



## The Potential Role of Geosynthetic Clay Liners in Acidic Rock Drainage Treatment Systems

K. Lange, R.K. Rowe and H. Jamieson, GeoEngineering Centre at Queen's-RMC, Kingston, Canada

### ABSTRACT

Acid rock drainage (ARD) is a well known environmental problem that occurs when water comes into contact with pyrite in oxidizing conditions and produces acidic water with a high dissolved metal content. Conventional effluent treatment typically involves raising the pH of the water with lime and producing metal-rich precipitates. The high cost associated with the operation and maintenance of such systems has prompted an increased use of passive treatment technologies. Passive systems are engineered to combine several stages of treatment separated by ponds and basins constructed of low permeability liners. The low permeability, ease of mobility and large attenuation capacity of geosynthetic clay liners (GCLs) have made them a popular alternative to conventional clay barriers, and potentially significant component of passive treatment systems. Once the ARD has passed through a limestone channel, it still possesses some dissolved metal concentrations and requires a minimum retention time in a holding pond, lined with a low permeability barrier prior to discharge into a receiving water body. The current research examined the advective and diffusive migration of treated ARD through a GCL. The GCL's ability to attenuate the low concentration of metals from the treated ARD water implies its potential long term usefulness in ARD treatment.

### 1. INTRODUCTION

Storage of waste rock and mine tailings has evolved over the last few decades as new regulations are imposed from government agencies. A costly environmental issue facing the mining industry is the generation and release of acidic rock drainage (ARD). For example, the 1993 British Columbia (BC) State of the Environment Report showed that '240 million tonnes of acid generating waste rock and 72 million tonnes of acid generating mine tailings (4% and 8 % of the Canadian total)' existed in the province of BC alone. ARD occurs as a result of oxidation of pyrite and other sulfidic minerals when they are exposed to oxygen and water. Mine tailings that contain sulfides and insufficient buffering minerals are particularly vulnerable to acid generation because finely ground material has a larger exposed surface area (Norman and Raforth, 1998). The greatest concern of regulatory agencies is that they will discover ARD after mine closure and abandonment when financial resources to fund mitigation are no longer available (Norman and Raforth 1998). Metals tend to dissolve and mobilize more easily in the acidic waters associated with ARD. Depending on the geological composition of the host rock, and mining extraction methods, the metals found in mining waste may include arsenic, cobalt, copper, cadmium, chromium, nickel, strontium, gold, iron, lead, silver, and zinc (e.g. Feng et al. 2000). For some metals, leaching may only be significant if the acid levels drop below a pH of 5.5 to 6. However this is not true for elements like molybdenum, zinc, cadmium, and arsenic that can remain soluble at pH values near and greater than 7.

Mine operators and engineers increasingly seek lower cost alternative storage techniques to remediate ARD. While chemical treatment or some other form of active effluent treatment has traditionally been conducted in Canada, greater consideration has been given recently to forms of passive treatment; or at least the combination of active and passive treatment (Sheoran and Sheoran 2006). Passive treatment of ARD offers lower costs of construction and can be conducted at remote locations with limited operational requirements (e.g. Champagne et al. 2005; Sheoran and Sheoran 2006).

#### 1.1 The role of geosynthetic clay liners in passive ARD treatment

Passive treatment systems rely on natural chemical and biological processes to remediate ARD. Passive treatment systems can be combined with active components (e.g. addition of lime) to tailor to the needs of the level of treatment required. In passive anaerobic treatment, bacterial reduction of sulfate and iron, and the precipitation of metal sulfides are important (e.g. Chen and Li, 2007). In surface, or aerobic treatments, the dominant process is oxidation of iron and precipitation of iron and other metal hydroxides. Water in aerobic wetlands must be kept sufficiently alkaline. An anoxic limestone drain can be installed before water enters the holding pond or wetland to add alkalinity and raise the pH. An anoxic limestone drain consists of a trench filled with crushed limestone, sealed under a low permeability liner through which the contaminant stream flows by gravity. A constructed pond or wetland is located to receive the ARD, where it is expected to undergo metal removal and neutralization (Sheoran and Sheoran 2006). Liner materials are needed to minimize the downward flux of contaminants. This research assessed the potential of GCLs for attenuating the metals from a treated ARD effluent, by considering both advective and diffusive transport. Geosynthetics clay liners offer a large attenuation capacity, low permeability, and an ease of mobility that could make them a potentially significant component of passive treatment systems.

## 1.2 Treatment and storage of ARD

The authors evaluated the potential for GCLs to attenuate the metals from ARD waters that have been treated with a neutralizing chemical such as calcium hydroxide via this mechanism:



Where M represents a metal, for example,



Since the minimum solubility for the different metals occur at different pH values, maximum removal efficiency of mixed metals can be achieved at a single pH level (e.g. Feng et al. 2000). Figure 1 shows how Zn and Al can precipitate at a pH of 9.5, but the pH needs to be raised to effectively precipitate other contaminants such as Cd. Feng et al. 2000 treated an ARD of pH=1.65 with successive levels of lime up to a pH to 12.50. At a pH of 5.70, metals such as Cu, Fe, Mn, Ni, Sr, Zn, and Cd were significantly reduced (see Table 1, column 1; however they still remained at levels above effluent standards. Other authors have shown similar results. For example, Champagne et al. (2005) showed that Cd only experienced a 66.5% removal rate from a combined passive system in comparison to other metals such as Fe, Al and Zn that had greater than 99% removal efficiencies.

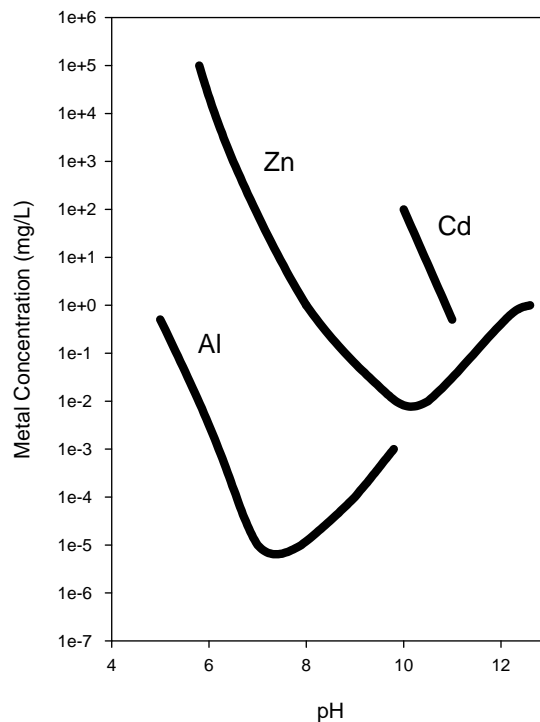


Figure 1: Metal Hydrolysis (hydroxide precipitation) (Aubé and Zinck, 1999)

## 2. EXPERIMENTAL

### 2.1 Mining Waters

This study used ARD that had been treated with lime (hereafter referred to as TARD for 'treated' ARD), provided by CANMET laboratories (Mining and Mineral Sciences, Ottawa). The TARD had a pH of 6.4. In order to simulate a TARD closer to that of Feng et al. 2000 (Table 1) the solution was spiked with metal sulfate salts. This raised the concentrations of Fe, Cd, Ni, and Zn, and decreased the pH to 5.83. For comparison, a synthetic (untreated) ARD (similar to that used by Lange et al. 2007) was also tested. Table 1 shows the composition of the TARD, synthetic ARD, and the solution by Feng et al. 2000. Metal determinations were performed with a Varian Inductively Coupled Plasma Atomic Spectrometer

(ICP-AES). Chloride content was measured with an ion specific electrode and sulfate was calculated based on total sulphur content.

Table 1. Composition of mine waters

Constituent (mg/L)	TARD	Feng et al. 2000 <sup>1</sup>	ARD
Cl	300	673	1700
Al	3.4	139	90
As	0.29	n/a	2.53
Ca	365	641	4.61
Cu	0.1	1.04	14
Cd	12	0.241	41
Fe	10	578	218
K	8	n/a	400
Mg	45	352	1
Mn	6	106	18
Ni	6	5.03	19
SO <sub>4</sub>	1440	4329	1034
Sr	0.5	1.39	0.1
Zn	8	5.67	135
Na	340	n/a	800
Eh (mV)	154	n/a	348
pH	5.83	5.70	2.18

<sup>1</sup>treated with Ca(OH)<sub>2</sub>

## 2.2 GCL Material

The GCL tested in this study was a BENTOFIX™ NW GCL (Terrafix Geosynthetics Inc.) and consisted of a nonwoven carrier geotextile, a layer of granular Wyoming sodium bentonite and a nonwoven cover geotextile needlepunched together with the fibers thermally treated on the carrier geotextile. Rowe et al. (2000) analyzed the properties of the granular bentonite for the same GCL. The procedure used to prepare the GCL specimens for hydraulic conductivity and diffusion testing was similar to that described by Petrov et al. (1997). A water-wetted steel cutting shoe was placed on the cover geotextile of the GCL, and slowly forced through the GCL specimen with a hand lever assembly. The average mass of the GCL was 4720 g/m<sup>2</sup>.

## 2.3 Fixed Ring Permeameter

The GCLs were permeated with TARD and ARD waters using the fixed ring (FR) permeameter designed by Fernandez (1989) and procedures described by Petrov et al. 1997. The FR permeameter consisted of a stainless steel cell where the GCL is encapsulated between an upper and lower porous stone (diameter of 54 mm and a height of 70.5 mm). A low static confining stress (18 kPa) was applied directly to the top of the specimen by springs sandwiched between locator caps. The GCL was hydrated, and then permeated with deionized de-aired water (DDW). Once the measured hydraulic conductivity and the effluent chemistry stabilized (this occurred at ~5 PVs), 10 pore volumes of the mine water were passed through the GCL. Effluent waters were analyzed for pH, Cl and cationic content. The GCL samples were then extruded from the test cells and subjected to aqua regia digestion to determine sorbed metal and other cation concentrations per gram of bentonite.

## 2.4 Diffusion Testing

Diffusion testing took place using a glass apparatus (cylindrical with a 70 mm diameter and ~80 mm height), that consisted of a top reservoir separated from a bottom reservoir by the GCL (Lake, 2000). Porous disks were used as spacers to ensure that the GCL swelled to a specified height. The GCL was hydrated under a small head (~20 mm). After the GCL was hydrated, (GCL final height =13 mm, porosity, n=0.82), DDW was placed above and below the sample. Cation concentrations (primarily Na and Ca) and Cl were measured over time, and once equilibrium was reached, a source solution was placed above GCL, while the water remained at the bottom. Samples from above and below the GCL were taken from both the source and receptor at different times and were replaced with the equivalent amount of water. The diffusive contaminant transport through the GCL was modeled using Pollute™ using the finite mass condition for the source (detailed in Rowe et al., 2000). Upon completion of the experiment, the GCL was digested by aqua regia for total sorbed metal determination.

### 3. RESULTS AND DISCUSSION

After permeation with 10 PVs of TARD, the pH of the effluent waters dropped from 8.3 to 6.4 (influent 5.83) and the pH of the ARD effluent waters dropped to 4.8. Figures 2 and 3 show normalized concentration data for Cl, Ni, Mn, SO<sub>4</sub>, Cd and Zn over time from the effluent sample port of the fixed ring apparatus for the ARD and TARD waters. The breakthrough line is highlighted on each figure (i.e. breakthrough time  $C/C_0=0.5$ , where C is the effluent concentration, and C<sub>0</sub> is the permeant initial concentration) to show how the metals are attenuated from the TARD permeant in comparison to the ARD. For example breakthrough of Mn in the TARD occurred at 10.2 PVs and at 6.4 PVs for the ARD (retardation factor, R=1.6). In both waters, the order of attenuation (from most to least attenuated) followed the order Ni>Cd>Zn>Mn. Chloride, SO<sub>4</sub> and Na effluent concentrations showed similar behaviour for both waters, despite their difference in initial concentrations. Lange et al. (2007) noted a delay in SO<sub>4</sub> breakthrough for a near-neutral pH gold mine solution and attributed it to gypsum precipitation; however that did not occur during this experiment, where SO<sub>4</sub> breakthrough occurred earlier than Cl. The large cation exchange of the GCL (noted by the loss of Na ions) was likely most responsible for attenuation of the metals. It should also be noted that the ARD had a much higher mass loading of metals than the TARD, which is not reflected on the normalized curves. The total mass retained for both solutions is shown in Table 2. Also shown is the difference between the measured cation content by soil digestion and the inferred percent retention by subtracting the effluent from the influent concentration(s). Most measurements were within a 10 percent of the predicted value, with the exception of Mn and SO<sub>4</sub> in the ARD-permeated GCLs. The Mn levels may fluctuate due to the dissolution of some Mn-bearing minerals in the background GCL bentonite. The SO<sub>4</sub><sup>2-</sup> difference however, could be due to the presence of sulfate-reducing bacteria or a sulfate precipitate that may have formed in the source reservoir (a black precipitate was found in the bentonite for this cell and is the subject of further investigation).

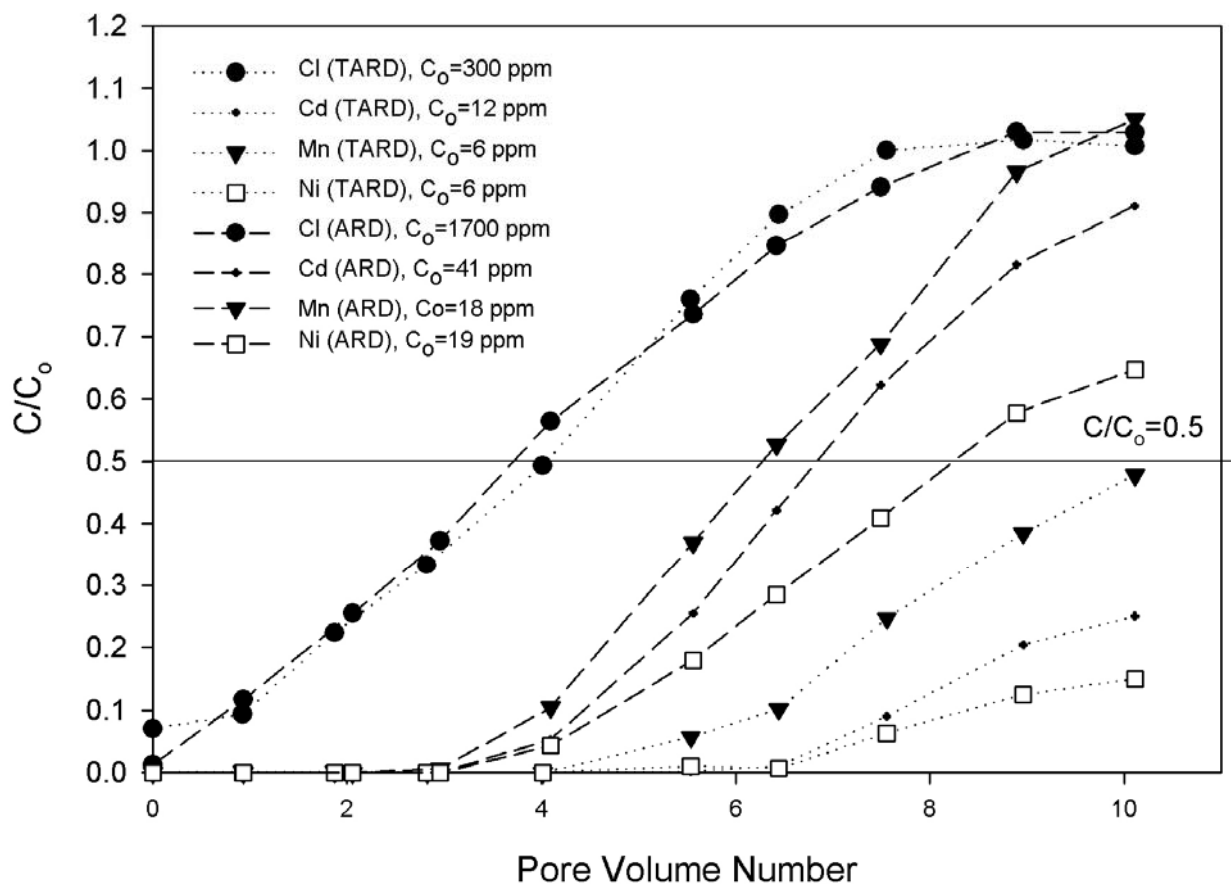


Figure 2: Normalized concentration of Mn, Cd and Ni and chloride versus pore volume number for TARD and ARD waters. Breakthrough line is highlighted.

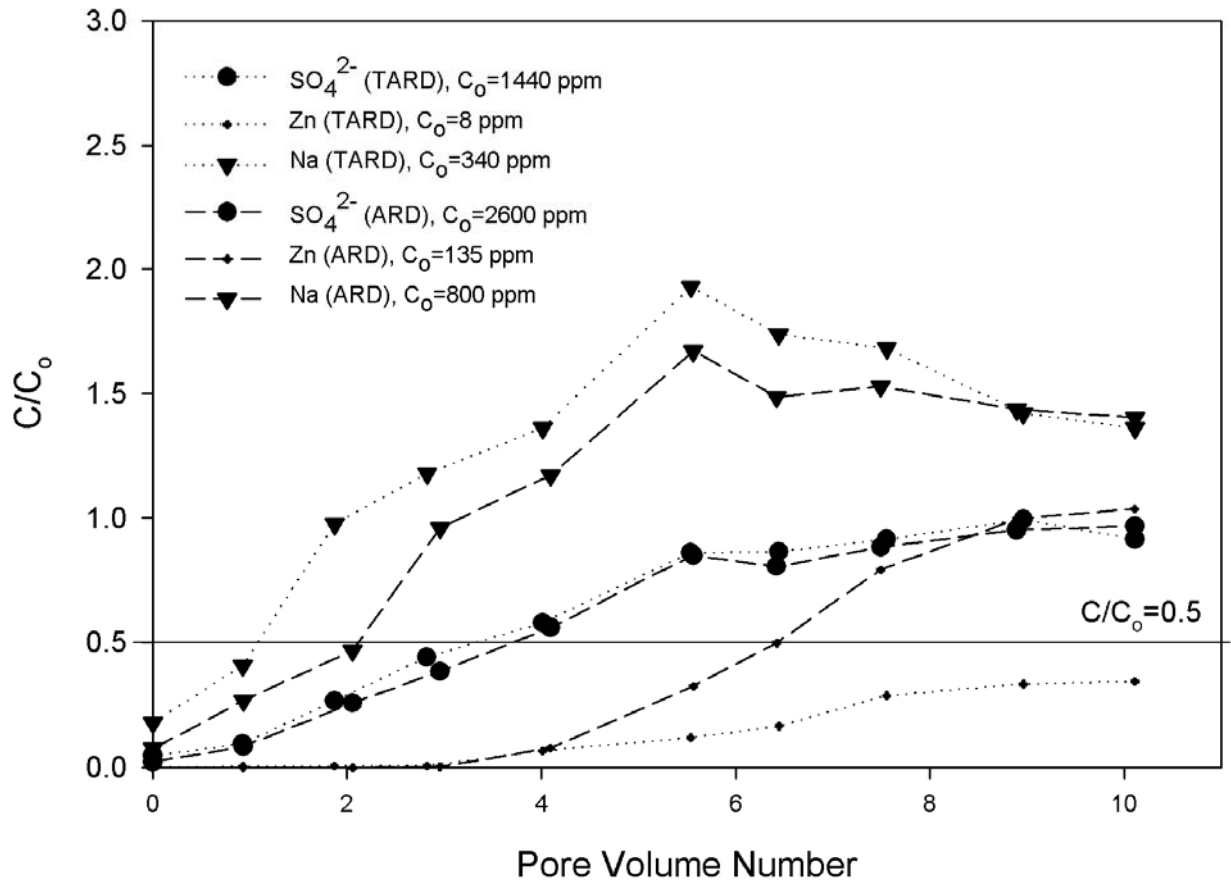


Figure 3: Normalized concentration of Na, Zn and dissolved sulfate versus pore volume number for TARD and ARD waters. Breakthrough line is highlighted.

Table 2. Mass Balance for TARD and ARD experiments

Constituent	Total mass in <i>mg</i>	Total mass out <i>mg</i>	Calculated mass ( $\mu\text{g}$ ) retained per <i>g</i> soil (mass in-mass out)	Measured metal (digested) mass ( $\mu\text{g}$ ) retained per <i>g</i> soil	Fraction sorbed <sup>1</sup>	Difference (%) <sup>2</sup>
<u>TARD</u>						
Cd	2.18	0.148	203	213	0.93	4.7
Mn	1.09	0.167	92.0	98	0.85	6.1
Ni	1.09	0.0474	104	110	0.96	5.5
Zn	1.46	0.233	122	127	0.84	3.9
SO <sub>4</sub> <sup>2-</sup>	262.0	181.0	8037	8564	0.31	6.1
Na	61.88	85.63	-2375	-2631	-0.38	9.7
<u>ARD</u>						
Cd	7.39	2.94	445	471	0.60	5.5
Mn	3.25	1.42	182	212	0.56	14.5
Ni	3.43	0.867	256	261	0.75	1.9
Zn	24.35	10.71	1364	1421	0.56	4.0
SO <sub>4</sub> <sup>2-</sup>	560	372	9734	8560	0.34	-13.7
Na	144	171	-2757	-2895	-0.19	4.8

<sup>1</sup> Fraction sorbed is based on the measured metal mass retained

<sup>2</sup> Percentage difference between calculated mass retained and measured mass retained (negative values indicate a loss)

The effective diffusion coefficients (porosity,  $n=0.81$ ) for Ni, Cd, Zn and Mn in the TARD and ARD were estimated using Pollute™ with  $R^2>0.97$ , and ranged from  $7.6 \times 10^{-11} \text{ m}^2/\text{s}$  for Ni (TARD) to  $9.9 \times 10^{-11} \text{ m}^2/\text{s}$  for Mn (ARD). Figure 4 shows the diffusion curve for Cd. Diffusion of most constituents including Cl was found to proceed at a faster rate within the ARD waters than the TARD waters. The  $K_d$  (distribution coefficient) is notably higher for the TARD, resulting in a very low receptor value. At 40 days, the receptor Cd concentration of the ARD and TARD were 3.5 mg/L and 0.1 mg/L respectively.

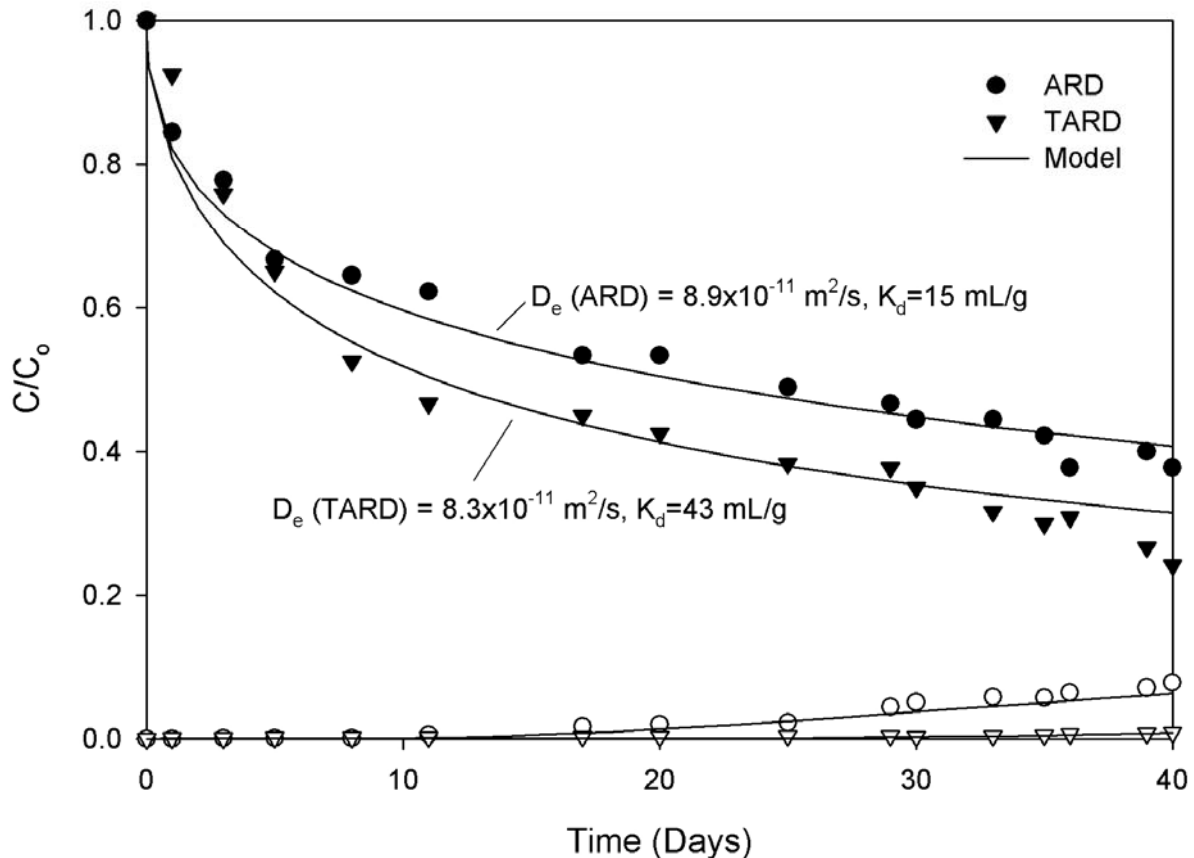


Figure 4: Diffusion of Cd from ARD and TARD waters. Normalized concentration of cadmium (Cd) versus the number of days (maximum of 40 d). Solid lines represent the predicted diffusion model from Pollute™.

#### 4. SUMMARY

Mitigation of ARD is difficult and expensive. Treatment of ARD has become essential to prevent contamination of surrounding areas, and as a result several methods have been developed (and are continuing to change) to treat ARD. The GCL's ability to resist pH changes and to attenuate the lower metal content of the TARD, implies its potential long term usefulness in ARD treatment. Metals that have been shown to be more difficult to precipitate by lime treatment such as Ni, Zn, Cd, and Mn showed greater than 80 percent removal efficiencies after 10 pore volumes of water permeation in the GCLs. In pure diffusion testing of TARD, the same contaminants showed concentrations much below effluent standards in the source reservoir.

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