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Combined neutralization-adsorption system for the disposal of hydrothermally altered excavated rock producing acidic leachate with hazardous elements

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Abstract

Hydrothermally altered rock excavated in a tunnel project produces acidic leachate containing hazardous elements that include arsenic (As), lead (Pb), copper (Cu) and zinc (Zn). To mitigate this problem, this paper evaluated a combined neutralization-adsorption system that used readily available and cheap reagents like calcium carbonate ($CaCO_3$) and partly-weathered volcanic ash. Batch neutralization experiments showed that $CaCO_3$ was effective in raising the pH of the leachate around neutral while the batch adsorption experiments illustrated that the volcanic ash sample collected near the tunnel project area was highly capable of adsorbing arsenate (As[V]), Pb, Cu and Zn. Under column conditions, the amount of hazardous elements released from the rock increased by several folds and their breakthrough curves had flushing-out trends. The mechanisms of As and heavy metals release probably include the dissolution of soluble phases and pyrite oxidation. Addition of $CaCO_3$ in the column experiments based on estimates from the batch results underestimated the amount of neutralizer needed to adjust the effluent pH to around 8, resulting only in slight increase of the pH. Nevertheless, the presence of $CaCO_3$ drastically reduced the amount of hazardous elements released from the altered rock especially during the initial stages of the column experiments. Combining neutralization and adsorption effectively reduced the amount of As and heavy metals in the effluent throughout the duration of the column experiments, which is attributed to the slight neutralizing effect of volcanic ash that raised the pH around circumneutral as well as its rich Al and Fe oxyhydroxide/oxide contents. The combined system immobilized the hazardous elements through a combination of co-precipitation and adsorption reactions and showed potential as an alternative method for the disposal of altered rocks producing acidic leachate.

Keywords: hydrothermally altered rock, arsenic, heavy metals, neutralization, adsorption

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1. INTRODUCTION

Hydrothermally altered rocks, which are widely distributed in geologically active volcanic regions like Japan, are formed due to the migration of superheated fluid/water called hydrothermal solutions through fractures and fissures in rocks. Enrichment of these rocks with toxic elements like Pb and As preferentially occurs in and around precipitated pyrite grains, which are oxidized upon exposure to the atmosphere producing acidic leachate containing these toxic elements (Igarashi *et al*., 2008; Tabelin and Igarashi, 2009). Tunnels for roads, railways and other projects in the island of Hokkaido have excavated these kinds of rocks, which are potential sources of soil and groundwater contamination. At the moment, excavated altered rocks are being disposed of by applying landfill liners to prevent the interaction of the rock and rainwater similar to those utilized in the disposal of municipal and industrial wastes (Katsumi *et al.*, 2001; Lundgren and Soderblom, 1985; Malusis *et al.*, 2003; Rapti-Caputo *et al.*, 2006; Wijeyesekera *et al.*, 2001), but this method is very expensive and impractical so that alternative methods are being explored.

Leaching of As and Pb from altered rocks and their mechanisms of release are both strongly pH dependent (Tabelin and Igarashi, 2009; Tabelin et al., 2012a). In addition, minor and trace minerals that have strong effects on the pH of the rock when in contact with water (e.g., calcite and pyrite) are important in the mobilization of these hazardous elements (Tabelin et al., 2010, 2012a,b). The best way to immobilize As and Pb from altered rocks is through adsorption and precipitation, respectively, and these processes are most effective in the circumneutral pH range (Tabelin and Igarashi, 2009; Tabelin *et al.*, 2010; Tabelin *et al.*, 2012a). Based on these previous studies, we have developed a disposal method called the neutralization-adsorption system as a simple and low cost alternative to special landfilling. The principles behind this system are simple: identify the mechanisms of As and heavy metal release from the altered rock, minimize the extent of these mechanisms, and provide

additional countermeasures to immobilize any hazardous element released from the rock. In contrast to traditional landfills that prevent the interaction of wastes with water through the use of special barriers, the concept of this system more closely resembles a permeable reactive barrier (PRB). In this proposed system, water is allowed to percolate into the waste, albeit at a lower infiltration rate, and the "loaded" leachate would then pass through the adsorption layer where immobilization of the hazardous elements would take place. A conceptual model of this new neutralization-adsorption system is presented in Figure 1.

The Teine mine area, which is located northwest of Sapporo, Hokkaido, Japan, consists of Late Miocene andessite tuff breccia and mudstone, extruded by altered andesite (propylite). The veins occur mainly in altered andesite, which are grouped into Mitsuyama, Koganezawa and Bannozawa (Imai, 1999). The mine produced gold (Au), silver (Ag) and copper (Cu) from 1893 until 1971 (Imai, 1978; Sugimoto, 1952; Watanabe, 1936; Watanabe 1943; Watanabe 1944). A new tunnel was constructed near the Mitsuyama deposit in 2006 to collect acid mine drainage for the new water treatment system installed in this mine. The construction of this new tunnel excavated hydrothermally altered rock rich in hazardous elements like As, Pb, Cu and Zn.

The main goal of this study is to evaluate the effectiveness of the neutralization-adsorption system in the immobilization of toxic elements like As and heavy metals such as Pb, Cu and Zn. The neutralizer and adsorbent selected for our experiments are calcium carbonate ($CaCO_3$) and partly-weathered volcanic ash, respectively. To achieve our goal, we first evaluated the effects of $CaCO_3$ on the leachate chemistry through batch neutralization experiments. Second, batch adsorption experiments using the ash sample with high amorphous aluminum (Al) and iron (Fe) mineral contents were carried out to characterize its adsorption capacity and affinity for As, Pb, Cu and Zn. Finally, column experiments were conducted using different neutralization and adsorption configurations to compare the effects

of using neutralization only and a combined neutralization-adsorption system. If this alternative disposal system is effective, it could provide a more economical, practical and safe way of disposing these hazardous excavated rocks.

2. MATERIALS AND METHODS

2.1 Hydrothermally altered rock, volcanic ash and calcium carbonate

The hydrothermally altered rock sample used in this study was collected from the bulk excavated rock stored in an interim disposal site that had already been exposed to the atmosphere for ca. 6 months. This interim disposal site is used until the final disposal of the rock and/or while waiting for the thawing of snow in winter. The test material (*i.e.*, partly-oxidized altered rock) was selected because it would most likely represent the actual waste rock for disposal. The rock sample was air dried, crushed and sieved using a 2 mm aperture screen. The partly-weathered volcanic ash sample was collected around the tunnel area. Volcanic ash was selected as an ideal adsorbent because it is inexpensive and widespread in Hokkaido. Furthermore, volcanic ash has been shown as an effective adsorbent of hazardous elements, such as As and heavy metals, because of the presence of amorphous and crystalline Al and Fe oxyhydroxide/oxide phases (Dixit and Hering, 2003; Toscano *et al*., 2008). The volcanic ash sample was also air dried and sieved using a 2 mm aperture screen. In preparation for the chemical and mineralogical analyses, the rock and ash samples were further ground to < 50 μm. Chemical analysis of the samples was carried out using an X-ray fluorescence spectrometer, Spectro Xepos (Rigaku Corporation, Japan), while their mineralogical composition was determined utilizing an X-ray diffractometer, MultiFlex (Rigaku Corporation, Japan). Both analyses were done using pressed powders of the samples. Amorphous Al and Fe phases in the ash, which are important in the adsorption of As and heavy metals, were determined using acidic oxalate solution extraction. Calcium carbonate

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was selected as the neutralizer of the acidic leachate because it is also inexpensive and widely used in the treatment of acid mine drainage.

2.2 Batch leaching, neutralization and adsorption experiments

Batch leaching experiments were carried out by mixing 15 grams of the crushed rock sample and 150 mL of deionized water at 120 rpm for 24 hours. A similar procedure was used for the neutralization experiments; the only difference was the addition of $CaCO_3$ (analytical grade powder) ranging from 0.5 to 25 % of the weight of the rock sample used. After shaking, the pH values of the leachates were measured, and then the leachates were filtered through 0.45 μm Millex® cellulose acetate membrane filters (Millipore Corporation, USA). The filtrates were acidified using hydrochloric acid (HCl) prior to the chemical analysis. The degree of concentration reduction of important metallic and metalloid species in the leachate was described as residual percentages. These values were calculated using the following equation:

$$\% \ residual = \frac{C_0 - C}{C_0} \times 100 \quad （1）$$

where, *% residual* is the residual percentage (%), C_0 is the initial concentration prior to neutralization (mg/L), and C is the concentration after neutralization (mg/L).

The batch adsorption experiments were done to characterize the adsorption properties of the volcanic ash sample for As[V], Cu, Pb and Zn. The ash was added in various amounts to solutions with known As[V], Cu, Pb, or Zn concentration prepared from reagent grade standard solutions. The mixtures were then shaken at 120 rpm for 24 hours. Leachates were then filtered through 0.45 μm Millex® filters prior to the chemical analyses. Adsorption isotherms were obtained using the following equation:

$$q = \frac{(C_0 - C) \cdot V}{W} \quad (2)$$

where, q is the adsorbed amount (mg/g), C_0 is the initial concentration (mg/L), C is the equilibrium concentration (mg/L), V is the volume of solution (L), and W is the amount of the ash sample added (g).

2.3 Column experiments

The columns used are made of acrylic tubes mounted on steel stands with each stand accommodating three columns. The columns have heights of 350 mm and inner diameters of 52 mm. Covers were also designed with small perforated holes to simulate rain and protect the columns from outside contaminants and dusts. A schematic diagram and details of the column dimensions are shown in Figure 2.

Five columns were constructed and details of their initial conditions are listed in Table 1. For standardization, the rock layer (with or without $CaCO_3$) and ash layer were compacted to have bulk densities of 1.83 and 0.77 g/cm^3, respectively. The neutralizer was mixed thoroughly with the altered rock prior to the construction of rock layers with neutralization. Fifty milliliters of deionized water (18 MΩ·cm) was poured into each column once a week through the rainfall simulator. This amount corresponds to a weekly precipitation of 23.5 mm, which is roughly equivalent to the average weekly rainfall in Sapporo. Deionized water was allowed to infiltrate by gravity to simulate the water movement at conditions close to the actual field setting. After ca. 2 days, effluents were collected, filtered through 0.45 μm Millex$^®$ filters, acidified using HCl and analyzed.

For the remainder of this paper, the columns are referred to by the following notations:

- column composed of the altered rock only is called case R,
- columns with neutralizer added are called cases R+N1 and R+N2 for 1% and 2% $CaCO_3$, respectively,

- columns with both neutralizer and adsorption layer are referred to as cases R+N1+A and R+N2+A corresponding to 1% $CaCO_3$ + 2 cm thick ash layer and 2% $CaCO_3$ + 2 cm thick ash layer, respectively.

In addition, "leachate" will be used to denote liquid samples from batch experiments while samples collected in the columns will be called "effluent".

2.4 Chemical analysis

Concentrations of As, Cu, Pb, Zn and coexisting ions greater than 0.1 mg/L were analyzed using an inductively coupled plasma atomic emission spectrometer (ICP-AES) (ICPE – 9000, Shimadzu Corporation, Japan). Arsenic concentrations less than 0.1 mg/L were analyzed using a hydride generation attachment coupled with the ICP-AES. In preparation for the hydride generation analysis, 30 ml of leachate or effluent was mixed with 15 ml of 12 M HCl, 2 ml of 20% potassium iodide (KI) solution and 1 ml of 10% ascorbic acid solution, and then diluted with deionized water to 50 ml. All chemicals used in the preparation and analysis were reagent grade. Low Cu, Pb and Zn concentrations (<0.1 mg/L) were determined using an ultrasonic aerosol generator attachment coupled with the ICP-AES. The standard ICP-AES method (*i.e.*, without attachments) used has a margin of error of ca. 2 – 3% whereas the more sensitive hydride generation and ultrasonic aerosol generator methods have uncertainties of ca. 5%.

2.5 Geochemical modeling

The saturation indices (*SI*) of Al and Fe oxides, oxyhydroxides and hydroxides were calculated from the measured leachate and effluent chemistries using PHREEQC (Parkhurst and Appelo, 1999) with the THERMODEM database compiled by the French Geological Survey (BRGM Institute). These thermodynamic calculations could provide additional insights into the processes controlling the mobilization and immobilization of the hazardous elements in our system.

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3. RESULTS

3.1 Properties of the altered rock and volcanic ash

The chemical and mineralogical compositions of the altered rock and partly-weathered volcanic ash used in this study are listed in Tables 2 and 3, respectively. The altered rock sample contains significant amounts of S at 10.6 wt%, which could be attributed to the presence of pyrite. It also has significant As, Pb, Cu and Zn contents at 150, 375, 68 and 62 mg/kg, respectively. Results of the leaching experiment of the altered rock sample using deionized water illustrated that its pH was acidic and it released significant amounts of As, Pb, Cu and Zn (Table 4). The leaching results also showed relatively high concentrations of Fe and SO_4^{2-}, which suggests that dissolution of soluble secondary minerals and oxidation of pyrite both occurred. The ash sample used as adsorbent is composed mostly of quartz, anorthite and chlorite, and is rich in Al and Fe bearing minerals (Tables 2 and 3). It also has significant amorphous Al and Fe contents at 24 and 13.6 mg/g, respectively, indicating that this ash sample is a potentially strong adsorbent of As and heavy metals.

3.2 Batch neutralization and adsorption experiments

Figure 3 illustrates the pH variation of the leachate as a function of the amount of neutralizer added to the altered rock. The leachate pH was initially acidic at 2.6 and addition of only 2.5% $CaCO_3$ (3.75 g) effectively increased the pH around neutral. Once the neutral pH range was reached, higher $CaCO_3$ addition had no significant effect on the pH of the leachate. The reduction in the concentrations of dissolved hazardous elements like As, Cu, Pb and Zn as well as major metallic species, such as Al and Fe as a function of pH are presented in Figures 4 and 5, respectively. The % residual of the hazardous elements decreased with increasing pH of the leachate. When the pH of the leachate increased to about 4, the % residual dropped to around 50 %. Increasing the pH until up to the neutral range effectively lowered the %

residual to almost zero. Similarly, the high concentrations of Al and Fe (Al: 70.8 mg/L; Fe: 378 mg/L) decreased to less than 1 mg/L after neutralization.

Calculated saturation indices (SI) of gibbsite (Al(OH)$_3$), diaspore (AlOOH), Fe(OH)$_3$ and goethite (FeOOH) as well as those of malachite (Cu$_2$(OH)$_2$CO$_3$), smithsonite (ZnCO$_3$), hydrocerrusite (Pb$_3$(CO$_2$)$_3$(OH)$_2$) and Pb(OH)$_2$ in the leachate are shown in Figure 6. Our results show that only Cu is predicted to precipitate as malachite due to the addition of the neutralizer while Pb, As and Zn remain dissolved in solution. Also, the precipitation of both Al and Fe-oxyhydroxides/oxides are thermodynamically possible at pH >4.

The sorption behaviors of As[V], Cu, Pb, and Zn onto volcanic ash and the corresponding Freundlich isotherms of best fit are shown in Figure 7. The partition coefficients (K_F) (*i.e.*, ratio of adsorbed amount q to liquid-phase equilibrium concentration C) for As[V], Pb, Cu and Zn are equal to 1.87, 0.37, 0.13 and 0.07 mg/g, respectively at C equal to 1 mg/L. These results indicate that the volcanic ash sample is capable of adsorbing As[V], Pb, Cu and Zn. Also, the values of K_F indicate that the ash sample has the highest adsorption affinity for As[V], followed by Pb, Cu and least for Zn.

3.3 Column experiments

3.3.1 pH change and breakthrough curves of As, Pb, Cu, Zn, Fe, Al and SO$_4^{2-}$

The column experiments lasted for 24 weeks and the evolution of the effluent chemistry is illustrated in Figure 8. The pH of case R (*i.e.*, rock only column) was strongly acidic throughout the duration of the experiment. The first effluent collected after 4 weeks had a pH value of 1.7, increased to ca. pH 3 and then stabilized in the range of 2 – 3. Addition of 1% CaCO$_3$ (case R+N1) did not have significant effects on the pH while doubling this amount of neutralizer added (case R+N2) only resulted in a slight increase of the pH. The combined neutralization-adsorption columns had the highest pH increase and approached the 6 – 7 range for case R+N2+A (Figure 8(a)).

The leaching curve of As had a "flushing-out" trend especially in case R as illustrated in Figure 8(b). The initial concentration of As in the effluent was 134 mg/L, which dropped to 0.11 mg/L after only three weeks. After this rapid decrease, the concentration of As in the effluent stabilized in the range of $0.02 – 0.5$ mg/L. The addition of 1% $CaCO_3$ had little effect on the pH, but dramatically decreased the concentration of As in the effluent. Increasing the amount of neutralizer to 2% further reduced the concentration of As in the effluent to below 0.01 mg/L. Combining neutralization and adsorption had the best results in terms of the immobilization of As (Figure 8(b)). The concentrations of As in the effluent collected from the combined system were less than the detection limit of the ICP-AES + hydride generation (<0.001 mg/L) regardless of the amount of neutralizer added.

The leaching behavior of heavy metals Pb, Cu and Zn was similar to As and also had "flushing-out" trends as illustrated in Figures 8(c), (d) and (e). The initial concentrations of these heavy metals in the effluent were very high ($70 – 200$ mg/L), decreased rapidly and stabilized in the concentration range of $0.02 – 0.1$ mg/L. The leaching behaviors of these heavy metals were also affected in similar fashions by the addition of neutralizer and adsorbent (Figures 8(c), (d) and (e)). The initial concentrations of Pb, Cu and Zn were reduced by ca. 80%, 70% and 30%, respectively after the addition of the neutralizer (cases R+N1 and R+N2). However, after this initial dramatic reduction, the leaching trends of heavy metals in the effluents decreased gradually with time, and their concentrations were higher than those collected in the column composed of the altered rock only. Immobilization of the heavy metals was more pronounced when a combined neutralization-adsorption system was employed as shown in Figures 8(c), (d) and (e). Using this system, the "flushing-out" leaching trends of Pb, Cu and Zn disappeared and more linear leaching curves with time were observed (cases R+N1+A and R+N2+A). Also, the addition of an adsorption layer effectively

reduced the concentration of Zn in the effluent to < 0.1 mg/L, which was not achieved by employing neutralization alone (Figure 8(e)).

The leaching behaviors of Fe and Al were similar to those of Pb, Cu and Zn, that is, "flushing-out" trends were observed only in columns composed of the altered rock only and those with neutralization while more linear leaching curves appeared in columns with both neutralization and adsorption (Figures 8(f) and (g)). Figure 8(h) shows that the leaching curve of SO_4^{2-} with time also had a "flushing-out" trend similar to As and the heavy metals especially in the column composed of the altered rock only. Addition of $CaCO_3$ resulted in a more gradual decrease of SO_4^{2-} with time while a combined neutralization-adsorption system resulted in a more linear leaching curve. Also, the SO_4^{2-} concentrations in all cases were close to each other after ca. 22 weeks, which suggests apparent equilibrium.

Mass balances of As, Pb, Cu, Zn, Al and Fe in case R+N2+A were calculated to estimate the amount of hazardous elements immobilized due to neutralization and adsorption (Table 5). The results showed that immobilization of As, Pb and Cu occurred mainly because of neutralization that retained ca. 99, 73 and 80% of the total mass released from the rock, respectively. In contrast, neutralization only retained ca. 24% of the total mass of Zn released from the rock. Furthermore, the adsorption layer reduced the amount of all hazardous elements released from the rock except As, the majority of which was already immobilized after neutralization. The amount of Al and Fe released from the rock also decreased dramatically because of the addition of neutralizer and adsorbent, which had strong positive effect on the immobilization of the hazardous elements via co-precipitation and adsorption reactions (Table 5; Figure 8).

3.3.2 Correlations of pH, As, Pb, Cu, Zn and Fe with SO_4^{2-}, and related geochemical modeling calculations
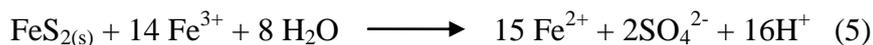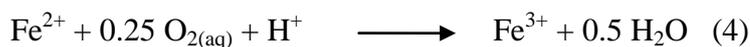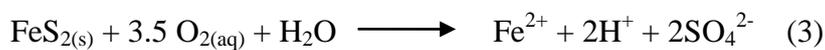
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Figure 9(a) illustrates the correlations of SO_4^{2-} with pH in all cases. There is a negative correlation between these two parameters, indicating that higher SO_4^{2-} concentrations mean lower pH values, and that the acidic pH produced by the altered rock is associated with processes that release SO_4^{2-} like dissolution of soluble Fe-sulfates and oxidation of pyrite. In contrast, the correlations of SO_4^{2-} with As, Pb, Cu, Zn and Fe were all strongly positive, which suggests that the leaching of SO_4^{2-} occurs in conjunction with the mobilization of these elements (Figures 9(b), (c), (d), (e) and (f)).

The calculated *SI*s with time for cases R, R+N2 and R+N2+A are presented in Figure 10. In the column composed of the altered rock only (case R), *SI* values of most Al and Fe oxyhydroxides/oxides except goethite (FeOOH) were less than zero, indicating that the precipitation of these minerals that are important in the immobilization of As and the heavy metals are not thermodynamically favorable. Also, exceptionally high concentrations of Pb, SO_4^{2-} and Ca^{2+} at the start of the experiments probably resulted in the precipitation of anglesite ($PbSO_4$) and gypsum ($CaSO_4 \cdot 2H_2O$) (Figure 10(a)). Solubility of $PbSO_4$ is relatively low, but gypsum could rapidly dissolve with time because of its generally high solubility. Addition of the neutralizer raised the *SI* values of Al and Fe oxyhydroxides/oxides close to saturation, but only diaspore (AlOOH) and goethite (FeOOH) are predicted to precipitate (Figure 10(b)). In columns with both neutralizer and adsorbent, the *SI* values of most Al and Fe oxyhydroxides/oxides were above zero, which suggests that the precipitation of these minerals is thermodynamically favorable (Figure 10(c)). Anglesite is also predicted to precipitate at the start of the experiment while gypsum is expected to precipitate in cases R+N2 and R+N2+A after week 4.

4. DISCUSSION

4.1 Dissolution of soluble phases and pyrite oxidation

Exposure of pyrite to the atmosphere results in its rapid oxidation commencing with the oxidation of S^{2-} species (Schaufuss *et al.*, 1998). This process is further enhanced in the presence of water or moisture that could strip reaction products exposing new sites on the pyrite surface. Reaction products from the atmospheric oxidation of pyrite include Fe-sulfates, Fe oxyhydroxides and oxides, which are more soluble than pyrite especially under acidic conditions (De donato *et al.*, 1993; Schaufuss *et al.*, 1998; Todd *et al.*, 2003). Because the altered rock sample used in this study was already exposed to the atmosphere and rain prior to sampling, it contains significant amounts of these soluble phases. The dissolution of these soluble phases was particularly evident in the breakthrough curves of SO_4^{2-} and Fe in the column composed only of the altered rock especially around the first 8 weeks (case R; Figure 8). These results suggest that the impact of the dissolution of soluble phases on acid production and mobilization of the hazardous elements is more pronounced at the start of the column experiments and significantly decreases with time. Mobilizations of As, Pb, Cu and Zn from the altered rock were also closely related to the dissolution of these soluble phases as suggested by their similar breakthrough curves to those of Fe and SO_4^{2-} as well as their strong positive correlations with Fe and SO_4^{2-} (Figure 8(f)). After the dissolution of most of these soluble phases, acidic leachate containing these hazardous elements persisted because of the continued oxidation of pyrite. This long-term acid production due to pyrite oxidation can be explained by the following chemical reactions:

$$FeS_{2(s)} + 3.5\ O_{2(aq)} + H_2O \longrightarrow Fe^{2+} + 2H^+ + 2SO_4^{2-} \quad (3)$$

$$Fe^{2+} + 0.25\ O_{2(aq)} + H^+ \longrightarrow Fe^{3+} + 0.5\ H_2O \quad (4)$$

$$FeS_{2(s)} + 14\ Fe^{3+} + 8\ H_2O \longrightarrow 15\ Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (5)$$

Ferric ions (Fe^{3+}) and O_2 are two of the most important oxidants of pyrite (Holmes and Crundwell, 2000; McKibben and Barnes, 1986; Moses *et al.*, 1987; Moses and Herman, 1991; Nicholson *et al.*, 1988). Oxygen further acts as an oxidant of Fe^{2+} to form Fe^{3+} as shown in

equation (4). These equations also explain that oxidation of 1 mole of pyrite could produce ca. $2 - 16$ moles of H^+. Based on these results, the dominant release mechanisms of these hazardous elements include the dissolution of soluble phases and pyrite oxidation consistent with our previously published works (Tabelin and Igarashi, 2009; Tabelin et al., 2012a,b).

4.2 Neutralization, precipitation and adsorption

The alternative disposal system proposed in this study focused on the retardation of acid dissolution and pyrite oxidation, which are the dominant release mechanisms of As, Pb, Cu and Zn in acidic/pyritic altered rocks. Addition of $CaCO_3$ effectively raised the pH close to neutral that resulted in lower concentrations of As, Pb, Cu and Zn in the batch tests (Figure 4). However, using a similar ratio of $CaCO_3$ (2%) in the column experiments did not have the same strong neutralizing effect on the effluent (Figure 8). These results suggest that batch neutralization tests underestimate the required amount of neutralizer. This difference could be attributed to the constant "renewal" of the pore water in the column experiments that probably results in more localized disequilibrium conditions. Results of the column experiments further showed that the addition of small amounts of neutralizer dramatically reduced the concentration of As in the effluent throughout the experiments, but not the heavy metals (Figure 8). The higher immobilization of As in comparison to the heavy metals could be attributed to its strong adsorption affinity to Al and Fe oxyhydroxide/oxide precipitates (Cornelis *et al.*, 2008; Dousova *et al.*, 2003; Dzombak and Morel, 1990; Gosh and Teoh, 1985; Lin and Puls, 2000; Wang and Mulligan, 2006). The similar leaching trends of Pb, Cu and Zn to those of Al, Fe and SO_4^{2-} suggest that the addition of $CaCO_3$ may affect the dissolution of soluble phases available in the rock. The $CaCO_3$ addition probably slowed down the dissolution of these soluble phases, resulting in the observed gradual decreasing trend and the higher concentrations of these heavy metals in comparison to the column composed of the rock only. Furthermore, our modeling calculations predict that because the

pH was not raised high enough, precipitations of Al and Fe oxyhydroxides/oxides, which are important in the immobilization of As and the heavy metals, were greatly limited (Figures 8 and 10). None the less, neutralization effectively lowered the concentrations of As, Pb, Cu and Zn in the column effluents especially during the first couple of weeks when very high concentrations of these toxic elements were observed in the effluent of the column composed of the altered rock only. Among the heavy metals, Pb is predicted to directly precipitate as anglesite ($PbSO_4$), which is relatively insoluble and could act as an important sink of dissolved Pb (Figure 10(b)). In contrast, direct precipitations of As, Cu and Zn either as sulfates, carbonates or oxyhydroxides were thermodynamically unfavorable. Thus, the observed decrease in the concentration of these hazardous elements in the effluent could be attributed to their co-precipitation and/or adsorption with and/or onto Al and Fe oxyhydroxides/oxides (Figures 8 and 10).

We achieved the best results in terms of the immobilization of the hazardous elements using a combined neutralization-adsorption system. The partly-weathered volcanic ash layer acted both as an adsorbent and neutralizer that resulted in the significant decrease in the concentrations of all the hazardous elements in the effluent. The ash sample had a pH of ca. 6 in water so that it was able to raise the effluent pH around $4 - 6$. This higher pH enhanced the precipitation of Al and Fe oxyhydroxides/oxides that lowered the concentrations of As, Pb, Cu and Zn in the column effluents (Figures 8 and 10). In addition, the rich Al and Fe oxyhydroxides/oxides originally present in the volcanic ash enhanced the adsorption of the toxic elements especially those of As, Cu and Zn (Figures 8 and 10). These results indicate that the combined neutralization-adsorption system is capable of reducing the amount of toxic metalloids and heavy metals released from altered rocks producing acidic leachate and could be utilized as an alternative method for their disposal.

4.3 Engineering Implications

Using $CaCO_3$ in powdered form may not be sustainable for the long term stabilization of the altered rock. This is because pyrite oxidation might take decades or even centuries to complete, depending on its relative abundance in the rock. Sufficient amounts of neutralizer are critical to the stability of the Al and Fe oxyhydroxide/oxide precipitates and those found in the volcanic ash. Therefore, the kind of neutralizer used must also be able to last as long as oxidizable pyrite is available in the rock. Potential neutralizers for this particular purpose would include limestone, calcite and dolomite. A combination of these "short" (powdered $CaCO_3$) and "long" (*i.e.*, limestone, calcite and dolomite) lasting neutralizers might also give better results if utilized. Finally, mixing of the neutralizer and the altered rock would be difficult during the actual disposal of the rock. Thus, other ways of introducing the neutralizer like applying it on the top of the rock or as a "sandwich"-like structure should be considered.

5. CONCLUSIONS

This paper describes the mitigation potential of a combined neutralization-adsorption system for excavated altered rocks producing acidic leachate. The findings of this paper are summarized as follows:

(1) Addition of at least 2% $CaCO_3$ in the batch experiments effectively neutralized the leachate of the altered rock and immobilized most of the As and heavy metals dissolved in it.

(2) The partly-weathered volcanic ash used in this study adsorbed both As and the heavy metals, and the corresponding K_F indicates that the ash had adsorption affinity in this order: As>Cu>Pb>Zn.

(3) Addition of 2% of $CaCO_3$ was insufficient to neutralize the effluent and reduce the concentrations of the toxic elements in the column experiments.

(4) The combined neutralization and adsorption method was more effective in neutralizing the acidic effluent from the rock layer and reducing the concentrations of As and the

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heavy metals than the method using neutralization alone.

(5) The mechanisms of As, Pb, Cu and Zn release from the altered rock include the dissolution of soluble phases and pyrite oxidation while the immobilization mechanisms of the proposed alternative disposal system include a combination of co-precipitation and adsorption reactions.

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FIGURE CAPTIONS

FIGURE 1   A schematic illustration of the combined neutralization-adsorption system.

FIGURE 2   A schematic illustration of the columns used.

FIGURE 3   Leachate pH as a function of $CaCO_3$ addition.

FIGURE 4   Residual percentages of As, Cu, Pb and Zn as a function of pH in batch experiments.

FIGURE 5   Concentrations of Al and Fe in the leachate as a function of pH in batch experiments.

FIGURE 6   Saturation indices of gibbsite ($Al(OH)_3$), diaspore (AlOOH), $Fe(OH)_3$, goethite (FeOOH), malachite ($Cu_2(OH)_2CO_3$), smithsonite ($ZnCO_3$), hydrocerrusite ($Pb_3(CO_2)_3(OH)_2$) and $Pb(OH)_2$ in batch experiments.

FIGURE 7   Adsorption isotherms of volcanic ash for As(V), Cu, Pb and Zn.

FIGURE 8   Evolution of the effluent chemistry with time in all cases; (a) pH change with time, (b) As concentration as a function of time, (c) Pb concentration as a function of time, (d) Cu concentration as a function of time, (e) Zn concentration as a function of time, (f) Fe concentration as a function of time, (g) Al concentration as a function of time and (h) SO_4^{2-} concentration as a function of time.

FIGURE 9   Relationship of SO_4^{2-} to (a) pH, (b) As, (c) Pb, (d) Cu, (e) Zn and (f) Fe in the effluents.

FIGURE 10   Saturation indices of gibbsite ($Al(OH)_3$), diaspore (AlOOH), $Fe(OH)_3$, goethite (FeOOH), anglesite ($PbSO_4$), gypsum ($CaSO_4.2H_2O$) and $Pb(OH)_2$ in the column experiments; (a) case R, (b) case R+N2, (c) case R+N2+A.
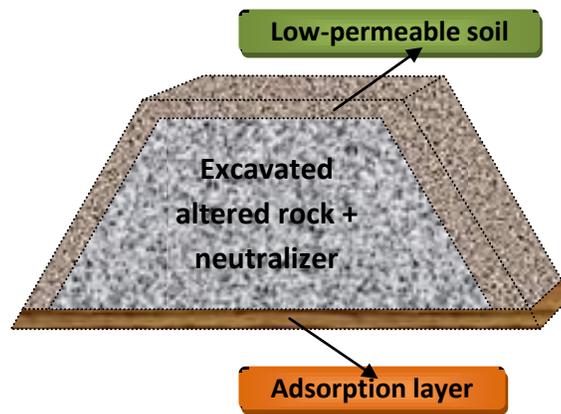
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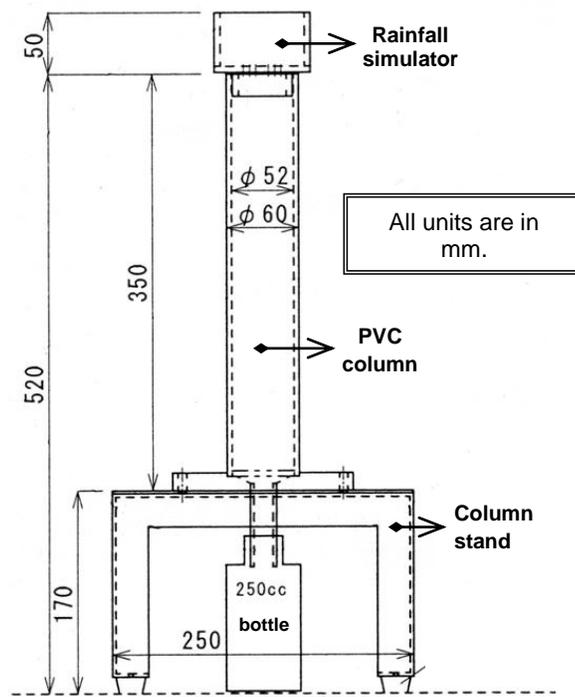
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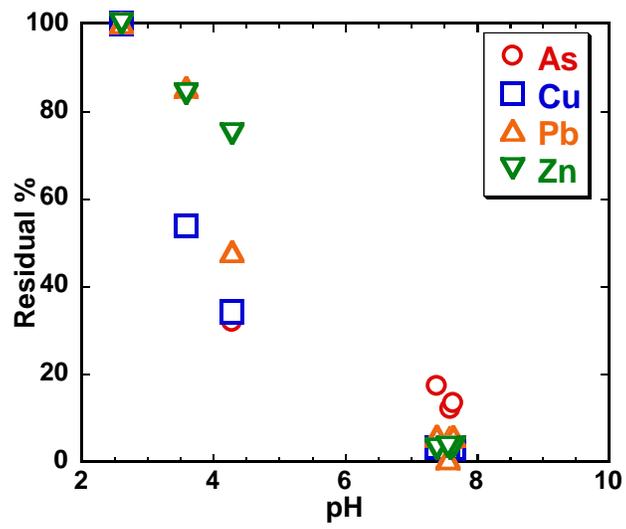
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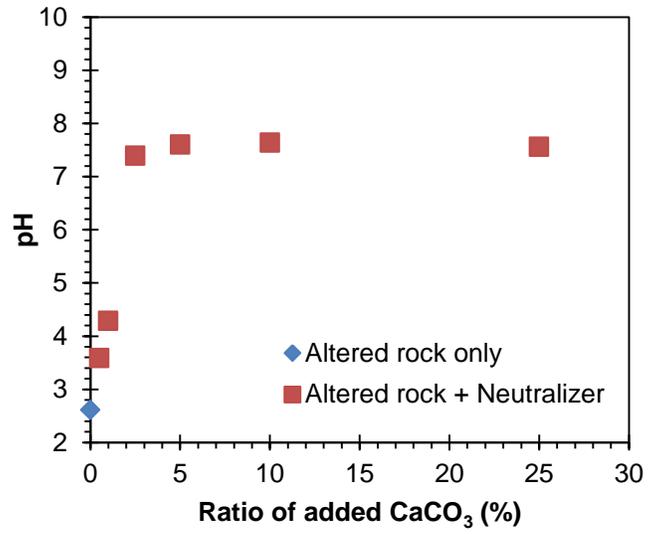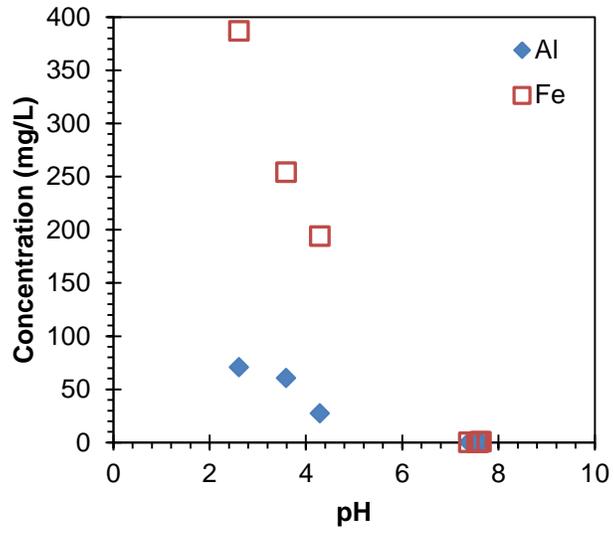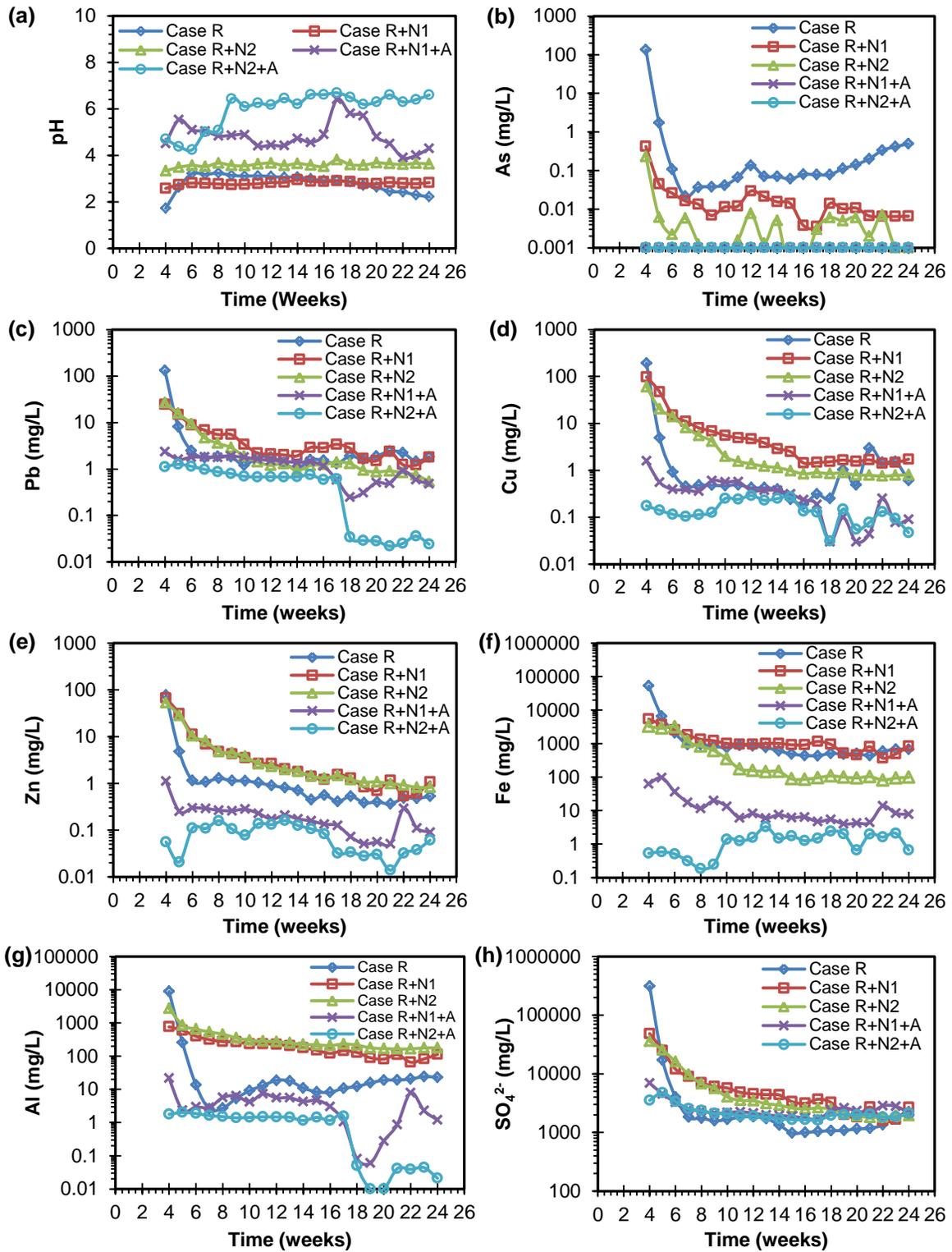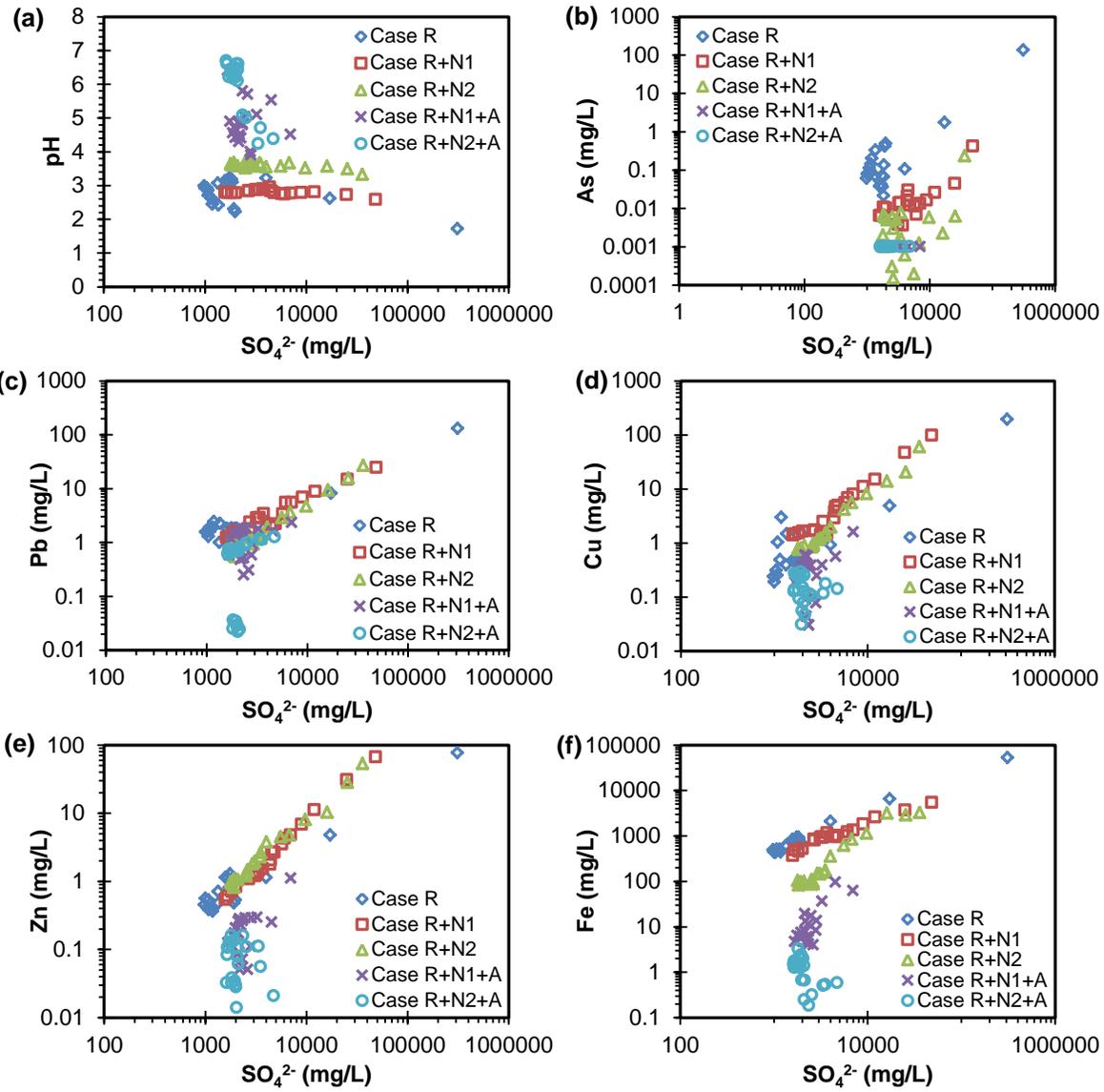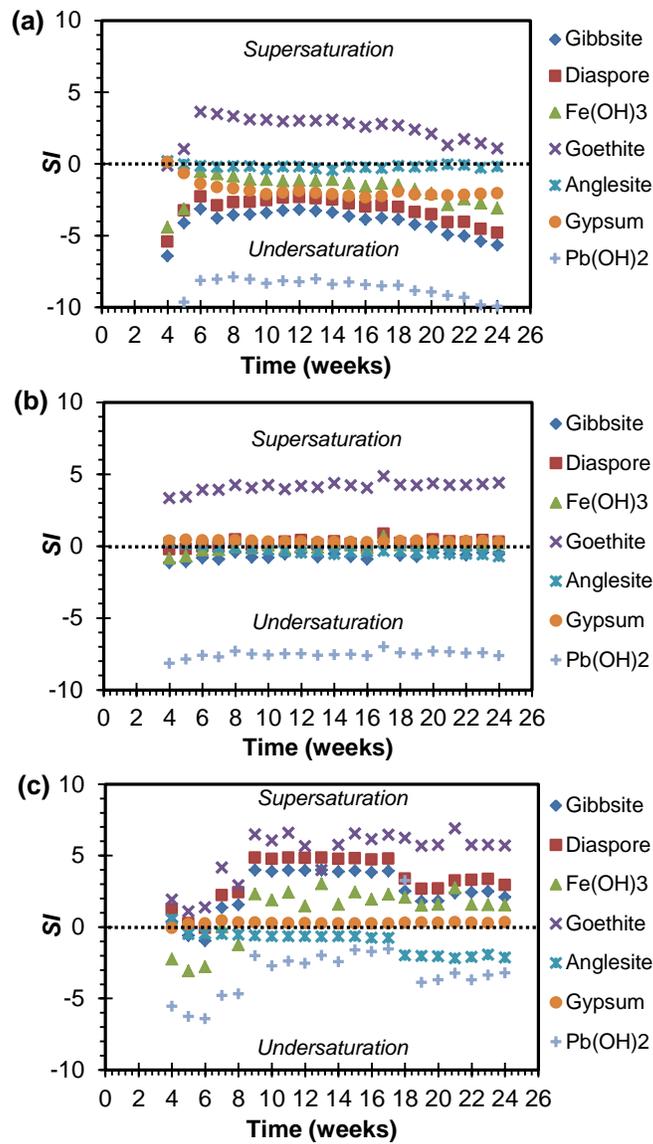
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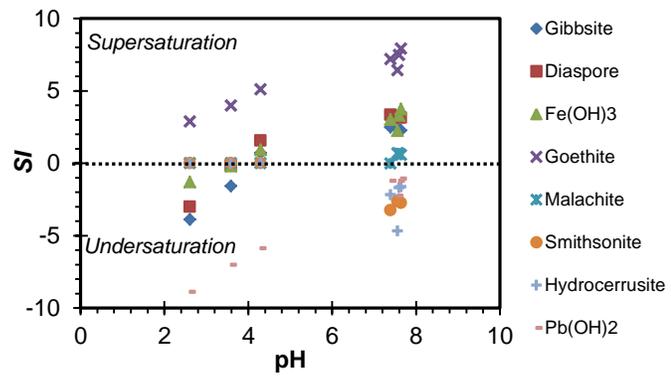
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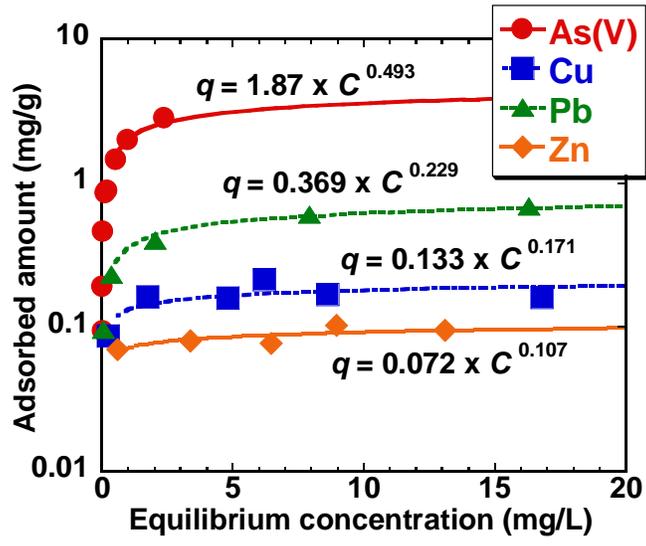
Figure 7

Figure 8

Figure 9

Figure 10

Table 1. Column experimental conditions

Case	Thickness of rock bed (cm)	Thickness of ash layer (cm)	Neutralizer-rock ratio (%)
R	20	0	-
R+N1	20	0	1
R+N2	20	0	2
R+N1+A	20	2	1
R+N2+A	20	2	2

Table 2. Chemical compositions of the altered rock and volcanic ash samples used

Sample	SiO_2 (wt.%)	TiO_2 (wt.%)	Al_2O_3 (wt.%)	Fe_2O_3 (wt.%)	MnO (wt%)	CaO (wt.%)	Na_2O (wt.%)	K_2O (wt.%)	P_2O_5 (wt.%)	S (wt.%)	As (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	Zn (mg/kg)
Altered rock	63.3	0.25	6.88	16	0.02	0.05	0.01	0.1	0.06	10.6	150	375	68	62
Partly-weathered volcanic ash	51.3	0.95	21.7	9.02	0.2	0.95	1.21	2.01	0.23	0.11	2.05	-	-	-

Table 3. Mineral compositions of the altered rock and volcanic ash samples used

Sample	Identified minerals
Altered rock	Quartz, Pyrite, Kaolinite
Volcanic ash	Quartz, Anorthite, Chlorite

Table 4. Leachate chemistry of the altered rock

pH	Concentration (mg/L)							
	As	Pb	Cu	Zn	Fe	Al	Ca	SO_4^{2-}
2.61	0.031	2.4	1.99	0.54	387	70.8	4.65	1,210

Table 5. Mass balances of As, Pb, Cu, Zn, Al and Fe in case R+N2+A

	As (mg)	Pb (mg)	Cu (mg)	Zn (mg)	Al (mg)	Fe (mg)
Total mass released (rock only)	10.2	11.8	15.3	6.62	686	4,898
Mass retained in neutralizer layer (2% CaCO3)	10.2	8.6	12.1	1.6	333	4,330
Mass retained in ash layer	<0.001	2.62	3.05	4.93	353	566
Total mass released after adding neutralizer and adsorbent	<0.001	0.501	0.139	0.073	0.926	1.2