

Evaluating the long-term leaching characteristics of heavy metals in excavated rocks

Évaluation des caractéristiques de lixiviation à long terme de métaux lourds dans les roches excavées.

Inui T., Katsumi T., Takai A.
Kyoto University, Kyoto, Japan

Kamon M.
Kagawa National College of Technology, Takamatsu, Japan,

ABSTRACT: When excavation works are executed at stratum that naturally contain heavy metals due to their geologic histories, time-saving and reliable assessment of contamination potential by these metals is a current geotechnical challenge. This paper addresses the long term leaching characteristics of arsenic and lead in several rock materials, which were weathered in outdoor for more than two years. In addition, applicability of several time-saving laboratory test methods were verified as a tool to estimate the actual leaching behaviour of heavy metals.

RÉSUMÉ : Lorsque des travaux d'excavation sont effectués dans des strates contenant naturellement des métaux lourds en raison de leurs antécédents géologiques, une évaluation fiable et économe en temps du potentiel de contamination par ces métaux pose à l'heure actuelle un problème géotechnique. Ce document traite des caractéristiques de lixiviation à long terme de l'arsenic et du plomb dans plusieurs matériaux rocheux, ces derniers ayant été exposés à l'extérieur aux intempéries pendant plus de deux ans. En outre, l'applicabilité de plusieurs méthodes de test en laboratoire économes en temps a été vérifiée comme outil d'évaluation du comportement de lixiviation réel des métaux lourds.

KEYWORDS: natural contamination, rock, arsenic, leaching test, outdoor exposure test

1. INTRODUCTION

When excavation works are executed at stratum that naturally contain heavy metals due to their geologic histories, time-saving and reliable evaluation to judge the contamination potential by these metals and metalloids is required for proper management of geomaterials with unacceptable contamination potentials. Heavy metals existing naturally in stratum are fundamentally stable and immobile under the anaerobic depositional environment. However, in some cases, leaching of these constituents is triggered when exposed to water and oxygen after excavation works. Acid drainage, which comes mainly from the interactions between water, oxygen, and sulfide minerals in soils and rocks, often produces sulfide acid and increases the leaching concentrations of metals. Thus, development of testing methodologies to assess their long-term leaching potential and behavior has been a great geoenvironmental issue in Japan (e.g. Hattori et al. 2003, Okumura et al. 2007). Generally, conventional batch and/or column leaching tests have been widely employed for evaluating the leaching potential of contaminated soils and waste-based geomaterials. However, when they are employed for rock materials, sample preparation including sampling and crushing is more likely to influence the leaching amount of trace elements (Inui et al. 2010). In addition, effects of oxidation after excavation on the leaching behavior should be considered since the acid rock drainage due to dissolution of sulfide minerals in rock is one of the main mechanisms which promote the leaching of heavy metals.

This study firstly presents the results of more than 27-month outdoor exposure tests conducted for five rock samples to assess their in situ leaching characteristics. They contain certain concentrations of natural-derived lead and arsenic, which are expected to be released if they are exposed to water and oxygen. The main focus is placed on the comparison of leaching characteristics of trace metals in outdoor exposure tests with those in various conventional laboratory tests, which include the

total trace metal content test, conventional batch leaching test, accelerated oxidation tests and column leaching test. Laboratory leaching tests were validated as an index of the long term leaching characteristics of trace metals by comparatively assessing the results with the outdoor leaching behaviors

2 MATERIALS AND METHODS




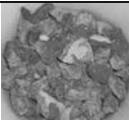
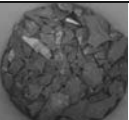
2.1 Materials

Five different rock materials were used. They were generated in construction works such as excavation and tunneling, which were executed in mountainous areas far from industrial and urban areas in Japan. Thus, it can be considered that heavy metals contained are derived from natural resources. Five rock samples consist of black shale, andesite, and three mudstones (MS-1, 2 and 3). They were all stored with their natural water content under the temperature of approximately 20 °C in sealed condition to prevent the exposure to oxygen and water. Table 1 shows their appearances and the total contents of As and Pb as well as chemical compositions which were determined by the X-ray fluorescence analysis. According to the Japanese guideline, excavated materials containing more than 9 mg-As/kg or 23 mg-Pb/kg should be assessed in terms of their contamination potential (Ministry of Land, Infrastructure, Transport and Tourism, Japan 2010). All the samples used in this study contains more than 9 mg-As/kg. Pb higher than this standard was detected only in black shale.

Figure 1 shows pH values of rock samples for distilled water and H₂O₂ solutions with 3% and 30% concentrations. pH measurement using H₂O₂ solutions were employed to evaluate the possible pH change of geomaterials when they are oxidized under weathering conditions. Geomaterials with pH < 3.5 for 30% H₂O₂ solution are considered to have acidification potentials (Japanese Geotechnical Society 2009). In this study, 3% H₂O₂ solution was also used to evaluate the acidification potential against weaker oxidation effects. Black shale and

andesite are fundamentally acidic even for distilled water. Three mudstone are considered to be alkaline rocks without oxidization effects. However, pH value of MS-2 for 30% H₂O₂ solutions were drastically reduced to 2-3, and pH values of MS-3 for 3% and 30% H₂O₂ solutions were lower than 3. These results supported that MS-3 is most easily acidifying among three mudstones.

Table 1. Chemical properties of rock samples used in this study

Sample ID	Black shale	Andesite
Appearance		
As content (mg/kg)	28	26
Pb content (mg/kg)	23	5
Chemical composition (% in mass)	SiO ₂ : 43.6, Fe ₂ O ₃ : 21.4, Al ₂ O ₃ : 4.6, CaO: 0.2, K ₂ O: 16.5, SO ₃ : 8.8, TiO ₃ : 3.0, Others: 1.9	SiO ₂ : 59.0, Fe ₂ O ₃ : 11.6, Al ₂ O ₃ : 13.5, CaO: N.D., K ₂ O: 8.9, SO ₃ : 5.4, TiO ₃ : 1.0, Others: 0.6
MS-1	MS-2	MS-3
		
23 13	15 6	23 1
SiO ₂ : 54.2, Fe ₂ O ₃ : 15.3, Al ₂ O ₃ : 10.4, CaO: 7.9, K ₂ O: 5.2, SO ₃ : 4.0, TiO ₃ : 1.4, Others: 1.5	SiO ₂ : 54.2, Fe ₂ O ₃ : 18.7, Al ₂ O ₃ : 12.3, CaO: 2.7, K ₂ O: 7.2, SO ₃ : 2.5, TiO ₃ : 1.9, Others: 0.5	SiO ₂ : 64.6, Fe ₂ O ₃ : 11.6, Al ₂ O ₃ : 9.9, CaO: 1.1, K ₂ O: 5.2, SO ₃ : 3.9, TiO ₃ : 1.5, Others: 0.5

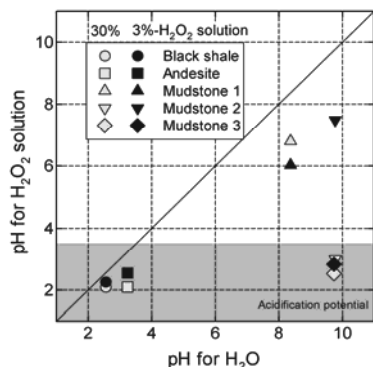


Figure 1. pH of each rock sample for distilled water and H₂O₂ solutions.



Photo 1. View of outdoor exposure test

2.2 Outdoor exposure test

Outdoor exposure tests have been conducted for five rock samples since October 2009. This paper presents the experimental results obtained until February 2012 (about 27 months). Each sample was crushed into 9.5 to 37.5 mm in grain size (2.0 to 9.5 mm in diameter for mudstone 1 due to its crushability). 4000g of rock sample with natural moisture content was stored in a cylindrical plastic container with a cross section of 0.05 m² with the dry density of 2.0 Mg/m³ for black shale, 1.1 Mg/m³ for andesite, 1.2 Mg/m³ for mudstone 1 and

1.6 Mg/m³ for mudstone 2 & 3, and exposed to the rainfall and air throughout the test (Photo 1). Rainfall intensity and percolation volume were continuously monitored. The leachate was periodically collected and subjected to chemical analyses.

2.3 Laboratory leaching tests

Leaching concentrations of As and Pb were analyzed according to the batch leaching test method for the soil quality regulated by the Notification No.46 of Japanese Ministry of the Environment in 1991. In the batch test, air-dried rock samples were crushed until its percentage passing at 2 mm became 100%. In addition, for black shale, the sample subjected to accelerated oxidation was also prepared. Accelerated oxidation was promoted by storing the crushed sample in an incubator under 80% O₂ and 100% humidity condition in 200 days.

As and Pb leaching concentrations during the aforementioned pH measurement using H₂O₂ solutions were analysed to evaluate the effects of accelerated acidification on the leaching behavior.

Tank leaching tests were conducted for monolithic rock samples with approximately 400 g in dry mass by submerging into distilled water for 28 days. The liquid to solid ratio (mL/g) of 10 was employed. Column leaching tests were performed for about 750 g rock samples, which were crushed until its percentage passing at 4.75 mm became 100%. A cylindrical specimen was prepared by vibratory compaction in an acrylic column (55 mm in inner diameter) and then permeated with the permeant by maintaining the constant water head (24 mL/hour in flow rate). The permeant was distilled water after its pH was adjusted to 4.7 using the nitric acid.

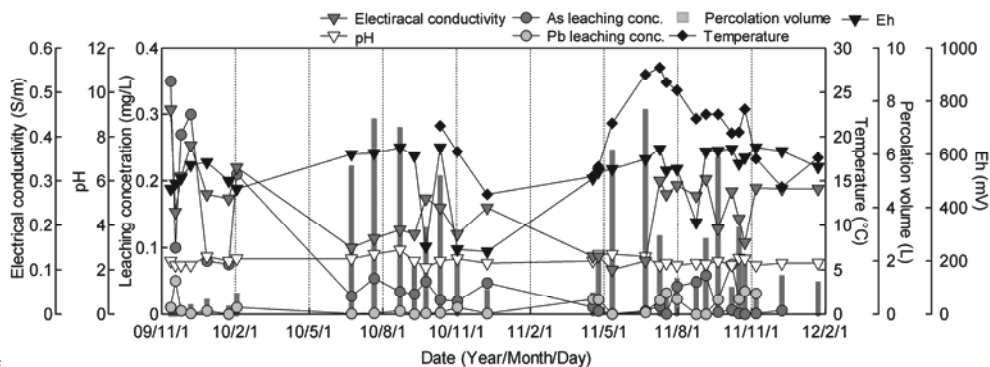
An atomic absorption spectrophotometer (Shimadzu, AA-6800) with a hydride generator and an electrothermal atomization system was used to determine the concentration of As and Pb in the solution. Chemical parameters of the solution (pH, Eh, Electrical conductivity (EC)) were also monitored.

3 RESULTS OF OUTDOOR EXPOSURE TESTS

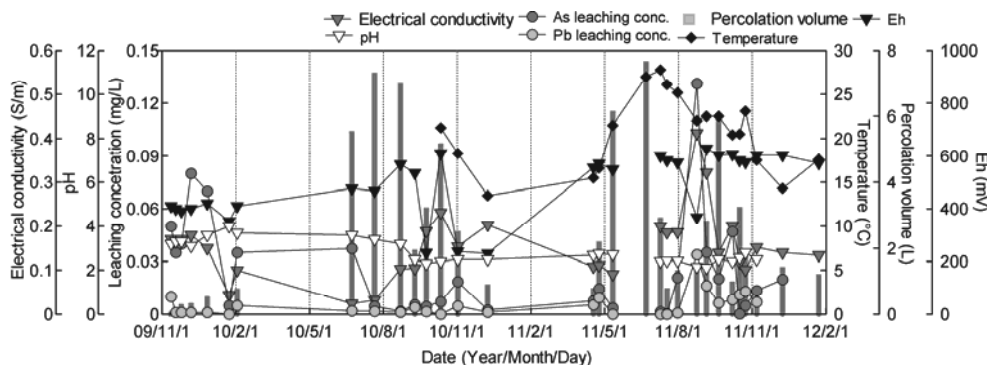
Figure 2 show profiles of percolation volume, pH, EC, Eh, temperature and concentrations of As and Pb of the leachate sample with time. This paper describes the results for black shale and andesite rock samples only. Cumulative flow volumes ranged from 16 to 19 in the liquid to solid ratio (mL/g) after 27 months since due to the difference in permeability.

The leachate from the black shale was acidic, and pH values ranged between 2.1 and 2.5 (Figure 2(a)). As concentrations were higher than 0.1 mg/L in the first three months, then decreased with time and reached 0.02 mg/L. Temperature rising during summer (July-September) were followed by slight decrease in pH and increase in EC and leaching concentrations. This is because the rock samples were subjected to wet and higher temperature conditions in summer and dissolution of the minerals was promoted due to the oxidization produces. Leaching of Pb was also detected but with much lower concentrations than As.

Testing results for the andesite (Figure 2(b)) had similarities with those for the black shale. pH values were ranging from 2.4 to 4.0. At the initial stage, EC values and As leaching concentrations were relatively high and then gradually decreasing and stabilized. However, 10 months after, with gradual lowering of pH values, the values of both parameters were getting larger particularly in summer as same as black shale. These profiles of pH, As leaching concentrations and EC were well explained well by the results of the accelerated oxidation test using H₂O₂ solutions (see Figure 1). Obvious pH drops were observed against the oxidization by H₂O₂ solutions. The andesite sample was gradually oxidized during the outdoor exposure test, and leaching of As and other minerals were promoted accordingly. Pb leaching higher than 0.01 mg/L were rarely observed throughout the test.



(a) Black shale



(b) Andesite

Figures 2. Profiles of pH, Eh, heavy metal concentrations, rainfall intensity and infiltration in outdoor exposure tests

4 DISCUSSION

In Figure 3, pH and Eh values of the leachate samples collected in both outdoor exposure tests and laboratory leaching tests for black shale are plotted on the pH-Eh/pe(electron activity) diagram of dominant forms of As and Fe in As-Fe-S-H₂O system (Zhu & Merkel 2001).

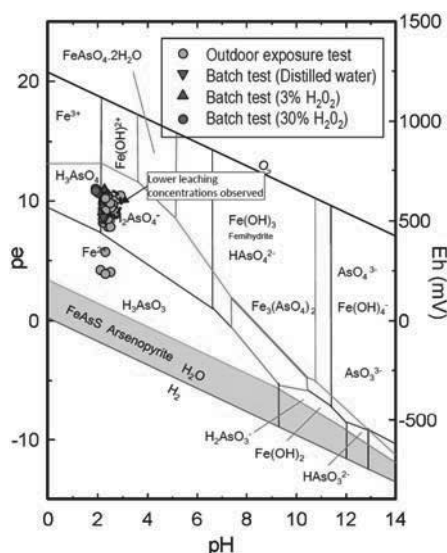


Figure 3. pH and Eh values observed in outdoor exposure tests and laboratory leaching tests combined with pH-Eh diagram of dominant forms of As and Fe in As-Fe-S-H₂O system (Zhu & Merkel 2001).

In the outdoor exposure test, higher leaching concentrations of As were observed even when Eh values were relatively low, where dominant forms of iron and arsenic are Fe²⁺ and H₃AsO₃ (arsenous acid), respectively. When lower leaching concentrations were observed (see the circle in Figure 3), the dominant form of As is expected HAsO₄⁻, which is more easily absorbed to iron compounds and less mobile than H₃AsO₃.

Comparing pH and Eh values monitored in laboratory leaching tests with those in outdoor exposure test, pH values in the batch test using 30% H₂O₂ solution was lowest, and pH for 3% H₂O₂ solution was almost similar to those in the outdoor exposure test. This indicates that 30% H₂O₂ solution is more influential than outdoor exposure in more than two years in terms of acidification, and accelerated acidification by 3% H₂O₂ solution is almost comparable to a few years outdoor exposure. This trend was consistent in all the rock samples used in this study and it can be concluded that pH changes against 3% and 30% H₂O₂ solutions could classify acidification potentials under the weathered condition, but the acceleration by 30 % H₂O₂ solution possibly overestimate the acidification progress in outdoor even for two years.

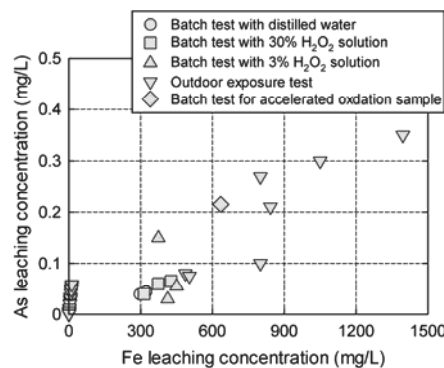
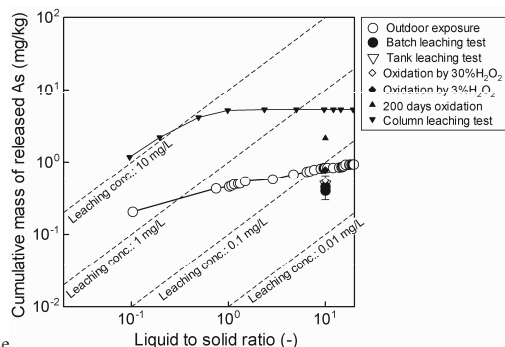


Figure 4. Relationship between Fe and As leaching concentrations in various leaching tests

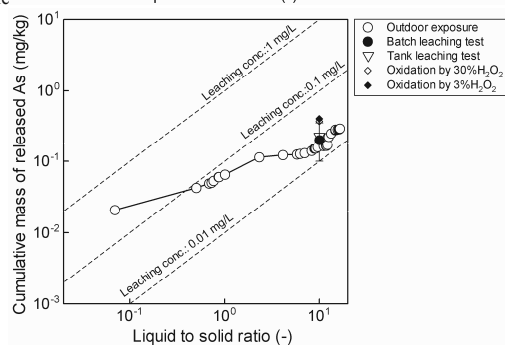
Figure 4 shows a relationship between Fe and As leaching concentrations in both outdoor exposure tests and laboratory leaching tests. A clear correlation between them indicates that dissolution of iron pyrite due to oxidization is a main driver for As leaching. In addition, Fe and As concentrations are correlated in laboratory leaching tests as well. From these observations, dissolution of pyrite due to oxidization was well simulated by the accelerated acidification/oxidization methods, such as adding H₂O₂ solutions and long term exposure to 80%

O₂ and water, which were employed in this study.

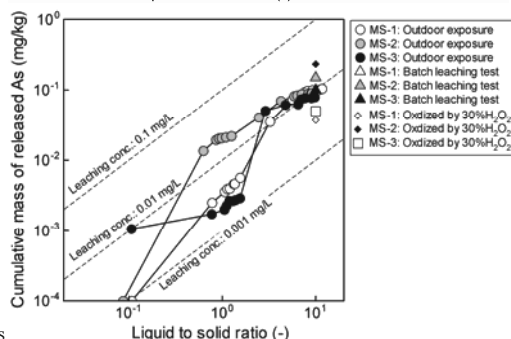
Figures 5 shows As leaching amounts of all the samples in outdoor exposure test and several laboratory leaching tests described in section 2.3. The leaching amounts of As from unit weight of each rock sample are plotted with the cumulative volume of solvent or percolated water contacting with the rock sample during laboratory leaching tests and outdoor exposure tests, which is represented by the liquid to solid ratio (L/S).



(a) Black shale



(b) Andesite



(c) Mudstones

Figures 5. Comparison of As leaching amounts obtained in 27 months outdoor exposure test and laboratory leaching tests.

For the black shale (Figure 5(a)), the leaching amount at L/S = approximately 10 reached 0.84 mg/kg, which is slightly larger than those in the conventional batch leaching test as well as the accelerated acidification test, which were conducted with L/S = 10. Considering that chemical activity of the black shale is relatively since EC values of the leachate collected were largest among all the rock samples, the chemical equilibrium achieved in the closed batch leaching systems was likely to limit the dissolution of As. Column leaching test gave 10 times larger leaching amount than the outdoor exposure test, probably because a crushed sample (< 4.75 mm in diameter) was used, and the permeant was continuously renewed in the column leaching test. Thus, sample preparation in the laboratory leaching test is also a key issue for the rock sample.

For the andesite (Figure 5(b)), the overall trends were almost similar to those of the black shale. However, a slope for the outdoor exposure test became steeper as the percolation volume increased (L/S > 10), since aforementioned As leaching associated with the oxidation was observed. For MS-2 and 3 (Figure 5(c)), the leaching amounts at L/S = approximately 10 were almost equal to those in the conventional batch leaching

test as well as the accelerated oxidation batch leaching test. However, similar to the black shale, MS-1 had a high chemical activity, and its leaching concentration in the batch leaching tests was limited to a negligible level although 0.1 mg/kg of As was released in the outdoor exposure test at L/S = 10.

From these testing results, the leaching amount of As obtained in the conventional batch leaching test can be a good index of the insitu leaching amount until L/S = 10 in the cases of rock samples with relatively low chemical activities. The accelerated oxidation tests using H₂O₂ solutions can simulate the in situ leaching amount for the safe side. However, the chemical equilibrium may limit the leaching of trace metals in the batch leaching test as observed in black shale and MS-1.

Pb leaching concentrations were negligible for all rock samples. According to the aforementioned criterion for total Pb content suggested by MLIT, all the rock samples are considered safe in terms of Pb leaching. These testing results support the validity of the criterion for total content of Pb.

5 CONCLUDING REMARKS

This manuscript verified several laboratory tests for estimating the long term leaching characteristics of As and Pb in several rock materials, by comparing the results of outdoor exposure tests. Total contents of trace metals can be regarded possibly as screening values to judge whether detailed evaluation of leaching characteristics are necessary. The leaching amount of As obtained in the conventional batch leaching test can be a good index of field leaching amount, and the accelerated oxidation tests can simulate the outdoor leaching amount for the safe side. These observations confirm the validity of a series of laboratory leaching tests as a tool to estimate the in situ leaching behavior of heavy metals in excavated rocks.

ACKNOWLEDGEMENTS

This research was financially supported by the Grant-in-Aid for Scientific Research (B) (No. 20360211), Japan Society for the Promotion of Science. The authors acknowledge Ms. A. Dejima and Ms. M. Katayama, former graduate students of Kyoto University, for their great efforts in laboratory experiment works.

REFERENCES

- Hattori, S., Ohta, T. and Kiya, H. 2003. Engineering geological study on exudation of acid water from rock mucks -Evaluation methods of rocks at the Hakkouda Tunnel near mine area, *Jour. Japan Soc. Eng. Geol.*, 43 (6), 359-371.
- Inui, T., Katsumi, T., Katayama, M. and Kamon, M. 2010. Effects of friability and grain size on the leaching of heavy metals in excavated rock materials, *Environmental Geotechnics for Sustainable Development*, M. Datta et al. (eds.), Tata McGraw Hill, New Delhi, 730-733.
- Japanese Geotechnical Society. 2009. *Japanese Standards and Explanations of Laboratory Tests of Geomaterials*, 314-315.
- Ministry of Land, Infrastructure, Transport and Tourism, Japan. 2010. *Technical Manual on the Countermeasures against Soils and Rocks Containing Natural-Derived Heavy Metals in Construction Works (Draft)*, 10.
- Okumura, K., Sakurai, K., Nakamura, N. and Morimoto, Y. 2007. Environmental impacts of naturally occurring heavy metals and countermeasures, *Journal of Geology*, 116 (6), 892-905.
- Zhu, Y. and Merkel, B.J.. 2001. The dissolution and solubility of Scorodite, FeAsO₄·2H₂O: Evaluation and simulation with PHREEQC2, *Wiss. Mitt. Inst. fur Geologie*, TU Bergakademie Freiberg, Germany, 18, 1-12.