Hydraulic and Diffusive Behavior of a Compacted Cemented Soil

E.P. Korf, P.D.M. Prietto, N.C. Consoli

Abstract. The study evaluated, through a series of permeability and diffusion tests, the hydraulic and the attenuation behavior of a compacted clayey soil, with and without the addition of Portland cement (0 to 2%). To evaluate the diffusive response, the specimens were subjected to a vertical static load (100 to 500 kPa), simulating the action of a waste mass, and to an acidic solution enriched with toxic metals Pb or Cd, prepared with pH varying from 1 to 6. The reactive behavior analysis indicated that retention by adsorption increased with the increase of pH, but was not affected by the applied static load. The combination of higher cement contents with higher pH caused precipitation to prevail over adsorption reactions.

Keywords: diffusion, lead, cadmium, acidic leachate, transport of contaminants, hydraulic conductivity.

1. Introduction

Leachates from industrial and mining solid wastes are a major source of environmental impact due to the presence of toxic metallic species and/or their acidic constitution. Some examples are the disposal in the ground of sludge and waste from electroplating and smelters activities, mining tailings from coal and minerals beneficiation, as well as accidental spills. In many cases, the managing of such leachates is inadequate, without any engineered solution to provide adequate containment and treatment of pollutants. The most aggravating aspect is that these wastewaters have the natural ground as their main destination, which unfortunately does not represent the endpoint for such toxic substances.

In this context, the improvement of technical solutions to ensure mitigation and prevention of environmental impacts plays a fundamental role. For instance, the use of reactive, compacted soil barriers, with low hydraulic conductivity, is a traditional technique used to reduce contaminant transport through side slope and bottom sealing in waste disposal facilities. Nevertheless, studies have shown that these barriers might be enhanced by the addition of small amounts of materials like Portland cement, lime, and bentonite, reducing hydraulic conductivity and compound mobility, and increasing adsorption/precipitation reactions (Lo et al., 1997; Lee, 1998; Tsai & Vesilind, 1988; Wu & Li, 1998; Basta et al., 2001; Elzahabi & Yong, 2004; Bartelt-Hunt et al., 2006; Adebowale et al., 2006; Lemos, 2006; Giannakopoulou et al., 2007; Knop et al., 2008; Thomé et al., 2014).

The objective of this research was therefore to evaluate, through a series of permeability and diffusion tests, the hydraulic response and the attenuation capacity of a compacted clayey soil, with and without the addition of Portland cement, aiming at its use as containment barriers for industrial and mining solid waste disposal facilities. To evaluate the diffusive behavior, specimens were submitted to the action of a static vertical load and to an acidic solution enriched with cadmium or lead.

2. Material and Methods

Laboratory experiments were planned, conducted, and analyzed to assess the effects of three main control variables - cement addition (0 and 2%), contaminant solution pH (1 and 6), and static vertical load (0 and 500 kPa) - on the attenuation capacity of a compacted clayey soil, subjected to the diffusive transport of an acidic contaminant solution enriched with cadmium or lead. In addition, the effect of cement content on the hydraulic conductivity of the compacted soil was evaluated.

The experimental program for the diffusion tests was conducted in two separate blocks, identically and independently for each of the metallic species investigated (cadmium and lead). For each block a 2³ factorial experimental design was used: three control variables at two levels each, with the addition of a central point (1% cement, pH 3.5, static vertical load of 250 kPa). Overall, the experimental design resulted in 9 combinations or treatments (8 factorial points and 1 central point) for each metal investigated (cadmium and lead). It should be noticed that replicates (n = 4) were performed only at central point, totaling 12 tests for each metal. Further details about the experimental design used in present work can be found in the specific literature (e.g. Montgomery, 2005, Box et al., 1999).
2.1. Soil sampling and characterization

The soil utilized was a basalt residual soil sampled from the Geotechnical Experimental Site at the University of Passo Fundo, located in the city of Passo Fundo, in southern Brazil. The sample was obtained by disturbed extraction from the B horizon (1.2 m depth).

The soil is classified as sandy clay (68% clay, 27% sand, and 5% silt), according to the NBR-7181 (ABNT, 1984c), has a specific gravity of 2.67 and a plastic index of 11, according to the NBR-6459 (ABNT, 1984a) and the NBR-7180 (ABNT, 1984b), respectively. It presents pH 5.4, low organic matter content (< 0.8%), and low cation exchange capacity (CEC = 8.6 cmolc/dm³), according to Tedesco (1995), as well as 33.86 m²/g of soil specific surface (EMBRAPA, 1997), typical of soils with the predominance of kaolinite minerals. The soil is also classified as humic oxisoil (Streck et al., 2008). According to X-ray diffraction analysis and chemical composition by X-ray fluorescence analysis, it is a kaolinite-based clay, with a significant presence of hematite (Fe₂O₃ content of 11.7%) and quartz.

The compaction characteristics of the residual soil, determined according to NBR-7182 (ABNT, 1984d) for the modified Proctor energy, are: maximum dry unit weight of 15.7 kN/m³, optimum moisture content of 24.5%, and degree of saturation at optimum moisture content of 94.8%.

The background concentrations (natural levels) of cadmium and lead available in the soil, as determined by the method of extraction by digestion (USEPA, 1996), are 1.63 and 30.74 mg/kg, respectively.

2.2. Cement and contaminant solution

Portland cement of high early strength [Type III, according to ASTM (2007)] was adopted as the cementing agent and also as a neutralizing element, because of its alkaline nature. The average cement composition is 0-5% of mineral admixtures and 95-100% of clinker, with nominal compressive strength at 28 days of 40MPa. According to the X-ray fluorescence analysis, the cement has a significant presence of CaO (66.2%) and SiO₂ (18%). The chemical composition of the mixture of soil with 2% hydrated cement indicated the presence of SiO₂ (45.1%), Fe₂O₃ (12.1%), Al₂O₃ (27.5%), and CaO (1.8%).

The contaminant solutions were prepared by diluting a 1000 mg/L standard solution of cadmium or lead (at 5% of nitric acidic by volume) into a solution of 10 mg/L. The metallic species concentrations were equivalent to extrapolating 3333 times and 1000 times, respectively for cadmium and lead, the values recommended by the World Health Organization (WHO, 2011). The solutions were prepared at different values of pH in the acidic range, adjusted with a sodium hydroxide and nitric acid solution.

2.3. Diffusion testing device

The testing device comprised a stainless steel cell, which functions as a rigid wall, downward-flow permeameter, allowing hydraulic conductivity determination as well as contaminant transport parameter evaluation. The device is described by Knop et al. (2008) and followed the requirements of the ASTM-D 4874 standard (ASTM, 1995) with modifications. The diffusion cell had dimensions of 100 mm in height and 70 mm in diameter and was adapted to a conventional consolidation frame to allow the application of a static vertical load to the specimen, simulating the action of a waste mass over a containment barrier (Fig. 1).

2.4. Specimens preparation and saturation

Mixture specimens with cement contents of 0, 1, and 2% of dry mass of soil, and nominal dimensions of 20 mm in height and 70 mm in diameter, were compacted into the diffusion cell at the specific unit weights and optimum moisture contents obtained in the modified Proctor compaction test (15.7 kN/m³ and 24.5%, respectively). The water/cement ratios for the cemented specimens were 24.5 and 12.25, respectively for the 1% and 2% cement contents.

To approximate saturation, the following procedure was carried out for all specimens: (1) distilled water percolation from an inlet pressurized cylinder connected to the top of the diffusion cell; (2) application of a hydraulic head equivalent to 80 kPa; (3) measurement of the volume percolated in a graduated burette attached to the bottom of the diffusion cell until steady flow was reached. The saturation procedure was complete in approximately seven days and the saturation degree resulted in values greater than 95%. This procedure was validated by measuring the degree of saturation of the specimens after the tests.

2.5. Diffusion tests

The procedures described below were adapted from Barone et al. (1989).

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*Figure 1 - Diffusion cell adapted to a conventional consolidation frame.*
Once the saturation phase was finished and the hydraulic conductivity measured, the outlet valve connected to the bottom of the diffusion cell was closed and remained so throughout the test. Subsequently, the distilled water inside the inlet cylinder was replaced by the contaminant solution, without any pressure applied, but subjected to constant agitation, with the aid of a pump, to maintain homogeneity. The diffusion cell was then coupled to a conventional consolidation frame and the vertical pressure applied. Then, the inlet valve connected to the top of the diffusion cell was opened and the contaminant diffusion phase initiated and conducted for seven days. After each diffusion test, the specimens were sectioned in four slices approximately 5 mm in height, by means of a steel cutting tool. The available metal concentration in each slice was then extracted by acidic digestion (USEPA, 1996) and analyzed in the atomic absorption spectrophotometer.

2.6. Determination of the contaminant transport parameters

In diffusion tests, the retardation factor \((R_d)\) was calculated from Eq. 1, in which \(\rho_d\) is the specimen dry density, \(n\) is the specimen porosity \((n)\), and \(K_d\) is the partition coefficient. The partition coefficient \(K_d\) was obtained (Eq. 2) by determining the adsorption \((S)\) for each slice of the tested specimens and calculating the equilibrium concentration of pore water \((C)\) by means of a mass balance.

\[
R_d = 1 + \frac{\rho_d}{n} K_d
\]

\[
K_d = \frac{S}{C}
\]

The effective diffusion coefficient \((D^*)\) was determined by back analyzing each slice of the tested specimens and fitting the experimental data to the analytical solution proposed by Carslaw and Jaeger (Shackelford, 1991), which is shown in Eq. 3, along with their initial and boundary conditions, and applies to the testing assembly previously described.

\[
\frac{c}{c_0} = \exp \left[ \frac{n R_d x}{H_f} + \left( \frac{n}{H_f} \right)^2 D^* R_d t \right] \\
\times \text{erfc} \left\{ \frac{x}{2 D^* t R_d} \sqrt{\frac{D^* R_d t}{H_f}} \right\}
\]

Initial condition:
\(c(x,0) = 0 \rightarrow x \geq 0\)

Boundary conditions:
\(c(0,t) = c_0 \rightarrow t \geq 0\)
\(c(\infty,t) = 0 \text{ and } \frac{\partial c(\infty,t)}{\partial x} = 0 \rightarrow t \geq 0\)

In Eq. 3, \(c\) is the contaminant concentration at the depth \(x\) from the top of the specimen; \(n\) is the specimen porosity; \(t\) is the time; \(c_0\) is the initial concentration of the contaminant solution; \(H_f\) is the effective height of the contaminant solution in the inlet cylinder; \(R_d\) is the retardation factor; \(D^*\) is the effective diffusion coefficient; and \(\text{erfc}\) is the complementary error function.

Figure 2 shows an example of fitting experimental data to the analytical solution in order to calculate the \(D^*\) parameter.

2.7. Statistical analysis

The results were statistically analyzed by using the Analysis of Variance (ANOVA) method, with a significance level of 5%.

3. Results and Discussion

3.1. Hydraulic conductivity

The average hydraulic conductivity (only for distilled water percolation) decreased with increasing cement content: 5.70 \(\times\) 10\(^{-10}\) m/s for 0% cement, 2.45 \(\times\) 10\(^{-10}\) m/s for 1% cement, and 1.96 \(\times\) 10\(^{-10}\) m/s for 2% cement, with coefficients of variation in the range of 56 to 60%. It should be noticed that the values observed are in the same order of magnitude, and vary within a range that could be most likely explained by experimental error. However, the trend observed is consistent with previous studies. Zhang et al. (2004), Lemos (2006), and Knop et al. (2008), for instance, have shown that the addition of Portland cement might con-
tribute to hydraulic conductivity reduction, mainly because of the reduction in porosity and changes in microstructure. Moreover, the values obtained are within the range proposed by Daniel (1993) for compacted clay barriers (< $10^{-9}$ m/s).

Figure 3 shows the hydraulic behavior observed in two tests carried out with 2% cement content and percolation of contaminant solutions at pH 1. It can be noticed that after the seventh day, when contaminant percolation initiated, the hydraulic conductivity showed a slight increase followed by a consistent decline, showing the presumable effect of the acidic percolation on the cemented soil structure. Dissolution and transport of soil particles was not observed in these tests. Similar results were obtained by Lemos (2006), who worked with a mixture of soil, cement, and bentonite subjected to sulfuric acid percolation over 20 weeks. Both results, however, are in disagreement with Daniel (1993), who points out that strong acids can dissolve soil compounds, forming preferential channels and increasing hydraulic conductivity. What probably occurred was the acidic dissolution of hydrated cement particles at first, resulting in the observed slight increase in hydraulic conductivity immediately after the contaminant solution insertion, followed by soil structure reorganization and collapse, which caused the reduction in hydraulic conductivity. However, the results presented herein should be interpreted cautiously, since long-term permeability tests are necessary to establish a complete pattern of behavior with time.

### 3.2. Contaminant transport parameters

The contaminant transport parameters obtained from diffusion tests and the corresponding statistical analysis (ANOVA) are summarized in Tables 1, 2, and 3. In Tables 2 and 3, the so-called $p$-values represent the probability or the margin of error associated to the conclusion that a control variable (cement content, pH, static load) has a significant effect on the response variable ($R_d$ or $D^*$).

The statistical analysis indicated that the vertical static load had no effect whatsoever on the transport parameters for both metals, possibly because there is no flow in diffusion tests and consequently no consolidation occurs. It should be noted, however, that this is not usually the case with field conditions, in which coupled diffusion-advection-consolidation phenomena can be relevant to actual barrier performance. Furthermore, the effective diffusion coefficient ($D^*$) was influenced only by cement content and only for lead. Consequently, only the average values of $D^*$ for each cement content are presented in Table 1 for lead. For the same reason, only the overall average value of $D^*$ is presented for cadmium. Figure 4 shows the average effect of cement content on the effective diffusion coefficient for lead. A noticeable reduction in $D^*$ is observed as the cement content increases.

Regarding the retardation factor, the statistical analysis showed that it was significantly affected by both cement content and pH, as well as by their interaction. Figures 5

![Figure 3 - Hydraulic behavior of the 2% cement content under the pH 1.](image)

<table>
<thead>
<tr>
<th>Cement content (%)</th>
<th>Solution pH</th>
<th>Retardation factor $R_d$</th>
<th>Effective diffusion coefficient $D^*$ (m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Lead</td>
<td>Cadmium</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>4.0</td>
<td>1.4</td>
</tr>
<tr>
<td>0</td>
<td>3.5</td>
<td>150.0</td>
<td>38.7</td>
</tr>
<tr>
<td>0</td>
<td>6</td>
<td>196.3</td>
<td>13.4</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>2.9</td>
<td>2.5</td>
</tr>
<tr>
<td>1</td>
<td>3.5</td>
<td>42.0</td>
<td>37.6</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>156.9</td>
<td>147.3</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>16.8</td>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
<td>3.5</td>
<td>20.1</td>
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</tr>
<tr>
<td>2</td>
<td>6</td>
<td>15.1</td>
<td>64.8</td>
</tr>
</tbody>
</table>
and 6 show the retardation factor ($R_d$) variation with cement content and pH, for both lead and cadmium, respectively.

It can be readily observed that for the metal lead (Fig. 5) the increase in pH caused an overall increase in $R_d$. However, with the addition of cement an interaction effect occurred: as the cement content increased from 0 to 1%, the effect of pH on $R_d$ became less pronounced, and for 2% cement no effect was observed. This behavior was probably caused by the immediate rise in pH due to cement addition, which produced a higher rate of precipitation rather than adsorption reactions. Thus, the reduction in the availability of lead to the adsorption process and diffusion resulted in

Table 2 - Summary of the statistical analysis (ANOVA) for $R_d$ and $D^*$ obtained from diffusion tests for lead.

<table>
<thead>
<tr>
<th>Control variable</th>
<th>p-value</th>
<th>Retardation factor - $R_d$</th>
<th>Effective diffusion coefficient - $D^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main effects:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cement content</td>
<td>0.02</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>0.01</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Static load</td>
<td>0.28</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>Interaction effects:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cement content vs. pH</td>
<td>0.03</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Cement content vs. static load</td>
<td>0.34</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>pH vs. Static load</td>
<td>0.46</td>
<td>0.51</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 - Summary of the statistical analysis (ANOVA) for $R_d$ and $D^*$ obtained from diffusion tests for cadmium.

<table>
<thead>
<tr>
<th>Control variable</th>
<th>p-value</th>
<th>Retardation factor - $R_d$</th>
<th>Effective diffusion coefficient - $D^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main effects:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cement content</td>
<td>0.06</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>0.02</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>Static load</td>
<td>0.36</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>Interaction effects:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cement content vs. pH</td>
<td>0.13</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>Cement content vs. static load</td>
<td>0.89</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>pH vs. Static load</td>
<td>0.97</td>
<td>0.99</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 4** - Effective diffusion coefficient variation with cement content for lead.

**Figure 5** - Retardation factor variation with pH and cement content for lead.
Regarding the metal cadmium, a different pattern is depicted in Fig. 6. It is likely that precipitation reactions have also occurred, but at lower intensity as compared to lead. As indicated in Fig. 6, it seems that the predominance of precipitation over adsorption reactions occurred only for the combination of pH 6 and 2% cement, which was not sufficient to reduce the effective diffusion coefficient $D^*$. Similar findings are reported in the literature. According to Raymond (2001), the metal lead is precipitated in soil at lower pH values when compared to cadmium, which explains the more pronounced effect of pH observed for the tests carried out with lead. This can also be explained by the larger chemical reduction potential of lead when compared to cadmium, resulting in a larger potential to receive electrons and precipitate in the form of salts. In addition, the influence of pH on the adsorption reactions has been investigated by various authors (e.g. Lee, 1998; Wu & Li, 1998), who explained that the adsorption is more significant for higher pH values because of the increased negative charges on soil particle surfaces. Also, as indicated by the transport parameters presented in Fig. 6, the metal lead shows lower mobility and greater retention when compared to cadmium (Yong et al., 1992).

4. Conclusion

The present study aimed to contribute to the understanding of the response of geomaterials submitted to boundary conditions similar to those encountered in the field, such as in the case of bottom barriers in industrial or mining waste disposal facilities. The transport parameters investigated are relevant to modeling studies of subsurface contamination plumes and decision-making processes associated with design and management of engineered systems.

The investigated compacted mixtures showed low hydraulic conductivity coefficients ($< 10^{-9}$ m/s), with values that decreased with increasing cement content. Regarding the reactive behavior, the retardation factor ($R_d$) increased mainly with the increment in the pH of the contaminant solution, thus increasing metal retention. The effective diffusion coefficient $D^*$ was not affected for the metal cadmium, but was reduced for lead. The coupled effect of increasing both pH and cement content caused a higher rate of chemical precipitation reactions, which predominated over adsorption reactions, in particular for the metal lead, allowing the contaminant to remain in solution and favoring its solubilization in acidic conditions.

Further studies are necessary to assess the effects of the variables studied on the long-term hydraulic behavior, advective-diffusive parameters, mechanical response (deformability and strength), and microstructure, such as variations in porosity, as well as chemical and mineralogical modifications.

Acknowledgments

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![Figure 6 - Retardation factor variation with pH and cement content for cadmium.](image-url)


**List of Symbols**

c: Contaminant concentration at the depth $x$ from the top of the specimens
c$_0$: Initial concentration of the contaminant solution
Cd: Cadmium
CEC: Cation Exchange Capacity
$D^*$: Effective diffusion coefficient and erfc: Complementary error function.
H_: Effective height of the contaminant solution in the inlet cylinder
$K_r$: Partition Coefficient
n: Specimen porosity
Pb: Lead
$R_d$: Retardation factor
S: Adsorption
t: Time
$x$: Distance
$\rho_{sd}$: Specimen dry density