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REMEDIATION OPTIONS FOR A CHROMIUM CONTAMINATED LANDFILL USING CEMENTITIOUS GROUTS

Marita L. Allan and Lawrence E. Kukacka, Department of Applied Science, Brookhaven National Laboratory, Upton, NY, 11973

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ABSTRACT

In-situ remediation of a chemical waste landfill with excessive chromium levels is being investigated as part of the Mixed Waste Landfill Integrated Demonstration. This paper is concerned with the design of advanced cementitious grouts for in-situ stabilization of chromium contaminated soil and in-situ installation of subsurface containment barriers. Grouts have been developed to improve the performance and cost effectiveness of remediation compared with conventional materials. In addition to restoration of chromium contaminated soils, the developed grouts have applications in other environmental operations where superior properties are required.

INTRODUCTION

As part of the Mixed Waste Landfill Integrated Demonstration (MWLID), the authors are developing advanced grouting materials for remediation of a chromium plume resultant from disposal of hexavalent chromium solutions. Further details of the MWLID have been given by Burford et al. (1). The site has an arid climate, a groundwater depth of approximately 160 to 170 m and alluvial type soil. The chromium is present in both the trivalent and hexavalent oxidation states, indicating that some transformation of redox state has occurred since the solutions were disposed. The remediation aims to convert hexavalent chromium into the less mobile and less toxic trivalent state and to contain the contaminated soil through use of subsurface barriers and a surface cover. The Brookhaven research is focused on 1) in-situ solidification/stabilization of the chromium contaminated soil and 2) in-situ subsurface containment barriers.

STABILIZATION OF CHROMIUM CONTAMINATED SOIL

Remediation of the chromium plume requires stabilization of both the trivalent and hexavalent states. Hexavalent chromium requires

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reduction to Cr(III) before stabilization as $Cr(OH)_3$ (2). For example, Cr(VI) contaminated soil can be pretreated with a ferrous sulphate solution, followed by cement or lime stabilization. However, a concern with this approach for in-situ remediation is that reduction of Cr(VI) may be incomplete and that verification of satisfactory reduction is necessary before proceeding with further treatment. Furthermore, the economics of remediation are detrimentally affected by the need to perform two separate stages.

Research has been directed towards simultaneous reduction of Cr(VI) to Cr(III) and stabilization so that soils contaminated with Cr(VI) or a combination of Cr(VI) and Cr(III) can be remediated in a one step in-situ process. The approach is to use grouts in which ordinary Portland cement is partially replaced with ground granulated blast furnace slag. Previous work has demonstrated reduction and stabilization of Cr(VI) by slag-modified cements (3-5). The low redox potential of slag-modified cements is responsible for the reduction of Cr(VI) (6,7).

The in-situ techniques under consideration for treating the contaminated soil with grout are jet grouting (8-11) and deep soil mixing (2,8,12,13). In these techniques grout is intimately mixed with soil to form soil cement. The choice of technique will depend on ability to meet stabilization objectives and regulatory acceptance, in addition to cost effectiveness for the scope of soil treatment.

Initial research investigated the effects of slag content, water/cementitious material ratio and soil/cementitious material ratio on the leachability, permeability, wet-dry durability and compressive strength of treated soils. Following successful stabilization of soils spiked with 200 ppm Cr(VI) and Cr(III) and of soil samples retrieved from the landfill under study, further leachability tests were conducted at a higher level of Cr. Additional details of the initial work on stabilization of Cr contaminated soils with slag-modified grouts are available (14,15).

Initial Leach Tests

The grouts consisted of Type I cement, ground granulated blast furnace slag, water, bentonite and superplasticizer. The slag used was ASTM C 989 Grade 100, supplied by Koch Minerals. Sodium montmorillonite type bentonite was added at a rate of 2% by mass of water to improve grout stability. Sodium naphthalene sulphonate formaldehyde superplasticizer with 42% solids by weight was used to enable reduction of the water/cementitious material ratio (w/c) while maintaining fluidity. Superplasticizer was added at a rate of 20 ml/kg cementitious material. Uncontaminated soil collected adjacent to the landfill of interest was spiked with known quantities of Cr and mixed with the grouts.

In the initial studies uncontaminated soil was spiked with either 200 ppm Cr(VI) or 200 ppm Cr(III) and then mixed with grout. The grout was added to soil at soil/cementitious material ratios (s/c) by weight of 1, 2 and 5. The corresponding water/cementitious material ratios were 0.48, 0.72 and 1.40. The concentrations of Cr in the specimens after dilution with grout were 80, 106 and 135 ppm for soil/cementitious material ratios of 1, 2 and 5, respectively. Slag was used at cement replacement levels of 0, 20, 40, 60 and 80% in the grouts. The treated soils were cured by burying in dry soil for 28 days. The objective of the curing was to simulate subsurface conditions under which the extent of hydration is expected to be reduced as compared with conditions where water is readily available. The cured specimens were crushed and subjected to EPA Toxicity Characteristic Leaching Procedure (TCLP) tests. The concentration of leached Cr from stabilized Cr(III) contaminated soil was less than 0.5 ppm for the range of grout slag contents and soil/cementitious material ratios. This compared with 6.3 ppm for the unstabilized soil and the EPA limit of 5.0 ppm. The amount of leached Cr(III) decreased with increasing slag replacement level.

The tests on soils spiked with 200 ppm Cr(VI) showed that the proportion of Cr(VI) to total Cr [Cr(III) plus Cr(VI)] was reduced as the slag replacement level increased. This indicates that reduction of Cr(VI) occurred. The concentrations of total Cr and Cr(VI) in the leachates increased as soil/cementitious material ratio increased. However, at slag replacement levels equal to or greater than 40% the concentrations remained below 0.5 ppm. The untreated soil spiked with 200 ppm Cr(VI) had leachate concentrations of 8.75 ppm Cr(VI) and 9.5 ppm total Cr. Hence, the slag-modified grouts were demonstrated to be potential stabilization agents on the spiked soils.

A significant finding from the TCLP tests on Cr(VI) contaminated soils stabilized with slag-modified grout was that 40% replacement of cement with slag was sufficient to cause reduction of Cr(VI). Studies by Angus and Glasser (7) on slag-modified cements showed that the redox potential was not significantly lowered until slag content reached around 85%. Curing conditions differed from those used in this work, but the curing period was approximately the same. Atkins and Glasser (16) comment that the level of slag replacement necessary for reducing behaviour depends on time since more S^{2-} is released as slag continues to hydrate. Thus, the redox conditions in the soils treated with slag-modified grout can be expected to change with time and with the availability of water for hydration.

Leach Resistance with Time

A question arises as to whether the observed immobilization of Cr(VI) with slag-modified grouts is permanent. Oxidation of S^{2-} may occur if oxygen diffuses into the treated soil. Consequently, the reducing characteristics may be diminished. Diffusion of oxygen into the stabilized landfill soil is not expected to be a major concern under subsurface conditions, but requires consideration. The potential deterioration of the reductive capacity of grout treated soil was investigated to determine whether this could result in increased leachability of Cr. Soils spiked with 200 ppm Cr(VI) and treated with grouts containing 40% and 80% slag were crushed as required for the TCLP test and left in laboratory air for periods of 7 and 14 months. The specimens were from the same batches used in the initial TCLP tests and, therefore, should not vary in content or properties except for inherent heterogeneity. At the conclusion of the exposure time the specimens were subjected to TCLP tests and the results were compared with those collected at an age of 28 days.

The soils treated with the 40% slag grout showed an increase in leached Cr(VI) and total Cr at both 7 and 14 months when the soil/cementitious material ratio equalled 5. At 14 months the material with 40% slag and a soil/cementitious material ratio of 2 had increased leachate concentrations compared to the initial and 7 month values. In contrast, the soil treated by grout with 80% slag did not demonstrate significant increased leachability at any soil content for either of the test periods. The limit of 5.0 ppm leached Cr was not exceeded for either grout and the maximum value for total Cr was 1.0 ppm. The results suggest increased potential for Cr release for soils treated with lower slag content grouts exposed to oxidizing conditions. Higher slag contents appear preferable in this respect and will continue to be monitored.

Leach Tests on 1000 ppm Cr Soil

The initial successful stabilization of spiked and landfill soils with the slag-modified grouts warranted further investigation with higher Cr contamination levels. Two grout mixes were used: 1) 100% cement, 2) 40% slag/60% cement. It is also intended to test grout with 80% slag on higher Cr concentrations for comparison, with emphasis on the long-term immobilization performance. The test specimens had a water/cementitious material ratio of 0.72 and a soil/cementitious material ratio of 2. The grouts were used to stabilize soils spiked with 1000 ppm Cr(III) and with 1000 ppm Cr(VI). Dilution by grout resulted in the Cr concentration of the stabilized soils being 532 ppm in each case.

The results for the leach tests on soil spiked with 1000 ppm Cr are presented in Figures 1 and 2. The leachate concentrations for the Cr(III) soil illustrated in Figure 1 were well below the limit of 5.0 ppm and showed enhancement of leach resistance due to addition of slag to the grout. Figure 2 shows that slag decreased the amount of Cr(VI) and total Cr that was leached. At 1000 ppm Cr(VI) in the original soil the grout without slag was unable to comply with EPA leachate requirements. Tests on stabilizing 1000 ppm

Cr(VI) soil with higher slag content grouts will determine whether reduction of Cr(VI) to Cr(III) and leach resistance can be improved further.

Future Work on Cr Stabilization

The laboratory prepared stabilized soils will be continually monitored for leachability to test that Cr stabilization remains acceptable. The practicality of using slag-modified grouts for in-situ stabilization of the chromium plume at the landfill will be investigated. The planned field trials will involve optimization of grout mix proportions and placement equipment parameters for the site conditions. The properties of the stabilized soil will be tested for leach resistance, durability and physical and mechanical properties. The safety, efficiency and economics of the grout stabilization process will be compared with other in-situ methods.

SUBSURFACE CONTAINMENT BARRIERS

Vertical and horizontal subsurface barriers in uncontaminated soil are required to reduce migration of any remaining leachates and to prevent penetration from external sources. Together with a surface cover, the subsurface barriers will effectively contain the landfill contents. Cementitious grouts containing admixtures have been evaluated for this purpose with the objectives of improving hydraulic and mechanical properties over conventional, high water/cement ratio grouts and producing a more cost effective and reliable solution than polymer or chemical grouts.

Jet grouting and deep soil mixing are under consideration for in-situ vertical barrier placement at the site of interest. Jet grouting can also be used to form horizontal barriers (10,17,18). Permeation grouting is not considered to have a high probability of producing continuous barriers in a controlled manner at the site with cementitious grouts due to the fine particle size and heterogeneity of the soil. Uncertainty of forming continuous barriers at the site is also a concern for claquage, or hydrofracture, grouting.

Two versions of jet grouting are of interest for the barrier construction. The first method is in-situ mixing of grout with soil to form a soil cement barrier. Replacement jet grouting is the second method and involves removal of soil by a jet of water and air, followed by placement of grout in the formed cavity. Of the two, the first method is more readily available and less expensive.

Containment barriers are required to be free from major defects that could give rise to leakage. Examples of such defects include cracks and discontinuities between successive grout or soil cement columns. The potential for cracking can be minimized to some degree through mix design, such as using minimum water/cementitious material ratio, and through materials selection to reduce shrinkage, increase fracture resistance and decrease thermal effects.

Another concern is that leakage may develop at column joints if the bond is insufficient. Jet grouted or soil mixed columns are usually overlapped and keyed together to form an interlocked barrier. Thus, a mechanical bond is formed. The chemical bond between columns is also of interest since this will influence the hydraulic integrity of the joint, and hence, the overall performance of the subsurface barriers. Studies of the permeability of bonded grouts and soil cements were initiated to examine the interfacial properties. The permeabilities were compared with those of bulk materials.

Bond Permeability Tests

Soil cements and sanded grouts determined to be barrier contenders from earlier property studies are currently being prepared and tested for bond permeability. Soil cements have been prepared from plain and from slag-modified grouts. Sanded grouts containing supplementary cementing materials such as silica fume and slag are being investigated for comparison with soil cements. The results for one soil cement and one grout have been selected for presentation. Both materials contained slag. The same types of superplasticizer and bentonite as used in the Cr stabilization described above were used for the barrier materials. Uncontaminated site soil collected from a location adjacent to the landfill was used. The mix proportions are presented in Table I.

Table I. Mix Proportions of Selected Soil Cement and Sanded Grout used for Bond Studies

Material	**Soil Cement**	**Sanded Grout**
Cement (kg/m^3)	322	563
Water (kg/m^3)	388	362
Slag (kg/m^3)	215	241
Sand (kg/m^3)	0	965
Bentonite (kg/m^3)	7.7	18.0
Soil (kg/m^3)	1075	0
Superplasticizer (l/m^3)	10.7	16.1

Permeability of bonded soil cements and sanded grouts was measured on cylindrical specimens cast in two halves. Wax coated cardboard cylinders 75 mm diameter and 150 mm long were fitted with a vertical insert which had a smooth polyethylene surface. The first half of each specimen was cast, covered with polyethylene sheet and allowed to sit for 24 hours. The insert was then removed and the second half of each specimen was cast. After 24 hours the cardboard mould was removed and the specimens were maintained in water until testing at 28 days age. A total of three specimens per mix were tested.

Figure 3 shows the permeabilities of the bonded materials in addition to the values for bulk materials at the same age and cured under the same conditions. Assuming that the permeabilities are normally distributed, *t*-tests were performed to determine whether the permeabilities of the bonded and bulk materials were significantly different. It was determined that the permeability of the bonded soil cement was significantly higher than the bulk material at a 5% level of significance. This can be attributed to shrinkage of the second half of the specimen, causing preferential flow to occur at the interface. The permeabilities of the bonded and bulk grouts were not significantly different. This suggests low shrinkage and sound bonding between successive grout batches. In each case, the permeability of the bonded material remained sufficiently low for containment purposes. It is necessary to repeat permeability measurements of column joints produced in the field with full scale in-situ placement equipment and subjected to subsurface shrinkage conditions to test that adequate performance can be achieved.

The bonded specimens will be subjected to wet-dry cycles and re-measured for permeability to determine the susceptibility to preferential flow at the interface. The permeability under unsaturated conditions is of interest since the barriers will be placed in the vadose zone in this case. The microstructure of the bond will also be investigated to elucidate potential means of improving interfacial properties.

Proposed Field Trials for Barriers

It is proposed to conduct extensive field trials at the landfill site so that the grout proportions, grouting process and barrier performance can be optimized for both vertical and horizontal barriers. Grouting parameters for the unique site conditions require further systematic variation with corresponding evaluation of barrier quality and continuity. The minimization of water/cementitious material ratio while retaining compatibility with the placement equipment is of particular importance since this parameter has the greatest influence on final permeability.

CONCLUSIONS

Slag-modified cementitious grouts have been found to be potential stabilization agents for soil contaminated with up to 1000 ppm Cr(VI). Further tests are in progress to assess the permanence of stabilization. Grouts with enhanced hydraulic, physical and mechanical properties have also been developed and characterized for subsurface barriers. The permeability of joints between barrier materials has been measured and found to be suitably low. The program is now at the stage of demonstrating the slag-modified grouts for in-situ stabilization of chromium plumes and demonstrating superplasticized cementitious grouts for subsurface containment barriers using placement techniques such as jet grouting.

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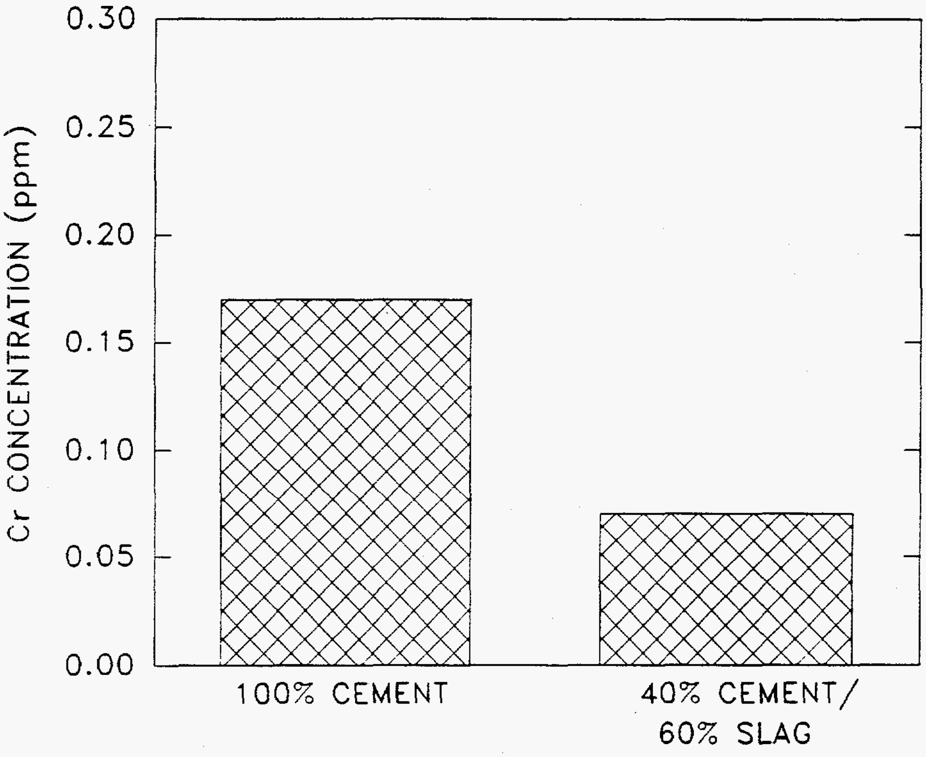

Figure 1. TCLP Results for 1000 ppm Cr(III) Soil.

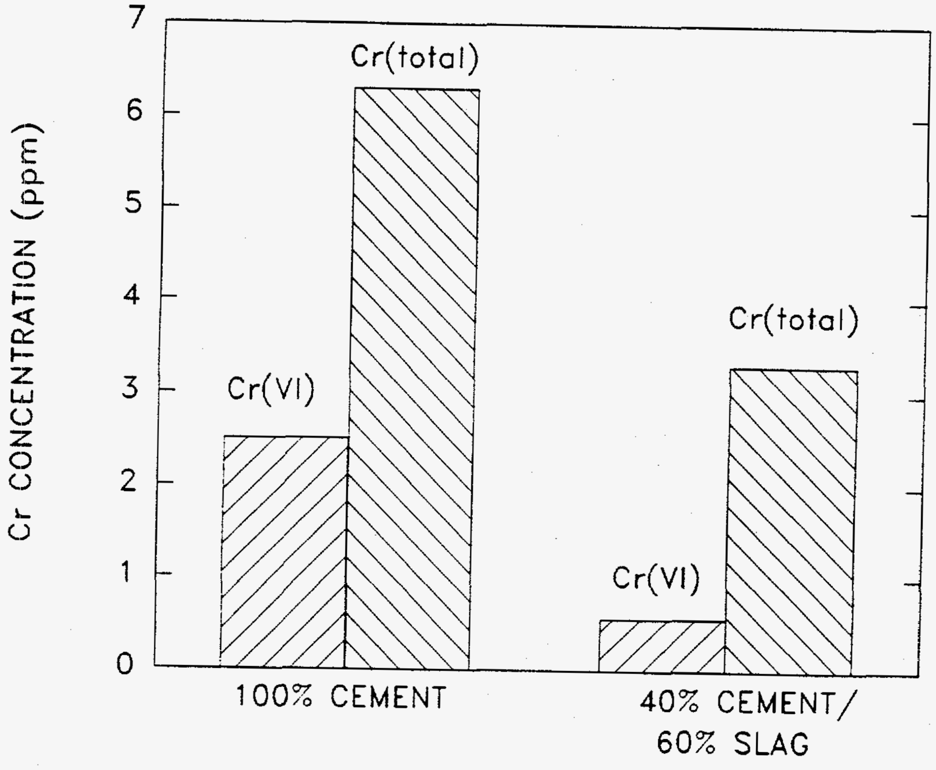

Figure 2. TCLP Results for 1000 ppm Cr(VI) Soil.

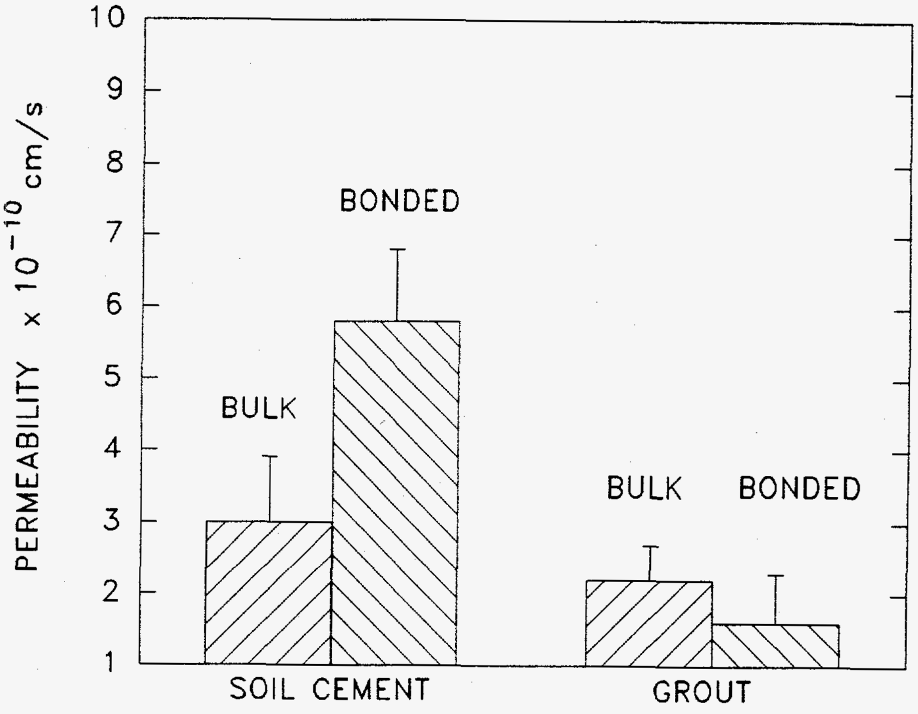

Figure 3. Permeability of Bonded and Bulk Materials