Removal characteristics of As(III) and As(V) from acidic aqueous solution by steel making slag

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ABSTRACT

This study focused on the environmental risk of steel making slag itself, arsenic removal mechanism and re-leaching possibility of arsenic to aqueous state after the adsorption. The purpose of the study is to promote the use of steel making slag as a low-cost adsorbent for arsenic in aqueous system. Calcium was easily dissolved out from the slag and become the dominant substance in the leachate. Some of the calcium could form amorphous calcium carbonate in alkaline condition, and arsenic in the aqueous solution would be removed by being co-precipitated with or adsorbed onto the amorphous calcium carbonate. Most of the amorphous calcium carbonate containing arsenic would be bound to amorphous iron oxide of the slag. When the slag was used as an adsorbent for arsenic removal, a little amount of toxic chemicals were leached from the slag itself under pH 0.8 to 13.6. Also, 70–80% of arsenic laden on the slag was bound to amorphous iron oxide which would not easily desorb unless given a reducing and complexing condition. Showing 95–100% removal efficiency near initial pH 2, the slag, therefore, could be used as an appropriate adsorbent for eliminating arsenic in acidic aqueous solution.

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1. Introduction

Arsenic (As) is naturally released in the environment by weathering of rocks and volcanism [1]. However its most important sources are human activities such as mining, pesticide use, burning of fossil fuels and timber treatment, and these activities have caused soil contamination [2,3]. Leaching of As from contaminated soils could cause a potential risk to groundwater quality as well as food safety through As uptake by plant [4–6]. Long-term drinking of groundwater exposed to As can bring about several dysfunctions and diseases such as loss of appetite and nausea, muscular weakness, neurological disorders, and cancers [7]. Consequently, U.S. Environmental Protection Agency (USEPA) has lowered the current maximum contaminant level (MCL) of As in drinking water from 50 ppb to 10 ppb [8].

As has a complex hydrochemistry that governs the speciation and distribution of its two most predominant oxidation states, arsenate (As(V)) and arsenite (As(III)), found in nature [9–12]. As(V) is dominant and stable in aerobic environments, whereas As(III) preponderate in moderately reducing anaerobic environments such as groundwater [13]. The most common forms of As in natural water are As(V) as $H_2AsO_4^-$ and $HAsO_4^{2-}$ and As(III) as H_3AsO_3, $H_2AsO_3^-$, depending on the pH of the solution [14].

Various methods including coagulation–flocculation, ion exchange, membrane processes, and adsorption have been used for As removal [15–17]. Coagulation–flocculation was inefficient for As(III), and the production of sludge containing As is not desirable [18]. Ion exchange was found to be susceptibly influenced by the competing ions and it is also inappropriate to remove As(III) because H_3AsO_3 is not dissociated in the relevant pH range for drinking water [19]. The membrane process needed relatively high cost for practical use [17]. The adsorption method has received more attention because of its various advantages such as high efficiency, simplicity, potential of regeneration, sludge free operation and cost-effectiveness [16]. Metal oxides and hydroxides of iron or alumina are generally known to be the most common adsorbents studied for the removal of As from wastewater [20]. However, there is a need to develop an adsorbent with a practical cost so that it can be applied to As contaminated groundwater in developing countries such as Bangladesh, India and Nepal [21].

Low-cost alternatives based on mineral adsorbents and agricultural or industrial byproducts have been researched for wastewater remediation [22]. Steel making slag, one of the industrial byproduct, is generated in enormous amount annually from steel manufacturing processes [22]. The slag consist mainly iron oxides and calcium hydroxides. The iron oxides in the slag could provide adsorption

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Table 1
Chemical composition of the steel making slag.

Element	Wt. (%)
SiO_2	14.23
Al_2O_3	5.23
TiO_2	0.62
FeO_3	35.67
MgO	2.95
CaO	35.01
Na_2O	0.31
K_2O	0.15
MnO	3.60
P_2O_5	1.34
LOI[a]	0.88

[a] Loss on ignition.

Table 2
Basic properties of the steel making slag.

pH	Specific surface area (m²/g)	CEC (cmol/100 g)	Hydraulic conductivity ($\times 10^{-3}$ cm/s)
12.6	5.74	1.33	1.01

sites for anions like As, Cr, and P [23,24]. Calcium hydroxides can also increase the pH of the surrounding system and catalyze the precipitation of dissolved heavy metal cations [25,26]. Because of the availability and its advantageous constituents as an adsorbent, studies regarding the utilization of the slag as an adsorbent for heavy metals have been conducted [26,27].

Most of the investigations on As removal using slag focused on its efficiency while only a few researchers have studied on the reaction mechanisms between As and the slag [25–27]. Moreover, additional research is required on As desorption of As adsorbed slag. Regardless of its high removal efficiency, when an adsorbent is used for the removal of hazardous materials, its chemical mechanisms should be well acquainted considering the possibility of re-leaching under certain conditions.

This research focused on the As removal mechanism and the possibility of secondary contamination to promote utilization of steel making slag as adsorbent for As in aqueous system. Sorption experiments were performed to characterize As removal with initial pH of the solution ranged from 0.2 to 7.3, and the chemical and mineralogical characteristics of the As-laden slag were analyzed by Fourier transform infrared (FTIR), scanning electron microscopy-energy dispersive spectroscopy (SEM–EDS), and X-ray diffraction (XRD). To ensure its practical use as the adsorbent, two types of leaching procedures were applied for analyzing chemical characteristics of the leachate from slag itself and sequential extractions were used to estimate a possibility of As re-leaching after initial bound to slag.

2. Materials and Methods

2.1. Materials

All chemicals used in this study were reagent grade. To prepare a 100 mg/L of 1 L As solution for the experiment, 100 mL of 1000 ppm As_2O_3 (As trioxide; Kanto, Japan) and 0.4165 g of $Na_2HAsO_4 \cdot 7H_2O$ (sodium arsenate heptahydrate; Sigma, Spain) – for As(III) and As(V), respectively were dissolved in deionized (DI) water from Milli-Q apparatus (Millipore, USA).11 M HCl (hydro chloride; Kanto, Japan) and 0.1 M NaOH (sodium hydroxide; Samchun, Korea) were used for pH adjustment.

The steel making slag obtained from the Kwangyang Iron & Steel Works in South Korea was used as an adsorbent in this study. All the slag was sieved to a diameter between 0.42 and 0.84 mm to simulate an adsorbent of sand size and ensure its homogeneity. The slag was then air-dried at room temperature. The chemical compositions of the slag were analyzed using an X-ray fluorescence (XRF) spectrometer (XRF-1700, shimadzu, Japan) and summarized in Table 1. The sum of the oxide contents which show high affinity toward heavy metals such as FeO_3, SiO_2 and Al_2O_3 were 58% and the total percentage of CaO, K_2O and MgO known as major alkalinity

contributors were 38% [28]. Therefore, it is expected that the slag could be used as an adsorbent for toxic metals and increase the pH of the solution. Physical and chemical properties of the slag including pH, specific surface area, cation exchange capacity (CEC) and permeability were measured and summarized in Table 2. The pH of the slag was measured using a pH meter (Orion 3-star, Thermo Scientific, US) by mixing 10 g of the dried slag with 25 mL of DI water for 1 h. The specific surface area of the slag was measured by BET (ASAP2010, Micrometrics, US) using nitrogen adsorption, and CEC of the slag was measured by the ammonium acetate method. The permeability of the slag was measured using the constant head method (ASTM D 2434-68) [29].

2.2. Methods

2.2.1. Leaching and sorption experiments

Steel making slag has been reported to contain various toxic metals. The Korean standard leaching test (KSLT) was performed to investigate the leaching possibility of toxic elements in the slag [30,31]. At first, 500 mL of DI water of pH 5.8–6.3 was mixed with 50 g of the slag and agitated at 200 rpm for 6 h. The KSLT was slightly modified and performed to analyze the leaching characteristics of elements in the slag at various pH values. 10 g of slag were added to 100 mL of DI water at various initial pH values adjusted to 0.8–13.6 and shaken at 150 rpm at room temperature for 24 h.

Batch sorption experiments using the slag were carried out separately on As(III) or As(V) solution at various initial pH values ranged from 0.2 to 7.3 at room temperature. The experiments were initiated by adding 1 g of the slag into 100 mL of 10 mg/L As(III) or As(V) solution and the solution was shaken on a flask rotary shaker at 170 rpm for 48 h to reach equilibrium state of the reaction [32]. The final pH of the solution was measured immediately after agitation and the slag reacted with As was removed by filtration through a 0.45 μm membrane filter paper (Millipore, USA). Each filtered sample was acidified by a drop or two of 11 M HCl before the concentrations of various elements including As and Ca were measured by inductively coupled plasma-emission spectrometer (ICP-ES; ICPS-7510, Shimadzu, Japan). All of the leaching and sorption experiments were carried out in duplicate.

2.2.2. Characterization of the As-laden slag

As-laden slag was a sample made by the reaction between the slag and As solution to examine their characteristics of the chemical combination of As. To analyze the characteristics of the As-laden slag, 100 mL of 100 mg/L As(III) and As(V) solutions were reacted with 1 g of slag. Samples of the resulting slag were subjected to testing. The concentration of As in this experiment was set higher than that in sorption experiments to increase the amount of As laden onto the slag. The experiments were separately carried out on As(III) and As(V). In addition, As solutions were prepared in two different conditions: acidified to pH 2 and non-acidified. The reason why these initial pH conditions were selected is to confirm why As removal rate was especially high in condition of initial pH 2 as checked in Fig. 1. Each experimental condition and the amount of As laden on the slag were summarized in Table 3.

Fourier transform infrared with attenuated total reflectance spectroscopy was performed to analyze functional groups in the As-laden slag. FTIR spectra were acquired from Nicolet 6700 (Thermo Scientific, USA) using potassium bromide (KBr) pellets. The spectra
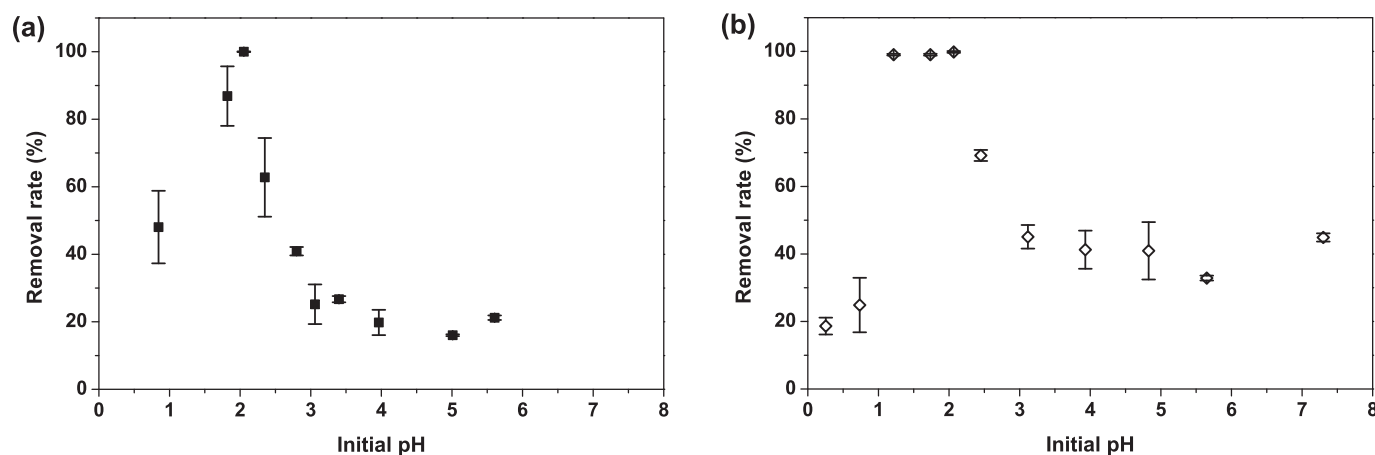
Fig. 1. Removal rate of (a) As(III) and (b) As(V) on the steel making slag at various pH values.

were recorded in the range of 4000–650 cm^{-1} with 8 cm^{-1} resolution and 32 scans were collected each time. Scanning electron microscopy-energy dispersive spectroscopy was conducted to understand the surface characteristics of the As-laden slag. SEM–EDS analyses were conducted using a SUPRA 55VP (Carl Zeiss, Germany) on Pt coated sample. X-Ray diffraction analysis was carried out to reveal information about the crystallographic structure. XRD patterns were made using D5005 (Bruker, Germany) operating with Cu Kα radiation source filtered with a graphic monochromator ($\lambda = 1.5406$) and 2θ angle was varied in the range 10–80° with 0.02 step size and 1°/min scan speed.

2.2.3. Sequential extraction of the As-laden slag

Sequential extraction experiments were conducted to investigate the distribution of As on the As-laden slag and to evaluate qualitative binding force of As on the slag. Gleyzes et al. [33] established a sequential extraction procedure suitable for As based on the methods proposed by Tessier et al. [34] and Shuman [35]. In our experiments, the procedure suggested by Gleyzes et al. [33] was slightly modified by subtracting two fractions related to manganese oxyhydroxides and organic matter and/or sulfides, since relatively small amount of manganese and organics exists in the slag and As has demonstrated a limited affinity for organic complexation in soils [36]. A detailed description of the sequential extraction procedure used in this study was given below.

2.2.3.1. Fraction F1: bound to exchangeable fraction.
The As species extracted in this fraction were retained on the slag by relatively weak electrostatic interaction. Mg^{2+} and Cl$^-$ ions would release As species by ion-exchange processes. 1 g of the slag was agitated at room temperature for 1 h with 8 mL MgCl$_2$·6H$_2$O (magnesium chloride hexahydrate; Kanto, Japan) of 1 M at pH 7. The slag was rinsed with 8 mL of DI water after extraction to collect the remaining As on the slag.

2.2.3.2. Fraction F2: bound to carbonate fraction.
The As species in this fraction is sensitive to pH changes and the release is achieved

through dissolution of the solid. The solid residue from *F1* was agitated at room temperature for 15 h with 8 mL of 1 M NaOAc (sodium acetate; Yakuri, Japan) at pH 4.5 adjusted by 17 M HOAc (acetic acid; Junsei, Japan). The slag was rinsed with 16 mL of DI water to collect the remaining As on the slag.

2.2.3.3. Fraction F3: bound to Fe oxides fraction.
The fractions bound to oxides are thermodynamically labile under reducing and complexing condition. By controlling the Eh and pH of decomposition reagents, dissolution of some or all the metal oxide phase can be achieved.

F3(a); amorphous Fe oxides: the solid residue from *F2* was agitated at room temperature for 4 h with 50 mL of 0.2 M NH$_4$Ox (ammonium oxalate; Yakuri, Japan) and 0.2 M HOx (oxalic acid; Junsei, Japan) in the dark. This reagent could not dissolve As bound to crystalline Fe oxides unless the catalyzing effect of light was present. The slag was rinsed with 3 mL of DI water to gather the remaining As.

F3(c); crystalline Fe oxides: the solid residue from *F3(a)* was agitated in boiling water bath for 0.5 h with 50 mL of 0.2 M NH$_4$Ox, 0.2 M HOx and 0.1 M C$_6$H$_8$O$_6$ (ascorbic acid; Yakuri, Japan). The slag was rinsed with 3 mL of DI water because of the same reason.

2.2.3.4. Fraction F4: residual fraction.
The solid residue from *F3(c)* was first digested on hot-plate with 10 mL of 28.2 M HF (hydrofluoric acid; JT Baker, USA) and 2 mL of 11.6 M HClO$_4$ (perchloric acid; Junsei, Japan) to near dryness; subsequently, the mixture was digested again with 10 mL of HF and 1 mL of HClO$_4$ to near dryness. Finally, 1 mL of HClO$_4$ alone was added to the residue and evaporated nearly totally. Afterward, 25 mL of 11 M HCl was added to dissolve and dilute the residue.

After each extraction, the slag suspension was centrifuged at 4000 rpm and the supernatant solution was filtered through a 0.45 μm membrane filter paper. The slag residues were washed with DI water, and then washing solution was carefully decanted and added to the each supernatant solution. This solution was analyzed for As by ICP-ES. The resulting residue was dried for the next step.

3. Results and discussion

3.1. Leachate analysis of steel making slag

The KSLT was conducted to examine the leachability of the toxic elements from the steel making slag. The concentrations of the selected toxic elements and their regulation levels in South Korea were summarized in Table 4. Most of the toxic elements were

Table 3
Experimental condition and the amount of As on the As-laden slag.

Experimental condition	As laden amount (mg/g)
As(III) in pH 2 solution	3.39
As(V) in pH 2 solution	6.37
As(III) in DI water	1.43
As(V) in DI water	2.83
DI water only	0 (without As)

Table 4
Concentrations of toxic elements in the leachate from the steel making slag by the Korea standard leaching test (unit: mg/L).

Contents	Steel making slag	Regulation level in Korea
Pb	<0.04	3.0
Cu	0.01	1.0
As	<0.05	1.5
Hg	<0.001	0.005
Cd	<0.002	0.3
Cr^{6+}	<0.007	1.5
CN	<0.01	1.0
P[a]	<0.0005	1.0
TCE	<0.008	0.3
PCE	<0.002	0.1

[a] Organophosphorus compounds.

scarcely leached from the slag. Cu leaching was only above detection limit, but it was much lower than its regulation. These results indicate that there is a low possibility of secondary contamination due to the slag itself as adsorbent.

The final pH values and the dissolved metal concentrations in the leachate from the slag obtained by the modified KSLT were listed in Table 5. The initial pH values of leaching solutions for the modified KSLT were adjusted from pH 0.8–13.6. All of the final pH values of the leachate were increased from the initial pH values with the exception of the initial pH 13.6. The dissolved Ca concentration was highest among all the elements in the various pH conditions. The most common constituent in the steel making slag was calcium oxide (CaO) (Table 1), presumably due to the CaO which was used as the addition agent in the steel making process. The dissolution of CaO in the slag could cause the Ca dissolution in the leachate and the pH increase [25], and these tendencies were enhanced as initial pH decreased. Iron oxide (FeO) also comprised a high fraction in the slag, but the leaching of Fe was not significant. The concentrations of toxic heavy metals including As, Cd, Cr, Pb, Se and Zn were below the detection limits (<0.1 mg/L) for the all pH ranges. Considering the solid to liquid ratio of 1:10 in the experiments, trace metal dissolved from the slag could be also negligible due to the excessive amount of groundwater in the field condition even under acidic or alkaline conditions.

3.2. As sorption characteristics of the steel making slag at various initial pH values

A series of batch sorption experiments with various initial pH values were conducted to investigate the characteristics of As removal by the slag. The removal rates of As(III) and As(V) by the slag as a function of initial pH were shown in Fig. 1. It is suggested that both As(III) and As(V) have a similar removal mechanism, since the tendencies of removal under series of initial pH conditions were similar to each other [30,31,37]. The removal rates of both As(III) and As(V) remained around 20% and 40%, respectively when the initial pH values were above 3. This yields similar results with those of other researches which show that As(V) is generally removed more efficiently than As(III) by adsorbents containing Ca or Fe elements [14,38,39]. The removal rate, however, increased sharply with the decrease of the initial pH from 3 to 2 for both As(III) and As(V) then inversely showed a dramatic decrease under the initial pH condition of less than 2.

The effects of the initial pH on the concentration of Ca leached from the slag and the final pH of the solution in contact with the slag were summarized in Fig. 2(a and b), respectively. Ca concentrations increased slightly as the initial pH decreased, however they jumped up rapidly in the initial pH less than 3. In the case of the final pH value, all the data showed a sharp increase compared to their initial values of pH after the As solution was reacted with the slag. The slag acted as a pH buffer due to its alkalinity and maintained the final pH of an acid solution to 9–10. However, when in a strong acid solution with a pH of less than 3, the acidity of the solution might exceed the slag's buffer capacity. As the acidity of the initial solution got gradually stronger, the final pH of the solution of which the slag was applied drops with. Eventually, when the initial pH of the solution is lower than 2, the final pH remained lower than 7, which is an acidic state. There was no significant difference between As(III) and As(V) in Fig. 2(a and b).

As is one of the well-known heavy metal anion and it could be efficiently adsorbed on various types of adsorbents including clay, oxides or hydroxides surfaces of Al, Fe and Mn, $CaCO_3$, and organic matter in low pH condition [36]. It has been proven that Ca enhances As removal via precipitation and several studies have shown that As removal increased with Ca concentration [18,40,41]. In our experiment, the final pH values and the Ca concentration were in a favorable condition to remove the As by adsorption or precipitation as the initial pH value was decreased. However, although the removal rate of As showed increasing tendencies when the initial pH value decreased until 2, it soon dramatically decreased when the initial pH value was below 2. These results indicate that adsorption and precipitation of As onto the slag surface could not be fully explained by the decline phenomenon of the removal rate under the initial pH lower than 2.

3.3. Characterization of the As-laden slag

The FTIR spectra of the slag reacted at various conditions in Table 3 are shown in Fig. 3. A wide band covered from 1400 cm^{-1} to 1500 cm^{-1} corresponding to amorphous $CaCO_3$ and another band was at 874 cm^{-1} corresponding to calcite [42] in the slag reacted with DI water. The reactions with As(III) and As(V) caused the

Table 5
Leaching results of selected elements from the steel making slag at various pH values by the modified KSLT (unit: mg/L).

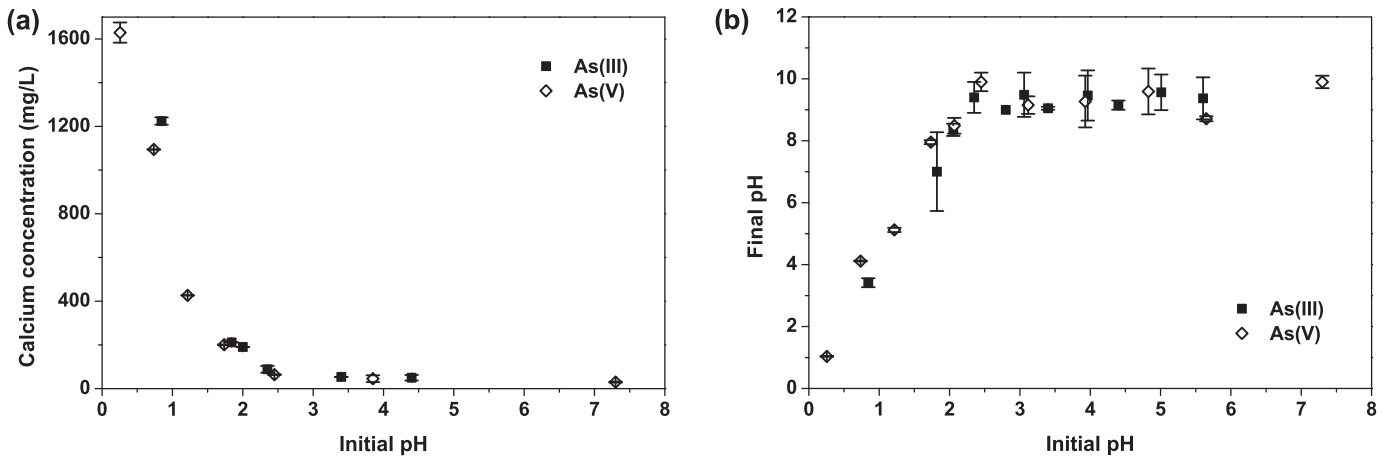| Initial pH	0.8	1.5	2.0	3.0	5.0	8.3	9.1	13.6
Al	<0.1	<0.1	2.7	0.7	1.3	2.2	2.2	4.0
Fe	241.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Mg	69.8	72.0	0.3	<1.0	<1.0	<1.0	<1.0	0.2
Ca	1746.0	1847.0	241.0	137.7	94.7	55.5	55.5	9.0
Mn	43.1	11.6	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
SO_4	128.7	59.3	14.6	8.8	<1.0	<1.0	<1.0	<1.0
B	0.6	0.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
As	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cd	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cr	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cu	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pb	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Se	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zn	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Final pH	5.6	8.5	11.9	12.3	12.5	11.6	11.5	13.1

Fig. 2. Effect of the initial pH on (a) the Ca concentration leached from the slag and (b) the final pH of the solution reacted with the slag.
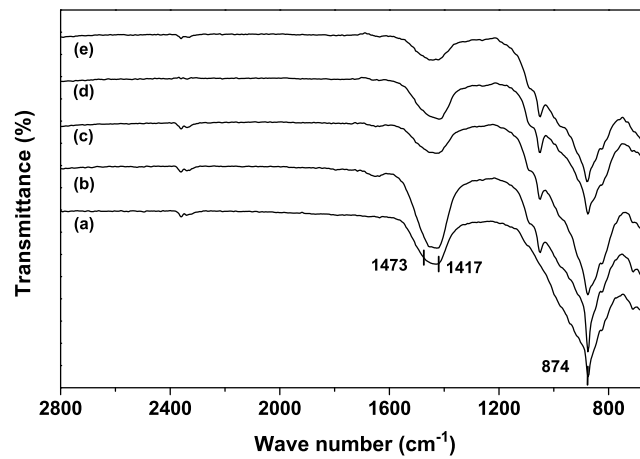

Fig. 3. FTIR spectra of the steel making slag reacted with (a) As(III) in pH 2, (b) As(V) in pH 2, (c) As(III) in DI water, (d) As(V) in DI water, and (e) DI water.

increase of transmittance with respect to amorphous $CaCO_3$ and calcite. The transmittance at $1417 \, cm^{-1}$ corresponding to amorphous $CaCO_3$ especially increased proportionally to the As laden amount on the slag (Fig. 4). The transmittance at $874 \, cm^{-1}$ corresponding to calcite was varied with the experimental conditions shown in Table 3, but showed irregular variations unlike the transmittance of amorphous $CaCO_3$. This result indicated that the formation of $CaCO_3$, especially amorphous $CaCO_3$, on the slag could play an important role in the removal of both As(III) and As(V) species.
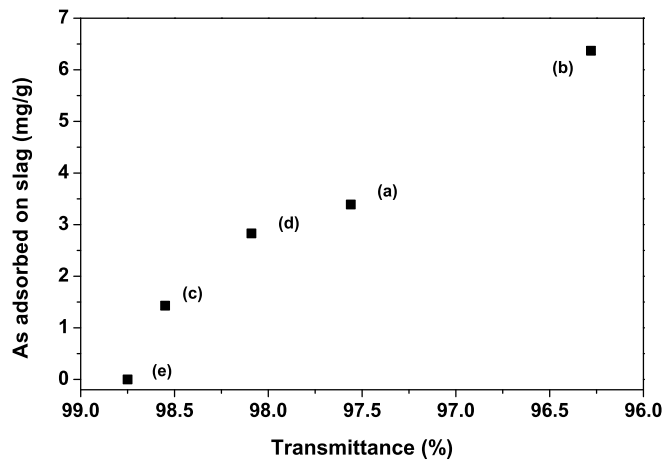

Fig. 4. Relationship of the As amount laden on the slag and the FTIR transmittance spectra ($1417 \, cm^{-1}$) of the slag reacted with (a) As(III) in pH 2, (b) As(V) in pH 2, (c) As(III) in DI water, (d) As(V) in DI water, and (e) DI water.
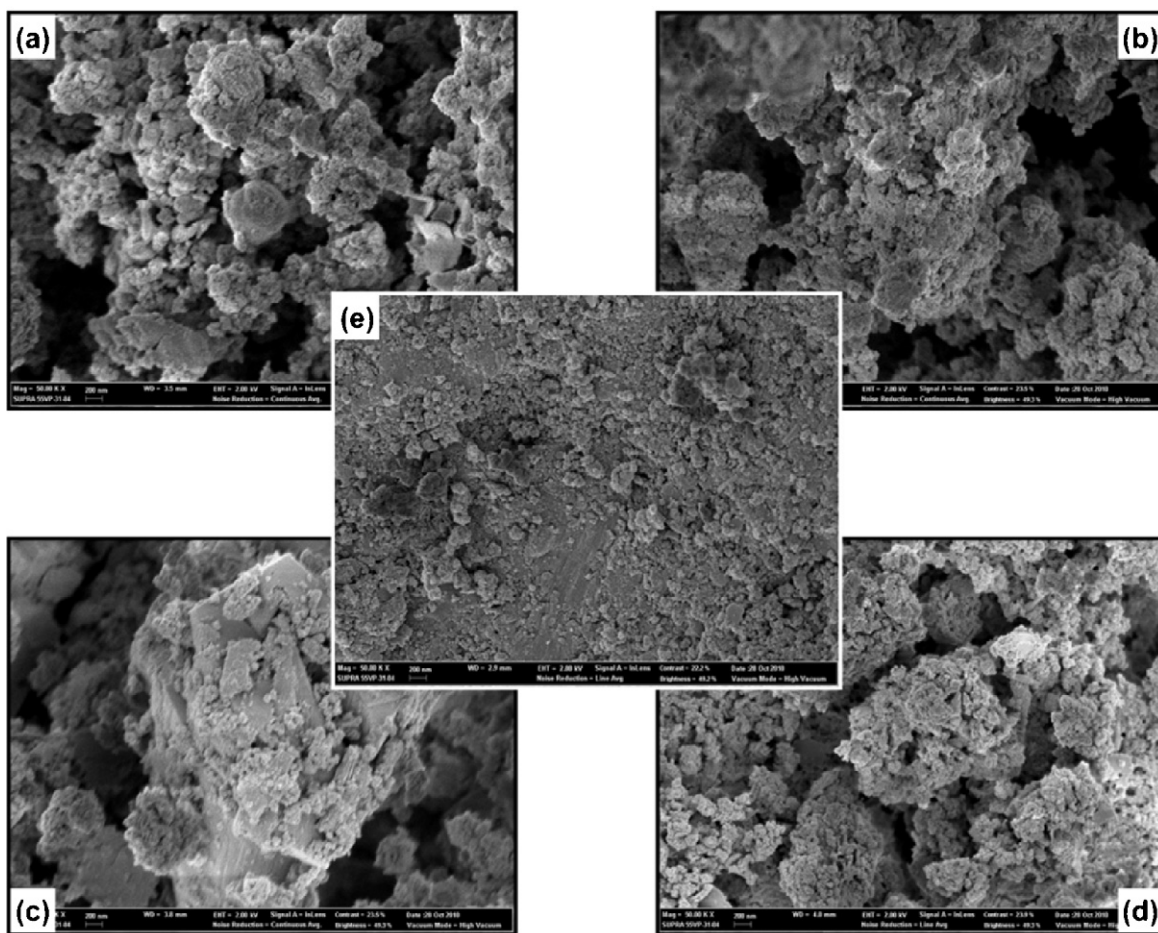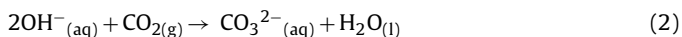
Fig. 5. SEM images of the steel making slag reacted with (a) As(III) in pH 2, (b) As(V) in pH 2, (c) As(III) in DI water, (d) As(V) in DI water, and (e) DI water ($\times$100,000).

$CaCO_3$ can be formed while Ca^{2+} ion in the solution reacts with carbon dioxide (CO_2) in the atmosphere. Dunsmore [43] suggested a reaction formula shown in (1) which shows that CO_2 in the atmosphere can be hydrated and form $CaCO_3$ with Ca^{2+}.

$$Ca^{2+}_{(aq)} + CO_{2(g)} + H_2O_{(l)} \leftrightarrow CaCO_{3(s)} + 2H^+ \tag{1}$$
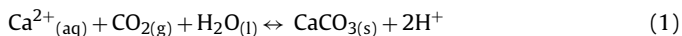
Also, CO_2 in ambient air could be spontaneously wet scrubbed by an alkaline solvent (reaction formula (2)) [44].

$$2OH^-_{(aq)} + CO_{2(g)} \rightarrow CO_3^{2-}_{(aq)} + H_2O_{(l)} \tag{2}$$

$$(\Delta G^\circ = -56.1 \, \text{kJ/mol})$$

$$Ca^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \leftrightarrow CaCO_{3(s)} \tag{3}$$

Carbonate (CO_3^{2-}) formed by (2) sequentially can form $CaCO_3$ with Ca^{2+} [45]. Forward reactions of these mentioned reaction formulae regarding formation of $CaCO_3$ can be accelerated in alkaline condition. These results were in agreement with our findings that the formation of $CaCO_3$ would be restricted in acidic condition.

It has been reported that As can be co-precipitated during formation of $CaCO_3$ or adsorbed on $CaCO_3$ by other researchers [18,46–49], and the formation of $CaCO_3$ could be accelerated with high concentration of Ca [50–54]. Guan et al. [18] reported that $CaCO_3$ could not be formed under acidic condition. An alkaline environment was more suitable for the formation of $CaCO_3$ and more significant at higher pH. In our experiment, the Ca concentration began to increase sharply below initial pH 3. And the final pH of

the solutions was in the alkaline condition when the initial pH was above 2 (Fig. 2(b)). Thus, the initial pH from 2 to 3 could be the most favorable condition to form $CaCO_3$ by providing abundant Ca quantity and maintaining the final pH as an alkaline condition. It could be also confirmed in Fig. 1 that the removal rate of both As(III) and As(V) increased below initial pH 3 as Ca concentration increased, but the removal rate soon dropped below initial pH 2, exceeding the pH buffer capacity of the slag, resulting in a final pH lower than 7. Therefore, it could be concluded that As would be co-precipitated with or adsorbed on $CaCO_3$. Amorphous $CaCO_3$, which showed linear relation with the amount of As laden on the slag in Fig. 4, was suggested to be a probable candidate among $CaCO_3$ forms in our experiment. Unless given an extremely acidic state of a pH lower than 2 which exceeds the buffer capacity of the slag, the slag, with its high removal and neutralization efficiency may be sufficiently reactive to be used as an adsorbent for As areas such as acid mine drainages. Ahn et al. [25] actually showed various types of slags that were more effective for acid mine drainages than alkaline leachates.

In Fig. 5, the SEM images of the As-laden slag illustrated that the reaction with As changed the surface morphology of the slag significantly. The surface morphology of the slag was changed more clearly at pH controlled conditions (Fig. 5(a and b)) than pH uncontrolled conditions (Fig. 5(c and d)). The surface morphology of the slag would also be affected with oxidation state of As. In the interaction between the As solution and the slag, increased precipitate formation was noticed in the case of As(V) (Fig. 5(b and d)) than As(III) (Fig. 5(a and c)). Based on the FTIR results, it could
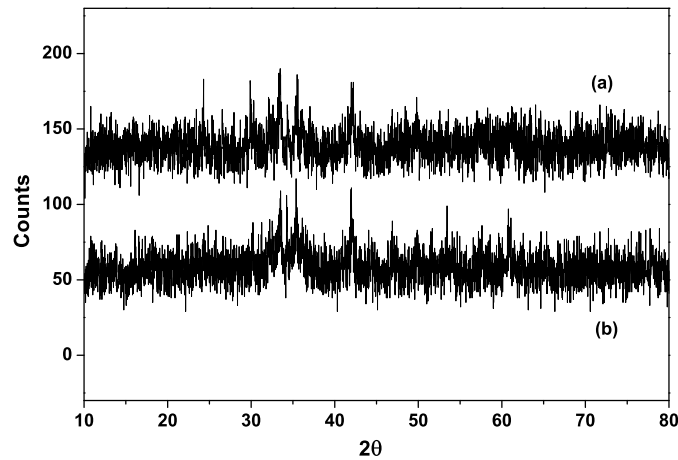
Fig. 6. X-ray diffraction pattern of the steel making slag reacted with (a) As(III) in pH 2 and (b) DI water.

be inferred that the newly formed precipitate from the reaction between the slag and As was amorphous $CaCO_3$. Thus, this SEM images could support the FTIR result that the amount of amorphous $CaCO_3$ increased proportionally to the quantity of As laden on the slag. The main purpose of the EDS analysis was to identify any possible mineral forms between As and other elements [55]. The elemental mass percentages calculated from the EDS analyses were in the similar order as those determined by XRF analysis; O, Fe, Ca, Si, Al, Mg and Mn. However, it was detected that Ca ratio was lowered in the EDS data than XRF in pH 2 condition, since a plenty of Ca were leached from the slag reacted by strong acid. Apparent relations about atomic ratio between As and Al or Fe which could form mineralogical structures were not found from the EDS data.

The XRD patterns of the slag reacted with As(III) and DI water were shown in Fig. 6. According to the XRD pattern of the slag reacted with DI water (Fig. 6(b)), the slag can be identified as a poorly crystalline material. The absence of crystallinity increase after loading As on the slag (Fig. 6(a)) indicated that there were a few crystalline phase transformations after As removal by the slag. The FTIR results showed that the precipitate newly formed in the reaction between As and the slag was amorphous $CaCO_3$, and this could explain the reason why any clear peak did not occur in the XRD pattern.

3.4. As-fractionation on the slag by sequential extraction experiment

The results obtained by the sequential extraction experiment could provide information on the As distribution and evaluate the qualitative binding force of As on the slag. As distributions on the slag at four different conditions (Table 3) were shown in Fig. 7. Both of As(III) and As(V) were mainly extracted in the fraction associated to amorphous iron oxides (*F3(a)*) particularly in the case of pH 2 solution which represents 76% and 88% in As(III) and As(V), respectively. As bound to oxides (*F3(a)* and *F3(c)*) can be extracted only in reducing and complexing conditions [55–57]. Although the amount of As extracted in the *F4* were below 25% in all cases, As laden on the slag might not be easily released to aqueous state, since sums of the *F1* and *F2* being easily soluble fractions were also low as average of 13%.

The FTIR and SEM results showed a noticeable change of the slag after its reaction with As. Through these phenomena, it was supposed that when As in aqueous solution was removed by the slag, most of the As would be removed by being contained to amorphous $CaCO_3$ formed from Ca which was leached from the slag. It could also be assured by the sequential extractions that most of these amorphous $CaCO_3$ containing the As were combined with amorphous iron oxides in the slag. The results of the sequential
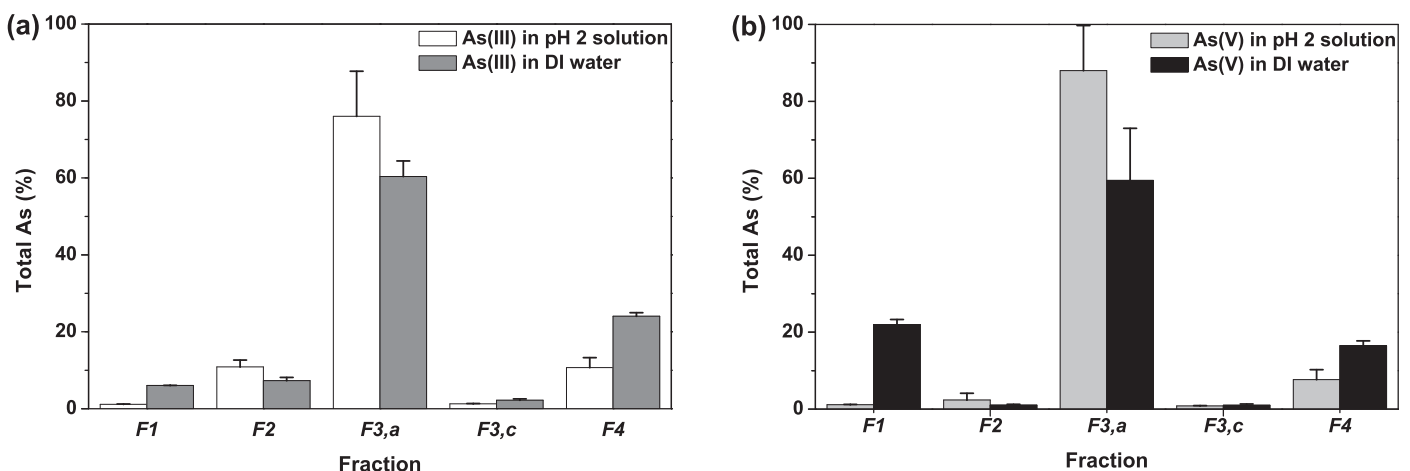

Fig. 7. As distribution on the steel making slag reacted with (a) As(III) and (b) As(V) by sequential extractions.

extractions can be supported by the XRF analysis that indicated a highest percentage of FeO_3 in the slag and the XRD pattern which showed that most of its form was identified as poorly crystallized form.

4. Summary and conclusion

This study focused on the As removal mechanism and the possibility of secondary contamination or As re-leaching to promote the use of steel making slag as a low-cost adsorbent for As in aqueous system.

The slag used in this study was made up with various elements; especially Fe (36%) and Ca (35%) consist mostly of the slag. Ca was relatively easy to dissolve out from the slag and become the dominant substance in the leachate. In addition, the Ca concentration showed a tendency to have a sharp increase when the initial pH was lower than 3. Some of these Ca could form amorphous $CaCO_3$ in alkaline condition resulted from the high pH of the slag, and As in the aqueous solution would be removed by being co-precipitated with or adsorbed onto the amorphous $CaCO_3$. Most of the amorphous $CaCO_3$ containing As would be bound to amorphous iron oxides of the slag.

When steel making slag was used as an adsorbent for As removal, As would be fixed to the slag following above mechanism and it would not be easily desorbed unless reducing and complexing condition was given. Also, a little amount of toxic chemicals such as heavy metals were leached from the slag itself even under acidic or alkaline condition. It meant the possibility of secondary contamination would be low in field. Showing a high removal efficiency at acid condition and relatively low possibility of secondary contamination, the slag, therefore, could be used as an appropriate adsorbent for eliminating As in aqueous solution.

Acknowledgments

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