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# Release Behaviors of Arsenic and Heavy Metals from Arsenic Sulfide Sludge during Simulated Storage

Liwei Yao <sup>1</sup>, Xiaobo Min <sup>1,2</sup>, Yong Ke <sup>1,2,\*</sup>, Yunyan Wang <sup>1,2</sup>, Yanjie Liang <sup>1,2</sup>, Xu Yan <sup>1,2</sup>, Hui Xu <sup>1</sup>, Jiangchi Fei <sup>1</sup>, Yuancheng Li <sup>1</sup>, Degang Liu <sup>1</sup> and Kang Yang <sup>3</sup> 

<sup>1</sup> School of Metallurgy and Environment, Central South University, Changsha 410083, China; yaoliwei0125@126.com (L.Y.); mxbcusu@163.com (X.M.); wyy@csu.edu.cn (Y.W.);

Liangyanjie2015@csu.edu.cn (Y.L.); yanxu1202@csu.edu.cn (X.Y.); Xuhui940303@163.com (H.X.); jack-fei@csu.edu.cn (J.F.); li245547278@hotmail.com (Y.L.); liudegang6669@163.com (D.L.)

<sup>2</sup> Chinese National Engineering Research Center for Control & Treatment of Heavy Metal Pollution, Changsha 410083, China

<sup>3</sup> School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China; csuyangkang@163.com

\* Correspondence: keyong000ke@csu.edu.cn; Tel.: +86-731-88830511; Fax: +86-731-88710171

Received: 21 December 2018; Accepted: 20 February 2019; Published: 23 February 2019



**Abstract:** Non-ferrous metal smelting enterprises produce hundreds of thousands of tons of arsenic sulfide sludge (ASS) each year in China. Most of the ASS are stored at the companies without enough preventive measures. During the storage and natural drying process, arsenic sulfide is easily oxidized, thereby causing secondary pollution and increasing environmental risks. In this paper, experiments of simulated storage were used to study the release characteristics of heavy metals. During the simulated storage, the release concentrations of As, Pb, and Cd increased rapidly at first and then slowly. Although the total amount of arsenic released was the largest, the release ratio was in the order of Cd > Pb > As. The effects of different atmospheres and conditions on the release of arsenic and heavy metals were explored. The more the H<sub>2</sub>SO<sub>4</sub> in the sludge, the higher the release concentration, and the addition of an appropriate amount of Ca(OH)<sub>2</sub> is beneficial for reducing the release of heavy metals. Finally, SEM, XRD and TG-DTG techniques were carried out to confirm that the release of heavy metals was caused by the oxidation process resulting from the residual H<sub>2</sub>SO<sub>4</sub> in the ASS and the air.

**Keywords:** arsenic sulfide sludge; simulated storage; heavy metals release; oxidization

## 1. Introduction

The toxicity and carcinogenicity of arsenic and heavy metals have caused serious environmental concerns throughout the world [1,2]. Arsenic pollution in the environment occurs mostly due to anthropogenic processes such as agriculture, mining and mineral processing operations [3–5]. It is universally believed that the extractive process of non-ferrous metal is one of the most important sources of arsenic and produces a large amount of strongly acidic wastewater with high arsenic concentration [6–8]. In the smelting of copper or lead-zinc ore, large amounts of acidic wastewater are discharged when the gaseous emissions containing SO<sub>2</sub>, As, Cu, Pb, Zn and other impurities are washed with diluted acid. Moreover, waste electrolyte with a high concentration of arsenic is produced abundantly in copper and lead-zinc electrolyte processes [9,10]. Generally, neutralization by Ca(OH)<sub>2</sub>/CaO and co-precipitation with ferric salt are the most useful industrial methods for the treatment of strongly acidic wastewater bearing arsenic and heavy metals. Nevertheless, large amounts of hazardous wastes are generated by these methods, which may cause environmental risks

and huge costs in the deposition. Therefore, precipitation employing sulfide as a precipitant via sodium sulfide or hydrogen sulfide, which generates  $\text{As}_2\text{S}_3$  precipitate with a higher purity and at a much lower amount compared to the sludge generated by neutralization or co-precipitation, has become a potential treatment technology for strongly acidic wastewater, to realize the recycling of metals and minimize the amount of arsenic waste [11]. Although the amount of arsenic sulfide sludge (ASS) produced is much less than that of the sludge of calcium or ferric arsenate, it is estimated that the ASS is still generated with an annual production of hundreds of thousands of tons in China. Accordingly, most of the ASSs are stored in the smelter without preventive action, which will lead to increased environmental risks [12].

At present, some ASSs have been developed to prepare arsenic trioxide, arsenate, arsenic chloride and arsenic sulfide. The disposal technology is mainly divided into two major categories: the pyrogenic process and the wet method. The pyrogenic process is a calcination method that leads to oxidation, where arsenic is directly recovered in the form of arsenic trioxide. This technology is mature, low cost and has a short process, but it is difficult to ensure a good working environment, which is easy to cause secondary pollution. Moreover, the product has low purity and a low arsenic recovery rate [13]. Some smelters in China have used a roasting furnace to treat ASSs. In addition, a vacuum separation method was proposed to recover elemental sulfur, arsenic sulfide and arsenic trioxide from ASS in a step by step fashion [14]. The wet method involves treatment by acid leaching or salt immersion, and the arsenic product is separated and further recovered. This technology does not produce dust, and has the advantages of low energy consumption, low pollution, high efficiency, etc., but the process is complicated, and the processing cost is high [13]. The wet methods mainly include copper sulfate replacement method [15], sulfuric acid oxidation leaching method [16], sulfuric acid high-iron oxidation leaching method [17], nitric acid oxidation leaching method and arsenic acid leaching method [18]. In addition, studies on the recovery of arsenate by alkaline leaching and electrolysis have also been reported [11]. However, as a typical arsenic-containing waste, the application of recycling technologies is limited because the market for arsenic is shrinking. Many companies are not interested in the recycling or disposal of ASSs, and most of the sludges are stored in the smelting plants. However, research on the heavy metals release of the ASS has not been reported during storage.

The crucial point of establishing the potential hazard of ASS is to know the chemical state in which metals are bounded to this waste, which determines their mobilization capacity [19]. In the process of storage of many waste residues, the forms of the heavy metals could be changed, which will increase or decrease the environmental risks. Many sludges from wastewater treatment or sediments tend to oxidize, dissolve and release heavy metals during the storage or deposition process in the nature environment [20]. Bioturbation, the influence of chemicals and the oxidation of air have been studied in the release of heavy metals from precipitated sludge or sulfide ore [21]. The long-term environmental risks of calcium arsenate and iron arsenate have been reported [22,23]. Therefore, it is necessary to study the environmental risks of the ASS during storage. The objective of this study is to investigate the release of arsenic and other heavy metals from ASS and the influencing factors under simulated storage.

## 2. Materials and Method

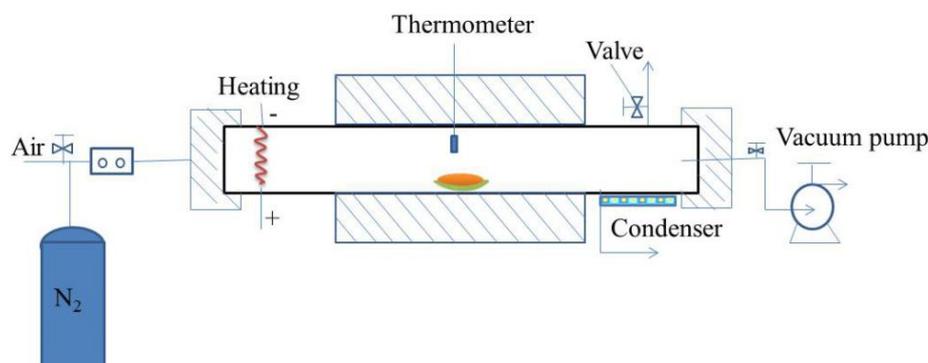
### 2.1. Materials

The arsenic sulfide sludge used in the experiments was obtained from a copper smelting plant located in Yunnan, China. The ASS was generated by the treatment of acidic wastewater with  $\text{Na}_2\text{S}$ . The collected ASS was stored in the plant for several months. The moisture of the raw ASS was 77% and the color was brown yellow.

### 2.2. Experimental Procedure

The collected ASSs ( $2 \pm 0.01$  g) or pre-treated ASSs by adding reagent without drying were added into a simulated accelerated storing reactor (Figure 1), which was heated to different temperatures

and then maintained for various periods of time at different atmospheres. The reactor volume of the inner room is 10 L, and the air flow is 5 L/min during the simulated storage experiment. Thereafter, the resulting products were cooled to room temperature to evaluate the characteristics of the sludges. The release concentrations of arsenic and other heavy metals were assayed by ICP-AES.



**Figure 1.** Simulated equipment for the experimental procedure.

### 2.3. Analysis

#### 2.3.1. Determination of Elemental Composition

The contents of heavy metals such as As, Cd, Cr, Pb, Cu and Zn, etc. in the raw material were determined using ICP-AES. Prior to the ICP-AES tests, the sample was digested through microwave-assisted acid digestion according to the procedure described in our previous study [24].

#### 2.3.2. Determination of Phase Composition

The arsenic-containing compound was analyzed by a chemical phase analysis method to obtain the phase composition of arsenic in the sludge. Based on the books of “Analytical Chemistry of Arsenic” [25] and “Chemical Phase Analysis of Ore and Industrial Product” [26], different arsenic phases were obtained by extraction and separation of different reagents. The separation process of each phase is shown in Table 1.

**Table 1.** The separation process of the arsenic phase of the raw ASS.

Extraction Step	Species	Reagent	Program
1	Oxidation states	Distilled water	Stir and boil for 1.5 h
2	Arsenate/arsenite	20% H <sub>2</sub> SO <sub>4</sub>	Stir for 0.5 h at room temperature
3	Arsenic and sulfur compounds	NaOH (2 mol/L)	Stir for 0.5 h at 80 °C
4	Residual	Aqua regia	Boil for 0.5 h

Step 1: 1 g dry “sludge” and 100 mL distilled water was added to a 250-mL Erlenmeyer flask with magnetic stirring (500 rpm) and boiled for 1.5 h. The extract was separated from the solid sludge by centrifugation (5000 rpm) for 10 min and decanted into a polyethylene container. The sludge was washed with 20 mL distilled water by shaking for 15 min, followed by a centrifugation procedure, and the supernatant was then decanted into the polyethylene container. The washing procedure was repeated twice to completely separate the leachate.

Step 2: The residue from Step 1 along with 50 mL 20% H<sub>2</sub>SO<sub>4</sub> was transferred back to the Erlenmeyer flask, and then stirred (500 rpm) for 30 min at room temperature. The extraction separation procedure was then performed as described above.

Step 3: 50 mL NaOH (2 mol/L) was added to the residue from Step 2 and the suspension was continually stirred for 30 min at 80 °C. The extraction separation procedure was then performed as described above.

Step 4: The solid residue from Step 3 was retained for digestion at 200 °C by adding 10 mL aqua regia. All of the extraction volumes were recorded and the concentrations of arsenic were analyzed by ICP-AES.

### 2.3.3. Leaching Test and Sequential Extraction Scheme

Chinese leaching tests were conducted to evaluate the arsenic and other heavy metals leaching behaviors from the raw sludge according to the China standard leaching test (CSLT) (GB 5085.3-2007, 2007) [6].

A three-step extraction procedure was first proposed by the Community Bureau Reference (BCR). In this work, Davidson's three-stage BCR sequential extraction procedure was used to analyze the effective combination forms of heavy metals in the sludges. The detailed procedure of the BCR tests was shown in our previous study [27].

### 2.3.4. Release Concentration and Release Ratio

The experimental samples after the simulated reaction process were transferred to a 125 mL PP bottle, and then immersed in 40 mL 0.1 mol/L acetic acid for 20 h. The supernatant was filtered, and then the concentration of arsenic and heavy metals was determined for the filtrate, which was defined as the release concentration.

The moisture content was measured by drying the raw samples at 60 °C under vacuum to a constant weight ( $\pm 0.01$  g). The release ratio was then calculated according to Equation (1) as follows:

$$\text{Release ratio} = \frac{(c' - c) \times 40}{2000 \times (1 - \varphi) \times w} \times 100\% \quad (1)$$

where 2000 (mg) is the raw weight of ASS;  $\varphi$  (%) is the raw moisture of ASS;  $w$  (%) is the content of heavy metal;  $c$  (mg/L) is the release concentration of the raw ASS;  $c'$  (mg/L) is the release concentration of the stored ASS; 40 (mL) is the volume of the leaching solution.

### 2.3.5. Other Analyses

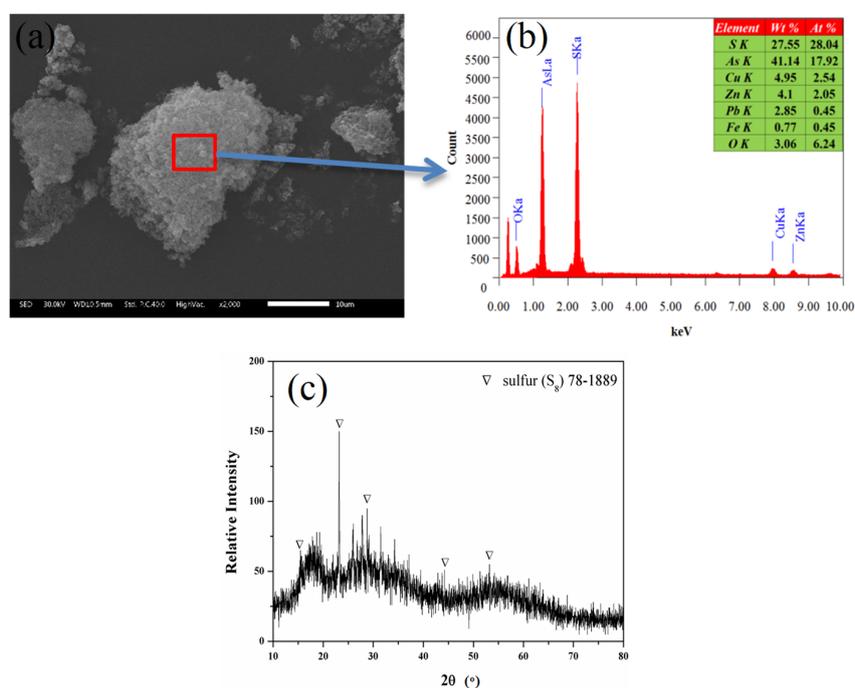
The crystallographic composition of the samples was characterized by X-ray diffraction (XRD, Rigaku D/max2550VB + 18 KW, Tokyo, Japan) with steps of  $0.02^\circ$  at  $10^\circ \text{ min}^{-1}$  in a  $2\theta$  range from  $10^\circ$  to  $80^\circ$ . The morphological change of the samples was observed through a scanning electron microscope (SEM-EDS, Nova NanoSEM 230, Brno, Czech Republic). Thermogravimetry-differential thermal analysis (TG-DTA) was carried out using a thermal analyzer (NETZSCH STA 449C; NETZSCH Pumps North America LLC, Exton, PA, USA) in flowing Ar at a heating rate of  $10^\circ \text{ C/min}$  from room temperature up to a final temperature of  $350^\circ \text{ C}$ , to confirm the reactions of the ASS. The concentration of sulphate was determined by barium chromate spectrophotometry, and the interference effect of arsenate/arsenite was eliminated by hydrogen sulfide precipitation and filtration separation. The concentration of hydrogen ions was calculated by the pH electrode.

## 3. Results and Discussion

### 3.1. Characterization and Chemical Composition of the ASS

The characterization and chemical composition of the ASS is presented in Figure 2 and Table 2. As shown in Figure 2a, the general particles were in irregular shapes, and no obvious crystal structure was found. The amorphous particles agglomerated into large particles. The EDS results (Figure 2b) show that the sludge was mainly composed of S and As, indicating that the amorphous particles were mostly As-S compounds. Figure 2c shows three broad peaks at  $2\theta$  values near  $18^\circ$ ,  $31^\circ$  and  $57^\circ$ , respectively, which was well fitted to that of amorphous  $\text{As}_2\text{S}_3$  [28]. A small amount of sulfur crystal ( $\text{S}_8$ ) peaks was also found, which was also reported in our previous research [29]. The generation

of elemental sulfur should be produced by the reaction of arsenate in the acidic wastewater with hydrogen sulfide [30,31].



**Figure 2.** Characterization of the raw sample: (a) SEM, (b) EDS, and (c) XRD.

**Table 2.** Main elemental composition and leaching concentration of the raw ASS.

Classification	As	S	Fe	Cu	Zn	Pb	Cd	Mg	Na	Ca
Elemental composition (wt %)	39.2	22.9	0.81	0.53	0.6	0.10	0.093	0.016	0.19	0.055
CSLT (mg/L)	1474	a	a	0.2	469.1	3.35	61	a	a	a
GB18598-2001 *	≤2.5	b	b	≤75	≤75	≤0.5	≤5	b	b	b
GB5085.3-2007 *	≤5	b	b	≤100	≤100	≤1.0	≤5	b	b	b
Arsenic Species (%)	Oxidation States		Arsenate and Arsenite		Sulfide		Residual			
	49.56		0.02		48.78		1.64			
Other ion concentration (wet mass)	SO <sub>4</sub> <sup>2-</sup> 72 mg/g			H <sup>+</sup> 8.125 mg/g						

\* The threshold of china. <sup>a</sup> Not detected. <sup>b</sup> Not limited in the standard.

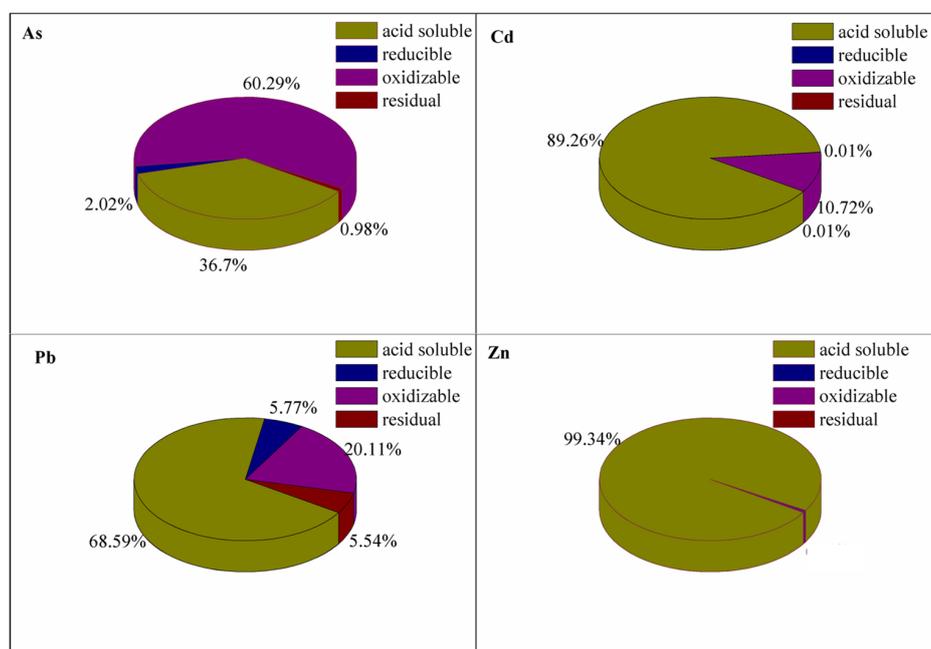
Table 2 shows the elemental contents of the ASS and leaching concentrations of heavy metals. The elemental composition is mainly arsenic and sulfur, and the other heavy metals are less than 1%, respectively. The leaching test was performed using the CSLT method, and the results indicated that the As, Zn, Pb, and Cd-leachate concentrations were higher than the Chinese regulation limits of “Identification standards for hazardous wastes: Identification for toxic substance content (GB5085.3-2007)” and “Standard for pollution control on the security landfill site for hazardous wastes (GB18598-2001)”.

Table 2 also shows the phase compositions of arsenic which are analyzed by a chemical phase analysis method. The result indicates that 49.56% of the As exists in the form of As<sub>2</sub>O<sub>3</sub>/As<sub>2</sub>O<sub>5</sub> and 48.78% in the form of As-S compounds. It is obvious that arsenic is mainly in the oxidation state and the sulfide state. It is surprising that the results of SEM and XRD measurements show that no crystals of arsenic oxide are observed. In our previous study, the phase compositions of As were also mostly oxide (79.9%) and sulfide (10.5%) for the Cu-As-containing filter cake which was obtained by Na<sub>2</sub>S deposition [15]. This phenomenon is possibly attributed to the oxidation of arsenic sulfide during the storage period and drying process. It should be noted that the arsenic sulfide sludge contains approximately 8% sulfuric acid (wt).

### 3.2. Chemical Speciation of As and Heavy Metals

Study on the chemical speciation of the heavy metals for the sludge is important for analyzing the release characteristics and the environmental activity during storage. The species from sequence extraction could lead to detailed information about the origin, chemical forms, biological and physicochemical availability, mobilization and transport of trace metals [29]. Generally, arsenic and other heavy metals in the acid soluble fraction are classified as direct effect phases for environmental availability and ecological risk because they are presented as a loosely bound phase or thermodynamically unstable phase, which are likely to release into the environment. Meanwhile, arsenic associated with the oxidizable fraction is identified as a potential effect fraction because it can be liberated or transformed into an acid soluble fraction under oxidizing conditions.

It can be seen from Figure 3 that the acid exchangeable and oxidizable states of As, Cd, Pb and Zn are 99.02%, 99.99%, 88.70% and 99.72%, respectively. The amount of acid exchangeable states is roughly equivalent to the sum of exchangeable and carbonate phases of the metal from the sludge [23]. The water soluble phase and exchangeable phase of acid exchangeable heavy metals will be easily released in an acid rain environment [27]. The contents of the acid exchangeable forms of Zn, Cd, Pb and As are 99.34%, 89.26%, 68.59% and 36.70%, respectively. The results show that all of them have high environmental activity and can be easily released into the environment quickly. The results are quite different from other studies, which may be related to the acidity of the sludge, the storage time, the concentration of heavy metal pollution in the acid wastewater, and the treatment effect of the sulfuration [29,32]. The oxidizable forms of heavy metals bound to organic matters and sulfides can be easily released under oxidizing conditions [33]. The contents of the oxidizable forms of Zn, Cd, Pb and As are 0.38%, 10.72%, 20.11%, and 60.29%, respectively (Figure 3). It reveals that the sulfides of Cd, Pb and As would be oxidized and released in an oxidizing environment.



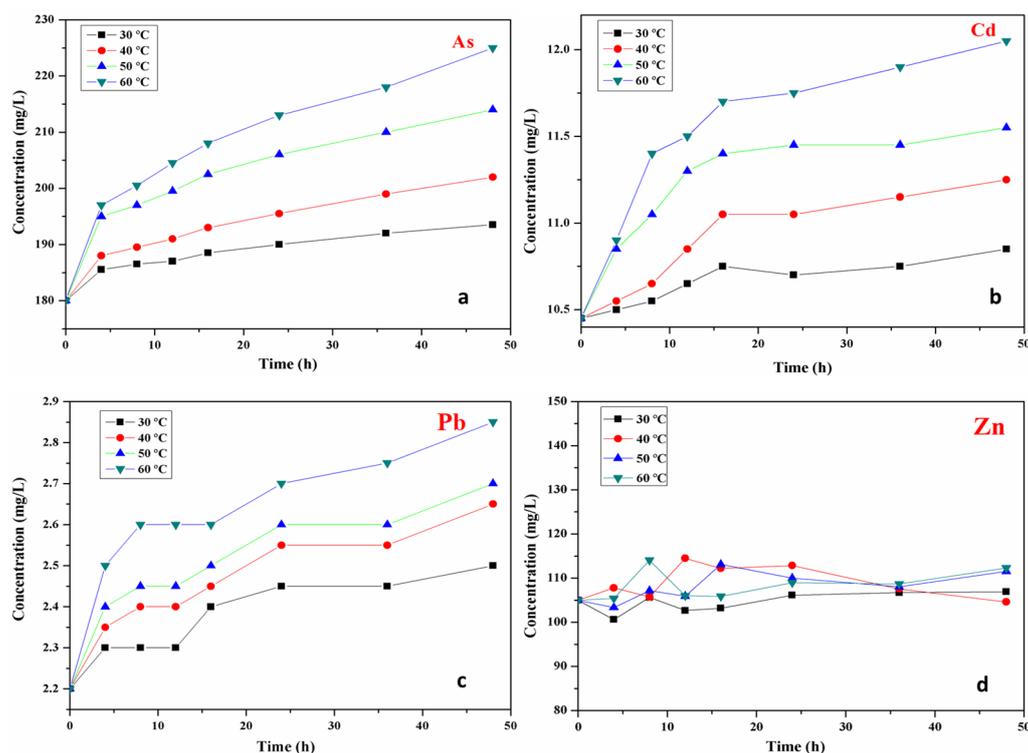
**Figure 3.** Chemical fractions of arsenic and heavy metal species in the ASS by the BCR sequential extraction procedure.

The amount of reducible forms from the BCR method is roughly equivalent to the content of the Fe–Mn phase of the heavy metal in the residue [27]. The contents of the reducible forms of Zn, Cd, Pb and As are 0.22%, 0.01%, 5.77% and 2.02%, respectively (Figure 3). The residual fraction, known as the stable fraction, contains mainly primary and secondary minerals that hold metals within their crystal structure [29]. The contents of the residual forms of Zn, Cd, Pb and As are 0.05%, 0.01%, 5.54% and

0.98%, respectively (Figure 3). These kinds of metals would steadily exist in the sludge for a long time. Above all, the stability of this sludge is very poor, and heavy metals are easily released in an acidic or oxidizing environment, and the results are consistent with other studies [32]. The analysis of BCR can be used to estimate the possibility of heavy metals release and environmental risk. However, the release characteristics and influencing factors in the storage process require more experimental verification.

### 3.3. Release Characteristics of Heavy Metals

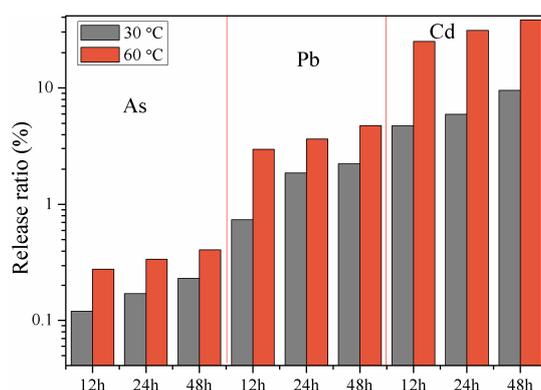
Figure 4 shows the different release concentrations of As, Cd, Pb and Zn at different temperatures maintained for various periods in the simulated environment of air. Apparently, as the temperature or time increases, the release concentrations of arsenic, lead and cadmium also increase. However, the trend of each heavy metal release concentration change is different. For arsenic, the release concentration increased quickly in the first 4 h. The concentration reached 185, 188, 195 and 197 mg/L at the simulated temperature of 30, 40, 50 and 60 °C for the first 4 h, respectively. For the next 44 h, the concentration of arsenic increased slowly, and the concentration increased to 193, 202, 214 and 225 mg/L, respectively. On the other hand, the release concentration of cadmium increased rapidly in the first 16 hours and then slowly increased. The concentrations are 10.75, 11.05, 11.40 and 11.40 mg/L at the temperatures of 30, 40, 50 and 60 °C for the first 16 h, respectively. However, the concentrations only increased to 10.85, 11.25, 11.55 and 12.05 mg/L for the next 32 h. For lead, the concentration increased quickly in the first 4 h, while it remained stable for the next 12 h, and then it slowly increased again for the last 32 h. Finally, the concentration of zinc varied little with the temperature and time, probably because zinc is mainly present in the acid soluble state and the oxidizable state is only 0.38%.



**Figure 4.** The release concentrations of As (a) and heavy metals for the simulated condition: Cd (b), Pb (c), and Zn (d).

Figure 5 shows the release ratios of As, Pb and Cd at 30 and 60 °C for times of 12, 24, and 48 h in the simulated environment of air. It is clear that the release ratio is as follows: Cd > Pb > As. The release ratio increases with increasing temperature and time. For arsenic, the release ratio at 60 °C (0.28% for 12 h, 0.34% for 24 h and 0.41% for 48 h) is almost twice than that at 30 °C (0.12% for 12 h, 0.17% for 24 h and 0.23% for 48 h). The effect of temperature on the release of lead is more pronounced than

that of arsenic. The release ratio at 60 °C is two to three times than that of 30 °C. What is surprising is that a doubling of the temperature leads to a 5–6 folds increase in the release of cadmium. The release ratio at 30 °C was 4.76%–9.53%, and it increased to 25.01%–38.12% at 60 °C. Obviously, although the content of cadmium is very low, the release ratio is the highest, and it is most affected by temperature. The release concentration may also be affected by a closed or open environment during the stocking process. In addition, the residual acid in the arsenic sulfide sludge may also have an effect on the release of heavy metals during the storage process.

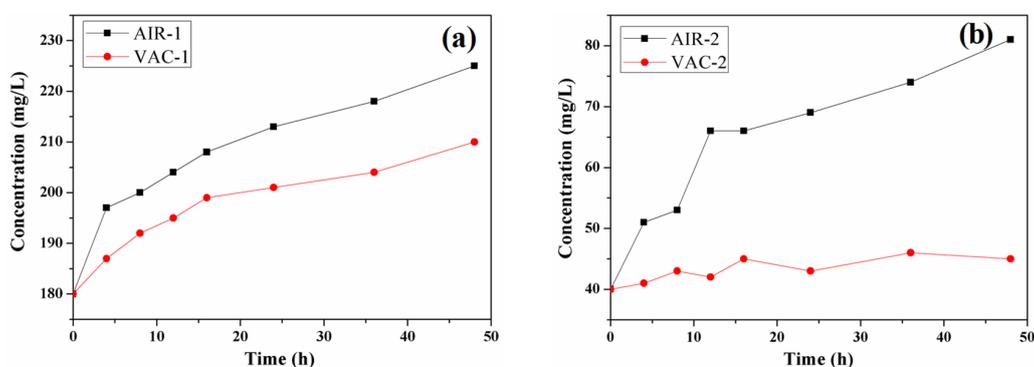


**Figure 5.** Release ratios of As, Pb and Cd at 30 and 60 °C for times of 12, 24, and 48 h in the simulated environment of air.

### 3.4. Influencing Factors

#### 3.4.1. Effect of Atmosphere

As seen in Figure 6a, the arsenic release concentrations increased both in air and vacuum condition, and this release effect in air was more significant than that in vacuum condition. During the simulated release process in air, the concentration of arsenic increased by 33 mg/L and 45 mg/L at 24 h and 48 h, respectively, while the concentration still increased by 21 mg/L and 30 mg/L under the simulated conditions without oxygen. The release of the vacuum simulation process is attributed to the chemical reaction inside the sludge. The sludge of sulfuric acid may promote the oxidation of arsenic sulfide to cause an increase in arsenic release concentration. To further confirm the oxidation of the sulfuric acid of the sludge, a water-eluting acid was designed to simulate the test and observe the change of the release concentration of arsenic.



**Figure 6.** Concentration of arsenic with respect to time in different atmospheres: (a) the raw acid ASS in air and vacuum; (b) the eluted ASS in air and vacuum.

Figure 6b shows the variation of the release concentration of arsenic from the ASS after elution (L:S = 10:1, cleaned three times with deionized water) in different atmospheres. Obviously, it can

be seen that the release concentrations of arsenic do not increase under vacuum condition. In air atmosphere, the release of arsenic exhibited a significant increase. Therefore, the release of arsenic is related to the oxidation by sulfuric acid.

### 3.4.2. Effect of $H_2SO_4$

Arsenic sulfide sludge is derived from the sulfidation of waste water with different acidity. Different companies have different acid contents, so it is necessary to explore the influence of different acidity on the release of heavy metals. The effect of sulfuric acid addition on the release concentrations of heavy metals is show in Figure 7. The addition of a small amount of sulfuric acid causes a significant increase in the release concentrations of arsenic, cadmium and lead. The release concentrations increase slowly with greater additions of sulfuric acid. The change trends of arsenic, cadmium and lead release with the increase of sulfuric acid dosage are similar. However, with the same excess of sulfuric acid, the arsenic release concentration increased from 213 to 298 mg/L, cadmium increased from 11.75 to 13.15 mg/L, and lead increased from 2.7 to 5.5 mg/L. The presence of sulfuric acid not only directly oxidizes sulfides to release heavy metals, but may also promote oxygen oxidation, but the mechanism of action may require further investigation. The concentration of zinc is basically not affected by the addition of sulfuric acid and maintains a relatively stable release concentration, which is because the amount of oxidizable form is less than 1% (Figure 3).

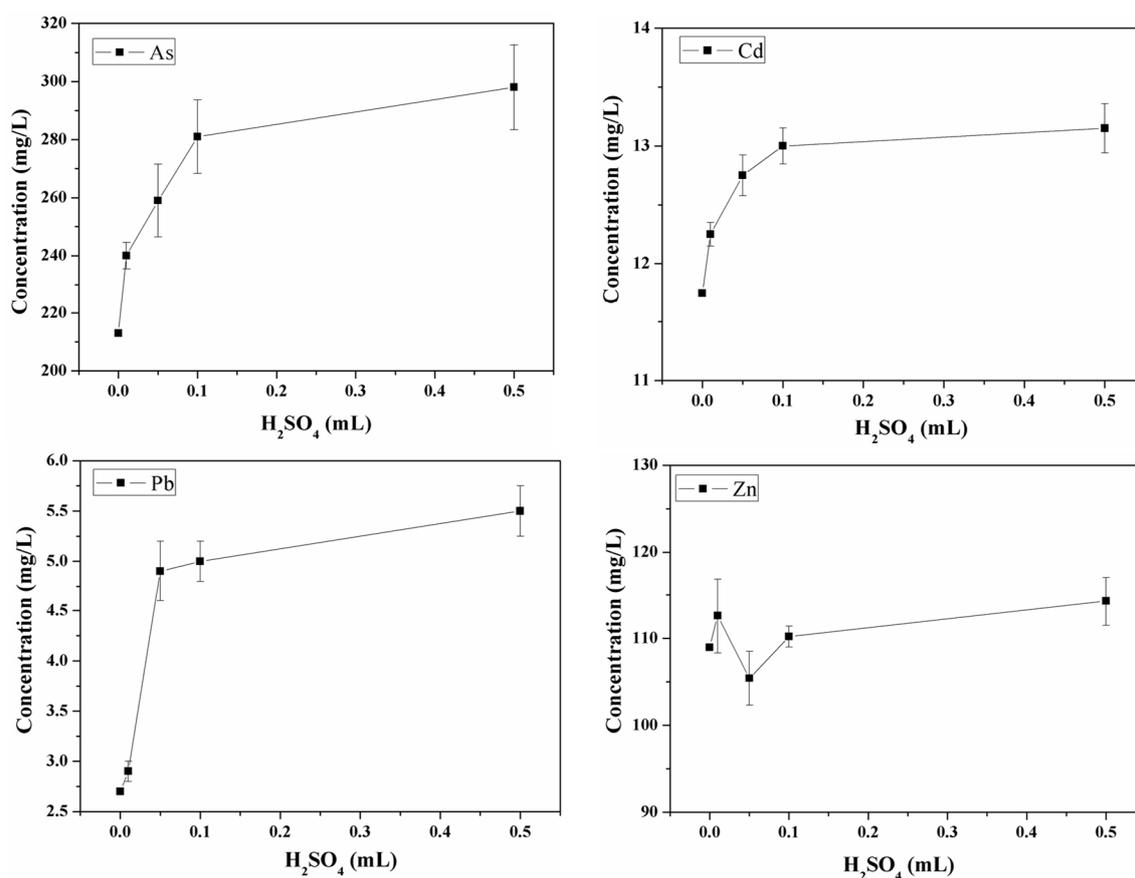


Figure 7. Effect of sulfuric acid addition on the release concentrations of heavy metals.

### 3.4.3. Effect of $Ca(OH)_2$

Previous experiments have shown that the elution of acid by water can reduce the release concentration of arsenic, and the increase of sulfuric acid content will result in the increase of the release concentration. Therefore, reducing the concentration of sulfuric acid in the sludge is beneficial to reducing the release of heavy metals. However, the method of washing to remove sulfuric acid is

difficult in engineering. The neutralization reaction of lime with sulfuric acid may be an economical and feasible solution.

The effects of adding  $\text{Ca}(\text{OH})_2$  on the release concentrations of heavy metals were investigated. As seen from Figure 8, adding  $\text{Ca}(\text{OH})_2$  can significantly reduce the release concentrations of heavy metals except for arsenic. After the addition of a small amount of  $\text{Ca}(\text{OH})_2$ , the concentration of arsenic slowly decreased. When the dosage of lime is 0.4 g, the release concentration of arsenic reaches a minimum of 186 mg/L, which is 27 mg/L lower than that without dosing. The concentration of arsenic rapidly increases after more  $\text{Ca}(\text{OH})_2$  is added. This is because too much alkali reacts or dissolves arsenic sulfide [34,35], and forms unstable calcium arsenate [36,37]. The release concentrations of cadmium and zinc first slowly decline with the increase of  $\text{Ca}(\text{OH})_2$  content, then rapidly decrease, and finally become slower. When the dosage was 0.8 g, the release concentration of zinc dropped sharply. The change in the release concentration of lead is special, and a small amount of 1 g  $\text{Ca}(\text{OH})_2$  greatly reduces the release concentration. The addition of 0.2 g directly reduced the lead release concentration from 2.7 mg/L to 0.58 mg/L. The variation of cadmium, lead and zinc release concentrations may be related to the formation of the precipitated hydroxide. In general, a proper amount of  $\text{Ca}(\text{OH})_2$  can slow down the release of heavy metals during the arsenic sludge accumulation process.

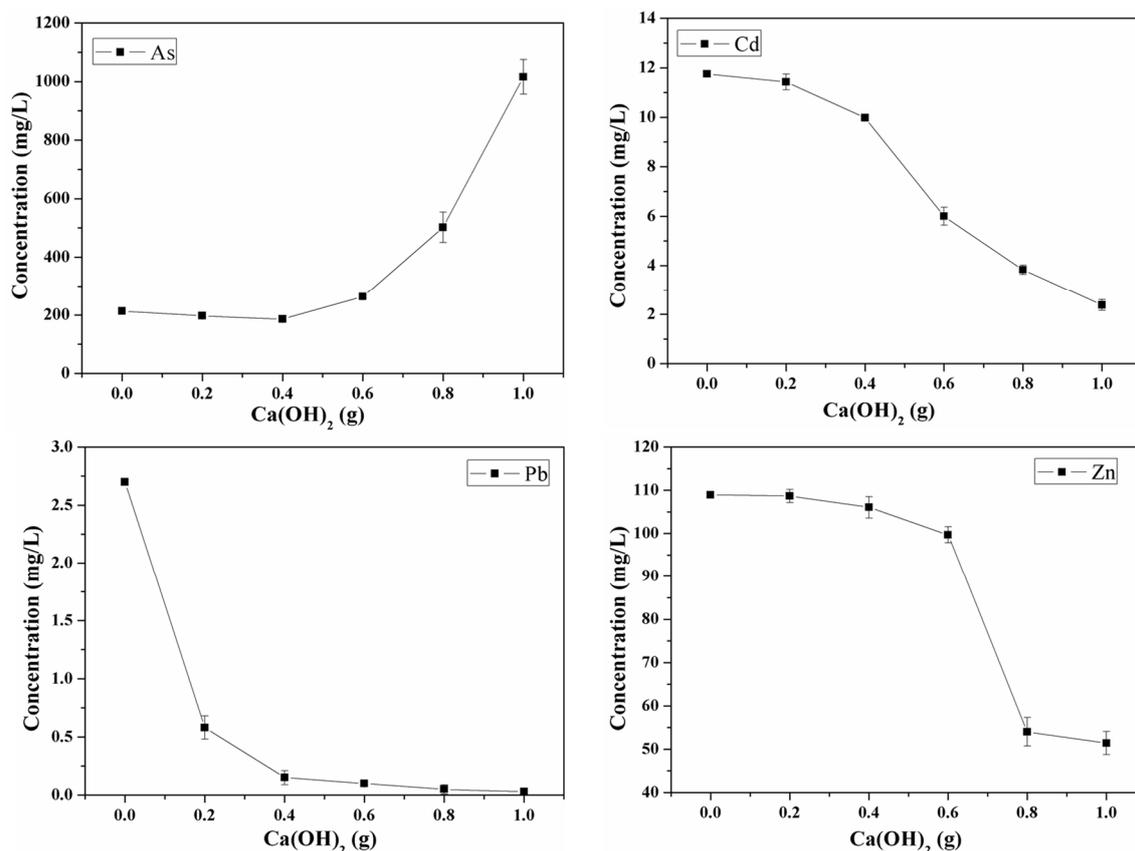


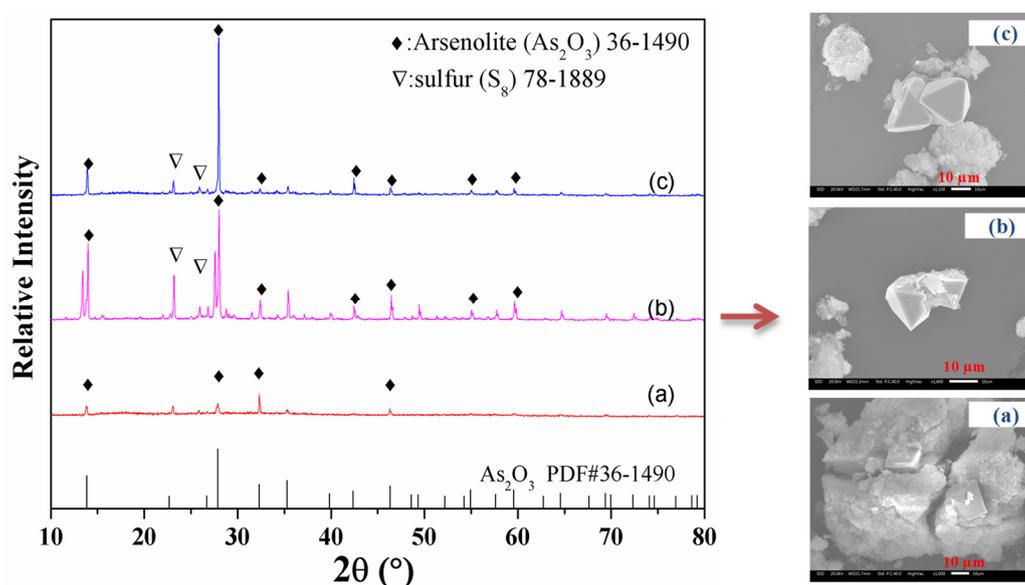
Figure 8. Effect of  $\text{Ca}(\text{OH})_2$  addition on the release concentrations of heavy metals.

### 3.5. Morphology, Change and Phase Transformation

The SEM images of vacuum-ASS and air-ASS were selected as a representative to illustrate the morphology changes during simulated storage. Figure 9 shows that there are obvious differences in the morphology and phase of the ASS after simulated storage. Before treatment, the ASS was flocculent particles which is similar to our previous studies [15,29], which were composed of extremely fine arsenic sulfide (Figure 2a). After simulated vacuum storage at 30 °C and 60 °C for 48 h, a small

amount of crystals has been found, probably due to the oxidation of small flocculent arsenic sulfide particles (Figure 9a,b). Meanwhile, crystals were also found after simulated air storage at 60 °C for 48 h (Figure 9c). In summary, whether an aerobic environment or a vacuum environment, the morphology of the arsenic sulfide sludge has been changed. Some new crystals are produced, and it is possible that the crystals of  $\text{As}_2\text{O}_3$  produced may be the reason for the increase of the release concentration.

Figure 9 also shows the XRD patterns of the ASSs after simulated storage. The raw ASSs were mainly amorphous with a few diffraction peaks (Figure 2). Crystalline sulfur ( $\text{S}_8$ ) was observed in the raw ASS, which might be attributed to the reaction of  $\text{H}_2\text{S}$  and  $\text{AsO}_4^{3-}$  during the treatment of acidic arsenic bearing wastewater by  $\text{H}_2\text{S}$  [28,31]. Moreover, for vacuum or air atmosphere,  $\text{As}_2\text{O}_3$  species were apparently detected and the intensity of the peaks increased with the increase of temperature. The XRD results also support the previous hypothesis that the storage process has changed the morphology and produced new crystals. This could account for the increase of the As release concentration. Similar changes may have occurred for the other sulfides of Cd and Pb, but the content was too low to be detected by the morphology or XRD analysis. Therefore, it is necessary to calculate the oxidation process theoretically.



**Figure 9.** XRD and SEM images of the ASS after simulated storage: (a) simulated storage in vacuum at 30 °C for 48 h; (b) simulated storage in vacuum at 60 °C for 48 h; (c) simulated storage in air at 60 °C for 48 h.

### 3.6. Release Mechanism

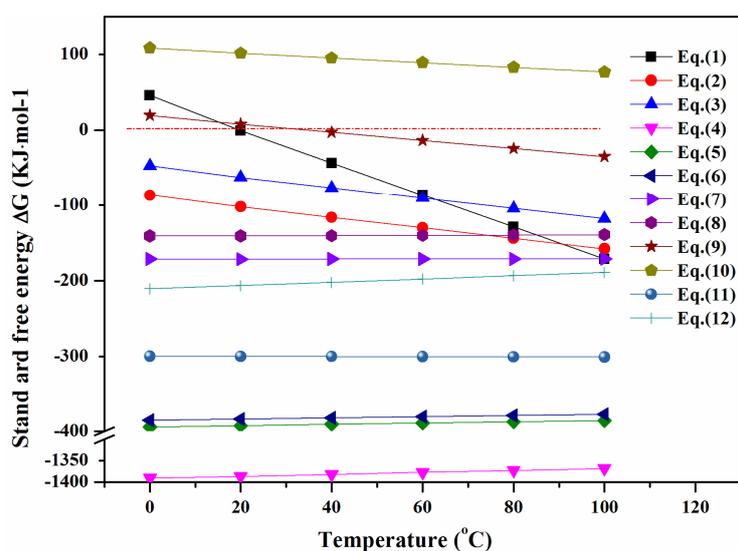
Table 3 shows the possible major chemical reactions during the simulated storage process under air or vacuum condition. The simulated oxidation process can be summarized as the two major categories of liquid-solid reactions (Equations (1)–(3)) and gas-solid reactions (Equations (4)–(6)). At the same time, other reactions (Equations (7)–(9), (11)–(12)) may also be accompanied. The standard free energy ( $\Delta G$ ) changes for Equations (1)–(12) over the temperature range of 0–100 °C are shown in Figure 10. In terms of thermodynamics, the sulfides of As can be oxidized by sulfuric acid if the temperature reaches 20 °C. The sulfides of Cd and Pb can be oxidized by sulfuric acid and oxygen and arsenic sulfide can be oxidized by oxygen over the temperature range of 0–100 °C. On the basis of thermodynamic calculations, the data of standard Gibbs free energy ( $\Delta G$ ) and heat of reaction  $\Delta H$ ) for Equations (1)–(12) at the temperature of 60 °C are shown in Table 2. The Gibbs free energy of the gas-solid reaction (Equations (4)–(6)) is higher than that of the liquid-solid reaction (Equations (1)–(3)), so the gas-solid reaction (Equations (4)–(6)) may be dominant. However, in the actual storage process, the solid of sulfides is encapsulated by the sulfuric acid, which will reduce the contact efficiency of

oxygen. In addition, it can be seen from the reaction function ( $\Delta H$ ) that the increase of temperature is beneficial to the liquid-solid reaction.

**Table 3.** Chemical reactions that may occur during the simulation.

Equation	$\Delta G$ (kcal·mol <sup>-1</sup> )	$\Delta H$ (kcal·mol <sup>-1</sup> )	Number
$\text{As}_2\text{S}_3 + 9\text{H}_2\text{SO}_4 = \text{As}_2\text{O}_3 + 12\text{SO}_2(\text{g}) + 9\text{H}_2\text{O}$	-20.634	149.383	(1)
$\text{PbS} + 4\text{H}_2\text{SO}_4 = \text{PbSO}_4^* + 4\text{SO}_2(\text{g}) + 4\text{H}_2\text{O}$	-31.115	24.368	(2)
$\text{CdS} + 4\text{H}_2\text{SO}_4 = \text{CdSO}_4 + 4\text{SO}_2(\text{g}) + 4\text{H}_2\text{O}$	-21.608	33.356	(3)
$\text{As}_2\text{S}_3 + 4.5\text{O}_2(\text{g}) = \text{As}_2\text{O}_3 + 3\text{SO}_2(\text{g})$	-329.242	-347.395	(4)
$\text{PbS} + 1.5\text{O}_2(\text{g}) = \text{PbO} + \text{SO}_2(\text{g})$	-93.030	-99.624	(5)
$\text{CdS} + 1.5\text{O}_2(\text{g}) = \text{CdO} + \text{SO}_2(\text{g})$	-91.008	-97.186	(6)
$\text{PbO} + \text{H}_2\text{SO}_4 = \text{PbSO}_4^* + \text{H}_2\text{O}$	-40.953	-41.552	(7)
$\text{CdO} + \text{H}_2\text{SO}_4 = \text{CdSO}_4 + \text{H}_2\text{O}$	-33.469	-35.113	(8)
$\text{S} + 2\text{H}_2\text{SO}_4 = 3\text{SO}_2(\text{g}) + 2\text{H}_2\text{O}$	-3.231	127.830	(9)
$\text{As}_2\text{O}_3 + 2\text{H}_2\text{SO}_4 = \text{As}_2\text{O}_5 + 2\text{SO}_2(\text{g}) + 2\text{H}_2\text{O}$	21.293	73.503	(10)
$\text{S} + \text{O}_2(\text{g}) = \text{SO}_2(\text{g})$	-71.810	-71.039	(11)
$\text{As}_2\text{O}_3 + \text{O}_2(\text{g}) = \text{As}_2\text{O}_5$	-47.287	-64.614	(12)

The thermodynamic data were calculated by the HSC Chemistry Software Version 6.0 (Outokumpu Research Oy, Pori, Finland) at 60 °C. \* Slightly soluble in water.



**Figure 10.** Standard free energy changes vs. temperature for Equations (1)–(12). The thermodynamic data was obtained from HSC Software Version 6.0 (Outokumpu Research Oy, Pori, Finland).

TG-DTG was performed to confirm the oxidization of sulfuric acid and the TG-DTG curves of the raw ASS and washed ASS (L:S = 10:1, cleaned three times with deionized water) are shown in Figure 11. As shown in Figure 10, two weight loss stages were observed for the raw ASS. In the first stage, at approximately from 50 to 145 °C, a heavy mass loss of 12% was observed. The DTG also reflects the dehydration peak P1 in this temperature range. That was attributed to the volatilization of adsorbed and bound water. In the second stage in the range of 145–210 °C (P2), a heavy mass loss of 12% was ascribed to the oxidization of sulfides to SO<sub>2</sub> by concentrated sulfuric acid. For the sample eluted by water, mass loss peaks could not be found below 200 °C. However, there is a significant weightlessness peak between 210 and 275 °C (P3). The heavy mass loss of 8% was possibly attributed to sulfur volatilization. The thermodynamics calculation shows that oxidation by sulfur acid and oxygen is theoretically feasible. The simulated oxidation process can be summarized as the two major categories of liquid-solid reactions and gas-solid reactions (Table 3). The sulfides of As, Cd and Pb can be oxidized by sulfuric acid and oxygen. The Gibbs free energy of the gas-solid reaction is higher

than that of the liquid-solid reaction, so the gas-solid reaction may be dominant. However, the solid of sulfides is encapsulated by the sulfuric acid, which will reduce the contact efficiency of oxygen.

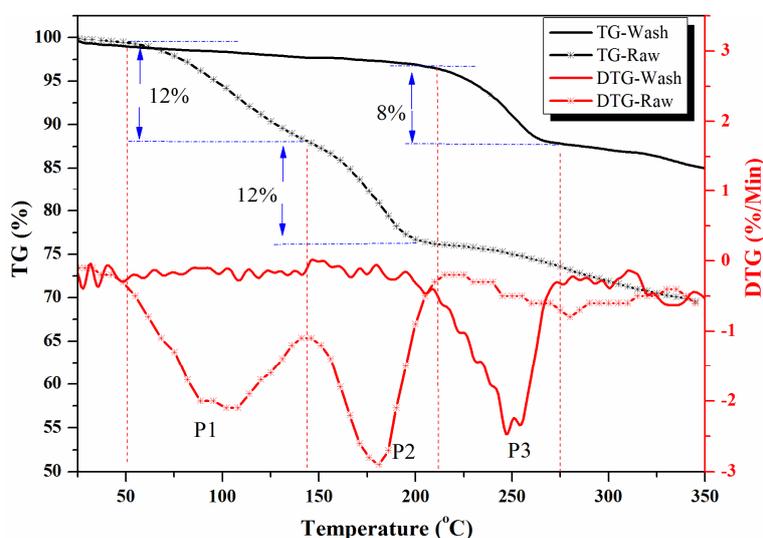


Figure 11. TG-DTG curves of the raw ASS and washed ASS.

Based on the changes of the release concentrations and SEM, XRD and TG-DTG results, it is believed that concentrated sulfuric acid had a significant influence on the heavy metals release of ASS. The schematic diagram for this mechanism is illustrated in Figure 12. First, the arsenic sulfide sludge is drying and dehydrated during the storage process, and the sulfuric acid solution becomes concentrated sulfuric acid. Second, the concentrated sulfuric acid oxidizes sulfides to increase the acid soluble heavy metals and the liquid film of the sulfuric acid is lost. At the same time, the sulfides are oxidized by oxygen, which causes an increase of release concentrations. Therefore, the combined oxidation mechanism of sulfuric acid and oxygen poses an environmental risk of heavy metals for the arsenic sulfide sludge. The strength and sequence of oxidation still require further research and exploration.

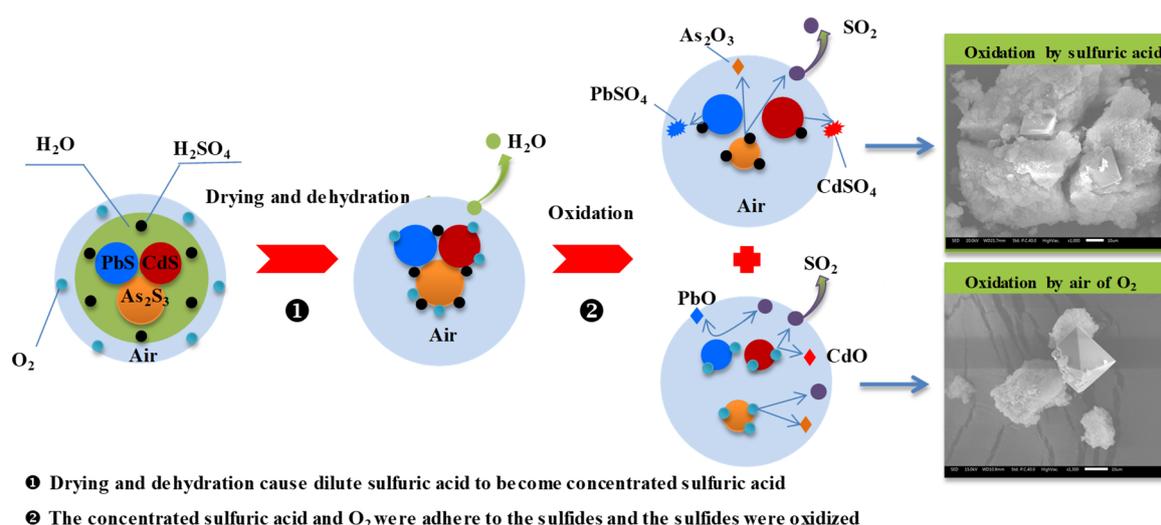


Figure 12. Schematic illustration of the simulated storage procedure.

#### 4. Conclusions

This paper investigated the characteristics, influencing factors and mechanism of heavy metals release during the simulated storage of ASS. The results showed that the release concentrations of arsenic, lead and cadmium increased with increasing temperature and time, except zinc. The increase of

release concentration was rapid in the initial stage and became slow in the following stage. At 30–60 °C and 12–48 h of simulation time, the release ratio was Cd (25.01%–38.12%) > Pb (4.76%–9.53%) > As (0.12%–0.28%). An anoxic environment or water-elution was beneficial for reducing the release of arsenic. Sulfuric acid significantly affected the release of arsenic, lead and cadmium. However, with the addition of more than 0.1 mL of sulfuric acid, the increase of release concentration was not significant. Neutralization of the sulfuric acid by adding Ca(OH)<sub>2</sub> could significantly reduce the release of lead, cadmium and zinc. A small amount of Ca(OH)<sub>2</sub> added was beneficial to reduce the release of arsenic, but the release concentration of arsenic was rapidly increased when the dosage was more than 0.4 g.

Based on the results of SEM, XRD and TG-DTG, the release mechanism of the sulfide arsenic sludge during simulated storage was inferred. The co-oxidation of sulfuric acid and oxygen caused the release of heavy metals such as arsenic, lead and cadmium and increased the environmental risk of the storage process. Both oxidation products of arsenic sulfide are As<sub>2</sub>O<sub>3</sub>, which is responsible for the increase of arsenic release concentration.

However, the correspondence between the release characteristics and oxidation mechanism needs further demonstration. In particular, since the simulation time is too short, the release process characteristics still require further systematic research and the release kinetics require modeling for research. In the next step, it is necessary to conduct an in situ study to evaluate the long-term environmental risk of an enterprise's arsenic sulfide sludge yard.

**Author Contributions:** Conceptualization, L.Y.; Data curation, L.Y. and H.X.; Formal analysis, L.Y.; Funding acquisition, X.M. and Y.W.; Investigation, X.M. and Y.K.; Methodology, L.Y. and D.L.; Project administration, X.M. and Y.K.; Resources, Y.K.; Software, Y.L. (Yanjie Liang) and Y.L. (Yuancheng Li); Supervision, Y.K.; Validation, L.Y. and Y.K.; Visualization, Y.W., Y.L. (Yanjie Liang), J.F. and K.Y.; Writing—original draft, L.Y.; Writing—review & editing, X.Y.

**Funding:** This research was supported by National Key R&D Program of China (2018YFC1900301, 2018YFC1903301), National Science Fund for Distinguished Young Scholars (51825403), the National Natural Science Foundation of China (51634010), Science and Technology Project of Hunan Province (2017RS3010).

**Conflicts of Interest:** The authors declare no conflict of interest.

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