BEHAVIOR OF POLYMER-MODIFIED BENTONITES WITH AGGRESSIVE LEACHATES

By

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A Thesis submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE
(Civil and Environmental Engineering)

at the

UNIVERSITY OF WISCONSIN-MADISON
August 2015

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ABSTRACT

Geosynthetic Clay Liners (GCLs) are hydraulic barrier systems in which a thin layer of bentonite (<10 mm) is fixed between two geotextiles by needle punching or glued to a geomembrane. Sodium bentonite (Na-B), the major constituent of GCLs, hydrates upon exposure to liquids such as deionized water and can swell significantly. The corresponding low hydraulic conductivity achieved makes GCLs effective barriers for waste containment systems. However, aggressive characteristics of the hydrating liquid in contact with bentonites in GCLs, such as salinity, cation type, and pH, may alter the bentonite fabric and lead to unacceptable increases in hydraulic conductivity.

Polymer-modified bentonites (PMBs) containing a blend of Na-B and various polymers have been introduced in recent years to improve the chemical compatibility and hydraulic performance of GCLs contacted with aggressive leachates. The purpose of this study is to demonstrate that the resistance of PMBs to increases in hydraulic conductivity when contacted with aggressive leachates is maintained over the long term, and to identify potential conditions where this is not the case (e.g., PMB types or permeant solution characteristics). A secondary goal is to improve basic understanding of the physical and chemical mechanisms by which polymer modification leads to improved hydraulic performance. A practical goal of the research is to identify the applicability of conventional index tests (e.g., free swell, fluid loss) and alternative index tests by which the long term hydraulic performance of PMBs may potentially be estimated from more easily determined short-term test procedures.

Hydraulic conductivity of GCLs containing natural sodium bentonite (Na-B) and GCLs containing various PMBs (Resistex and Resistex plus) were measured in flexible

wall permeameters for specimens permeated with synthetic leachates corresponds to leachates obtained from coal combustion, municipal solid waste combustion (MSW) and heap leach facilities impoundments. Hydraulic conductivity of GCLs were measured for specimens permeated with eight CCP leachates, an MSW incinerator ash (MSW-I) leachate and a gold pregnant leach solution (Gold PLS). Five of the synthetic CCP leachates were selected from CCP leachate database of Electric Power Research Institute (EPRI) representing CCP disposal facilities in the U.S. and referred here as EPRI leachates: typical CCP leachate, predominantly divalent cation ash leachate (low RMD), flue gas desulfurization residual (typical FGD), high ionic strength leachate and trona ash leachate. Chemical characteristics of remaining three CCP leachates (CCP 1, CCP 2 and CCP 3), MSW-I leachate and gold PLS leachate were obtained from coal combustion, municipal solid waste combustion (MSW) and heap leach facilities impoundments around the U.S. and used to produce corresponding synthetic leachates in the laboratory. These leachates were referred here as site-specific leachates.

Hydraulic conductivity results are presented for tests that have reached both hydraulic and chemical equilibrium, and for on-going tests where equilibrium has not yet been reached but can be reasonably approximated. Hydration characteristics of Na-B and PMBs in various aggressive solutions and correlations to steady state hydraulic conductivity for GCLs permeated with these solutions are evaluated using conventional (swell index, fluid loss) and an alternative fall cone index test and loss on ignition test.

Hydraulic conductivity test results for Na-B GCL with site-specific leachates varied from 9.61 x 10^{-7} m/s to 2.2 x 10^{-11} m/s. Four orders of magnitude increase in hydraulic conductivity for Na-B GCL permeated with the site-specific leachates was observed as the ionic strength of the leachate increased by a factor of 100. Hydraulic conductivity values for GCLs containing PMB permeated with the site-specific leachates were variable, and ranged from 10^{-12} to 10^{-8} m/s. The highest hydraulic conductivity value for these tests (2.27×10^{-8} m/s) was obtained with permeant solution MSW-I (the highest ionic strength leachate, I=1042 mM). Each test with PMB GCLs displayed lower hydraulic conductivity to the site-specific leachates than tests with conventional Na-B GCL. Permeation of PMB GCLs with EPRI leachates resulted in very low hydraulic conductivity values, and within the same order of magnitude (10^{-12} m/s), regardless of the ionic strength of leachate. PMB GCLs having higher polymer loading had lower hydraulic conductivity to both EPRI leachates and site-specific leachates in all but one case.

The long term hydraulic conductivity of Na-B GCL to the EPRI leachates and site-specific leachates was inversely related to swell index (ASTM D5890-11) and directly related to fluid loss (ASTM D5891-02). For the PMB materials, however, no systematic correlation between hydraulic conductivity and either conventional swell index or fluid loss was observed.

Liquid limit values extrapolated from laboratory fall cone tests (BS 1377-part 2) was found to be inversely related to hydraulic conductivity of one type of PMB GCL (old generation Resistex) and Na-B GCL to EPRI leachates. No systematic correlation was observed between hydraulic conductivity of other PMB GCLs (Resistex and Resistex plus) and liquid limit obtained from fall cone test.

Loss on ignition (LOI) values before any permeation was inversely related to hydraulic conductivity of PMB GCLs having various polymer loading with trona leachate.

For the PMB GCLs used in this study, an increase in LOI from 3.15 % to 6.17 % resulted in decrease in hydraulic conductivity to trona leachate by a factor of two. For the other PMB GCLs permeated with trona leachate, increasing polymer loading from 4.0 % to 6.5 %, hydraulic conductivity decreased by 2 order of magnitude (from 8.67 x 10^{-10} m/s to 4.82 x 10^{-12} m/s).

ACKNOWLEDGEMENTS

Foremost, I would like express my gratitude to my advisor Prof. William J. Likos for his continuous support for my M.S. study and research, for his encouragement, enthusiasm and patience. His guidance, persistent help and valuable feedback are appreciated deeply.

I wish to express my sincere thanks to Prof. Craig Benson and Prof. Tuncer Edil for accepting my invitation to be on my defense committee and for sharing their immense knowledge with me during weekly research meetings. Their continuous support helped me to remain dedicated and motivated in this academic endeavor.

I am also grateful to Xiaodong ‘Buff’ Wang for his time and willingness to help whenever I needed. I also would like to thank to Sabrina Bradshaw for sharing her experiences with me and assistance.

I would like to extend my thanks to my friends for their confidence in me. I would like to give special thanks to the GCL research group, especially Jiannan ‘Nick’ Chen, Faith Zangl, Kuo Tian and Weijuan Geng. Their valuable ideas contributed to my research work and enlightened me throughout my research path. Endless thanks go to the GLE family, particularly Merve Gizem Bozkurt, Brigitte Brown, Ayse Ozdogan Dolcek and Yibo Zhang for their precious friendship.

I also owe a great debt of gratitude to my undergraduate research assistants, Alexander Newell and Aaron Felhofer. This research work couldn’t be accomplished without their assistance in the laboratory.

Special thanks to my family, particularly my mom Asiye Salihoglu, my dad Saadettin Salihoglu and my brother Emre Salihoglu. Their love and faith in me kept me motivated all the time. Many thanks to my friends in Turkey for their encouragement and endless support.

Financial support of this research work was provided by Colloid Environmental Technologies Co. (CETCO). This support is gratefully acknowledged.

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CHAPTER 1: LONG TERM HYDRAULIC CONDUCTIVITY OF NA-BENTONITE AND POLYMER MODIFIED BENTONITES TO SITE-SPECIFIC LEACHATES AND COAL COMBUSTION PRODUCT LEACHATES

1.1. ABSTRACT

Hydraulic conductivity tests were conducted for two polymer-modified bentonite (PMB) GCLs (Resistex and Resistex Plus) in order to investigate their long term hydraulic performance when permeated with aggressive leachates. Permeant solutions included eight synthetic CCP leachates, an MSW incinerator ash leachate and a gold pregnant leach solution.

Five of the synthetic CCP leachates were selected from CCP leachate database of Electric Power Research Institute (EPRI) representing CCP disposal facilities in the U.S. and referred here as EPRI leachates: typical CCP leachate, predominantly divalent cation ash leachate (low RMD), flue gas desulfurization residual (typical FGD), high ionic strength leachate and trona ash leachate. Chemical characteristics of EPRI leachates used in this study were the same as those reported in Sustainability Report of Office of Sustainability at University of Wisconsin-Madison in 2014 (Report No. OS-14-11). Remaining five synthetic leachates corresponds to leachates obtained from coal combustion, municipal solid waste combustion (MSW) and heap leach facilities impoundments around the U.S. and referred here as site-specific leachates: gold pregnant leach solution (gold PLS), CCP 1, CCP 2, CCP 3 and municipal solid waste

incinerator ash leachate (MSW-I). Site-specific leachates were synthesized to mimic the chemical characteristics of leachates obtained from various sites around the U.S.

Control experiments were also conducted with a “conventional” GCL (Bentomat) containing natural sodium bentonite (Na-B) permeated with the site-specific leachates. Hydraulic conductivity tests on non-prehydrated GCLs were performed at effective confining stress of 20 kPa and average hydraulic gradient of 190 using flexible-wall permeameters according to ASTM D5084 and ASTM D6766-12. Hydraulic conductivity tests on Na-B GCLs with site-specific leachates showed classical high ionic strength-high hydraulic conductivity relationship. Hydraulic conductivity of Na-bentonite GCL increased as the ionic strength of the permeant increases. Highest hydraulic conductivity (9.61 x 10^{-7} m/s) was obtained with MSW-I leachate which has the highest ionic strength. Hydraulic conductivity tests on PMB GCLs showed step increase in hydraulic conductivity (four orders of magnitude) around one molar ionic strength. Below this ionic strength, permeation of the PMB GCLs with both EPRI and site-specific leachates resulted in very low hydraulic conductivity (k) values and within the same order of magnitude (10^{-12} m/s), regardless of the ionic strength (I) of leachate. In all tests, PMB GCLs maintained lower hydraulic conductivity than Na-B GCL. In general, PMB GCLs having higher polymer loading had lower hydraulic conductivity to both EPRI and site-specific leachates.

1.2. INTRODUCTION

There has been increased interest for containment of coal combustion products (CCP) to protect the environment from contaminants existing in the solid waste stream. Requirements and guidelines for CCP management were proposed by U.S. Environmental Protection Agency (EPA) in 2010 (USEPA, 2010). Requirements for composite liners, which includes use of a flexible membrane (geomembrane) over compacted clay soil to prevent the leaching of contaminants to groundwater, was established in subtitle D of the Resource Conservation and Recovery Act (RCRA). A final report was signed on December, 2014 and published on April, 2015 further clarified the technical requirements for CCP disposal (USEPA, 2015).

Geosynthetic clay liners (GCLs) are commonly used as bottom liners for solid waste containment in place of compacted clay soil under the geomembrane. Sodium bentonite forming the low hydraulic conductivity component in GCLs mostly consists of the mineral montmorillonite (Grim, 1968). Upon exposure to water, bentonite hydrates and expands to large volumes. Corresponding low hydraulic conductivity (e.g., $<10^{-10}$ m/s) makes it an effective hydraulic barrier (Jo et al., 2004). However, aggressive characteristics of the hydrating liquid in contact with bentonite such as high ionic strength, polyvalent cation type, or low or high pH, may alter the bentonite fabric, leading to an often unacceptable increase in hydraulic conductivity (Gleason et al., 1997; Petrov et al., 1997; Shackelford et al., 2000; Jo et al., 2001; Egloffstein, 2001). In particular, pore fluids having high ionic strength and low RMD (ratio of total molarity of monovalent cations to square root of total molarity of divalent cations) tend to increase hydraulic conductivity of sodium bentonites (Kolstad et al. 2004). Previous studies have also shown that prevalence of polyvalent cations in solution can cause increases in hydraulic conductivity (Shackelford 2000, Kolstad et al. 2004, Katsumi et al. 2007). CCPs generated from power generation can have variety of cations and anions in solution upon exposure to water (Chen et al., 2015), which may render conventional Na-B susceptible to increases in hydraulic conductivity. Chemical compatibility of CCPs with GCLs is thus of primary concern.

Polymer-modified bentonites (PMBs) have been introduced in recent years to improve chemical compatibility of GCLs with aggressive leachates (Kondo, 1996; Flynn and Carter, 1998; Trauger and Darlington, 2000; Scalia, 2012). In this study, hydraulic conductivity data for three different GCL products (one GCL with conventional sodium bentonite and two GCLs with polymer-modified bentonite) permeated with leachates representative of different coal combustion products (CCPs) and site-specific synthetic leachates are presented. CCP leachates used in the study have the same chemical characteristics as CCP leachates reported in Sustainability Report of Office of Sustainability at University of Wisconsin-Madison (Report No. OS-14-11) entitled "Engineering Properties of Geosynthetic Clay Liners Permeated with Coal Combustion Product Leachates: Final Report". The material properties and chemistry of leachates are described in Sections 1.4 and 1.5.

The primary objective of this study is to evaluate the hydraulic conductivity of GCLs containing PMBs in contact with CCP leachates and site-specific leachates and to demonstrate that the resistance of PMBs to increases in hydraulic conductivity is maintained over long term. A secondary objective is to understand physical and chemical mechanism underlying the observed hydraulic behavior of PMBs.

1.3. BACKGROUND

Bentonite is commonly used in GCLs for waste containment systems. Many studies have been conducted to investigate the effects of aggressive inorganic solutions on hydraulic performance of bentonite (Shan and Daniel 1991; Egloffstein 2001; Ruhl and Daniel 1997; Shackelford et al. 2000; Katsumi et al. 2004, 2007; Jo et al. 2004, 2005). Such studies have shown that when bentonite is permeated with aggressive inorganic salt solutions (I>500 mM), hydraulic conductivity can be very high (10^{-7} to 10^{-9} m/s) (Jo et al. 2004). Permeant liquids having high ion concentration and valence generally cause increases in attractive interparticle forces associated with a reduction in diffuse double layer (DDL) thickness (Mitchell and Soga, 2005). A decrease in DDL thickness generally promotes contraction or flocculation of the particle fabric with consequent increases in hydraulic conductivity (Ashmawy et al., 2002). This increase can be several orders of magnitude (Shackelfold et al., 2000).

In recent years, bentonites have been treated or blended with polymers in order to maintain low hydraulic conductivity in aggressive leachate environments. Many studies have investigated the effect of polymer treatment on hydraulic properties of bentonites (Katsumi et al. 2001; Ashmawy et al. 2002, Schenning 2004; Katsumi et al. 2008; Mazzieri et al. 2010, Di Emidio 2011, Puma et al. 2011; Scalia et al. 2014). Many different types of polymer amended bentonites have been developed and tested. For example, Katsumi et al. (2001 and 2008) evaluated the chemical compatibility of multiswellable bentonite (MSB) developed by Kondo (1996) and dense-prehydrated GCL (DPH-GCL) developed by Flynn and Carter (1998) with NaCl and $CaCl_2$ solutions. That study found that MSB and DPH-GCL maintained osmotic swelling of bentonite and thus have lower hydraulic conductivity than untreated sodium bentonite for solutions with a molar concentration of ≤ 1.0 M. Trauger and Darlington (2000) developed bentonite-polymer alloy (BPA) by polymerizing an organic molecule in bentonite slurry. BPA permeated with sea water was four orders of magnitude lower than hydraulic conductivity of untreated bentonite with the same solution. Di Emidio et al. (2011) permeated HYPER clay, a bentonite treated with an anionic polymer (Sodium Carboxymethyl Cellulose (Na-CMC)), with deionized water, sea water and 5 mM $CaCl_2$ solution using an average effective stress of 14 kPa. Hydraulic conductivity of the HYPER clay was one order of magnitude lower than untreated bentonite in sea water and 2.6 times lower in 0.5 mM $CaCl_2$ solution for the same amount of polymer loading. The lower hydraulic conductivity of HYPER clay was attributed to the effect of polymer on clay structure. The study proposed that intercalation of polymer in the interlayer of montmorillonite platelets may result in a more tortuous flow path and consequently low hydraulic conductivity. Bentonite-polymer a composite (BPC) in which sodium bentonite is treated by in-situ polymerization of acrylic acid was tested with a range of $CaCl_2$ solutions by Scalia et al. (2012). Hydraulic conductivities for those materials were more than four orders of magnitude lower than untreated sodium bentonite permeated with the same solutions.

Polymer-Clay Interactions

Understanding the underlying mechanisms of polymer interactions with clay surfaces is key to understanding the index and hydraulic properties of polymer-modified bentonites. With physical adsorption, clay surface properties may change without altering the clay structure (Liu et al., 2007). In an aqueous environment, polymers will compete with water molecules for adsorption to the clay surface. The presence of water on clay surfaces may either promote or inhibit polymer adsorption, depending on whether the water molecule is an electron donor or acceptor in reaction. 2:1 silicates such as montmorillonite have considerable enthalpies of hydration (-300 to -1500 kJ/mol) due to inorganic cations that balance the clay surface net negative charge. These cations attract water molecules, effectively desorbing them from the clay surface and opening up more space for polymer accommodation. Entropy gained by the system drives polymers to be adsorbed to clay surface.

In uncharged polymers, adsorption occurs when polar functional groups along the polymer chain interact with clay minerals. Intercalation of uncharged polymer between interlayer spaces of smectites leads to spreading out of polymer at the solid/solution interface if the surface is accessible (i.e. in dilute solutions).

In positively charged polymers, adsorption occurs by largely electrostatic interactions between cationic groups of polymer and negative surface charges of clay, which causes collapse of polycation on clay surface. Adsorption of negatively charged polymers on clay surfaces is generally limited due to repulsive forces between negatively charged polymer and the negative electric field along with basal surface of smectites (Theng 1982). However, intercalation of polymer in interlayer spaces may occur if the surface charge of clay is satisfied under acidic conditions or in the presence of high ionic strength solutions and anionic groups are protonated (Theng 1982, Lagaly et al. 2006).

In negatively charged polymers, adsorption can occur through electrostatic attraction of polymer to the clay mineral edge at slightly alkaline and acid pH; hydrogen bonding between the functional groups of polyanion and edge surface hydroxyls and; cation bridging between anionic group of polymer and clay surface (Deng et al. 2006; Laird 1997; Huang et al 2012). Adsorption is also promoted with an increase in molecular weight, since Van der Waals forces contribute to the adsorption energy (Theng, 1982).

1.4. MATERIALS

1.4.1. GCLs

One conventional Na-B GCL (Bentomat) and two polymer modified bentonite (PMB) GCLs (Resistex and Resistex plus) were used in this study (materials and trade names supplied by Colloid Environmental Technologies Company, CETCO). Granular Na-B or PMB in each GCL was fixed between a woven and nonwoven geotextile by needle punching. Digital microscope camera views of GCLs used in this study are provided in Fig. 1.2. Granule size distributions were obtained by dry sieving of either the bentonite or bentonite-polymer dry mixture (Fig. 1.1). Other physical properties are provided in Table 1.1. A summary of X-Ray Diffraction (XRD) analysis results is provided in Table 1.2.

1.4.1.1. Bentomat

X-Ray Diffraction (XRD) analysis showed that Bentomat consists mainly of the montmorillonite mineral (84%). Cation exchange capacity (CEC) was determined to be 84.03 cmol+/kg (ASTM D7503) from three replicate tests, with a standard deviation of 4.42. The dry bentonite mass per unit area is provided by manufacturer as 3.6 kg/m^2 at 0% moisture content. Initial (air-dry) water content of Bentomat was determined to be

4.84%. These and additional physical and chemical properties of the Bentomat Na-B are summarized in Table 1.1.

1.4.1.2. Resistex

Resistex is a reinforced GCL containing a dry mixture of bentonite and polymer in between a woven and nonwoven geotextile. Polymer treatment of the bentonite in the Resistex GCL provides chemical resistance and is intended to make the product more effective than standard Na-bentonite in aggressive leachate environments. Initial (air-dry) water content of PMB sampled from the Resistex GCL is 3.22%. Polymer loading of the Resistex GCL was determined via loss on ignition (LOI) as suggested by Scalia (2012), and is 3.70% with a standard deviation of 1.80% from 13 replicate tests. Cation exchange capacity (CEC) was determined to be 79.1 cmol+/kg (ASTM D7503) from three replicate tests, with a standard deviation of 5.95. A summary of the physical and chemical properties of the PMB in the Resistex GCL product is provided in Table 1.1.

1.4.1.3. Resistex Plus

Resistex plus GCL is also a polymer-treated GCL consisting of a dry blend of bentonite and polymer. Initial water content of air-dried material sampled from the GCL is 4.42%. The difference between Resistex and Resistex plus GCL appears to be the extent of polymer loading, based on results from loss on ignition tests conducted according to procedures described by Scalia (2012). Mass loss on ignition for PMB sampled from the Resistex plus GCL was determined to be 6.17% from 16 replicate tests with a standard deviation of 1.93%. Relative abundance of minerals obtained from X-Ray Diffraction (XRD) analysis is given in Table 1.2. Cation exchange capacity (CEC) was determined to be 85.51 cmol+/kg (ASTM D7503) from six replicate tests with a standard deviation of 16.75. Physical and chemical properties of Resistex plus GCL are given in Table 1.1.

1.4.2. Permeant Liquids

Characteristics of site-specific synthetic leachates used in this study were obtained from various sites around U.S. and EPRI leachates selected from CCP leachate database of Electric Power Research Institute (EPRI) representing CCP disposal facilities in the U.S. EPRI leachates used in the study have the same chemical characteristics as CCP leachates reported in Sustainability Report of Office of Sustainability at University of Wisconsin-Madison (Report No. OS-14-11) entitled "Engineering Properties of Geosynthetic Clay Liners Permeated with Coal Combustion Product Leachates: Final Report". (Benson et al., 2014). Fig. 1.5 shows the RMD vs ionic strength of both EPRI and site-specific leachates.

1.4.2.1. Site-Specific Leachates

Chemical characteristics of leachates were obtained from coal combustion, municipal solid waste combustion (MSW) and heap leach facilities impoundments around the U.S. and used to produce corresponding synthetic leachates in the laboratory. Three CCP leachates (CCP 1, CCP 2 and CCP 3), one gold pregnant leach solution (Gold PLS) and a municipal solid waste incinerator ash leachate (MSW-I) were evaluated in this study. Leachate ionic strengths increase in the order of gold PLS< CCP 1<CCP2<CCP3<MSW-I. Ionic strengths are plotted together with the ratio of monovalent cations to square root of divalent cations (RMD) in Fig. 1.3. The regression line included in the figure is a regression of data for representative leachates from Subtitle D landfill cells (Bradshaw and Benson, 2013).

Major ionic species in each synthetic leachate are summarized in Table 1.3. Activity coefficients for the ionic species accounted for deviation from ideal mixture behavior with solution charge balance satisfied at 25 °C using the Visual Minteq (KTH, Sweden) chemical equilibrium model. Synthetic solutions were also checked for mineral saturation index, which is defined as the ratio of the ion activity product of dissolved ions of a mineral in solution to its equilibrium constant, and is an indication of whether the solution is over-saturated or under-saturated with respect to a solid phase. CCP1, CCP2, CCP3 and Incinerator ash leachate were determined to be over-saturated with respect to mineral gypsum ($CaSO. 2H_2O$), which leads to precipitation. Ca ion in these leachates was thus replaced by Mg, which has higher solubility, in order to prevent precipitation and maintain the target ionic strength and RMD. Ca and Mg have the same valence and similar hydrated radii. Therefore, the preference for Ca and Mg in the exchange complex is essentially the same.

Mg is the predominant cation in the CCP 1 and CCP 2 leachates, whereas Gold PLS, CCP 3 and Incinerator ash leachates have appreciably higher concentrations of Na than Mg. The predominant anion is Cl in all leachates, except Gold PLS, which has higher SO_4 concentration than Cl. Cl and SO_4 concentrations in all leachates are comparable, except for the incinerator ash leachate, where the Cl concentration is an order of magnitude higher than the SO_4 concentration.

1.4.2.2. EPRI Leachates

Chemical compositions of EPRI leachates used for this study are the same as the composition of leachates reported in Electrical Power Research Institute (EPRI) final report entitled “Engineering properties of geosynthetic clay liners (GCLs) for disposal facilities for coal combustion products (CCPs)" (Benson et al., 2014). Characteristics of all leachates in the EPRI study (except for trona leachate) were established by analyzing a leachate database based on 33 CCP management landfills. Characteristics of trona leachate were based on high trona injection rates (Benson et al., 2014). Five synthetic leachates with different I and RMD combinations were selected in the EPRI study to represent various conditions in CCP disposal facilities (Fig.1-4): typical CCP leachate, predominantly divalent cation ash leachate (low RMD), flue gas desulfurization residual (typical FGD), high ionic strength leachate and trona ash leachate. The concentrations of leachate constituents, pH, ionic strength and RMD for each of these leachates are summarized in Table 1.4.

The predominant cation in Typical CCP and Low RMD leachate is Ca, whereas Na is the predominant cation in High ionic Strength, Typical FGD and Trona leachates. Major anions in all CCP leachates are Cl and SO_4, except Trona leachate in which Cl is not present. For leachates having both Cl and SO_4, SO_4 is the predominant anion. Trona leachate has an SO_4 concentration an order of magnitude higher than all the other CCP leachates.

1.5. METHODS

1.5.1. Hydraulic Conductivity Tests

Hydraulic conductivity tests were conducted with a Na-bentonite GCL and two polymer-modified bentonite GCLs (Resistex and Resistex Plus) using flexible wall permeameters according to ASTM D5084 Method B (Falling head-water, constant tail-water) and ASTM D6766. An average hydraulic gradient of 190 was maintained for all tests. ASTM D 5084 suggests a maximum hydraulic gradient of 30 for materials having low hydraulic conductivity ($k < 10^{-9}$ m/s). Petrov (1995) has shown that using higher hydraulic gradient results in seepage-induced consolidation, leading to decrease in void ratio of bentonite. However, higher hydraulic gradient was used in the laboratory in order to conduct the tests over the required time interval. Hydraulic gradients of 150 to 200 are typical for laboratory hydraulic conductivity testing of GCLs (Dunn and Mitchell, 1984). However, hydraulic gradient has negligible effect on hydraulic conductivity of GCLs. For example, Shackelford et al., (2000) showed that hydraulic conductivity of GCLs was not affected significantly by hydraulic gradient if it is less than 500.

GCL specimens were hydrated in the permeameter cell with the leachate of interest for 48 hours at an average cell pressure of 27 kPa prior to initiation of the test. The influent valve was initially left open to allow the specimen to hydrate with leachate with the effluent valve closed to prevent outflow. Flow-through hydraulic conductivity tests were then conducted at an effective stress of 20 kPa until termination criteria according to ASTM 6766 were reached.

1.5.2. Termination Criteria

Following ASTM 6766, hydraulic equilibrium was considered established when steady hydraulic conductivity was maintained for three consecutive measurements and the volumetric outflow to inflow ratio was within 1±0.25 (i.e., %25). Chemical equilibrium was considered established when the ratios of effluent to influent pH (pH_{out}/pH_{in}), electrical conductivity (EC_{out}/EC_{in}), and major cation (Ca, Mg, Na, K) concentrations were within 1.0±0.1 (i.e., 10%). Equilibrium hydraulic conductivity values were reported by taking the average of the last three consecutive readings at steady state.

1.5.3. Chemical Analysis of Effluent

Concentrations of major cations (Na, K, Mg, Ca) in effluent samples were analyzed using Varian MPX inductively coupled plasma atomic emission spectroscopy (ICP-AES) in accordance with method 6010B defined by the U.S. Environmental Protection Agency (EPA). Calibration standard solutions were prepared by adding appropriate volumes of stock solutions preserved in 1% nitric acid. Prior to analysis, samples were diluted 10 times and digested with 1 mL of nitric acid.

1.5.4. Soluble Cations, Bound Cations and Cation Exchange Capacity (CEC)

Soluble cations, bound cations and cation exchange capacity (CEC) were determined for bentonite (or PMB) obtained from each GCL according to procedures described in ASTM D 7503. Prior to testing, the material was ground to 100% passing the no 10 U.S. standard sieves. Two grams and ten grams of material were used for soluble cation determination and bound cation determination, respectively.

For the determination of soluble cations, the material was mixed with 100 mL of type II DI water and tumbled at 30 rpm in an end-over-end shaker for one hour. The mixture was then vacuum filtered. Extract was transferred to a 100 mL volumetric flask, preserved with 1 mL nitric acid (HNO_3) and filled to 100 mL volume with Type II DI water (ASTM D1193-91). The extract was then analyzed in ICP-AES for cation concentration.

For determination of bound cations, 10 g of material was mixed with 1 M extraction liquid (NH_4OAc). After tumbling the mixture for 5 minutes at 30 rpm, the sample was agitated for 24 hours. At the end of 24 hours, the sample was tumbled again for 15 min at 30 rpm and the extract was vacuum filtered using 2.5 µm ashless filter paper. Four 30 mL portions of 1 M NH_4OAc were used to wash the material. Extract was then transferred to a 250 mL volumetric flask, washed with NH_4OAc, preserved to pH of 2, and then filled to 250 mL volume with 1 M NH_4OAc. Cation concentrations were analyzed using ICP-AES.

Previously NH_4OAc washed material was used for cation exchange capacity (CEC) determination. Three 40 mL portions of isopropanol were used to wash residual NH_4OAc. After discarding the residual NH_4OAc, the material was washed with four 50 mL portions of 1 M KCl to replace the adsorbed cations with K. Extract was then transferred into a 250 mL volumetric flask, washed with KCl, and filled to 250 mL volume with Type II DI water. The KCl extract was analyzed for nitrogen concentration using spectrophotometry. The CEC of the soil material then can be calculated from ammonium concentration using the following equation given in ASTM D7503-10.

$$\mathrm{CEC} = \mathrm{N} \times \frac{1\,\mathrm{cmol}^{+}}{140\mathrm{mg}} \times \frac{0.25\mathrm{L}}{\mathrm{M}_0(\mathrm{g})} \times 1000\,\frac{\mathrm{g}}{\mathrm{kg}}$$

where;

N: concentration of nitrogen (mg/L)

M_0: oven-dry mass of soil

CEC: cation exchange capacity $(\mathrm{cmol}^{+}/\mathrm{kg})$

1.6. RESULTS

The Bentomat, Resistex and Resistex plus GCLs were permeated with EPRI and site-specific synthetic leachates within a time period of 1 to 12 months. A summary of hydraulic conductivity results is presented in Table 1.5. The same results are summarized in the form of bar chart in Fig. 1.6. Hydraulic conductivity results to EPRI and site-specific leachates were also presented in the form of bar chart in Fig. 1.7 and Fig. 1.8 separately.

Fig. 1.9 shows the hydraulic conductivity vs ionic strength of the permeant relationship for Bentomat, Resistex and Resistex Plus GCLs. Bentomat GCL shows smooth increase in hydraulic conductivity with increasing ionic strength whereas PMB GCLs show a step increase in hydraulic conductivity around one molar ionic strength. This might be due to the fact that local elution of polymer within the sample opens the pore spaces and controls the hydraulic conductivity. In this case, free water would preferentially move through the point where polymer elution occurs causing sudden increase in hydraulic conductivity.

Bentomat GCL permeated with site-specific leachates having I ≤ 179 mM displayed relatively low hydraulic conductivity (<10^{-9} m/s). Hydraulic conductivity of Bentomat GCL with these leachates initially increased slightly and then decreased. Permeation with site-specific leachates having I≥975 mM resulted in higher hydraulic conductivity (>10^{-8} m/s) as compared to low ionic strength site-specific leachates. For these leachates, hydraulic conductivity of the GCL initially increased and then leveled out (with the exception of CCP-2 leachate). For the CCP-2 leachate, the hydraulic conductivity vs. PVF plot was steady from the beginning (Fig. B.7).

Hydraulic conductivity of polymer modified bentonite (PMB) GCLs with site-specific leachates showed two distinct trends: for leachates having relatively low (I≤370 mM) and high (I≥975 mM) ionic strength. For site-specific leachates having relatively low ionic strength (Gold PLS, CCP 1 and CCP 2), an initial slight decrease in hydraulic conductivity was maintained over time. For leachates having high ionic strength (CCP 3 and MSW-I), hydraulic conductivity showed a trend of initial increase followed by leveling out. Typical hydraulic conductivity, pH ratio and EC ratio vs. pore volume of flow (PVF) graphs for tests conducted on Resistex plus GCL with MSW-I (I=1042 mM) and CCP 1 (I=179 mM) leachates are provided in Fig. 1.10 and Fig. 1.12. EC ratio decreases as the salts are washed away from pore spaces. pH ratio is within the 1±0.1 indicating pH equilibrium. Corresponding cation ratios are also presented in Fig. 1.11. A gradual increase in Mg ratio and decrease in Na ratio suggests that cation exchange is occurring. As the Mg ions replaces Na ions in the exchange complex, decrease in volume of bound water to montmorillonite surface and increase in volume of free water lead to enlargement of flow paths and consequently increase in hydraulic conductivity.

The PMB GCLs (Resistex and Resistex Plus GCLs) permeated with site-specific synthetic leachates showed lower hydraulic conductivity than corresponding Bentomat GCL. Fig. 1.13 is a comparison of hydraulic conductivity tests with PMB GCLs and the Na-B GCL. All data points fall below the 1:1 line, suggesting that the hydraulic performance of PMB GCLs to site-specific leachates is better than the Na-B GCL. As a control, hydraulic conductivity tests on Resistex and Resistex plus GCL with deionized water (DI) were also conducted. Fig. 1.14 shows a comparison between hydraulic conductivity to site-specific leachates and to DI water. All data points for Resistex plus GCL fall above to 1:1 line suggesting that the Resistex plus GCL is more permeable to the site specific leachates than to DI water. Hydraulic conductivities for the Resistex GCL with site specific leachates having relatively low ionic strength solutions (I≤370 mM) fall below 1:1 line and above 1:10 line. However, tests with DI water are reported for relatively short period of time (<3 months) and have not reached hydraulic and chemical equilibrium yet. Although result from LOI suggests that the polymer loading of the PMB GCLs are different from each other, permeation with site-specific leachates having I≤370 mM resulted in hydraulic conductivity of same order of magnitude (10^{-12} m/s) for both the Resistex and Resistex plus GCLs. On the other hand, permeation with leachates having I≥975 mM resulted in hydraulic conductivity on the order of 10^{-8} m/s, except for the Resistex GCL with incinerator ash leachate. For this leachate, the Resistex plus GCL was more permeable than the Resistex GCL. Due to its higher polymer loading, the Resistex plus GCL was expected to have better hydraulic performance with incinerator ash leachate than corresponding Resistex GCL. Therefore, a replicate test was conducted for both Resistex and Resistex plus GCL with incinerator ash leachate. The replicate test yielded hydraulic conductivity on the order of 10^{-9} m/s for Resistex and 10^{-10} m/s for Resistex plus. However, hydraulic and chemical equilibrium has not been reached yet for this test and may change over the long term.

Hydraulic conductivity tests with EPRI leachates were conducted with only PMB GCLs. Permeation with EPRI leachates resulted in hydraulic conductivity values on the same order of magnitude (10^{-12} m/s) for both GCL products, regardless of the ionic strength of leachate used. Hydraulic and chemical equilibrium haven't yet been satisfied for tests, and the results might change over the long term.

Hydraulic conductivity of Resistex GCL with EPRI leachates showed two distinct trends for leachates having relatively low (I≤96.8 Mm) and high (I≥178 M) ionic strength. For leachates having relatively low ionic strength (typical CCP, low RMD and typical FGD), an initial slight decrease in hydraulic conductivity was maintained within the same order of magnitude over time. For leachates having high ionic strength (trona and high ionic strength), hydraulic conductivity showed an initial increase followed by gradual decrease and final leveling out. Typical hydraulic conductivity, pH ratio and EC ratio v. pore volume of flow (PVF) graphs for tests conducted on Resistex GCL with trona (I=755 mM) and typical FGD (I=96.8 mM) leachates are provided in Fig. 1.15 and Fig. 1.16. An increase in hydraulic conductivity for the Resistex GCL with trona by 2 orders of magnitude around 5 PVF was attributed to unplugging of the confining cell pressure tubing connected to permeameter. Decrease in confining pressure is likely to cause change in packing of grains and increase in pore size leading to higher hydraulic conductivity. An increase in hydraulic conductivity at 6.4 PVF was also observed for Resistex GCL with trona leachate. No significant change in chemical indicators (EC, pH and cation ratios) was seen at that time.

Rhodamine tracer dye was used to observe the distribution of flow through the GCL specimen and to determine possible reasons for the observed increase in hydraulic conductivity (Fig. 1.17). One mL of dye was poured into the influent burette and allowed to pass through the GCL specimen until the dye was observed in the effluent. The permeameter was then temporarily disassembled to observe the flow distribution in GCL specimen from the dye trace. Observation of dye around the outside of the GCL specimen leads to the conclusion that sidewall leakage occurred around the specimen (Fig. 1.17). A paste was thus made by mixing Resistex material and trona and placed around the exposed edges of the specimen to minimize sidewall leakage. However, after reassembly, hydraulic conductivity decreased for a short period of time and then increased again. Therefore, the permeameter was disassembled for a second time, the GCL specimen was trimmed into smaller size (100 mm in diameter) and the test was continued. After 7.5 PVF hydraulic conductivity of Resistex with trona leachate decreased to same level where it had initially reached an apparent steady state.

Hydraulic conductivity of Resistex plus GCL with relatively low and high ionic strength EPRI leachates showed a trend similar to that observed in Resistex GCL, except for tests with typical CCP and high ionic strength leachate. Hydraulic conductivity for Resistex plus with high ionic strength leachate was maintained within the same order of magnitude over time, much like the trend observed with low ionic strength leachates with Resistex GCL. For typical CCP, an initial slight increase in hydraulic conductivity was followed by a gradual decrease. Tests with Resistex and Resistex plus GCLs have not reached hydraulic and chemical equilibrium. Therefore, hydraulic conductivities are subject to change over long term. Two GCL products (Resistex and Resistex Plus) will be permeated until the termination criteria is satisfied.

Comparison of hydraulic conductivity test results with previous EPRI study

An old generation Resistex GCL (CR) having lower polymer loading (2.2 %) and produced by the same company (CETCO) was previously tested with EPRI leachates by Benson et al. (2014). Hydraulic conductivity tests with EPRI leachates in this study were conducted under the same conditions with tests conducted by Benson et al. (2014). GCL specimens were hydrated in cell with the leachate of interest for 48 hours at an average cell pressure of 27 kPa prior to initiation of the test. An average hydraulic gradient of 190 was applied. Fig. 1.18 shows ionic strength vs. hydraulic conductivity plot of tests conducted in this study together with results from Benson et al. (2014). Benson et al. (2014) observed a trend of increasing hydraulic conductivity as the ionic strength of the leachate increased. However, in the current study, low hydraulic conductivity (on the order of 10^{-12} m/s) was maintained, even with the highest ionic strength leachate (trona). Hydraulic conductivity to trona leachate was five orders of magnitude lower in this study than observed by Benson et al. (2014). Comparison of these two studies suggest that when polymer loading is below a threshold value, PMB GCLs behaves similar to Na-B GCL.

1.7. DISCUSSION

PMB GCLs (Resistex and Resistex plus) showed resistance to increases in hydraulic conductivity for all EPRI leachates. Even tests with trona leachate, which has the highest ionic strength (I=755 mM) among the EPRI leachates, resulted in hydraulic conductivity on the order of 10^{-12} m/s. However, PMB GCLs tested with site-specific leachates having I≥975 mM were more permeable than same GCLs tested with high ionic strength EPRI leachates. For example, CCP 3 leachate has ionic strength close to trona leachate, but the difference between hydraulic conductivities was four orders of magnitude. However, divalent cations are more abundant (RMD= 1.86) in CCP 3 leachate than trona leachate (RMD=4.4.), which might lead to an increase in hydraulic conductivity due to cation exchange. Another possible explanation might be the ineffective adsorption of polymer for tests conducted with high ionic strength site-specific leachates (CCP 3 and MSW-I). The presence of salts in solution affects the nature of polymer-solvent interactions (Atesok et al. 1988). Depending on whether the solvent is good or poor, the polymer configuration can change in the solution, which would eventually affect the polymer adsorption. In a poor solvent, monomer-monomer interactions are more favorable than monomer-solvent interactions. Therefore, polymer chain minimizes the contact with solvent and collapses into a coiled configuration. In a good solvent, monomer-solvent interactions are favored. Therefore, the polymer chain is more extended and flexible. A more extended polymer chain would result in more interaction with clay surface through exchangeable cations (Burchill et al. 1983) and form a 3D network structure. Upon this interaction, the polymer can absorb significant amounts water, swell, and retain low hydraulic conductivity. However, in a coiled configuration there will be less bound water on the polymer due to minimized contact with the solvent. Therefore, free water would move more easily and give rise to an increase in hydraulic conductivity.

In general, higher polymer loading resulted in lower hydraulic conductivity for testing with site specific leachates. However, hydraulic conductivity testing on Resistex GCL (which has lower polymer loading) with MSW-I leachate yielded lower hydraulic conductivity than Resistex plus GCL with the same leachate. This might be due to the fact that polymer elution during the testing makes the PMB ineffective to maintain low hydraulic conductivity. Preliminary results from total organic carbon tests conducted on effluent samples showed that initial flushing of polymer around 0.2 PVF was higher in the case of Resistex plus GCL with MSW leachate than Resistex GCL with the same leachate (Fig. A.1). Due to this polymer elution, fraction of pore space available for free water to flow increases and consequently hydraulic conductivity increases. This might be an explanation for higher hydraulic conductivity of Resistex plus to MSW-I leachate.

1.8. CONCLUSIONS

Hydraulic conductivity tests were conducted on a Na-B GCL and two PMB GCLs (Resistex and Resistex plus) with EPRI leachates and site-specific synthetic leachates. The following conclusions have been drawn based on the testing results.

1. Hydraulic conductivity of NaB GCLs is affected primarily by the ionic strength of leachates.
2. PMB GCLs are more chemically resistant than Na-B GCLs.
3. PMB GCLs having higher polymer loading (i.e. Resistex plus) lead to lower hydraulic conductivity (by a factor of 2) when contacted with aggressive leachates.
4. When polymer loading is below a threshold value, PMB GCLs behave like Na-B GCL.
5. PMB GCLs show step increase in hydraulic conductivity at high ionic strengths rather than a ductile failure observed in the case of Na-B GCL. Polymer elution controls the hydraulic conductivity.

1.9. TABLES

Table 1.1: Physical and chemical properties of GCLs.

Property		Bentomat	Resistex	Resistex Plus	Method
Initial Water Content (%)		4.84	3.22	4.42	ASTM D 2216
Swell Index to DI water (mL/2 g)		29.5	27.5	27.0	ASTM D 5890-11
Loss on Ignition (%)		1.92 ± 0.10	3.70±1.80	6.17± 1.93	Scalia (2012)
Initial Thickness (mm)		7.3 - 8.2	7.2 - 8.8	7.1 - 8.3	-
Bentonite mass per unit area (kg/m^2)		3.6	3.6	3.6	-
Cation Exchange Capacity (cmol+/kg)		84.0	79.1	85.5	ASTM D 7503-10
Bound Cations (cmol$^+$/kg)	Na	28.7	40.4	18.0	
	K	2.94	1.1	0.5	
	Ca	23.6	20.7	10.3	
	Mg	11.1	9.9	5.3	

Table 1.2: Mineralogy of GCL bentonites

Mineral Constituent	Chemical Formula	Relative Abundance (%)		
		Bentomat	Resistex	Resistex plus
Quartz	SiO_2	9	7	8
Cristobalite	SiO_2	-	5	2
Albite feldspar	$NaAlSi_3O_8$	-	2	7
Augite	$Ca(Fe, Mg)Si_2O_6$	1	1	-
Plagioclase Feldspar-Oligoclase	$(Na_{0.82}Ca_{0.18})AlSi_3O_8$	3	-	-
K-Feldspar-Orthoclase	$KAlSi_3O_8$	Trace	1	trace
Calcite	$CaCO_3$	1	-	-
Gypsum	$CaSO_4 . 2H_2O$	trace	1	1
Clinoptilolite	$(Na,K,Ca)6(Si,Al)_{36}O_{72} . 20H_2O$	2	2	2
Kaolinite	$Al_2Si_2O_5(OH)_4$	trace	-	trace
Illite/Mica	$KAl_2(Si_3AlO_{10})(OH)_2$	1	1	1
montmorillonite	$(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2 . xH_2O$	84	80	79

Table 1.3: Concentrations of major ionic species, pH, ionic strength and RMD for site-specific leachates

Cation or Anion	Gold PLS	CCP-1	CCP-2	CCP-3	MSW-I
Ca (mg/L)	45.38	189.32	186.1	154.6	93.24
Mg (mg/L)	1.70	1049.49	1469	3173	6815
Na (mg/L)	175.94	911.87	344.1	12500	7700
K (mg/L)	-	645.12	658.4	5470	4900
Cl (mg/L)	187.90	4340.16	3906	22000	33000
SO_4 (mg/L)	241.92	1480.32	2544	16000	4600
pH	7.9	8.2	5.7	7.9	6.6
Ionic Strength (mM)	13.2	179.0	369.5	974.5	1042.0
RMD ($M^{1/2}$)	0.21	0.26	0.12	1.86	0.87

Table 1.4: Concentration of major ionic species, pH, ionic strength and RMD for CCP leachates.

Cation or Anion	Typical CCP	Low RMD	High ionic strength	Typical FGD	Trona
Ca (mg/L)	311	616	512	542	500
Na (mg/L)	254	28.8	2500	968	14800
Mg (mg/L)	29.4	24.3	140	73.1	150
K (mg/L)	72.2	10.6	22.2	49.9	200
Cl (mg/L)	70.7	23.2	1720	784	-
SO_4 (mg/L)	1390	1620	4720	2620	33000
pH	8.0±0.5	8.0±0.5	8.0±0.5	8.0±0.5	11.0±0.5
Ionic Strength (mM)	39.5	48	177	96.8	755
RMD ($M^{1/2}$)	0.16	0.01	1.00	0.39	4.4

Table 1.5: Summary of hydraulic conductivity results for CCP leachates and site-specific leachates

GCL	Permeant	Hydraulic Conductivity (m/s)
Resistex	DI water	$4.07\text{x}10^{-12}$
	Typical CCP	$3.33\text{x}10^{-12}$
	Low RMD	$3.44\text{x}10^{-12}$
	Typical FGD	$7.81\text{x}10^{-12}$
	High ionic strength	$9.78\text{x}10^{-12}$
	Trona	$5.58\text{x}10^{-12}$
Resistex Plus	DI water	$1.52\text{x}10^{-13}$
	Typical CCP	$1.24\text{x}10^{-12}$
	Low RMD	$4.98\text{x}10^{-12}$
	Typical FGD	$5.13\text{x}10^{-12}$
	High ionic strength	$2.63\text{x}10^{-12}$
	Trona	$7.30\text{x}10^{-12}$
Bentomat	Gold PLS	$1.47\text{x}10^{-11}$
	CCP 1	$1.00\text{x}10^{-10}$
	CCP 2	$3.93\text{x}10^{-8}$
	CCP 3	$5.08\text{x}10^{-7}$
	MSW-I	$1.36\text{x}10^{-6}$
Resistex	Gold PLS	$6.34\text{x}10^{-12}$
	CCP 1	$4.63\text{x}10^{-12}$
	CCP 2	$2.36\text{x}10^{-12}$
	CCP 3	$1.77\text{x}10^{-8}$
	MSW-I	$1.32\text{x}10^{-10}$
	MSW-I-Replicate	$2.53\text{x}10^{-9}$
Resistex Plus	Gold PLS	$7.25\text{x}10^{-12}$
	CCP 1	$3.03\text{x}10^{-12}$
	CCP 2	$4.75\text{x}10^{-12}$
	CCP 3	$1.15\text{x}10^{-8}$
	MSW-I	$2.27\text{x}10^{-8}$
	MSW-I-Replicate	$2.50\text{x}10^{-10}$

1.10. FIGURES

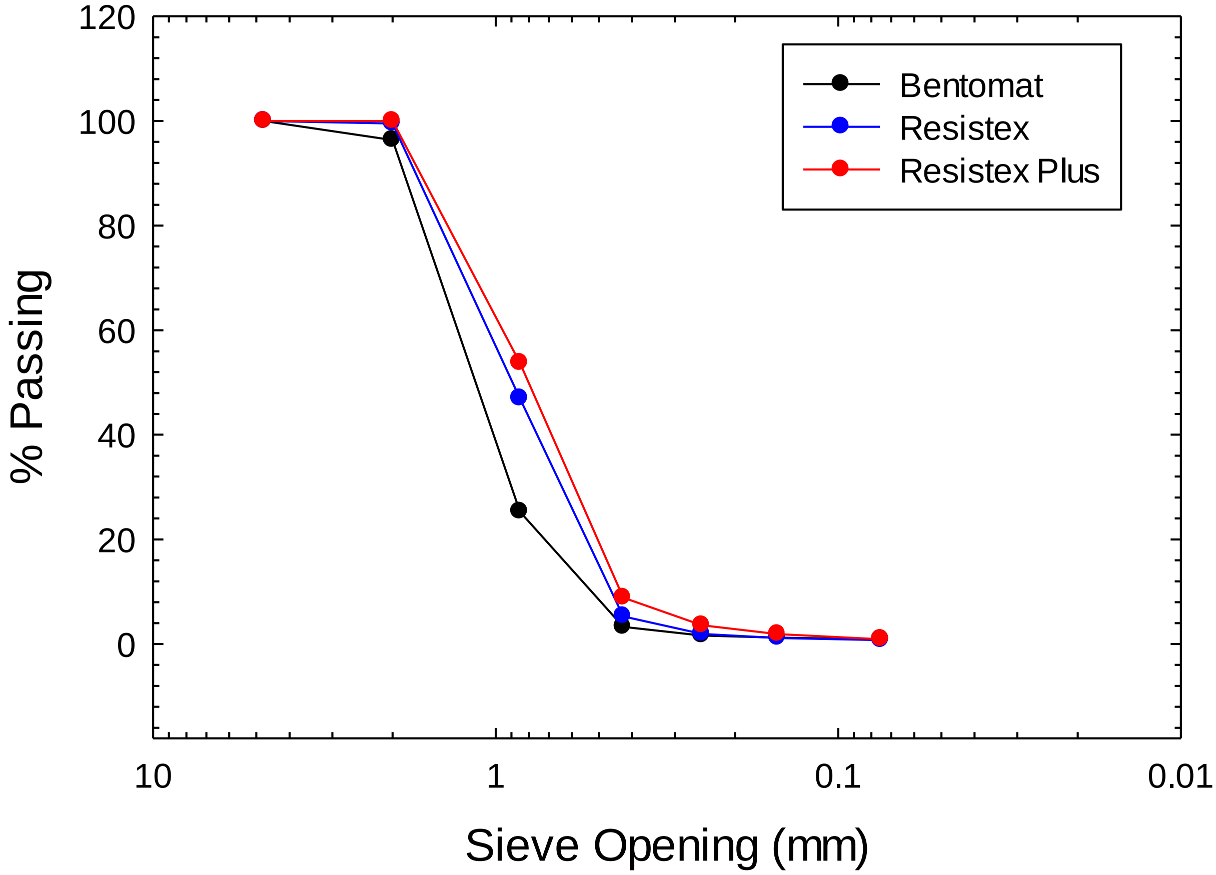

Figure 1.1: Granule size distributions of each GCL obtained by dry sieving of bentonite and bentonite-polymer dry mixtures.

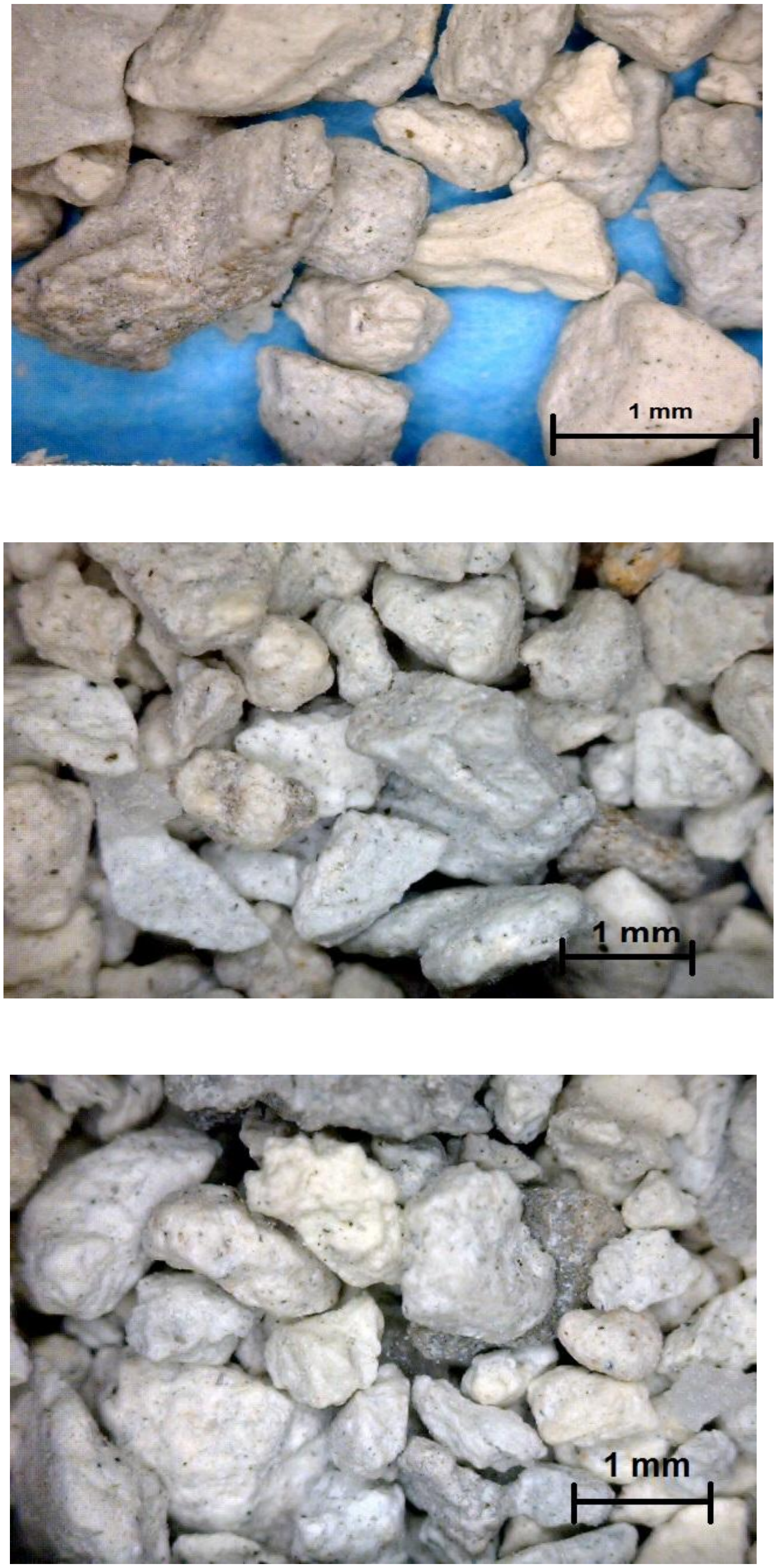

Figure 1.2: Digital microscope camera view of GCLs: a) Bentomat, b) Resistex and c) Resistex plus GCL

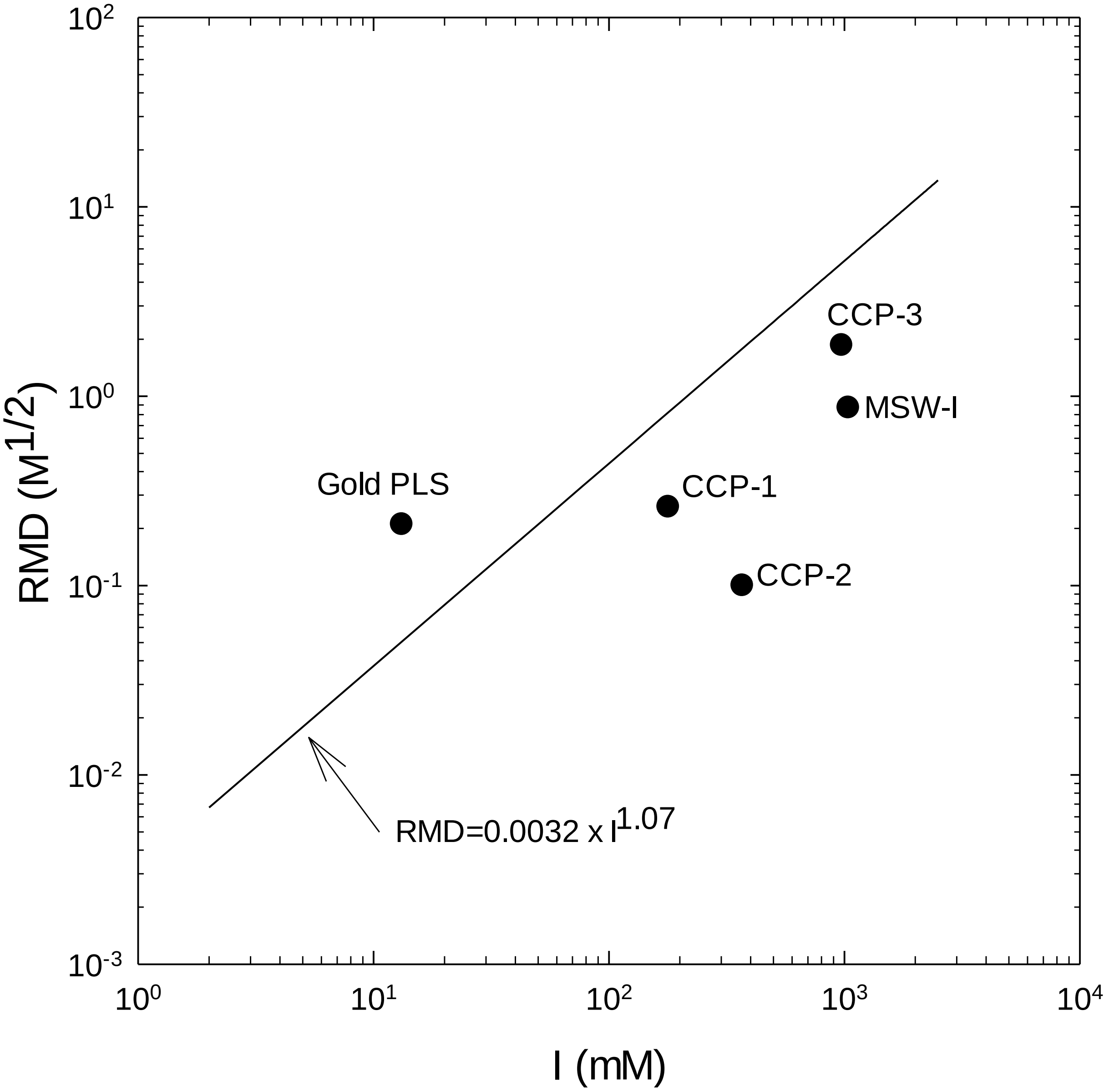

Figure 1.3: RMD vs. I for site-specific leachates. The solid line represents a regression of leachate data from Subtitle D landfill cells reported in Bradshaw and Benson (2013)

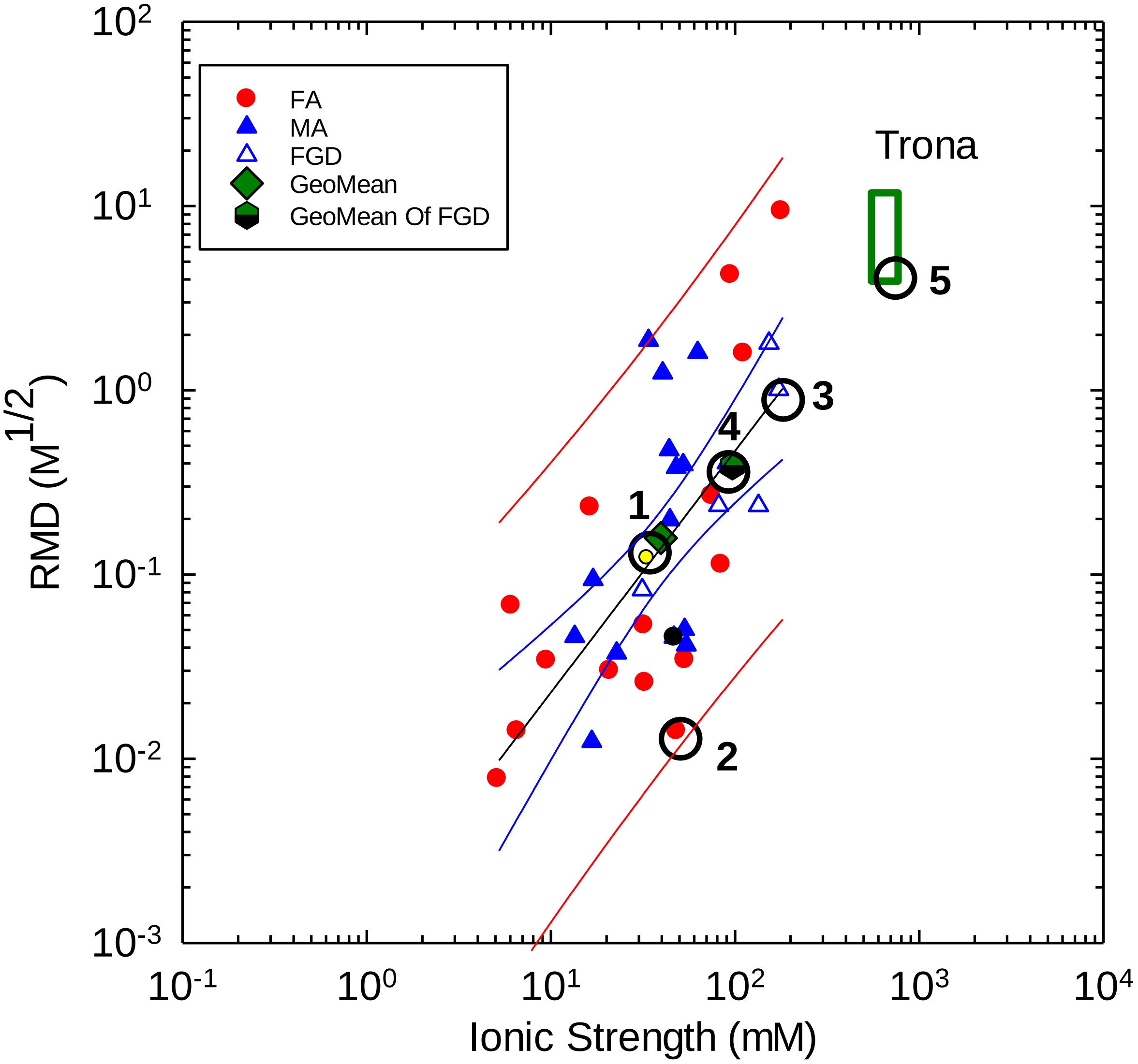

Figure 1.4: RMD vs. I for CCP leachates (Benson et al., 2014): 1.Typical CCP leachate, 2.Low RMD ash leachate, 3. High ionic strength leachate, 4.Typical FGD leachate, 5.Trona ash leachate

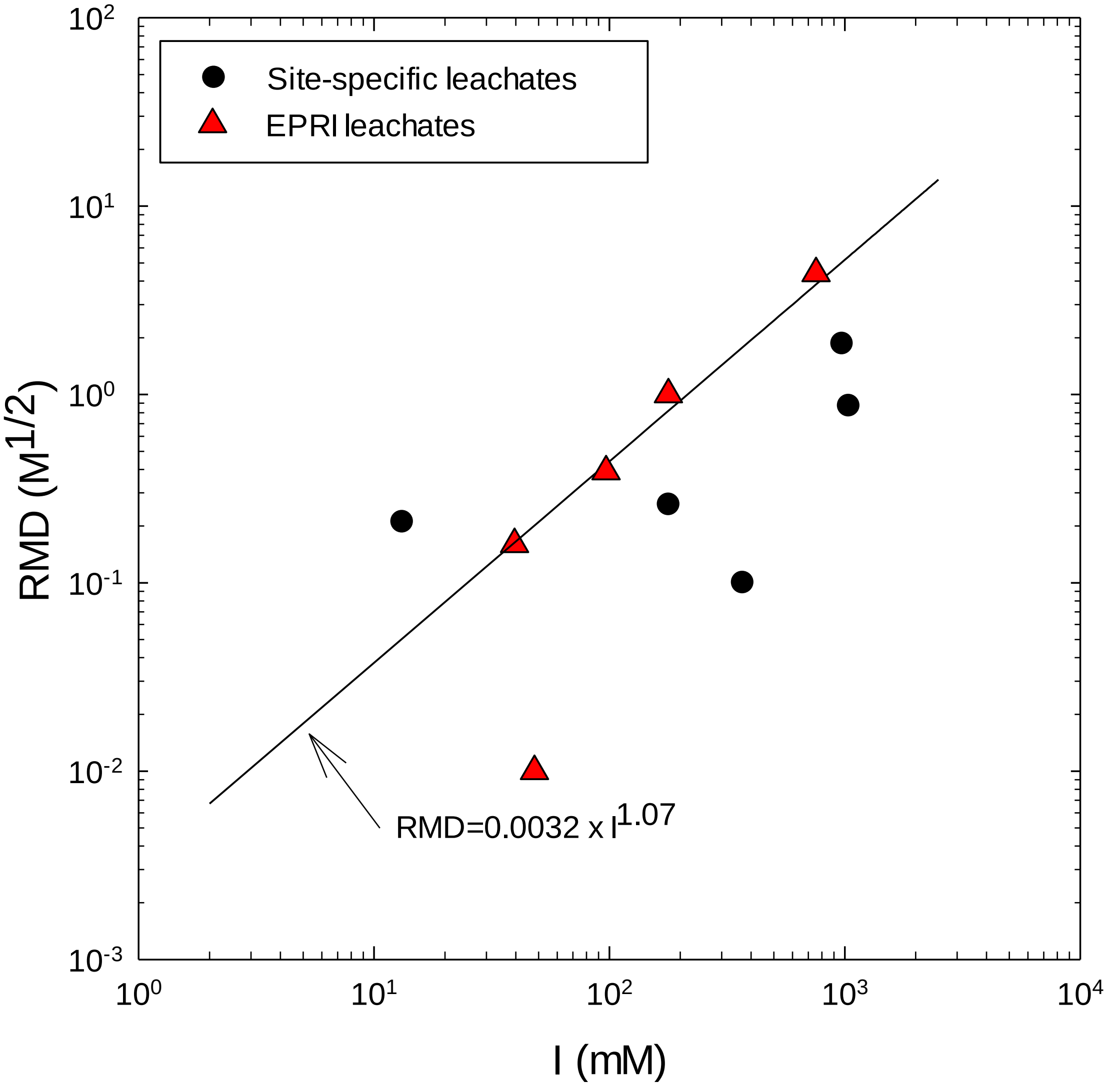

Figure 1. 5: RMD vs. I for EPRI leachates and site-specific leachates

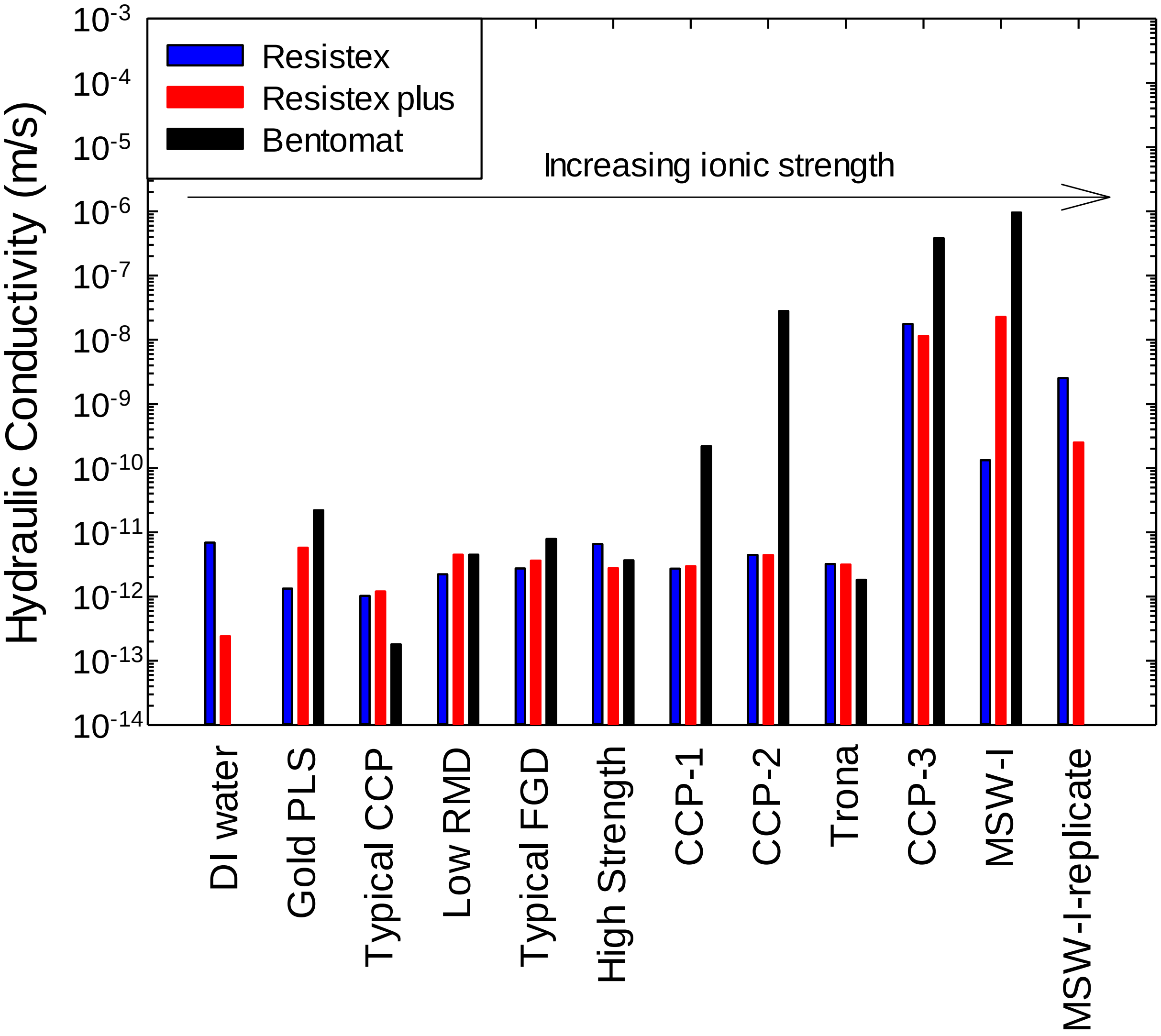

Figure 1. 6: Hydraulic conductivity of Bentomat, Resistex and Resistex plus GCLs to EPRI and site-specific leachates

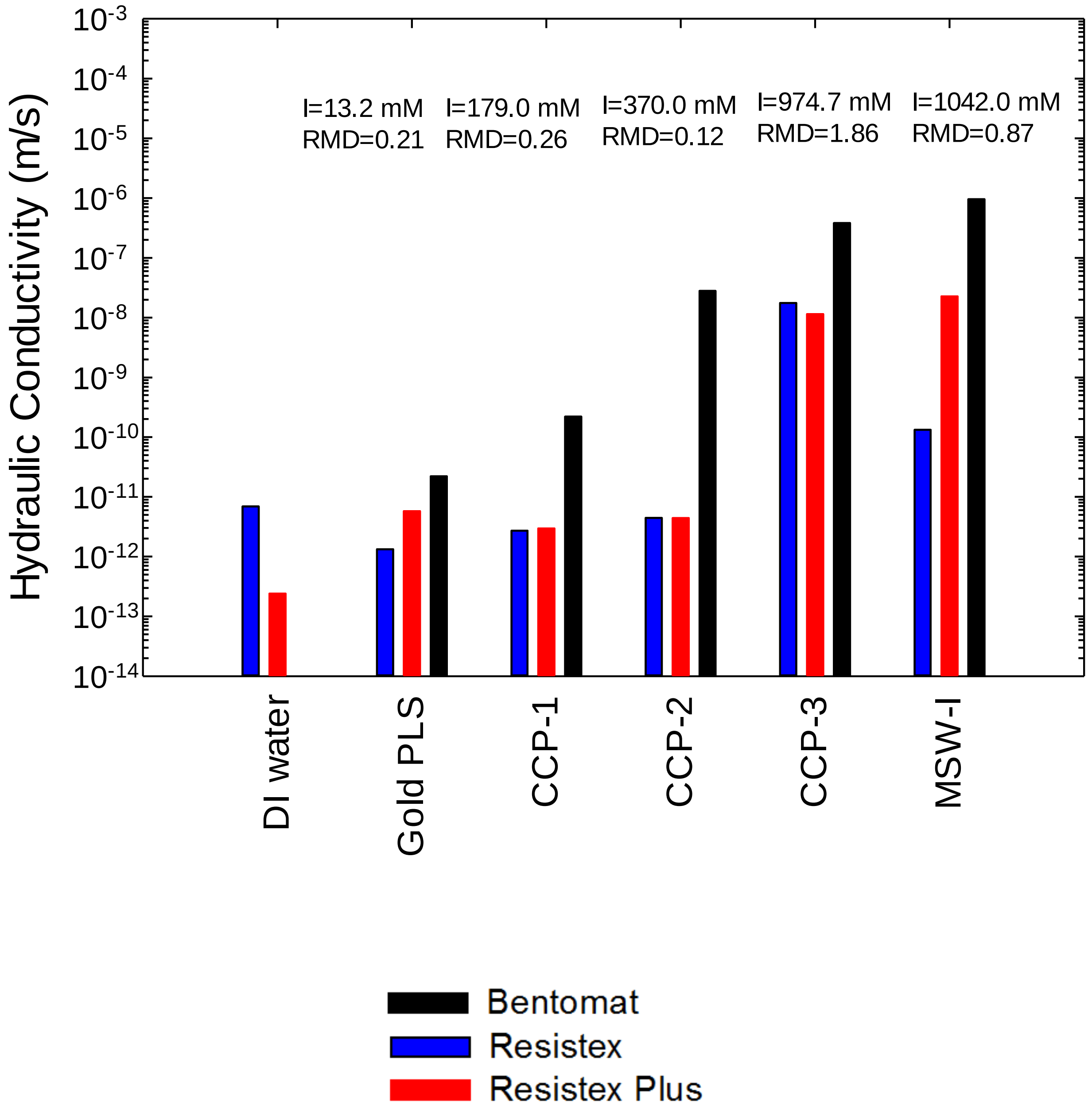

Figure 1.7: Hydraulic conductivity of Bentomat, Resistex and Resistex plus GCLs to site-specific leachates

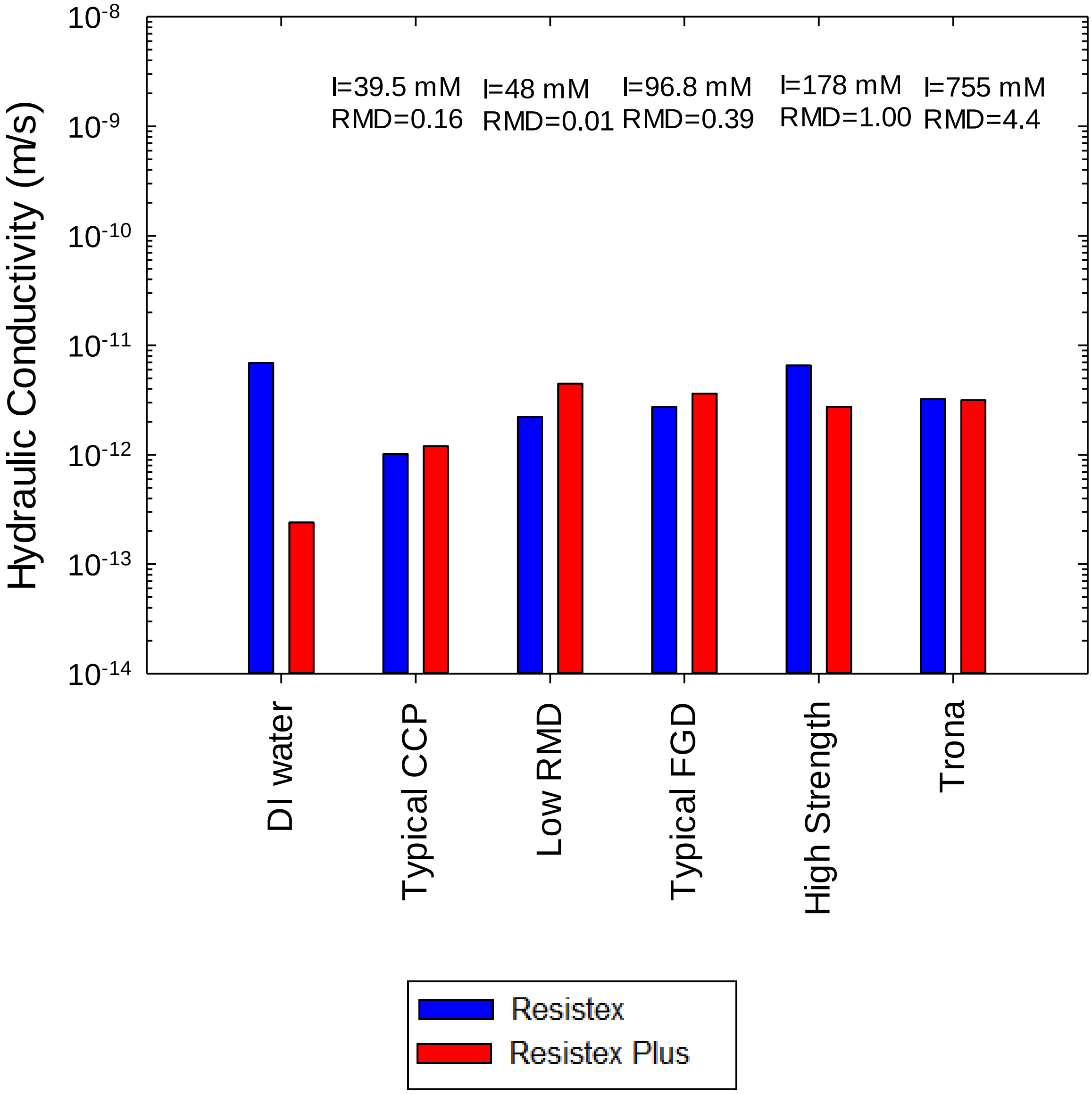

Figure 1. 8: Hydraulic conductivity of PMB GCLs to EPRI leachates

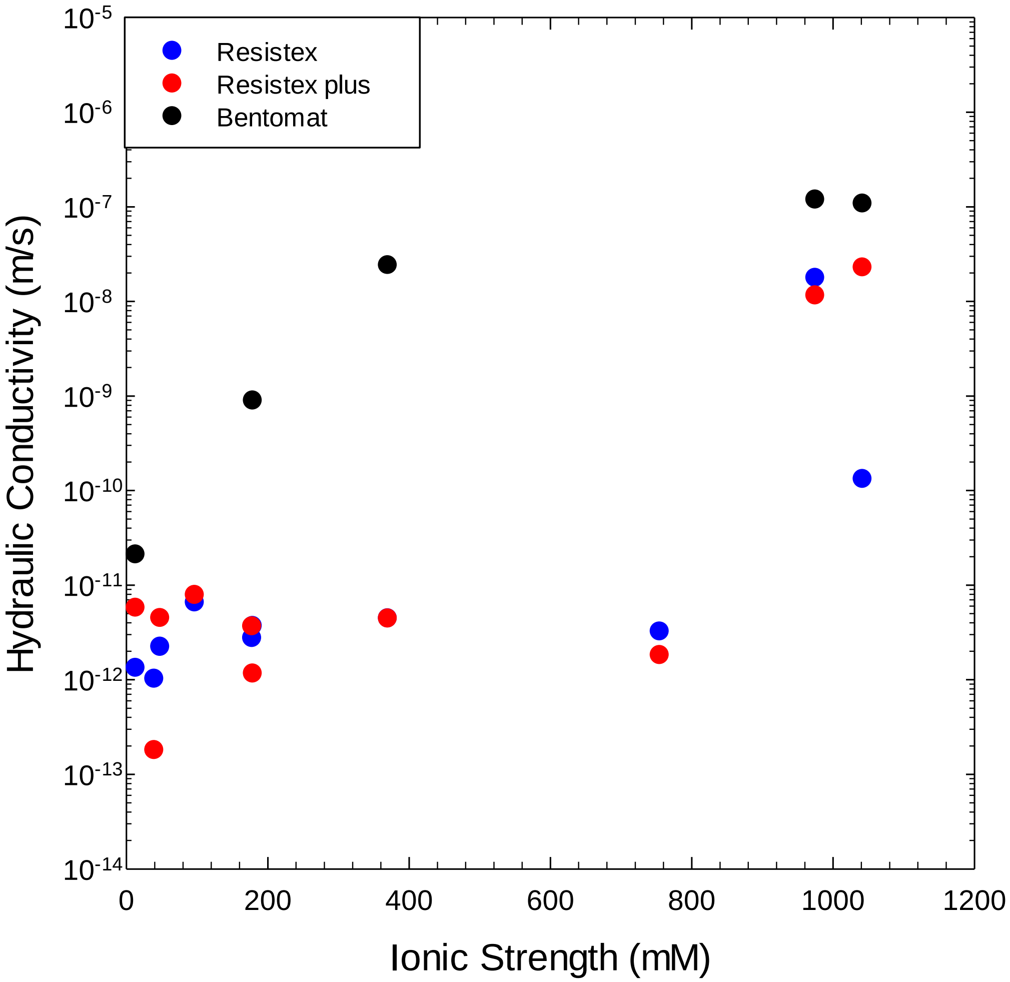

Figure 1. 9: Hydraulic conductivity vs ionic strength for Bentomat, Resistex and Resistex plus permeated with EPRI and site-specific leachate

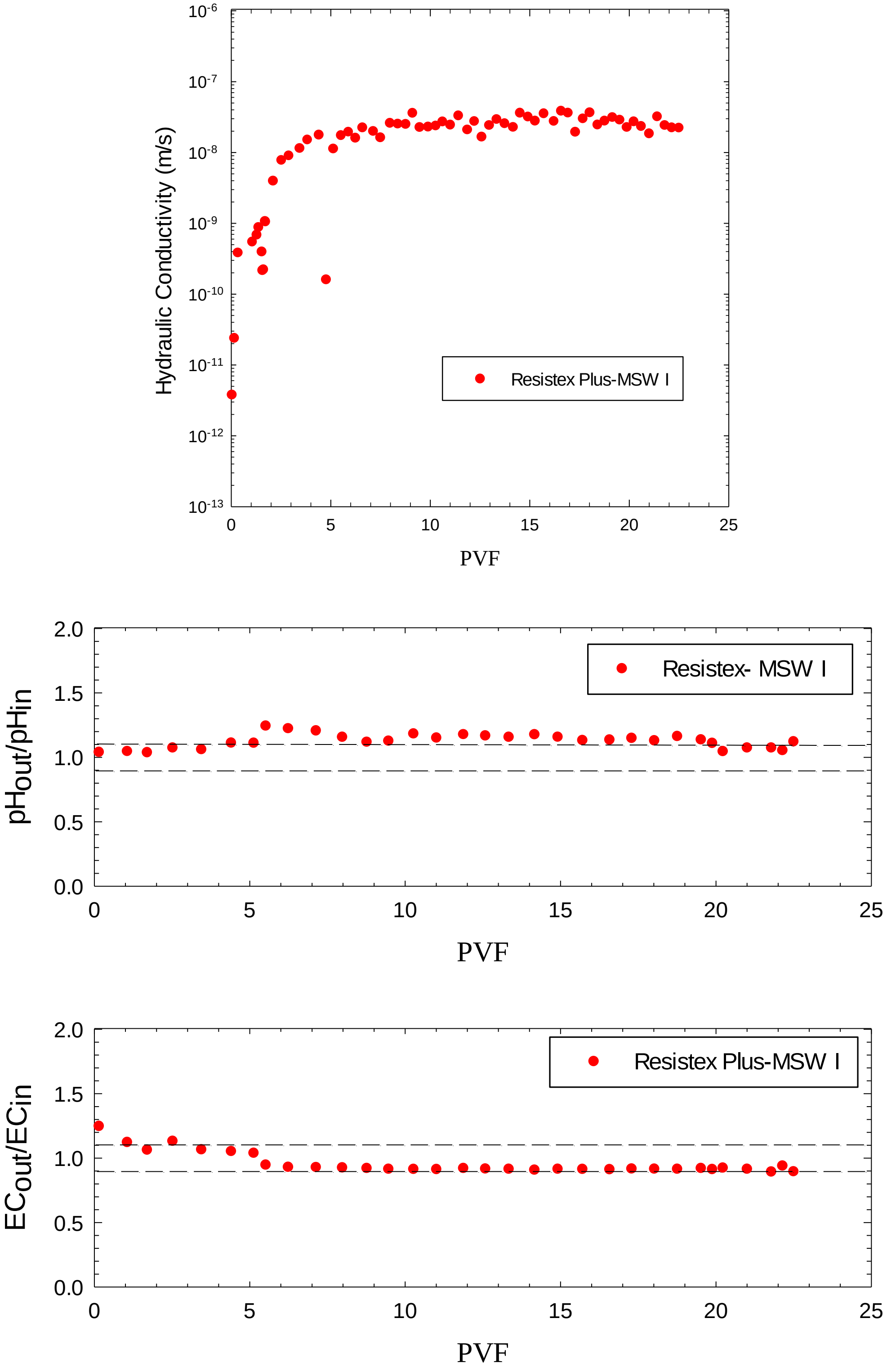

Figure 1. 10: Hydraulic conductivity, pH_{out}/pH_{in} and EC_{out}/EC_{in} vs. PVF for Resistex plus with MSW-I leachate

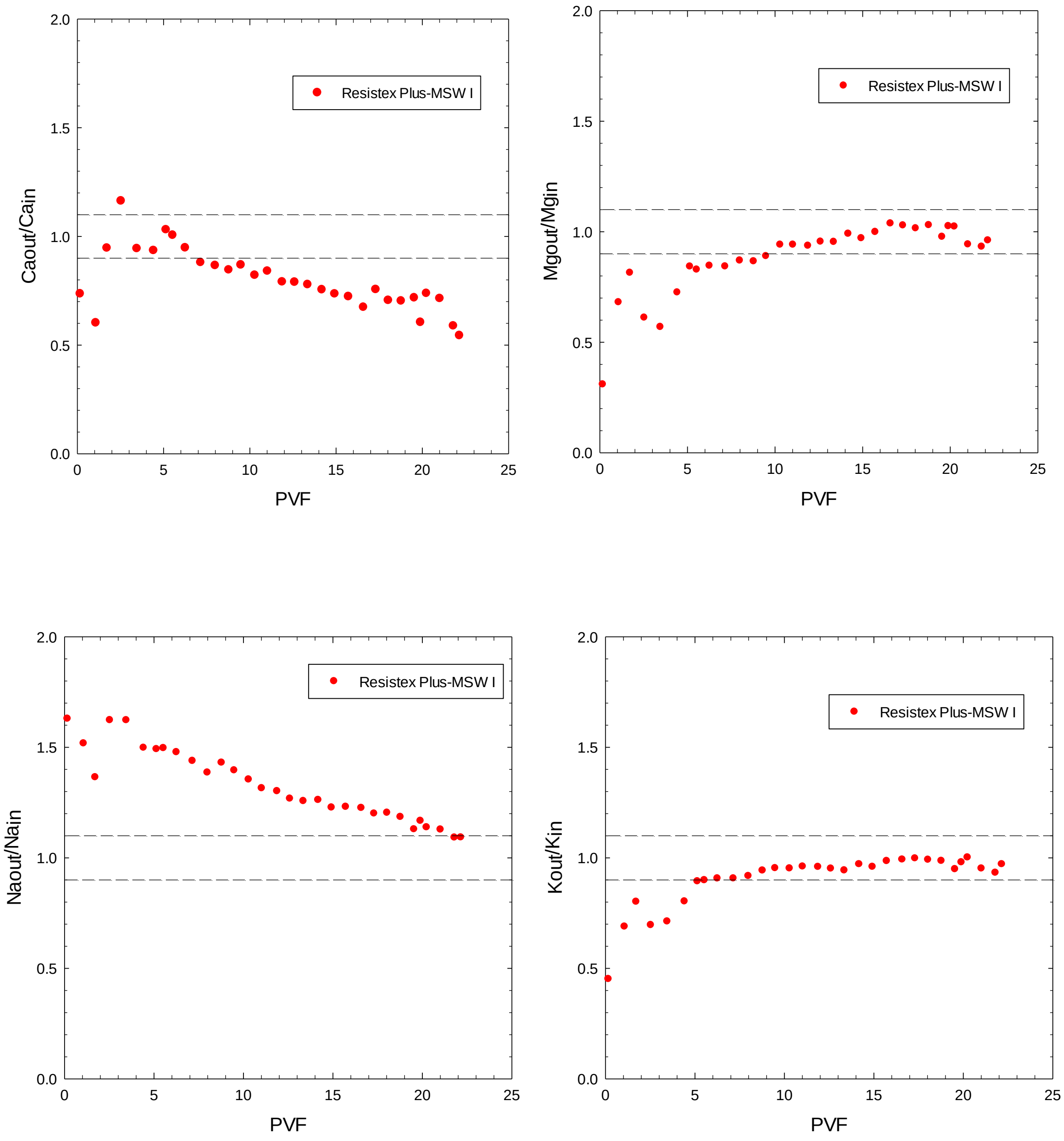

Figure 1. 11: Ratio of major cation concentrations in effluent to influent as a function of PVF for Resistex plus with MSW-I leachate

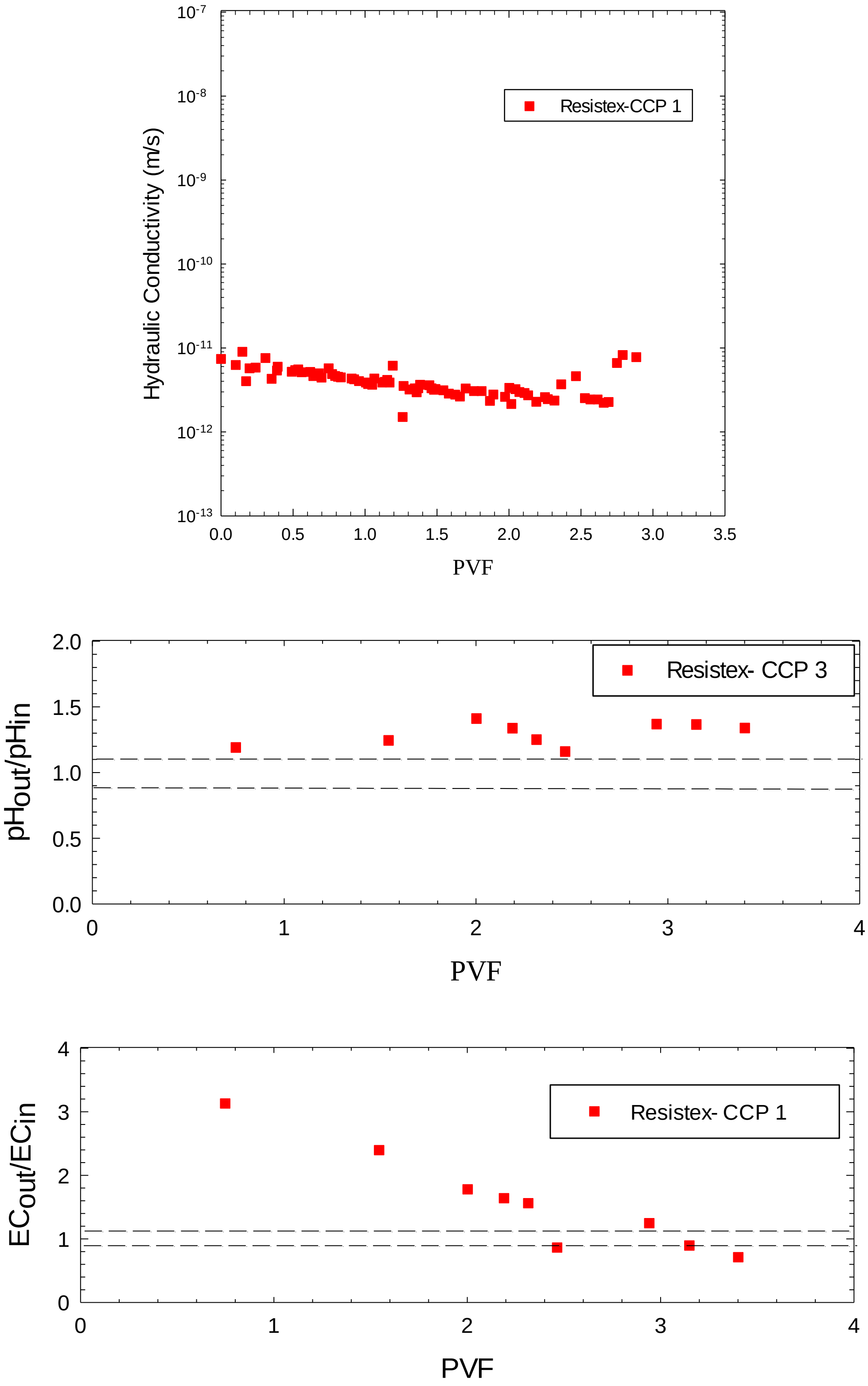

Figure 1. 12: Hydraulic conductivity, pH_{out}/pH_{in} and EC_{out}/EC_{in} vs. PVF for Resistex with CCP 1 leachate

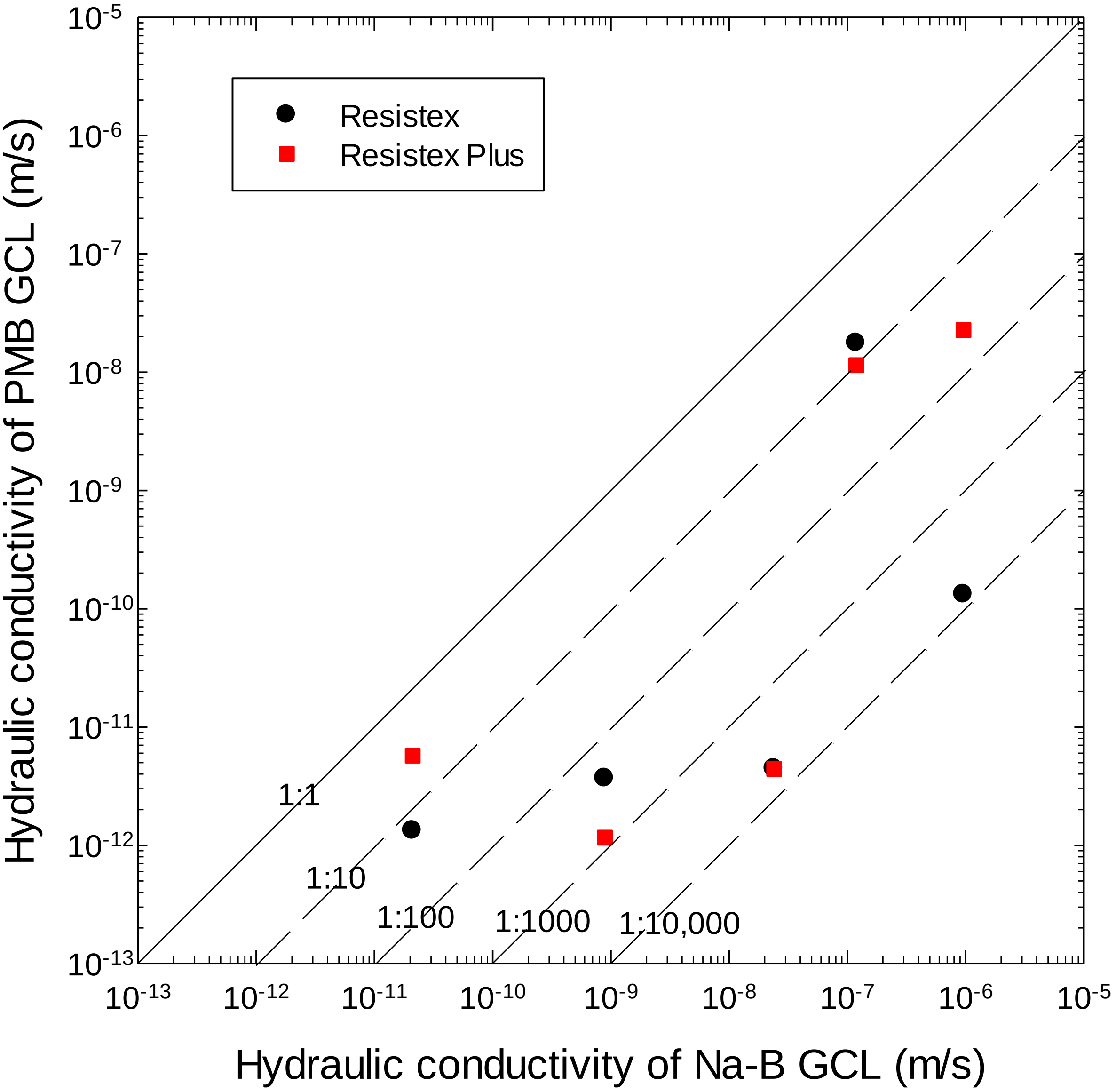

Figure 1. 13: Hydraulic conductivity of PMB GCLs in comparison to Na-B GCL for site-specific leachates

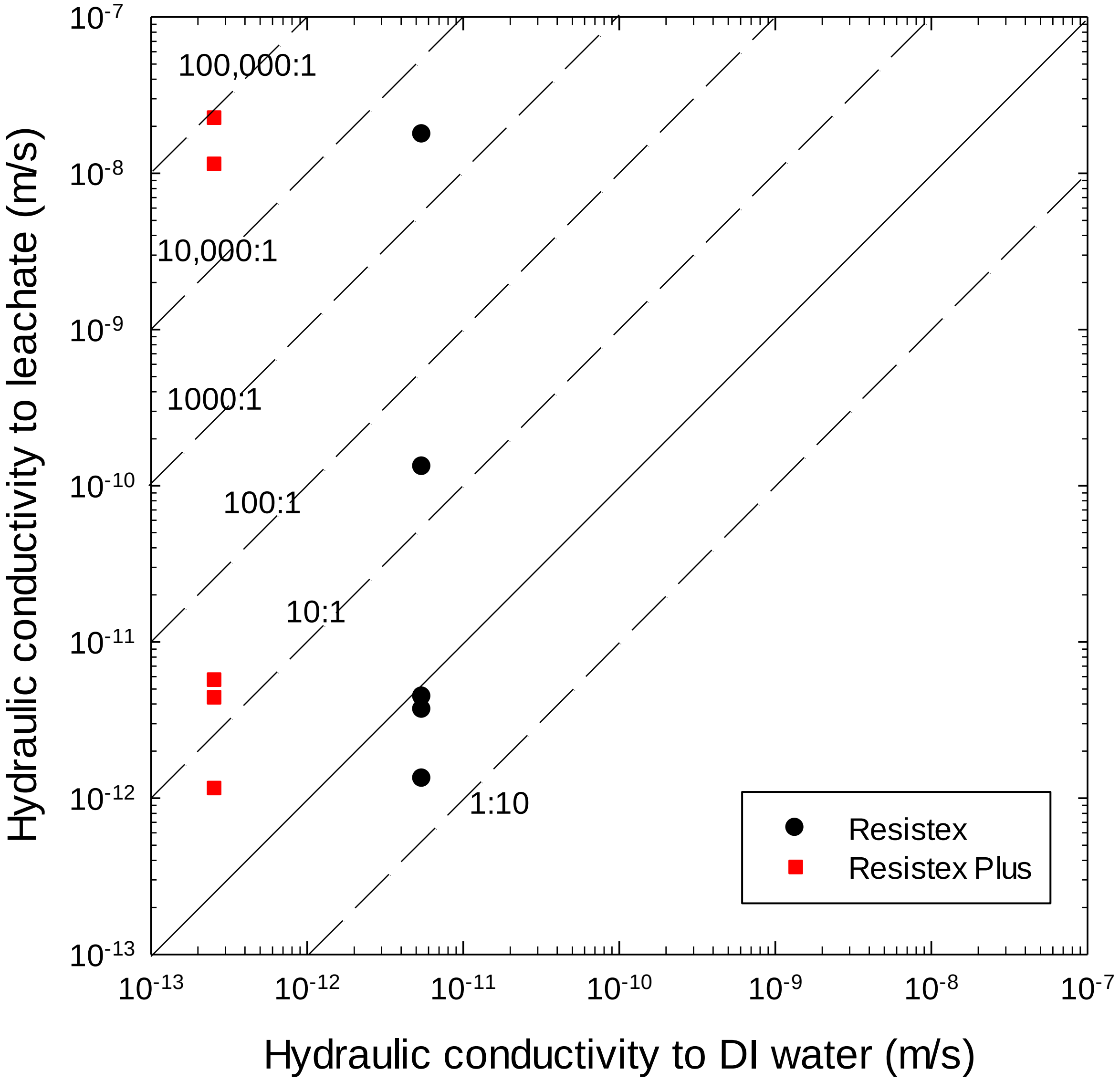

Figure 1. 14: Comparison of hydraulic conductivity of PMB GCLs to site-specific leachates and DI water

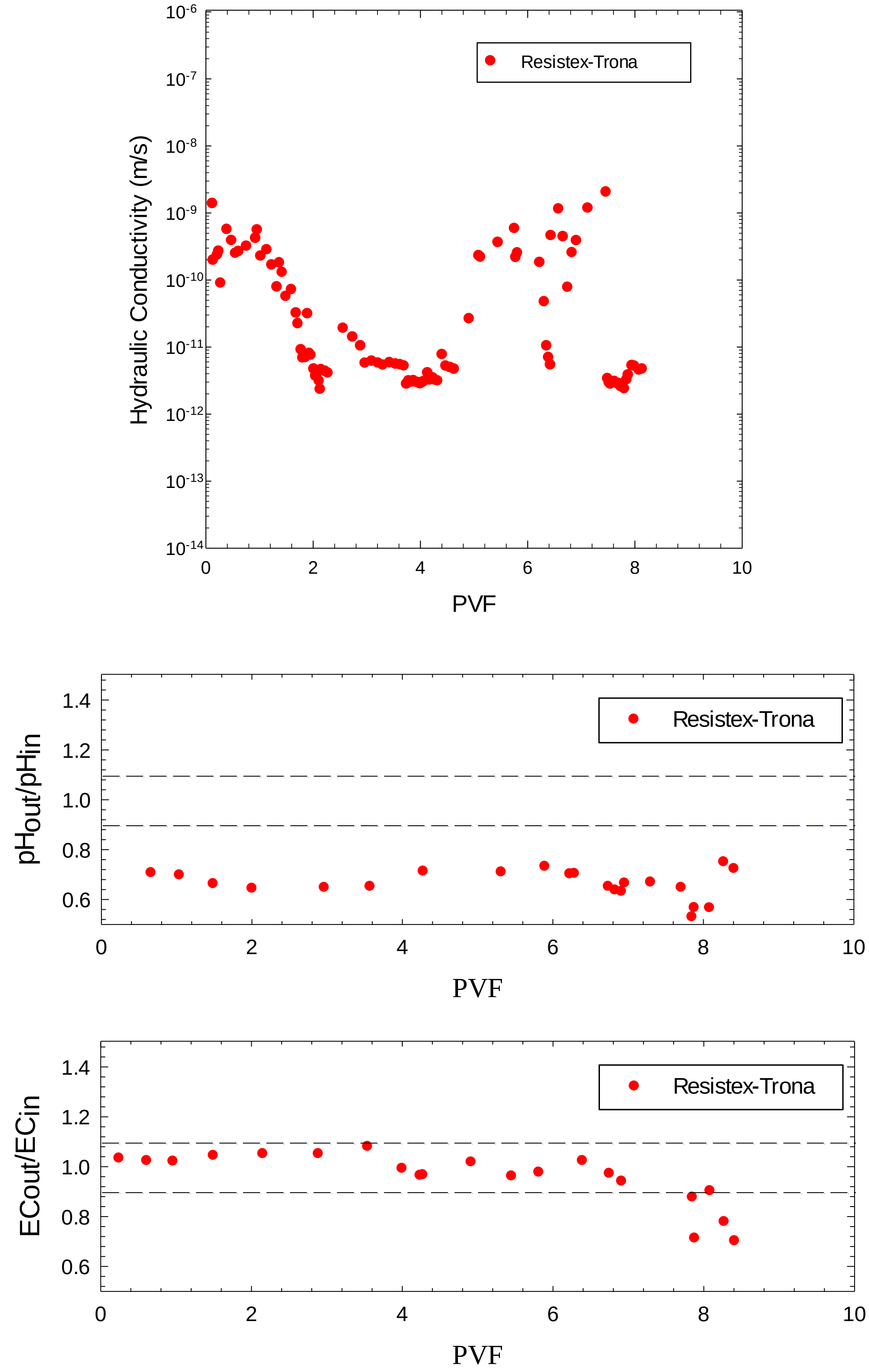

Figure 1. 15: Hydraulic conductivity, pH_{out}/pH_{in} and EC_{out}/EC_{in} vs PVF for Resistex with trona leachate

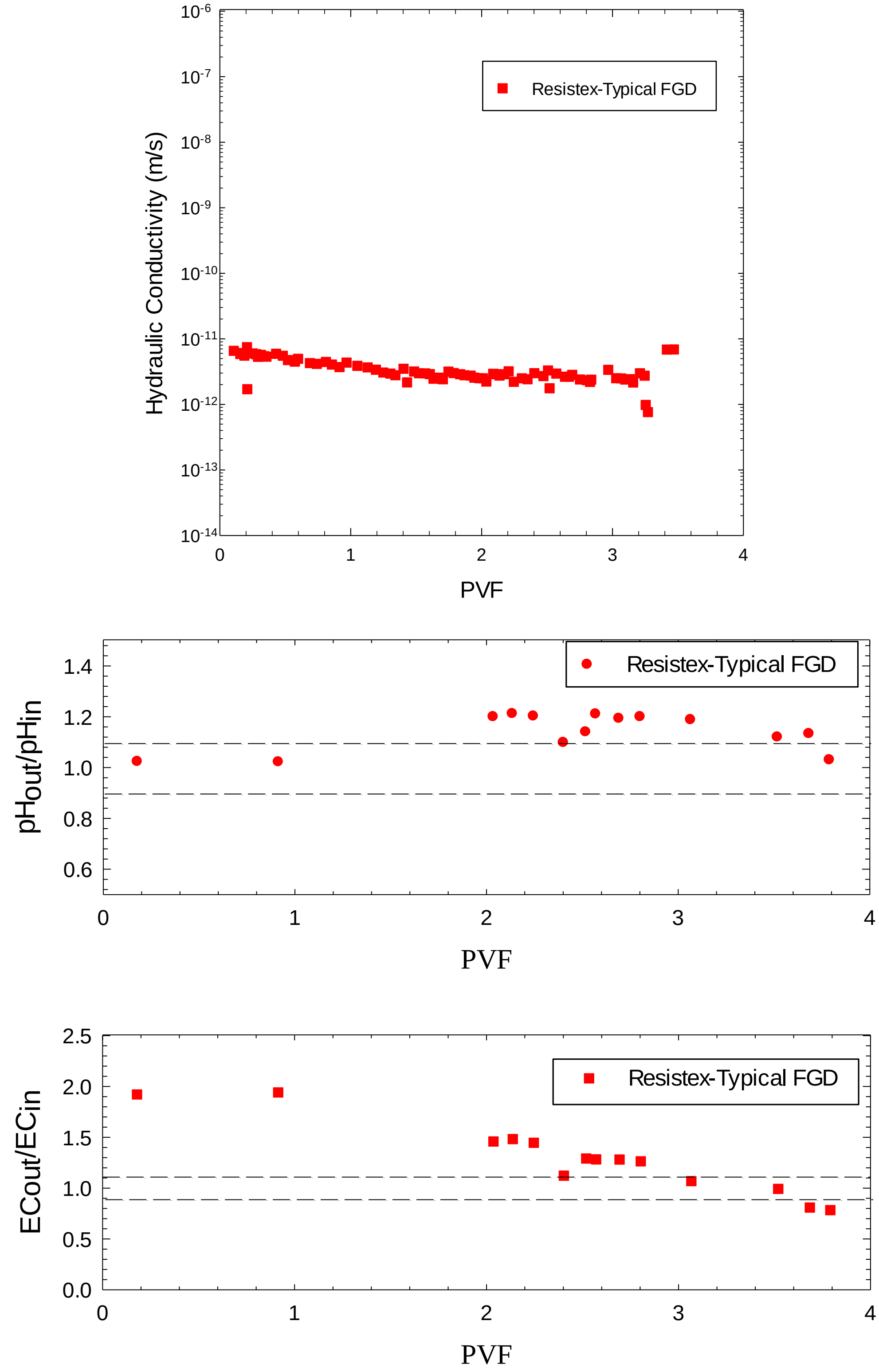

Figure 1. 16: Hydraulic conductivity, pH_{out}/pH_{in} and EC_{out}/EC_{in} vs PVF for Resistex with typical CCP leachate

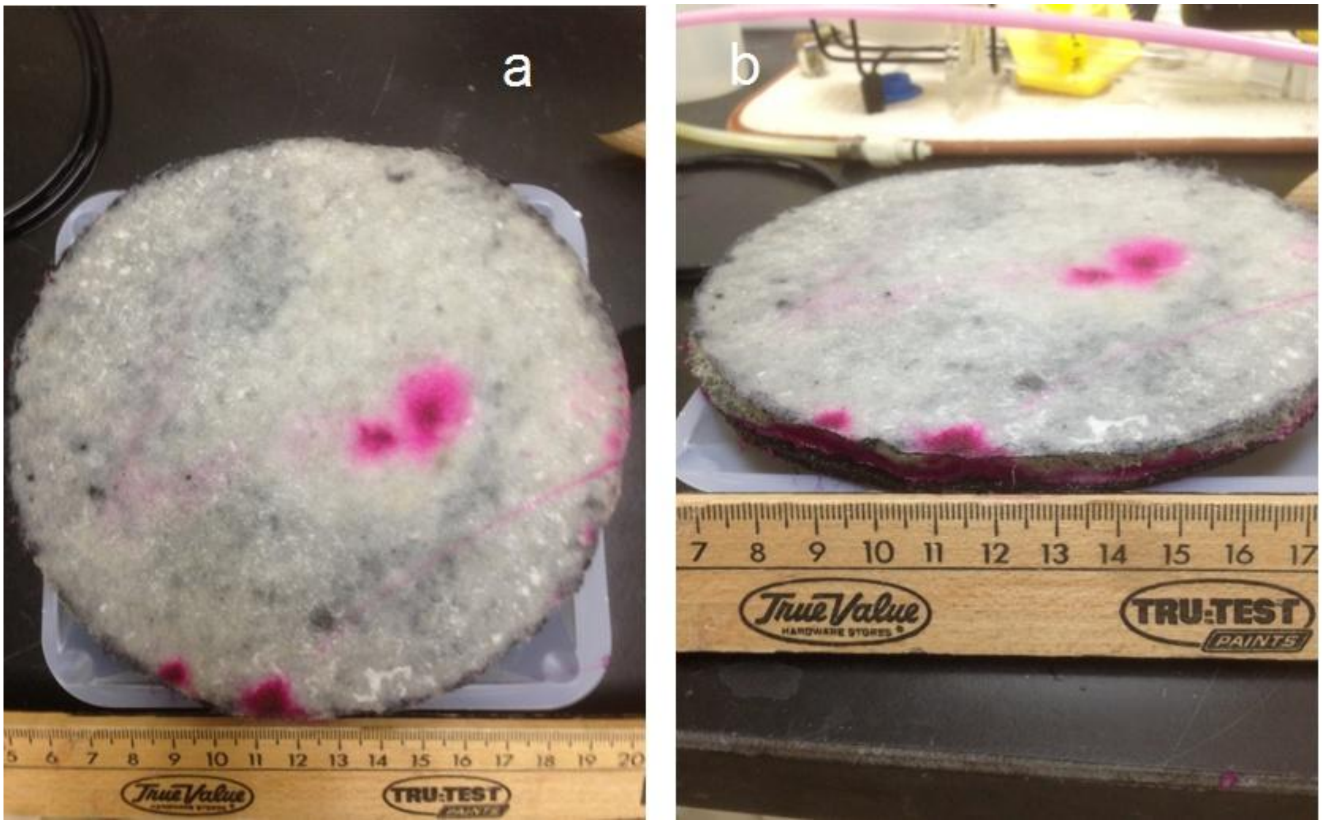

Figure 1. 17: Rhodamine dye tracer test for Resistex GCL with trona: a) top view b) side view

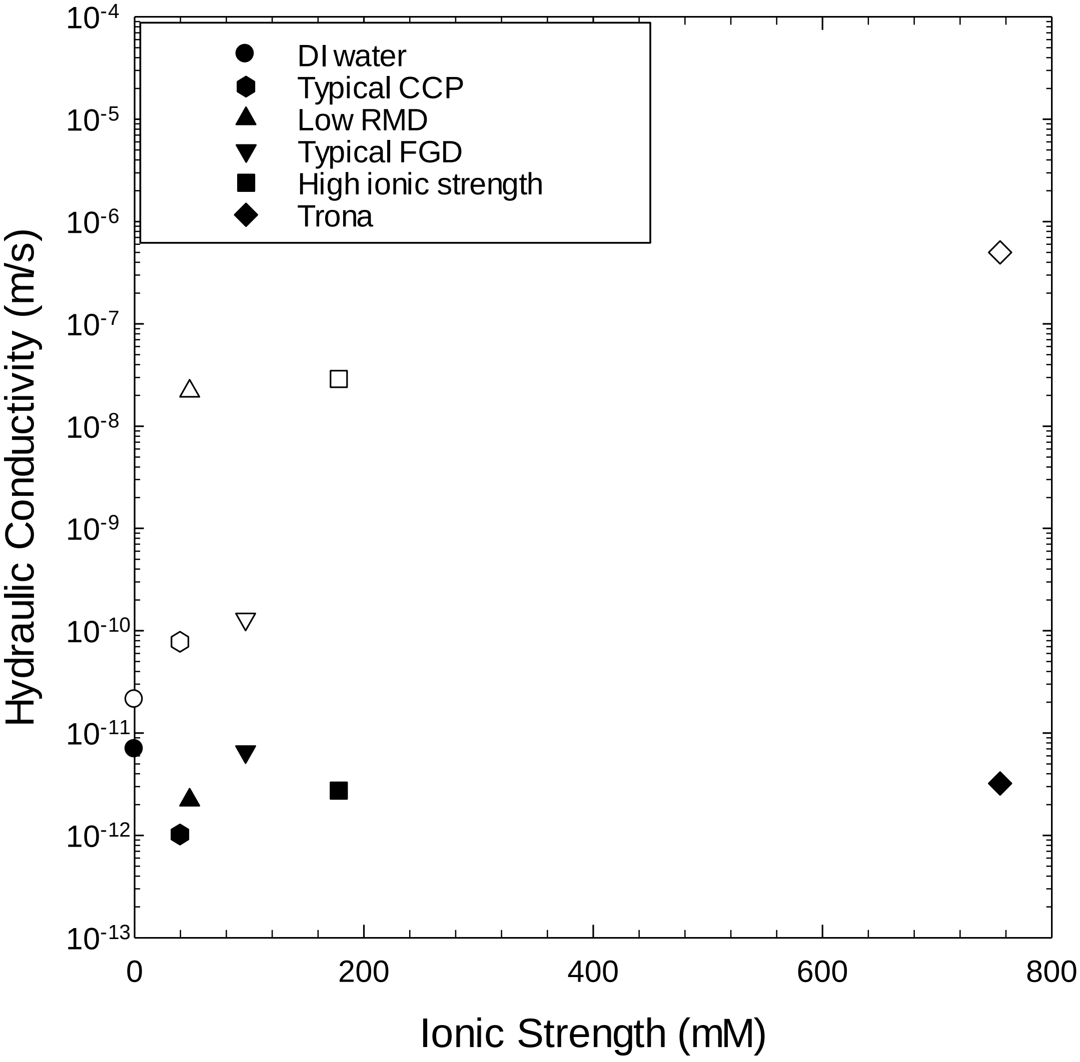

Figure 1. 18: Hydraulic conductivity of Resistex GCL to CCP leachates in this study (closed symbols) in comparison to Benson et al. 2014 (open symbols)

1.11. REFERENCES

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CHAPTER 2: CONVENTIONAL AND ALTERNATIVE INDEX TESTS AS INDICATORS OF HYDRAULIC CONDUCTIVITY OF POLYMER-MODIFIED BENTONITES (PMBs)

2.1. ABSTRACT

Hydration characteristics of Na-B (Bentomat) and polymer-modified bentonite GCLs (Resistex, Resistex plus and an old generation Resistex product) were evaluated using conventional and alternative index tests. Swell index tests (ASTM D 5091) and fluid loss tests (ASTM D5891) were conducted using eight synthetic CCP leachates, one MSW incinerator ash leachate and a gold pregnant leach solution. Five of the synthetic CCP leachates were selected from CCP leachate database of Electric Power Research Institute (EPRI) representing CCP disposal facilities in the U.S. and referred here as EPRI leachates: typical CCP leachate, predominantly divalent cation ash leachate (low RMD), flue gas desulfurization residual (typical FGD), high ionic strength leachate and trona ash leachate. Remaining five synthetic leachates corresponds to leachates obtained from coal combustion, municipal solid waste combustion (MSW) and heap leach facilities impoundments around the U.S. and referred here as site-specific leachates: gold pregnant leach solution (gold PLS), CCP 1, CCP 2, CCP 3 and municipal solid waste incinerator ash leachate (MSW-I).

Results of these tests were correlated with hydraulic conductivity. Hydraulic conductivity of Na-B GCL was systematically related to conventional index tests (swell index and fluid loss test) whereas no systematic trend was observed for PMBs. However, lowest swell was observed for highest ionic strength leachate. Above the

threshold swell index value of 15 mL/ 2g and below the threshold fluid loss value of 45 mL/22.5 min, PMB GCLs yielded low hydraulic conductivity (~10^{-12} m/s).

The fall cone test (BS-1377) was examined as an alternative index test for correlation to hydraulic conductivity for PMB GCLs. Liquid limit values obtained from the fall cone test were inversely correlated to hydraulic conductivity of Bentomat and old generation Resistex product for EPRI leachates. Fall cone liquid limit with Resistex and Resistex plus yield step function like the one observed in hydraulic conductivity and ionic strength relationship for PMBs. Above the threshold liquid limit of 175 %, PMB GCLs showed low hydraulic conductivity.

In a separate study, effect of polymer loading on hydraulic conductivity of PMB GCLs was also investigated. Increasing polymer loading from 4.0 % to 6.5 %, 2 orders of magnitude decrease in hydraulic conductivity was observed (from 8.67 x 10^{-10} m/s to 4.82 x 10^{-12} m/s).

2.2. INTRODUCTION

Hydraulic performance of GCLs depends on the compatibility of bentonite with permeating liquid, i.e. no significant change in hydraulic conductivity caused by the permeating liquid (Shakelford et al. 2000, Shan and Lai 2002). Many studies have been conducted to observe the effect of pore fluid chemistry on hydraulic behavior of bentonite in GCLs (Petrov and Rowe 1997; Ruhl and Daniel 1997; Shackelford et al. 2000; Jo et al. 2001). Previous studies have shown that hydraulic conductivity tests need to be conducted until the influent and effluent concentrations of permeant are comparable to ensure the completion of reactions between permeant liquid and bentonite in GCL (Bowders et al. 1986; Shackelford et al. 2000; Jo et al. 2005).

However, the duration for hydraulic conductivity tests to reach comparable influent and effluent chemical concentrations might be long depending on the chemical characteristics of permeant liquid, hydraulic gradient and interactions between soil and liquid. Especially for PMB GCLs, testing duration might be extensive. Therefore, there is motivation to explore the applicability of rapid and less expensive index tests in lieu of direct hydraulic conductivity measurements to evaluate hydraulic performance of PMB GCLs from engineering practice point of view.

Swell index (ASTM D5890-11) and fluid loss (ASTM D5891-02) tests have been used as index tests in the past. Previous studies with Na-B, for example, have shown direct correlation between hydraulic conductivity and swell index (Jo et al. 2001, Kolstad et al. 2004, Katsumi et al. 2007, Lee et al. 2005). However, GCLs with polymer treatment do not show clear correlation with such index tests. For example, Scalia (2011) tested bentonite-polymer nanocomposites (BPN) containing polymerization of organic molecule in bentonite slurry with varying concentrations of $CaCl_2$. Weak correlation between hydraulic conductivity data and swell index test results suggested that swell index was decoupled from the hydraulic conductivity of BPN.

The main objective of this study is to explore alternative index tests as indicators of hydraulic conductivity of PMBs. Swell index (ASTM D5090-11) and fluid loss tests (ASTM D5891-02) were performed using CCP leachates and site-specific leachates to evaluate the hydration characteristics of polymer-modified bentonties (PMBs). In addition to these two tests, an alternative index test, fall cone (BS-1377) test, was conducted on both Na-B and PMB extracted from GCLs. Results from the conventional and alternative index tests were correlated with hydraulic conductivity data.

2.3. BACKGROUND

2.3.1. Swelling behavior of bentonite in relation to hydraulic conductivity

GCLs are widely used as hydraulic barriers for waste containment systems since they are easy to install, cost effective, and maintain low hydraulic conductivity to water (Katsumi et al. 2007). Whether a GCL is an effective barrier or not is controlled by the hydraulic conductivity of the bentonite (Shackelford et al. 2000). The bentonite component of GCL materials is composed predominantly of the clay mineral montmorillonite. When bentonite comes into contact with water, penetration of water molecules into 2:1 layers within the montmorillonite causes an increase in basal spacing which is termed as interlayer swelling or crystalline swelling. Crystalline swelling can result increase in volume two times higher than that of dry clay when four layers of water are imbibed (Van Olphen, 1966). A much higher degree of swelling can be observed due to osmotic swelling (Van Olphen, 1966; Onikata et al. 1999; Jo et al. 2004) or sometimes referred as diffuse double layer swelling (Laird, 2006).

Researchers have shown previously that there is a significant correlation between low hydraulic conductivity and high swelling of bentonite. For example, Jo et al. (2001) permeated sodium bentonite GCLs with single species salt solutions and showed an inverse relationship between swell and hydraulic conductivity of bentonite. That study attributed the low swell-high hydraulic conductivity relation to an increase in solution concentration and presence of multivalent cations. Increase in ionic strength of the solution and replacement of multivalent cations for Na in the exchange complex leads to decrease in osmotic swelling. As the multivalent cations replace Na in the exchange complex, volume of bound water (immobile) decreases and volume of mobile water increases. Thus, the presence of exchangeable cations in permeant solutions causes an increase in hydraulic conductivity (Shackelford 2000, Kolstad et al. 2004, Jo et al. 2005, Kolstad et al. 2007). Kolstad et al. (2004) permeated sodium bentonite GCLs with multispecies inorganic solutions and showed that swell is directly related to ratio of monovalent cations to square root of divalent cations (RMD) and inversely related to ionic strength of the permeant solution, which is directly related to hydraulic conductivity of GCLs. There have been many studies that have investigated the effect of inorganic aggressive solutions on hydraulic barrier behavior of bentonite (Shan and Daniel 1991; Egloffstein 2001; Ruhl and Daniel 1997; Shackelford et al. 2000; Katsumi et al. 2004, 2007; Jo et al. 2004, 2005).

2.3.2. Filtrate Loss of Bentonite

In drilling applications, water-based muds (e.g., bentonite slurries) are used to prevent diffusion of drilling fluids into surrounding porous media and maintain wellbore stability. In a drilling operation, bottom hole pressure should not be greater than pore pressure of soil media and fracture pressure of drilled rocks. Otherwise, drilling fluids can invade into soil formation and lead to instability of well. In order to prevent possible invasion of drilling fluid into soil formation, a film of mud having low permeability is generally formed at the well wall (Peysson, 2004). Bentonite slurries are commonly used for this purpose and hydraulic conductivity of bentonite is tested using American Petroleum Institute (API) fluid loss test or sometimes referred as API filter press test for quality assurance and control (Filz et al. 2001). In a similar manner, the fluid loss test can be used to rapidly evaluate the effect of different chemical solutions on hydraulic performance of GCLs in waste containment scenarios. Fluid loss tests (ASTM D5891) for GCLs is adopted from American Petroleum Institute drilling fluid specifications (API Specification 13A and 13B) as a measure of capability of bentonite suspension to form a hydraulic barrier (filter cake). However, the method cannot substitute for flexible wall permeameter test since the stress state for the specimen in fluid loss test is different than the one in flexible wall permeameter test. Constant preconsolidation pressure conditions are satisfied throughout the specimen in flexible wall permeameter test whereas consolidation by seepage forces is achieved in fluid loss test. This difference in consolidation pressure may cause variation in void ratio of the specimen and correspondingly hydraulic conductivity. Therefore, average hydraulic conductivity from API fluid loss test is related to a particular consolidation pressure (Filz et al., 2001).

Several studies have been conducted to estimate hydraulic conductivity from fluid loss tests (Barvenick and Ayres 1987; Filz 2001; Nguyen et al. 2012; Liu et al. 2012; Liu et al. 2013; Rosin-Paumier and Touze-Foltz 2012). Rosin-Paumier et al. 2010 used fluid loss test with collection of effluent throughout the test, as an indicator of bentonite-leachate interactions. Rosin-Paumier and Touze-Foltz (2012) performed permeameter tests on natural sodium bentonite and sodium-activated calcium bentonite GCLs with four different types of leachates over a year, and compared the results with hydraulic conductivities obtained from the filter test. However, results obtained from permeameter test and fluid loss test didn't match. They hypothesize that the differences were due to prehydration of bentonite in permeameter tests, high ammonium concentration of leachate and biological clogging. Liu et al. (2013) evaluated the hydraulic conductivity of GCLs under acidic conditions using the fluid loss test and flexible-wall permeameter test. They concluded that hydraulic conductivity estimated from fluid loss is conservative in low acid concentrations, whereas it is non-conservative for high acid concentrations.

2.3.3. Liquid Limit in relation to hydraulic conductivity

Pore fluid chemistry has a significant effect on the fabric and hydraulic properties of fine-grained soils. Pore fluid chemistry can control interparticle forces and corresponding particle arrangement, which directly influences the effective pore size controlling fluid flow (Mitchell and Soga 2005). At high electrolyte concentrations and in the presence of multivalent exchangeable cations, repulsion forces decrease and promote particles to flocculate at shorter interparticle distances (Warkentin 1961). Liquid limit, which can be defined as particle distance at which interparticle interactions are weak enough so that particles can move easily relative to each other (Warkentin, 1961), can be useful to evaluate the effect of pore fluid chemistry on hydraulic properties of fine-grained soil. A limited number of studies have been conducted to relate index properties such as liquid limit to hydraulic conductivity of fine-grained soils (Sridharan and Nagaraj 2005). Previously, Mishra et al. (2009 and 2011) correlated hydraulic conductivity of sand-bentonite mixtures with liquid limit. They found that hydraulic conductivity of mixtures are function of liquid limit of both bentonite and sand-bentonite mixtures. At high electrolyte concentration, they observed a decrease in liquid limit.

2.4. MATERIALS

Materials used for index tests were same as described in section 1.4. In addition to materials described in section 1.4, an old generation polymer-modified bentonite provided by the supplier was also used. Only difference for the old generation Resistex product was the polymer loading. This product has polymer loading of 2.2 % which is lower than Resistex GCL.

2.5. METHODS

2.5.1. Swell Index

Swell Index tests were conducted on fresh (before any permeation) bentonites removed from each GCL product (Bentomat, Resistex and Resistex plus) in accordance with procedures described in ASTM D5890. Bentonite was ground with a mortar and pestle to 100% passing the no 200 US standard sieve (ASTM E11). Ground bentonite was dried to constant mass at 105 ± 5 °C for 16 hours. After cooling it to room temperature, 2.00 ± 0.01 g of the oven-dried bentonite was dusted over the surface of 90 mL test solution and placed into 100 mL graduated cylinder in 0.1 g increments over a period of approximately 30 s until 2 g of bentonite was consumed. Between each increment, the bentonite was allowed to hydrate and settle to the bottom of the graduated cylinder. After the final increment, the graduated cylinder was gently tipped at a 45° angle to homogenize the settled particles and then filled to the 100 mL volume with test solution by rinsing particles stuck to the side sides of the cylinder. After allowing for at least 16 hours of hydration, swell volume was recorded in mL to obtain the corresponding swell index. Swell index results are reported in Table 2.1.

2.5.2. Fluid Loss

Fluid loss tests were performed on fresh bentonites obtained from GCLs according to ASTM D5891. Prior to testing, the bentonite was ground with a mortar and pestle to 100% passing the no 200 US standard sieves. A 350 ± 5 mL volume of test solution was added into a mixing cup and 22.50 ± 0.01 g (6% solids) of bentonite was slowly added over 30 s time period. After stirring the suspension for 5 ± 0.5 min., bentonite that had adhered to sides of container was removed by a spatula and incorporated into the suspension. The mixture was then stirred for an additional 20 ± 0.1 min. Suspensions were aged for minimum of 16 hours in a sealed container at ambient (room) temperature. After aging, the mixtures were shaken to break gel strength and placed into a mixer for 5 ± 0.5 min for dispersion into slurry. The fluid loss test cell, filter paper, and gaskets were assembled. Bentonite slurry was poured into the fluid loss test cell and 690 kPa air pressure was applied to the fluid loss cell (Fig. 2.1). Filtrate was collected under the drain tube after both 7.5 min and 30 min. Filtration rate was high for filtrate collected after 7.5 min., which is referred to as spurt loss. Fluid loss was calculated by multiplying filtrate volume for the last 22.5 min. interval by 2 and reported in mL. Filter cake thickness was also measured with a Vernier caliper. Fluid loss test results are reported in Table 2-2.

2.5.3. Loss on Ignition

Loss on ignition (LOI) tests was conducted according to procedures described by Scalia (2012) to determine polymer content of PMBs before and after hydraulic conductivity testing. PMB was ground to 100% passing the no 20 US standard sieve (ASTM E11) and dried to constant mass at 105 ± 5 °C in an oven for 16 hours. Oven-dried PMB was then placed into pre-heated crucibles and subjected to sequential heating up to 550 °C for 4 hours. After 4 hours of ignition, the crucibles were allowed to cool in a container with desiccant and the mass loss on ignition was recorded. The raw polymer used in one of the PMB GCLs (Resistex) was also provided by supplier. This polymer lost 84.8% of its mass on ignition with a standard deviation of %0.5 from 3 replicate tests. Mass loss on ignition of bentonite was 1.92% with a standard deviation of 0.1%. Loss on ignition test is a way to determine unburned carbon content of the sample. Associated LOI value of bentonite (1.92±0.5) was due to $CaCO_3$ present in bentonite. By knowing mass loss on ignition for bentonite and polymer separately, amount of polymer retained in GCL after permeation was directly estimated from LOI by eliminating bentonite effect from bentonite-polymer dry mixture.

2.5.4. Fall Cone

Liquid limits of fresh bentonites removed from GCL products were determined by the British Fall Cone test in accordance with the method described in BS 1377, part 2 (BSI, 1990). Tests were conducted on Resistex, Resistex plus and an old generation Resistex product provided by the supplier in contact with different leachates as described in section 1.4.1.1 and 1.4.1.2. Prior to testing, air-dried bentonite (or PMB) granules were sifted to 100% passing the no 10 US standard sieve and mixed with leachate of interest. The mixture was sealed in a plastic bag for at least 24 hours. After 24 hours, the sample was remixed and placed in a straight-sided cup having 55 mm diameter and 40 mm depth. The surface of sample was leveled off and positioned under fall cone (30° apex angle and 80 g mass) with its apex just touching the sample surface. An initial penetration gauge reading was recorded at this time. The cone was released for 5 s (until the cone is at rest) and depth of penetration was recorded from the dial gauge. This procedure was repeated over 5 different locations of the sample (Fig. 2.2) and depth of penetration was recorded by taking average of 5 measurements. Water content corresponding to this penetration depth was determined using the method described in ASTM D2216. Depth of penetrations was correlated with water contents to determine liquid limit. Liquid limit was defined as the water content corresponding to 20 mm of depth of penetration in BS 1377. Liquid limits obtained from fall cone test for each GCL product contacted with different leachates are summarized in Table 2.4

2.6. RESULTS AND DISCUSSIONS

2.6.1. Swell Index

Results from swell index tests conducted on Bentomat, Resistex and Resistex plus GCLs with varying concentrations of both site-specific synthetic leachates and CCP leachates are shown in Fig. 2.3 and Fig. 2.4. Reported swell indices are average values from at least three replicate tests.

For the Na-B (Bentomat) GCL, swell index decreases with increasing ionic strength, an observation similar to findings in previous studies (Shackelford et al. 2000, Jo et al. 2001, Kolstad et al. 2004, Lee et al. 2005, Katsumi et al. 2007, Scalia and Benson 2011). Hydraulic conductivity of PMB GCLs didn't indicate a systematic correlation with swell index. However, lowest swell index was observed with highest ionic strength MSW-I leachate (10.5 mL/2g with Resistex GCL). The swell index of typical CCP leachate was slightly higher than DI water. Similar findings were also reported in Benson et al. (2014). Slightly higher swell index than DI water was also observed for gold PLS leachate. Additionally, polymer loading didn't affect the swell index of PMBs. Resistex plus has two times higher polymer loading than Resistex GCL. However, the swell index values obtain with these two PMBs were similar.

Fig. 2.5 shows the relationship between hydraulic conductivity for all GCLs permeated with EPRI and site-specific leachates and swell indices. It can be concluded from the figure that swell index can be used as indicator of hydraulic conductivity for Na-

B GCLs. Nevertheless, the correlation for PMB GCLs is not as clear as the case for the Na-B GCL. For PMB GCLs, when swell index exceeds 15 mL/2 g, low hydraulic conductivity (~10^{-12} m/s) to all leachates was observed. For example, swell index of trona leachate was 16.88 mL/2 g and swell index of typical CCP leachate was 29.7 mL/ 2 g with Resistex GCL recorded in this study. However, the hydraulic conductivity of Resistex with trona was higher than Resistex with typical CCP by only factor of 3. Benson et al (2014) reported a threshold swell index value of 23 mL/ 2 g for PMB GCLs to EPRI leachates above which low hydraulic conductivity is maintained ($k<10^{-9}$ m/s). However, this study shows that low hydraulic conductivity to EPRI leachates can be maintained with swell index values below this threshold value.

However, only testing with leachates having high ionic strength (CCP 3 and MSW-I) reached hydraulic and chemical equilibrium. Permeability tests are still ongoing and haven't reach to chemical equilibrium. Results are subject to change over long term.

2.6.2. Fluid Loss

Average fluid losses from at least 3 replicate tests were recorded for Resistex and Resistex plus GCL with both EPRI leachates and site-specific leachates. Fluid losses ranged from 10.6 mL/ 22.5 min to 78.9 mL/22.5 min for Resistex GCL and from 10.8 mL/22.5 min to 83.26 mL/ 22.5 min. for Resistex plus GCL with increase in ionic strength of the solution. Fluid loss of PMB GCLs does not show a systematic trend with ionic strength of the leachate. For example, the low RMD leachate has lower ionic strength than trona leachate. However, fluid loss for low RMD was two times higher than that of trona leachate for both Resistex and Resistex plus GCL (Table 2.2). On the other hand, fluid losses were inversely related with swell index for PMB GCLs (Fig. 2.6).

Fluid loss of Na-bentonite GCL indicated a direct correlation with hydraulic conductivity and inverse relationship with swell indices (Fig. 2.6 and Fig. 2.7). For PMB GCLs, hydraulic conductivity wasn't systematically related to fluid loss (Fig. 2.7). Similar findings were reported in Benson et al. (2014). When the fluid loss was less than 45 mL/22.5 min, low hydraulic conductivity was maintained for both PMB GCLs (~10^{-12} m/s). Additionally, effect of polymer loading in fluid losses wasn't observed. Fluid losses were comparable for Resistex and Resistex plus GCL.

2.6.3. Loss on ignition

Hydraulic conductivity tests were conducted on PMB GCLs different than Resistex and Resistex plus having different polymer loading with trona leachate. Same conditions were valid for these tests as testing with Resistex and Resistex plus (20 kPa effective stress, average hydraulic gradient of 190 and non-prehydrated). Polymer loading via loss on ignition (LOI) was determined. Fig. 2.8 shows relationship between LOI and hydraulic conductivity of PMB GCLs including Resistex and Resistex plus with trona. It can be observed that as the polymer loading (LOI) before any permeation increases, hydraulic conductivity decreases. For the PMB GCLs used in this study (Resistex and Resistex plus), an increase in LOI from 3.15 % to 6.17 % resulted in decrease in hydraulic conductivity by a factor of two. For the other PMB GCLs, increasing polymer loading from 4.0 % to 6.5 %, hydraulic conductivity decreased by 2 order of magnitude (from 8.67 X 10^{-10} m/s to 4.82 X 10^{-12} m/s). This might be due to type and/or structure of polymer used in GCL products.

2.6.4. Fall cone

Hydraulic conductivities of PMB GCLs were decoupled from index tests such as swell index and fluid loss test. Therefore, an alternative index test potentially well correlated with hydraulic conductivity of PMB GCLs is needed. For this purpose, fall cone tests were completed on Na-bentonite and an old generation Resistex product used in Benson et al. (2014) with EPRI leachates as well as Resistex and Resistex plus GCL with site-specific leachates. Liquid limits defined as water content corresponding 20 mm depth of cone penetration were determined from depth of penetration vs. water content plot of each GCL.

Fig. 2.9 shows the relationship between liquid limit and hydraulic conductivity of old generation Resistex GCL and Na-B GCL. From the graph, it can be observed that liquid limit obtained from fall cone test is related to hydraulic conductivity of old generation Resistex GCL and Na-bentonite GCL with EPRI leachates reported in Benson et al. (2014). Hydraulic conductivity of Resistex and Resistex plus to site-specific leachates does not show as string a correlation with liquid limit (Fig. 2.10). Fall cone liquid limit with Resistex and Resistex plus yield step function like the one observed in hydraulic conductivity and ionic strength relationship for PMBs. Above the threshold liquid limit of 175 %, PMB GCLs showed low hydraulic conductivity. However, these tests are still ongoing and correlation is subject to change over time as the hydraulic conductivity changes. Besides correlation to hydraulic conductivity, it can be seen from Fig. 2.10 that as the ionic strength of the leachate increases, liquid limit decreases. This is expected due to decrease in repulsive forces. However, this decrease is more dramatic in Resistex plus. Resistex plus specimens have lower liquid limits to all site-specific leachates except MSW-I than Resistex GCL, suggesting that Resistex plus is more sensitive to chemical changes than Resistex GCL (Fig. 2.11).

2.8. CONCLUSIONS

Swell index, fluid loss, loss on ignition and fall cone tests were conducted on a Na-bentonite GCL and PMB GCLs with EPRI leachates and site-specific synthetic leachates. Results were correlated to hydraulic conductivity of GCLs to evaluate the hydraulic behavior of bentonite component in GCLs from engineering practice point of view. The following conclusions have been drawn based on testing results:

1. Hydraulic conductivity of Na-B GCL was systematically related to conventional index tests (swell index and fluid loss test) whereas there is no systematic trend for PMBs. Therefore, conventional index test are not applicable for PMB GCLs.
2. Index test results were comparable for Resistex and Resistex plus. However, comparison of this study with Benson et al. (2014) indicated that below a threshold polymer loading PMB GCLs behave like Na-B. Therefore, index tests are affected by the polymer loading.
3. LOI before permeation was an effective indicator of hydraulic conductivity of PMB GCLs. However, this relationship is also dependent on polymer type and/or structure.
4. Resistex plus is more sensitive to chemical changes than Resistex GCL based on the fall cone liquid limit values.

2.9. TABLES

Table 2. 1: Swell indices of GCLs with CCP leachates and site-specific leachates

Permeant	**Swell Index (mL/2 g)**		
	Bentomat	**Resistex**	**Resistex Plus**
DI	31.0	27.5	27.5
Gold PLS	30.0	32.2	29.0
CCP1	18.5	22.7	23.3
CCP2	16.0	23.5	23.5
CCP3	10.0	12.0	14.0
Incinerator	7.5	10.5	12.3
Typical CCP	28.0	29.7	29.2
Low RMD	24.0	21.3	23.3
Typical FGD	18.0	24.5	23.2
High Strength	15.0	22.0	24.1
Trona	13.0	19.0	16.9

Table 2. 2: Fluid losses of GCL bentonites with CCP leachates and site-specific leachates

Leachate	**Fluid loss (mL/ 22.5 min)**		
	Bentomat	**Resistex**	**Resistex Plus**
Gold PLS	13.6	10.6	10.8
CCP 1	21.6	16.2	16.3
CCP 2	30.8	16.0	28.8
CCP 3	54.8	41.9	43.2
MSW-I	85.2	78.9	83.3
Typical CCP	-	8.5	9.5
Low RMD		39.7	36.5
Typical FGD		16.3	17.6
High ionic strength		15.5	18.4
Trona		15.3	16.6

Table 2. 3: Liquid limits from fall cone test for Bentomat and old generation Resistex with CCP leachates

Leachate	**Liquid limit from fall cone test (%)**	
	Bentomat	**Old Generation Resistex**
DI	288.7	313.4
Typical CCP	235.1	286.0
Low RMD	237.5	245.7
Typical FGD	194.7	270.0
High Strength	179.2	234.1
Trona	113.1	167.0

Table 2. 4: Liquid limits from fall cone test for Resistex and Resistex plus GCL bentonites with site-specific leachates

Leachate	**Liquid limit from fall cone test (%)**	
	Resistex	**Resistex Plus**
DI	242.3	218.0
Gold PLS	235.3	199.0
CCP 1	202.6	180.1
CCP 2	209.8	185.5
CCP 3	182.4	150.1
MSW-I	135.0	190.8

2.10. FIGURES

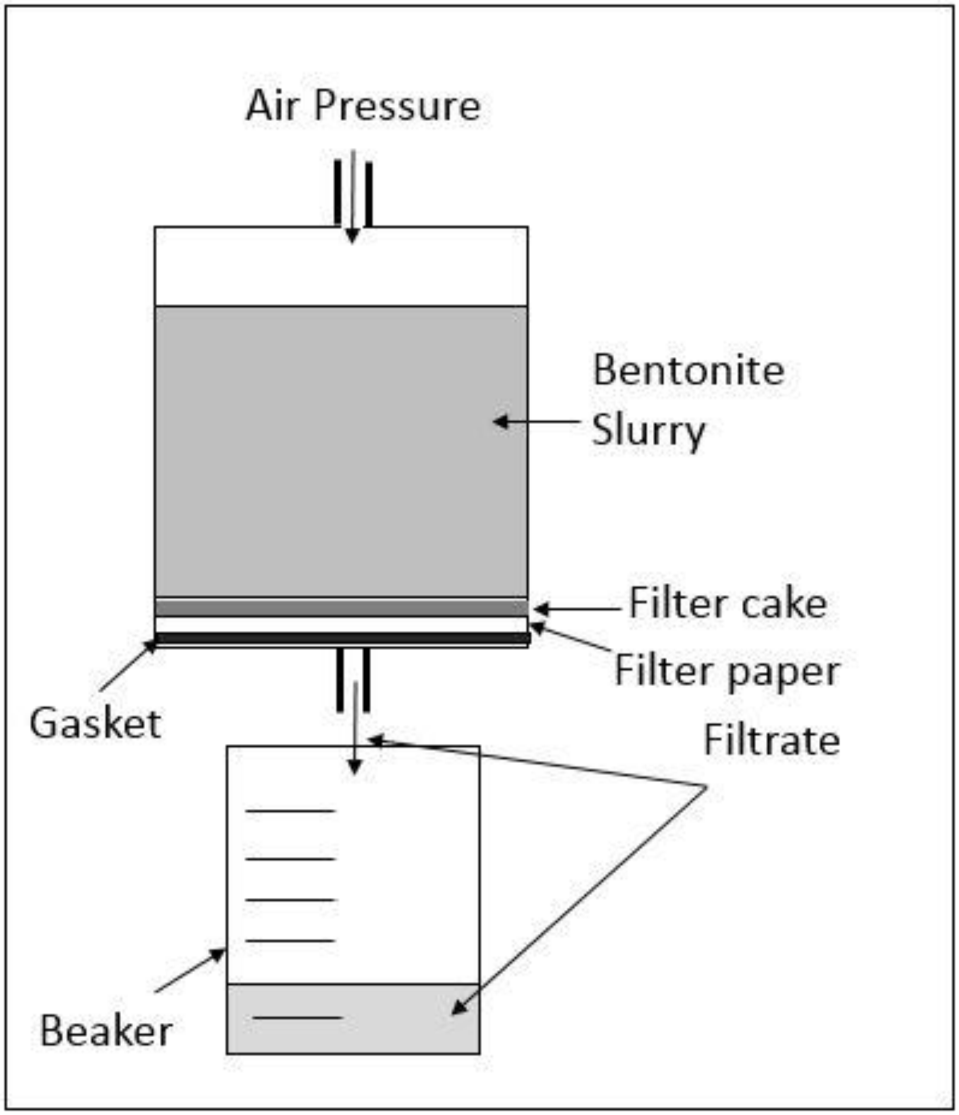

Figure 2.1: Sketch of fluid loss device

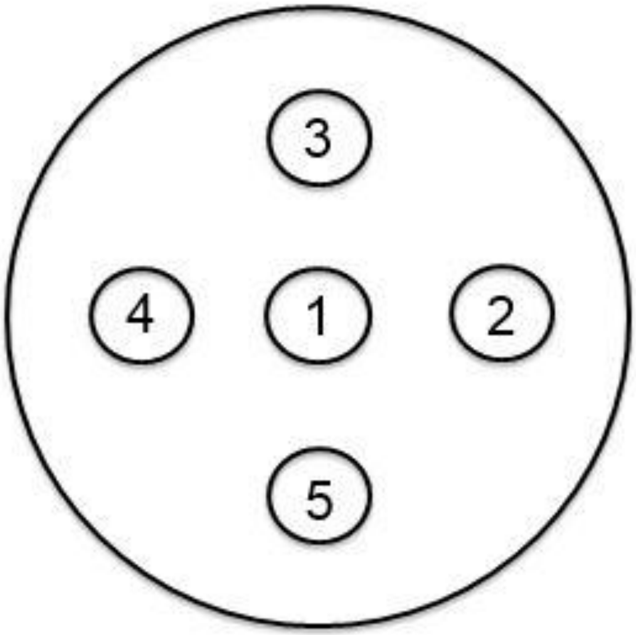

Figure 2.2: Fall cone testing locations on sample

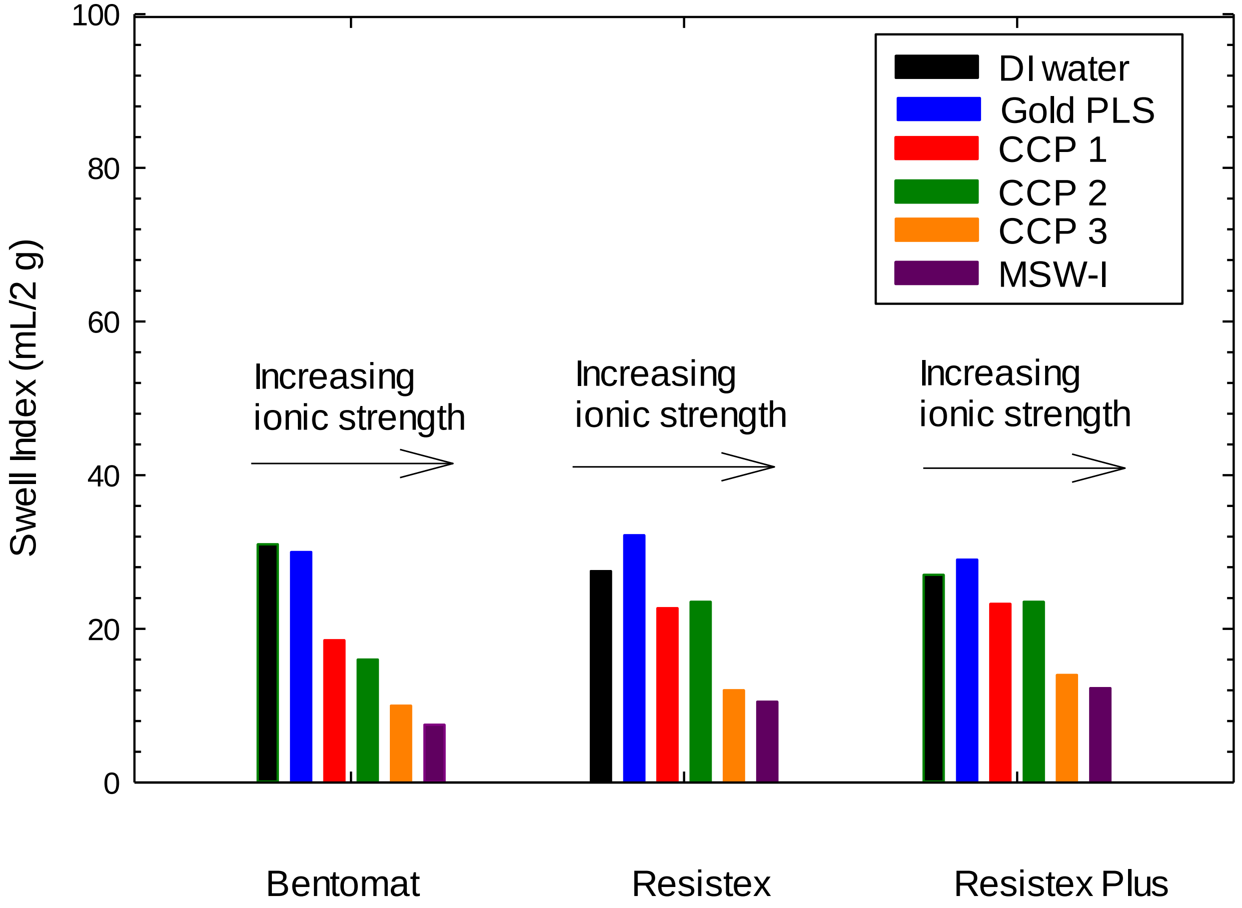

Figure 2.3: Swell indices of GCLs to site-specific leachates

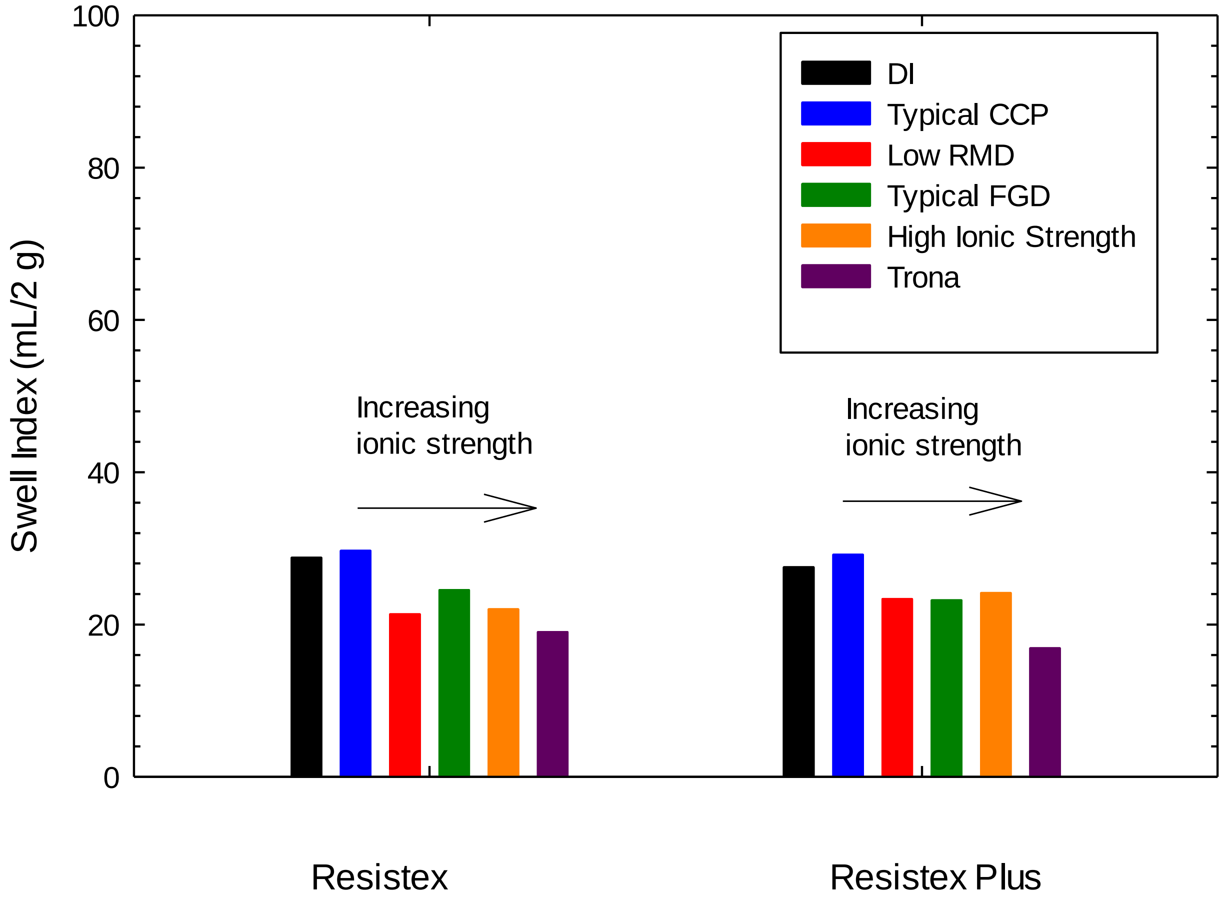

Figure 2.4: Swell indices of PMB GCLs to EPRI leachates

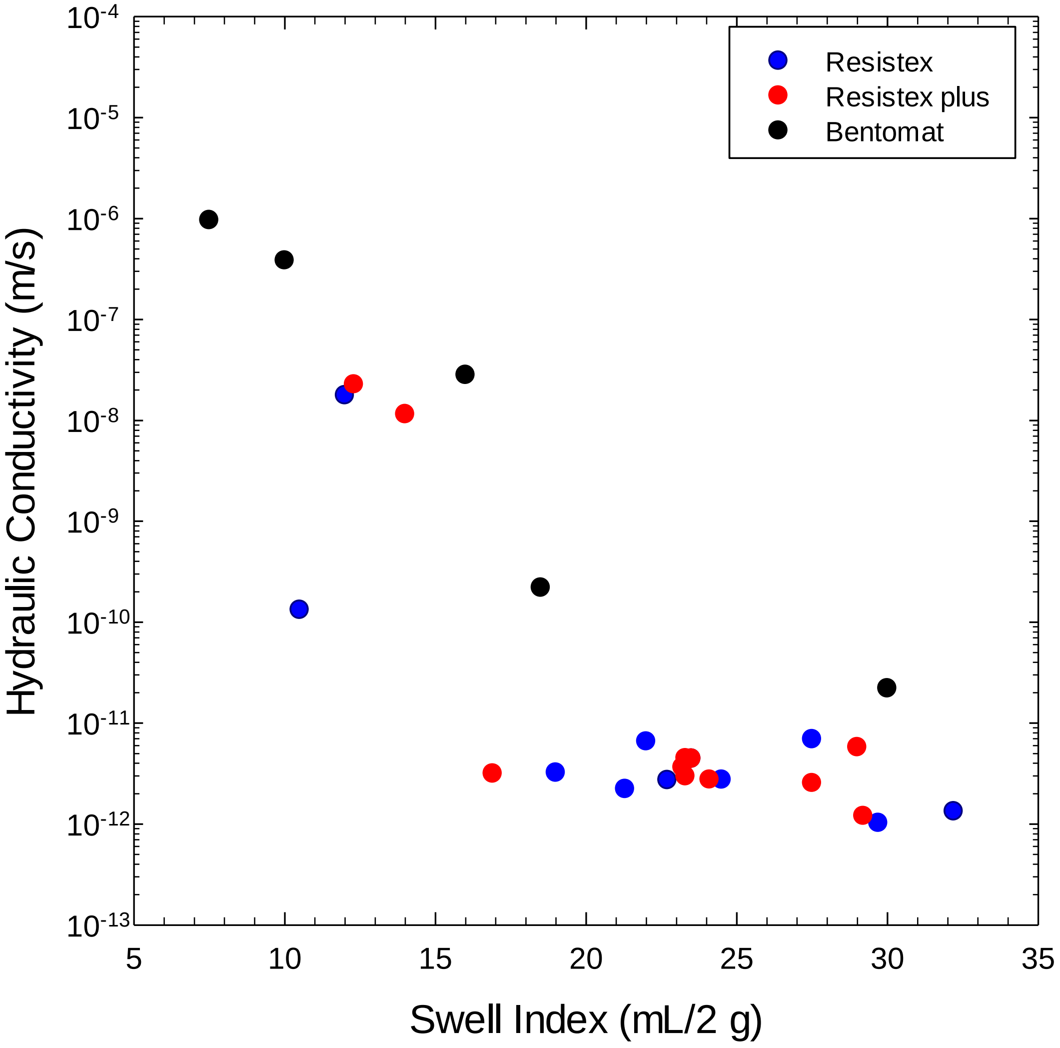

Figure 2.5: Hydraulic conductivity of GCLs to EPRI and site-specific leachates vs swell index

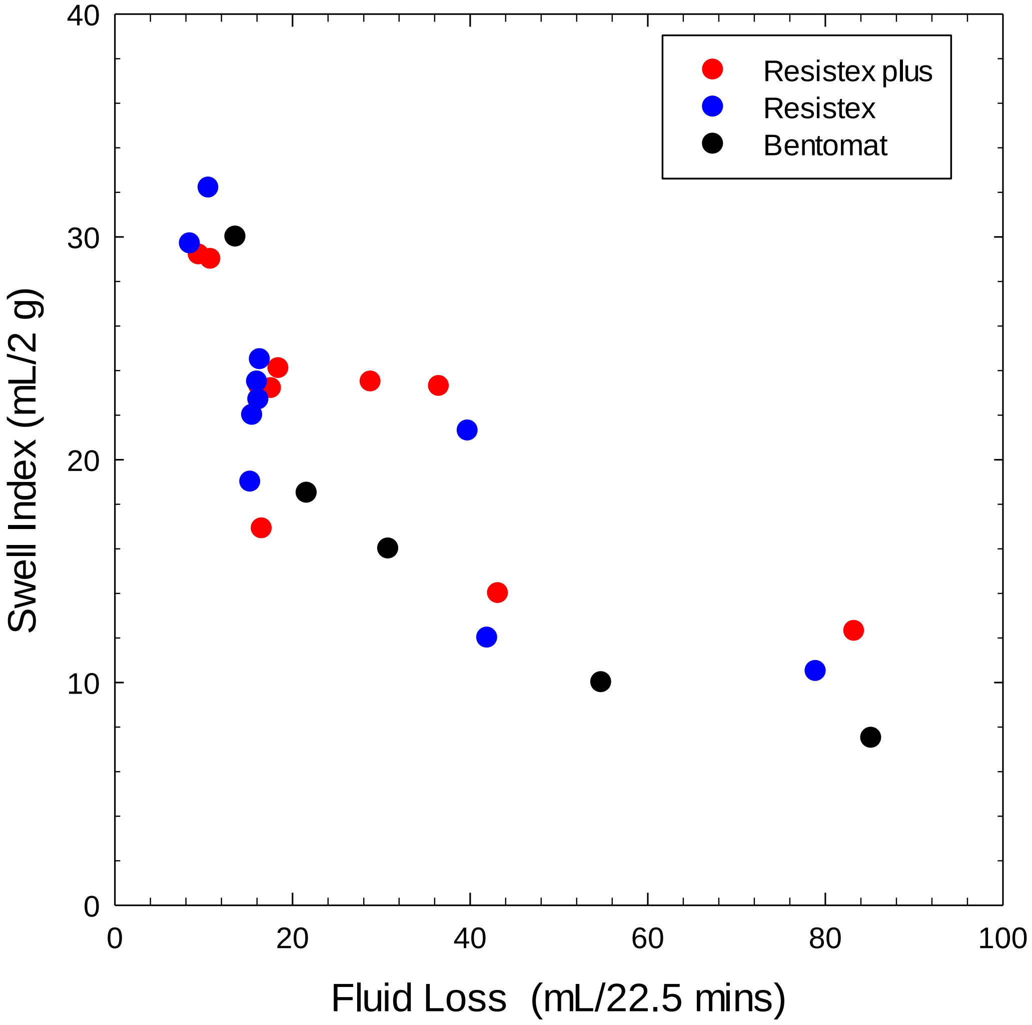

Figure 2. 6: Fluid loss vs swell index to EPRI and site-specific leachates for all GCLs

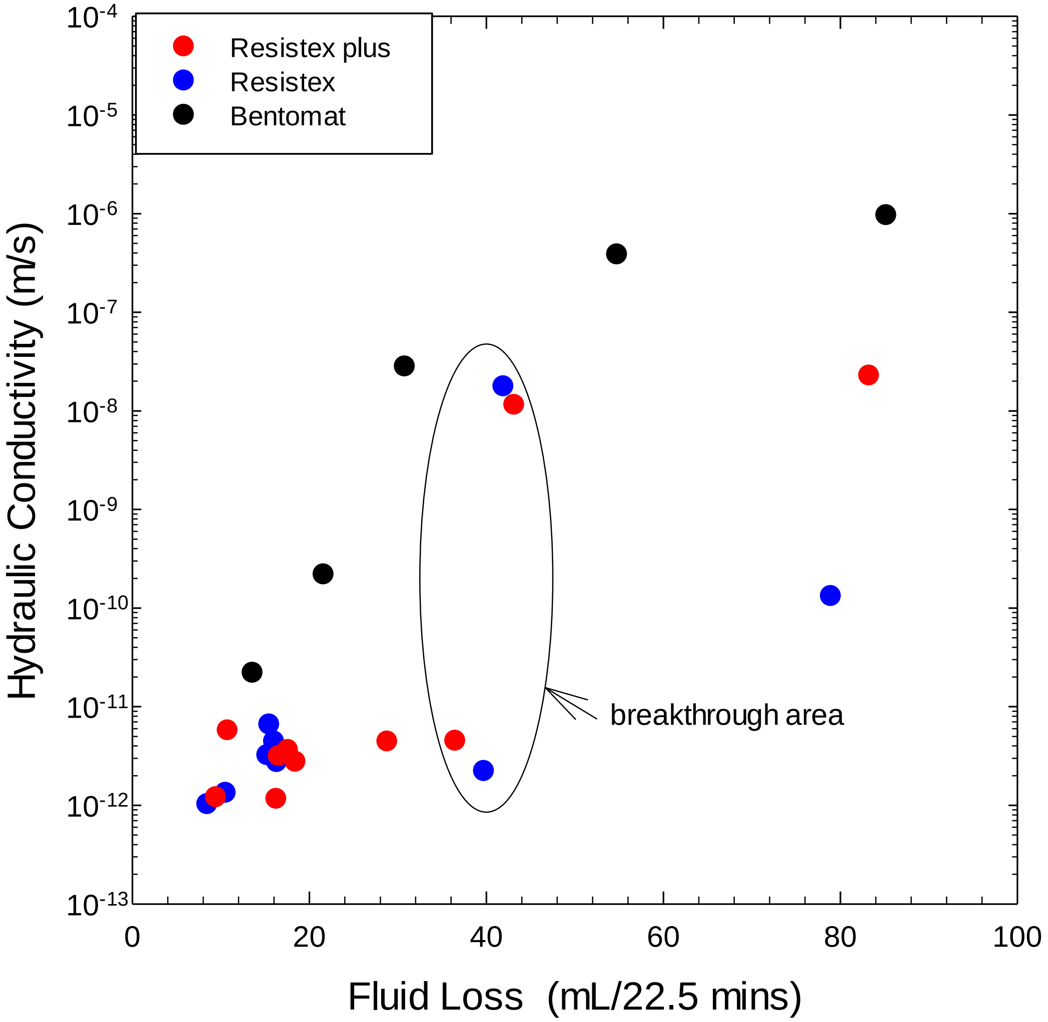

Figure 2. 7: Hydraulic conductivity of GCLs to EPRI and site-specific leachates vs fluid loss

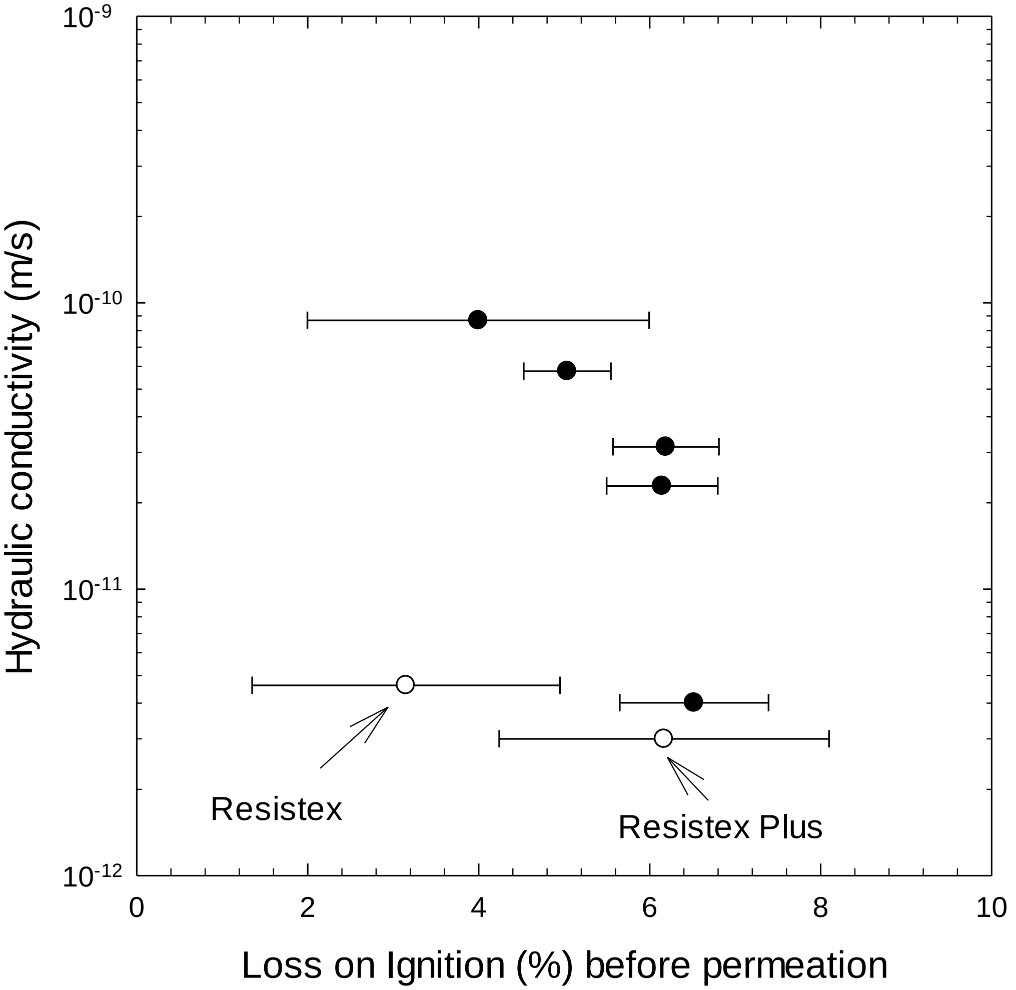

Figure 2. 8: Hydraulic conductivity of various GCLs with different polymer loading vs LOI

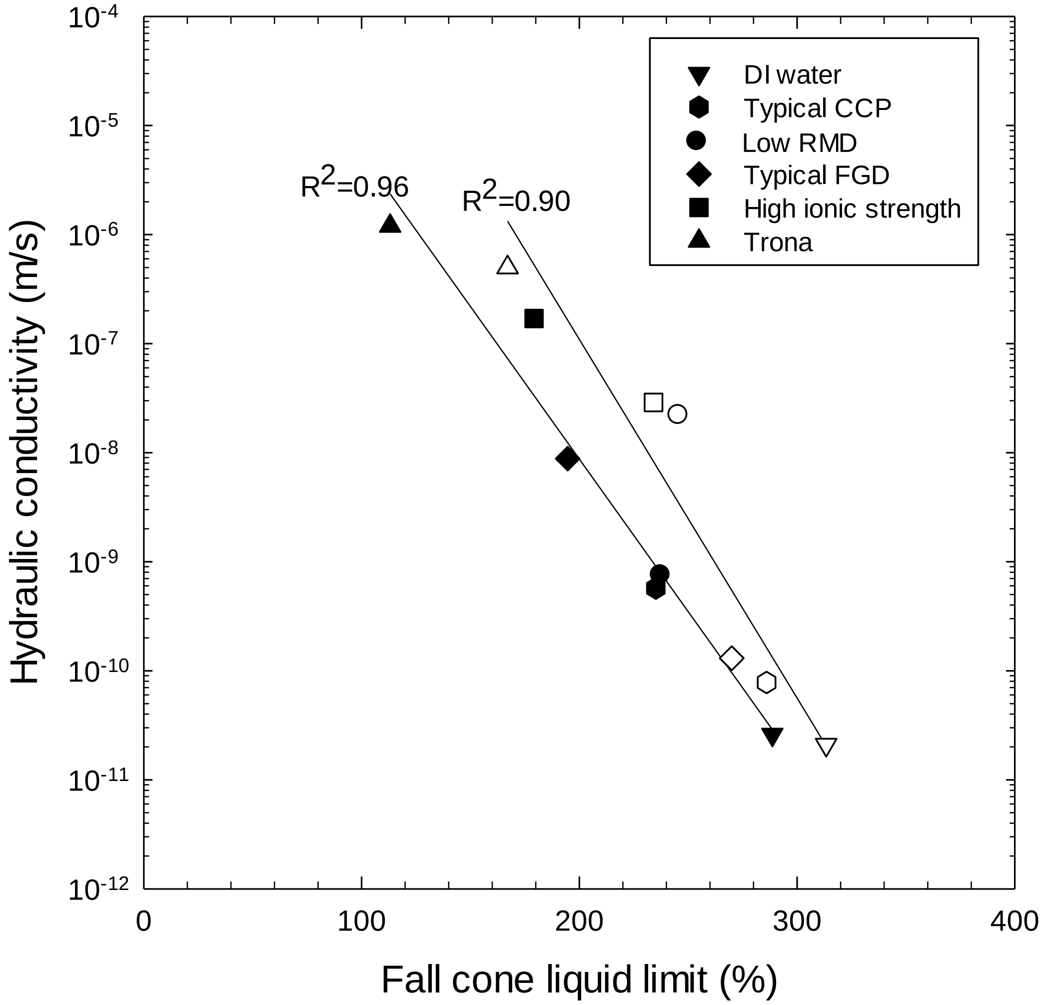

Figure 2. 9: Hydraulic conductivity of Bentomat and an old generation Resistex GCL to EPRI leachates vs. liquid limit obtained from fall cone test

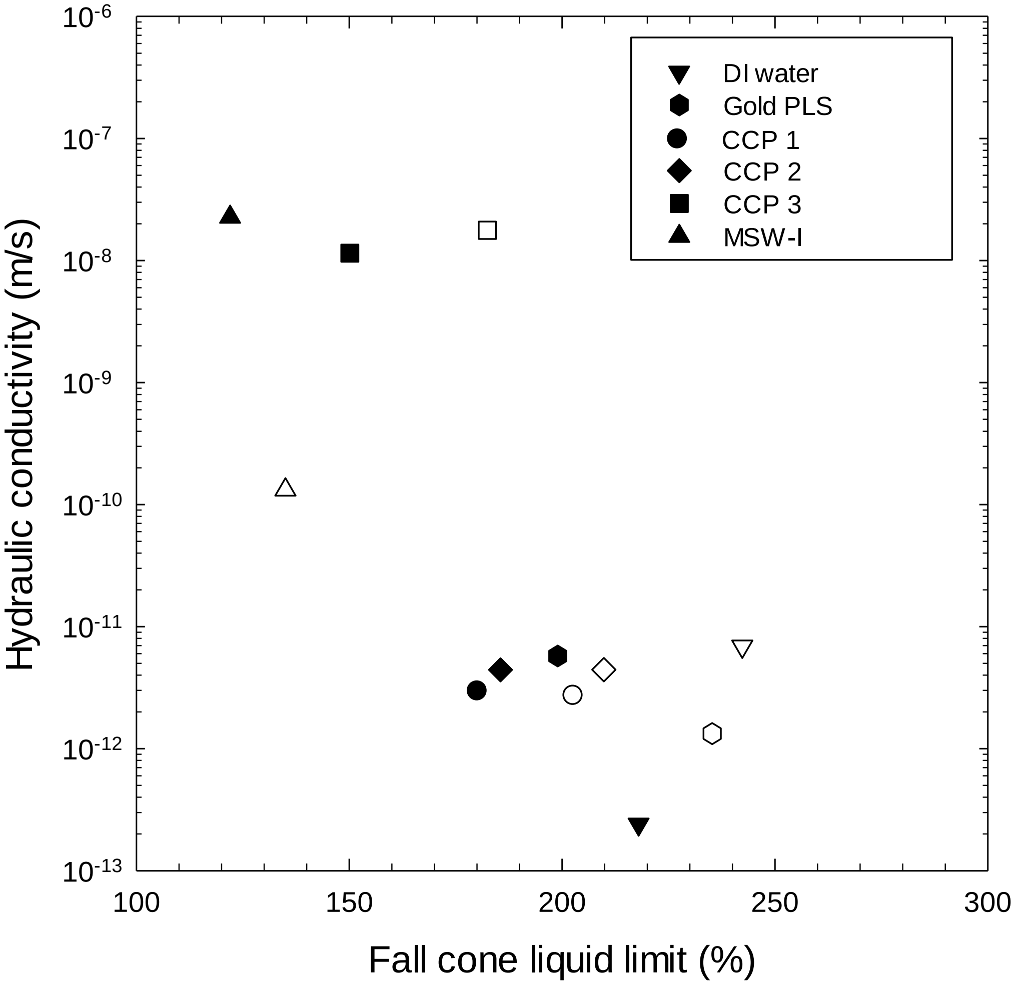

Figure 2. 10: Hydraulic conductivity of PMB GCLs to site-specific leachates vs. liquid limit obtained from fall cone test.

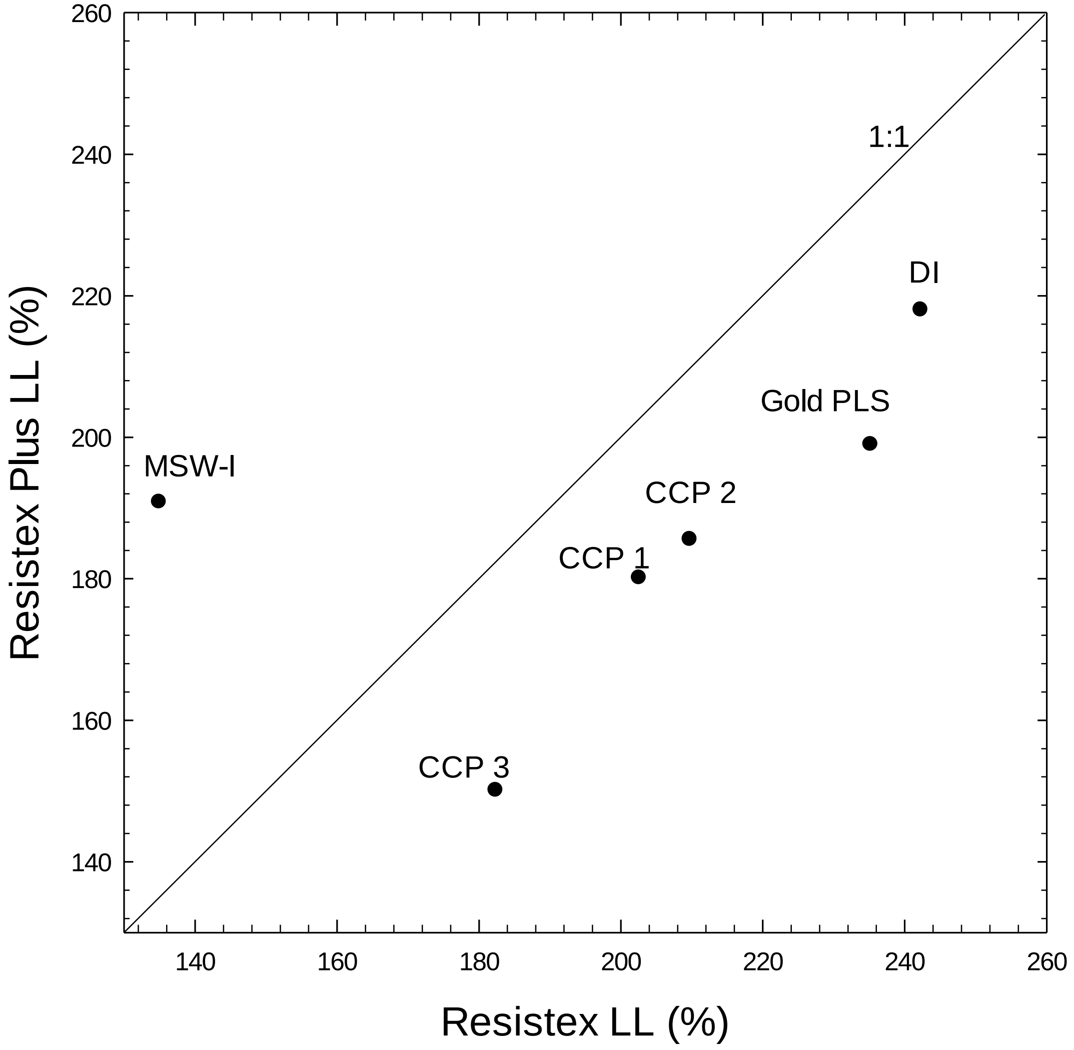

Figure 2. 11: Comparison of Resistex and Resistex plus liquid limits to site-specific leachates.

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APPENDIX A

DETERMINATION OF POLYMER ELUTION IN POLYMER-MODIFIED GEOSYNTHETIC CLAY LINERS CONTACTED WITH AGGRESSIVE LEACHATES

A.1. INTRODUCTION

Polymer-modified bentonites have been developed in order to provide resistance to increase in hydraulic conductivity in aggressive environment. Many studies have investigated the effect of polymer treatment on hydraulic properties of bentonites (Katsumi et al. 2001; Ashmawy et al. 2002; Katsumi et al. 2008; Mazzieri et al. 2010, Di Emidio 2011, Puma et al. 2011; Scalia et al. 2014). However, there are limited studies on effect of polymer elution after long term permeation to hydraulic conductivity. Previously Scalia (2012) studied the polymer elution for BPN material as a function of varying concentrations of $CaCl_2$ solution via loss on ignition test. That study concluded that polymer elution was linearly related with the concentration of the solution. Maximum % (92 % on average) of original polymer content within BPN was retained in the case of highest ionic strength solution (500 mM $CaCl_2$). It was hypothesized that clogging of pore spaces by polyacrylate resulted in high polymer retention and maintain low hydraulic conductivity.

In this study, TOC content of effluent samples for completed and on-going hydraulic conductivity tests with CCP leachates and site specific leachates were analyzed. The main purpose of this study was to discover the effect of polymer elution on hydraulic conductivity.

A.2. MATERIALS

PMB GCLs (Resistex and Resistex plus) were used in this study. Material physical properties were discussed in detail in section 1.4.1.

A.3. METHODS

A.3.1. Total Organic Carbon (TOC) Analysis

Total organic carbon (TOC) concentrations in effluent samples were analyzed using the Shimadzu TOC analyzer in accordance with ASTM D 4839-03. Non-purgable organic carbon (NPOC) method was used since samples were free of purgable organic content. Calibration standard solutions were prepared by diluting 1000 mg/L anhydrous potassium hydrogen phthalate to various concentrations with high purity water (electrical resistivity>18.0 megaohms-cm). Prior to analysis samples were diluted 25 times to keep the carbon content within the range of the standard solutions. At least 11 mL of each sample was placed into 24 mL glass vials. Samples were injected into analyzer and acidified to pH of two with concentrated acid (2 M HCl). Inorganic carbon component of the sample was removed by sparging of a gas free of CO_2 through sample. Remaining total carbon content was converted to carbondioxide (CO_2) by burning the sample in combustion tube. After the gas was cooled and dehydrated, chlorine and other halogen components were removed in halogen scrubber. Finally CO_2 was detected in non-dispersive infrared (NDIR) gas analyzer.

A.4. RESULTS

Total organic carbon (TOC) content of effluent samples for completed and ongoing tests on Resistex and Resistex plus GCL were presented in Fig. A.1. as a function of cumulative outflow (mL). TOC content of effluent samples for all tests showed exponential decaying trend. From the Fig. A.1, it can also be observed that initial and residual TOC contents where the TOC concentrations were stabilized were different for each test. Highest initial flush of polymer (Highest TOC) and residual TOC content were observed for Resistex plus GCL with MSW-I leachate (I=1042 mM). Fig. A.2 shows initial and residual TOC content of each test as a function of cumulative outflow. Both initial and residual TOC shows similar inverse S shaped curve. Graph suggests that for the same amount of initial or residual TOC content, both low and high hydraulic conductivity can be obtained. For example, Resistex with MSW-I leachate and Resistex with high ionic strength leachate have similar initial and residual TOC content. However, the difference between hydraulic conductivities is two orders of magnitude. Fig. A.3 shows the relationship between % polymer eluted and ionic strength of the solution used. Total amount of polymer eluted was obtained by computing area under TOC vs. cumulative outflow curve for each GCL-leachate pair and % polymer eluted was determined based on the initial polymer content of the GCL. From the graph, it can be observed that as the ionic strength of the leachate increases, % of polymer eluted increases as well. Scalia (2012) previously did polymer elution tests on BPN material with varying concentrations of $CaCl_2$ using loss on ignition test and concluded that polymer elution decreases as the ionic strength of the leachate increases. However, it should be noted that polymer type and polymer treatment in this study were different than BPN material tested before by Scalia (2012). Na-B was dry mixed with polymer in this study whereas in-situ polymerization of polyacrylate within Na-B slurry was utilized for studies performed by Scalia (2012). Additionally, multi-species inorganic salt solutions were used for this study which is likely to affect the amount of polymer eluted. Fig. A. 4 shows the relationship between % polymer eluted from TOC test and hydraulic conductivity of each GCL-leachate pair. As the amount of polymer eluted increases, hydraulic conductivity increases since polymer is not retained in GCL and adsorbed effectively onto Na-B. Amount of polymer eluted was also calculated from loss on ignition test and results were compared to TOC test (Fig. A.5). Data points for Resistex plus GCL falls below 1:1 line suggesting that TOC overestimates the amount of polymer elution. However, this might be due to high standard deviation associated with initial % polymer calculated from LOI test for Resistex plus GCL (5.5 ± 2.0). This might be due to non-uniform distribution of the polymer in GCL roll.

TOC testing of effluent samples will continue for hydraulic conductivity tests reached to hydraulic and chemical equilibrium and results will be analyzed by a subsequent researcher. It is also suggested that TOC results are compared with LOI results after permeation. Ultimate goal should be finding a relationship between TOC and simple LOI test from multiple tests and relating results to hydraulic conductivity.

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A.6. FIGURES

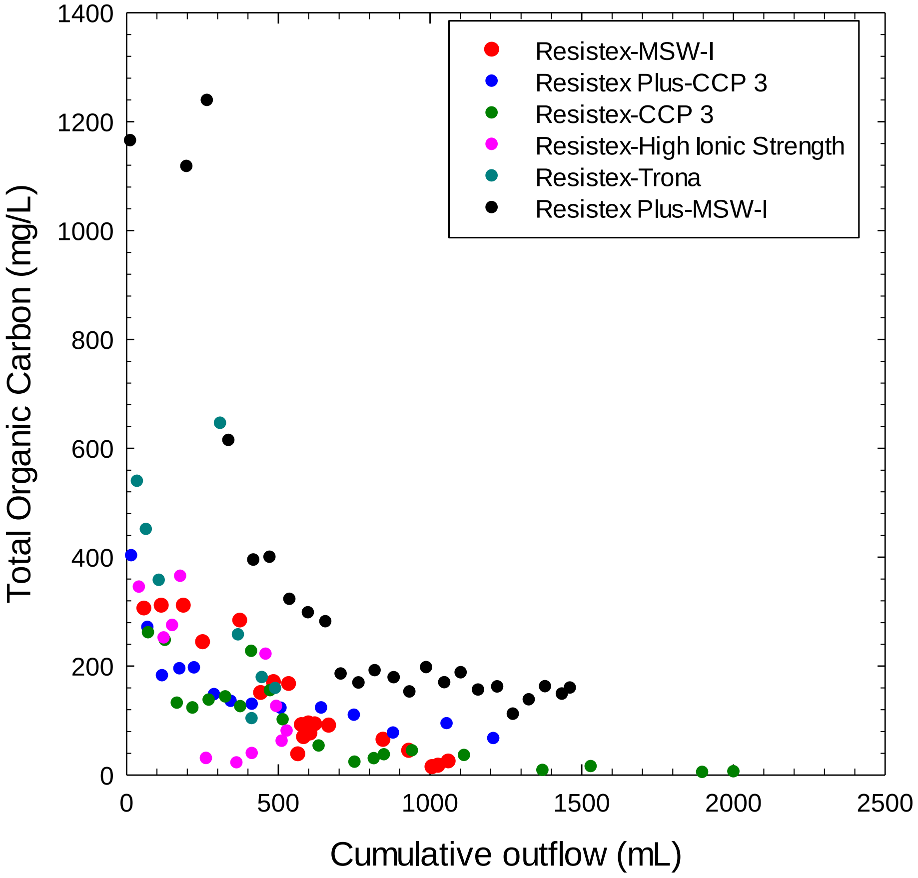


Figure A. 1: Total organic carbon content (TOC) of effluent samples as a function of cumulative outflow

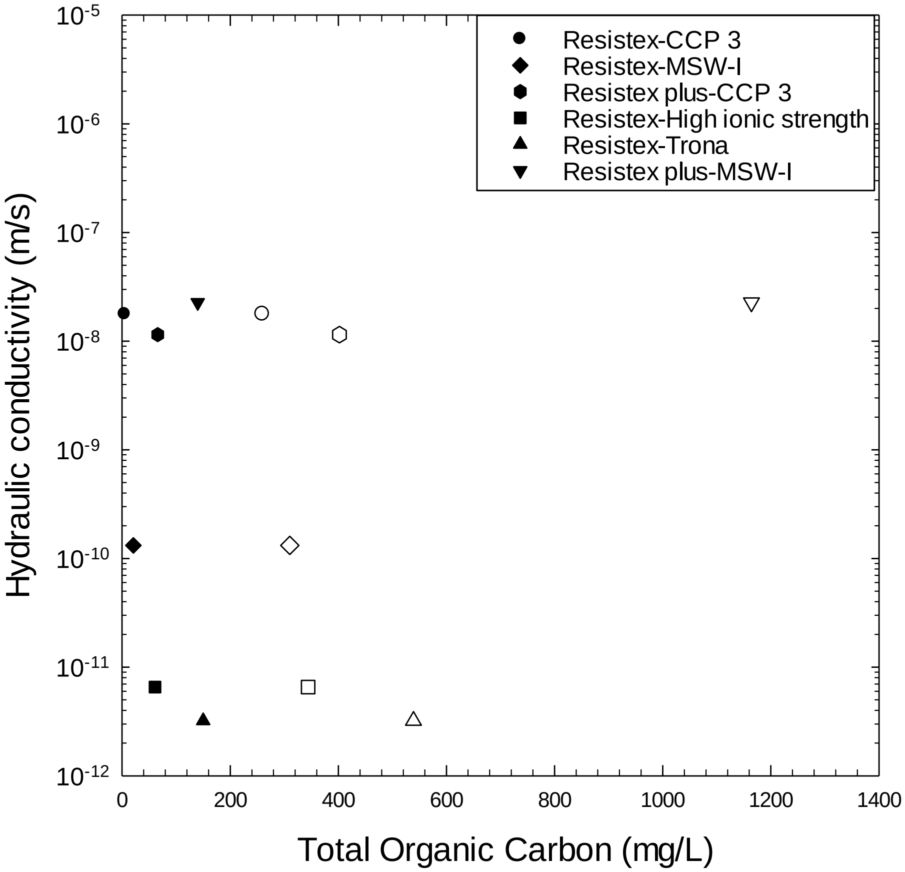


Figure A. 2: Initial and residual TOC content of effluent samples vs. hydraulic conductivit

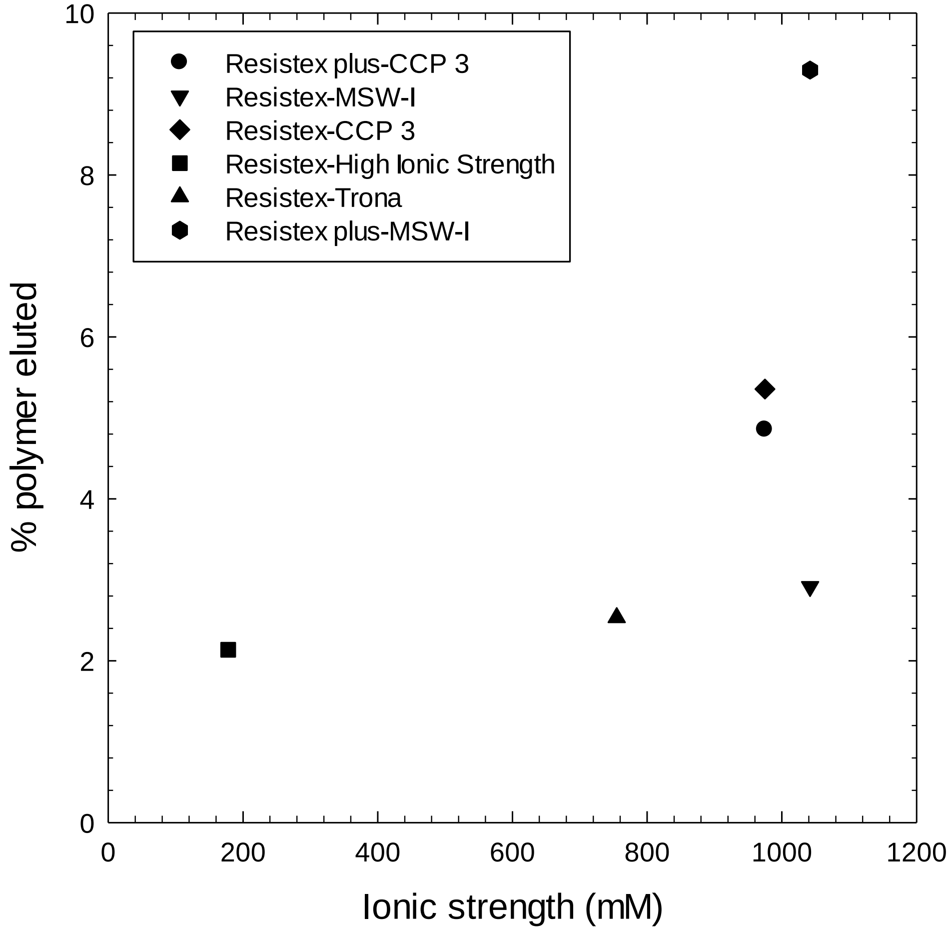


Figure A. 3: Polymer eluted (%) calculated from TOC test as a function of ionic strength

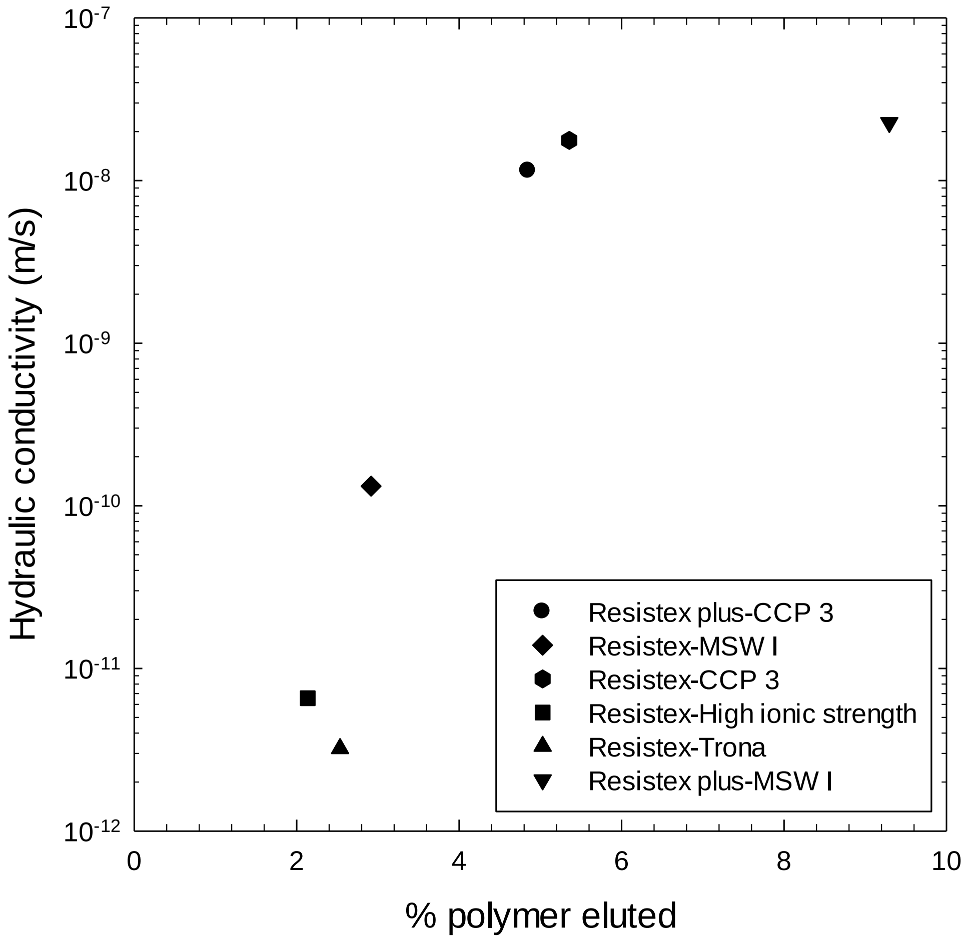


Figure A. 4: Polymer eluted (%) calculated from TOC test vs. hydraulic conductivity

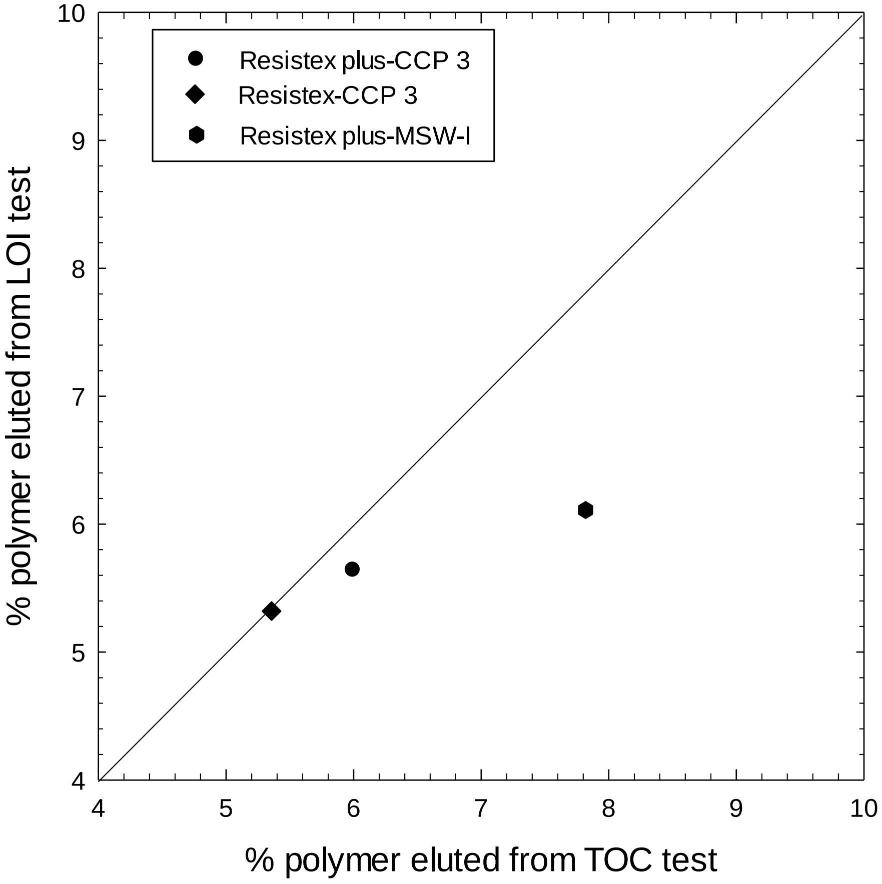


Figure A. 5: Comparison of polymer elution from TOC and LOI tests

APPENDIX B: Figures

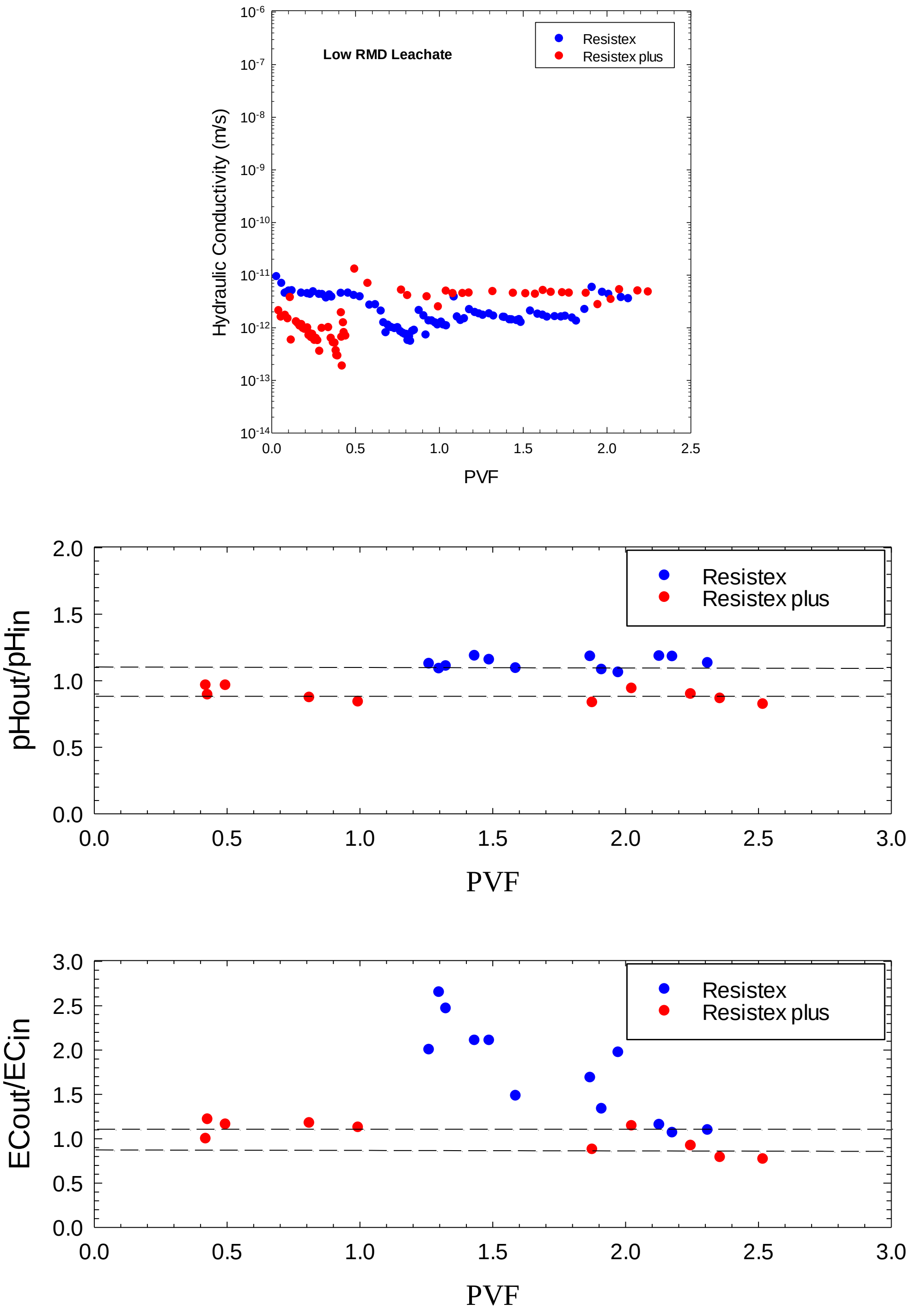


Figure B. 1. Hydraulic conductivity, pH_{out}/pH_{in} and EC_{out}/EC_{in} vs PVF for Resistex and Resistex plus with low RMD leachate

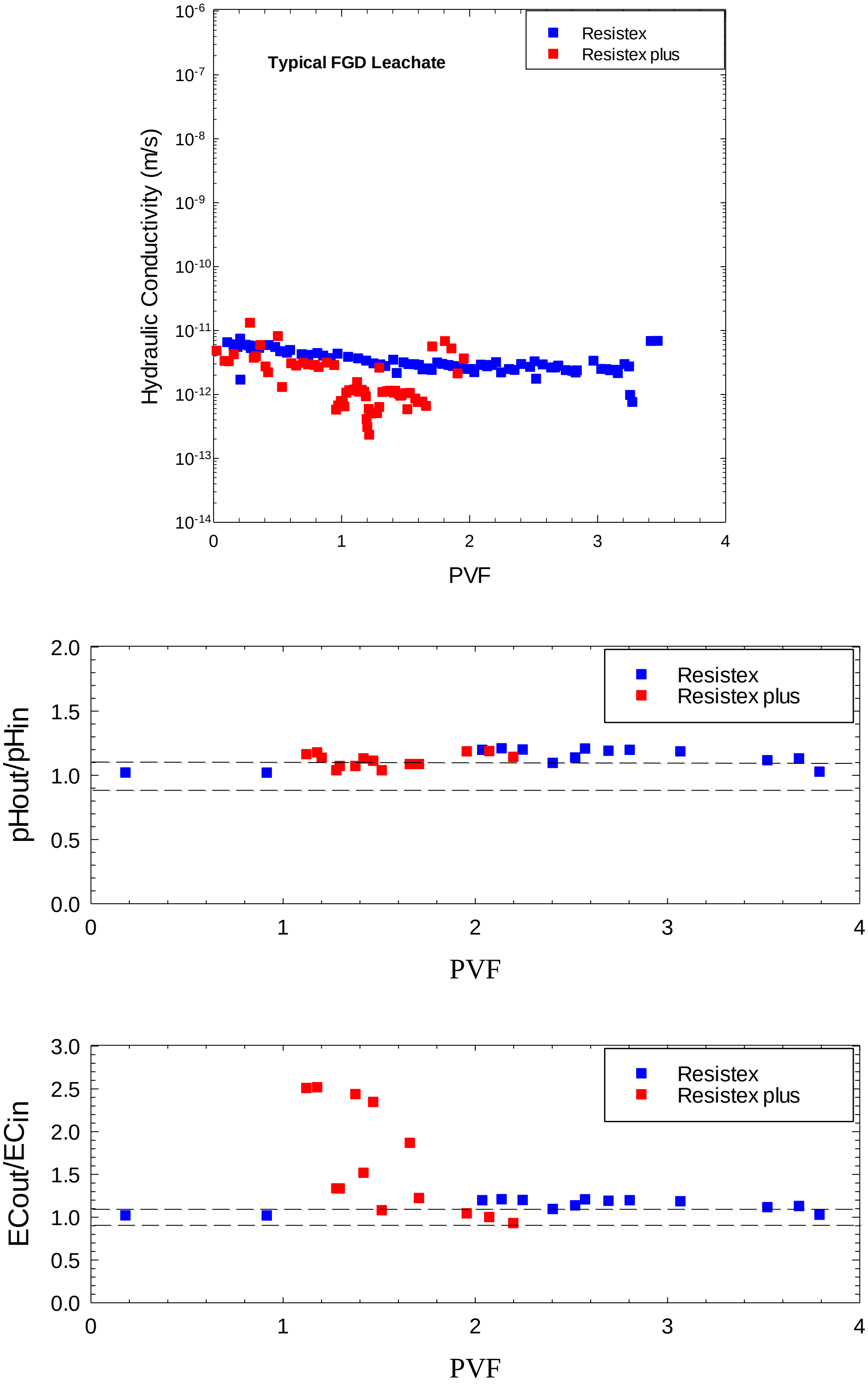


Figure B. 2: Hydraulic conductivity, pH_{out}/pH_{in} and EC_{out}/EC_{in} vs PVF for Resistex and Resistex plus with typical FGD leachate

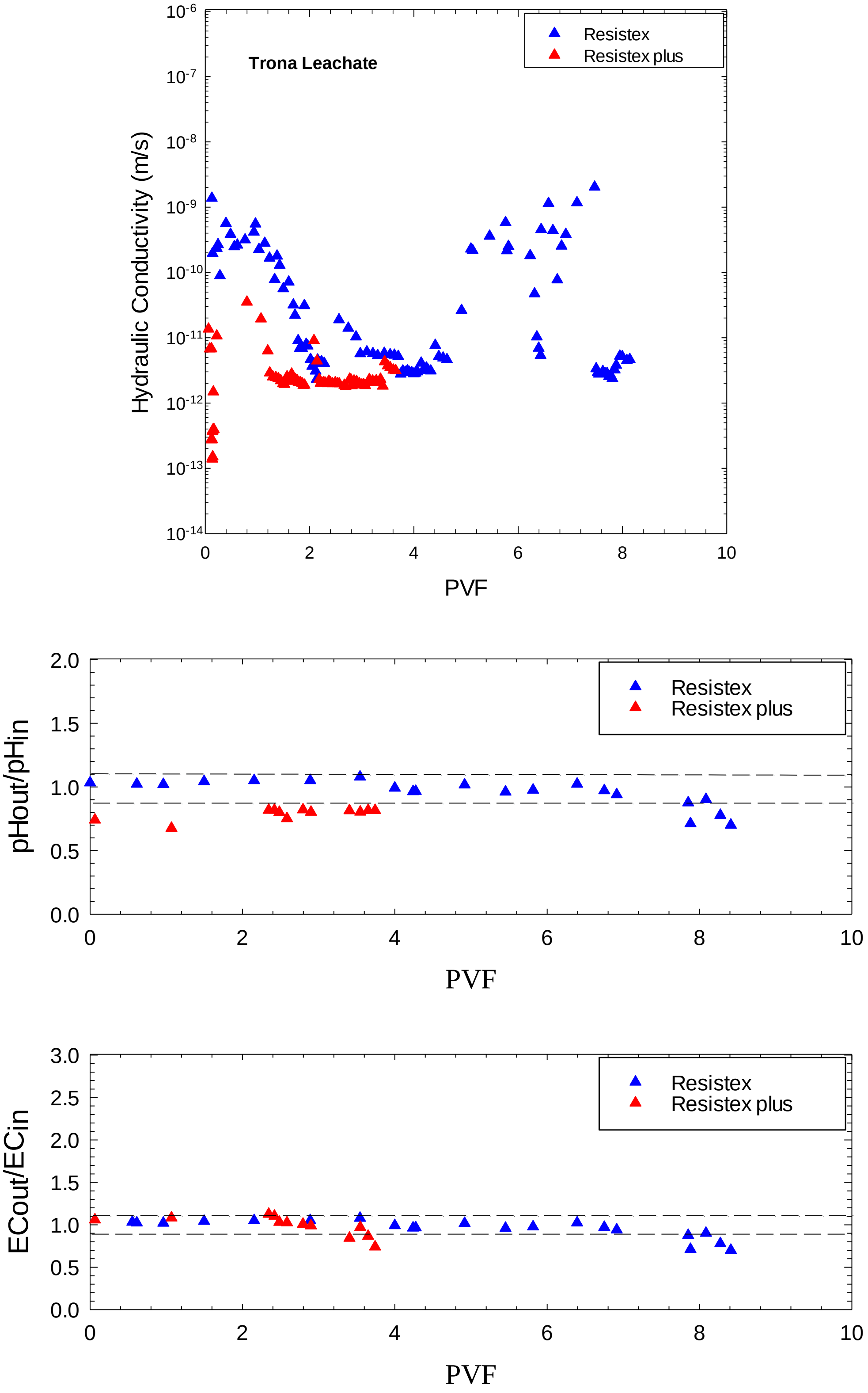


Figure B. 3: Hydraulic conductivity, pH_{out}/pH_{in} and EC_{out}/EC_{in} vs PVF for Resistex and Resistex plus with trona leachate

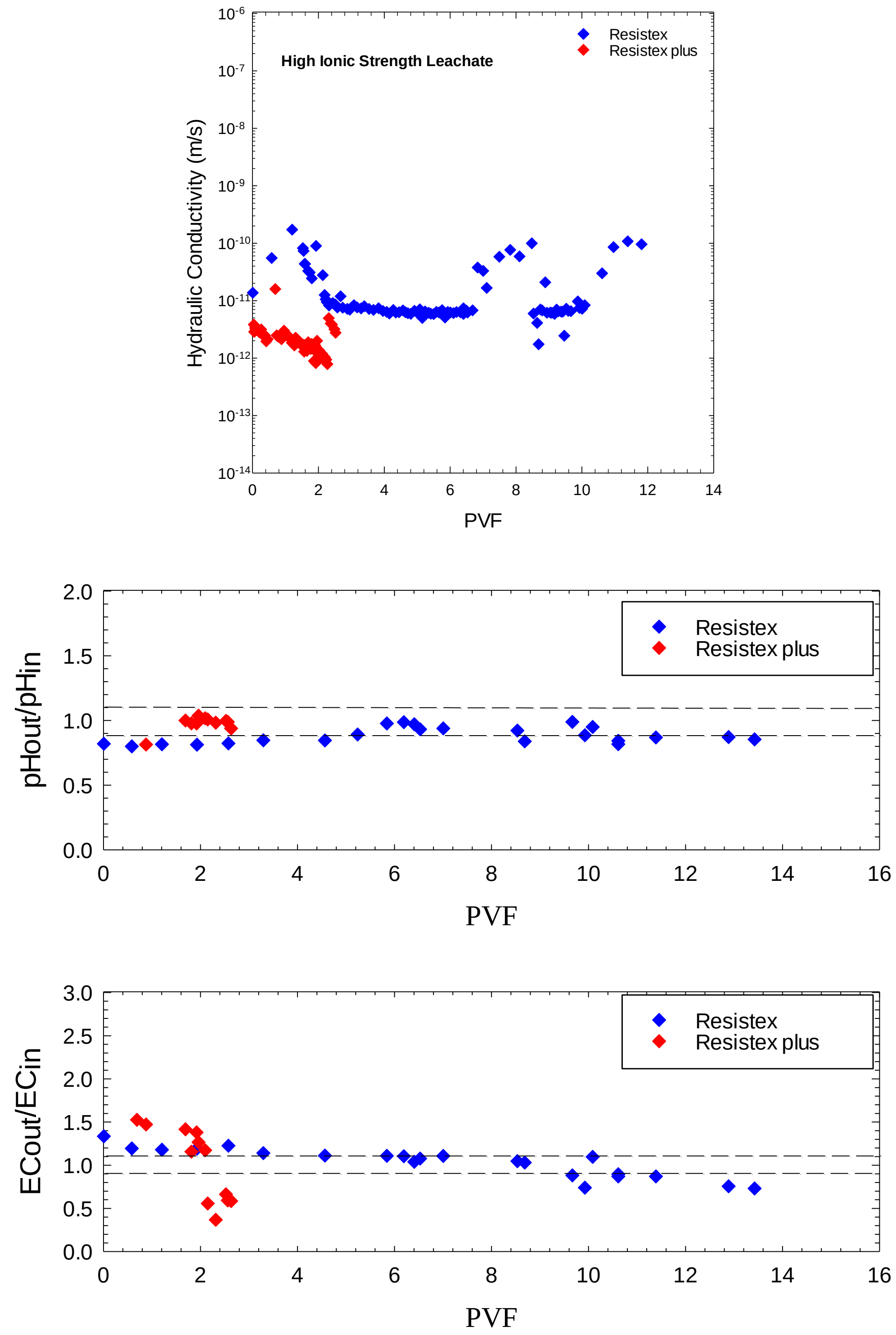


Figure B. 4: Hydraulic conductivity, pH_{out}/pH_{in} and EC_{out}/EC_{in} vs PVF for Resistex and Resistex plus with high ionic strength leachate

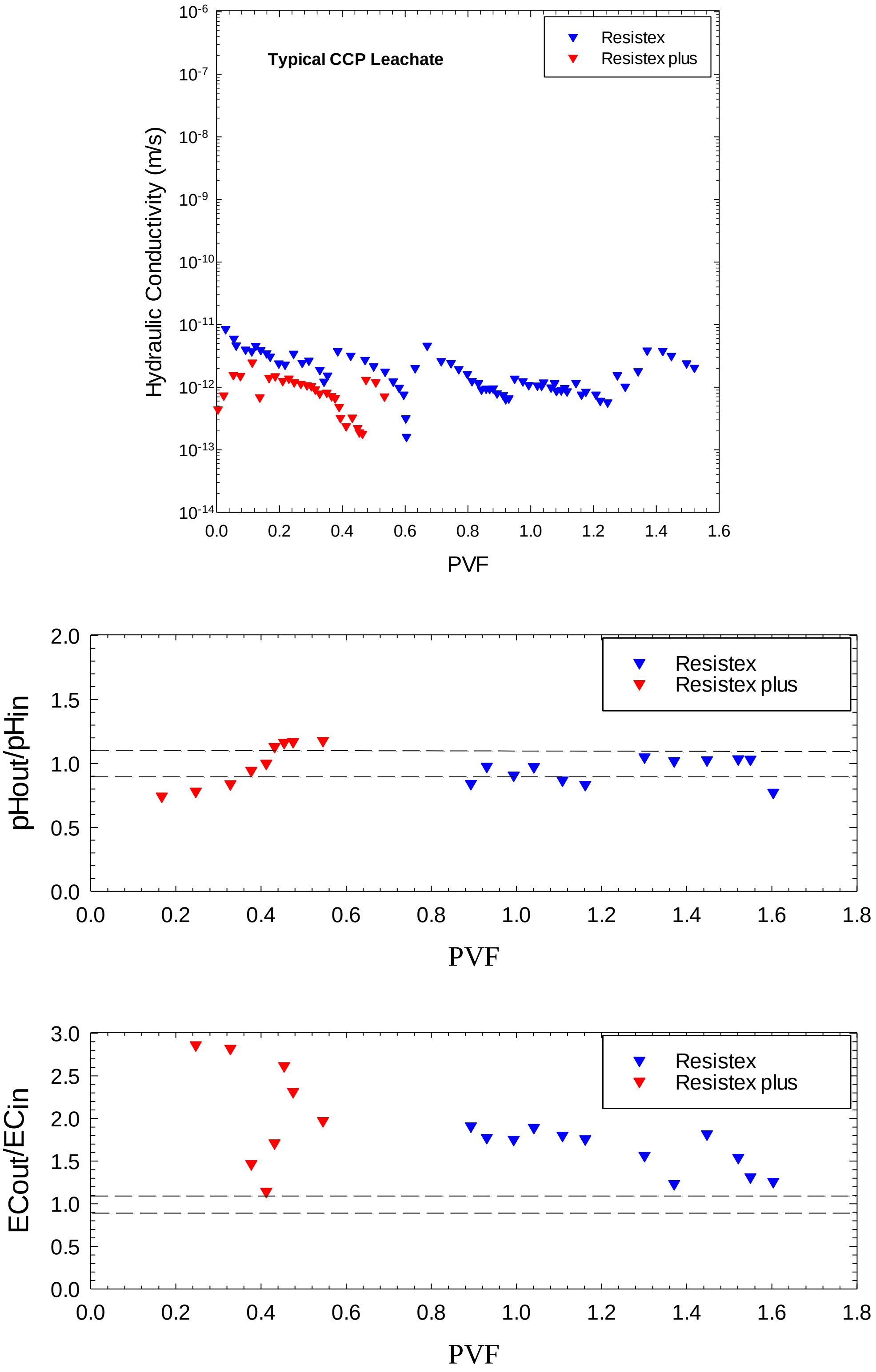


Figure B. 5: Hydraulic conductivity, pH_{out}/pH_{in} and EC_{out}/EC_{in} vs PVF for Resistex and Resistex plus with typical CCP leachate

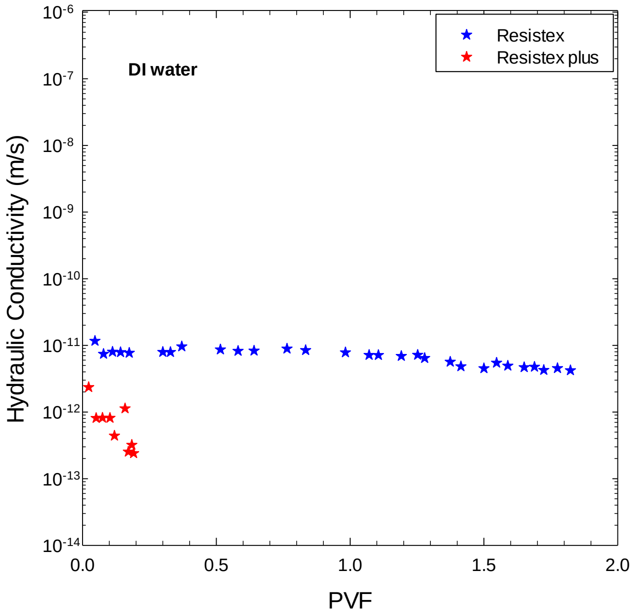


Figure B. 6: Hydraulic conductivity profile for Resistex and Resistex plus with DI water

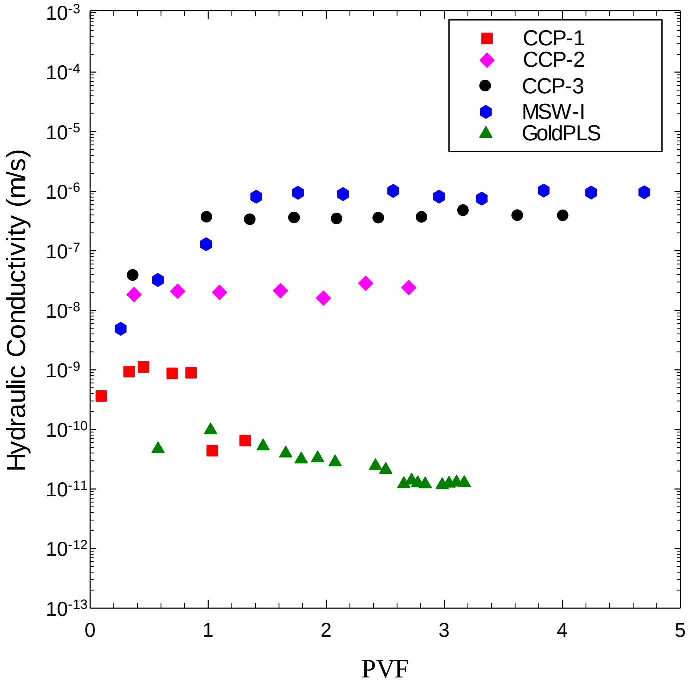


Figure B. 7: Hydraulic conductivity profile for Bentomat with site-specific leachates

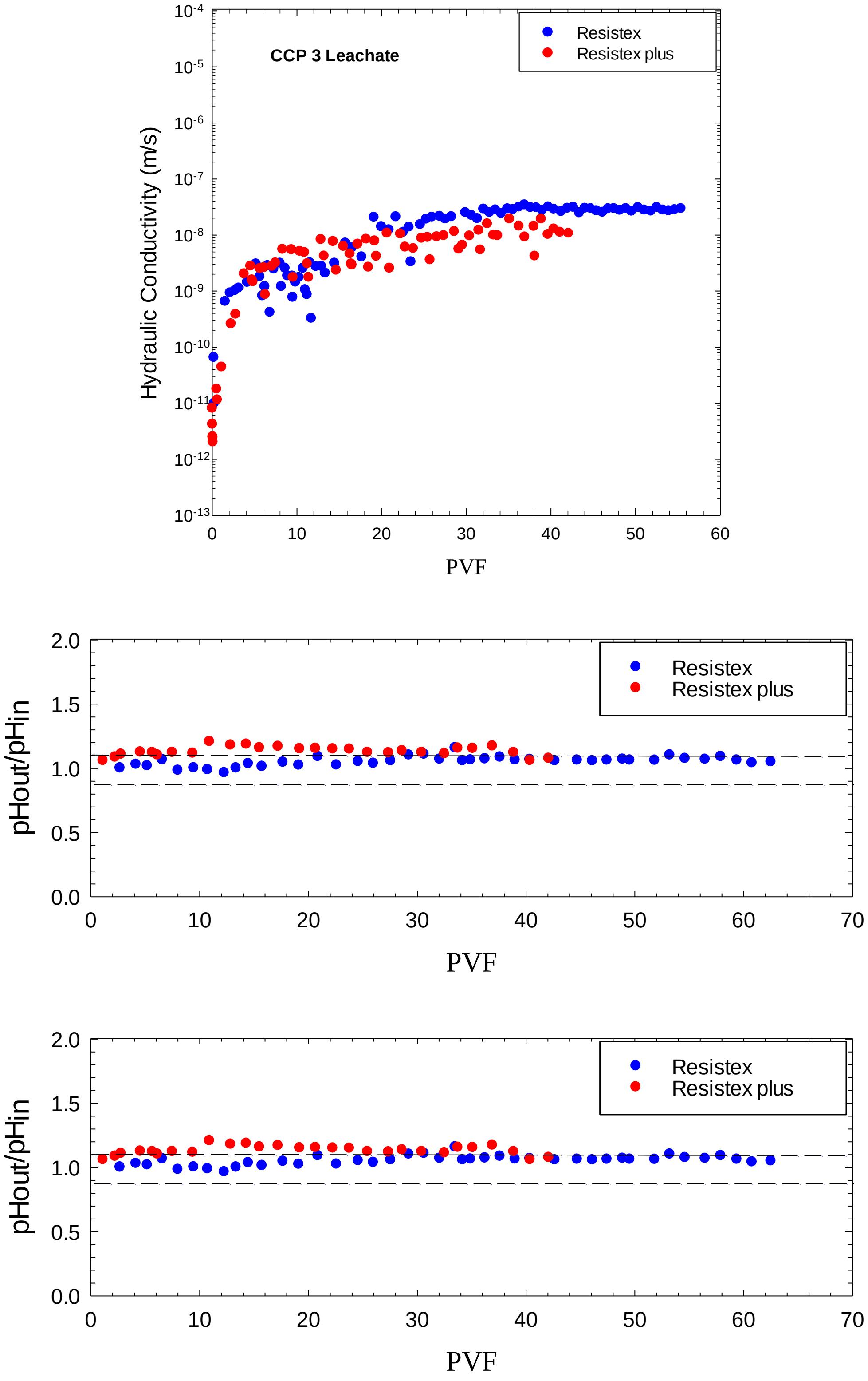


Figure B. 8: Hydraulic conductivity, pH_{out}/pH_{in} and EC_{out}/EC_{in} vs PVF for Resistex and Resistex plus with CCP 3 leachate

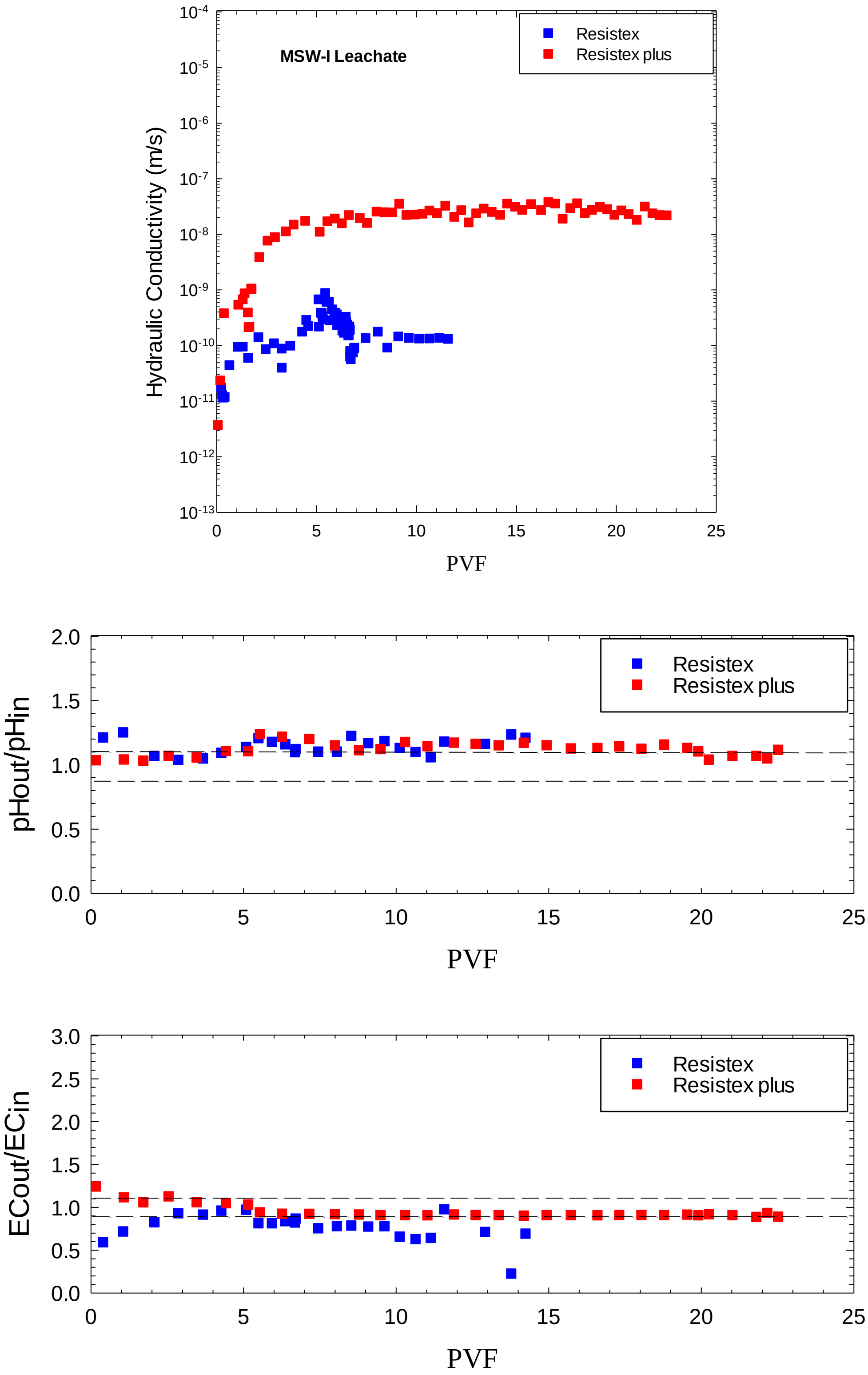


Figure B. 9: Hydraulic conductivity, pH_{out}/pH_{in} and EC_{out}/EC_{in} vs PVF for Resistex and Resistex plus with MSW-I leachate

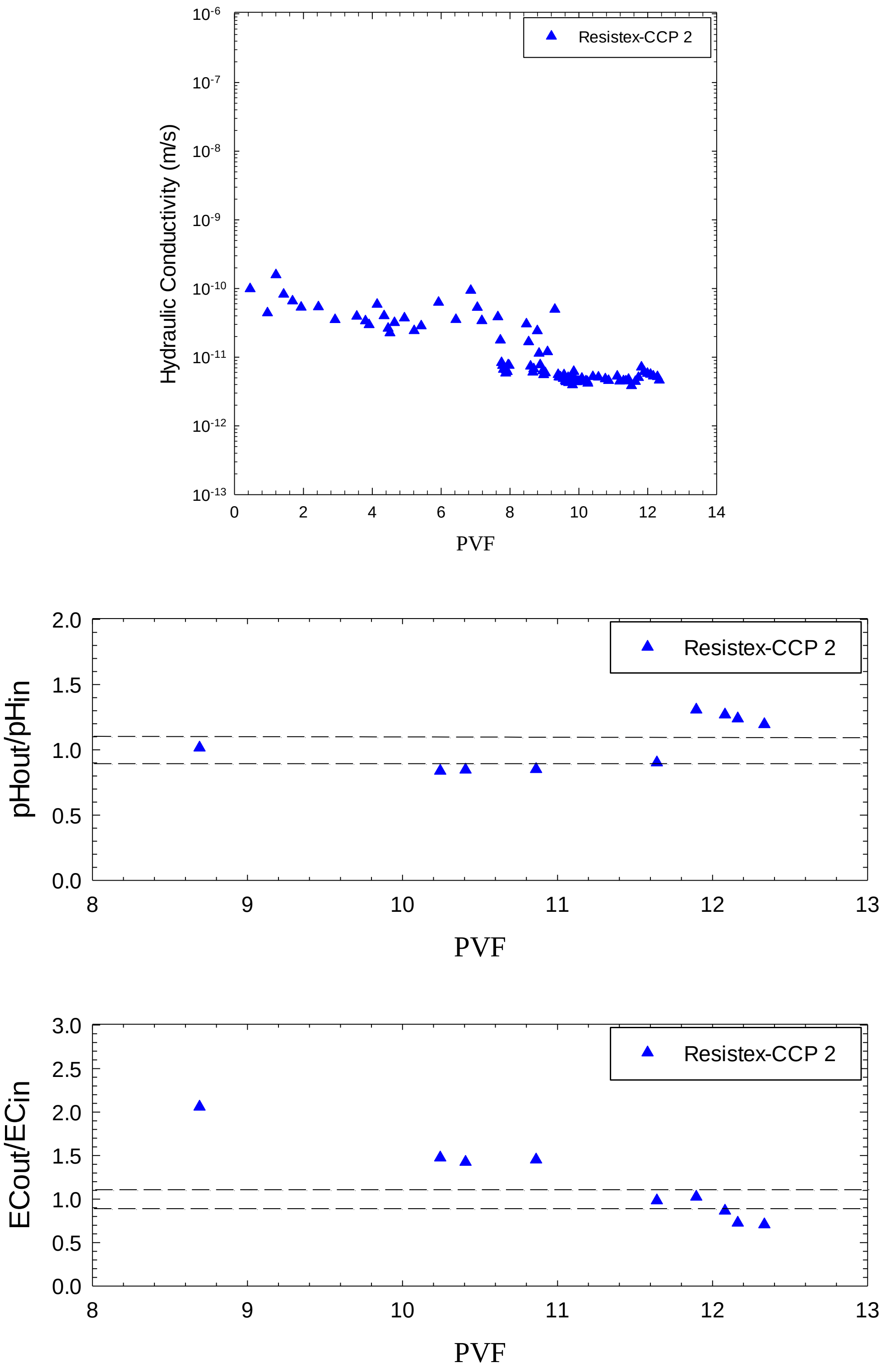


Figure B. 10: Hydraulic conductivity, pH_{out}/pH_{in} and EC_{out}/EC_{in} vs PVF for Resistex with CCP 2 leachate

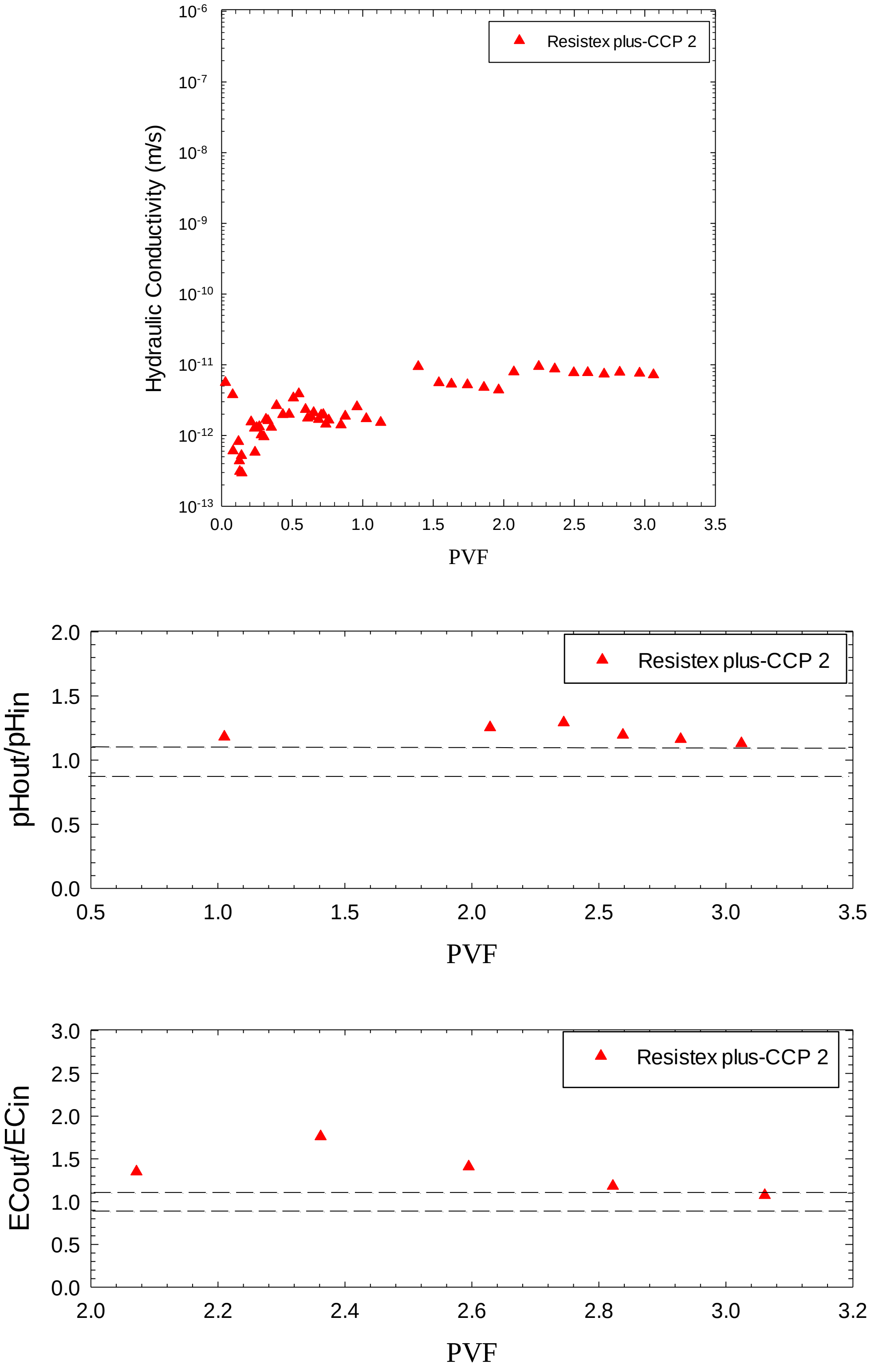


Figure B. 11: Hydraulic conductivity, pH_{out}/pH_{in} and EC_{out}/EC_{in} vs PVF for Resistex plus with CCP 2 leachate

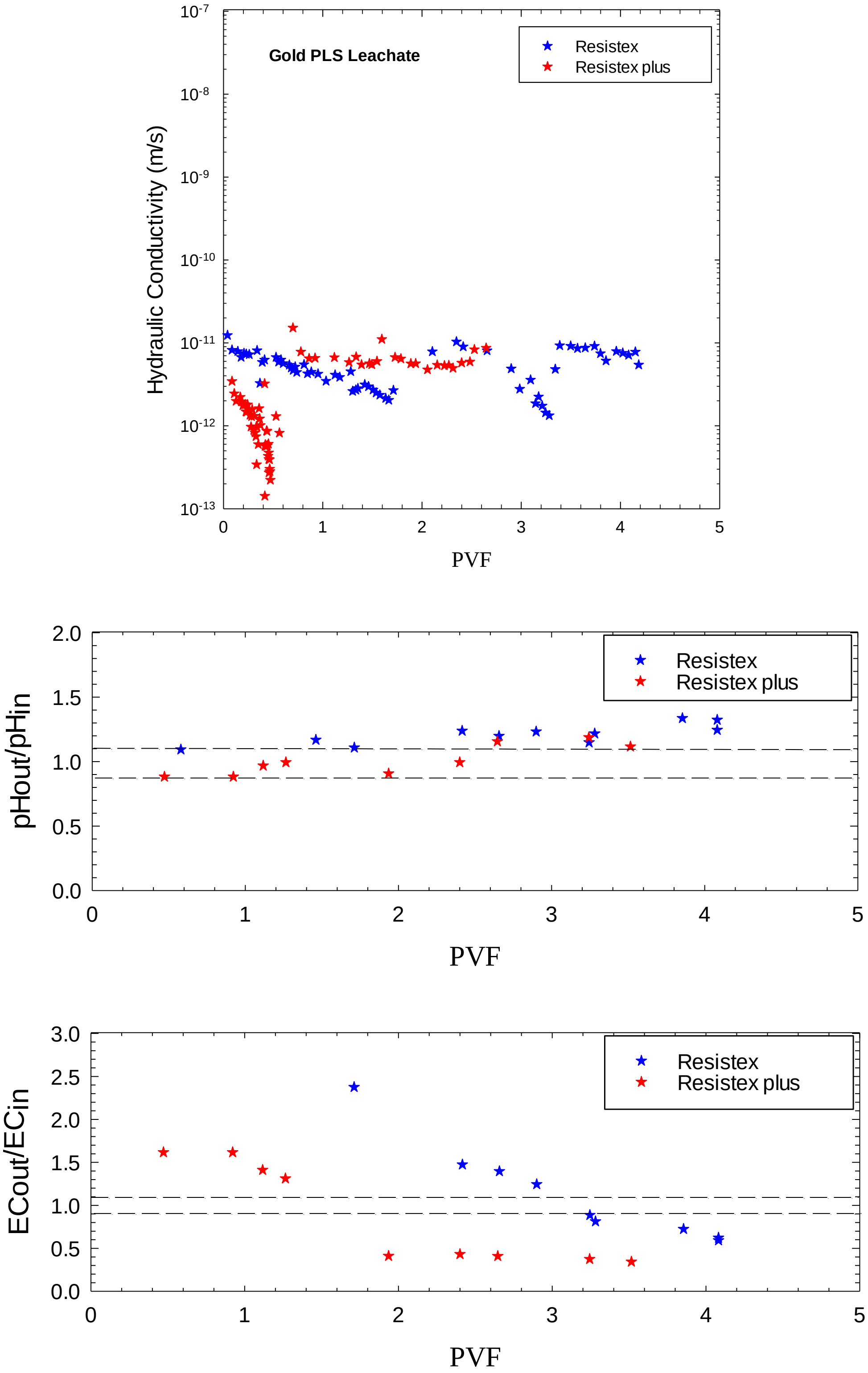


Figure B. 12: Hydraulic conductivity, pH_{out}/pH_{in} and EC_{out}/EC_{in} vs PVF for Resistex plus with Gold PLS leachate

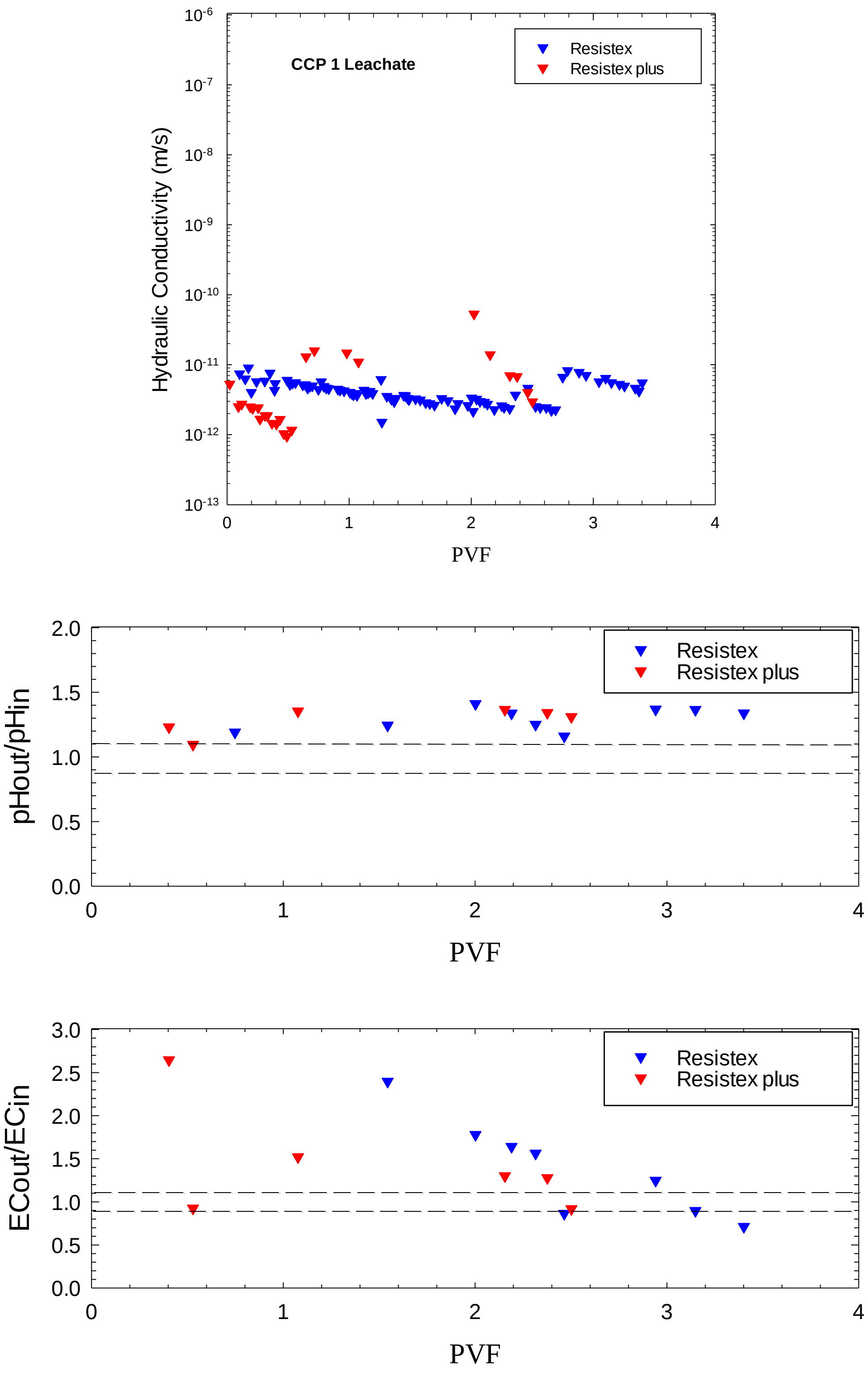


Figure B. 13: Hydraulic conductivity, pH_{out}/pH_{in} and EC_{out}/EC_{in} vs PVF for Resistex and Resistex plus with CCP 1 leachate

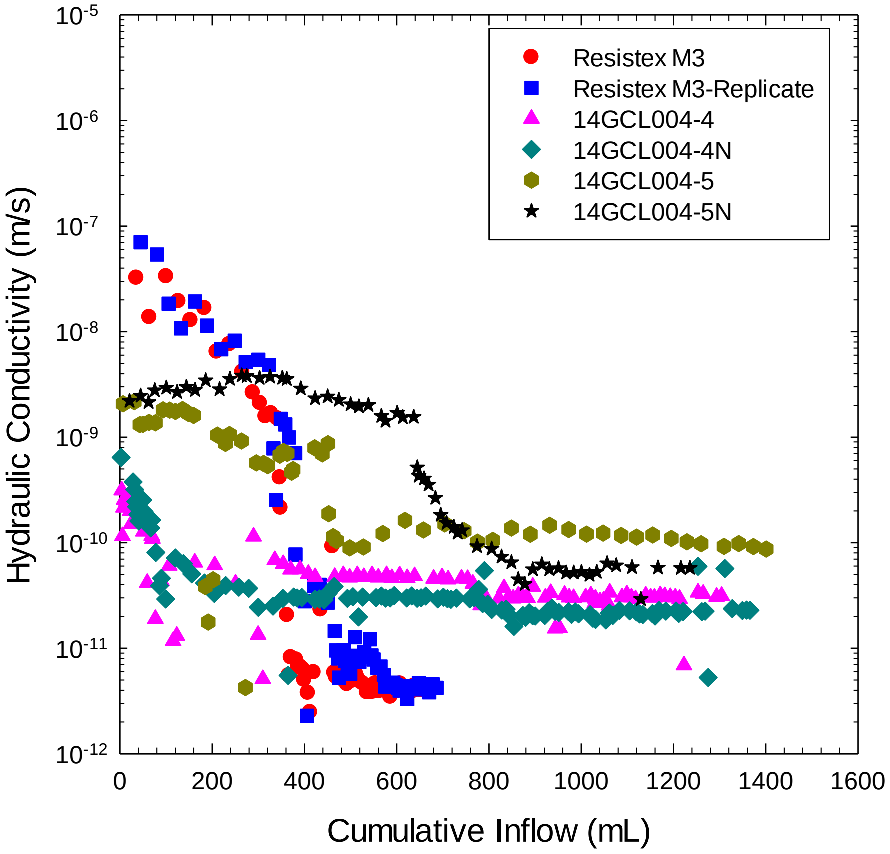


Figure B. 14: Hydraulic conductivity profiles for variety of GCLs with trona leachate.

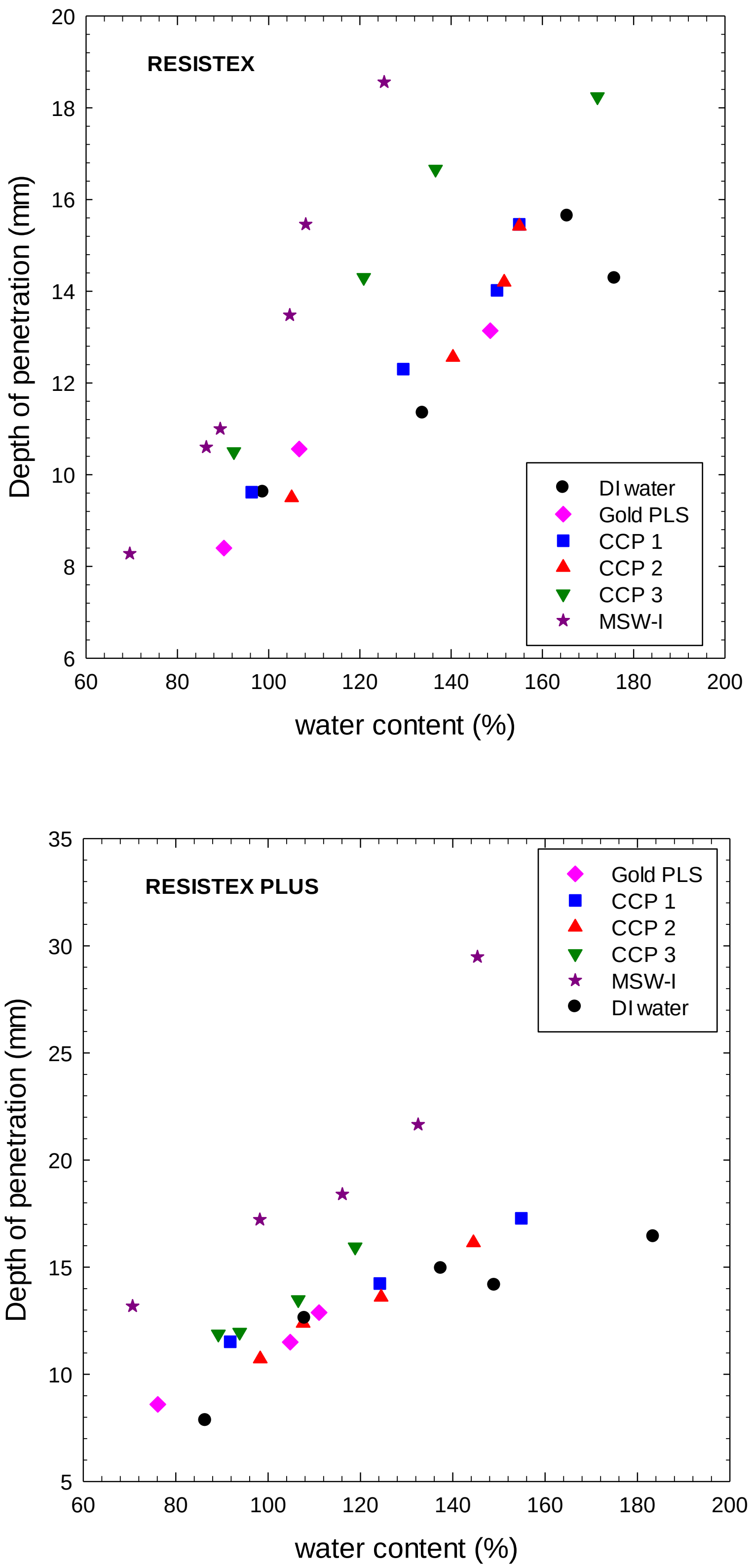
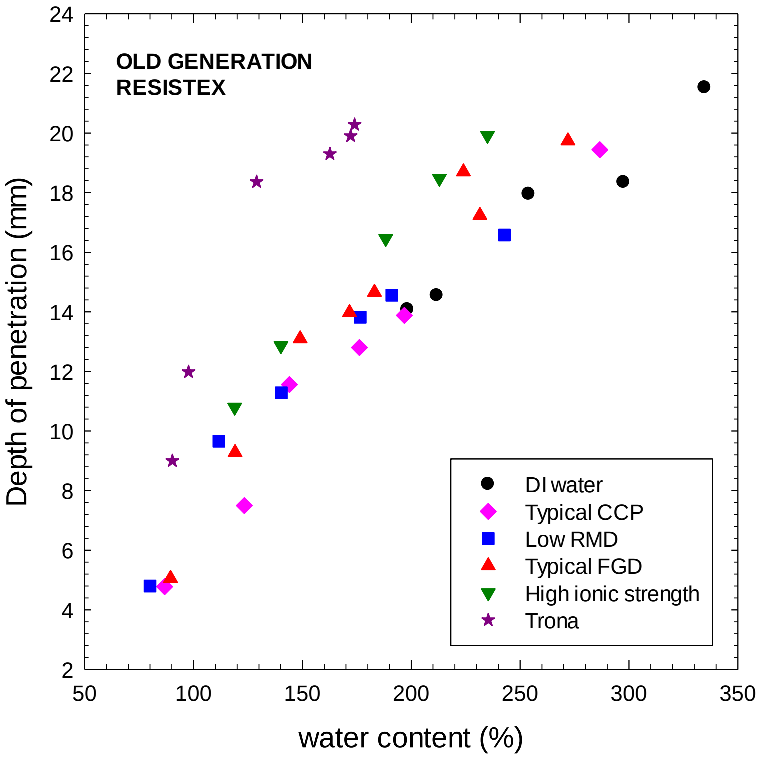


Figure B. 15: Fall cone test data for Resistex and Resistex plus with site-specific leachates



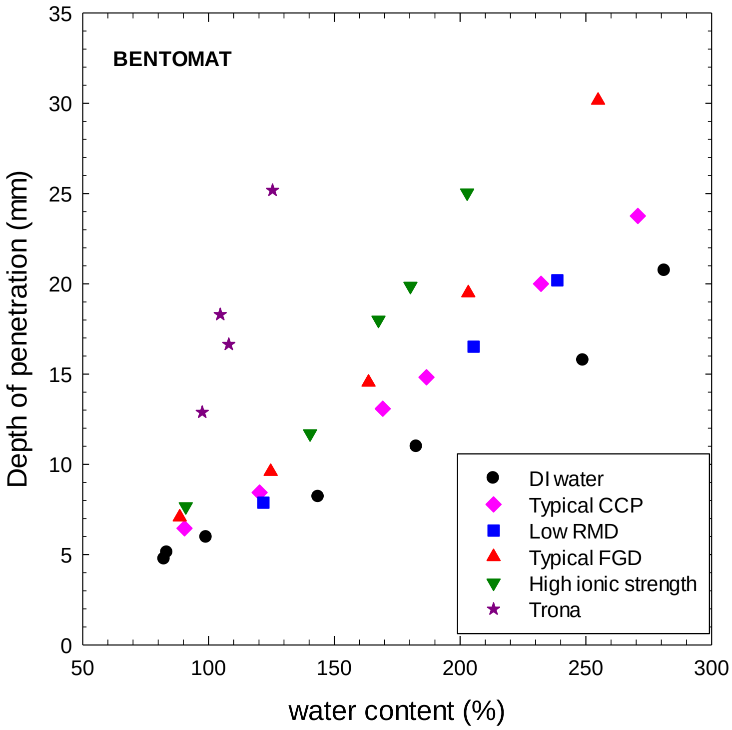


Figure B. 16: Fall cone test data for old generation Resistex and Bentomat with CCP leachates