Geosynthetic Clay Liner Permeated with Acid Rock Drainage: The Role of Iron in Arsenic Immobilization

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Geosynthetic clay liners (GCLs) have the potential to immobilize cations present in solution. Due to this, GCLs have been considered suitable materials not only in landfill bottom liners, but also in rock containments with the potential of acid rock drainage (ARD) generation. However, the bentonite inside GCLs does not have affinity towards anions such as arsenic, which is one of the toxic components present in ARDs. Based on the authors' previous research on swelling, sorption, and hydraulic conductivity of GCL against ARD, thorough discussion on the role of Fe in As immobilization was done in this paper. Swelling test showed that the presence of metals, especially a high concentration of Fe (4,500 mg/L approximately) due to its high concentration, negatively impact the swelling of bentonite by increasing the hydraulic conductivity value. The hydraulic conductivity remained low during the test duration but was one order of magnitude higher in the ARD permeation case (5.0×10^{-10} m/s) than in the water permeation case (1.4×10^{-11} m/s). Single metal sorption tests showed that Fe was sorbed by the bentonite while As was not. Sorption tests with different ARD dilutions showed that the increase of iron concentration positively impacts on As sorption. Considering that GCLs do not retain As, but Fe does, an additional Fe layer could be placed in the bottom liner system in order to immobilize it. However, if the ARD contains high Fe concentration, this additional layer would not be necessary as the Fe in solution will prevent As migration.

Keywords: Geosynthetic clay liner, Acid rock drainage, Hydraulic conductivity test, Swelling test, Sorption test

1. INTRODUCTION

The use and disposal of large amounts of materials coming from construction has become an important issue in Japan due to the growing interest in saving space in landfills and reducing the use of new natural resources^{1), 2), 3)}. Thus, reusing excavated materials has become a solution that reduces the amount of waste rock produced, as well as the consumption of new material. However, when rocks and soils are reused in geotechnical applications, the potential for pollution or natural contamination should be considered. In Japan, particularly, several types of metals such as As and Pb are present in a higher concentration compared to the average global level. Moreover, in mountainous areas of Japan, there are several rock formations which contain pyrite (FeS_2) and other minerals that may contain high amount of As and Pb. Therefore, acid rock drainage (ARD) generated by the decomposition of sulfides with subsequent As, Pb and other heavy metal leaching becomes a critical issue^{4), 5)}. ARD is produced when sulfide minerals such as FeS_2 , Cu_2S , PbS , ZnS , CuFeS_2 , or FeAsS are oxidized in the presence of oxygen and

percolating water. Although this phenomenon occurs naturally, mining and excavation accelerate the generation of ARD by increasing the quantity of sulfides exposed. Because sulfides are only stable under strongly reducing conditions, exposing them to oxidizing conditions will destabilize these rocks and oxidation occurs through a variety of mechanisms⁶⁾.

Heavy metals have negative effect on the environment and health; as natural processes do not degrade them, they remain in the ecosystem having a toxic effect on food chain through bioaccumulation. In order to prevent ARD surface and groundwater pollution, using an adsorption layer in rock containment facilities is considered a relatively new and cost-effective measure³⁾. This method places a layer of material in the bottom part of the waste rock containments that has adsorption capacity against heavy metals, such as geosynthetic clay liners (GCLs).

GCLs are bentonite-based liners that have large specific surface area, high metal adsorption capacity, and low hydraulic conductivity^{7), 8), 9)}.

Bentonite, specifically montmorillonite, can absorb heavy metals through two different pH dependent

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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 edges¹⁰⁾. In acid conditions, the hydrogen ion competes with the heavy metals towards the superficial sites; additionally, most silanol and aluminol groups are less deprotonated which favours metal mobility¹⁰⁾. 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.¹¹⁾ have demonstrated that, in addition to montmorillonite clay's cation exchange capacity, minerals comprising less than 5% of the bentonite, such as goethite, gypsum and pyrite, play an important role in sequestering a range of metals, specifically Ni, Zn, and Cu. Besides the crystalline initially present in the materials, 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 mobility¹¹⁾.

In the author's previous research^{12), 13)} the barrier performance of geosynthetic clay liners (GCLs) against a pH 3 artificial ARD was investigated through swelling, hydraulic conductivity, and sorption tests. Based on these experimental results, a thorough discussion focused on Fe and As retention/release interactions, which seems to play an important role in As immobilization, is presented in this study. The bentonite inside GCLs has special affinity toward cations such as Pb, Mn, Cd, etc., but not anion species, such as As, one of the toxic components present in ARDs. Thus, discussion was mainly focused on arsenic as it has a different behavior and sorption mechanism compared to the ARD's cations. Almost no migration of As was found due to its retention or precipitation mainly caused by the presence of Fe. This research differs from other studies in the type of ARD used (high metal concentrations, especially Fe), the long-term nature of the hydraulic conductivity experiments, and the study of the relationship between Fe and As.

2. MATERIALS AND METHODS

Experiments were conducted using a needle-punched GCL (Bentofix® NSP 4900) which contains powdered Na-bentonite sandwiched between woven and non-woven geotextiles (4,670 g bentonite/m², at natural moisture content). It had 10% water content, a specific gravity of 2.85 and a smectite content of 80%. An artificial ARD was prepared in the laboratory based upon the drainage composition of a Pb-Zn-(Cu) deposit located in Cerro de Pasco, Peru¹⁴⁾, as shown in Table 1. 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^{8), 9)}. The ARD was prepared by mixing guaranteed reagent (GR) grade FeSO₄·7H₂O, Al₂(SO₄)₃·16H₂O, CuSO₄·5H₂O, ZnSO₄·7H₂O, Na₂HAsO₄·7H₂O, PbCl₂, K₂SO₄, Na₂SO₄, CaSO₄, and MgSO₄. The pH was adjusted to 3, using

H₂SO_{4(cc)} and the electrical conductivity (EC) was 1195 mS/m.

Table 1. Chemical composition of the artificial ARD

Metal	Concentration (mg/L)
Fe	4330.2
Cu	86.9
Zn	493.1
Al	259.2
As	49.1
Pb	2.9
Na	413.9
K	31.8
Mg	214.0
Ca	397.0

A swelling test was conducted for different dilutions and bi-metal mixtures of the artificial ARD, according to the ASTM D 5890 "Standard Test Method for Swell Index of Clay Mineral Component of Geosynthetic Clay Liners". Two grams of dry powdered bentonite from the GCL was dusted into a 100 mL graduated cylinder filled with 90 mL of solution. The same solution was then used to fill the cylinder to 100 mL. The cylinder was covered and allowed to stand undisturbed for 24 hours, with the volume level (in mL) recorded.

Hydraulic conductivity tests on GCL were conducted according to the ASTM D 5084 "Standard Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter" and ASTM D 7100 "Standard Test Method for Hydraulic Conductivity Compatibility Testing of Soils with Aqueous Solutions", using a falling headwater-constant tailwater system. A typical diagram of this system is presented in Figure 1. It consisted of a flexible wall permeameter, with a cell pressure of 30 kPa and an average hydraulic gradient of 85–95, at a constant room temperature of 25°C. The test specimen (GCL) was placed between filter papers, geotextiles, and plastic caps (cap and pedestal) with holes to connect the tubes, and confined by a latex membrane on the sides. The following variables were measured periodically: (1) the thickness of the GCL by a cathetometer; (2) the electrical conductivity (EC); (3) the pH; (4) the effluent amount; and the (5) metal content by inductively coupled plasma spectroscopy method (ICP). Experiments were conducted using both distilled water and ARD as permeant solutions. All cases were monitored for 9 months. In the water permeation case, the GCL was directly permeated with water from the influent port. In the ARD permeation case, it was first prehydrated with the ARD solution before the long-term ARD permeation from the influent port. The prehydration was done by placing the GCL into a containment with the ARD solution for 7 days with a constant application of 30 kPa.

For the sorption test, different dilutions of ARD (from 2 to 100%), and Fe and As single metal solutions (0 to 100 mmol/L approximately) were mixed with bentonite (obtained from the GCL) in a solid liquid ratio of 2 g

bentonite/L solution for single metal and 20 g bentonite/L solution for ARD. In addition, different solid-liquid ratios were tested over ARD solution (4 to 80 g bentonite/L). Experiments were conducted in 100 mL plastic bottles with caps, and the volume of the solution was fixed to 50 mL. Once bentonite was added, the mixture was placed on a shaking table at 100 rpm for 24 hours at 25°C. Next, the mixture was centrifuged and filtered using a filter with a 0.45- μ m pore size. Metal concentration before and after the sorption tests were analyzed by ICP-MS (ICPS- 800 Shimadzu).

Figure 1. Schematic view of a flexible-wall permeameter. (Note: Closed valves $\otimes$ were kept closed through the test)

3. RESULTS AND DISCUSSIONS

(1) Swelling test

The results of the free swelling tests using different dilutions of the artificial ARD are shown in Figure 2. These indicate that a high metal concentration, corresponding to high ARD percentage in Figure 2, has a negative effect on the swell volume by making it lower. The swell index of 0% ARD (or distilled water adjusted to pH 3 using $H_2SO_{4(cc)}$) was 32 mL/2 g bentonite, while the swell index of 100% ARD was around 8 mL/2 g bentonite. This reduction in swell volume can be mainly attributed to the presence of iron due to its high concentration in the ARD (around 4,500 mg/L). This assumption can be demonstrated in Figure 3 and 4 in which the swell index of different Fe and As single metal concentrations (Figure 3) and the effect of Fe and As present in the ARD to the swell index (Figure 4) were evaluated.

From Figure 3, it can be seen that a Fe concentration higher than 100 mg/L negatively impacts the swell index by decreasing it. However, As does not affect the swell index even at concentrations higher than 100 mg/L.

Swelling, in combination with the diffuse double layer (DDL), constitutes one of the most important reasons why GCLs provide the low levels of hydraulic conductivity⁷⁾ necessary to prevent the migration of toxic substances from rock containment facilities into groundwater. The reduction in swell index caused by metals was studied by Jo et al.¹⁵⁾. They indicate that the increase in metal concentration makes water move out of the mineral interlayer and then a reduction in swell volume occurs.

As swell index reduction was observed (from 32 to 8 mL/2 g bentonite) due to high metal concentration in the ARD (Figure 2), an increase in hydraulic conductivity was expected in the GCL permeated with ARD. The 9-month hydraulic conductivity tests, presented in the next section, Figure 5, showed that the hydraulic conductivity of GCL was one order of magnitude higher in the ARD permeation case than the water permeation case. Although the high concentration of iron in this experiment negatively impacts the performance of the GCL, it seems to have a crucial role in the As retention in the GCL.

Figure 2. Swell index at different ARD percentage (data from Naka et al, 2011¹²⁾)

Figure 3. Swell index at different metal concentration

Figure 4. Swell index of ARD (100 %ARD), Fe effect on swelling (4330.2 mg/L), and As effect on swelling (49.1 mg/L)

(2) Hydraulic conductivity test

Changes in hydraulic conductivity values (k) versus pore volumes of flow (PVF) are illustrated in Figure 5. PVF, which is a non-dimensional parameter, was calculated by dividing the cumulative amount of effluent collected during the test (m^3) by the volume of voids in the specimen (m^3).

The hydraulic conductivity of GCL permeated with distilled water was constant over time (correlated to PVF and vice versa), with an average value of 1.4×10^{-11} m/s. The hydraulic conductivity of the ARD prehydrated and permeated with ARD gradually increased over time, until 150 PVF approximately. After this point, it stabilized, reaching an average permeability value of 5.0×10^{-10} m/s. At approximately 300 PVF it started decreasing again due to physical clogging, mainly attributed to iron precipitation observed in Figure 6 (brown-red color on the specimen).

Figure 5. Hydraulic conductivity of GCL a) permeated with distilled water and b) prehydrated and permeated with ARD (data from Naka et al., 2011¹²⁾)

Figure 6. GCL after hydraulic conductivity test a) water permeation and b) ARD prehydration and permeation

One of the most important factors of bottom liner systems for rock containment facilities is to achieve a low permeability since they prevent waste leachates from having an adverse impact on soil and groundwater. The hydraulic conductivity differs according to the type of soil. The low hydraulic conductivity of GCLs, attributed to the swelling and water retention capacity of bentonites, make them suitable for barrier systems, according to the regulations established by different countries. The regulated hydraulic conductivity value in North America

and Europe is 10^{-9} m/s. In Japan, the regulation permits a natural clay ≥ 5 m in thickness with hydraulic conductivity $\leq 10^{-7}$ m/s to be utilized as a liner. Otherwise, one of the following liner systems is required: (1) two geomembranes (GMs) which sandwich a non-woven fabric or other cushion material, (2) a GM underlain by an asphalt-concrete layer ≥ 0.05 m in thickness and having hydraulic conductivity $\leq 10^{-9}$ m/s, or (3) a GM underlain by a clay liner ≥ 0.5 m in thickness and having hydraulic conductivity $\leq 10^{-8}$ m/s¹⁶⁾.

Besides hydraulic conductivity, pH, as well as EC, and metal release over time also constitute important factors to be considered. Effluent analysis of each case was conducted.

In the water permeated GCL case, the pH of the effluent was constant over time at approximately 10 (Figure 7). These high pH values can be attributed to the temporary alkalinity contribution of the cations released from the GCL (Ca, Mg, Na, and K) and/or the adsorption of H^+ onto the GCL. From Figure 8, it can be seen that the EC changed over time. At 6 PVF, the EC was 619 mS/m and after 35 PVF, it decreased to 140 mS/m (Figure 8).

Figure 7. Change of pH over time for GCL permeated with ARD and water (data from Naka et al., 2011¹²⁾)

Figure 8. Change of EC over time for GCL permeated with ARD and water (data from Naka et al., 2011¹²⁾)

Effluent analysis in case of GCL prehydrated and permeated with ARD showed that after 4 PVF the pH

was 8, but after 10 PVF it decreased to 3.8 and continued decreasing until pH 3, which was equivalent to the pH of the initial solution (Figure 7). It indicates that the pH equilibrium was reached at around 50 PVF. EC equilibrium was also observed, with an average value of 1000 mS/m (Figure 8). Variation in EC values can be attributed to metal leaching and/or desorption.

In order to study the role of Fe in As retention, data presented from Figure 9 to 12 will be limited to these two metals. Information of the other metals, such as release and sorption are presented in the authors' previous publications^{12), 13)}.

Figure 9 illustrates the metal concentration ratio of Fe and As over time. The metal concentration was reported in terms of metal concentration ratio, which is the ratio between the outflow and the inflow.

$$\text{Metal concentration ratio} = \frac{C}{C_0}$$

where C is the metal concentration in the outflow and C_0 is the metal concentration in the inflow.

At 210 PVF for Fe, an increase above the influent concentration values (ratio larger than 1) were observed, which may indicate a release of these species from GCL (desorption). The metal concentration ratio for As remained below the influent concentration value (ratio lower than 1), even after 600 PVF. This suggests that As was prevented from breaking through the GCL by sorption onto other metals present in the ARD (mainly Fe) which will be discussed more in section 3. Evidence of it is the red/orange layer of iron hydroxide in the GCL (Figure 6), observed also by Lange et al.¹¹⁾.

Figure 9. Heavy metal concentration ratio on GCL prehydrated and permeated with ARD (data from Naka et al., 2011¹²⁾)

(3) Sorption test

Figure 10 presents the isotherm for Fe and As sorption onto bentonite. It shows that Fe sorption onto bentonite is around 3 mmol/g bentonite. On the other hand, almost no adsorption was observed for As. Figure 11 shows Fe and As sorption at different ARD percentages (from 2 to 100% ARD) using 20 g/L of bentonite. When the ARD percentage was lower than 10%, all the Fe was sorbed onto bentonite. In case of As, at low ARD proportions, the As sorption was low. However, as the Fe concentration increased with the

increase of the ARD proportion, more As was removed from the solution. However, Fe sorption was decreasing due to the saturation of bentonite. This suggests that Fe is retained in bentonite though ion exchange, whereas for As, an additional mechanism that involves Fe may occur. The partition coefficient, K_d , was calculated from the soil concentration (C_s) and respective porewater concentration (C_{aq}) at test termination, based on:

$$K_d = \frac{C_s}{C_{aq}}$$

For the artificial ARD, assuming that the equilibrium was reached between the bentonite and the porewater at the end of the test, the K_d (batch) value for Fe and As at 100% ARD was 12 mL/g and 135 mL/g, respectively. The partition coefficient was calculated for every ARD dilution or ARD percentage that was used in the experiments. These values are presented in Table 2.

Figure 12 shows the sorption percentage of each metal using different amount of bentonite (from 4 to 80 g bentonite/L solution). In the case of Fe (initial concentration, 4330.2 mg/L), 75% was sorbed by 80 g/L of bentonite. For As, it was observed that the sorbed amount was constant, even at high adsorbent concentration, due to the presence of Fe in the solution. It suggests that As is immobilized on the precipitated iron oxides or iron hydroxide, $\text{Fe}(\text{OH})_3$, through a surface complexation reaction (Figure 13), and probably to other metals presents in ARD as well.

Figure 10. Fe and As sorption on bentonite at 20 g bentonite/L solution (excerpt from Naka et al.^{12), 13)})

Figure 11. Fe and As sorption on bentonite at different ARD percentage (data from Naka et al., 2010 and 2011^{12), 13)})

Table 2. Partition coefficient at different ARD percentage

ARD percentage	K_d for Fe (mL/g)	K_d for As (mL/g)
2	838	0
4	6,988	2
8	21,864	15
20	256	62
40	47	107
80	17	198
100	12	135

Figure 12. Fe and As sorption on bentonite at different sorbent amount (data from Naka et al., 2011¹³)

The sorption reaction of As onto Fe is different depending on the specie. For di- and monovalent anions, the equation can be defined as follows¹⁷:

(1) Iron hydroxide formation:

(2) Anion adsorption onto iron hydroxide:

where $\equiv$ refers to adsorption sites and w to weak adsorption sites in the two-layer surface complexation model.

For arsenate or As(V), Dixit and Hering¹⁸) have proposed the following equations with their respective intrinsic surface complexation constants:

High values of the intrinsic surface complexation constants suggest that the reaction or interaction between

As and Fe is favored.

Figure 13 shows the possible pathways of As secondary sorption on bentonite, proposed by Davis et al.¹⁹). This illustrates both monodentate and bidentate bonding using arsenate complexes.

Figure 13. Possible pathways of As secondary sorption (sorption on Fe) on bentonite¹⁹)

Figure 14 shows the As sorption (1 mM) in the presence of a second metal of the same concentration (1 mM). It suggests that for As immobilization onto bentonite, a secondary metal such as Fe plays an important role. In addition this graph shows that As has higher affinity towards Fe. At 1 mmol/L of Fe and 1 mmol of As, 70% of As was sorbed. Besides, in presence of Al 50% of As was sorbed, in presence of Cu, 35%, in presence of Zn, 60 % and in presence of Pb, 55%. This slightly higher affinity towards Fe and the high concentration of Fe in the ARD suggests that Fe is the main binding site for As present in the ARD solution and the responsible for its immobilization.

Figure 14. Sorption of As in presence of a second metal (bi-metal sorption test)

4. CONCLUSIONS

The swell index of distilled water adjusted to pH 3 using H_2SO_4 was 32 mL/2 g bentonite, while the swell volume of bentonite in presence of ARD was 8 mL/2 g bentonite. This value is highly influenced by the amount of Fe in the ARD.

The hydraulic conductivity for distilled water

remained constant at around 1.4×10^{-11} m/s. The hydraulic conductivity of the GCL prehydrated and permeated with an artificial ARD solution gradually increased, but between 150 and 300 PVF it became stable and reached a k value of 5×10^{-10} m/s. After 300 PVF, k started decreasing due to physical clogging caused by metal precipitation.

The sorption test with single metal solution showed that bentonite has affinity for Fe, but not for As. Different ARD dilutions showed that the increase of Fe concentration impacts on the As sorption.

Considering that GCLs do not retain As, an additional Fe layer should be placed in the bottom liner system in order to immobilize it. However, if the ARD contains high Fe concentration, this additional layer is not necessary as the Fe in solution will prevent the As migration.

Although an increase of an order of magnitude was observed after ARD permeation, the hydraulic conductivity remained low enough to meet the standard requirement. In addition, a relatively high metal attenuation capacity even under extreme conditions was observed which make GCLs a solution for ARD mitigation.

Other factors such as mineral-metal interactions, metal ion transport through minerals, pH effects, desorption processes, etc. must be thoroughly studied prior to field applications to assure long-term performance. In other words, additional systematic studies about the chemical compatibility of bentonite are required before applying GCLs to bottom liners in rock waste containment facilities, especially because the metal concentration and composition in ARD, which strongly influence GCL performance, differ by location.

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酸性廃水に対するジオシンセティッククレイライナーの性能評価：砒素の固定化における鉄の役割

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ジオシンセティッククレイライナー(GCLs)には重金属の固化効果が期待できるため、これまで廃棄物処分場の底部遮水ライナーや、酸性廃水(ARD)を生じる可能性のある掘削ずりの封じ込め等に用いられてきた。しかしARD中の有害物質の一つである砒素は陰イオンとして存在することから、陽イオンとの親和性があるGCLs中のベントナイトに吸着されにくい。本研究では、既往研究で著者らが実施したベントナイトの膨潤試験、吸着試験、GCLsの透水試験の結果をとりまとめ、鉄の存在が砒素のベントナイトへの固化効果、GCLsの遮水性能に与える影響について考察を行った。その結果約4,500 mg/Lの鉄イオン等、高濃度で金属イオンが存在する場合にはベントナイトの膨潤量が低下しGCLsの透水係数が上昇することが明らかとなった。GCLsの透水係数は条件に関わらず透水試験実施期間を通して低い透水係数を示したものの、透水溶液にARDを用いた場合 5.0×10^{-10} m/sであり、水を用いた場合の 1.4×10^{-11} m/sと比較して1オーダー高い値を示した。単一金属イオン溶液を用いた吸着試験結果から、濃度に関わらず砒素は吸着されないものの鉄は濃度の上昇に伴い吸着量が増加することがわかった。異なる希釈濃度のARDを用いた場合には、ARD濃度が高く金属イオン濃度が高くなるほど砒素の吸着量も増加することがわかった。これらの結果からGCLsそのものの砒素吸着能は低いものの鉄の存在下では砒素が吸着されうると言え、底部遮水層として砒素の吸着を見込む場合においては鉄を含有する層を複合的に設置する必要があると考えられる。しかしARD中に鉄が存在する場合にはそれが砒素の固化に寄与するため不要であると考えられる。

KEYWORDS: ベントナイト, 重金属, 透水試験, 透水係数, 膨潤試験, 吸着試験