Evaluation of Mineral Barriers against Acid Rock Drainage

Angelica Naka¹, Takeshi Katsumi¹, Giancarlo Flores², Toru Inui¹, Takehiro Ohta³, Takuya Urakoshi³, and Tomokazu Ishihara³

¹Graduate School of Global Environmental Studies, Kyoto University, Kyoto, Japan

²Graduate School of Engineering, Kyoto University, Kyoto, Japan

³Disaster Prevention Technology Division, Railway Technical Research Institute, Tokyo, Japan

E-mail: katsumi.takeshi.6v@kyoto-u.ac.jp

ABSTRACT: The barrier performance of geosynthetic clay liners (GCLs) containing Na-bentonite, zeolite, and ferrihydrate against acid rock drainage (ARD) was evaluated through hydraulic conductivity and sorption tests in order to determine their applicability as adsorption layers in waste rock containment facilities. The hydraulic conductivity (*k*) of GCL permeated with water was 1.4×10^{-11} m/s and this increased by one order of magnitude with ARDpermeation ($k = 5.0 \times 10^{-10}$ m/s). The *k* of zeolite permeated with water was 3.0×10^{-10} m/s and this also increased with ARDpermeation ($k = 1.4 \times 10^{-9}$ m/s). The *k* value of ferrihydrate was 7.3×10^{-9} m/s when permeated with water and this remained constant after ARD permeation ($k = 8.6 \times 10^{-9}$ m/s). Metal sorption of bentonite, zeolite, and ferrihydrate were different in terms of sorption capacity and selectivity, which can be summarized as follows: bentonite: Cu>Fe>Zn>Al>As>Pb, zeolite: Cu>Fe>Zn>Pb≈Al≈As, and ferrihydrate: Cu>Zn>Al>As>Pb. According to experimental results, the tree minerals appear to be good candidates for ARD mitigation.

1. INTRODUCTION

Reutilization or recycling of excavated soils and rocks from construction works, mining operations, and other activities—that formerly were considered as waste—has become an important geoenvironmental issue in some countries such as Japan. It is due to the growing awareness to reduce the amount of materials that are being used and disposed, as well as to deal with the limitation of landfill space. Therefore, Japan is moving towards the reuse of waste materials that are generated in large quantities.

Associated with that development, a goal and challenge to limit the environmental impact of using recycled materials has emerged. It is because when recycled materials are used in geotechnical applications, such as embankments, there is the potential for pollution or natural contamination. Some by-product materials, such as industrial waste (coal ash, slag, and scrap tyres) and municipal solid waste (MSW) incinerator ash may contain toxic chemicals (heavy metals, boron, fluorine, among others). In addition, some of them are not environmentally compatible even if they have been treated prior to geotechnical applications. Thus, a proper characterization of soil and waste as well as monitoring or predicting the release of contaminants from them become a necessary tool to assess environmental impacts properly (Katsumi et al. 2008a; Katsumi et al. 2010; Susset and Grathwohl 2011). For this purpose, leaching (or elution) and composition (human availability) tests are conducted and the results are used to determine if the leaching level exceed the environmental standards. If it does, necessary measures should be taken in order to prevent a negative environmental impact.

In Japan, particularly, several types of metals such as arsenic and lead and other harmful substances are naturally present in higher concentration compared to the average level in the world and so do the soils and rocks from excavation and mining. The reason of this is because Japan is located in a geological active area, which favors the accumulation of these elements. Moreover, in mountainous areas of Japan, there are several rock formations which may contain pyrite (FeS₂) and other minerals that contain high amount of As and Pb(Katsumi et al. 2008a; Katsumi et al. 2010). These constituents are basically stable and immobile under anaerobic conditions, but they may leach due to the exposure to water and oxygen after excavation(Katayama et al. 2011).

Thus, the need to control natural contamination by metals and metalloids coming from mining and construction waste becomes an important environmental issue and represents a current challenge in many countries such as Japan (Ohta et al. 2006). In the past, remediation technologies were focused on the development of covers systems that prevented infiltration of water and oxygen (Lange et al. 2010b). However, recent researches have suggested that some hazardous elements, such arsenic, selenium, nickel, and zinc are mobile even under neutral pH-conditions (Rowe 2006; Lange et al. 2010b). Moreover, the reductive dissolution of Asbearing minerals has resulted in the release of arsenic(Rowe 2006). As a result, disposal of excavated rocks with potential of acid rock drainage (ARD) generation is going towards storage of hazardous materials in lined containment facilities (Lange et al. 2007; Katsumi et al. 2008a), or the reuse of these materials in technical constructions such as road dams, embankments prior an adsorption layer installation. The latter, is a relatively new and cost-effective method that proposes the use of materials that have high adsorption capacity towards heavy metal. Besides, it is expected to provide low hydraulic conductivity and a low enough metal release that meet the environmental standards.

Minerals such as bentonite (geosynthetic clay liners or GCLs), zeolite, and ferrihydrate seems to be potential materials to be used as adsorption layer, since previous studies have suggested that some of them have relatively large specific surface area, medium to high metal adsorptive capacity, self-healing capacity, and low hydraulic conductivity (Naka et al. 2010a; Naka et al. 2010b; Varank et al. 2011).

GCLs, which usuallyconsist of granular or powdered bentonitesupported by geotextiles and/or geomembranes, play an important role in providing cost effective barriers for environmental protection for a wide range of application (Bouazza 2002), including recent potential applications in mining industry (Lange et al. 2007, 2009, 2010a). For liner applications, the bentonite is generally sodium bentonite because of its higher swelling ability and cation exchange capacity compared to calcium bentonite(Kashir and Yanful 2001). Sodium bentonite may be the result of natural geological processes or the result of an activation of calcium bentonite using soda ash to force the Ca-Na exchange (Guyonnet et al. 2009). Zeolite is a geographically widely distributed mineral. It has a cage-like negatively charged structure, which results from isomorphous replacement of Al³⁺ with Si⁴⁺ in the structure. This negative charge is balanced by innocuous cations (Na⁺, Ca⁺, K⁺) that are exchangeable with certain cations. As a result, zeolite can adsorb cations such as Pb²⁺, Cd²⁺, Zn²⁺, and Mn²⁺ selectively through ion exchange mechanism. Even though the adsorption capacity of each zeolite is different, previous studies have reported that this mineral generally shows preference for metals in the following order: Pb²⁺> Cd^{2+} Cs⁺> Cu²⁺> Co²⁺> Cr³⁺> Zn²⁺> Ni²⁺> Hg²⁺ (Erdem et al. 2004). Ferrihydrate is an amorphous iron oxy-hydroxide material, usually present in clays, soils, and sediments. Research about ferrihydrate has shown that this material has high potential to remove arsenic, lead, and cadmium from contaminated water due to their large surface areas and abundance of binding sites (Srivastava et al. 1988; Satpathy and Chaudhuri 1995; Benjamin et al. 1996).

Even though bentonite, zeolite, and ferrihydrate are found to have intermediate to high capacity to attenuate certain metals, their

performance when exposed to acid rock drainage is still under investigation. Therefore, this research aims to investigate the barrier performance of bentonite, zeolite, and ferrihydrate against acid rock drainage, through hydraulic conductivity and sorption tests, and determine their applicability as adsorption layers in waste rock containment facilities.

1.1 Mechanisms involved in metal retention

Heavy metals can be immobilized in minerals through numerous mechanisms such ascation exchange, surface complexation, surfaceinduced precipitation, surface co-precipitation, colloid formation at surface, and diffusion into particle micropores. It is sometimes difficult to separate sorption and other types of reactions involving solid such as precipitation and dissolution (Sposito 1984).

Bentonite, specifically montmorillonite, can absorb heavy metals through two different mechanisms: (1) Cation exchange in the interlayers and (2) formation of inner-sphere complexes through Si-O- and Al-O- groups at the clay particle edges (Abollino et al. 2003). Both mechanisms are pH dependent. In acid conditions, the hydrogen ion competes with the heavy metals towards the superficial sites and, besides, most silanol and aluminol groups are less deprotonated which favours metal mobility (Abollino et al. 2003). It was also found that the presence of ligands in solution influences the adsorption of heavy metals due to the formation of metal-ligand complexes.Lange et al. (2010b) have demonstrated that, in addition to the cation exchange capacity from the montmorillonite clay, minerals comprising less than 5% of the bentonite, such as goethite, gypsum, and pyriteplay an important role in sequestering a range of metals, specifically Ni, Zn, and Cu. Besides the crystalline phases present in the starting materials bentonite, those formed as a result of interaction between species present in the ARD (newly-precipitated minerals) can have a significant long-term impact on metal mobility (Lange et al. 2010b).

Zeolites, in general, are weakly acidic in nature and sodiumform exchangers are selective for hydrogen (R–Na + $H_2O \leftrightarrow RH +$ Na⁺ + OH⁻), which leads to high pH values when the exchanger is equilibrated with relatively dilute electrolyte solutions. In this condition, metal hydroxide precipitation most likely occurs. The sorption on zeolitic particles is a complex process because of their porous structure, inner and outer charged surfaces, mineralogical heterogeneity, existence of crystal edges, broken bonds, and other imperfections on the surface(Peri et al. 2004).

In case of ferrihydrate, previous spectroscopic studies, pressurejump relaxation kinetics measurements, and titration measurements discussed in Sherman and Randall (2003)have shown that As strongly adsorbs to iron oxide and hydroxides. The attenuation mechanismis assumed to be by forming inner-sphere surface complexes by ligand exchange with hydroxyl groups at the mineral surface(Sherman and Randall 2003).

2. MATERIALS AND METHODS

2.1 Materials

Bentonite used for the tests was obtained from a needle-punched geosynthetic clay liner (GCL) Bentofix® NSP 4900. This GCL contains natural powered sodium bentonite sandwiched between woven and nonwoven geotextiles, with a mass per unit areaequal to 4670 g bentonite/m². According to the manufacturer, this was measured using the EN 965 standard at natural moisture content(NAUE 2005). Bentonite contained in this GCL had a water content of approximately 10.0%, a specific gravity of 2.85, and a smectite content of 80%. The zeolite (Clinoptilolite) was provided by Mitsui Mineral Development Engineering Co., Ltd. (MINDECO) and has a particle size of 0.5 mm sieve pass. The ferrihydrate, FeO(OH), was a commercial yellow powder material obtained from NacalaiTesque.

Species investigated in this study include Fe, Al, Cu, Zn, As, and Pb, which are common metals present in ARD. Considering that ARDs usually contain sulfate ions in their composition, most

solutions were prepared using sulfate species: $FeSO_4$, $Al_2(SO_4)_3$, $CuSO_4$, and $ZnSO_4$. However, in case of As, the pentavalent salt $(Na_2HAsO_4, '7H_2O)$ was used, and in case of Pb, the chloride specie was used (PbCl₂), as it has slightly higher solubility than the sulfate compound.

An artificial ARD was prepared in the laboratory based on the drainage composition of a Pb-Zn-(Cu) deposit located in Cerro de Pasco, Peru (Wibkirchen et al. 2005). This ARD was selected because it represents a very severe case of ARD in terms of metal concentration, much higher than the ones reported by other authors who studied acid rock drainage against GCLs (Lange et al. 2010a; Shackelford et al. 2010). Metal composition of the artificial ARD is presented in Table 1. GR grade FeSO₄.7H₂O, Al₂(SO₄)₃·16H₂O, CuSO₄·5H₂O, ZnSO₄·7H₂O, Na₂HAsO4·7H2O, PbCl₂, K₂SO₄, Na₂SO₄, CaSO₄, and MgSO₄ were mixed, and then the pH was adjusted to 3 using H₂SO₄. The electrical conductivity (EC) was 1195 mS/m.

Table 1 Artificial ARD composition

Element	Metal source	Concentration (mg/L)	
K	K_2SO_4	31.7	
Na	Na_2SO_4	281.4	
Ca	$CaSO_4$	432.8	
Mg	$MgSO_4$	251.3	
Al	$Al_2(SO_4)_3 \dot{\cdot} 16H_2O$	263.5	
Fe	FeSO ₄ ·7H ₂ O	5022.2	
Cu	CuSO ₄ ·5H ₂ O	91.7	
Zn	ZnSO ₄ ·7H ₂ O	500.6	
As	Na ₂ HAsO ₄ ·7H ₂ O	3.1	
Pb	PbCl ₂	1.6	

2.2 Methods

2.2.1 Sorption test

The chemical performance of bentonite, zeolite, and ferrihydrate was studied through batch sorption tests. Batch sorption test is a quick method that provides information about metal affinity of these minerals, as well as the mechanisms involved. For this test, single metal solutions of Fe, Cu, Zn, Al, As, and Pbwith concentration ranging from 2 to 800 mg/L were used.

Batch sorption tests were conducted adding 0.1 g of bentonite, zeolite, or ferrihydrate in 50 mL of solution contained in 100 mL plastic bottles. Samples were taken after 24 hours on an incubator shaker at 100 rpm and 20°C. This time was proved to be enough to reach equilibrium (Naka et al. 2011b). After shaking, every mixture was centrifuged and filtered using a filter with a 0.45- μ m pore size. The concentrations of Fe, Cu. Zn, Al, As, Pb, Na, Ca, Mg, and K before and after the sorption tests were analyzed by inductively coupled plasma (ICP), ICPS-800 Shimadzu.

2.2.2 Hydraulic conductivity test

Hydraulic conductivity tests were conducted on GCL, zeolite, and ferrihydrate following the procedures described in ASTM D 5084 (2009b) and ASTM D 7100(2009a), using a falling headwater-constant tailwater system. Figure 1shows a typical diagram for this system, which consists of a flexible-wall permeameter with a cell pressure of 30 kPa and an average hydraulic gradient of 85–95 at constant room temperature of 20°C. The specimen (GCL, zeolite, or ferrihydrate) was placed between filter papers, geotextiles, and plastic caps and was confined by a latex membrane on the sides. The filter paper was used to retain any particle that could block the holes where the effluent passes, while the geotextile was used to make the flux uniform in all directions.In case of the GCL, prehydration with

ARD was done before the setup, as previous studies suggest that the first permeant solution has an impact on the hydraulic conductivity(Naka et al. 2011a).Forthis prehydration process, the GCL was placed into a containment with the ARD solution for seven days and 30 kPa of pressure was applied. The thickness of the GCL was measured regularly using a cathetometer. The thickness of the zeolite and ferrihydrate was adjusted to 2 cm and they were prepared by compaction in a consolidation machine using the optimum water content (45% for zeolite and 66% for ferrihydrate, as shown in Figure 2) and applying 40 kPa of pressure (20 kPa for 24 hours and 40 kPa for 24 hours). The optimum water content was calculated from compaction test results, following the procedures described in ASTM 698(2007). The bulk void ratio of the GCL was 1.5, and the void ratios of the zeolite and ferrihydratewere 2.2, and 4.3, respectively.Effluent analysis were done periodically in all cases by measuring the electrical conductivity (EC), pH,volume, and metal content by ICP. For this purpose, 50 mL plastic reservoirs were placed in the outflow of the system to collect the effluent. Once the volume was about 40 mL, the bottles were replaced by new ones. Hydraulic conductivity test of each specimen with the artificial ARD and distilled water (control) was conducted.



Figure 1 Scheme of a flexible-wall permeameter



Figure 2 Compaction test results of zeolite and ferrihydrate

3. RESULTS AND DISCUSSION

3.1 Sorption test

Sorption test on single metals was conducted in order to determine the metal sorption capacity of each mineral. The isotherms for each metal are presented in Figure 3 and the sorption capacity, in Table 2. According to these results, metal selectivity of each mineral is as follows:

(a) Bentonite: Cu > Fe > Zn > Al >> As >>Pb

(b) Zeolite: Cu > Fe > Zn >>Pb \approx Al \approx As

(c) Ferrihydrate: Cu > Zn >> Al > As >>Pb

Table 2 Metal sorption capacity of bentonite, zeolite, and ferrihydrate

Metal	Bentonite (mg/g bentonite)	Zeolite (mg/g zeolite)	Ferrihydrate (mg/g ferrihydrate)
Al	13.2	1.0	3.1
Fe	71.0	23.7	NA
Cu	93.7	43.1	22.4
Zn	47.1	13.1	17.7
As	0.6	0.9	2.3
Pb	0.01	1.07	0.34

These results show that As sorption on bentonite and zeolite is very low (0.6 mg/g bentonite and 0.9 mg/g zeolite), whereas for ferrihydrate is the highest among these three minerals (2.3 mg/g ferrihydrate). It proves the hypothesis that As is also sorbed or coprecipitated by Fe and other metals present in ARD. Bentonite, zeolite and ferrihydrate show high affinity for Cu (93.7 mg/g bentonite, 43.1 mg/g zeolite, and 22.4 mg/g ferrihydrate), followed by Fe (71 mg/g bentonite and 23.7 mg/g zeolite) and Zn (47.1 mg/g bentonite, 13.1 mg/g zeolite, and 17.7 mg/g ferrihydrate), but lower for Al (13.2 mg/g bentonite, 1 mg/g zeolite, and 3.1 mg/g ferrihydrate), and Pb (0.01 mg/g bentonite, 1.1 mg/g zeolite, and 0.3 mg/g ferrihydrate). Bentonite has higher sorption capacity than zeolite and ferrihydrate except in case of As and Pb, in which zeolite and ferrihydrate seems to work better.

Sorption test results may represent ideal conditions and overestimate the sorption capacity because the surface area of contact between metal and mineral is the maximum in these experiments. Besides, application of these data to ARD may raise some concern as multiple metal ions in the solution may interact due to the synergetic and antagonistic effect that they extert on each other (Kaoser et al. 2005). In multi-metal solutions, metal sorption tends to increase with the decrease in ion exchange, or less competitive species (Lange et al. 2009). Therefore, to evaluate field application of bentonite, zeolite, and ferrihydrate as adsorption layer in waste rock containments, additional tests, such as hydraulic conductivity, become necessary.

3.2 Hydraulic conductivity test and effluent analysis

The results of the hydraulic conductivity test are presented in Figures 4 (water permeation) and 5 (ARD permeation). A summary of hydraulic conductivity values is presented in Table 3. The hydraulic conductivity of GCL permeated with distilled water (control) was constant, with an average of 1.4×10^{-11} m/s. The hydraulic conductivity value of the GCL permeated with artificial ARD was around 5.0×10^{-10} m/s, 10 times higher compared to water permeation case. The hydraulic conductivity of zeolite permeated with water was 3.0×10^{-10} m/s and this value increases one order of magnitude when it was permeated with ARD, with an average a value of 1.4×10^{-9} m/s. The hydraulic conductivity of ferrihydrate is the highest among the three species with a hydraulic conductivity value of 7.3×10^{-9} m/s. The hydraulic conductivity of this material when permeated with ARD does not show any change, with an average value of 8.6×10^{-9} m/s.

Table 3 Hydraulic conductivity of different specimens permeated with water and ARD

Specimen	Permeant solution		
Specifien	Water	ARD	
GCL	1.4×10 ⁻¹¹ m/s	5.0×10 ⁻¹⁰ m/s	
Zeolite	3.0×10^{-10} m/s	1.4×10 ⁻⁹ m/s	
Ferrihydrate	7.3×10 ⁻⁹ m/s	8.6×10 ⁻⁹ m/s	



Figure 3 Sorption of single metals on bentonite, zeolite and ferrihydrate



Figure 4 Hydraulic conductivity of minerals permeated with water (control)



Figure 5 Hydraulic conductivity of minerals permeated with ARD

From the point of view of the hydraulic conductivity value, these three materials are suitable to be employed as lining systems, as the hydraulic conductivity remains relatively low after being exposed to ARD. In the case of bentonite, previous studies have reported that hydraulic conductivity values increases as the concentration of electrolytic solution increases (Petrov and Rowe 1997; Ruhl and Daniel 1997; Shackelford et al. 2000; Jo et al. 2001; Kolstad et al. 2004; Katsumi et al. 2007; Katsumi et al. 2008b). It is because high metal concentration makes water moves out of the mineral interlayer and then, a reduction in swell volume occurs (Jo et al. 2001). Swelling, in combination with the diffuse double layer (DDL), constitutes one of the most important reasons why GCLs provide low levels of hydraulic conductivity (Katsumi 2010), which is necessary for rocks containment facilities with leachingpotential of toxic substances.

The increase of hydraulic conductivity of zeolite permeated with ARD can be attributed to the change in morphology or cristallinity of the structure, most probably produced by low pH high metal concentration. Even though clinoptilolite is quite stable chemically in low pH environments, small changes observed in X-ray diffraction (XRD), electron diffraction X-ray fluorescence (ED-XRF) and transmission electron microscopy (TEM) (Li et al. 2008) indicate that pH may have effect on the mineralogical, chemical and morphological properties of clinoptilolite. Thus, it may negatively impact on the hydraulic conductivity by making it one order of magnitude higher. Transport or migration of metals through the adsorption layer is another important parameter to be considered as the presence of chemicals may have an impact on the surrounding environment.

Analysis of the effluents based on pH, EC, and metal release was done for each mineral in order to evaluate their adsorption behavior and capacity. Results are presented in Figure 6 and 7 and Table 4. Figure 6 shows that the pH and EC equilibrium (ratio of outflow-to-inflow pH and ECdiffer by <0.1)was reached in all cases. For bentonite case, the pH and EC equilibrium was reached at around 250 PVF, while for zeolite and ferrihydrate it was reached at around 20 and 15 PVF, respectively. Figure 7 shows the metal concentration ratio in the effluent during ARD permeation. It was observed no metal migration in the beginning, but after 10 PVF for bentonite and 5 PVF for zeolite and ferrihydrate some metals started to leach out the system. The duration of all tests was different, butin order to compare metal migration and retention among minerals, discussion will be limited up to35 PVF. According to these results, the metal affinity for each mineral can be summarized as follows:

(a) Bentonite: Fe >> Zn \approx Al > Cu>>As >Pb (b) Zeolite: Fe > Al \approx Zn>Cu>>As>>Pb

(c) Ferrihydrate: Fe> Al ≈Zn>Cu>As >Pb



Figure 6 pH and EC analysis of effluents after ARD permeation (a) GCL, (b) zeolite and (c) ferrihydrate





Figure 7 Metal analyze of effluents after ARD permeation (a) GCL, (b) zeolite and (c) ferrihydrate

The removal or sorption of metals in multiple-species occur either through ion exchange (bentonite and zeolite),or specific binding to the surface (ferrihydrate). In the latter, heavy metals are sorbed from solution without releasing other ion in equivalent proportion as it happens in the ion exchange mechanism. In both mechanisms, the selectivity is determined by the strength of electrostatic forces. Thus, metal sorption is governed by the ion valence of cations, the free energy of hydration of the cations, molecular size, and hydrated radius of cations. In that case, the order would be Al > Fe > Cu > Zn >Pb. However, these results differ slightly from what it was observed in experiments. It is probably due to the competition among metals for binding sites, the difference in metal concentration, and other mechanisms such as precipitation. Table 4 shows the amount of metal sorbed on bentonite, zeolite and ferrihydrate taking into considereation the amount of mineral used in each case. After similar amount of PVF (35 PVF), more metal retention was observed for bentonite than zeolite and ferrihydrate. However, according to the results presented in Table 4, none of them has reached the maximum sorption capacity (Table 2), except for the system zeolite-Al. It may indicate that the values obtained in sorption testswere overestimated or the contact time between minerals and metals were not enough to favor sorption mechanisms.In case of bentonite, for Cu, it was observed that the ratio went up to 2, which can be attributed to the release of Cu that was sorbed into the GCL during the prehydration process with ARD solution.

Table 4 Metal sorption capacity at 35 PVF according to the effluent analysis in hydraulic conductivity test

Metal	Bentonite	Zeolite	Ferrihydrate
	(mg/g bentonite)	(mg/g zeolite)	(mg/g ferrihydrate)
Al	2.3	1.1	1.0
Fe	26	10.9	13.4
Cu	0.7	0.4	0.3
Zn	2.8	0.9	0.8
As	0.05	0.01	0.02
Pb	0.01	0.001	0.005

3.3 Practical implications

Constructing an adsorption layer using a readily or locally available material that can minimize migration of contaminants is considered a relatively new and cost-effective measure for waste containment facilities and embankments. However, the performance of the adsorbent material should be carefully examined beforehand in order to guarantee an effective long term barrier performance. Moreover, the use of certain materials as adsorption layer in the field should be determined not only by chemical compatibility, but also by the availability of the material, the type of contaminants that may leach from rocks, and the price of the material, including transportation and installation. Thus, they constitute part of the next steps, as they would be good indicators of the suitability of this contamination mitigation method. Moreover, as the construction of an adsorption layer involves the use and transport of large amount of materials, and therefore may be very costly, the possibility of mixing these adsorbents with local soil or material generated in excavation sites in different proportions is also going to be evaluated.Future research will be also performedon the relationship between parameters such as EC, pH, swell volume or metal sorption capacity and hydraulic conductivity in order to predict field application of these three minerals. In addition, economic evaluation and environmental risk assessment are also considered part of the future steps in thisstudy.

4. CONCLUSIONS

Three materials that can be potentially used as adsorption layer, such as bentonite, zeolite and ferrihydrate, were proposed and evaluated in this paper. According to experimental results, these materials appear to be suitable for acid rock drainage mitigation, as the hydraulic conductivity remained low and they all showed sorption capacity toward metals even under severe conditions.

Among the threestudied minerals, bentonite is a better sorbent for Al, Fe, Cu, Zn, and Pb, whereas ferrihydrate seemed to be better for As.

The hydraulic conductivity of GCL permeated with distilled water was 1.4×10^{-11} m/s, while when permeated with ARD, it was 5.0×10^{-10} m/s. The hydraulic conductivity of zeolite permeated with water was 3.0×10^{-10} m/s, while when permeated with ARD, 1.4×10^{-9} m/s. The hydraulic conductivity of ferrihydrate was the highest among the three species with a hydraulic conductivity value of 7.3×10^{-9} m/s in the case of permeation with water. This value remained constant after ARD permeation, with a value of 8.6×10^{-9} m/s.

The effluent analysis of the hydraulic conductivity test showed that the pH and EC equilibrium was reached and that the presence of other metals in the ARD affects the sorption capacity of these materials, making it lower than the predicted from single metal sorption test.

5. ACKNOWLEDGMENTS

The Nikkei Scholarship granted by The Nippon Foundation (Nippon Zaidan) has been provided to the first author's postgraduate study. The authors express a deep gratitude to MsHermelinda Plata (Kyoto University) for herhelpful comments and suggestions.

6. **REFERENCES**

- Abollino, O., Aceto, M., Malandrino, M., Sarzanini, C., and Mentasti, E. (2003) "Adsorption of heavy metals on Namontmorillonite. Effect of pH and organic substances". Water Research, Vol.37, No.7, pp.1619-1627.
- ASTM, 2007. D 698-07 Standard Tets Methods for Laboratory Compaction Characteristics of Soil Using Standard Effort (12 400 ft-lbf/ft³ (600 kN-m/m³)), Vol 04.08, pp.84-96.
- ASTM, 2009a. D 7100-06 Standard Test Method for Hydraulic Conductivity Compatibility Testing of Soils with Aqueous Solutions, Vol 04.09, pp.1213-1229.
- ASTM, 2009b. D 5084-03 Standard Tets Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter, Vol 04.08, pp.1045-1067.
- Benjamin, M. M., Sletten, R. S., Bailey, R. P., and Bennett, T. (1996) "Sorption and filtration of metals using iron-oxidecoated sand". Water Research, Vol.30, No.11, pp.2609-2620.
- Bouazza, A. (2002) "Geosynthetic clay liners". Geotextiles and Geomembranes, Vol.20, No.1, pp.3-17.
- Erdem, E., Karapinar, N., and Donat, R. (2004) "The removal of heavy metal cations by natural zeolites". Journal of Colloid and Interface Science, Vol.280, No.2, pp.309-314.
- Guyonnet, D., Touze-Foltz, N., Norotte, V., Pothier, C., Didier, G., Gailhanou, H., Blanc, P., and Warmont, F. (2009) "Performance-based indicators for controlling geosynthetic clay liners in landfill applications". Geotextiles and Geomembranes, Vol.27, No.5, pp.321-331.
- Jo, H. Y., Katsumi, T., Benson, C. H., and Edil, T. B. (2001) "Hydraulic Conductivity and Swelling of Nonprehydrated GCLs Permeated with Single-Species Salt Solutions". Journal of Geotechnical and Geoenvironmental Engineering, Vol.127, No.7, pp.557-567.
- Kaoser, S., Barrington, S., Elektorowicz, M., and Wang, L. (2005) "Effect of Pb and Cd on Cu adsorption by sand-bentonite liners". Canadian Journal of Civil Engineering, Vol.32, No.1, pp.241-249.
- Kashir, M., and Yanful, E. K. (2001) "Hydraulic conductivity of bentonite permeated with acid mine drainage". Canadian Geotechnical Journal, Vol.38, No.5, pp.1034-1048.
- Katayama, M., Hirota, M., Inui, T., Katsumi, T., and Takai, A., 2011. Long-term leaching of heavy metals from excavated soils and rocks with natural contamination, 10th Japan-Korea-France-Canada Joint Seminar on Geoenvironmental 2011, Takamastu, Japan, pp.41-46.
- Katsumi, T., Ishimori, H., Ogawa, A., Yoshikawa, K., Hanamoto, K., and Fukagawa, R. (2007) "Hydraulic conductivity of nonprehydrated geosynthetic clay liners permeated with inorganic solutions and waste leachates". Soils and Foundations, Vol.47, No.1, pp.79-96.
- Katsumi, T., Inui, T., and Kamon, M. (2008a). "Wastes and byproducts used in geotechnical applications in Japan". Geo-Environmental Engineering 2008 -Proceedings of the Eighth Japan-Korea-France Joint Seminar on Geoenvironmental Engineeringpp.275-282.
- Katsumi, T., Ishimori, H., Onikata, M., and Fukagawa, R. (2008b) "Long-term barrier performance of modified bentonite

materials against sodium and calcium permeant solutions". Geotextiles and Geomembranes, Vol.26, No.1, pp.14-30.

- Katsumi, T. (2010) "Hydraulic conductivity of geosynthetic clay liners". Geosynthetic Clay Liners for Waste Containment Facilities. A. Bouazza and J. Bowders. London, CRC Press/Balkema: 55-83.
- Katsumi, T., Inui, T., and Kamon, M. (2010). "Sustainable geotechnics for reuse of by-products". Environmental Geotechnics for Sustainable Development - Proceedings of the 6th International Congress on Environmental Geotechnics, New Delhi, India, pp.302-317.
- Kolstad, D. C., Benson, C. H., and Edil, T. B. (2004) "Hydraulic conductivity and swell of nonprehydrated geosynthetic clay liners permeated with multispecies inorganic solutions". Journal of Geotechnical and Geoenvironmental Engineering, Vol.130, pp.1236.
- Lange, K., Rowe, R. K., and Jamieson, H. (2007) "Metal retention in geosynthetic clay liners following permeation by different mining solutions". Geosynthetics International, Vol.14, No.3, pp.178-187.
- Lange, K., Rowe, R. K., and Jamieson, H. (2009) "Diffusion of metals in geosynthetic clay liners". Geosynthetics International, Vol.16, No.1, pp.11-27.
- Lange, K., Rowe, R. K., and Jamieson, H. (2010a) "The potential role of geosynthetic clay liners in mine water treatment systems". Geotextiles and Geomembranes, Vol.28, No.2, pp.199-205.
- Lange, K., Rowe, R. K., Jamieson, H., Flemming, R. L., and Lanzirotti, A. (2010b) "Characterization of geosynthetic clay liner bentonite using micro-analytical methods". Applied Geochemistry, Vol.25, pp.1056-1069.
- Li, L. Y., Tazaki, K., Lai, R., Shiraki, K., Asada, R., Watanabe, H., and Chen, M. (2008) "Treatment of acid rock drainage by clinoptilolite--Adsorptivity and structural stability for different pH environments". Applied Clay Science, Vol.39, No.1-2, pp.1-9.
- Naka, A., Li, Z., Inui, T., and Katsumi, T. (2010a). "Evaluation of heavy metal attenuation capacity of geosynthetic clay liners and its applicability to acid rock drainage cases". 9th International Conference on Geo-Environmental Engineering 2010, Seoul, Korea, pp.111-118.
- Naka, A., Ohta, T., Urakoshi, T., Ishihara, T., Katsumi, T., and Inui, T. (2011b). "Sorption capacity of minerals materials against heavy metals and acid drainage from excavated rocks". 10th Japan-Korea-France-Canada Joint Seminar on Geoenvironmental 2011, Takamastu, Japan, pp.15-22.
- NAUE, 2005. Fibre-reinforced Geosyntetic Clay Liner (GCL) Bentofix NSP 4900 Product Sheet.
- Ohta, T., Enomoto, H., and Tokunaga, T. (2006) "Evaluation and prediction of pollution caused by acid water exuded from mud sediment in urban ground". IAEG 2006, No.265, pp.1-9.
- Peri, J., Trgo, M., and Vukojevi Medvidovi, N. (2004) "Removal of zinc, copper and lead by natural zeolite--a comparison of adsorption isotherms". Water Research, Vol.38, No.7, pp.1893-1899.
- Petrov, R. J., and Rowe, R. K. (1997) "Geosynthetic clay liner (GCL)-chemical compatibility by hydraulic conductivity testing and factors impacting its performance". Canadian Geotechnical Journal, Vol.34, No.6, pp.863-885
- Rowe, R. K. (2006). "Some factors affecting geosynthetics used for geoenvironmental applications". 5th International Conference on Environmental Geotechnics, London, pp.43-69.
- Ruhl, J. L., and Daniel, D. E. (1997) "Geosynthetic clay liners permeated with chemical solutions and leachates". Journal of Geotechnical and Geoenvironmental Engineering, Vol.123, pp.369.
- Satpathy, J. K., and Chaudhuri, M. (1995) "Treatment of cadmiumplating and chromium-plating wastes by iron oxide-coated sand". Water Environment Research, pp.788-790.

- Shackelford, C. D., Benson, C. H., Katsumi, T., Edil, T. B., and Lin, L. (2000) "Evaluating the hydraulic conductivity of GCLs permeated with non-standard liquids". Geotextiles and Geomembranes, Vol.18, No.2-4, pp.133-161.
- Shackelford, C. D., Sevick, G. W., and Eykholt, G. R. (2010) "Hydraulic conductivity of geosynthetic clay liners to tailings impoundment solutions". Geotextiles and Geomembranes, Vol.28, No.2, pp.149-162.
- Sherman, D. M., and Randall, S. R. (2003) "Surface complexation of arsenic (V) to iron (III)(hydr) oxides: structural mechanism from ab initio molecular geometries and EXAFS spectroscopy". Geochimica et Cosmochimica Acta, Vol.67, No.22, pp.4223-4230.
- Sposito, G. (1984) "The surface chemistry of soils". New York, Oxford University Press.
- Srivastava, S. K., Bhattacharjee, G., Tyagi, R., Pant, N., and Pal, N. (1988) "Studies on the removal of some toxic metal ions from aqueous solutions and industrial waste. Part I (Removal of lead and cadmium by hydrous iron and aluminium oxide)". Environmental Technology, Vol.9, No.10, pp.1173-1185.
- Susset, B., and Grathwohl, P. (2011) "Leaching standards for mineral recycling materials-A harmonized regulatory concept for the upcoming German Recycling Decree". Waste Management, Vol.31, No.2, pp.201-214.
- Varank, G., Demir, A., Top, S., Sekman, E., Akkaya, E., Yetilmezsoy, K., and Bilgili, M. S. (2011) "Migration behavior of landfill leachate contaminants through alternative composite liners". Science of the Total Environment, Vol.409, No.17, pp.3183-3196.