# Chemical Compatibility of Conventional Geosynthetic Clay Liners to Aggressive Low-Level Radioactive Waste Leachate – 17296

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## ABSTRACT

Experiments were conducted to evaluate how two aggressive leachates representative of leachates in low-level radioactive waste (LLW) disposal facilities affected the hydraulic conductivity of a conventional sodium-bentonite (Na-B) geosynthetic clay liner (GCL) used in composite liner systems. One leachate was highly alkaline (H-pH) and the other had a low abundance of monovalent cations relative to divalent cations (L-RMD). Tests were also conducted with a typical radioactive synthetic leachate (RSL) and with deionized (DI) water as control. Na-B from the GCL had a swell index of 24 mL/2 g in RSL, 22 mL/2 g in H-pH leachate, and 16 mL/2 g in L-RMD leachate, whereas the swell index was 36 mL/2 g in DI water. Hydraulic conductivity tests were conducted in flexible-wall permeameters using the falling headwater with an effective confining stress at 20 kPa. Hydraulic conductivity of Na-B GCL was low when permeated with RSL (1.8 x $10^{-10}$ m/s) and H-pH leachate (2.4 x $10^{-10}$ m/s), but higher than the hydraulic conductivity to DI water (2.5 x$10^{-11}$ m/s). The GCL was two orders of magnitude more permeable when permeated with L-RMD leachate (7.9 x $10^{-8}$ m/s). The higher hydraulic conductivity of the GCL to the leachates is attributed to reduced swelling of the Na-B in leachates with higher ionic strength solution (H-pH, RSL) or a predominance of divalent cations (L-RMD). Increasing the effective confining stress from 20 to 450 kPa reduced the hydraulic conductivity approximately two orders of magnitude for the L-RMD and H-pH leachates.

## INTRODUCTION

Low-level radioactive waste (LLW) and mixed waste (MW) disposal facilities are operated by the US Department of Energy (DOE) for long-term containment of wastes associated with clean up and decommissioning activities in the US nuclear weapons complex. These facilities employ multilayer barrier systems to control the flux of contaminants into the surrounding environment, including geosynthetic clay liners (GCLs) [1, 2, 3]. The long-term compatibility of GCLs and other geosynthetics used for barriers in contact with LLW leachate is of particular importance because the design life of LLW and MW barrier systems is required to be 1000 yr or longer [2, 3].

GCLs are hydraulic barriers consisting of a thin layer of bentonite clay (≈3–5 kg/$m^2$) sandwiched between two geotextiles that are bonded by needle-punching or stitching [4]. GCLs primarily contain conventional sodium bentonite (Na-B) and have low hydraulic conductivity to water (typically < $10^{-10}$ m/s), but can be affected by chemical interactions between the bentonite and the permeant solutions [4, 5, 6, 7]. Previous studies have shown that permeating GCLs with more concentrated leachates or leachates containing predominantly polyvalent cations reduces swelling of the bentonite and increases the hydraulic conductivity significantly [2, 4, 5, 6, 8, 9, 10].

Several studies have examined the hydraulic conductivity of GCLs permeated with synthetic municipal solid waste (MSW) leachates [11, 12, 13] and synthetic LLW leachate [2]. In a very long-term study, Bradshaw and Benson [13] show that the hydraulic conductivity of GCLs to MSW leachate is no more than a factor of six higher than the hydraulic conductivity to Deionized (DI) water under similar conditions. Tian et al. [2] evaluated the hydraulic conductivity of two Na-B and six polymer-modified GCLs to radioactive synthetic leachate (RSL) representative of LLW leachates. They indicate that the hydraulic conductivity of the Na-B GCLs to RSL were approximately 10 times higher than the hydraulic conductivity to DI water. Bentonite-polymer GCLs with a polymer loading >5% had much lower hydraulic conductivity to RSL ($3.8–6.9 \times 10^{-12}$ m/s) due to polymer clogging the intergranular pores. Limited studies have been conducted to date to evaluate how more aggressive LLW leachates affect the hydraulic conductivity of GCLs. Additionally, the influence of effective confining stress on the hydraulic conductivity of GCLs to LLW leachates has not been explored.

Hydraulic conductivities of a conventional Na-B GCL to two aggressive LLW leachates and one typical LLW leachate were evaluated in this study over a range of effective confining stresses. Tests were conducted on GCLs directly permeated with the three synthetic leachates at effective confining stresses of 20, 100, 250, and 450 kPa.

## MATERIALS AND METHODS

### Geosynthetic Clay Liner (GCL)

The GCL used in this study consists of granular Na-B sandwiched between a non-woven geotextile (top) and a woven geotextile (bottom). Both geotextiles are polypropylene and are bonded together by needle punching. The GCL had an initial thickness of 5.1 mm, water content of 15.9%, and a swell index of 36 ml/2 g in DI water (per ASTM D5890). Cation exchange capacity (CEC) of the Na-B in the GCL is 73.2 $\text{cmol}^+$/kg, with the following bound cation mole fractions: Na (0.45), K (0.04), Ca (0.29), and Mg (0.12) (per ASTM D7503). X-ray diffraction showed that montmorillonite is the major mineral component in the bentonite (84%), with other measureable quantities of quartz, plagioclase, feldspar, oligoclase, illite, mica, and calcite.

### Permeant Liquids

Three synthetic leachates were used in this study based on leachate compositions reported by Tian [14] and Abdelaal and Rowe [15]: (1) typical radioactive synthetic leachate (RSL), (2) a LLW leachate with a low abundance of monovalent to divalent cations (L-RMD leachate), and (3) a highly alkaline LLW leachate (H-pH leachate). Major cations and major anions in the leachates are summarized in Table 1. DI water was used as control.

The major cations in leachates at DOE disposal facilities are $Ca^{2+}$ (0.77–24.9 mM), $Mg^{2+}$ (0.20–30.2 mM), $Na^+$ (0.19–38.13 mM), and $K^+$ (0.04–1.94 mM). The major anions are $SO_4^{2-}$ (0.39–29.6 mM) and $Cl^-$ (0.12–19.3 mM). The predominant radionuclides are total uranium (U-234, U-235, and U-238) (6.4–3060 µg/L), tritium (40–4625 Bq/L), and technetium-99 (0.3–47.8 Bq/L). The pH ranges from 5.7 to 9.1 and is 7.2, on average. RMD and ionic strength of the three synthetic leachates are shown in Fig. 1 along with data for LLW leachates from the four DOE facilities evaluated by Tian [14].

Table 1. Characteristics of synthetic LLW leachate used in this study.

| Group | Components | Quantity in RSL | Quantity in L-RMD | Quantity in H-pH | Unit |
|---|---|---|---|---|---|
| Major cation concentrations | $Ca^{2+}$ | 4 | - | - | mM |
| | $Mg^{2+}$ | 6 | 25 | 0.0013 | mM |
| | $Na^{+}$ | 7 | 1.6 | 100 | mM |
| | $K^{+}$ | 0.7 | - | 5 | mM |
| Major anion concentrations | $SO_4^{2-}$ | 7.5 | 25 | 2.5013 | mM |
| | $Cl^{-}$ | 8 | 1.6 | - | mM |
| | $NO_3^{-}$ | 1.5 | - | - | mM |
| | $HCO_3^{-}$ | 3.5 | - | - | mM |
| Bulk characteristics | pH | 7.2 | 6.9 | 13.0 | - |
| | Ionic Strength | 43.6 | 101.6 | 107.5 | mM |
| | RMD | 0.077 | 0.010 | 2.91 | $M^{0.5}$ |

Note: hyphen represents component is not in leachate.

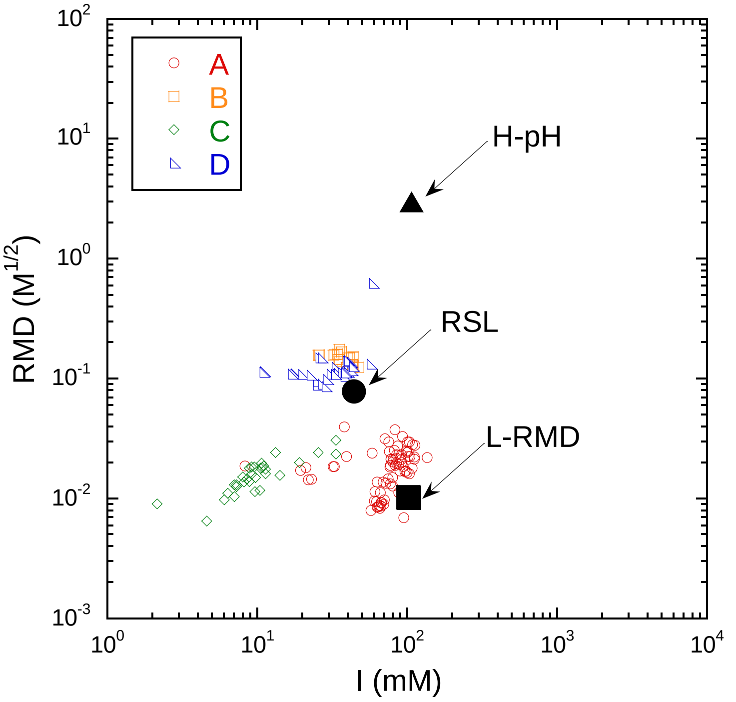

Fig. 1. RMD versus ionic strength for the synthetic and actual LLW leachates. RSL, L-RMD, and H-pH leachates are shown as a solid black circle, square, or triangle. A, B, C, and D designate the four DOE disposal facilities used to characterize LLW leachate.

The typical radioactive synthetic leachate (RSL) is the formulation in Tian et al. [2] based on the average concentration of each non-radioactive component in the DOE LLW leachates and the highest concentrations of radionuclides in the DOE leachates. L-RMD leachate was created to simulate a worst-case scenario with ionic strength (101.6 mM) near the maximum recorded in the field and the ratio of monovalent to divalent cations (RMD = 0.010 $M^{0.5}$) near the lowest recorded in the field. L-RMD represents a worst case because, at the same ionic strength, leachate with lower RMD results in less swelling of bentonite and higher hydraulic conductivity [6].

The H-pH leachate is based on data reported in Abdelaal and Rowe [15] for six LLW disposal facilities, with pH ranging from 8.0 to 12.3. The H-pH synthetic leachate (pH =13) is more alkaline than any of the leachates in Abdelaal and Rowe [15], representing a worst-case scenario.

### Hydraulic Conductivity Testing

Hydraulic conductivity tests on the GCL specimens were conducted in flexible-wall permeameters using the falling headwater-constant tailwater method described in ASTM D6766. GCL specimens were hydrated with the permeant liquid in the permeameter for 48 hr at an effective confining stress of 10 kPa and without a hydraulic gradient. After hydration, the effective confining stress was increased to 20 kPa and the hydraulic gradient was set at 150. Influent for the tests was contained in 50-mL burettes sealed with parafilm to prevent evaporation. Effluent was collected in 60-mL polyethylene bottles.

Equilibrium was defined using the hydraulic and chemical equilibrium criteria in ASTM D6766 along with an additional criterion for influent and effluent concentrations. The criteria in D6766 require no temporal trend in the hydraulic conductivity measurements, hydraulic conductivity falling within 25% of the mean for three consecutive measurements, incremental effluent volume ($Q_{out}$) within 25% of the incremental influent volume ($Q_{in}$) for at least three measurements, and the ratio $Q_{out}/Q_{in}$ exhibiting no temporal trend. Chemical equilibrium is defined in D6766 as the electrical conductivity of the effluent ($EC_{out}$) showing no temporal trend and falling within 10% of the electrical conductivity of the influent ($EC_{in}$). In addition, concentrations of major cations and pH of the effluent were required to be within 10% of those in the influent.

### Effective Confining Stress

After the hydraulic conductivity tests reached chemical equilibrium at 20 kPa, the effective confining stress was increased incrementally to 100, 250, and 450 kPa to simulate increasing depth of waste on the liner. Hydraulic conductivity testing commences 48 hr after the GCL specimens were consolidated to the next highest effective confining stress.

## RESULTS AND DISCUSSION

GCL specimens were permeated directly with the RSL, L-RMD, and H-pH leachates or DI water. Summary information from the hydraulic conductivity tests is reported in Table 2. The pore volume of flow (PVF) reported in Table 2 are based on the initial pore volume. At the time this paper was prepared, the tests had been conducted for 0.5-1.8 yr. GCL specimens permeated directly with RSL met all of the termination criteria before the tests were terminated. Tests conducted with the L-RMD and H-pH leachates have not reached equilibrium and were ongoing when this paper was prepared.

Table 1. Hydraulic conductivity of GCLs permeated with RSL, L-RMD, H-pH leachates, and DI water.

| Test Time (yr) | Permeant Liquid | PVF | D6766 Termination Criteria | | Effective confining Stress (kPa) | Hydraulic Conductivity (m/s) |
|---|---|---|---|---|---|---|
| | | | Hydraulic | EC and pH | | |
| 1.8 | RSL | 208 | Yes | Yes | 20 | $1.9\times10^{-10}$ |
| | | | | | 100 | $6.1\times10^{-11}$ |
| | | | | | 250 | $1.5\times10^{-11}$ |
| | | | | | 450 | $9.3\times10^{-12}$ |
| 0.7 | L-RMD | 50 | Yes | Yes | 20 | $7.9\times10^{-8}$ |
| | | | | | 100 | $1.1\times10^{-8}$ |
| | | | | | 250 | $2.1\ \times10^{-9}$ |
| | | | | | 450 | - |
| 0.5 | H-pH | 39 | Yes | No | 20 | $2.4\times10^{-10}$ |
| 0.7 | DI | 3.8 | Yes | No | 20 | $2.5\times10^{-11}$ |

Hydraulic conductivities of the GCL specimens permeated with the RSL, L-RMD, and H-pH leachates at an effective confining stress of 20 kPa are shown in Fig. 2 along with the hydraulic conductivity to DI water. Hydraulic conductivities of the GCL to L-RMD leachate ($7.9\times10^{-8}$ m/s), H-pH leachate ($2.4\times10^{-10}$ m/s), and RSL ($1.9\times10^{-10}$ m/s) are one to three orders of magnitude higher than the hydraulic conductivity to DI water ($2.5 \times 10^{-11}$ m/s). Higher hydraulic conductivity to the H-pH leachate relative to DI water is attributed to reduced swelling due to the higher ionic strength of these H-pH leachate (Table 1) [2, 4, 5, 6, 7]. The much higher hydraulic conductivity to the L-RMD leachate relative to DI water is attributed to combined effects of higher ionic strength and replacement of native $Na^+$ by $Ca^{2+}$ and $Mg^{2+}$ in the leachate, both of which reduce swelling [6].

The impacts of L-RMD, H-pH, and RSL leachates on swelling of the Na-B are shown in Fig. 3. Swell indices of the Na-B are 16 mL/2 g in L-RMD, 22 mL/2 g in H-pH, and 24 mL/2 g in RSL, whereas the swell index in DI water is 36 mL/2 g in DI water. The higher hydraulic conductivities to the L-RMD and H-pH leachates relative to DI water are consistent with the relative magnitudes of these swell indices.

Bound cations in the exchange complex of bentonite from the GCL permeated with RSL are summarized in Table 3. Essentially all of the native $Na^+$ in the exchange complex was replaced by $Ca^{2+}$ or $Mg^{2+}$. The impact of cation exchange is evident in the swell index of Na–B in RSL after permeation with RSL (14 mL/2 g), which is just above the range typical of Ca-bentonite (8-10 mL/2 g) [5].

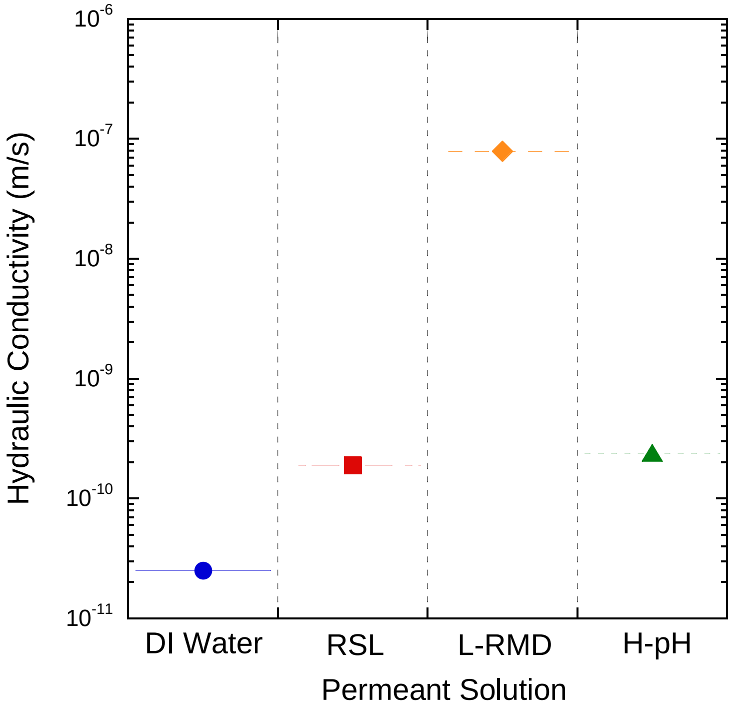

Fig. 2. Hydraulic conductivity of GCL to DI water and RSL, L-RMD, and H-pH leachates at 20 kPa effective confining stress.

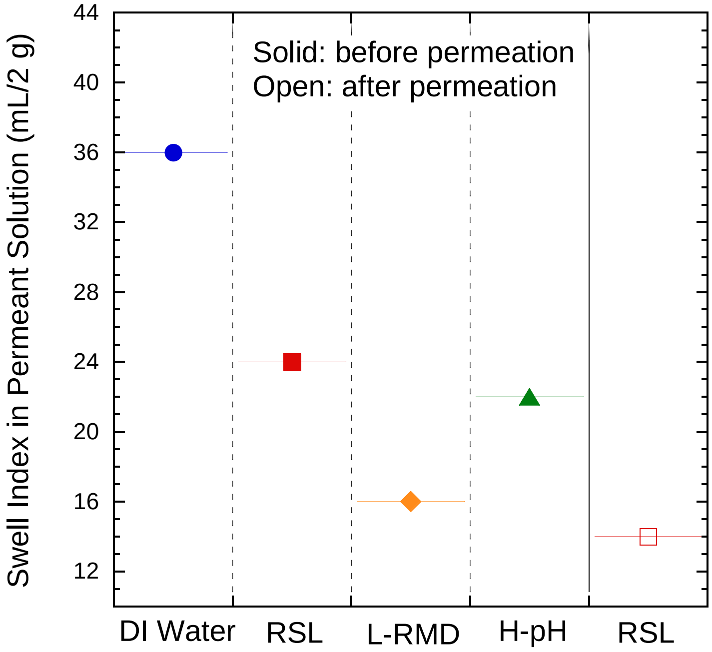

Fig. 3. Swell index of Na-B bentonite in DI water, RSL, L-RMD, and H-pH leachates before permeation (closed symbols) and swell index in DI water after permeation with RSL (open symbol). Data not shown after permeation for L-RMD and H-pH leachates as tests are ongoing.

Table 3. Mole fractions of bound cations of bentonite from GCL before and after permeation with RSL.

| Cation | Mole fraction of bound cations in exchange complex | |
|---|---|---|
| | Initial | After permeation with RSL |
| $Na^+$ | 0.45 | 0.01 |
| $K^+$ | 0.04 | 0.02 |
| $Ca^{2+}$ | 0.29 | 0.45 |
| $Mg^{2+}$ | 0.12 | 0.52 |

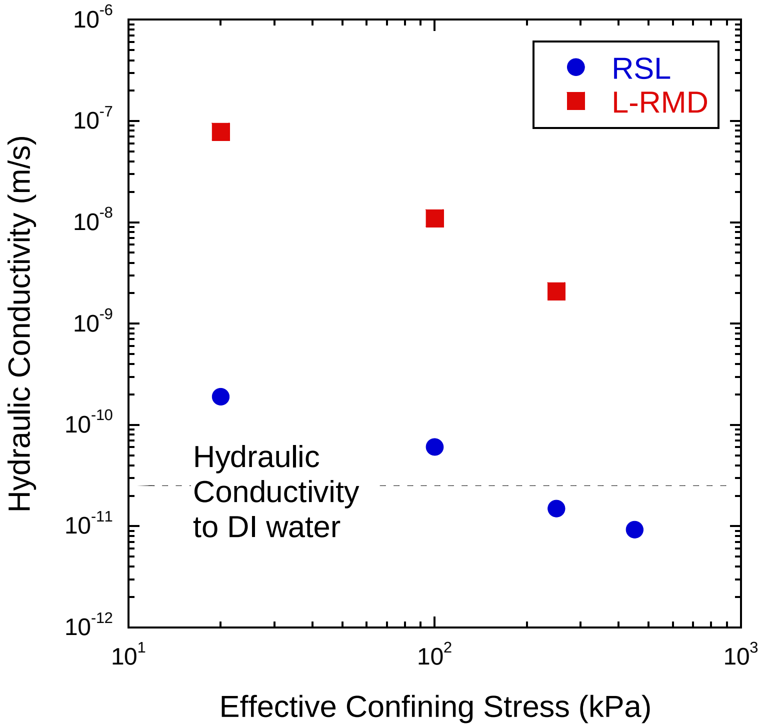

Fig. 4. Hydraulic conductivity vs. effective confining stress for GCL specimens permeated with RSL and L-RMD leachate.

**Effective Stress**

The hydraulic conductivity of GCLs to RSL and L-RMD leachates decreased as the effective confining stress was increased (Fig. 4). At 450 kPa, the hydraulic conductivity to RSL was lower than the hydraulic conductivity to DI water at 20 kPa ($2.5x10^{-11}$ m/s). For L-RMD leachate, the hydraulic decreased from $7.9 \times 10^{-8}$ m/s at 20 kPa to $2.1 \times 10^{-9}$ m/s at 250 kPa. The rate of decrease in hydraulic conductivity with increasing effective confining stress is essentially the same for both leachates, and reflects the reduction in void ratio due at higher stress. For the RSL leachate, reductions in pores size due to stress are dominant relative to increases in the pore sizes due chemical phenomenon (ionic strength and cation exchange), resulting in very low hydraulic conductivity at high stress. In contrast, for the L-RMD leachate, the impact of the chemical phenomenon (ionic strength and cation exchange) on pore size is predominant relative to the impact of the physical phenomenon, resulting in high hydraulic conductivity even at high effective confining stress.

## CONCLUSIONS

Hydraulic conductivities of a conventional Na-B GCL to typical LLW leachate and aggressive LLW leachates (predominantly divalent cations or highly alkaline) were evaluated in this study. The impact of effective confining stresses on the hydraulic conductivity to LLW leachate was also evaluated. The following are findings of this study:

- The hydraulic conductivity of a conventional GCL permeated with L-RMD leachate is approximately three orders of magnitude higher than the hydraulic conductivity to DI water at an effective confining stress of 20 kPa. Hydraulic conductivities to the H-pH and RSL leachates are approximately 10 times higher than the hydraulic conductivity to DI water.

- The higher hydraulic conductivity to L-RMD leachate and RSL is attributed to replacement of $Na^+$ in the exchange complex by divalent cations in the leachate ($Ca^{2+}$, $Mg^{2+}$), which reduces of swelling of the bentonite. For the GCL permeated with H-pH leachate, the increase in hydraulic conductivity is attributed to the reduction in swelling associated with higher ionic strength.

- Increasing the effective confining stress from 20 to 450 kPa results in a similar reduction in hydraulic conductivity for both the RSL and L-RMD leachates. For the RSL leachate, the pore size reduction due to increasing stress (physical effect) was sufficient to counter the increase in pore size due to chemical effects, at least when the stress was very high, resulting in very low hydraulic conductivity to RSL at high stress. In contrast, the increase in pore size due to chemical effects for the L-RMD leachate was predominant relative to the reduction in pore size due to stress, resulting in high hydraulic conductivity for all stresses.

## ACKNOWLEDGEMENT

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