



# Article Mechanisms at Different pH for Stabilization of Arsenic in Mine Tailings Using Steelmaking Slag

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Abstract: The mechanisms at different pH for the stabilization of arsenic (As) in mine tailings (MTs) using steelmaking slag were investigated using laboratory experiments. Two types of steelmaking slag were used in the experiments. Ca-slag has high pH and high calcium oxide content due to its short period of aging. In contrast, Fe-slag is oxidized for a long time and is richer in Fe than in Ca. The As-contaminated MTs were taken from a tailing-storage dam around an abandoned gold mine in Korea. The tailings had an average As concentration of 2225.3 mg/kg. The As-removal batch experiment was performed to investigate the As-removal characteristics of the steelmaking slag. From SEM/EDS analyses after each batch experiment, Ca-As bearing precipitates were broadly found on the surface of Ca-slag particles and the final pH of the solution increased to 12.3. However, for Fe-slag, the As was locally found as forms adsorbed to the surface of Fe and Mn oxides contained in the Fe-slag particles. The final pH of this solution was 8.4. The efficiency of removal of As from water using the Ca-slag was >97% and that with Fe-slag was 79%. This suggests that As ions in solution were removed by Ca-(co-)precipitation (which occurs comprehensively on the Ca-slag surface), or by restrictive adsorption of Fe- and Mn-oxides (on limited parts of the Fe-slag). To determine the efficiency of As-extraction reduction from MTs using steel slags, arsenic-extraction batch experiments with two slags were performed under acidic conditions, simulating the leaching environment formed around a mine tailing storage dam. The As concentration in the extracted solution was decreased by 69.9% (even at pH 2) after the addition of 5% Fe-slag. However, when 5% Ca-slag was added, the As concentration decreased by 42.3% at pH 2. These results suggest that Fe-rich steel slag can be more effective than Ca-rich steel slag as a stabilizer for As in contaminated mine tailings at low pH.

Keywords: steelmaking slag; soil stabilization; arsenic; mine tailing; soil remediation

# 1. Introduction

Arsenic (As) is a metalloid belonging to the nitrogen group in the periodic table and is considered a highly toxic substance that requires environmental countermeasures. Arsenic has affinity with thiol groups (-SH: sulfhydryl group) in cysteine, one of the amino acids containing sulfur, because it is similar to the phosphate molecule. Arsenic is known to damage the protein function of the human body, causing neurological disorder and cancer, and to attack the receptors and cells [1]. The US Environmental Protection Agency (USEPA) has designated arsenic as highly toxic even at low concentrations and, in 2001, the Maximum Contaminant Level (MCL) of As for drinking water was decreased from 50  $\mu$ g/L to 10  $\mu$ g/L [2].

As contamination is mainly caused by human activities, such as glass melting, petroleum refining, and mining for gold, silver, copper, zinc, and lead [3,4]. Arsenic spilled during artificial mine activities contaminates the soil and groundwater, after which As absorbed by fish and plants can directly or indirectly impact humans. Among the various kinds of damage originating from domestic mine activities from 2016 to 2018 in Korea, the portion related to deforestation and waste rock was the highest (30.4%). Next were soil pollution and tailing dams, which accounted for 24.7% and 7.8%, respectively [5]. A large number of mine tailing storage sites in Korea have been left alone without proper care; therefore, the development of techniques for economically and prospectively treating mine tailings (hereafter "MTs") has become necessary. The As was one of the metals and metalloids which were commonly found in gold mines and the maximum As content in some Korean gold mines was >5% [5]. These arsenic-contaminated tailings, which exist in a variety of forms (arseniosiderite, arsenolamprite, bernardite, titanium oxide arsenate, etc.), can adversely affect an ecological system when they are released into the environment [6,7]. Recently, the pH and sulfur contents of domestic MTs from different metal mines in Korea were reported by Park et al. (2018) [8]. The pH of the tailings ranged from 2.5 to 8.5 (average 5.5) regardless of the mineral species, indicating that the pHs of tailings are directly affected by the amount of sulfur. Most of the tailing environments were acidic. Therefore, acidic effluent or leachate generated by sulfide minerals in tailings can create a risk to the surrounding environment to which more arsenic at high concentrations could leach out from the tailings.

Many treatment processes have been studied to remove As from soils. These processes include soil washing, electrokinetic extraction, adsorption, phytoremediation, and stabilization [9–12]. Despite the disadvantages of stabilization treatments, in the USA, solidification/stabilization technologies are considered the best treatment for arsenic-contaminated soils and wastes [13]. For the last two decades, stabilizers, such as lime, oyster shell, steel slag, and Mn/Fe-oxides have been studied for use on As-contaminated soil and most As is stabilized in soil by forming complexes or by (co)precipitating with other elements [14–18]. From the previous research, it has become clear that the mobility of other metal ions (except As) during a stabilizer, the result was an extreme reduction in As-extraction when used in arsenic-contaminated soils, but the leaching of other heavy metals (such as Zn, Pb, Cu, and Cd) increased [19]. Moreover, the pH of the soil affects the As-stabilization capacity because the pH controls the final forms of As-bearing minerals or precipitates that occur during the stabilization process and an optimal stabilizer should be selected according to the pH of the soil medium [20].

Steelmaking slag (hereafter "steel slag") is a by-product generated by the process of charging quicklime to remove silicon, phosphorus, and sulfur during the steelmaking process. The slag contains useful resources, such as oxides, silicates, and carbonates. Steel slag is mainly divided into Basic Oxygen Furnace Slag (FOB-Slag) and Electric Arc Furnace Slag (EAF-Slag), according to the steel refining process [21,22]. Most steel slags have a great deal of highly soluble alkali components on the surface, as a result of the quicklime charging process. To prevent environmental pollution by the quicklime and sulfur leachate from steel slag, and to suppress volume expansion caused by the hydration of free-CaO, MgO, and dicalcium silicate, an aging treatment is required before the slag is recycled [23,24]. However, the aging process is not necessary if the steel slag is used for soil stabilization or water quality improvement. For example, in several studies, unaged steel slag (having high pH) was used as an improver of soil, a stabilizer for waste, and as flocculent/precipitant for water-quality improvement [25,26]. In 2018, the domestic steel industry produced about 72.5 million tons in Korea, which emerged as the world's fifth-largest steel industry by country [27]. Steel slag has been recycled, mainly in the form of aggregate, for filling and covering at road construction sites in the past, but recent active research has been focused on using it as a stabilizer for contaminated soils [28]. This is because it has been proven to have excellent ability to adsorb harmful heavy metals, including As [29,30]. However, only a few studies have been performed on the use of steel slag to stabilize MTs, and its use for the stabilization of arsenic in tailings at low pH has never been studied before. Clear understanding of the various reactions among steel slag, tailings, and water is essential for selecting the steel slag most suitable for use with a specific tailing. However, studies into the reaction mechanisms involving steel slag and MTs are also very limited [31]. For the successful stabilization of arsenic in MT, not only the characteristics of the steel slag, but also the pH of the steel tailings should be taken into account.

This study was focused on identifying the behavior and the existing forms of As during the stabilization process, and on investigating the reaction among water, tailings, and steel slag at different pH levels. In this paper, we also present how to increase As stabilization efficiency in MT using the different characteristics of two steel slags (Ca-rich slag (Ca-Slag) and Fe-rich slag (Fe-Slag)). These results provide insights not only into the use of steel slag as a stabilizer for arsenic-contaminated tailings and soils, but also for finding other recycling purposes for steel slag.

## 2. Materials and Experimental Methods

## 2.1. Preparation of MTs and Steel Slags

For the experiments, MT samples were collected at a 0–25 cm depth from a landfill site at which more than 5000 m<sup>3</sup> of MTs generated by the mining activities of an Au-Ag mine near Cheonan, Korea is stored. After removing debris and rock fragments from the MTs, they were naturally dried indoors at room temperature. Dried samples of the MTs were separated using a no. 10 sieve (<2 mm) and then used in the experiments. The aqua regia extraction method (ISO 11466 method) was applied to extract the heavy metal contents (including AS) from the MTs, and an inductively coupled plasma/optical emission spectrometer (ICP/OES; Optima 7000DV, Perkin Elmer, Waltham, MA, USA) was used to measure their concentrations [32]. The mineralogical and chemical properties of the MTs were analyzed using an X-ray diffractometer (XRD: X'Pert-MPD System, PHILIPS, Amsterdam, The Netherlands) and X-Ray fluorescence spectrometry (XRF-1800, SHIMADZU, Kyoto, Japan). The pH of the MTs was measured using a pH meter (ORION Star-A211, Thermo scientific, Waltham, MA, USA) based on the standard method in Korea (ES 06304).

Two types of steel slag were used as tailing stabilizer in this study. To investigate the efficiency of the As stabilization in the MTs, the reductions in arsenic extraction were compared according to their different characteristics. One of the steel slags was a BOF Slag, obtained without aging treatment after being produced at a steel mill company in Korea. This slag has very high Ca content (hereafter "Ca-slag"). The other is a steel slag that has been landfilled as a form of industrial waste at a coastal site in Korea since the 1980s. Because it had been buried for a long time, the surface was quite oxidized and the Fe content was higher than the Ca content (thus, hereafter "Fe-slag"). The steel slags used in the experiment were pulverized into powder particles of 0.075 mm (or less) in diameter using a tungsten carbide ring mill. The pulverized Ca-slag and Fe-slag was analyzed for components using XRF, and the pH of each was measured using a pH meter. Before these steel slags were used as stabilizers for the arsenic-contaminated MTs in this study, several toxicity leaching tests were also performed to evaluate the risk that toxic heavy metals and metalloids might be leached from them. The toxicity characteristic leaching procedure (TCLP) test was conducted according to the US-EPA 1311 method [33]. The TCLP is a method for simulating heavy metal leaching for wastes in municipal solid waste landfills. Because both steel slags were measured and found to have pH higher than 5 (Ca-slag: pH 12.39; Fe-slag: pH 8.43), the extraction solution was titrated to pH of  $2.88 \pm 0.05$  by adding acetic acid. The synthetic precipitation leaching procedure (SPLP) test was also conducted according to the US-EPA 1312 method [34]. The SPLP test was used to estimate the amount of outflow of heavy metal in an acid-rain condition, and the mixture of dilute nitric acid and sulfuric acid was used as an extraction solution (pH  $4.2 \pm 0.05$ ). To identify the total amount of heavy metals, including As in the steel slag, they were extracted using the aqua regia extraction method and the total heavy-metal content was analyzed using an ICP/OES, which results represented their concentrations in the steel slag.

#### 2.2. Batch Experiments for Investigating the Mechanism of As Removal by the Steel Slags

In order to identify the main mechanisms in the steel slags that cause stabilization of arsenic in the MTs, the two kinds of steel slag were reacted with artificially As-contaminated solution at batch scale. The As solution used in the experiment was prepared using an ICP standard solution of As (1000 mg/L, purchased from Anapure Co., Beijing, China), which was diluted with distilled water to prepare the As-contaminated solution (100 mg/L As). The solution was titrated to pH 5.5 using 0.1 M HNO<sub>3</sub> solution to confirm the stabilization of the mine tailings under field conditions because the average pH of MTs in Korea is 5.5 [8]. A more acidic solution (pH 4.0) was also prepared to represent acidic drainage from the MTs. Forty milliliters of the prepared As-contaminated solution was mixed with 8 g of each steel slag powder at a ratio of 1:5 w%/v%, and the mixed solution was stirred at 25 °C and 150 rpm condition for 12 h in a shaker. This was followed by a standstill for 24 h. After a total reaction time of 36 h, some of the supernatant was collected from the solution using a 0.8 µm syringe filter (16592-K, Sartorius, Göttingen, Germany). The As-concentration in the collected sample was analyzed using an ICP/OES attached with a hydride generator. The efficiency of As removal from the solution by the steel slag was calculated using Equation (1).

$$Removal efficiency(\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100$$
(1)

where  $C_0$  is the initial concentration of As in solution (mg/L) and  $C_e$  is the final concentration in solution after reaction with the steel slag (mg/L). The batch experiments were repeated three times and their average value was used as the final result for the experiment. The pH and oxidation-reduction potential (ORP) of the solution were also measured using a multi-analyzer (PDC-70N, iSTEK, Seoul, Korea) before and after the reaction to confirm the change in the pH and ORP by the steel slag in the aqueous environment. These results were plotted in a pH-Eh diagram to estimate the chemical species of As remaining in solution after reaction with the steel slags.

After the reaction, Ca-slag or Fe-slag was separated from the solution and washed sufficiently with distilled water (1:50 w%/v% ratio) using a vacuum pump. The washing solution was filtered through 5B filter paper and the solids were dried in an oven at 50 °C for 48 h. Before and after the reaction, the surface of the steel slag was visualized using a scanning electron microscope (SEM: S-2700, Hitachi, Tokyo, Japan) with energy dispersive spectroscopy (EDS: EX-250, Horiba Scientific, Kyoto, Japan) to identify the precipitation and adsorption configurations of As on the steel-slag surface. Angle-resolved X-ray photoelectron spectrometry (XPS: KRATOS, Kyoto, Japan) analysis was also conducted to observe the existence of the Fe- and Mn-oxides on the steel slag effective for As adsorption.

#### 2.3. Batch Extraction Experiment for the Efficiency of As-Extraction Reduction from MTs by Steel Slag

The As stabilization efficiency of steel slag could be evaluated from how much the As in the solution, extracted from the MT, decreased after the slag was added to MTs. Batch extraction experiments were performed to investigate the reduction in As-extraction from MTs caused by the two steel slags. The arsenic-contaminated MTs, steel slag, and distilled water were mixed in a 50 mL conical tube at the ratio of 20:1:20 (MT (20 g) + steel slag (1 g) + distilled water (20 mL)) [16]. They were stirred for 12 h at 25 °C and 150 rpm in a shaker during the stabilization process and then were left for 24 h. After a total reaction time of 36 h, the solution was passed through a 5B filter paper and the recovered solids dried in an oven at 50 °C for 48 h. The filtered solution was analyzed for its As concentration using an ICP/OES and the stabilized MT was prepared for additional experiments (such as SEM/EDS analysis).

The effect of  $\text{HPO}_4^{2^-}$ , MnO, and MnO<sub>2</sub> as supplementary materials for stabilization of the As in MTs by steel slag was also investigated experimentally. Because the As adsorption capacity is greater when the aqueous As ion is in the form of arsenate (As<sup>5+</sup>) rather than arsenite (As<sup>3+</sup>), MnO and MnO<sub>2</sub> may act as oxidants to maintain the final state of As in water as arsenate [35]. According to Nesbitt's

study using XPS, birnessite ((Na,Ca) $Mn_7O_{13}$ ·13 $H_2O$ ) induces oxidation to elemental As through a two-step chemical process, as indicated in Equations (2) and (3) [35].

$$2MnO_2 + H_3AsO_3$$
 (Arsenite) +  $H_2O \rightarrow 2MnOOH + H_3AsO_4$  (Arsenate) (2)

$$2MnOOH + H_3AsO_3 \text{ (Arsenite)} + 4H^+ \rightarrow 2Mn^{2+} \text{ (aq)} + H_3AsO_4 \text{ (Arsenate)} + 3H_2O \tag{3}$$

In this test, only 1% MnO and MnO<sub>2</sub> were added to confirm how the Mn ion acts for As stabilization. Because the structure of molecular As is similar to that of phosphate, the phosphate in MTs or steel slag may affect the reduction of As-extraction. In addition, 1%  $K_2$ HPO<sub>4</sub> was also added to ascertain if ion-exchange competition occurred between phosphorus (HPO<sub>4</sub><sup>2–</sup>) and arsenic (HAsO<sub>4</sub><sup>2–</sup>) in an aqueous environment.

To simulate the acidic drainage caused by sulfide minerals in the tailings, the As extraction batch test was duplicated using a solution at low pH. Acidic solutions at pH 2.0, 2.5, 3.0, 4.0, and 5.5 used in the experiments were made using a solution of distilled water and 0.1 M HNO<sub>3</sub>. The MTs, steel slag, and acidic solutions were mixed at a ratio (w%/v%) of 1:0.05:20 of MT (1 g) + steel slag (0.05 g) + acidic solution (20 mL), of which the solid and solution ratio was similar to that of the TCLP test. The mixture was reacted for 12 h at a stirring speed of 30 rpm using a rotating stirrer. The supernatant of the solution was passed through a 0.8 µm syringe filter for the measurement of the As concentration in the extracted solution.

#### 3. Results and Discussion

#### 3.1. Evaluation of the Characteristics of the MTs and Steel Slags

The results of the particle size analysis of the MTs showed that the weight ratio was 87.3 % for sand (0.075–2 mm) and 12.7% for clay and silt (<0.075 mm). This indicates that the MT particles had a "sand" texture based on the USDA soil texture diagram [36]. The results of the XRF analysis of the MTs are shown in Table 1. The contents of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were 76.5 wt% and 12.8 wt%, respectively. Lesser amounts of other components occurred in the order K<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, and P<sub>2</sub>O<sub>5</sub>. The average concentrations (mg/kg) of the heavy metals and As in the MTs are shown in Table 2 and the MTs were seriously contaminated by As (concentration 2225.3 mg/kg, exceeding by > 10 times the Korean Soil Pollution Warning Limit (KSPWL) at Area 3 [32]. Figure 1 shows the results of the SEM/EDS analysis for the MT particles. The results indicate that the tailing particles show high As content (4–7 wt% of a particle) mostly as Fe-combined minerals (see the EDS results in Figure 1b,d,f).

In the flocculation/precipitation reaction of As in a water system, oxysalts, such as sulfate, silicate, and phosphate, are known to affect the reaction activity [37]. From the results of the XRF analysis (Table 1), the Ca-slag was characterized by the high CaO content (46.9 wt%), indicating that it has not gone through a long aging time. However, the Fe-slag contained less than 20 wt% CaO, and instead included a relatively large amount of SiO<sub>2</sub> (29.7 wt%), Fe<sub>2</sub>O<sub>3</sub> (24.3 wt%), Al<sub>2</sub>O<sub>3</sub> (12.1 wt%), and MnO (6.7 wt%), of which oxidation resulted in an outstanding ability to adsorb metal and metalloid ions. The Ca-slag showed a high pH (12.39), suggesting that the addition of Ca-slag increases the pH of MTs because of CaO hydration. However, Fe-slag showed a pH of 8.43 and is considered to have little effect on the change of pH of the MTs.

The concentrations of heavy metal and As in the steel slags are shown in Table 2. The total heavy metal content in the Ca-slag is lower than that in the Fe-slag. The concentrations of the main toxic heavy metals (including As) for both Ca-steel and Fe-steel slag are lower than for the KSPWLs at Area 3. As a stabilizer for MTs, <10 % of steel slag (mostly <5 %) has generally been added to tailings and thus the increase of heavy metal amounts in tailing by adding steel slag is considered to be very small. Results from the TCLP and the SPLP tests in Table 3 show that very small amounts of heavy metals (Zn, Cu, Cd, and Pb) and As were leached from both Ca-steel and Fe-steel slags, suggesting that they could be used as stabilizers for heavy-metal contaminated sites, from the viewpoint of toxic metal leaching.

		Component Portion from XRF Analysis (wt %)								
Material Type	pН	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	MgO	MnO	CaO	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>
MTs	5.5	76.5	12.8	5.4	2.6	1.3	-	0.6	0.4	-
Ca-slag	12.4	13.1	2.0	-	26.6	5.8	3.1	46.9	0.2	0.8
Fe-slag	8.4	29.7	12.1	-	24.3	4.3	6.7	19.3	-	0.6

**Table 1.** The pH and XRF analysis for MTs and two slags.

"-": <0.1%, All values represent the arithmetical mean from triple measurements.

Table 2. Average heavy metal and As concentrations of MTs and two slags.

Material Type	Concentration (mg/kg)						
Waterial Type	Zn	Cu	As	Cd	Pb		
MTs	133.2	33.0	2225.3	3.5	39.6		
Ca-slag	3.1	-	-	-	5.1		
Fe-slag	222.2	172.7	-	-	97.9		
KSPWL at Area 3	2000	2000	200	700	700		

"-": <0.1 mg/kg; KSPWL: Korean Soil Pollution Warning Limit; All values represent the arithmetical mean from triple measurements.



Figure 1. SEM/EDS analyses for As-bearing MT particles ((a,c,e): SEM images; (b,d,f): EDS peaks).

Type of Steel Slag	Looching Test Type	Concentration (mg/L)					
Type of Steel Stag	Leaching lest type	Zn	Cu	As	Cd	Pb	
Caslag	TCLP	DL	DL	DL	DL	DL	
Ca-slag	SPLP	DL	DL	DL	DL	DL	
Focilar	TCLP	4.545	0.024	DL	DL	0.107	
re-slag	SPLP	DL	0.005	DL	DL	DL	
Extraction Tolerance Limit			3	1.5	0.3	3	

Table 3. Heavy metal and As concentrations in extracted solution for TCLP and SPLP test.

DL: <Detection Limit (0.001 mg/L).

## 3.2. Batch Experiments for Investigating the Mechanism of Arsenic Removal by Steel Slag

Inorganic As in aqueous systems exists in the form  $As^{3+}$  (arsenite:  $H_3AsO_3$ ,  $H_2AsO_3^-$ ,  $HAsO_3^{2-}$ , and  $AsO_3^{3-}$ ) under reducing conditions and in the form  $As^{5+}$  (arsenate:  $H_3AsO_4$ ,  $H_2AsO_4^{-}$ ,  $HAsO_4^{2-}$ , and  $AsO_4^{3-}$ ) under oxidizing conditions. It is known that their chemical characteristics change depending on the redox potential and pH conditions [20,38]. Arsenite, as the dominant species in an aqueous reducing environment, is weakly adsorptive because it tends to exist as a zero-valent form of H<sub>3</sub>AsO<sub>3</sub> (without charge) in neutral and acidic pH conditions. Arsenite is also known to be 25 to 60 times more toxic than arsenate, usually requiring a pretreatment process that removes it after it is oxidized to As (V) [39]. One of the main purposes for the stabilization of As in MTs is to maintain the As ions in solution in the form As<sup>5+</sup>, thereby producing more As-bearing solids in the MTs. The pH and redox potential of the solution before or after the reaction of the steel slag-As solution were measured and plotted on a pH-Eh diagram to investigate change in the form of As in the solution due to the steel slag (Figure 2). Before the addition of the steel slag to the solution, the As ions in solution (the initial pH of each solution: 4.0 and 5.5) mainly existed in the form of arsenite ( $As^{3+}$ ). However, after the steel slag was added,  $As^{3+}$  ions changed to arsenate ( $As^{5+}$ ), which was more conveniently fixed in the MTs. With MT stored in the field, the addition of steel slag can increase the pH of the MTs, causing the As ions in solution to exist mostly in the form of arsenate over a wide range of redox potential. If this phase transformation of As ions can occur when the steel slag is added to the MTs, the arsenate starts to form stable solids and the amount of As that can be extracted from the stabilized MTs naturally decreases. This represents the goal of successful As stabilization treatment.



Figure 2. Eh-pH diagram of arsenic status in solution during the slag-As-contaminated water reaction.

The As concentration in solution after reaction of the steel slag with the arsenic-contaminated solution was measured and the As removal efficiency with each steel slag was calculated using Equation (1) (Table 4). The pH of the solution increased to 12.2 and 12.3 (strong base) from 4.0 and 5.5 by adding Ca-slag, and the average As concentration in solution decreased to 3.0 and 2.1 mg/L, respectively, showing more than 97 % of the average As-removal efficiency. When Fe-slag was added, the pH of the solution increased to 8.2 and 8.4 from 4.0 and 5.5. The average As concentration in the solution decreased from 100.0 to 20.4 mg/L, showing As removal efficiency of 79.6%. Results from the experiments supported the conclusion that both of the steel slags have enough potential as As stabilizers for MTs because of the high As removal efficiency (>79%).

Steel Slag Type	The pH before the Reaction	The pH after the Reaction	Initial As Concentration (mg/L)	As Concentration after the Reaction (mg/L)	As Removal Efficiency (%)
Ca-slag	4.0 5.5	12.2 12.3	100.0	3.0 2.1	97.0 97.9
Fe-slag	4.0 5.5	8.2 8.4	100.0	21.3 20.4	78.7 79.6

Table 4. Average As removal efficiency from solution by steel slags at two pH conditions.

All values represent the arithmetical mean from triple measurements.

To investigate how the soluble As ions were fixed on the steel slag, SEM/EDS analysis was performed for Ca-slag and Fe-slag before and after reaction with the As-contaminated solution. The results are shown in Figures 3 and 4. From analysis of the SEM/EDS data, the original Ca-slag was composed of Ca-silicate and carbonate minerals, having high content of Ca, O, and Si (Figure 3a–c). After the reaction, most of the Ca-slag surfaces were covered by As-containing precipitates of various sizes and shapes. These were considered forms of calcium-arsenate or As-bearing CaCO<sub>3</sub> produced by co-precipitation of As because of the contents of Ca, O, and C (Figure 3d–f). Alkali components, such as free-CaO and dicalcium silicate contained in the Ca-slag, caused a sharp increase in the solution pH when Ca-slag was mixed with the As solution. Under high pH conditions (>12.0), As ions present in solution combine with large amounts of dissolved calcium ions to form stable solids, resulting in 97% efficiency for the removal of As from the solution. The EDS results for Ca-slag in Figure 3f show that, after the reaction, arsenic is evenly distributed over the slag surface (0.39 wt%). These calcium-arsenate precipitation mechanisms have been studied previously and the related chemical equations for these Ca-As co-precipitations in solution are listed in Equations (4)–(9) [40–42].

$$H_2AsO_4^- \leftrightarrow HAsO_4^{2-} + H^+$$
(4)

$$HAsO_4^{2-} \leftrightarrow AsO_4^{3-} + H^+$$
(5)

$$2AsO_4^{3-} + 2HAsO_4^{2-} + 5Ca^{2+} + 9H_2O \rightarrow Ca_5H_2(AsO_4)_4.9H_2O$$
(6)

$$3Ca^{2+} + 2AsO_4^{3-} + xH_2O \rightarrow Ca_3(AsO_4)_2 \cdot xH_2O$$
<sup>(7)</sup>

$$4Ca^{2+} + 2AsO_4^{3-} + 2OH^- + 4H_2O \rightarrow Ca_4(OH)_2(AsO_4)_2 \cdot 4H_2O$$
(8)

$$5Ca^{2+} + 4AsO_4^{3-} + OH^- \rightarrow Ca_5(AsO_4)_3OH$$
(9)

From the results of SEM/EDS analysis of the Fe-slag particles before the reaction (Figure 4a–c), the particles contained a certain number of Fe and Mn oxides, which are known to have high capacity for As adsorption [43]. The existence of Fe and Mn oxides in the Fe-slag can also be observed from XPS analyses. Figure 5 shows that Fe<sup>3+</sup>-oxide and Mn<sup>2+</sup>-oxide are found in the Fe-slag, whose oxides can provoke As adsorption to the Fe-slag surface when the Fe-slag is added to the solution. From the EDS results for the Fe-slag after the reaction (Figure 4f), it was found out that existing Fe- and Mn-oxide minerals in the Fe-slag come to contain relatively high As content (average of 2.84 %), comparing with only 0.39 % of As contents newly precipitated on the Ca-slag surface. The pH of the solution was 8.1

after the addition of the Fe-slag. Thus, it appears that the main mechanism for As removal by Fe-slag was the adsorption of Fe- and Mn-oxides rather than of newly formed calcium-arsenate and CaCO<sub>3</sub> precipitates. The typical adsorption form of As on the surface of Fe<sup>3+</sup>-oxides, such as ferrihydrite and goethite, was identified using an extended X-ray absorption fine structure instrument (EXAFS) [43,44]. They calculated the distances between Fe and As atoms on the As adsorption surface and divided the forms of As adsorption into three inner-sphere surface complexes according to their As-Fe-binding structures (Figure 6). It is considered that most of the As in solution was removed by forming these As-Fe binding structures on the Fe-slag surfaces.



Figure 3. SEM/EDS analyses of the Ca-slag before (a-c) and after (d-f) the reaction of the slag with As-contaminated water.



**Figure 4.** SEM/EDS analyses of Fe-slag before (**a**–**c**) and after (**d**–**f**) the reaction of slag with the As-contaminated water.



Figure 5. XPS analyses for Fe-slag having peaks for Fe-oxide (a) and Mn-oxide (b).



**Figure 6.** Surface complexes demonstrate arsenate (V) adsorbed to ferrihydrite ( $Fe_5O_7OH \cdot 4H_2O$ ) and goethite ( $\alpha$ -FeOOH) (modified from [43,44]).

The results from these batch experiments supported the notion that the As removal mechanism of steel slag can be divided into the precipitation of the calcium arsenate (including the co-precipitation of CaCO<sub>3</sub>) available with Ca-slag, and the adsorption of Fe and Mn oxides with Fe-slag. After reaction with the Ca-slag, the pH of the solution increased from 4.0 to 12.2, and calcium-arsenate or CaCO<sub>3</sub> was precipitated in the high-pH environment. The SEM analysis of the filtered Ca-slag after reaction showed that As-bearing carbonate minerals, such as CaCO<sub>3</sub> were evenly distributed on the Ca-slag surface. As the pH of the arsenic solution increased, the precipitation reaction of calcium and arsenic occurred over the Ca-slag surface, resulting in rapid decrease in the As concentration in solution. However, after the Fe-slag reacted with the solution, the pH was only 8.1 and most of the As was locally adsorbed to iron oxide in the Fe-slag, which is known to be effective for As adsorption. The average As content of As-bearing Fe and Mn oxides on the Fe-slag (2.8 wt%) was much higher than that of new precipitates on Ca-slag (0.4 wt%). These results suggest that the As-stabilization characteristics of Ca-slag and Fe-slag for MTs, as well as their As removal efficiencies, will be different in the field.

#### 3.3. Batch Extraction Experiment for the Efficiency of As-Extraction Reduction from MTs by Steel Slag

The As extraction experiment using the mixture of MT + stabilizer + distilled water (20:1:20 wt% ratio) was performed and the results are shown in Figure 7. The As concentration of the solution extracted from original MTs (without stabilizer and additives) was 2.34 mg/L (the leftmost in Figure 7). When 5 % Ca-slag and Fe-slag were added as stabilizers to the MTs (CS-MT and FS-MT in Figure 7), the concentration of the extracted As decreased to 0.65 and 0.62 mg/L, respectively. The reduction in As extraction efficiency by the two slags was 72.2% and 73.5%, respectively, showing high and similar As stabilization capacity. The effect of MnO as a supplementary additive on the stabilization of the As in MTs could be ignored because the change in the As concentration

in the extracted solution was very small, even after MnO was added to the MTs (CS-MnO-MT and FS-MnO-MT in Figure 7). This is because both of the steel slags contained a sufficient amount of Mn-oxide to produce arsenate from MTs (see the XRF result in Table 1). However, when the potassium phosphate ( $K_2$ HPO<sub>4</sub>) was added to MT (CS-P-MT and FS-P-MT in Figure 7), the extracted As concentrations abruptly increased to 17.95 and 14.70 mg/L (more than six times that with only MT: 2.34 mg/L). These results are similar to those of a previous study [45]. Phosphorus, which has a chemical form similar to that of As, was more successful in competition than As when the Ca-precipitation and the adsorption of As occurred; thus, much more As was extracted after the addition of potassium phosphate. These results suggest that this effect of the existence of phosphate in a stabilizer should be considered for the stabilization of As in the field.



Figure 7. As concentration of the solution extracted from MTs after the addition of slag and additive.

To observe the effect of pH on the stabilization efficiency of As in MTs in detail, an extraction experiment using a mixture of MT (1 g) + steel slag (0.05 g) + distilled water (20 mL) was performed and their results are shown in Figure 8. The As concentration in the solution extracted from the MTs increased with the decrease in the pH in solution, regardless of type of steel slag added to the MTs. However, the slope of increase was very different depending on the slag type (Figure 8). The As concentration in the solution extracted from MTs without addition of slag was 0.18 mg/L at pH 5.5 (the original pH of the MTs) and increased to 2.39 mg/L when the solution pH was 2.0. This suggests that the As concentration in the solution extracted from the MTs depends on the pH and could increase more than 13 times if the pH decreases to 2.0. When 5% Ca-slag was added to MT, the As concentration in the extracted solution was 0.02 at pH 5.5, which is similar to that of MTs with Fe-slag, but was much lower than that of MTs without slag (0.18 mg/L). As the pH of the solution decreased to 2.0, the As concentration increased to 1.38 mg/L. In the case of Ca-slag addition, the As concentration at pH 2.0 was only 58% of the As concentration of MT without slag, showing a comparative stabilization effect on As even at low pH. However, when Ca-slag was added to the MTs, the trend of increase in the As concentration with decrease of the pH in the solution was similar to that in MTs without Ca-slag. This suggests that the As stabilization efficiency of Ca-slag in MTs clearly decreases with a decrease in the pH and that the maintenance of high pH is very important for achieving the effect of extreme stabilization of As by the Ca-slag. At the early stage of stabilization for MTs in the field, the use of Ca-slag may show a high As stabilization effect because of the formation of calcium arsenate and calcium carbonate, followed by a sudden increase in pH. However, when the pH of stabilized MTs goes back down (<4.0), the amount of As extracted from the stabilized MTs also starts to increase. Moreover, the As stabilization efficiency of Ca-slag dramatically decreases to < 50 %, which does not seem to match the result in Section 3.2, in which the removal efficiency of As from the solution by Ca-slag was very high (>97%) at pH 12.5.



**Figure 8.** As concentration of the solution extracted from MTs after the addition of slag at different initial pH of the solution.

When the initial pH of the solution was 5.5, the As concentration extracted from MTs with 5% Fe-slag was 0.02 mg/L, which is similar to that from MTs with Ca-slag. However, it only increased to 0.72 mg/L when the pH of the solution was 2.0, indicating that a relatively small amount of As was extracted from the MTs, compared with that when Ca-slag was added. This increasing slope of the concentration of As in solution with decrease of the pH was very gentle. This is because of the existence of Fe or Mn oxides that strongly adsorbed As in the MTs with Fe-slag and because their solubility was low compared to that of calcium arsenate in the MTs with Ca-slag under acidic conditions (pH 2-4). Trivalent oxides such as goethite and ferrihydrite are known to have a high adsorption affinity with As (V) even at low pH and it is also considered that this adsorption of As-anions on inner-sphere surface complexes becomes stronger due to the electrical attraction at low pH (below the point of zero charge (PZC) of goethite, ferrihydrite, and hematite at pH 7.2–9.4, 7.4–8.4, and 7.4–9.5, respectively) [46]. Therefore, the reduction in the As extraction for MTs after adding 5% Fe-slag at pH 2.0 and 4.0, was 69.9% and 65.2%, respectively. This is higher than the extraction efficiencies after adding 5 % Ca-slag under the same pH conditions (42.3% and 52.2%). The results suggest that this As-extraction reduction efficiency by Fe-slag can stand out in the field, where low-pH leachate or drainage is produced by the oxidation of sulfide minerals, specifically at mine tailing storage sites. When Fe-slag was applied to As-contaminated MTs as the As stabilizer, Fe and Mn oxides in the slag and MTs strongly adsorbed As to reduce the concentration of As flowing out into the surrounding water system. Even the dissolution of As-combined Fe-oxides occurred again at low pH, but the solubilities of Fe and Mn oxides in water were much lower than those of As-bearing carbonates. Thus, they maintained relatively high reduction of the As extraction, showing high As stabilization efficiency in MTs even at low pH.

From the results of this study, the stabilization of As in MTs by steel slags can be divided into processes with two different mechanisms. The As stabilization mechanism of Ca-slag was the precipitation of Ca-source materials, which contain much calcium at high pH. This process stabilizes the As leached out from the tailings either by precipitation of the calcium arsenate (Ca-As-O(OH)) or by co-precipitation with CaCO<sub>3</sub> during the slag-MT-water reaction [16,47,48]. The high efficiency of As stabilization with Ca-slag was maintained only at high pH, and at low pH, the dissolution of As from the newly formed precipitates may occur to severely lower the stabilization efficiency. The second stabilization mechanism was the adsorption of As onto the Fe and Mn-oxide surfaces in the Fe-slag, which was relatively less affected by pH. Moreover, the comparatively high As stabilization efficiency was maintained at pH 2. Even the As stabilization efficiency of Fe-slag was lower than that of Ca-slag at high pH. At neutral pH, their stabilization efficiencies became similar, and the Fe-slag showed much higher As stabilization efficiency than Ca-slag did at low pH (<4 in Figure 8). Because this study was

based on the assumption of a leachate environment in mine tailing storage dams under acidic pH conditions, the As adsorption process of Fe or Mn-oxide minerals in Fe-slag could be a more important stabilization mechanism than the precipitation of As-bearing calcium carbonates. This paper focused on the evaluation of As stabilization mechanisms by using slags.

## 4. Conclusions

This study was focused on how to maintain the high efficiency of As stabilization by steel slag even at low pH, and how to identify the major mechanisms by which As in MTs is stabilized by steel slags. Mine tailings highly contaminated with As were selected as the target media because of very limited study on tailing-content stabilization. Two very different steel slags were used as As stabilizers. The conclusions derived from this study are listed below.

The stabilization of MT using Ca-slag resulted in the formation of (co-)precipitates, such as either calcium arsenate or CaCO<sub>3</sub> at high pH. As the pH of the solution extracted from the MTs increased, the precipitation reaction of calcium and arsenic occurred throughout the Ca-slag and MT surfaces, resulting in a rapid decrease in the As concentration in solution.

When Fe-slag was used as the stabilizer in MTs, most of the As was locally adsorbed on Fe and Mn oxides in the Fe-slag and MTs, which are known to be effective for As adsorption. The potential stabilization process of Fe-slag in MTs at low pH can be summarized in three parts: (1) The adsorption of As anions onto the surface of Fe- and Mn-oxides was accelerated because the pH condition < the PZC, which generated induced complexes for arsenate (V) at the inner-sphere. (2) The Fe-slag reduced the dissolution of As-combined iron in MTs because many of the Fe- and Mn-oxides in the Fe-slag dissolved competitively in the MTs (as well as the As-bearing minerals). (3) Precipitation of insoluble Fe-As compounds was also induced, effectively reducing the As leaching from the MTs. The As content of the As-bearing precipitates was much greater on Fe-slag than on Ca-slag, suggesting that the As adsorption process on Fe and Mn oxides in Fe-slag and MTs was a more stable mechanism than with Ca-precipitation, for binding the As in MTs. For further study to investigate the stabilization capacity in field, the long term pilot test, as well as the column test considering kinetic effects, should be performed.

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