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Project Summary

Reactivity of Various Grouts to Hazardous Wastes and Leachates

Andrew Bodocsi, Mark T. Bowers and Roddy Sherer

A laboratory study was conducted to evaluate the potential of selected grouts for controlling the percolation of leachates from hazardous solid waste landfills or hazardous waste ponds. In the course of the study, seven different grouts were subjected to permeability tests and four of the grouts were tested for their reactivity by an immersion type test. Eight different chemicals, some with two concentrations, and two real-site wastes were used as permeants in the permeability tests, and as liquids for the immersion baths.

Of the seven grouts, the acrylate, cement-bentonite (mix 2), and urethane grouts had the lowest baseline permeabilities with water, ranging from 2.3 x 10^{-10} to 3.6 x 10^{-9} cm/sec. During permeability testing with chemicals, the acrylate grout exhibited excellent resistance to the paint and refinery wastes, 25% acetone, 25% methanol, and sodium hydroxide. It performed satisfactorily with cupric sulfate, ethylene glycol, and xylene, and was seriously damaged by aniline, 100% acetone, hydrochloric acid, and 100% methanol. The permeability of the cement-bentonite (mix 2) grout was tested with acetone, aniline, cupric sulfate, hydrochloric acid, methanol, and sodium hydroxide. With every one of these chemicals the permeability of the grout improved, ultimately reaching a practically impervious state. The urethane grout maintained its low permeability with acetone, aniline, ethylene glycol, methanol, paint waste, refinery waste, and hydrochloric acid and it performed marginally well with cupric sulfate. However, the urethane lost its low permeability with sodium hydroxide and xylene.

Based on the comparison of permeability and reactivity test results, a scheme was proposed to correlate the permeability changes of grouts to the weight and consistency changes that may occur during their reactivity testing.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research 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

One of the major environmental problems facing the nation is the threat of contamination of groundwater from leaking hazardous waste landfills and hazardous waste ponds. If a waste site is underlain by an impervious stratum, the most cost-effective remedy may be using a cutoff slurry wall constructed around the site and keyed into the aquiclude. However, if there is no impervious stratum below the waste, the remedy may be the construction of a bottom seal created by injection grouting, in conjunction with a vertical slurry wall. Alternately, both the bottom seal and side wall may be made by injection grouting.

Injection grouting has been used for many years for stabilizing soils, to provide cutoff curtains under dams, for stabilizing tunnels, and more recently it was proposed for containment of hazardous waste.

When constructing an impervious barrier by injection grouting under a waste site, the grout must thoroughly penetrate the soil. After expelling the waste from the voids the grout must set and harden in the soil. In addition, the hardened grout must provide a durable impervious seal even when permeated by hazardous leachate.

The purpose of this study was to test the permeability and reactivity of selected grouts with 10 chemicals to determine if the grouts had the durability to withstand the typical hazardous waste site environment, and thus could be considered for horizontal seal construction.

The permeability test results indicate that certain grout-chemical combinations caused the deterioration of the permeability of the grout, while others resulted in little or no detrimental changes. The reactivity test results show what effect chemical baths had on grout samples; some combinations caused weight gains, others weight losses, and still others caused no changes. In addition, changes in sample consistency were observed. The combined analysis of the two tests resulted in correlations that allow prediction of permeability changes from reactivity test results.

Materials and Methods

All permeability tests and most reactivity tests were conducted on grouted soil samples. The permeability testing was conducted in specially constructed permeameters and safe environmental boxes, using selected chemicals as the permeants. The reactivity samples were tested by their immersion in selected chemical baths.

The detailed description of the grouting procedure, the permeameters, the permeability measuring apparatuses, and the permeability and reactivity testing procedures may be found in a separate report of the same title as this summary.

Grouts Used

In the typical batch of the cement-bentonite (mix 1) grout 3000 g Type III cement, 120 g bentonite, and 6000 ml water was used, resulting in a water-cement ratio of 2.0. The batches of cement-bentonite (mix 2) grout were made up of 3000 g MC-500 microfine cement, 120 g bentonite, 30 ml dispersant, and 2250 g water, yielding a water-cement ratio of 0.86. For ease of injection, pea gravel was used as the soil with both grouts.

The sodium silicate grout selected was SIROC 132*, distributed by Raymond International, Inc. It consisted of 60% modified silicate, 25% water, 10% formamide, and 5% calcium chloride. A fine Mason's sand was used as the soil to avoid syneresis. Later extensions to the work included a glyoxal-modified sodium silicate grout and a sodium aluminate-modified sodium silicate grout in order to reduce the permeability of these grouts.

The urethane grout selected was CR360, a product of the 3M Company. A mixture of 89.2% water, 5.7% CR361 (gel inhibitor), and 5.1% CR360 (urethane polymer solution) was chosen. A silica sand was used with this grout.

AC-400, distributed by Avanti International, was chosen to represent the acrylate grouts. A mixture of 73.44% water, 24.99% AC-400, 0.74% triethanolamine (catalyst), 0.74% ammonium persulfate (initiator), and 0.074% potassium ferricyanide (inhibitor) was used. Silica sand was used as the soil.

Chemicals and Hazardous Leachates Used

For this study, eight different chemicals and two real-site leachates were selected. Acetone, aniline, cupric sulfate, ethylene glycol, hydrochloric acid, methanol, sodium hydroxide and xylene were used. The real-site leachates used were a refinery waste and a paint waste, which were obtained from lysimeter studies conducted at the Center Hill Solid and Hazardous Waste Research Facility in Cincinnati, Ohio.

Results and Discussion

Permeability Test Results with Water

Before the samples were tested with chemicals, they were permeated with deionized water to establish their equilibrium baseline permeabilities. Three of the grouts tested had very low baseline permeabilities with water: acrylate ($k = 5.1 \times 10^{-10}$ cm/sec), cement-bentonite (mix 2) ($k = 2.3 \times 10^{-10}$ cm/sec), and urethane ($k = 3.6 \times 10^{-9}$ cm/sec). The permeabilities of the other four grouts with water exceeded 1×10^{-7} cm/sec.

Permeability Test Results For Urethane Grout with Chemicals

Figure 1 illustrates in a bar chart form the overall permeability changes of urethane grout with 10 selected chemicals. On the left vertical axis of the chart permeability is plotted on a log scale. On the right vertical axis the equilibrium permeabilities of the urethane grout samples with water are indicated. Each shaded bar represents the average changes in the permeability of the grout with one of the chemicals. Each bar starts at the equilibrium permeability of the grout with water, and may go up or down, or remain unchanged, depending on the reaction of the grout with the specific chemical. In most cases the bar first rises to a dashed line that represents the permeability of the grout at the first peak of its permeability with flow. The bar may rise further and terminate at a permeability level that corresponds to the final equilibrium permeability of the grout with the specific chemical. The number on each line gives the number of pore volumes of chemical which flowed through the sample before it reached the indicated permeability.

As shown, the urethane grout remained quite impervious with the majority of the chemicals. With 20% cupric sulfate and 4N hydrochloric acid the grout performed marginally, as its final permeability slightly exceeded the 1×10^{-7} cm/sec level. The most detrimental to the urethane grout were the 25% sodium hydroxide and xylene. The sodium hydroxide caused a 4.5 orders of magnitude increase, raising the equilibrium permeability of the grout to much above the 1×10^{-7} cm/sec level.

The bar chart in Figure 2 shows the effects of concentration of selected chemicals on the final permeability of the urethane grout. As shown, varying the concentrations can have varying effects on the permeability of this grout.

Permeability Test Results for Acrylate Grout with Chemicals

The acrylate grout exhibited excellent resistance to real-site paint and refinery wastes, and 25% sodium hydroxide. Its performance was satisfactory with 20% cupric sulfate, 100 % ethylene glycol and xylene. The aniline 100% acetone, 4N hydrochloric acid, and 100% methanol were very detrimental to the permeability

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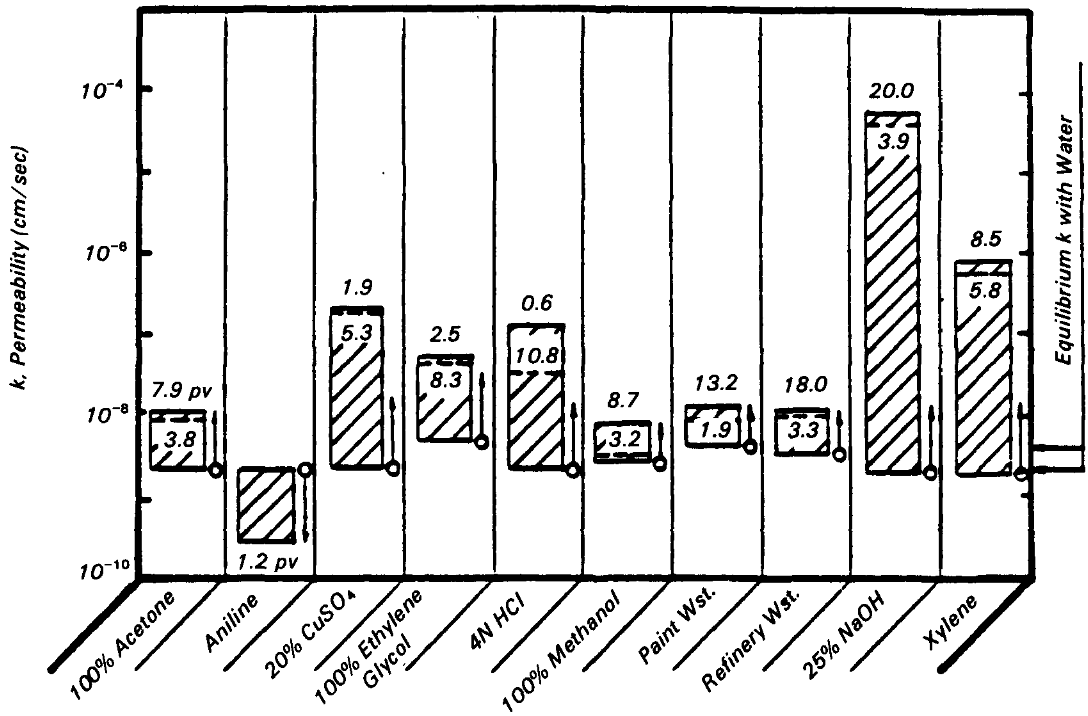

Figure 1. Permeability of urethane grout with various chemicals.

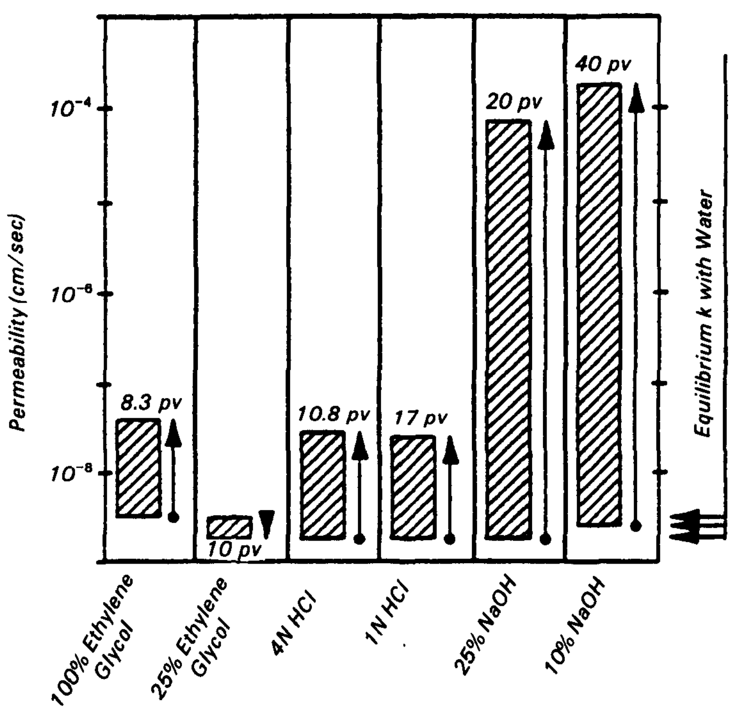

Figure 2. Effect of leachate concentration on the permeability of urethane grout.

of this grout. The permeability of the grout actually decreased with the introduction of 25% sodium hydroxide.

Permeability Test Results for Cement-Bentonite (Mix 2) Grout with Chemicals

With both water and chemicals, this grout was the most impervious of all tested. The introduction of every chemical caused the permeability of the grout samples to decrease from their baseline permeabilities with water. With very small amounts of flow of between 0.1 and 0.6 pore volumes, the permeabilities of the samples dropped to between 3 x 10^{-11} and 6 x 10^{-11} cm/sec, or to a practically impervious state. Because of their very low permeability, these samples allowed very low flow volumes, even though they were tested on the average for more than 120 days. It is possible that given enough time and flow, these chemicals could increase the permeability of the grout, but it would take very long testing times.

Permeability Test Results for Other Grouts with Chemicals

In addition to the above discussed grouts, cement-bentonite (mix 1), sodium silicate, glyoxal-modified sodium silicate, and sodium aluminate-modified sodium silicate grouts were also tested.

A detailed description of the test results, including bar chart summaries, may be found in a separate report of the same title as this summary.

Reactivity Tests

The objectives of the reactivity tests were to observe the weight and volume changes that small samples of the various grouts underwent during their immersion in selected chemical baths, and to explore if these observations could be correlated with the corresponding permeability test results.

In this research the four grouts tested for their reactivity were acrylate, cement-bentonite (mixes 1 and 2), and urethane. The testing consisted of immersing the grout samples in selected chemicals and weighing them after elapsed times of 1, 7, 14, 28, 56, and 84 days. Plots of percent weight change versus time were prepared for each sample and replicate series. In addition, subjective observations were made and recorded on the shrinkage, swelling, spalling, hardening, softening and stickiness of the samples. The results ranged from total disintegration to as much as a 40% weight increase.

Comparative Analysis of Permeability and Reactivity Tests

The results from the two types of tests were analyzed, compared, and a scheme was proposed to allow the prediction of the permeability behavior of grouts with various chemicals from their behavior with the same chemicals in the reactivity tests. This scheme is summarized in Table 1, where weight and volume changes in the vertical columns, and consistency changes in the horizontal rows are correlated with permeability changes indicated in the boxes. For example, the urethane samples in xylene baths underwent medium (10%, authors' classification) weight losses, and they also became hard. This case corresponds to the matrix location of column 2 and row 2, which reads: "Permeability increases significantly." Indeed, going back to Figure 1, it is seen that the permeability of the urethane grout with xylene increased almost three orders of magnitude before it came to an equilibrium. It is proposed that with the presented correlations, the choice of the most suitable grout for a site could possibly be made based on reactivity tests only, and furthermore, the tests could be conducted at the site of the hazardous waste.

Conclusions

1. When tested for permeability, the urethane grout remained quite impervious with the majority of the chemicals tested, except it performed only marginally with a 20% solution of cupric sulfate and the 1N and 4N concentrations of hydrochloric acid, and poorly with the 25% solution of sodium hydroxide and reagent grade xylene.
2. The acrylate grout exhibited excellent to satisfactory resistance to all chemicals, except reagent grade aniline, 100% acetone, 1N and 4N concentrations of hydrochloric acid, and 100% methanol. These caused increases of several orders of magnitude in its permeability.
3. With all the chemicals tested, the permeability of the cement-bentonite (mix 2) grout decreased from its baseline permeability with water to a practically impervious permeability of approximately 3 x 10^{-11} cm/sec.
4. The effects of the concentration of chemicals on the permeability of grouts varied. It was found from the limited data that certain chemicals with reduced concentrations caused smaller increases in the permeability of grout than those with higher concentrations, while varying the concentration of other chemicals had no significant effects on the permeability of the grout.
5. From the analysis of reactivity and permeability test results, a scheme was proposed that correlates the weight and consistency changes of the reactivity samples of a grout immersed in a chemical to expected changes in its permeability when permeated by the same chemical. This may allow an engineer to make at least the preliminary selection of suitable grouts for a site by using reactivity tests in place of the more costly permeability tests.

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Table 1. *Predicted Permeability Behavior Based on Reactivity Test Results*

Weight/Volume Changes / *Consistency Changes*	*Volume Increase/Weight Gain*	*Volume Decrease/Weight Loss*	*Weight Loss by Spalling*	*Initial Volume Increase, Later Shrinkage (Initial Weight Gain, Weight Loss as Test Proceeds)*	*Initial Volume Decrease, Later Volume Increase (Initial Weight Loss, Weight Gain as Test Proceeds)*
None			*Moderate increase in permeability*		
Remains hard or becomes hard		*Permeability increases significantly*		*Considerable increase in permeability*	*Large increase in permeability*
Softens	*Permeability decreases somewhat, or at worst, increases minimally*			*Permeability affected minimally*	
Softens quickly		*Increase in permeability is small*			*Moderate increase in permeability*
Softens slowly		*Increase in permeability is large*			
Disintegrates	*Permeability increases greatly*				

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