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Leaching behavior of arsenic from various rocks by controlling geochemical conditions

Igarashi, T.[*], Imagawa, H.[**], Uchiyama, H.[***], and Asakura, K.[*]

* Graduate School of Engineering, Hokkaido University

** Nippon Mining & Metals Co., Ltd.

*** Nuclear and Industrial Safety Agency, Ministry of Economy, Trade and Industry

Abstract

Hydrothermally altered igneous rock and mudstone formed under the sea are often rich in arsenic (As). Therefore, As leaching from these rocks excavated during construction work may affect the surrounding soils and groundwater. High-volume, low-concentration contaminants contained in the waste rock as muck have been a major concern in Japan since the Soil Contamination Countermeasures Law was enforced in 2003.

The aim of this study is to develop ways to reduce As concentration leached from muck by controlling the geochemical conditions. Batch leaching experiments were carried out to determine the leaching behavior of As as a function of mixing period, solution pH, oxygen concentration, or mixing ratio of different rocks. The results showed that the As concentration in the leachate approached almost constant after 1 to 7 days mixing and increased with the As content in the rock, and that the maximum As leaching was observed at around pH 9. The concentration of oxygen gas and the mixing ratio of different rocks also affected the As leaching by changing the leachate pH. This indicates that the solution pH as well as the As content in the rock greatly affects the As leaching from rocks.

Keywords: Leaching, Oxidation, and Environmental

1. Introduction

Hokkaido, in the north of Japan, has many active volcanoes, hot springs, and abandoned mines. This implies that hydrothermally altered rock is widely distributed throughout Hokkaido. The arsenic (As) content of altered rock is known to be higher than that of unaltered rock (Tanaka, 1988), and it may induce higher As concentrations in seepage through altered rock layers. In particular, the leachate through impounded altered rock excavated in relation to tunnel or dam construction, called muck, often displays noticeably elevated As levels. This is because the geochemical conditions of the rock have been changed from anoxic to oxic and because the specific surface area of excavated rock is dramatically higher than that of the intact rock, causing an enhancement in the mobility of As (Smedley and Kinniburgh, 2002; Yoshimura and Akai, 2003).

The extensive As pollution of groundwater as in the cases of Bangladesh (Acharyya et al., 2000; Ahmed et al., 2003; Akai et al., 2004; Anawar et al., 2003; Nickson et al.,1998; Nickson et al., 2000; Welch and Stollenwerk, 2003), West Bengal (Acharyya et al., 2000; Das et al., 1996; Dowling et al, 2002; Nickson et al., 2000), and other locations (Chen et al., 1994; Kim et al., 2000; Kelley et al., 2005; Nimick, 1998; Peters et al., 1999; Robertson, 1989; Schreiber et al., 2000; Smedley and Kinniburgh, 2002; Smedley et al., 2002; Yoshimura and Akai, 2003; Welch et al., 1988; Welch and Stollenwerk, 2003; Williams et al., 2005) is a well known concern worldwide. There are also reports of As pollution of groundwater, sediments, soils, and/or rocks in Japan (Shimada, 1996; Masuda et al., 1999). The origin of the As has been reported to be As-containing minerals in sediments (Akai et al., 2004; Dowling et al, 2002; Kim et al., 2000; Peters et al., 1999; Shimada, 1996). There has been exhaustive research into the behavior of As leaching and migration in subsurface environments (Livesey and Huang, 1981; Manning and Goldberg, 1997; Nickson et al., 2000; Yoshimura and Akai, 2003) and to remediate polluted groundwater (Welch and Stollenwerk, 2003). However, As leaching from crushed rock has never been systematically studied. Thus it is necessary to evaluate As leaching from rock and the subsequent migration in the subsurface in the disposal of muck excavated from hydrothermally altered regions. In fact, an attempt at reducing As leaching is offered by the Hakkoda tunnel with a length of 25.45 km for the Superexpress in Japan where a considerable part of the muck related to the construction was closely disposed in a similar manner to the landfills of industrial wastes (Hattori et al., 2003).

The objective of this study is to elucidate the leaching behavior of As from crushed rock samples by batch experiments and to consider reasonable methods for reducing As leaching. Hydrothermally altered rock samples as well as samples of sedimentary rock formed below sea level were used for the experiments. The information obtained here will be useful to predict the underground migration of leached As and to evaluate the risks involved in disposing of As-rich muck.

2. Materials and methods

2.1 Rock samples

Eleven igneous rock samples (K1~K11) were collected in a hydrothermally altered area of Hokkaido. The samples were crushed by jaw crusher or agate mortar and pestle, and sieved <2mm for use in the measurement of the mineralogical and chemical properties as well as in leaching experiments. Complementary samples, K4', K10' and K11' were taken at the same site as the K4, K10 and K11 samples, respectively, because the original samples were used up during the experiments. The rock types involved were andesite, pyroclastic rock, and tuff, except for samples K4 and K11 that were from a gouge in a fault.

Four sedimentary rock samples (N1, N2, Y1, and Y2) were also collected from the areas different from K-series of samples. The N1 and N2 samples are slate, the Y1 sample is mudstone, and the Y2 sample is sandstone. The sedimentary rock samples were pretreated in a similar manner to the altered igneous rock samples.

The mineralogical properties of the rock samples were determined by X-ray diffraction (XRD),

and a powder X-ray diffractometer, Multiflex produced by Rigaku Corporation, Tokyo, Japan was used for the identification. Table 1 lists the identified minerals in the samples. Pyrite (FeS_2) was detected in the K1, K2, K4, K8, K11, K12, and Y1 samples whereas As-bearing minerals were not detected.

The chemical compositions of the samples were measured by the X-ray fluorescence method (XRF). An energy dispersive X-ray fluorescence spectrometer, Xepos, produced by Rigaku Corporation was employed for the chemical analysis. The results are shown in Table 2. The contents of major elements in the rock were expressed in wt% as their oxide forms because it was difficult to analyze their chemical forms in the rock by the XRF method. The As contents of the samples ranged from 3 to 611 mg/kg. The sulfur (S) contents of the samples ranged from <0.01 to 0.8 wt%; the S contents were higher for samples with pyrite. The altered igneous rock samples in which FeS_2 was detected contained more than 40 mg/kg of As whereas the sedimentary rock sample in which FeS_2 was detected contained only 9 mg/kg of As. The average As content of rock or soil is reported to be less than 2 mg/kg (Tanaka, 1988). Recently, the Public Works Research Institute reported the background As content of soils to be less than 39 mg/kg (Public Works Research Institute, 2004), and the Geochemical Survey of Japan has determined the background As content of river sediments as 9 mg/kg (Geological Survey of Japan, AIST, 2004). Several altered igneous rock samples used in these experiments have higher As contents than the background level whereas the sedimentary rock samples used have As contents similar to the background.

2.2 Experimental procedures

A series of batch leaching experiments were carried out as shown in Table 3. Fifteen grams of a crushed-rock sample and 150 mL of deionized water were mixed in a 200-mL Erlenmeyer flask at room temperature. The reaction flask was shaken at approximately 120 rpm by a reciprocal shaker. To compare oxic and anoxic conditions, batch experiments both under atmospheric conditions (oxic batch experiments) and in a glove box filled with argon gas (anoxic batch experiments) were conducted. The shaking period was changed from 6 hours to 28 days. Mixtures of different rock samples with different As contents were also used in oxic batch experiments to determine the effects of the mixing ratio of rock samples on As leaching.

After a specified period of shaking, the temperature and pH of the leachate were measured, and the aliquot of the leachate was sampled for filtration with a 0.45-μm cellulose acetate membrane filter. The filtrated sample was first provided for the measurement of alkalinity by titrating with 0.01 M sulfuric acid (H_2SO_4). Hydrochloric acid (HCl) or nitric acid (HNO_3) was added to the remainder of the sample to preserve it at approximately pH 2 in a polyethylene bottle for chemical analysis. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used in the analysis of Ca, Mg, Na, K, Si, S, Fe, Mn, and Al, and inductively coupled plasma mass spectrometry (ICP-MS) or hydride generation ICP-AES was used in the analysis of As in the acidified samples.

Consecutive batch leaching experiments were also carried out to evaluate the long-term leaching behavior of As under atmospheric conditions (consecutive oxic batch experiments). In this experiment, the whole leachate after 1 day mixing was replaced with 100 mL fresh deionized water

and the suspension was mixed again. The replacement and mixing were repeated 5 to 10 times. The leachate from every cycle was provided for the pretreatment and chemical analysis described before.

3. Results and discussion

3.1 Oxic batch experiments

The As concentration changes in the leachate with the mixing period for altered igneous rock samples are presented in Figs. 1(a) and (b). The As concentration in the leachate increased with the mixing period from 6 hours to 7 days, and then reached almost constant values or decreased slightly from 7 to 28 days for most of the samples used. This means that the As concentration nearly reached apparent equilibrium after 1 to 7 days of reaction. The As concentrations in the leachate of K2, K4, K4', K8, K11', and K12 were higher than 0.01 mg/L, the drinking water standard of Japan and World Health Organization. The pH of the leachate is shown in Figs. 2(a) and (b). A weakly alkaline leachate was obtained for all the samples except K4. The alkaline pH decreased with time and reached 8 to 8.5 for all the samples except K4. This indicates that the equilibrium As concentration is related to the stability of the leachate pH. The acidic leachate for K4 may be a result of much higher content of pyrite than that of calcite (Igarashi et al., 2001; Igarashi et al., 2002).

The As concentrations in the leachate changed with time for sedimentary rock samples as presented in Fig. 3. The As concentration of N1 increased with time and asymptotically approached equilibrium, and the As concentration of Y1 reached constant after 1 day mixing. The apparent equilibrium As concentrations of these samples were higher than 0.01 mg/L. This trend is the reverse of the change in leachate pH as shown in Fig. 4. The As concentrations of N2 and Y2 were less than 0.01mg/L, and remained almost constant regardless of mixing period. The As leaching experiments by using sulfide-bearing rock samples showed that the apparent equilibrium was attained within a few days unless the solution pH was unchanged (Shreiber et al., 2000). The similar leaching experiments by using sandstone also showed that the As concentration in the leachate approached equilibrium before 4 days reaction (Kim et al., 2000). The As concentration changes obtained in this study agreed with the tendency with the other rock samples.

The concentrations of the other constituents in the leachate were also analyzed. As a result, the concentrations of sulfate (SO_4^{2-}) and iron (Fe) were found to correlate with the As concentration in the leachate. Figures 5 and 6 illustrate the relationship between the As and SO_4^{2-} concentrations in the leachate and the relationship between the As and Fe concentrations in the leachate, respectively. The results for the 1 and 7 day mixing periods are plotted in these figures, because the As concentration and pH were considered to be almost in equilibrium. The As concentration in the leachate correlated with the SO_4^{2-} concentration in the leachate of both altered igneous rocks, except K4, and sedimentary rocks, suggesting that As leaching results from pyrite dissolution that produces SO_4^{2-}. A similar correlation between the As concentration and the SO_4^{2-} concentration was observed for sulfide-bearing rocks (Shreiber et al., 2000). The As concentration in the leachate also correlated with the Fe concentration in the leachate of igneous rock samples, except K4 that produced an acidic leachate. On the other hand, the As concentration in the leachate did not correlate well with the Fe

concentration in the leachate of sedimentary rock samples, since the Fe concentration was nearly at the detection limit. The correlation between the As concentration and Fe concentration has been reported by many researchers (Ahmed et al., 2003; Dowling et al., 2002; Kim et al., 2000; Nickson et al., 2000; Shreiber et al., 2000).

The relationship between the solid-phase and liquid-phase concentrations was examined based on the chemistry of the leachate and the chemical composition of the rock samples. The As concentration in leachate versus the As content of rock is presented in Fig. 7. The As concentration in the leachate correlated with the As content of the rock for both altered igneous rocks and sedimentary rocks. Figures 8 shows the relationship between the As concentration in the leachate and the S content of the rock. From this figure, the As concentration in the leachate increased with the S content of sedimentary rock samples whereas the As concentration in the leachate weakly correlated with the S content of altered igneous rock samples. The weak correlation between As leaching and S content of altered igneous rock might be due to the difference in the leachability of As from sulfide-bearing minerals.

Figure 9 shows the relationship between the As content of the rock and the S content of the rock. The As content of the rock increased with the S content of the rock for both sedimentary rock samples and altered igneous rock samples. This relationship suggests that the As leaching primarily results from pyrite oxidation of the rock samples. Indeed, Imagawa et al. (2007) observed the higher As content on pyrite grain surfaces for altered igneous rock samples by scanning electron microscope/energy dispersive X-ray spectrometer (SEM/EDX) although arsenopyrite was not detected by XRD analysis. This indicates that the As in the altered igneous rock samples exists in pyrite as impurities. Akai et al (2004) also clearly observed the As existence on pyrite grain. However, this approach was not applicable to sedimentary rock samples used because of their much finer grains.

By comparing altered igneous rock samples with sedimentary rock samples, the As contents of altered igneous rock samples were higher than those of sedimentary rock samples although the As concentrations in the leachate of altered igneous rock samples were similar to those of sedimentary rock samples. The difference in the leachability between the altered igneous rocks and sedimentary rocks might be due to the grain size of pyrite and pH of leachate.

The effect of mixing different rock samples with different As contents on the As leaching was examined to understand the solid-liquid partitioning of As. The K12 and K13 samples were selected as examples of altered igneous rock, and the Y1 and Y2 samples as examples of sedimentary rock. The relationship between the As concentrations in the leachate and the weight ratio of K12 to the K12 and K13 mixture is presented in Fig. 10. The As leaching was linearly related to the mixing ratio irrespective of the mixing period. This indicates that the As leaching is in response to the As content of the rock sample, suggesting that As leaching can be evaluated by the mixing ratio of the samples and their As contents. The relationship between the As concentration in the leachate and the weight ratio of Y1 to the Y1 and Y2 mixture is presented in Fig. 11. The results show peak As concentrations that were higher than the concentrations leached from Y1 and Y2 individually at two

different mixing ratios. This unexpected behavior of altered igneous rocks and sedimentary rocks may be explained by the leachate pH. Figures 12 and 13 show the pH changes of the leachate from the mixtures of K12 and K13, and Y1 and Y2. The pH of the leachate was not greatly dependent on the mixing ratio for the altered igneous rock samples whereas the pH of the leachate was dependent on the mixing ratio for the sedimentary rock samples. Since the leachate pH of Y1 was higher than that of Y2, the pH of the mixture of Y1 and Y2 changed depending on the mixing ratio. The leachate pH of the mixture changed from 8 to 10 with changing the mixing ratio. However, a maximum of As leaching was observed at around pH 9. The pH change of the leachate results in a convex As concentration change as a function of the mixing ratio. This indicates that the pH of the leachate plays an important role in As leaching from rock samples as the content of As in the rock does.

3.2 Anoxic batch experiments

Batch experiments in a globe box filled with argon gas were carried out to compare the leaching behavior of As in an anoxic condition with that in an oxic condition. The K4' sample was selected as an altered igneous rock, and the N1 sample as for a sedimentary rock. Figure 14 illustrates the As leaching concentration changes with the mixing period for K4' and N1. The As concentrations in the leachate in the anoxic condition were higher than those in the oxic condition. This suggests that the anoxic condition enhances As leaching. This phenomenon contradicts the mechanism of As leaching during pyrite oxidation. The pH in the anoxic condition was 9 to 9.5, higher than the pH in the oxic condition, 8 to 8.5, as shown in Fig. 15. The pH difference is due to the dissolution of CO_2 from air to the leachate. Therefore, the difference in As leaching was caused by the difference in pH rather than that in the oxygen concentration. In the experiments, the anoxic condition led to a pH increase of the leachate. This indicates that the pH of the leachate is a critical parameter for As leaching, and that the control of pH is necessary to reduce As leaching.

3.3 Consecutive batch experiments

Consecutive batch leaching experiments were conducted to obtain the long-term leaching behavior of As by using altered igneous rock samples of K2, K8, and K11', and sedimentary rock samples of Y1, Y2, Y3 (a 1:1 mixture of Y1 and Y2), N1, and N2. The As concentration in the leachate versus the number of extractions is shown in Fig. 16. The As concentration decreased with the number of extractions, irrespective of the samples used. This trend was observed both for the altered igneous rocks and for the sedimentary rocks. In particular, the decrease in As concentration was more noticeable when the initial As concentration in the leachate was higher. This indicates that As leaching from crushed rock samples decreases with water volume that passes through the crushed rock layer. The pH of the leachate was nearly constant, depending on the sample as shown in Fig. 17.

The leaching behavior of As for crushed rock samples consists of initial higher and subsequent lower leaching rates, indicating that a highly reactive surface is generated when freshly crushed surfaces of rock are generated, however, the reactivity of the surface decreases with time as the leaching proceeds. This means that the As concentration leached from rock does not remain constant, and that instead the concentration decreases with time. This property is advantageous to risk assessments when silty or clayey soils that retain As by a reversible adsorption are used as sealing

materials.

To compare the results of consecutive batch experiments with those of oxic batch experiments, the As concentration in the leachate was transformed to the leached As content from unit mass of rock (mg-As/kg-rock). The cumulative leached As changes with the number of extractions or time were presented in Figs. 18 (a) and (b). The cumulative leached As content increased with the number of extraction and asymptotically approached a specific value, depending on the sample. The As content obtained by consecutive batch experiments was higher than that by oxic batch experiments. The difference between the two might be due to the initial As concentration in the leachate. Thus, the As leaching rate from crushed rock samples decreased with time regardless of the experimental method.

4. Conslusions

A series of batch leaching experiments of As from altered igneous rock samples and sedimentary rock samples from Hokkaido, Japan were conducted. The results obtained are the following.

(1) The As leaching depended on the As content of the rock and the leaching pH. The As concentration in the leachate increased with the As content of the rock when the pH remained constant. A higher As concentration in the leachate was observed at around pH 9.

(2) The mixing of different rocks with different As contents changed the As concentration in the leachate in response to the As content of the mixture when the leachate pH remained constant. However, the As concentration in the leachate depended on the As content as well as pH when the leachate pH changed with the mixing ratio.

(3) An anoxic condition increased the leachate pH by preventing the CO_2 in air from dissolving into the leachate and induced As leaching.

(4) The As concentration of the leachate decreased with the number of extractions. This property is favorable to the risk assessment of disposing high-As-content rock.

The As leaching under in situ conditions and subsequent adsorption by surrounding soils need be solved for reasonable disposal of high-As-content waste rock by controlling As leaching.

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Captions

Table 1 Mineralogical properties of rock samples used
Table 2 Chemical compositions of rock samples used
Table 3 Details of the batch experiments

Fig. 1(a) As concentration changes of the leachate from altered igneous rock samples of K1 to K7
Fig. 1(b) As concentration changes of the leachate from altered igneous rock samples of K8 to K13
Fig. 2(a) pH changes of the leachate from altered igneous rock samples of K1 to K7
Fig. 2(b) pH changes of the leachate from altered igneous rock samples of K8 to K13
Fig. 3 As concentration changes of the leachate from sedimentary rock samples
Fig. 4 pH changes of the leachate from sedimentary rock samples
Fig. 5 As concentration in leachate vs SO_4 concentration in leachate
Fig. 6 As concentration in leachate vs Fe concentration in leachate
Fig. 7 As concentration in leachate vs As content in rock
Fig. 8 As concentration in leachate vs S content in rock
Fig. 9 As content vs S content in rock samples
Fig. 10 As concentration in leachate as a function of mixing ratio of K12 sample
Fig. 11 As concentration in leachate as a function of mixing ratio of Y1 sample
Fig. 12 pH change of the leachate from K12 and K13 mixture
Fig. 13 pH change of the leachate from Y1 and Y2 mixture
Fig. 14 Comparison of As leaching in oxic and anoxic conditions
Fig. 15 Comparison of leachate pH in oxic and anoxic conditions
Fig. 16 As concentration changes of the leachate with the number of extractions
Fig. 17 pH changes of the leachate with the number of extractions
Fig. 18(a) Cumulative leached As content from altered igneous rock samples
Fig. 18(b) Cumulative leached As content from sedimentary rock samples

Table 1 Mineralogical properties of rock samples used

Sample	Identified minerals
K1	Quartz, Feldspar, Muscovite, Calcite, Kaolinite, Pyrite
K2	Quartz, Feldspar, Chlorite, Muscovite, Pyrite
K3	Quartz, Feldspar, Muscovite, Kaolinite
K4	Quartz, Feldspar, Muscovite, Chlorite, Pyrite
K4'	Quartz, Feldspar, Muscovite, Kaolinite, Albite
K5	Quartz, Feldspar, Calcite, Muscovite, Chlorite
K6	Quartz, Feldspar, Muscovite, Chlorite, Pyrophyllite
K7	Quartz, Feldspar, Chlorite
K8	Quartz, Feldspar, Chlorite, Pyrite
K9	Quartz, Feldspar, Calcite, Chlorite
K10	Quartz, Feldspar, Chlorite
K10'	Quartz, Feldspar, Chlorite
K11	Quartz, Calcite, Muscovite, Chlorite, Pyrite
K11'	Quartz, Feldspar, Calcite, Muscovite, Chlorite
K12	Quartz, Feldspar, Muscovite, Chlorite, Calcite, Pyrite, Montmorillonte
K13	Quartz, Feldspar, Chlorite, Muscovite, Calcite, Kaolinite
N1	Quartz, Feldspar, Chlorite, Muscovite, Calcite, Kaolinite
N2	Quartz, Feldspar, Chlorite, Muscovite, Calcite, Kaolinite
Y1	Quartz, Feldspar, Calcite, Chlorite, Muscovite, Montmorillonte, Pyrite
Y2	Quartz, Feldspar, Calcite, Chlorite

Table 2 Chemical compositions of rock samples used

Sample	SiO_2 (wt.%)	TiO_2 (wt.%)	Al_2O_3 (wt.%)	Fe_2O_3 (wt.%)	MnO (wt.%)	MgO (wt.%)	CaO (wt.%)	Na_2O (wt.%)	K_2O (wt.%)	P_2O_5 (wt.%)	S (wt.%)	C (wt.%)	As (mg/kg)	LOI (wt.%)	$H_2O(+)$ (wt.%)	$H_2O(-)$ (wt.%)
K1	64.2	0.42	13.6	4.53	0.38	1.31	2.42	0.16	8.48	0.08	0.45	0.59	107	2.63	2.05	0.40
K2	55.2	1.12	18.2	7.84	0.45	2.42	0.80	1.17	8.75	0.18	0.53	0.17	265	3.68	2.97	0.74
K3	64.0	0.62	16.2	4.58	0.22	2.13	1.41	1.30	5.87	0.11	0.03	0.33	27.0	3.16	3.09	1.75
K4	67.4	0.58	14.3	4.70	0.08	1.81	0.27	0.06	6.30	0.12	0.55	0.11	116	3.94	2.35	0.72
K4'	71.7	0.34	15.2	2.72	0.06	2.98	0.95	0.24	4.49	0.05	0.16	-	52.2	-	-	-
K5	65.9	0.37	13.5	4.06	0.14	3.16	2.03	0.47	5.57	0.08	0.25	0.47	15.0	3.41	2.97	1.04
K6	49.0	0.92	17.7	8.37	0.15	7.23	5.12	2.79	1.78	0.22	0.11	0.72	5.0	6.05	5.80	1.63
K7	55.8	0.88	17.1	7.07	0.13	5.18	8.04	2.61	1.32	0.22	<0.01	0.12	5.0	1.55	1.50	0.83
K8	54.3	0.92	17.6	7.45	0.14	6.15	1.87	4.96	2.15	0.21	0.32	0.13	611	3.84	3.60	0.95
K9	54.1	0.86	16.5	7.60	0.11	5.67	5.29	3.50	1.55	0.20	<0.01	0.51	4.0	4.11	4.00	1.75
K10	55.7	0.90	17.3	7.16	0.08	4.51	7.66	2.83	0.66	0.22	0.03	0.38	7.0	2.72	2.59	0.77
K10'	53.4	0.98	14.4	7.70	0.10	7.93	6.41	1.93	1.29	0.19	0.12	-	2.5	-	-	-
K11	38.4	1.20	22.8	11.4	0.11	5.80	3.91	0.10	4.91	0.28	0.76	0.78	40.0	9.34	4.85	9.84
K11'	49.9	1.19	19.2	6.96	0.14	9.41	6.65	0.22	3.55	0.22	0.33	-	14.3	-	-	-
K12	62.2	1.05	17.1	7.14	0.2	5.69	2.85	1.13	3.76	-	0.38	-	75.9	-	-	-
K13	58.1	0.98	17.6	6.54	0.16	5.45	3.9	0.41	4.14	-	0.53	-	29.3	-	-	-
N1	43	0.41	12.1	5.43	0.1	2.85	1.59	0.5	3.02	0.04	0.27	-	10.5	-	-	-
N2	38.3	0.69	17.4	7.68	0.06	3.67	0.72	0.24	4.07	0.11	0.3	-	7.6	-	-	-
Y1	72.6	0.59	14.5	1.32	0.29	1.98	2.54	0.26	2.38	-	0.65	-	8.7	-	-	-
Y2	39.6	0.96	10.9	5.23	0.87	1.76	20.9	2.19	1.49	-	0.041	-	5.3	-	-	-

C: inorganic carbon content, LOI: loss of ignition, $H_2O(+)$: bound water, $H_2O(-)$: adsorbed water, -: not analyzed.

Table 3 Details of the batch experiments

Category	Samples used
Oxic batch experiments using unmixed samples	K1,K2, K3, K4, K4', K5, K6, K7, K8, K9, K10, K10', K11, K11', K12, K13, N1, N2, Y1, Y2
Anoxic batch experiments using unmixed samples	K4', N1
Oxic batch experiments using sample mixtures	Mixing ratio K12:K13=3:1, 1:1, 1:3 Y1:Y2=3:1, 1:1, 1:3
Consecutive oxic batch experiments	K2, K8, K11', Y1, Y2, Y3(Y1:Y2=1:1), N1, N2

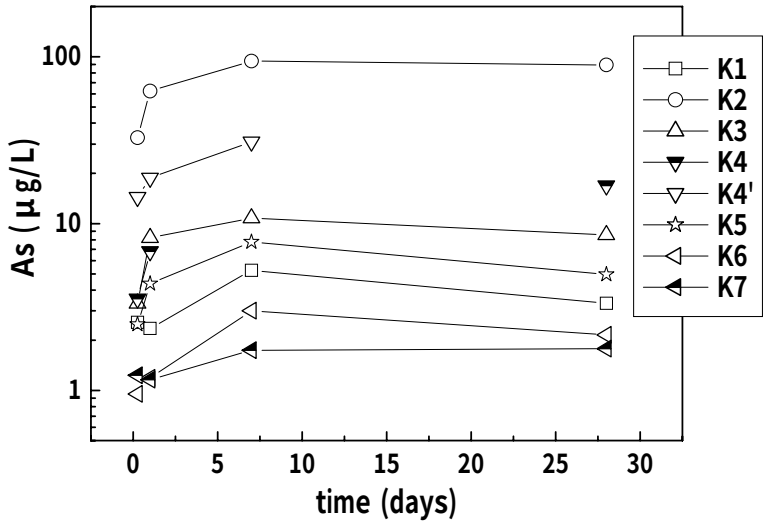

Fig. 1(a) As concentration changes of the leachate from altered igneous rock samples of K1 to K7

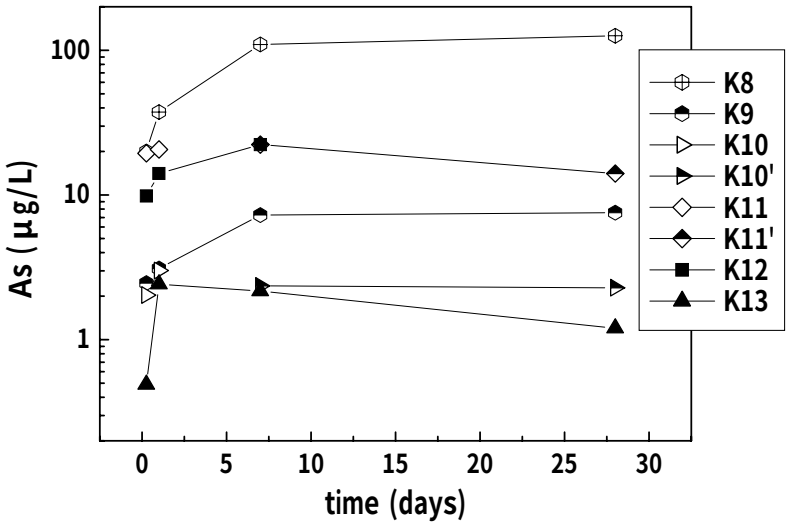

Fig. 1(b) As concentration changes of the leachate from altered igneous rock samples of K8 to K13

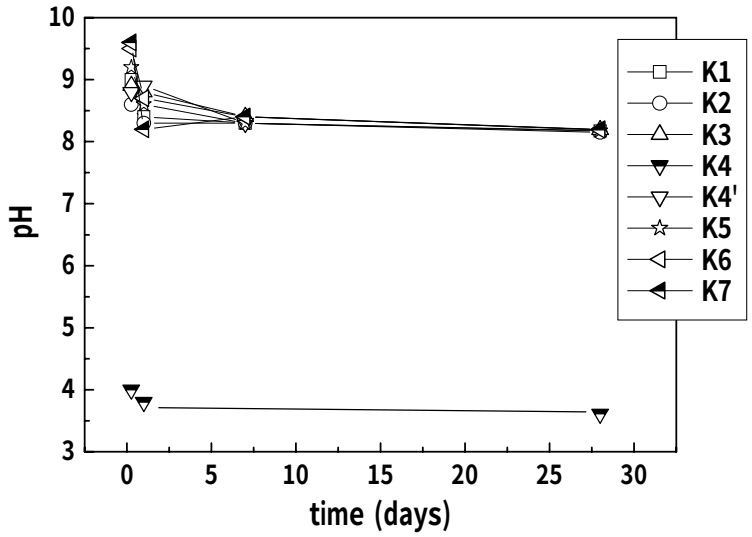

Fig. 2(a) pH changes of the leachate from altered igneous rock samples of K1 to K7

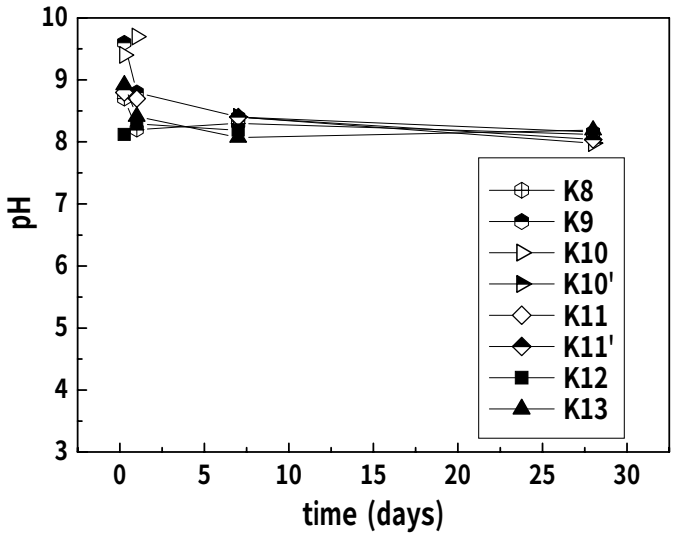

Fig. 2(b) pH changes of the leachate from altered igneous rock samples of K8 to K13

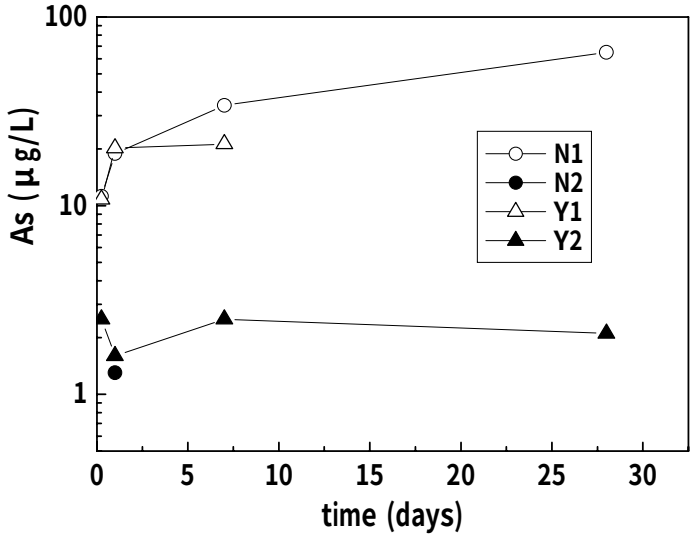

Fig. 3 As concentration changes of the leachate from sedimentary rock samples

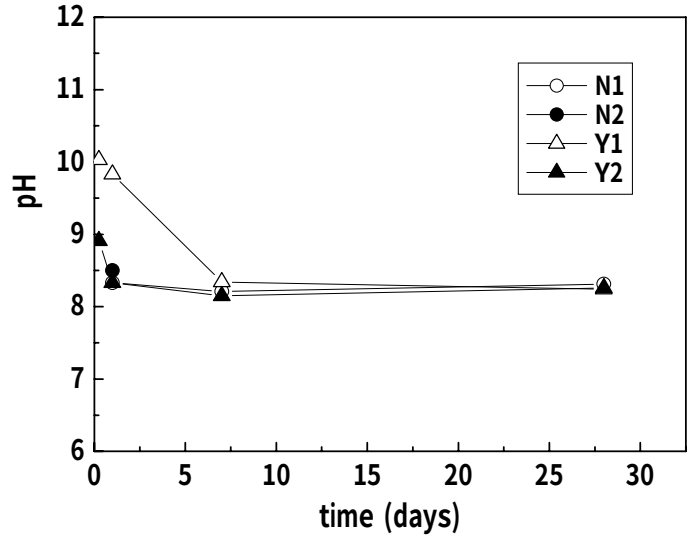

Fig. 4 pH changes of the leachate from sedimentary rock samples

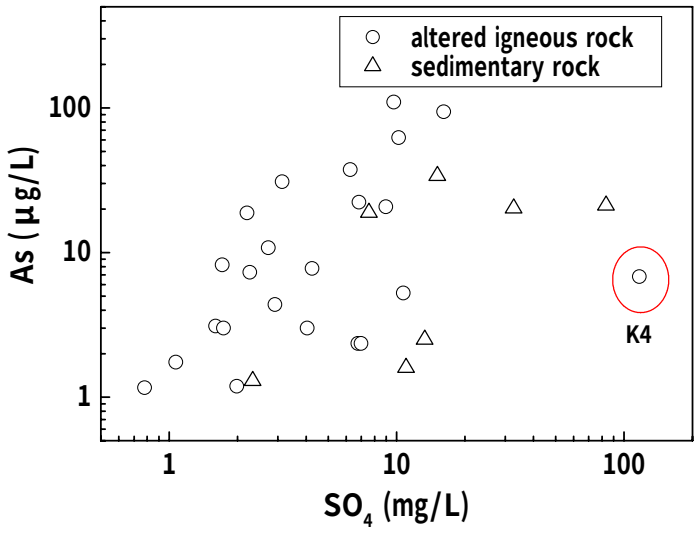

Fig. 5 As concentration in leachate vs SO_4 concentration in leachate

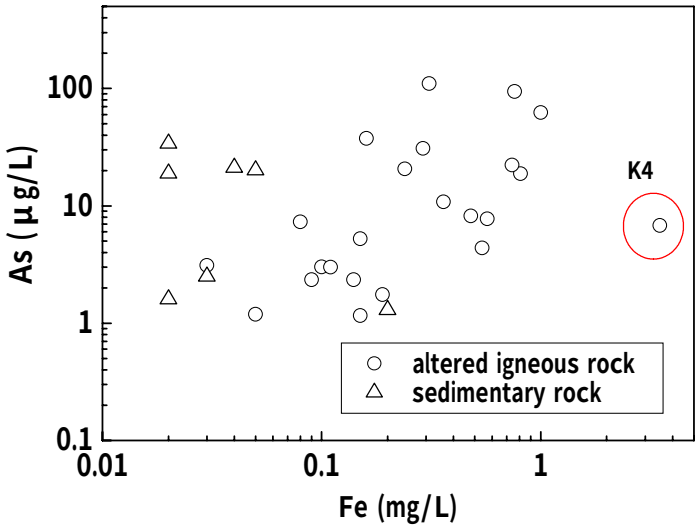

Fig. 6 As concentration in leachate vs Fe concentration in leachate

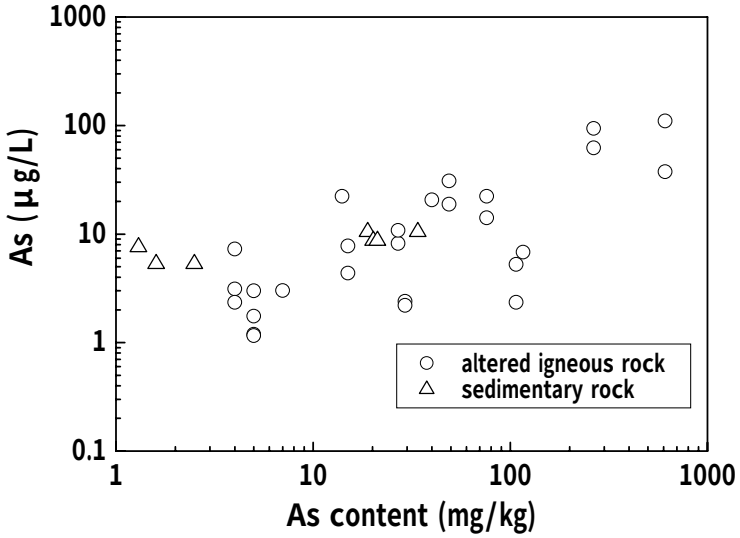

Fig. 7 As concentration in leachate vs As content in rock

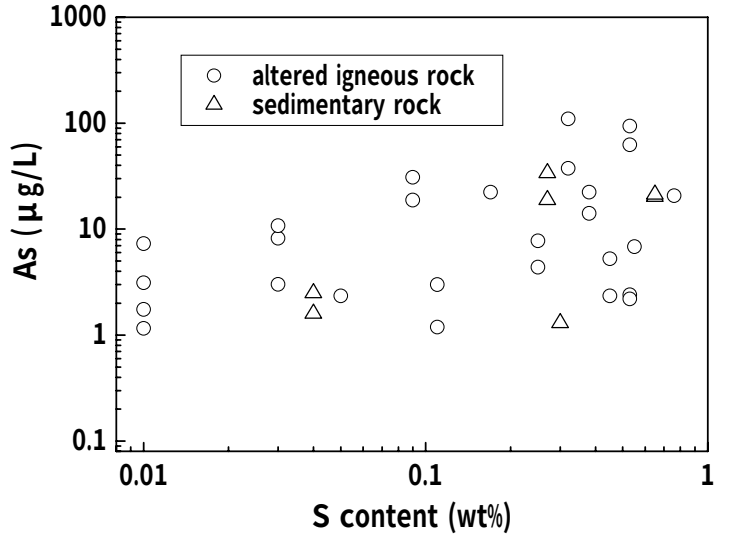

Fig. 8 As concentration in leachate vs S content in rock

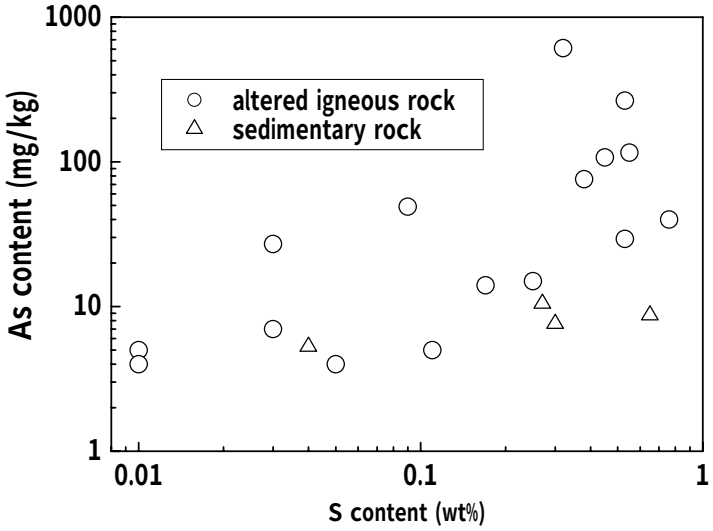

Fig. 9 As content vs S content in rock samples

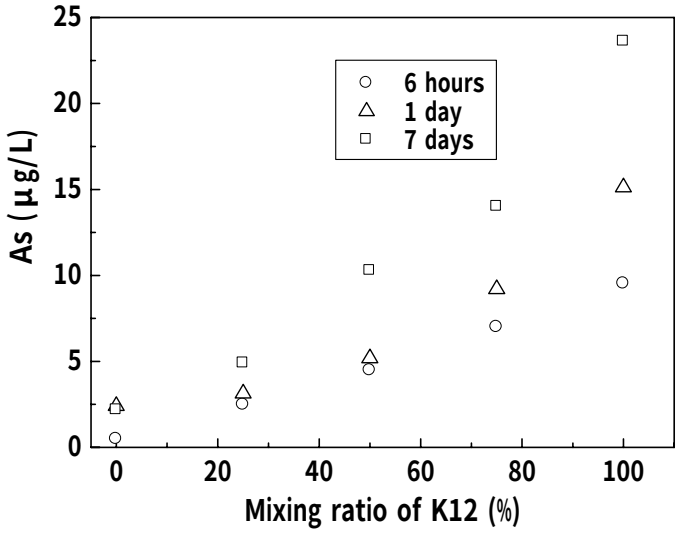

Fig. 10 As concentration in leachate as a function of mixing ratio of K12 sample

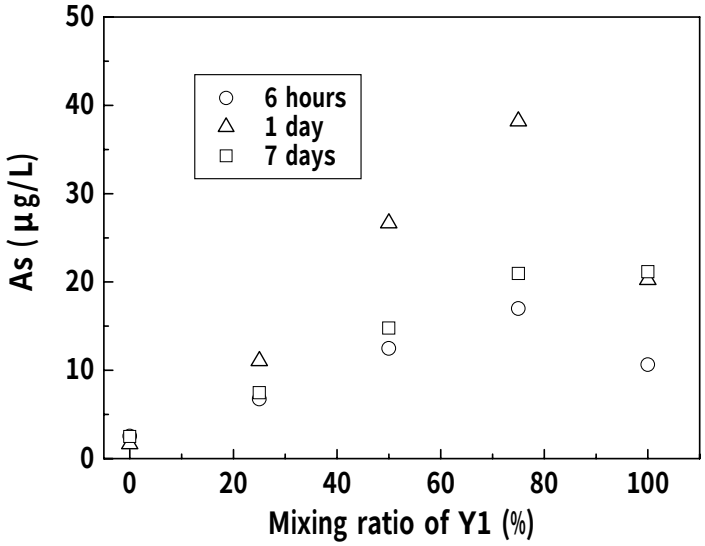

Fig. 11 As concentration in leachate as a function of mixing ratio of Y1 sample

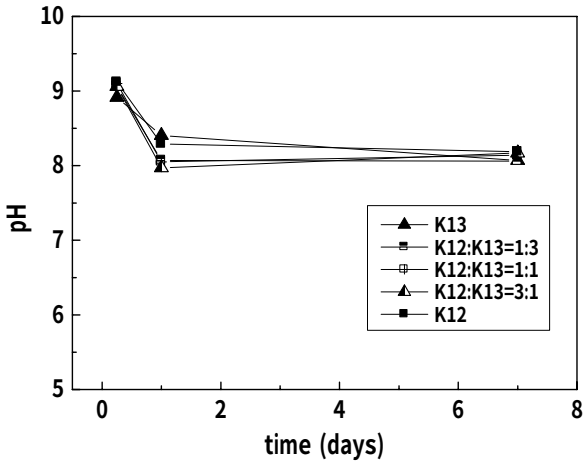

Fig. 12 pH change of the leachate from K12 and K13 mixture

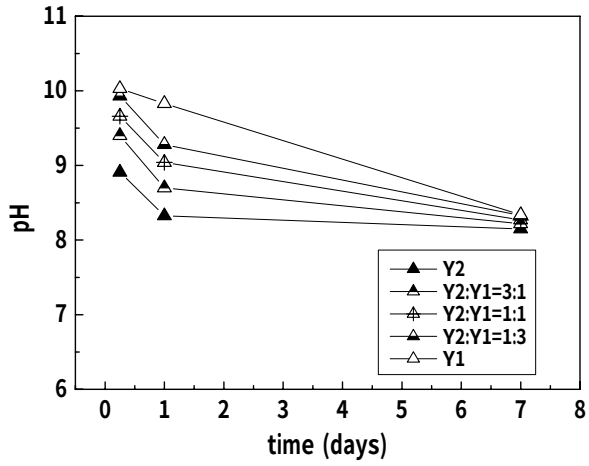

Fig. 13 pH change of the leachate from Y1 and Y2 mixture

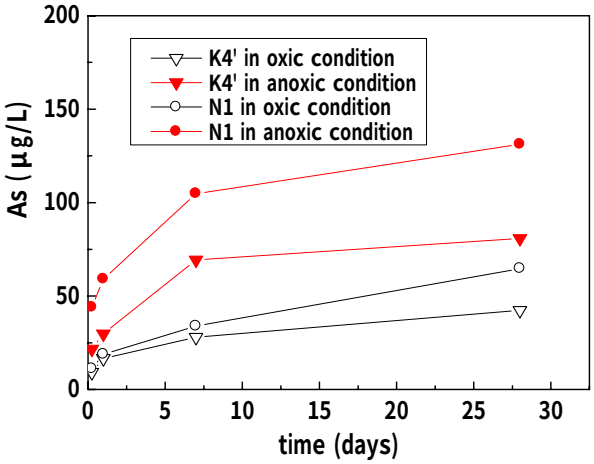

Fig. 14 Comparison of As leaching in oxic and anoxic conditions

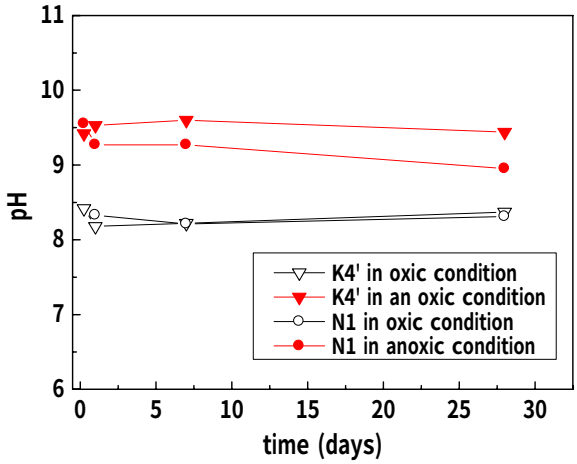

Fig. 15 Comparison of leachate pH in oxic and anoxic conditions

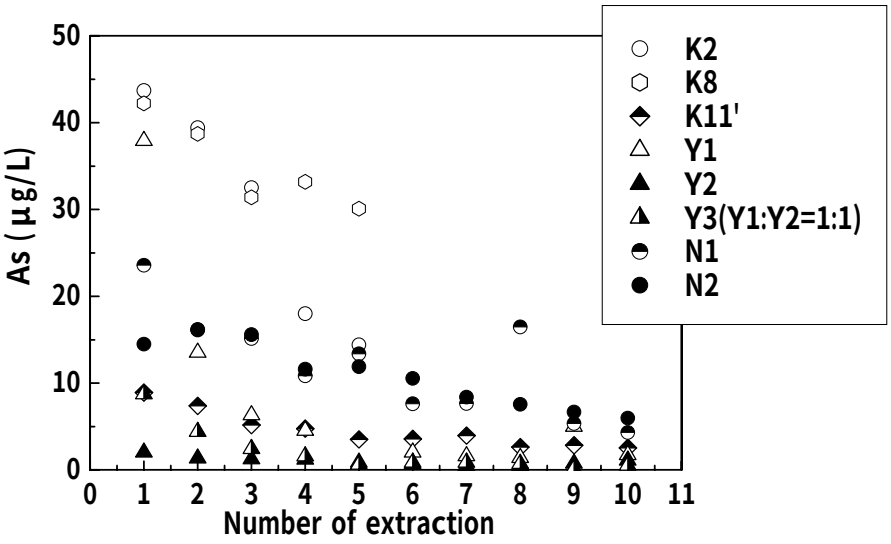

Fig. 16 As concentration changes of the leachate with the number of extractions

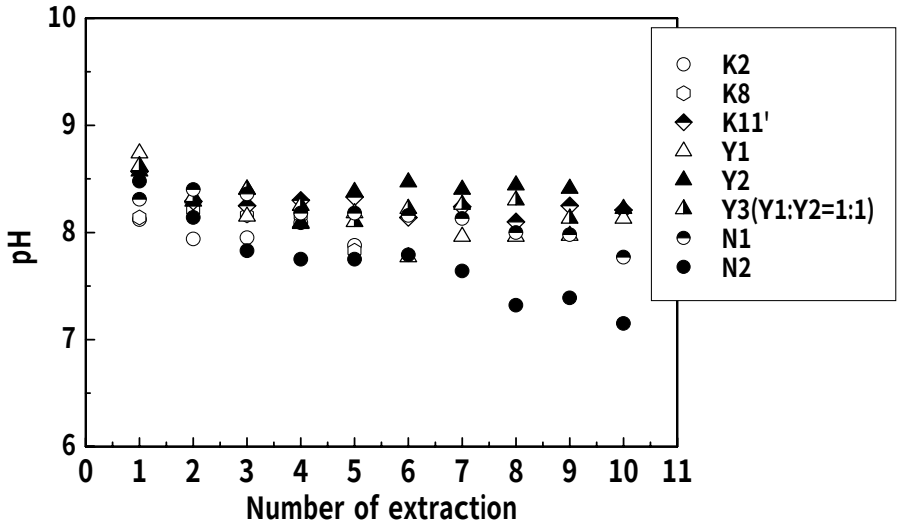

Fig. 17 pH changes of the leachate with the number of extractions

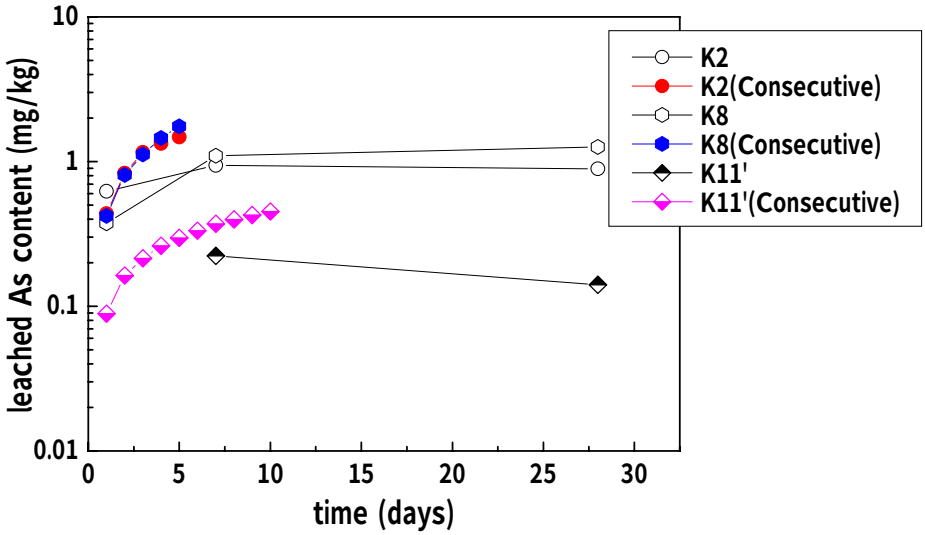

Fig. 18(a) Cumulative leached As content from altered igneous rock samples

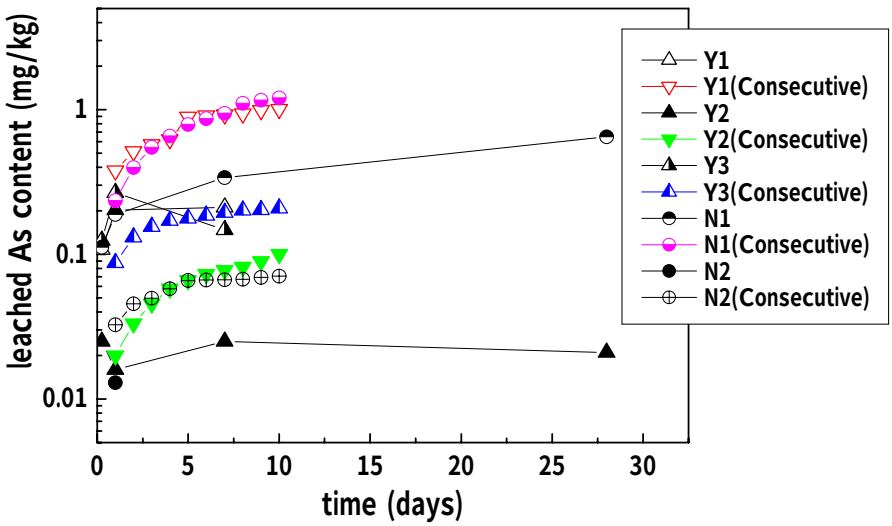

Fig. 18(b) Cumulative leached As content from sedimentary rock samples