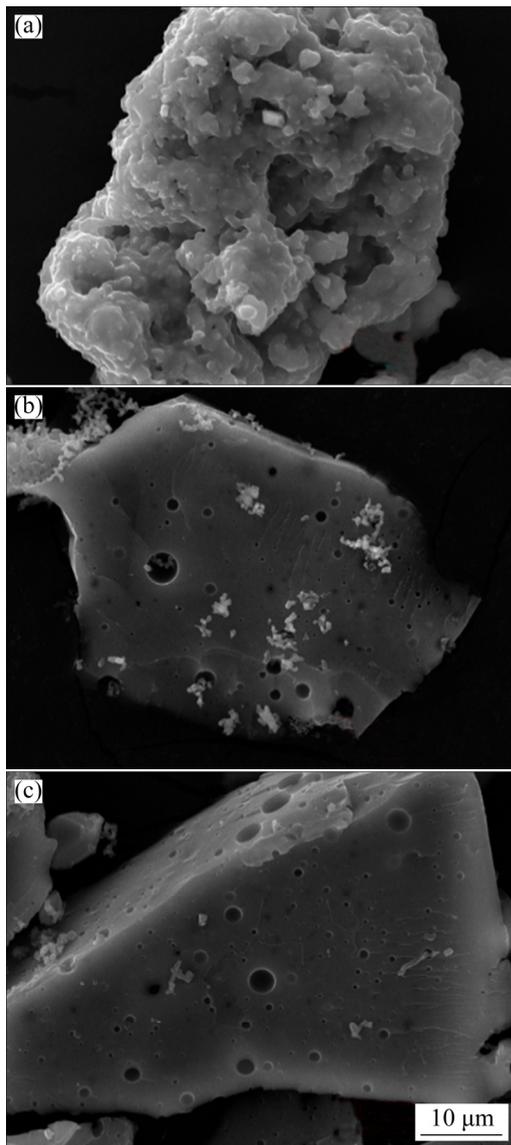


Fig. 4 SEM images of treated sludge (2 h, L/S ratio of 1:1, and initial pH of 2): (a) 120 °C; (b) 150 °C; (c) 160 °C

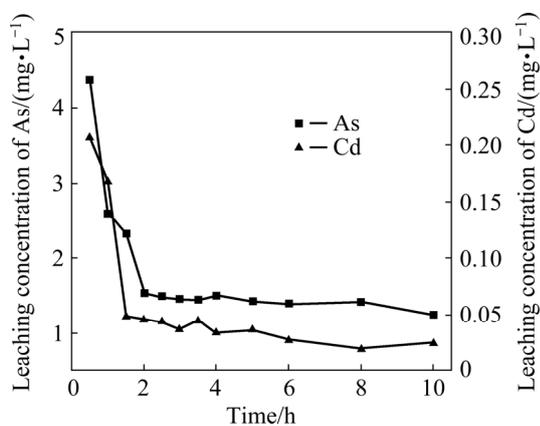


Fig. 5 Concentrations of As and Cd in leachate with different reaction time (160 °C, L/S ratio of 1:1, and initial pH of 2)

while slowly decreased with the reaction time prolonging. The concentration tendency of Cd was consistent with that of As. Besides, the concentrations of As and Cd in leachate remained lower than the limited values within the whole range of reaction time.

The morphologies of the treated ASS of the initial 2 h are shown in Fig. 6. It is obvious that the sludge with a flocculent and porous structure began to bond together at 0.5 h (Fig. 6(a)). With reaction time increasing to 1 h, the sludge became dense (Fig. 6(b)) and gradually aggregated into a smooth bulk at 2 h (Fig. 6(c)). In addition, the original particles gradually grew with the reaction time prolonging. When the reaction time reached 2 h, the particle size increased to around 50 μm, as shown in

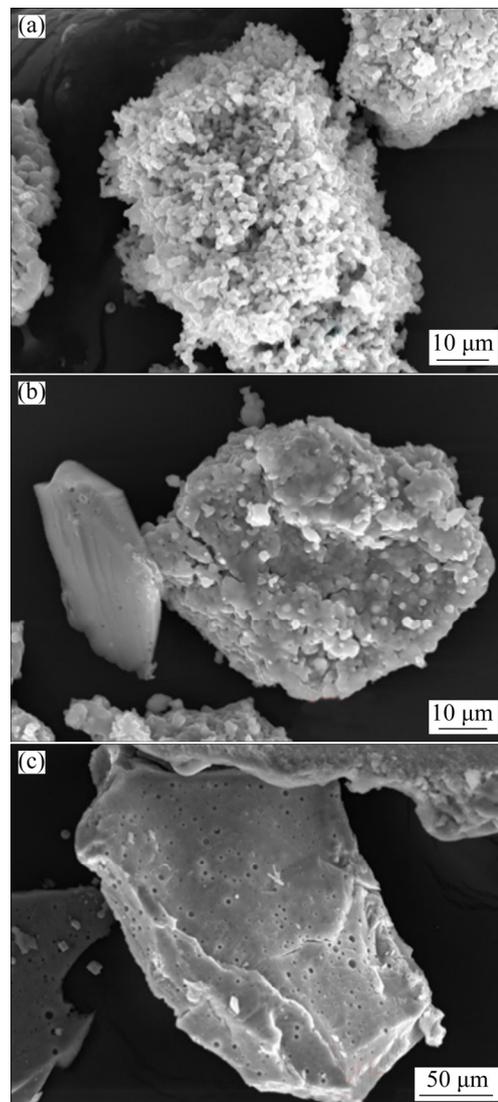


Fig. 6 SEM images of treated sludge with different reaction time (160 °C, L/S ratio of 1:1, and initial pH of 2): (a) 0.5 h; (b) 1 h; (c) 2 h

Fig. 6(c). The densification was achieved because the amorphous and flocculent particles aggregated into a bulk structure, which may result in the decrease of As and Cd concentrations in leachate.

3.1.3 Effect of liquid-to-solid ratio

To investigate the influence of the liquid-to-solid ratio on the hydrothermal stabilization process, the ratios from 0:1 to 3:1 have been tested. As shown in Fig. 7, the concentrations of As and Cd in leachate decreased as the liquid-to-solid ratio increased. In terms of As, the concentration decreased to 1.23 from 4.31 mg/L with the ratio changing from 0:1 to 1:1. However, the concentration increased to 2.57 mg/L with the ratio changing to 2:1. When the ratio further increased to 3:1, the concentration slightly decreased. The hydrothermal process involved the dissolution process of the original ASS and the formation process of the treated ASS with dense structure. When liquid-to-solid ratio was larger than 1.5:1, the content of the dissolved ASS in the solution was relatively low, which was unfavorable to stabilize ASS. Therefore, the leaching concentration of As at liquid-to-solid ratio >1.5:1 was generally higher than that at low liquid-to-solid ratio. In terms of Cd, the tendency of the concentration in leachate was similar to that of As.

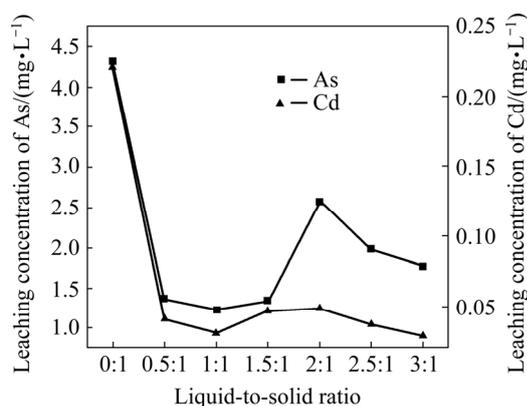


Fig. 7 Concentrations of As and Cd in leachate at different liquid-to-solid ratios (160 °C, 2 h, and initial pH of 2)

3.1.4 Effect of initial pH

The existing speciation of As is greatly affected by pH through influencing their dissolution behavior during the hydrothermal process [26]. Figure 8 presents the effect of initial pH. For As, the concentration in leachate slightly fluctuated when the initial pH varied from 1 to 4, and then rapidly

increased to 40.2 mg/L with the initial pH increasing to 8. This suggested that strong acidic system could benefit the hydrothermal stabilization. With regard to Cd, the concentration in leachate was below the specified values within pH of 1–8. Comprehensively considering that pH of the original sludge was about 2, the optimum initial pH was considered to be 2.

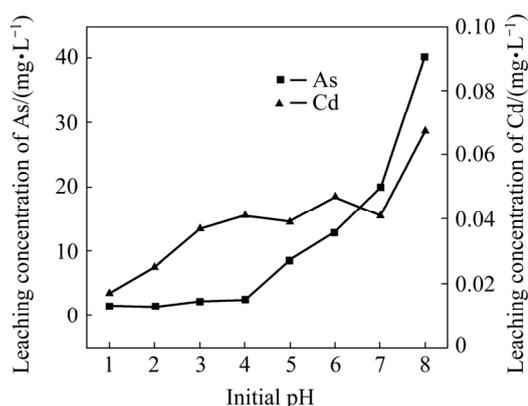


Fig. 8 Concentrations of As and Cd in leachate at different initial pH values (160 °C, 2 h, and L/S ratio of 1:1)

Herein, it is obvious that temperature has the greatest influence on the hydrothermal stabilization process, and the optimum conditions are as follows: 160 °C, 2 h, 1:1 of liquid-to-solid ratio and 2 of the initial pH. Under these conditions, the concentrations of As and Cd in leachate of the treated ASS reduced to 1.23 and 0.03 mg/L, which were all lower than the specified values. Besides, densification of the ASS has been realized by the hydrothermal process. It could also be concluded that the ASS containing elemental sulfur originally is easier to achieve stabilization compared to the hydrothermal process of ASS without elemental sulfur originally (200 °C, 4 h, 1:1 of liquid-to-solid ratio and 2 of the initial pH) [21].

Stabilization

3.2 Stabilization

3.2.1 Leaching concentration

Table 2 summarizes the concentrations of As, Cd, Pb, Cr, and Zn in leachate of the original and the treated ASS. After hydrothermal treatment, the As and Cd concentrations reduced to 1.23 and 0.03 mg/L, and the Pb, Cr and Zn concentrations decreased to 0.04, 0.1 and 0.08 mg/L, respectively. It should be noted that the stabilization of the As

and Cd that were excessive originally has been achieved during the hydrothermal process.

Table 2 Leaching concentrations of original and treated arsenic sulfide sludge (mg/L)

Element	Threshold	Original ASS	Treated ASS
As	≤ 5	504.0	1.23
Cd	≤ 1	12.0	0.03
Pb	≤ 5	3.0	0.04
Cr	≤ 5	0.13	0.1
Zn	Not specified	20.0	0.08

3.2.2 Speciation variation

To evaluate the environmental activity and long-term stability of As and Cd in the original and the treated ASS, the BCR method has been employed. The speciation can be divided into the acid soluble fraction (F_1), the reducible fraction (F_2), the oxidizable fraction (F_3) and the residual fraction (F_4). The acid soluble fraction and the reducible fraction are identified as the direct effect fractions, the oxidizable fraction is classified as a potential effect fraction, and the residual fraction is considered as a stable fraction [27].

The chemical speciations of As and Cd in the original and the treated ASS are shown in Fig. 9. For As, the percentages of F_1 , F_2 , F_3 and F_4 were 1.16%, 0.08%, 90% and 8.76%, respectively, while in the treated sludge they were 0.01%, 0.01%, 36.23% and 63.75%, respectively. In the original sludge, As existed mainly in the speciation of the

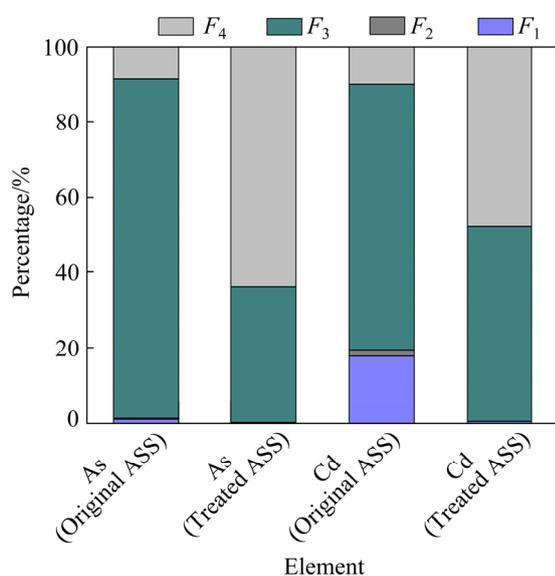


Fig. 9 BCR chemical speciations of As and Cd

oxidizable state. After hydrothermal treatment, most of the oxidizable fraction converted into the residual fraction, which became the main speciation in the treated sludge. It can be inferred that the stabilization of As may be attributed to the speciation transformation. For Cd, it mainly existed as the oxidizable state of 70.37% in the original sludge, and then it decreased to 51.98% after the hydrothermal treatment. Meanwhile, the percentage of the residual fraction increased from 10.08% to 47.62%. Cd of the residual state increased to some extent, which suggested that it turned into a more stable chemical form during the process. It is obvious that As and Cd in the original ASS transformed into the more stable forms via the hydrothermal process.

3.3 Mechanism

3.3.1 XRD analysis result

To analyze the phase changes of the ASS during the hydrothermal process, the XRD analysis of the sludge before and after the treatment under the optimum conditions have been conducted. Figure 10 shows that S_8 was the main phase in the original sludge. For arsenic sulfide compound, three broad bands located at $2\theta=18^\circ$, 32° and 56° could be assigned to amorphous As_2S_3 [10]. After hydrothermal treatment, the diffraction peaks of S_8 disappeared and no significant change occurred in arsenic sulfide compound. The results illustrate that the original sludge mainly consisted of S_8 and As_2S_3 , while the S_8 disappeared after the hydrothermal treatment. It could be speculated that the densification of the ASS may be promoted from the melting and polymerizing of the S_8 [17], and the densification would result in the decrease of As and

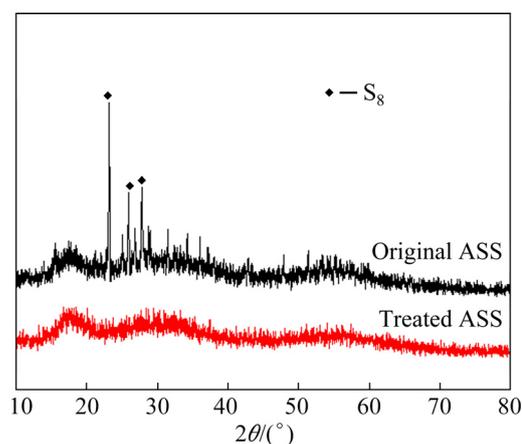


Fig. 10 XRD patterns of original and treated ASS

Cd leaching concentrations. Compared to the hydrothermal process of the ASS without elemental sulfur originally, the presence of elemental sulfur greatly improves the stabilization.

3.3.2 XPS analysis result

The chemical state of the ASS was analyzed by XPS for the sludge before and after the treatment under the optimum conditions. Figure 11(a) shows the As 3d_{5/2} spectra, which consisted of two prominent peaks at 43.6 and 44.8 eV corresponding to As₂S₃ of 72.58% and As₂O₃ of 27.42%, respectively [28,29], indicating that the amorphous As₂S₃ was the main component in the original sludge. Due to the natural oxidation of arsenic sulfide, As partially existed in the form of As₂O₃ [30]. After hydrothermal treatment, a new XPS peak located at 43.20 eV appeared, which was attributed to As₄S₄. The contents of As₂S₃, As₂O₃ and As₄S₄ in the treated ASS were 63.92%, 24.45% and 11.63%, respectively. The results show that part of As₂S₃ in the ASS transformed into As₄S₄ during the hydrothermal process.

As for S, it has been reported that the binding energies of S 2p spectra for S²⁻, S₂²⁻ and S⁰ are in the range of 161.2–162.8, 162.7–164.1 and 162.9–164.8 eV, respectively [31–33]. The original sludge showed three peaks associated at 162.8, 163.8 and 164.5 eV (Fig. 11(b)), which were assigned to S²⁻, S₂²⁻ and S⁰ species with a content of 39.34%, 31.76% and 28.90%. The S²⁻ and S₂²⁻ species were commonly found on the surfaces of arsenic/metal sulfides [34,35]. Besides, S⁰ (α -sulfur crystals of cycloocta-sulfur (S₈)) may result from the oxidation of S²⁻ [36,19]. After hydrothermal treatment, the content of S²⁻, S₂²⁻ and S⁰ species were 32.03%, 51.51% and 16.46%, respectively. The main reason may be that S₈ began to melt when temperature reached 120 °C and even began to polymerize at 159 °C [25], which contributed to the ASS changing from particles to a bulk.

In summary, the XRD and XPS results illustrate that the original ASS was mainly composed of S₈ and amorphous As₂S₃, while S₈ disappeared and As₄S₄ occurred with the decrease of As₂S₃ content after the hydrothermal process. The stabilization of the ASS has been achieved due to the possible change from particles to a bulk through structure transformation. And, the melting and polymerizing of the elemental S promoted the hydrothermal sintering of As₂S₃, As₄S₄ and S at

lower temperature. It could be concluded that the presence of elemental S in the ASS significantly improves its stabilization property.

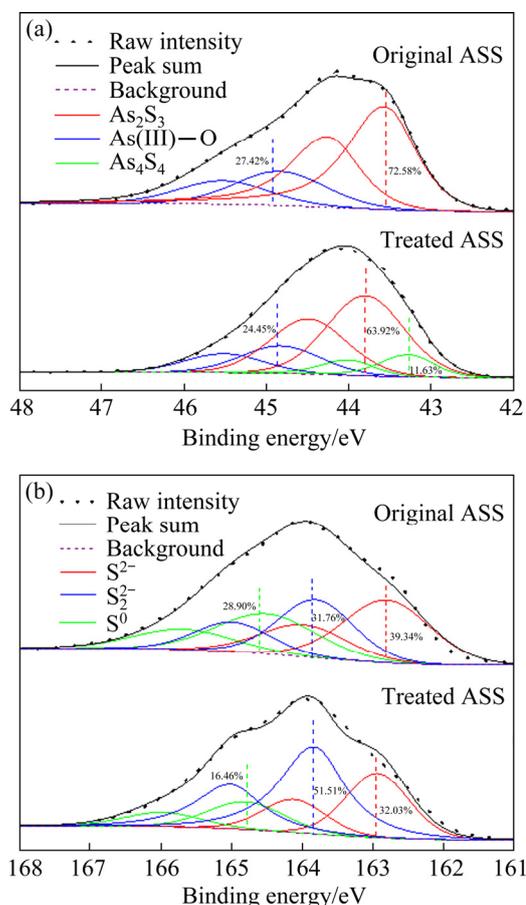


Fig. 11 As 3d (a) and S 2p (b) XPS spectra of original and treated ASS

4 Conclusions

(1) Hydrothermal treatment could effectively achieve the densification and stabilization of the ASS especially consisting of sulfur.

(2) The optimized conditions of hydrothermal process are 160 °C, 2 h, liquid-to-solid ratio of 1:1 and the initial pH of 2. After treatment, the As and Cd concentrations in leachate reduced to 1.23 and 0.03 mg/L, and the Pb, Cu and Zn concentrations decreased to 0.04, 0.1 and 0.08 mg/L, respectively, which were all lower than the specified values set by USEPA.

(3) The BCR results show that As and Cd in the original ASS transformed into the stable structure via the hydrothermal process. The XRD and XPS results illustrate that the original sludge was mainly composed of S₈ and As₂S₃, while S₈ disappeared by melting and polymerizing during

the hydrothermal process. The melting and polymerization of S_8 contribute to the ASS changing from the particles to a bulk.

(4) The stabilization of the ASS containing sulfur has been realized through structure transformation from the particles into a bulk and the speciation transformation of As and Cd. Besides, the presence of elemental sulfur in the original sludge greatly improves its stabilization process compared to the hydrothermal process of the ASS without elemental sulfur.

Acknowledgments

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含单质硫的硫化砷渣水热稳定化的过程及机理

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摘要: 提出一种水热处理方法以稳定硫化砷渣。在最优条件(160 °C、2 h、液固比 1:1、初始 pH 2)下, 水热处理后 As 和 Cd 元素的浸出毒性分别由 504.0 和 12.0 mg/L 降低至 1.23 和 0.03 mg/L。硫化砷渣的稳定化主要通过颗粒转化成块状的结构转变及 As 和 Cd 化学形态的转变来实现。此外, 硫化砷渣中具有熔融和聚合特性的单质硫的存在极大促进其水热稳定化。

关键词: 水热稳定化; 硫化砷渣; 单质硫; 结构转变

(Edited by Bing YANG)