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Project Summary

Parameters Affecting the Measurement of Hydraulic Conductivity for Solidified/ Stabilized Wastes

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A series of experiments conducted at the Alberta Environmental Centre examined the variation in hydraulic conductivity (K) within and among three matrices formed by steel mill baghouse dust treated with 8%, 9% and 10% Normal Portland Cement at a water/cement ratio of 1:1. Within the 8% and 9% matrices, test gradient (i) and back pressure (P) were combined into 3 x 3 factorial treatments. Commercially available equipment was modified to allow sensitive and continuous monitoring of hydraulic conductivity. A permeant-matrix interaction was indicated by K decreasing with time at a rate that increased with higher cement contents. After hydraulic conductivity testing, the samples were examined by scanning electron microscopy and energy dispersive x-ray analysis. A cement hydration product, identified as ettringite, had formed in the solidified/stabilized waste pores. This product reduced hydraulic conductivity by two orders of magnitude by restricting conducting pores. Four to seven weeks of testing were required before an acceptable equilibrium had been reached and statistical comparisons among the i x P treatments were made. Within each matrix, gradient was statistically the most significant parameter accounting for 60% of the variation in results. The response to gradient was different than that observed with clay and soil-liners in the literature. The overall mean hydraulic conductivity of the 8% matrix ($10 \pm 5 \times 10^{-6}$ cm.sec^{-1}) was significantly greater ($p \leq 0.01$) than that of the 9% matrix ($0.06 \pm 0.03 \times 10^{-6}$ cm.sec^{-1}). Temporal effects, gradient and cement content were identified as important factors affecting hydraulic conductivity measurements and must be considered in regulatory tests. Bulk density was a useful quality control criterion for minimizing sample variance within each matrix.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Solidification/stabilization processes are widely used to treat wastes before their disposal, especially those containing heavy metals. These processes reduce the potential for release of such contaminants by removing free water, i.e., forming a monolith (thereby reducing the surface area available for leaching) and by reducing contaminant solubility by alkaline precipitation or incorporation into cement hydration products.

One of the routes of contaminant release is through dissolution and flow through the bulk of the treated waste. Hydraulic conductivity, defined below by Darcy's law, is thus important:

$$K = \frac{Q}{iA}$$

where K is hydraulic conductivity (cm. sec^{-1}), Q is flow rate (cm^3. sec^{-1}) through a cross-sectional area of A (cm^2), and i is gradient (dimensionless), defined as head loss or pressure drop (cm H_2O) per unit length of the solid (cm).

Hydraulic conductivity and permeability, which are often incorrectly interchanged, are related by:

$$\kappa = \frac{K\mu}{\rho g}$$

where κ is permeability (cm^2), μ and ρ are absolute viscosity ($g.cm^{-1}.sec^{-1}$) and density ($g.cm^{-3}$) of the fluid, respectively, and g is gravitational acceleration (980 $cm.sec^{-2}$).

When there is no fluid-solid interaction, permeability is an intrinsic and useful property of a solid: the flow rates of different fluids through it can be computed from its permeability and the properties of the liquids. As shown in the report as summarized here, however, this is not necessarily the case with solidified/stabilized waste. Moreover, since it is not the solid property *per se*, but the flow rate of aqueous permeant through it which is of interest, hydraulic conductivity will be used herein.

The available literature deals predominantly with clay and soil liners. Test and instrument parameters, such as saturation, gradient and back pressure, as well as temporal effects and sample preparation, have been identified as being important factors in hydraulic conductivity measurements. The corresponding information on solidified/stabilized waste is, however, practically non-existent. Nor is there sufficient information that addresses the differences between clay or soil liners and solidified/stabilized waste, such as those in compressive strength and permeant-matrix interactions.

This report deals with the effects of parameters affecting the measurement of hydraulic conductivity of solidified/stabilized waste. The study was undertaken to form bases for the development of a regulatory test method - to improve intra- and inter-laboratory precision - and for correlating accelerated laboratory test results to those occurring under field conditions.

The scope of the investigation was limited to:

- one waste, steel mill baghouse dust, treated with Normal Portland Cement at different formulations to produce a range of hydraulic conductivities typical of those achieved by other commercial solidification/stabilization processes, and
- the following test and instrument parameters: sample preparation, temporal effects, gradient and back pressure.

New equipment was acquired and modified to allow for sensitive, accurate, and continuous flow measurements. Particular attention was given to minimize variance due to sample preparation, statistical methods, and experimental designs. Electron microscopy, chemical analyses, and measurements of physical properties were conducted to assist in the interpretation of the observed phenomena.

Materials, Methods and Procedures

Sample Preparation

Equal portions of steel mill baghouse dust and silica sand (42, 41, and 40 wt.%) were treated with equal portions of Normal Portland Cement and water (8, 9 and 10 wt.%). The products are referred to as 8%, 9% and 10% matrices, respectively.

The waste and the treatment were chosen to be those commonly encountered in practice. The formulations, including the use of sand, were selected to produce samples with a range of hydraulic conductivities typical of solidified/stabilized wastes (10^{-6} to 10^{-8} $cm.sec^{-1}$). To obtain samples, the dry ingredients were mixed, water was added and mixed, and the product was compacted into cylindrical plastic molds (7.6 cm diameter by 15.2 cm long) with the use of a standard method. The samples were cured for at least 28 days at 23°C and a minimum relative humidity of 95%.

After curing, the samples were removed from the molds and then trimmed to ensure parallel end faces. The bulk density of each sample was computed from measurements of its mass and dimensions. For each matrix, the mean bulk density of all the samples prepared was computed. Only those samples with bulk densities within 0.5% of the mean were used.

Sample Characterization

In addition to bulk density and water content, the specific gravity of the dried samples (true density) was measured, from which porosity and degree of saturation could be computed. To determine the effect of hydraulic conductivity testing, these destructive measurements were made on samples after testing as well as on companion samples that had not undergone testing. The unconfined compressive strengths of these companion samples were also measured.

Equipment

Three flexible-wall permeameters were used. The equipment featured a novel method for measuring permeant flow rate, using the movement of a piston inside a permeant interface. This piston was connected to a linear variable displacement transducer, the output of which was digitized and logged in a data logger. The inlet and outlet flow rates were simultaneously measured.

Two major modifications were made. The first was the replacement of the transducers to achieve 0.001-mm accuracy over a 30-mm range. The second was the use of a bladder interface to isolate the pneumatic pressurization system from the permeameter cell water.

Hydraulic Conductivity Measurements

After vacuum saturation was applied, the inlet and outlet flow rates were computed using volume measurements, from the calibrated piston movement, and the corresponding elapsed times. Hydraulic conductivity was computed when the inlet and the outlet flows were within 5%.

Other Measurements

Electron microscopic analyses were performed on a Hitachi S510* scanning electron microscope (SEM), a Hitachi X-650 (SEM) with energy dispersive X-ray spectrometer, and a Hitachi H-600 scanning transmission electron microscope (STEM) equipped with a Kevex Be window X-ray detector. Chemical analyses of the waste and the exuded permeant were performed with the use of ion coupled spectroscopy, atomic absorption spectroscopy, colorimetry and potentiometric titration.

Experimental Design

The effects of sample formulation, time and instrument parameters (gradient, i, and back pressure, P) were studied as follows. A 3 x 3 full factorial design was used to determine the effects of i and P. The values for i were 8, 116, and 227, and for P were 14, 69, and 124 kPa.

The hydraulic conductivity of each of the 8%, 9%, and 10% matrices was concurrently measured using the three permeameters. To study the initial temporal effects, median levels of i and P were used. After suitable equilibrium was reached, i and P were then varied in a random manner according to that design. Equilibrium was defined as when the variation of hydraulic conductivity with time, as computed from the slope of a linear regression, could not be proven to be different from zero. Because of time constraints, the full factorial design was applied only to the 8% and 9% matrices. In addition, three 8% matrix samples were tested concurrently at median levels of i and P over

* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

a 29-day period to obtain precision values.

Results and Discussion

Bulk Density

Although a standard compaction procedure was carefully applied, there were overlaps in bulk density among the selected matrices, as shown in Table 1.

The criterion of selecting only those samples within ±0.5% of the sample mean of each matrix was thus applied to ensure distinct populations.

Temporal Effect

The hydraulic conductivity of each matrix decreased with time in a manner that could be described by the following equation:

$$K \times 10^6 = A\,(T+1)^B$$

where T is elapsed time, in days, from the first day of testing at T=0. The least-squares values of A and B (referred to as the power function intercept [initial value] and slope, respectively, and computed over 80 days of testing at median levels of i and P) are given in Table 2.

Two interesting observations can be made: there was a marked difference in initial value between the 8% and 9% matrices but not between the 9% and 10% matrices; and the negative slope increased in magnitude with increasing cement content. The first observation can be readily explained in terms of granular versus paste-like behavior resulting from differences in cement and water contents. The second, which suggests some form of cement hydration reaction, will be discussed in the following section.

The decrease in hydraulic conductivity with time, up to two orders of magnitude for the 10% matrix, was the opposite of what was anticipated at the onset of the project. Due to matrix dissolution, it was expected that the connecting pores in the matrix, and hence hydraulic conductivity, would increase. Matrix dissolution did occur quite significantly. In some cases, more than 1% of the sample weight was lost over 80 days of testing. Yet, the hydraulic conductivity decreased with time. The results of the investigation into this phenomenon are described below.

Mechanisms of the Decrease in Hydraulic Conductivity

Visual inspections of the samples after testing showed the presence of white materials in the dark-colored matrix. SEM examinations revealed profuse fibrous growth, the morphology of which was similar to that of ettringite ($3CaO.Al_2O_3.CaSO_4.31H_2O$), rather than to that of a cement hydration product, such as calcium silica-hydrate or calcium hydroxide. X-ray analyses of the individual fibres revealed the presence of Ca, Al, S and traces of Fe, and a Ca/S ratio of 2.62±0.52. These results suggest the presence of mainly aluminoferrite trisulphate (Ca/S=2.1) and some aluminoferrite monosulphate (Ca/S=4.1).

The formation of fibrous materials was a result of permeant-matrix reactions. No such formation was observed in companion samples that were kept in a humidity chamber.

The above phenomenon has been previously reported. The hydraulic conductivity of cement pastes could be reduced by six orders of magnitude as a result of curing under water. The explanation was given in terms of expansion in volume of hydrated paste and hydration products filling the pores and cavities, thereby reducing and blocking flow channels.

Effect of Matrix

As previously mentioned, there was a marked difference in hydraulic conductivity between the 8% and 9% matrices. Even when the effects of time, i and P are not considered, a statistically significant difference ($p<0.01$) in hydraulic conductivity exists between them: $10\pm5 \times 10^{-6}$ cm.sec^{-1} versus $0.06\pm0.03 \times 10^{-6}$ cm.sec^{-1}. Hydraulic conductivity is thus very sensitive to matrix composition.

Effect of Instrument Parameters

The effects of i and P were investigated after equilibrium conditions were reached. By the criterion used, these were reached after 27, 34, and 59 days of testing for the 8%, 9% and 10% matrices, respectively. Note however that the criterion is based on failure to reject the null hypothesis of zero slope. The power of the test and the Type II error were not considered. Temporal effect could still be present, and this would be considered as random errors.

The variation of hydraulic conductivity with gradient and back pressure was modelled according to a second order polynomial of the form:

$$Kx10^6=b_0+b_1x_1+b_2x_2+b_{11}x_1^2+b_{22}x_2^2+b_{12}x_1x_2$$

where x_1 and x_2 are the transformed (range from -1 to +1) i and P, respectively. The regression results are shown in Table 3.

The results show statistically significant effects of gradient for the 8% matrix, with a positive linear term and a negative quadratic term; and gradient and back pressure for the 9% matrix, with only positive linear terms. The equations show that K is less sensitive to i and P at high and median levels, and thus is the region where hydraulic conductivity should be measured to minimize variability.

The gradient was varied by a factor of 25, and the back pressure by 8. Yet the

Table 1. *Bulk Density of Stabilized Waste Samples*

	Matrices, cement percent weights		
	8%	*9%*	*10%*
Mean Bulk Density, (SD) * *(gms per cm³)*	*2.398 (±0.024)*	*2.480 (±0.043)*	*2.527 (±0.363)*
Relative Standard Deviation (n)⁺	*1.00 (16)*	*1.73 (18)*	*0.36 (16)*

* *SD = Standard Deviations.*
⁺ *= Number of Samples.*

Table 2. *Temporal Effect: Regression Analysis Results* *

	Matrix		
	8%	*9%*	*10%*
Initial Value, ±se ⁺	*82.4 ± 4.4*	*1.571 ± 044*	*1.356 ± 0.148*
Slope, ±se	*-0.413 ± 025*	*-0.743 ± 0.032*	*-1.476 ± 0.070*

* *The models account for more than 98% of observed variation in hydraulic conductivity.*
⁺ *Standard error; significance levels p<0.001.*

Table 3. *Regression Analysis Results*

Matrix	Coefficient b_0	b_1	b_2	b_{11}	b_{22}	b_{12}	n^+
8%	13.01* (0.8)§	2.33× (0.7)	0.18 (0.7)	-4.3× (1.1)	-1.2 (1.1)	-0.3 (0.9)	22
9%	0.06× (.005)	0.023× (.005)	0.015× (.0005)	-0.013 (.008)	0.003 (.008)	-0.001 (.006)	26

* The models account for 68% and 58% of the total variance for the 8% and 9% matrices, respectively.
n^+ Number of data points.
§ Standard error of the coefficient.
× Significant effect at $p<0.01$.

variation in hydraulic conductivity was less than 4-fold for the 9% matrix, and less than 3-fold for the 8% matrix. Therefore, as a first approximation and only with respect to the effects of i and P, accelerated laboratory conditions produced results close to what might be found in the field.

Distribution and Precision

Log-transformation has been suggested as a way to normalize the data and obtain constant variance. The triplicate measurement results for the 8% matrix were log-transformed. The null hypothesis of normal distribution could not be rejected for the transformed data. The precision values are shown in Table 4.

For comparison, a precision of x/÷ 7.3 for four replicates was reported in a previous study on solidified/stabilized waste. The improvement could be attributed to sample preparation, sample acceptance criterion and measurements at higher levels of i and P.

Correlation with Porosity

For the 8%, 9%, and 10% matrices, the hydraulic conductivity and porosity E could be correlated by:

$$K=2.83 \times 10^{-29}\ 10^{72.5E}$$

with $p<0.0001$ and $r^2=0.89$. It should be emphasized, however, that only one waste/treatment combination was used.

Saturation

Saturation is defined as the ratio of free water to pore volume. Changes in saturation as a result of testing are shown in Table 5.

There was a marked increase in saturation, which in part was effected in the beginning of the testing when vacuum saturation was applied. In the field, however, the treated waste would not be saturated. The effect of not saturating the sample, coupled with applying low levels of gradient and back pressure, still needs to be investigated.

Table 5. *Permeant Saturation Before and After Testing*

Testing	Matrix 8%	9%	10%
Before	35%	42%	52%
After	96%	93%	94%

Table 4. *Results of Log-Transformation for the 8% Matrix*

Log Transformation	Test Day 1	8	15	22	29
Mean	-3.94	-4.31	-4.48	-4.61	-4.78
(SD)*	(.18)	(.25)	(.23)	(.26)	(.24)
Precision +: x/÷	3.80	4.4	4.25	4.48	4.36

* Standard Deviation.
\+ 95% confidence limits for mean K for three samples.

Effect of Gradient: Comparison with Soil/Clay Liners

High gradients applied to soil/clay samples have been reported to cause consolidation and the consequent reduction in hydraulic conductivity. This seems reasonable considering that clay, with a typical unconfined compressive strength (UCS) of 100 kPa, would be subjected to a pressure of up to 450 kPa (for 15 cm sample length at a gradient of 300). For comparison, the samples used in this study had a range of UCS from 3000 to 6000 kPa, and were subjected only to a maximum pressure of 340 kPa. This may explain the difference in the effect of gradient between soil/clay and solidified/stabilized waste.

Conclusions and Recommendations

Conclusions

1. Hydraulic conductivity was sensitive to matrix composition. Significantly different hydraulic conductivities were measured between samples differing only by 1% in cement content. The ability to distinguish such samples was attributed to the institution of a strict quality control criterion on the basis of bulk density. The corollary is that variance resulting from sample preparation can be minimized by using that criterion.
2. Hydraulic conductivity decreased with elapsed time during testing. A power function in the form of $y=ax^b$ describes the relationship. The decrease could be explained by long-term cement hydration reactions forming ettringite in the permeant-conducting pores. Although matrix dissolution occurred, no effect was observed over the testing period of up to 80 days.
3. The effects of gradient and back pressure on hydraulic conductivity were the following:
   - Gradient was the most significant parameter, and its correlation with hydraulic conductivity was positive, the opposite to that for soil and clay liners. This was attributed to the higher unconfined compressive strength and the corresponding lesser degree of sample consolidation.
   - Medium and high levels of gradient and back pressure were the less sensitive region for hydraulic conductivity measurements. Falling-head permeameters, in which low levels of these parameters are used, are thus operated in the more sensitive region.

- Over the entire region of the chosen experimental levels, the measured hydraulic conductivities varied by a factor of four or less. Values obtained in the laboratory are thus reasonable estimates of those in the field conditions, provided that compaction and curing conditions are similar.

4. An exponential relationship between hydraulic conductivity and sample porosity was shown to be statistically significant. How such a relationship varies with different matrices was not investigated.

Recommendations for Regulatory Test Development

1. Bulk density should be used as a quality control criterion to reduce variance resulting from sample preparation.
2. To improve precision, temporal effects should be taken into account and measurements carried out at high levels of gradient and back pressure.
3. To estimate maximum hydraulic conductivity, measurements should be made as soon as the sample is cured.

Recommendations for Future Work

1. Other common waste/treatment systems should be studied to investigate permeant-matrix interactions and the effect of instrument parameters.
2. Saturation effects should be studied to predict field hydraulic conductivity.

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The complete report, entitled "Parameters Affecting the Measurement of Hydraulic Conductivity for Solidified/Stabilized Wastes," (Order No. PB93-199 396/AS; Cost: $19.50, subject to change) will be available only from:
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