7. VENDOR BID ESTIMATE

Applied Geotechnical Engineering and Construction prepared a vendor bid. The grouting vendor was asked to prepare the cost estimate as if it was the company bidding on the job. This company was the grouting contractor on this and past INEEL projects. This bid estimate was prepared using two different approaches to grouting 11 acres in the SDA. The first approach was to use the thrust block or cover block approach as described in the field testing portion of this report. The other technique was for an x-y positional system gantry crane approach as described in Appendix A. For both approaches, the cost estimate did not include the costs of remedial design, Federal Facility Agreement and Consent Order management and oversight, remediation oversight, and remedial design. However, the costs reflected that the contractor set up a permanent operation with a 10-year duration with onsite management. Appendix I gives the details of both of these cost estimates.

To summarize, the gantry crane approach was much lower in total cost over the 10-year period than the cover block or thrust block approach. This is almost entirely due to the cost of the cover blocks relative to the cost of the gantry crane systems. The total cost for the gantry crane approach was $251M and the cost of the thrust block approach was $621M. For the thrust block approach, the cost of the thrust blocks were $283M of the total of $621M. Both approaches assumed using the same grout (GMENT-12 @ $2.55/gal for the dry ingredients) and the use of an on site batch plant. Both approaches used 20,000 holes per acre and assumed the same escalation of 3% starting with 2002 dollars. Both approaches used 10% profit and 30% overhead in the estimation. Again, Appendix J gives detailed assumptions and costs for the two approaches.

INEEL cost estimating made a preliminary evaluation of this bid and found the following points:

- the bid did not include a "basis of estimate"
- estimate should be broken down into capital and operation costs
- concrete for footings on page J-6 is inconsistent with spread sheet
- more detail required on cost of thrust blocks (it is a multi-million dollar term and requires more detail)
- units are missing on spread sheet
- not clear whether state and local taxes included.

8. DISCUSSION OF RESULTS

The results presented in Volume 1 of this report represent both detailed bench data as well as full-scale qualitative demonstration of the technology during field applications. In general, there was a continuous down-selection of grouts from a total of six grouts to one grout for field application. Even though only one grout was chosen for the field test, all of the grouts tested had desirable properties for application to in situ grouting. What follows is a discussion of results relative to the bench, implementability, and field testing work.

8.1 Bench Studies

Bench testing resulted in a logical down-selection of grouts from six promising candidates to three grouts recommended for field studies. The three grouts selected showed excellent durability properties (high leach indexes and pH's compatible with INEEL soils), low hydraulic conductivities, high tolerance to interferences, and high strength. The three grouts were: GMENT-12, TECT HG, and U.S. Grout. In a study involving the microencapsulation of volatile organics by the neat grout mixtures, there was an unexpected retardation in the release of the various volatile organics (TCE, TCA, PERC, CCl4) to a control volume over a period of 90 days of testing. The reference organic sludge mixture released the VOCs immediately to the control volume but when uniformly mixed with the grout, the release was on the order of "hundredths" of a percent of the source term per 10-day testing period. This can translate to a much retarded release of the material. The other three grouts (Waxfix, Enviro-Blend, and Saltstone) displayed properties that require some work to be considered applicable to field use. During testing, it became obvious that certain areas required more work. These areas include 1) suspension of the boron-10 in the Waxfix material, 2) the too early gel time for the Saltstone grout, 3) the poor strength for neat grout and neat grout and interferences, and a too-high hydraulic conductivity for the Enviro-Blend material. Another area that required more work was the unexpected result that the macroencapsulation test displayed a too-high release of Volatile organics relative to the microencapsulation testing for the three grouts recommended for field work. It is suspected that end plug cracking lead to this poor performance.

8.1.1 Boron-10 Suspension in Waxfix

Basically, no physical or chemical testing was performed on the Waxfix grout due to the poor suspension results of the glycerin/sodium tetraborate solution in the curing Waxfix. Instead of the desired 1g/L of boron-10 in the cooled matrix, there was an almost complete settling of the boron material. This was most unfortunate in that Waxfix in prior studies had demonstrated the capability once grouted to penetrate all voids in the buried waste such that the resultant monolith was virtually water-proof and self healing relative to crack formation. The problem of boron suspension could not be solved in time to commit to a complete evaluation of the Waxfix grout; however, this study will an important addition to the Remedial Investigation/Feasibility Study database and should be undertaken as soon as possible. Waxfix has the potential to not only support the concept of grouting for in situ disposal but also has great potential to support cheaper, safer retrieval of buried transuranic waste (see Appendix I). One such concept was developed called RETRIEVABLE DISPOSAL discussed in Appendix I. This concept involves grouting with Waxfix, retrieving the waste, shredding the retrieved material using cryogenics, and then mixing the shredded material with low temperature polyethylene. The resultant material is poured into polyethylene boxes with lifting lugs and disposed of in the pits from which the material was originally retrieved. After this process, the waste is considered disposed but easily retrieved should a better disposal site be determined.

8.1.2 Too Early Gel Time for Saltstone

There were two grouts from the Savannah River Plant that were investigated in this study including Saltstone and Tank Closure grout (reformatted as GMENT-12). The test plan (Grant et al. 2000) called for adjustments to these grouts to make them "jet groutable" in that neither of these materials had been applied in that way. There was only time and budget to "adjust" the formulation of one of the grouts-Tank Closure grout. In fact, the effort to reformulate the base ingredients in this grout were so extensive that the University of Akron subcontractor renamed the grout GMENT-12. Meanwhile the Saltstone grout was tested with minimal reformulation. As a result, the Saltstone grout had an initial gel time of less than 2 hours, which cannot support jet grouting in the field. If an effort were made to adjust the admixture to support jet grouting, it is possible that the Saltstone could be a viable grout.

8.1.3 Poor Performance of Phosphate-Based Grout

It was recognized that including at least one phosphate based grout in the initial list was prudent because of the excellent scavenging properties of the phosphate material for hearing metal contaminants. Evidence of this is in the Phosphate Beds in South Eastern Idaho and the high thorium concentrations. This natural analog geological evidence is useful when convincing regulators about the concept of in situ disposal. To this end, a vendor of a phosphate based strippable paint product used in Rocky Flats remediation was contacted. The vendor was American Minerals, Inc. American Minerals agreed to develop a "grout" material at no cost to the government and supply the material for our testing protocol. The development time was short and the resultant Enviro-Blend grout was developed and tested during the Bench testing. While it displayed the highest Leach Indexes during ANS 16.1 testing, it also displayed the poorest performance for hydraulic conductivity and tolerance to interference materials. It is possible to improve the properties of the neat grouted tested in this program; however, until these properties are improved, the Enviro-Blend grout cannot be recommended for in situ jet grouting.

8.1.4 Cracked End Plug for Macroencapsulation Testing

The results of evaluation for Volatile Organic release in a special sealed volume test using gas chromatography was performed for both micro and macro encapsulation scenarios. The results of the microencapsulation testing (the grout and organic sludge was intimately mixed and allowed to cure) was encouraging in that there was a large unforeseen decrease in the release rate such that the release of VOCs could be retarded for hundreds of years. Macroencapsulation testing involved filling a hollow cylinder made of neat grout with the organic sludge. After sealing the central hollow containing the sludge with a cap made of the grout and further sealing the grout cap with epoxy, the cylinder was placed in the same sealed volume test facility as was used for the microtest. Surprisingly, there was not a marked decreased in the offgas rate of VOCs for the macro compared to the micro testing. Examination of the end plug seal showed a visible cracking which could allow a tortuous but a definite flow path for the VOCs to the chamber air. To perform this experiment correctly would involve accounting for the crack by allowing the hollow cylinder to cure, place the sludge in the cylinder, seal in a cured plug of neat grout, and then, apply various coats of water based epoxy resin coat by coat until the cracks are filled. At this point, the 90-day test could be re-run with the expected result that the VOC release would be hardly measurable in that it was expected that the release would be diffusion controlled.

8.1.5 Durability

The ANS 16.1 leaching protocol provides a conservative durability estimate compared with grout dissolution into the natural ground water because the SDA ground waters are virtually saturated in calcium (with respect to calcite, CaCO3) and silicon (with respect to chalcedony, microcrystalline SiO2) whereas the ANS 16.1 leach tests specifies demineralized water, which remains unsaturated. The effect of composition difference between the pore water and solvent water is illustrated by considering the Fick's law relationship given as $F = A(D_p\Delta C)/\Delta X$ (Kemper 1986), where F is the grout material flux, A is the area, Dp is the diffusion coefficient of material p, ΔX is thickness of the diffusion medium and ΔC is the difference in concentration between the pore water composition and the surrounding ground water composition.

In the case of the SDA, ΔC is virtually zero and the grout material flux would also be virtually zero, indicating that the material loss rates would probably be significantly slower that those used in the computations. In addition, the fact that the ground waters are saturated with calcium and silica means that these materials would probably reprecipitate at the boundary of the waste form. This is borne out by the fact that calichie, natural deposits of calcite, is forming in the SDA soils at the present time. (J. R. Weidner, personal observation, 1991) The data indicate that all the tested grout materials would provide mechanical stability and chemical buffering for thousands of years and easily meet a 1,000-year durability goal (Armstrong 2002).

8.2 Implementability Testing

During implementability testing it was demonstrated with full-scale field equipment that the three grouts recommended from the Bench Testing (TECT HG, U.S. Grout, GMENT-12) could be applied for in situ grouting. All three grouts could be mixed and delivered at 400 bar (6,000 psi) via jet grouting. Two of the grouts (U.S. Grout, GMENT-12) required using a 2.4-mm nozzle and the third grout could pressurize the system using a 3-mm nozzle. The size of the nozzle is important in that the larger the nozzle, the less prone to plugging due to small debris in the system or the effects of filter caking in a stagnant condition (as was required with the thrust block contamination control strategy). Also demonstrated at the implementability testing was the ability to place a 7 cm (2.75 in.) polyethylene rod into the just grouted hole to create, once cured, a borehole for performing hydraulic conductivity tests. In addition, it was further demonstrated that a thermocouple probe consisting of a 1.27 cm (½ in.) copper pipe could be inserted for measuring the centerline temperature of the pit. It was demonstrated that the fluid in the drill stem could be drained in a matter of a few minutes; however, what was observed was a stoppage of flow out the nozzles, in that during Field testing it was shown that there was still fluid "held up" by a vacuum that was spilled out the nozzles when tilting the drill stem and moving between holes.

A single grout –GMENT-12- was chosen from the three grouts based on factors such as basic cost, ease of mixing and clean-up of the grout, grout returns in creating a triplex column, and formation of the monolith. It must be mentioned that all three grouts displayed the capability to be jet grouted and form solid stand-alone monoliths in an INEEL type soil condition(tightly packed silty-clay soils). This clay soil condition is thought to be the more restrictive for jet grouting in that there are low voids. For a buried waste case involving soil and debris there is a marked increase in easily accessible void fraction in the debris. U.S. Grout had the lowest specific gravity and therefore displayed the largest amount of grout returns during grouting (when grouting two holes, the space under the simulated thrust block was filled with grout and the third hole could not be grouted). With a lower specific gravity grout, there is not as much kinetic energy imparted to the surrounding medium as with the higher specific gravity grouts, the velocity of the grout being the same. Even though the U.S. Grout displayed a too-high grout return for use on the thrust block concept, this grout would certainly be recommended as a candidate grout for using the x-y positional system discussed in Appendix B.

8.3 Field Testing

Even though an injury accident occurred after successfully grouting only 12 holes, much data on using the thrust block concept and actual data on the capability of the thrust block to contain the terbium tracer was obtained. The project was not abandoned because of technical/safety issues rather, there was a need for the remaining budget for more pressing INEEL projects at exactly the same time frame as the resultant extensive accident investigation. In short, the remaining budget was needed elsewhere. Completion of the testing would have resulted in, a better statistical approach to evaluating contamination control data, more data on durability of the shroud, knowledge of the hydraulic conductivity of the cured pit, and an extensive evaluation of the monolith and physical and chemical testing of select samples of the monolith during destructive examinations. These monolith samples would have completed an evaluation of the durability of the monolith and supported the data obtained from the Bench testing and the analytical studies on durability found in Volume 2 of this report.

Prior to the accident, there was a learning curve to using the thrust block concept. Since a trickle flow of grout in the nozzles had been utilized on all other grouting at the INEEL (Loomis 1995, 1997, 1998), this test represented the first attempt at grouting without allowing a continuous flow. During implementability testing, the drain of the drill stem was noted to be on the order of minutes and in fact this knowledge was applied for the first two holes. For the first hole, the process worked as planned. When moving from the second hole to the third hole, the sack formed by the twist and tape action of the thrust block sleeve filled with draining grout. Gravity pulled the sack full of fluid off of the stinger and the potentially terbium contaminated neat grout material flowed onto the top surface of the thrust block. This lead to measurable terbium tracer on some of the thrust block smears. This event led to two actions. One action was to separate the high-pressure hose at the fitting near the weather structure wall and relieve the vacuum in the drill stem (caused by the draining fluid which holds up material in the drill stem). In fact, compressed air was introduced to blow the grout out the nozzles. The other action was to provide a separate bag at the bottom of the sack to help contain any dripping that may occur due to sack filling in the twist-off section. In a hot application, however, it would be desirable to have a special self-cleaning relief valve in the system to relieve the vacuum and the possible automatic actuation of compressed air to blow out the remaining grout. Another major issue was the amount of nozzle plugging and time spent using rotopercussion to unstick plugged nozzles. This issue may be related to the grout chosen for the test (GMENT-12). In prior studies using the TECT HG grout there was an allowed trickle flow for most of the grouting; however, there were times when the grout was stopped and start-up was accomplished without much plugging of the nozzles. What was needed in the implementability testing was a separate-effects test to determine which of the grouts displayed the least nozzle plugging in a stopped flow condition. As an alternative to excessive use of the rotopercussion hammer for nozzle clearing during hot application, it is recommended to use a glovebox adjacent to the grouting area with glove ports to allow clearing the nozzles with a wire inside the glovebox.

At the time of the accident, all systems were working as planned with minor modifications required. One modification is the need for a better view of the void space under the thrust block using the remote TV cameras which would involve a deeper Lexan well for the TV camera. Another minor modification would be to provide a hard pipe for the inlet and outlet of the thrust block HEPA filtration system to avoid collapse of the hose. It was obvious that a better weld connection of the shroud to the top bracket was required as well as an engineered twist in the shroud material itself to avoid the rotating drill steel touching the inner shroud.

During the testing, grout was mixed in Idaho Falls at a Ready Mix plant and transported 50 miles to the INEEL Cold Test Pit South three time a day (3,024 L [800 gal] per trip). This distance factor lead to a poor utilization of mixed grout in that many loads were dumped unused because of schedule delays in grouting. In order to meet schedule, a batch was prepared based on grouting performance several hours earlier. When the grout actually arrived at the Cold Test Pit, the grouting system may not have been functioning for the entire 2 hours and a full truck of grout was still available. The obvious solution to this problem is to utilize a ready-mix plant at the Cold Test Pit South.

Data quality objectives were listed in the test plans covering the bench, implementability and field testing phases of the treatability study. Most of the data quality objectives discussed in the test plans were addressed by the treatability study; however, there are definite missing gaps in data due to truncation of the field testing program. All of the data quality objectives were met for the bench and implementability testing phases and even with only limited testing in the field testing phase, many of the objectives associated with the field testing involving the thrust block and contamination control system were addressed. Overall, the main data quality objective relating to implementability of the in situ grouting process using the thrust block contamination control system was demonstrated. Only minor design changes are required as discussed above. The overall grouting process is not as rapid on a time per hole basis compared to that expected using alternative grouting concepts (the x-y positional system discussed in the report); however, the thrust block concept process could be applied for a variety of applications in buried waste regions. For instance, the thrust block concept could be used to grout a series of interconnected columns (say 10 hole columns) at various regions within a pit to support a cap and leave the thrust block in place. Another application would be to grout small very specific hot spots within a buried waste region. For this case, the relatively long time to grout a hole would not matter and the complications of using an x-y positional system would not be warranted for such a limited application. The time issue only becomes important when grouting hundreds of thousands of holes over a 10-year period. Finally, to fully evaluate the missing data quality objectives (those relating to the characteristics of the emplaced monolith like void filling, and monolith durability), would require completion of the grouting in the pit followed by hydraulic conductivity testing and excavation of the monolith with further chemical and physical testing of samples from the resultant monolith.

9. DATA EVALUATION RELATIVE TO DATA QUALITY OBJECTIVES

Because the treatability study was performed under CERCLA guidance, the results of bench, implementability, and field studies are compared to data quality objectives defined in the bench test plan (Grant et al. 2000) and in the implementability and field test plan (Loomis 2000). Table 38 makes that comparison for the bench testing results, and Table 39 provides that comparison for implementability. Table 40 covers field testing. It is noted that, because the field testing was not completed, many data quality objectives were not met.

Table 38. Data quality objectives compared to bench testing results.

Data Quality Objective	Measurement	Discussion of Results
Test Objective 1-Estimate the Durability of the Grouted Waste Monoliths	ANS 16.1 leach testing for Sr, Al, Ca,Si, KNO_3	High leach indexes between 10-15 for constituent materials suggests long durability
Test Objective 2 Evaluate the Hydraulic Properties of the Grouted Waste Monoliths	Hydraulic Conductivity	There are a variety of grouts with low hydraulic conductivity on the order of e-9 cm/s suggest essentially no flow through neat grout regions and for the case with soil/nitrate/organic interferences on the order of e-7 cm/s to e-8 cm/s suggest low hydraulic conductivity in a monolith application
	Shrinkage	Screening test results show relatively high shrinkage numbers in the range of 0.25% to 3% as measured as a drop in level in a curing cylinder of neat grout.
	Porosity	Data not taken in that neat grout samples dissipated upon roasting. Testing protocol designed for aggregate concrete.
	Tensile strength	Relative high tensile strength in the range of greater than 600 psi for neat grouts and greater than 200 psi for neat grouts mixed with interferences. Enviro-Blend grout displayed essentially no tensile strength for both neat grout and neat grout mixed with interferences.
Test Objective 3-Identify Grout Material Suitable for Monolith Application	Tensile Strength	See above
	Shrinkage	See above
	Hydraulic conductivity	See above
	Porosity	See above

Table 38. (continued).

Data Quality Objective	Measurement	Discussion of Results
	Estimate Fracture Development	Fractures observed in macroencapsulation tests in the end plug. Other than this obvious fracture, none observed
	Measure change in test cylinder height	See measurement of shrinkage. The range was a drop in height of 0.25 to3%.
	Measure fracture development; tensile strength	Not directly done by measurement-issue addressed in Volume 2 of this report
	Measure Free water	See height of cylinder discussion
	Hydrogen ion activity	PH measured for leachate for the ANS 16.1 testing. System is completely alkaline and moderately oxidizing basic with pH in the range of 10-13 for the leachate water. Compatible with INEEL soil conditions.
	Oxidation Reduction Potential	Measured range in 225-390 mV suggesting moderately oxidizing conditions
	Compressive Strength	Relative high compressive strength for a large variety of grouts for both neat grouts and grouts with interferences. Range of compressive strengths for neat grout 1,500-9,000 psi range and for grouts with interferences 600 to 5,000 psi range.
	Density	Range of density was sg = 1.6 to 2.16 for cementitious grouts tested
	Viscosity	All grouts showed to be jet groutable with Marsh funnel at 56 to165s.
	Cure time /temperature of cure	Only Saltstone showed a too fast cure time. All other grouts showed initial gel times greater than 2 hours. All grouts had a temperature of set lower than 100°C.
Test Objective 3-Evaluate Chemical Buffering Properties of grouted waste forms	PH and eH measured in ANS 16.1 leachate water.	Demonstrated chemical compatibility with INEEL buried waste soil conditions (see ph/eh discussion above)
Test Objective 4-Determine the effects of soil, organic materials and nitrate salts on grout properties	Compressive strength	All grouts showed high compressive strength (greater than 1,000 psi) with 50 wt% soil/12 wt% nitrate salts, and 9 wt% organic sludge.

Table 38. (continued).

Data Quality Objective	Measurement	Discussion of Results
	Leach of Sr tracer	High leach indexes relatively unchanged over the case for neat grout (range 10-15)
	Hydraulic conductivity	A large variety of grouts showed only a 1-order-of-magnitude change in hydraulic conductivity with interferences present
	Fracture development/tensile strength	Fracture not observed except in macroencapsulation end plug. Tensile strength remained above 200 psi with interferences
	Free water	Not reported with interferences
	Compressive strength	Compressive strength greater than 1,000 psi for all grouts except Enviro-Blend with the interferences present
Noncritical Objective B-Determine the effectiveness of retaining volatile organic compounds	Microencapsulation testing	Exhibited on the order of "hundredths of a percent" of source term release per 10-day period. Surpassed expectation for VOC entrapment.
	Macroencapsulation testing	Exhibited results similar to the microencapsulation testing ; however, the macro testing was expected to display less release than the microencapsulation testing. Results flawed by presence of cracks in the end plug
Test Objective 1-Confinement during retrieval-properties of grout based on additives	Sodium tetraborate added to molten paraffin and cooling and separation properties examined	Almost complete separation of the sodium tetraborate during the slow cool down.
Test Objective 2-Confinement during retrieval-Evaluate the combustion hazard of the paraffin based grout	Department of Transportation Oxidizer testing	Not done due to failure of boron suspension results
Test Objective A-Confinement during retrieval-non critical	Btu content	Not done due to failure of boron suspension results.

Table 39. Data quality objectives compared to testing results (implementability).

Data Quality Objective	Measurement	Discussion of Results
Test Objective 6-Evaluate INEEL administrative feasibility for in situ grouting process implementation	Observe pit construction and layout/stage equipment/grout equipment parameter settings/time to grout/total grout returns/heaving/temperature of cure/	Implementability testing performed at vendor site in a timely manner with down-time less than a total of 4 hours. All three grouts (U.S. Grout, TECT HG, and GMENT-12) dry/wet materials were easily shipped to the vendor site. Pit was built to specification and equipment easily arranged to expedite grouting. Key data included time to grout, total grout returns and pit heave. In addition, the temperature of set was easily measured. Basically all data called for in the test plan was obtained.
Test Objective 8-Evaluate field implementability of the grout emplacement process for monolith design and application	Pit construction and layout, position of thrust block, stage equipment, set parameter settings	Silty-Clay soil Pit constructed as per test plan with 3-simulated thrust blocks with 12 in. space for grout returns located on top of pits. Equipment oriented to optimize grouting process and pretest nozzle setting tests recommended U.S. Grout and GMENT-12 should use the 2.4-mm nozzle while the 3-mm nozzle should be used for the TECT HG grout. These nozzles would allow pressurizing the system to 6,000 psi.
	Measure dry/liquid components and mixed amounts of grout during testing	Mixing of grouts simplified to use dry (and some cases wet ingredients) and water in a vortex mixing system. One column batch produced at a time. Some concerns that there was sufficient GMENT-12 in that an excessive amount was used during nozzle optimization testing; however, enough product was left to create a triplex column
	Measure total depth of drill rig and grouted region	Drill stem was inserted 11 ft and the bottom 8 ft was grouted as measured by a mark on the drill string
	Measure parameter settings (injection pressure, step distance, step time, drill string rotation rate, total injection volume, nozzle size/total volume of grout returns, heaving, grout physical properties such as density and viscosity	Injection pressure was always 6,000 psi with the step distance always set at 5 cm. The step time was varied depending upon the measured amount of grout that went into the pit. It was attempted to keep the amount of grout injected for each grout the same; however, the injection of U.S. Grout had the volume under the thrust block filled with grout after only two holes. The density of the grout was measured with a mud balance prior to injection and the density was in agreement with the bench values. There was no heaving of the blocks however, in a weakened area for the TECT HG pit there was a grout return outside the thrust block. The weakened are was caused by test holes that had been grouted to set the injection parameters just prior to grouting the triplex column. For both the U.S. Grout and the TECT HG there was remaining space under the thrust block

Table 39. (continued).

Data Quality Objective	Measurement	Discussion of Results
	Temperature of cure	Measured for each pit less than 100C
	Excavation of columns	All three grouts created stand-alone grout columns
	Rock Quality description	No free water was observed in surround soils nor under thrust block; however, surround soils displayed a wet nature, the monoliths were cohesive enough that all three monoliths could be brought out of the pit in one large piece. Banging on the monolith with a standard backhoe bucket required 10-15 blows from 3 ft to obtain small take-a-way sample.
	Grout Quality(set hardness, impeded curing, free water, fracture development, soil inclusions, mixing,	See above, monolith consisted of cured mixtures of soil and grout with occlusions of clay soil similar to that observed in prior INEEL testing, no fractures could be observed in the monoliths even after removal with the large front-end loader, no incomplete curing was observed.
	Column development(diameter, height, overlap)	Column diameter was nominally 48 in. and 8 ft high for three holes on 20 in. center. No ungrouted regions were observed within the column
Test Objective 3-Identify grout material to support monolith application during in situ grouting	Equipment check-out, time to grout, grout returns, heaving of pit, temperature of cure	GMENT-12 was chosen as the grout to carry to the field testing based on groutability, mixability, monolith formation, and other factors discussed in the main text of this report.
Test Objective 7-Determine contaminant release during in situ grouting	Grout returns	U.S. Grout was eliminated as the choice for field testing on the amount of grout returns which were excessive and would have compromised contamination control systems. U.S. Grout, should be considered as a candidate grout for application of in situ grouting using the x-y positional system described in this report.
Noncritical test objective D-Determine time, equipment, and labor requirements for mobilization demobilization, and operations	Stage equipment, establish material laydown areas, equipment check-out	Vendor gained experience in mobilizing and demobilizing equipment which was factored into cost estimates made in this report.

Table 40. Data quality objectives compared to test results (field testing).

Data Quality Objective	Measurement	Discussion of Results
Test Objective 1-Estimate durability of grouted monolith	Rock Quality Designation/Water infiltration/monolith grab samples-leach testing etc. (see test plan)	Not obtained-monolith not completed
Test Objective 2-Evaluate hydraulic properties of the monolith	Hydraulic conductivity testing in special wells in the monolith	Not obtained-monolith not completed
Test Objective 4-Evaluate the chemical buffering qualities of the monolith	Measure eh and pH in leachate for ANS 16.1 leach testing	Not obtained-monolith not completed
Test Objective 5-Evaluate the physical stabilization of the waste site to control subsidence	Water infiltration, rock quality	Limited excavation showed solid monolith
Test Objective 6-Evaluate INEEL feasibility for in situ grouting process implementation	Pit construction and layout	Pit constructed in a typical manner to the INEEL SDA transuranic pits and trenches, weather structure installed and thrust blocks and associated cameras, and contamination control equipment installed on pit in the required time
	Stage equipment	Grouting equipment staged to allow safety of INEEL workers relative to the high pressure grouting equipment. All ancillary drill string shrouds laid out to allow easy access, high pressure pump near clean out pit with easy access for grout delivery tanks
	Parameter settings	Initial settings based on Implementability testing, some difficulty keeping the exhaust hoses for the thrust block open due to design issues; however problem not critical as negative pressure was maintained. Camera wells should have been deeper to allow better view of region under the thrust block.
	Time to grout	Grouting was taking too long relative to production rates required to remediate the SDA in a timely manner. Some of the delay is due to the inherent design of the thrust block sleeve system and some of the delay is due to inexperience.(see extensive discussion of this in the discussion of results section)
	Total volume of grout returns	Minimal grout returns observed in 12 holes grouted under the thrust block
	Heave observed	None observed in 12 holes of grouting
	Temperature of cure	Not obtained-grouting terminated after 12 holes

Table 40. (continued).

Data Quality Objective	Measurement	Discussion of Results
	Product costs	Grout costs for the test were considerably higher than for an actual application. GMENT-12 should cost $2.55 per gal of liquid grout in an actual application
	Contamination control monitoring	Smears and air sampling did not interfere with operations
	Volume increase in the monolith	Not obtained-monolith not completed
Test Objective 7-Determine Contaminant release during in situ grouting	100 cm^2 smears on top of thrust block	Twisted sleeve fell off drill string shroud when moving from hole 2 to hole 3 spilling potentially terbium-contaminated neat grout on top of the thrust block. Evaluation of samples showed slightly elevated levels on some smears-no airborne release to air monitors surrounding the pit.
Test Objective 8-Evaluate field implementability of the grout emplacement process for monolith design and application	Thrust block foundation	Pea gravel provided a good base for the metal thrust block
	Positioning thrust block	INEEL standard lifting and moving techniques utilized
	Parameter settings	Initial settings for first 12 holes based on implementability testing results and the results of the first few holes. Step time adjusted as need to achieve 60% void filling. This was accomplished using the Jean Lutz flow meter.

Table 40. (continued).

Data Quality Objective	Measurement	Discussion of Results
	Grouting Process	The grouting process was complicated by use of the glove-box contamination control system involving the thrust block, sleeves, and shrouds on the drill rig; however, the process worked as designed except for a spill of neat grout on the top surface of the thrust block which pointed to several design issues. The first issue is the need to account for a stagnant system between grout holes relative to allowing a trickle flow of grout. Without a trickle flow, the nozzles are prone to plugging using the GMENT-12 grout. The second issue was the need for a drill string drainage system to allow complete drainage of grout between holes. The third was the need for a engineered twist in the shroud to maintain a space between the rotating drill steel and the inner shroud. Of particular importance was the lesson learned from the accident about the proper use of high pressure fitting, tie-downs, and hoses. Additionally, it was learned to employ automatic pressure relief for the high pressure pump during overpressurization events. Otherwise, the emplacement of grout in a buried transuranic waste environment is completely implementable. The thrust block concept should be particularly useful for small "hot spot" applications.
	Equipment Clean-Out (drill string, subassembly, grout supply system, pumps)	The drill string/shroud assembly removal process took on the order of 1 hour and is completely implementable. Although not demonstrated in the field test, cleaning the used shroud could easily be done in a partial glove-box environment for reuse. It is also anticipated that in actual practice, the plugged nozzles could be cleaned in a small portable glovebox assembly within the weather structure adjacent to the thrust block. It is possible that ice build up in the vortex mixing system could have caused plugging problems. The bottom line is that clean-up using a manifold to attach to the top of the drilling system once the shroud has been removed is completely implementable

Table 40. (continued).

Data Quality Objective	Measurement	Discussion of Results
	Volume of grout material	Even though the grout was mixed at an Idaho Falls Ready Mix plant 50 miles from the Cold Test Pit South, grout delivery to support the drilling/jet grouting process was accomplished. The grout was mixed in 800-gal batches with density and viscosity measurements essentially the same as in the laboratory bench studies. To avoid wastage of the grout and to allow better coordination between the grout batch plant and the jet grouting operation, it is recommended that the batch plant be located at the scene of jet grouting.
	Total Depth Measurements	Bottom of the pit, Elevation where grouting stopped, easily measured by using a painted mark on the top of the drill rig which gives a relative distance from the top surface of the thrust block. Time to drill recorded in the log books and was accomplished in a matter of minutes. However, there were multiple delays caused by nozzle plugging and time spent in rotopercussion trying to unplug the nozzles. In addition, there were up to 20 minutes lost in each hole trying to drain the drill stem of grout to disallow any build-up of grout in the plastic sack formed by twisting off the plastic sleeve on the bottom of the drill stem.

Table 40. (continued).

Data Quality Objective	Measurement	Discussion of Results
	Parameter Settings(injection pressure, step distance, step rate, drill string rotation rate, total injection volume, nozzle size)	The test used GMENT-12 grout which demanded using a 2.4-mm nozzle as per the implementability test. The pressure was as planned 6,000 psi and the step size was 5 cm with the step time varied depending upon the measured amount of grout as measured by the Jean Lutz. The desire was to achieve an overall void filling of 60% of the pit excavated volume; however, for edge holes, a lower amount of grout could be tolerated because of the predominant presence of low void soil. The string rotation rate was to get 2 revolutions of the drill stem per step thus ensuring complete coverage of grout in any 5 cm axial region.
	Grout returns(total volume, per hole)	In the 12 holes grouted during the field test, there were only minor returns observed; however, the cameras worked sufficiently to control the total grout return to a level such that the thrust block void space was not compromised. Therefore, use of the cameras within the thrust block worked as designed and is completely implementable.
	Grout Specifications(viscosity, density, sheer strength)	Field measurements made at the batch plant showed density and viscosity essentially identical as those in the laboratory. Limited Mud balance testing for density showed no change at the Cold Test Pit South after delivery. Initial batch of grout had multiple small debris that could have plugged nozzles but after double screening of the material at the batch plant, this problem was eliminated. The material appeared to be a mouse nest in either the vortex mixer, the "new" grout delivery trucks or in some part of the process at the batch plant. During one day of testing, there were multiple hours delay due to nozzle plugging events and overpressurization events that left the system in a stuck high pressure condition which resulted in the delivered grout going beyond the "pot" life of 4.5Hours. Use of a batch plant at the site of grouting would eliminate this timing problem.
	Volume of rinse water	Not measured only 12 holes grouted

Table 40. (continued).

Data Quality Objective	Measurement	Discussion of Results
	Contamination Control System Evaluation(time to switch shroud assembly, time to apply plastic sleeves from thrust block etc.	The shroud assembly could be removed in approximately 1 hour; however, with practice, this time could be halved. The time to attach the plastic sleeves, grout a hole, allow the system to drain, twist-off the sleeve and cut the twist off and move the rig to a new hole, took nominally 1 hour; however by attaching the sleeves with only one band and using an automatic drain system to keep the nozzles open, this process could be reduced to a 30min time period. This compares to the estimated time to grout using the x-y positional system discussed in the appendix of under 10 min. per hole.
	Contamination Control System (100 cm^2 smears of thrust block, drill string, shroud)	Thrust block smears showed elevated levels of terbium tracer following the spill in going from hole 2 to 3. No terbium was found on the outer shroud; however, the drill string and inner shroud showed terbium at the point where the inner shroud wore through due to twisting of the shroud during insertion. Samples above the seal on the shroud showed no terbium tracer indicating that the grease seals worked as designed. If the bag had not fallen on the top surface of the thrust block, there would not have been terbium present.
	Contamination Control (grout returns)	Only 1 in 12 holes showed a grout return with terbium above background (hole 12). This sample was barely above background and standard deviation. Minimal grout returns for the limited testing of 12 holes.
	Contamination Control (backgrounds-air, thrust block, and personnel monitors)	11 backgrounds taken for 7 high volume air samplers and multiple smears taken for top of thrust block, personnel monitors not taken. Adequate backgrounds taken for comparison to assess the implementability from a contamination control standpoint.
	Contamination Control-Air monitoring	During 2 days of grouting covering 12 holes no terbium tracer above background was found in the composited filters from the high-volume samplers suggesting that the in situ grouting process from a contamination spread standpoint is implementable.

Table 40. (continued).

Data Quality Objective	Measurement	Discussion of Results
	Camera Coverage under the thrust block	Cameras worked well in tracking the grout returns under the thrust block and in determining orientation of the drill string and nozzles during the grouting operation. To increase the view the camera Lexan well should be lowered to allow a more wide-angle view of all positions in the thrust block. Another possible solution (completely implementable) would be to install more wells in the thrust block to enhance the view.
	Relative humidity, pressure and temperature under the thrust block	Completely implementable and worked as planned. Only problem with the thrust block HEPA filtration system was in setting up the outlet flow flexible hose which collapsed when trying to establish a too low negative pressure; however by correct placement of the flexible hose a slight "hundredths of an inch" negative pressure was maintained during grouting.
	HEPA filter samples	Inconclusive in that there was no established background for HEPA filters. Pre-filler valves were higher than HEPA filler valves. Negative pressure was maintained under the thrust block; however, hose management needs redesign. Negative pressure under the thrust block did not puncture the plastic diaphragms under the thrust block for the ungrouted holes. Personnel monitors not evaluated in that enough holes were not grouted to warrant this action.
	Field-scale testing; tests/measurements postgrouting (volume increase, temperature of cure, excavation of the monolith, rock quality designation)	None made-testing postponed. Recommended that the pit be completed using the x-y positional system and a complete post grout test evaluation be performed as planned in Loomis 2000.
Test Objective 9-Evaluate effects of soil, organic sludge, and nitrate salt on grout properties	Grout/Interference Matrix Interaction-degree of void filling, degree of object bonding, encapsulation vs. permeation, extent of matrix distribution	Not made-testing postponed-recommended for future testing

Table 40. (continued).

Data Quality Objective	Measurement	Discussion of Results
Test Objective B-non critical-Evaluate effectiveness of grout microencapsulation in retaining VOCs Also Test Objectives 1 2 4 5 9 see above for description.	Grout integrity, set hardness, impeded curing, free water (surface and associated with source containers), Grout/ Interference Matrix Interaction, degree of void filling, degree of object bonding, encapsulation vs. permeation, extent of matrix distribution from source container, source container destruction, source container relocation/movement, extent of multiple source term interaction, soil inclusions mixing, void filling, fracture development, column development, water infiltration by U.S. Bureau of Reclamation, monolith grab sample testing to duplicate bench studies (leach, hydraulic conductivity, etc.)	Not made-testing postponed-recommended for future testing.
Test Objective C-Evaluate volume, type and expected disposition of secondary waste	Rinse water evaluation by ICP-MS-qualitative observation of shroud ware	Water evaluation rinse water showed terbium at below detection limits. As described in text, inner shroud was cut by rubbing on drill string; however outer shroud was intact. Complete failure of the weldment of the shroud to the top bracket as described in text requires new type of weldment. Grease fittings appear to have worked in that no contamination above the grease seal in yet terbium contamination was found on the drill string.

In summary, all of the data quality objectives were met for the bench and implementability testing phases. Even with only limited testing in the field testing phase, many of the objectives associated with the field testing involving the thrust block and contamination control system were addressed.

The bench studies produced a data set for a wide variety of grouts that can be used to address the monolith durability questions and expected performance relative to reducing the migration of contaminants from the grouted site. These data quality objectives will be discussed in detail in Volume 2 of this report. By comparing the performance in laboratory studies for neat grouts as well as mixtures of neat grout and expected interferences, it was possible to down-select from six candidate grouts to three grouts for recommendation in the implementability studies. As part of that process, parameters affecting the implementability of those grouts for application in the jet grouting process were measured.

The implementability testing proved that the three candidate grouts could be mixed on site and jet grouted at 6,000 psi. These tests focused on implementability issues such as cleanup, mixing difficulties, grout returns, in situ temperature of set, capability to create a hydraulic conductivity well in the matrix with a polyethylene rod, nozzle plugging and grout pressurization issues. Although the three grouts were found to be implementable from a jet grouting standpoint, the U.S. Grout created a too-high grout return because of the lower density relative to the TECT HG and GMENT-12 grout. In addition, comparison of the mixing and clean-up properties between TECT HG and GMENT-12 along with the fact that monolith formation was similar, the GMENT-12 grout was chosen for the field testing. The fact that the system could be mobilized, configured for jet grouting and monoliths were formed contributed to the conclusion that the whole process was implementable at the INEEL Cold Test Pit South which is a main data quality objective.

Prior to performing the field test, special system check out testing was performed involving the integration of the thrust block/drill string shroud assembly with the jet grouting process. As a result of the special testing, it was concluded that the system could be mobilized and applied at the INEEL. During the field testing many of the objectives on jet grouting implementability in the field were assessed. Several areas were found lacking specifically the need for complete draining of the drill stem prior to moving the system to a new hole. This was simulated in the test by breaking the system at the high-pressure hose as it exited the weather structure; however, it was recognized that a automatic bleed of the system was required. By removing all neat grout in the drill stem, the problems with filling the bag (on the end of the drill stem formed by twisting and cutting the plastic sleeve) with draining grout will be eliminated. Additionally, by using "hard piped" entrance and exit piping to the thrust block HEPA filtration system would eliminate the problems encountered with collapsing hoses. The shroud on the drill string required an "engineered" twist to avoid the inner shroud from contacting the rotating drill string and thus tearing the material.

In summary, the main data quality objective relating to implementability of the in situ grouting process using the thrust block contamination control system was demonstrated to be practical. Only minor design changes are required as discussed above. The overall grouting process is not as rapid (on a time per hole basis) compared to that expected using the alternative idea of the x-y positional system, which is discussed in the Appendix A of this report. However, the thrust block concept process could be applied for limited hot spots in buried waste regions. For instance, the thrust block concept could be used to grout a series of interconnected columns (say 10 hole columns) at various regions within a pit to support a cap and leave the thrust block in place. Another application would be to grout small very specific hot spots within a buried waste region. For this case, the relatively long time to grout a hole would not matter. The time issue only becomes important when grouting hundreds of thousands of holes over a 10-year period. Finally, to fully evaluate the missing data quality objectives (those relating to the characteristics of the emplaced monolith like void filling, and monolith durability), would require completion of the grouting in the pit followed by hydraulic conductivity testing and excavation of the monolith with further chemical and physical testing of samples from the resultant monolith.

10. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions are made relative to the in situ grouting technology:

- In situ grouting of buried transuranic waste using the thrust block concept is technically feasible at the INEEL with several modifications to the system. Modifications include providing a nozzle cleanout glovebox adjacent to the grouting area and developing a better pressure relief system to facilitate draining of fluid in the drill stem. In addition use of an additional plastic bag on the end of the taped plastic sleeve would avoid minor dripping of grout when moving the system. By using double screening in the grout preparation phase debris in the grout that could block nozzles can be avoided. Finally, modifications to the shroud assembly that would prevent wear on the inner shroud and disallow detachment at the upper bracket are required.

- Based on the quality of the monoliths formed in simulated buried waste pits during past testing and during the implementability and field testing phase of the current in situ grouting treatability study, it would be expected that the in situ grouting technology can be expected to fill voids in the waste and provide an excellent barrier to subsidence.

- A variety of grouting material are available for application to jet grouting. The current list includes TECT HG, U.S. Grout, and GMENT-12. With minor modifications, the paraffin based Waxfix and the Saltstone grout could most likely also be candidate grout materials. By reformulation of American Minerals, Inc.'s Enviro-Blend grout, it too could be considered a candidate grout.

- Bench studies of U.S. Grout, TECT HG, Enviro-Blend, and GMENT-12 show excellent retention of constituent elements aluminum, silicon, calcium, and the tracer strontium during ANS 16.1 leach testing.

- Bench studies suggest that U.S. Grout, TECT HG, and GMENT-12 show a strong tolerance to interferences commonly occurring within the transuranic buried waste at the INEEL including organic sludge (up to 9 wt% tolerance), soil (up to 50 wt% tolerance) and nitrate salts (up to 12 wt% tolerance).

- Bench studies of volatile organic retention show that there is only a few hundredths of a percent of source term lost per 10-day interval in special microencapsulation testing involving cured mixtures of neat grout and 9 wt% organic sludge (for U.S. Grout, TECT HG, and U.S. Grout).

- The contamination control features of thrust block/drill string shroud concept worked as planned. As expected, there was no terbium tracer spread to the high volume air monitors even though neat grout with potential terbium contamination was spilled onto the top surface of the thrust block when the sack containing grout drippings fell off the drill string stinger. In fact, ICP-MS of smears taken on the top surface of the thrust block following the clean-up of the spill showed terbium contamination; however, even with eventual extensive foot traffic and movement of the drill rig, there was no spread to the high volume filters. The idea is that the grout locks the tracer material up in larger less easily aerosolizable particles. It is speculated that if the bag had not dropped, there would only have been terbium tracer within the containment of the drill string shroud and under the negative pressure of the thrust block.

- Applying the lessons learned from the accident evaluation should ensure that an overpressurization event causing projectile motion of fittings does not happen on future grouting projects. It is not clear whether an ice mass blocked flow at the outlet of the pump and caused a sudden impulse in pressure leading to the accident or rather, it was normal blockage at the nozzles that led to the overpressurization. By using proper pressure gauges and pump power pressure feedback deactivation technologies and further by using rated fittings, hoses, and whip checks, an accident of the magnitude suffered on the in situ grouting treatability study will not happen again.

- With grouting limited to two rows, a hard stand-alone monolith was created by injecting GMENT-12 grout. Although only a limited excavation was accomplished, the monolith was consistent with the grouting of two rows in the pit. A special nitrate drum with metal sides was embedded in the monolith and this drum was examined in detail. The drum had been penetrated by the drill steel and the voids in the drum had been filled with the grout. The drum was embedded in the monolith and the soil/grout matrix actually stuck to the side of the drum when excavated. All voids in the drum were filled neat grout while the interior appeared to be a low compressive strength mixture of grout and nitrate salts. Other waste forms examined in the pit included a grouted combustible drum in which a large void had been filled with grout and the large waste box at the bottom of the pit had large voids filled by grout.

- The following recommendations are made based on the studies of the in situ grouting technology:

- There should be a tradeoff study comparing the thrust block concept and the x-y positional system remote grouting ideas. On paper, the x-y positional system answers all the problems encountered with the thrust block concept. With the x-y positional system, a trickle flow of grout can be allowed and there are no real limitations on grout returns which improves the chances of complete pit void filling (grout returns are allowed and even encouraged to ensure complete void filling). In addition, the x-y positional system has more flexibility when encountering large hard objects that might cause refusal of the drill bit. Finally, a cost comparison of the thrust block testings versus the x-y positional system show an approximate factor of 2.5 savings.

- If the tradeoff study shows that the x-y positional system is effective, then a system should be designed and tested with rare earth tracers in a pit similar to the in situ grouting pit at Cold Test Pit South. This study should focus on the implementability of the grouting delivery system but also should evaluate expected contamination spread if any within the grouting area. In this testing, all data quality objectives associated with monolith formation, hydraulic conductivity, and durability of the monolith should be completed as was planned for the subject in situ grouting treatability study.

- High-pressure jet grouting pumping equipment should include redundant pressure relief systems in the event of a stuck high-pressure event. In addition, to avoid these events (usually caused by nozzle blockage), a low-pressure gauge should be valved in to operate the pump during insertion of the drill string. During grouting, the low pressure gauge should be valved out and the high pressure gauge valved in. It is further recommended that the pumping equipment be located inside a heated weather structure to avoid potential ice build-up inside a pump system. Most importantly any high pressure equipment should be operated within the design range using easy to read gauges calibrated for the range of operation and the system should utilize only fittings, hoses, whip checks, and valves that are rated for the operating pressure expected in this case 400 bar (6,000 psi).

- In future excavations, the concept of using a quarry saw to cut the monolith may be desirable to avoid the collapse of the monolith due to the large stress caused by a backhoe bucket. In addition, use of the quarry saw will eliminate the excessive smearing of loose soil on the monolith that obscures the view.

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Appendix A

Preconceptual Design for In Situ Grouting

Appendix A
Preconceptual Design for In Situ Grouting

Introduction

The concept of creating a solid monolith within the buried transuranic waste by filling void space with grout materials using jet grouting was originated at the INEEL. In a series of EM-50 sponsored research projects, the technology was developed and culminated in a 1997 hot CERCLA treatability study in the INEEL Subsurface Disposal Area Acid Pit. Currently, the technology is part of treatability studies for the INEEL WAG 7-13/14 (INEEL SDA transuranic PITS and TRENCHES). The technology involves drilling into the waste and jet grouting specially formulated grouts at nominally 6,000 psi such that interstitial clay soil is pulverized and incorporated with the grout into the voids in the waste seam. The result is a solid monolith with low hydraulic conductivity and by using special additives to the grouts, a certain degree of chemical fixation of contaminants can be obtained. The grouts considered for application at the INEEL SDA all have natural analogs, which have been shown to be durable for geological times. The past work in INEEL jet grouting has developed a detailed design to mitigate migration of plutonium fines during the grouting process, which involves a complicated thrust block, and drill string shroud assembly. While considered safe and effective, the design is fairly complicated and involves difficult operations. Because of this an alternative idea has been developed at the INEEL involving a more straightforward approach. What follows are preconceptual design features of a novel application of the jet grouting process for creating a final disposal scenario for the INEEL buried transuranic waste.

Design Features

The design involves using a remotely operated bridge crane mounted jet grouting drill string assembly to deliver the grout with total x,y, z control. The overall idea is to create a total monolith out of the waste, side and bottom burdens, and the overburden material. The main departure from the past designs is that some grout returns will be allowed to the surface to facilitate grouting soil side, bottom and over-burden soils. This is accomplished by performing the whole operation in a weather structure with flexible inner liner under negative pressure. While the weather structure is costly, it is relatively straightforward to design and build and allows a very simplified operation of the grouting process. By using a bridge crane mounted system, access to all points within a pit is assured. For instance if a certain hole shows refusal of the drill steel, the bridge crane assembly can position the drill a few inches away and perform the drilling/grouting operation. By suspending the drill system considerably above the top surface, the need to control grout returns diminishes and the risk of overfilling the thrust block used in the original concept is eliminated. What follows are details of the grouting system.

Grouting Rig-Bridge Crane/Concrete Side Walls

Construction of the system would first involve placing a concrete containing wall just outside the boundaries of the waste pit. This concrete wall also acts as a support structure for the bridge crane as shown in Figure 1. Depending upon support requirements this wall could be constructed of driven "H" piles or slurry walls depending upon characterization of the suspected clean sideburden soils. The wall extends above the surface of the overburden and allows an ample space to contain grout returns and to also allow burial of the inner flexible shroud in the weather structure at the completion of grouting. The drill mast and associated hydraulic tubing for rotopercussion drilling and jet grouting are placed on a special platform on the bridge crane that allows exact x,y,z positioning for the sub assembly of the drill rig. Figure 1 also shows a top view of the weather structure and the relative position of a RadCon support building which allows personnel entry for manned maintenance. The high-pressure injection pump, all hydraulic motors, and associated grout receiving hopper are also shown as being external to the grouting operation.

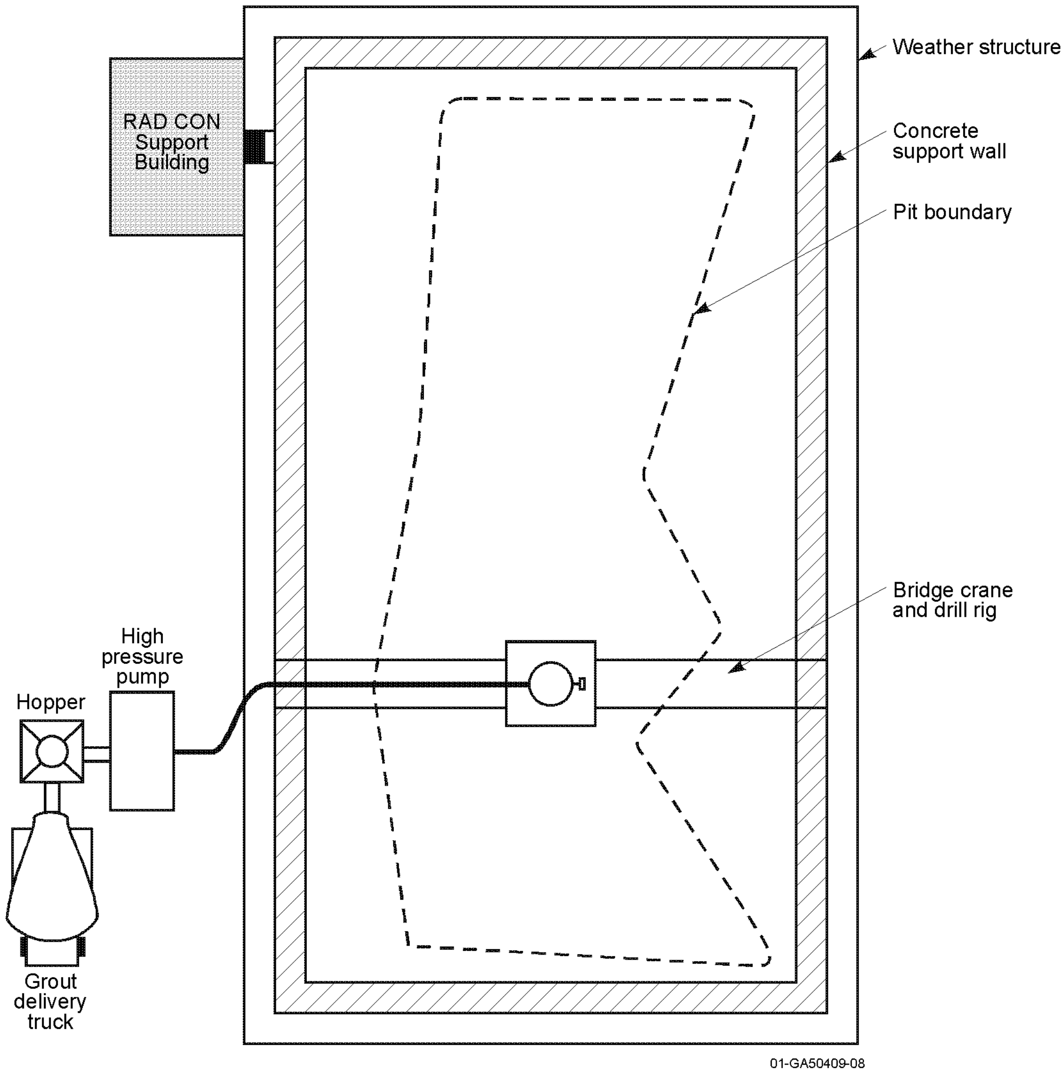

Figure 1. Top View Grouting Process.

Weather Structure/RADCON Building

The weather structure is assumed to be a negative pressure building with a TBD designation relative to status as a DOE nuclear materials handling facility. It is assumed as in all past SDA related projects that this weather structure will be designated and defined through negotiation with the agencies and regulators. Regardless it will be used to house the grouting operation allowing year-long grouting. It is also assumed that there will be an inner flexible "plastomer" wall that is considered disposable and the outer building is rigid "Butler Building" type of construction. Pit-9-Phase II has developed adequate requirements for such a structure; however, the inner flexible disposable inner sheath would require fire resistance materials and minimum volume for disposal. It is intended that when grouting is completed that the inner sheath is placed in the space at the top of the pit and covered with a final grout cap. Figure 2 shows the conceptual operation in a side view with the HEPA ventilation system and the inner flexible shroud material.

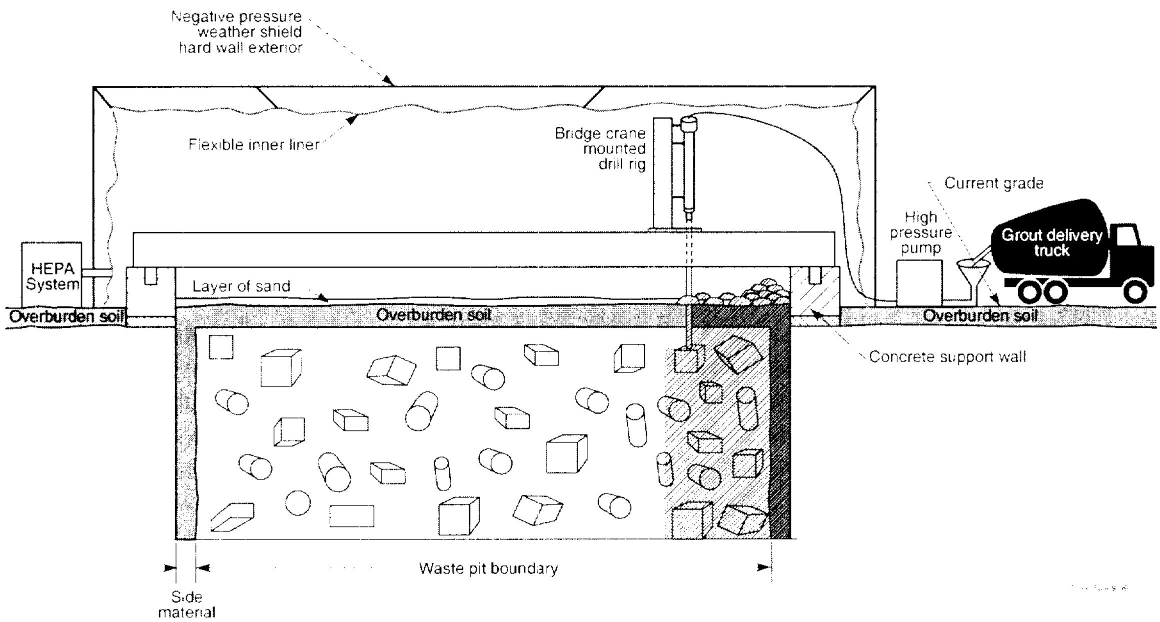

Figure 2. End View Grouting Operation.

This figure also shows how the grouting and hydraulic hoses enter the weather structure. On both Figure 1 and 2, only one drill/grouting assembly is shown on a single bridge crane. However, to expedite operations it may be desirable to have two grouting operations going at the same time or a separate rig in reserve in the event of injection nozzle plugging or other unforeseen events requiring operations shutdown for maintenance.

Details of Grouting

For this grouting concept the main departure from past operations is the inclusion of the top overburden in the grout monolith. To make a solid monolith out of the top overburden would require at least a 35 wt% grout 65 wt% soil mixture and accomplishing this task will create considerable grout returns. From a contamination control standpoint, this should present no problems in that the finely divided plutonium particulate will be incorporated into the liquidous grout/soil material. In addition, the top overburden material is essentially free of contaminants to start the operation. Therefore, grouting the top material is not expected to create a contamination spread problem only a fairly substantial amount of grout returns which can easily be handled by controlling the space between the top of the overburden and the top of the "H" piles or concrete support walls.

Figure 3 shows details of the grouting operation including a layer of clean sand on top of the overburden to act as a containment for the grout stream as the very top positions of the overburden are grouted jet grouted under high pressure.

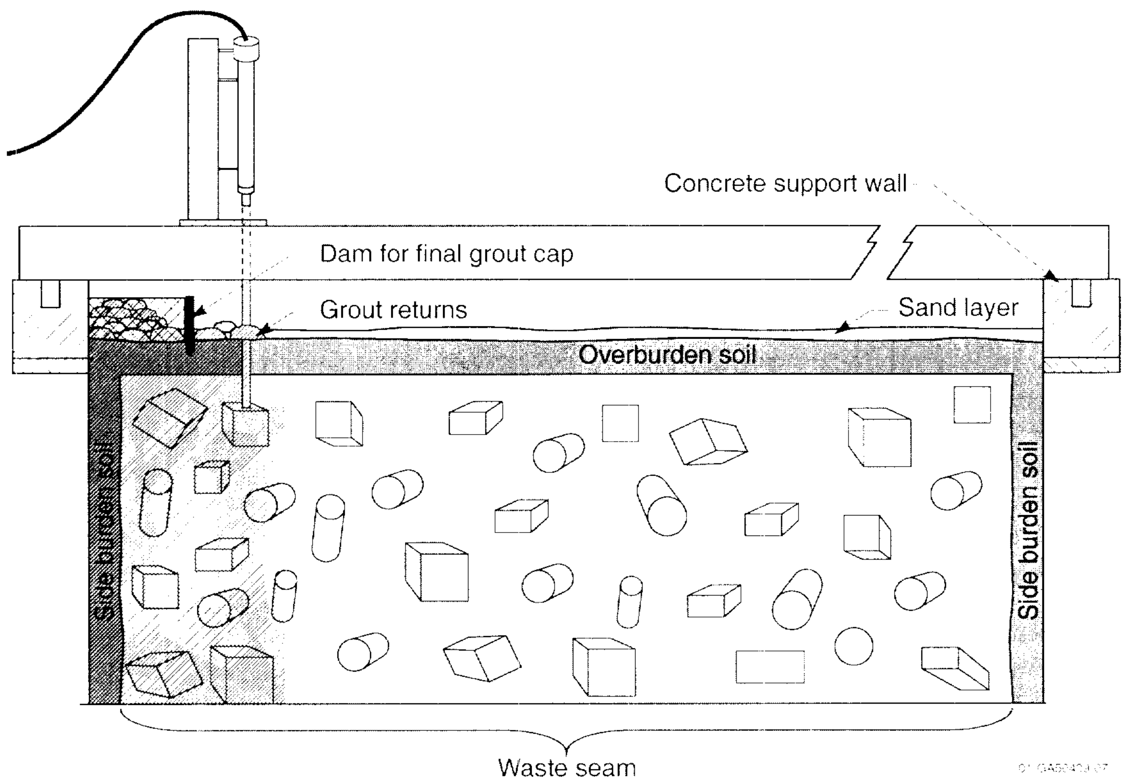

Figure 3. Detail Side View.

A sand layer above the overburden allows grouting to extend the monolith to the very top layer using a relatively low pressure (100 psi) without a violent spray associated with 6,000 psi jet grouting. Sand allows easy penetration of the grout and column formation under much lower pressures than that required for the tightly packed silty clay materials in the overburden. During the grouting operation, a region that has been completed can be isolated using a solid cofferdam block to allow partial filling of a just grouted region. By covering the grout returns in these regions with a neat grout, contamination spread via solidification and aerosolization are eliminated allowing a clean inner working area. During grouting operations, it will be initially assumed that maintenance will be performed using manned entry in bubble suits; however, an aggressive filter, smear and grout return sampling campaign will be performed using radiochemistry to determine loose surface and aerosolized spread of the plutonium oxide particulate which may allow manned entry in less restrictive personnel protective equipment.

Grouting will be accomplished identical to past grouting operations in that the drill stem is driven into the waste and when inserted to refusal in the basalt, the high-pressure pump is started and the rotating drill string is withdrawn in discrete steps. The other grouting variables are the time spent on a step and the number of revolutions of the drill string per step. If refusal is encountered on the way down (encountering heavy metal etc.) the drill string can be withdrawn and moved to several different positions near the refusal hole until penetration can occur. In this manner, "shadowing" effects can be eliminated.

Advantages of this grouting technique are that difficult materials like low-void organic sludges can be thoroughly mixed with grout without fear of excessive grout returns. While the operation will still be monitored with remote TV cameras, the amount of returns are not critical because ample space is provided by using the "wall" concept.

Final Disposal Cap

Following completion of grouting, the inner shroud assembly will be pulled into the remaining space provided by the wall and covered with a final pour of grout. To the extent possible, the drill string assembly will have been decontaminated prior to placing the shroud in the space. It is also possible that the drill string will simply also be disposed in the space provided by the wall prior to a final grout pour. In any case used or plugged drill steel will definitely be disposed of in the final pour. Following the final pour, the entire inner surface of the weather structure should be isolated from the contaminants and the weather structure can be removed for use on the next pit. Once the building has been removed, a final soil freeze cap will be placed to prevent freeze thaw cycles from degrading the monolith as shown in Figure 4.

This freeze cap will then be armored with 3-4 ft native basaltic cobble to prevent wind and water erosion of the cap (note: it is assumed that this basaltic cobble cap will be a soil collection zone that will eventually self vegetate with native plants). There will be no special monitoring with an individual pit rather monitoring for migration of contaminants will be part of the overall site-monitoring program.

Performance Standard

A performance standard for this type of operation would be to deliver on a pit wide basis nominally a volume of grout equal to 60% of the volume of the pit. On an average basis, this would ensure complete void filling within the waste seam. An additional performance standard would be to create a grouted overburden/sand region of nominally 35 wt% grout.

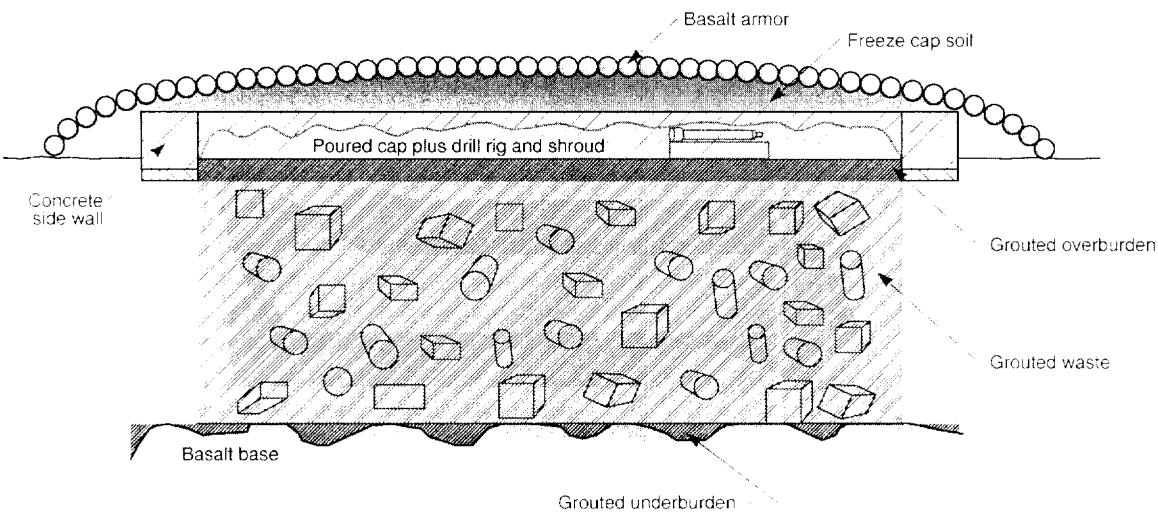

Figure 4. Monolith with Final Cap.

Grouting Schedule

It is estimated that the design could support grouting and placing a final cap for 9 acres in 6 years as follows: Using the x-y positional system in the single grout delivery system it is estimated that using a double grouting shift with a back shift for maintenance 64 holes per day can be grouted. It is estimated that grouting on a 20 in. triangular pitch matrix would involve up to 22,000 insertions per acre or about 343 days of operation, which is basically an 18-month operation with contingency. It is assumed that a grout batch plant would be built adjacent to the INEEL SDA and this plant would feed three systems operating simultaneously such that each system would grout 3 – 1acre sites each. It is assumed that the outer weather shield will be dismantled and placed on the next available pit. Allowing down time for moving between sites, the process could be accomplished in a 6-year timeframe including final freeze caps and basaltic cobble installation. This allows for slightly less than a year for initial set up and moving from pit to pit and 1 year for dismantlement of the weather structures and placement of the soil cap and cobble. It is assumed that at least a 2-year period will be required to permit and plan such a task and this is in addition to the 6 years for the actual process.

Preliminary Cost Estimate

- It is estimated that the weather structure system design/fabrication and construction including inner flexible disposable shroud, concrete retaining walls and total management and planning and waste management of the HEPA filtration systems would be $25M each. Since three weather structures will be used the total cost would be $75M.
- Grouting systems with bridge crane and controls with special control room in the RADCON building would be on the order of $3M for each pit (the drilling assembly is considered disposed of within the void created by the wall. However, the system control apparatus can be reused but this is offset by the need for new instrumentation as the project unfolds therefore it is assumed that the full price will be used for each pit. For 9 pits this would cost $27M.
- Batch Plant-$5M
- Planning for the whole operation would take 2 years of negotiations with the regulatory agencies and DOE as well as a complete internal design and ES&H RADCON review. This would involve approximately 20 people for 2 years or approximately 40 man-years or $6M.
- Operations would involve a staff of 30 plus nine shift supervisors x 6 years x $150,000/person for a total of $35.1M
- Assuming that the lowest cost grout that made the implementability testing criteria during the current in situ grouting treatability study is used at $2/gal and further assuming 60% void filling would result in approximately 2M gal/acre x 9 acresx$2/gal=$36M.
- Final cap pour would involve 400,000 gal per acre or 3.6M gal per 9 acres @$2/gal would be $7.2M
- Final soil and Basaltic Cover would cost $5M.
- Totals for 9 acres in 6 years:
- Planning/permitting-$6M
- Weather structure and construction of walls-$75M
- Grouting Systems-$27M
- Batch Plant-$5M
- Operations-$35.1M
- Grout-$36M
- Final Cap Pour-$7.2M
- Final Soil/Basaltic cover-$5M
- Total for 9 acres=$196.3M

  (If $5/gal grout is used the total is; $250.3M and if $8/gal grout is used the price is $304.3M.)

Appendix B

Data for Interference Tolerance Testing

Appendix B
Data for Interference Tolerance Testing

Table 1. Individual compressive strength test results in psi for the interference tolerance testing of neat grout specimens and specimens containing the INEEL soil interference at various loadings.

			Grout Product				
			C75	E	S	T	U
Specimen	Interference Type	Interference Percentage	Modified Tank Closure	Enviro-Blend	Salt Stone	TECT HG	U.S. Grout
Specimen A	None		7,502	147	1,619	6,232	2,355
Specimen B	None		8,909	160	1,605	6,378	2,643
Specimen C	None		6,505	142	693	6,349	2,748
Specimen A	INEEL Soil	12	5,734	61	1,407	3,759	3,980
Specimen B	INEEL Soil	12	5,145	59	1,167	4,227	3,803
Specimen C	INEEL Soil	12	6,774	65	1,202	4,464	3,904
Specimen A	INEEL Soil	25	5,876	25	919	3,501	2,995
Specimen B	INEEL Soil	25	5,855	23	933	3,762	3,159
Specimen C	INEEL Soil	25	6,413	29	877	3,698	3,139
Specimen A	INEEL Soil	50	2,722	41	1,351	1,884	1,186
Specimen B	INEEL Soil	50	2,263	45	1,386	1,927	1,421
Specimen C	INEEL Soil	50	2,602	43	1,216	1,962	1,228
Specimen A	INEEL Soil	75			403		757
Specimen B	INEEL Soil	75			382		835
Specimen C	INEEL Soil	75			424		823

Table 4. Individual compressive strength test results in psi for the interference tolerance testing of specimens containing the nitrate salt interference at various loadings.

			Grout Product				
			C75	E	S	T	U
Specimen	Interference Type	Interference Percentage	Modified Tank Closure	Enviro-Blend	Salt Stone	TECT HG	U.S. Grout
Specimen A	Nitrate Salts	12	1,906	36	771	3,224	5,298
Specimen B	Nitrate Salts	12	2,906	43	615	3,254	4,617
Specimen C	Nitrate Salts	12	4,702	37	714		4,490
Specimen A	Nitrate Salts	25	2,948	3	385	1,198	1,306
Specimen B	Nitrate Salts	25	2,298	4	424	1,184	1,420
Specimen C	Nitrate Salts	25	3,408	3	400	1,196	1,423
Specimen A	Nitrate Salts	50	3		2		1,819
Specimen B	Nitrate Salts	50	3		2		1,765
Specimen C	Nitrate Salts	50	2		1		1,857
Specimen A	Nitrate Salts	75	98	12	3		873
Specimen B	Nitrate Salts	75	102	12	3		866
Specimen C	Nitrate Salts	75	113	11	4		868

Table 5. Individual compressive strength test results in psi for the interference tolerance testing of specimens containing the organic sludge interference at various loadings.

			Grout Product				
			C75	E	S	T	U
Specimen	Interference Type	Interference Percentage	Modified Tank Closure	Enviro-Blend	Salt Stone	TECT HG	U.S. Grout
Specimen A	Organic Sludge	3	7,460	128	1,386	4,230	3,202
Specimen B	Organic Sludge	3	6,456	138	1,237	4,266	3,084
Specimen C	Organic Sludge	3	8,131	133	1,202	4,391	3,542
Specimen A	Organic Sludge	5	5,077	136	905	3,764	3,010
Specimen B	Organic Sludge	5	6,788	135	1,117	3,664	2,736
Specimen C	Organic Sludge	5	6,434	125	1,202	3,690	2,887
Specimen A	Organic Sludge	7	6,463	98	1,110	2,805	2,501
Specimen B	Organic Sludge	7	5,897	107	693	2,827	2,746
Specimen C	Organic Sludge	7	6,286	102	1,153	2,828	2,685
Specimen A	Organic Sludge	9	6,123	104	1,054	2,586	3,161
Specimen B	Organic Sludge	9	6,194	105	933	2,650	3,047
Specimen C	Organic Sludge	9	5,932	107	1,075		3,201
Specimen A	Organic Sludge	12		105	955	2,349	
Specimen B	Organic Sludge	12		126	820	2,308	
Specimen C	Organic Sludge	12		118	997	2,383	
Specimen A	Organic Sludge	25			615	204	
Specimen B	Organic Sludge	25			339		
Specimen C	Organic Sludge	25			566		
Specimen A	Organic Sludge	50		53		6	
Specimen B	Organic Sludge	50		44		7	
Specimen C	Organic Sludge	50		58			

Appendix C

Neat Grout American Nuclear Society 16.1 Individual Sample Data

Appendix C

Neat Grout American Nuclear Society 16.1 Individual Sample Data

Table 1. U Grout replicate A neat grout American Nuclear Society (ANS) 16.1 data.

Time (d)	Sr (mg/L)	Al (mg/L)	Ca (mg/L)	Si (mg/L)	NO_3^- (mg/L)
0.083	0.100	0.334	18.971	0.800	0.180
0.292	0.055	0.320	10.865	0.749	0.235
1.000	0.105	0.602	13.455	1.824	0.255
2.000	0.109	0.589	21.745	2.354	0.310
3.000	0.082	0.472	17.634	2.126	0.265
4.000	0.083	0.484	16.978	2.144	0.280
5.000	0.055	0.394	13.629	2.054	0.230
19.000	0.167	1.853	23.673	11.719	2.090
47.000	0.082	1.558	9.313	13.261	1.590
90.000	0.073	1.331	6.659	15.115	1.110

Time (d)	De (cm^2/s) Sr	Al	Ca	Si	NO_3^-
0.083	1.38E-10	8.97E-12	1.28E-09	2.74E-11	4.22E-10
0.292	5.48E-11	1.07E-11	5.50E-10	3.13E-11	9.32E-10
1.000	5.97E-11	1.13E-11	2.51E-10	5.57E-11	3.26E-10
2.000	7.87E-11	1.33E-11	8.06E-10	1.13E-10	5.95E-10
3.000	7.59E-11	1.46E-11	8.98E-10	1.57E-10	7.39E-10
4.000	1.09E-10	2.15E-11	1.18E-09	2.24E-10	1.16E-09
5.000	6.18E-11	1.84E-11	9.78E-10	2.67E-10	1.01E-09
19.000	7.05E-12	5.00E-12	3.64E-11	1.07E-10	1.04E-09
47.000	1.23E-12	2.58E-12	4.05E-12	9.90E-11	4.30E-10
90.000	8.78E-13	1.70E-12	1.89E-12	1.16E-10	1.89E-10

Time (d)	PH	eH (mV)
0.083	10.8	368.2
0.292	11.0	183.6
1.000	10.6	176.5
2.000	10.8	217.9
3.000	10.3	213.9
4.000	9.9	227.3
5.000	10.8	187.5
19.000	11.0	128.1
47.000	11.1	380.1
90.000	11.1	389.0

Table 2. U Grout replicate B neat grout ANS 16.1 data.

Time (d)	Sr (mg/L)	Al (mg/L)	Ca (mg/L)	Si (mg/L)	NO_3^- (mg/L)
0.083	0.046	0.238	6.622	0.048	0.180
0.292	0.055	0.324	9.998	0.704	0.270
1.000	0.118	0.612	14.661	1.924	0.255
2.000	0.118	0.589	25.172	2.461	0.290
3.000	0.091	0.492	19.872	2.179	0.240
4.000	0.082	0.456	17.230	2.133	0.280
5.000	0.056	0.401	15.345	2.161	0.230
19.000	0.155	1.859	21.558	11.016	1.890
47.000	0.082	1.549	9.683	13.534	1.500
90.000	0.073	1.376	11.107	16.710	1.110

Time (d)	De (cm^2/s) Sr	Al	Ca	Si	NO_3^-
0.083	2.94E-11	4.58E-12	1.57E-10	9.89E-14	4.22E-10
0.292	5.48E-11	1.10E-11	4.67E-10	2.77E-11	1.23E-09
1.000	7.50E-11	1.17E-11	2.98E-10	6.18E-11	3.26E-10
2.000	9.24E-11	1.33E-11	1.08E-09	1.25E-10	5.22E-10
3.000	9.29E-11	1.58E-11	1.14E-09	1.64E-10	6.09E-10
4.000	1.07E-10	1.92E-11	1.21E-09	2.21E-10	1.16E-09
5.000	6.41E-11	1.90E-11	1.24E-09	2.93E-10	1.01E-09
19.000	6.09E-12	5.07E-12	3.02E-11	9.46E-11	8.41E-10
47.000	1.23E-12	2.54E-12	4.40E-12	1.03E-10	3.85E-10
90.000	8.78E-13	1.79E-12	5.21E-12	1.41E-10	1.89E-10

Time (d)	PH	eH (mV)
0.083	11.1	355.0
0.292	10.9	181.0
1.000	10.8	178.0
2.000	10.9	216.0
3.000	10.3	203.0
4.000	10.8	212.0
5.000	10.8	193.0
19.000	11.2	134.0
47.000	11.1	366.0
90.000	11.1	391.0

Table 3. U Grout replicate C neat grout ANS 16.1 data.

Time (d)	Sr (mg/L)	Al (mg/L)	Ca (mg/L)	Si (mg/L)	NO_3^- (mg/L)
0.083	0.036	0.236	7.334	0.129	0.170
0.292	0.055	0.329	11.274	0.746	0.225
1.000	0.100	0.621	13.808	1.869	0.250
2.000	1.092	0.593	25.606	2.556	0.290
3.000	0.082	0.484	19.060	2.132	0.260
4.000	0.046	0.423	5.390	2.031	0.270
5.000	0.065	0.391	13.301	2.123	0.235
19.000	0.155	1.867	25.424	11.452	2.090
47.000	0.091	1.557	14.040	15.135	1.490
90.000	0.082	1.378	10.326	15.808	1.010

			De (cm^2/s)		
Time (d)	Sr	Al	Ca	Si	NO_3^-
0.083	1.80E-11	4.48E-12	1.93E-10	7.12E-13	3.75E-10
0.292	5.48E-11	1.14E-11	5.91E-10	3.10E-11	8.59E-10
1.000	5.37E-11	1.20E-11	2.64E-10	5.77E-11	3.14E-10
2.000	7.87E-09	1.35E-11	1.12E-09	1.33E-10	5.22E-10
3.000	7.59E-11	1.53E-11	1.05E-09	1.57E-10	7.13E-10
4.000	3.36E-11	1.65E-11	1.18E-10	2.01E-10	1.08E-09
5.000	8.65E-11	1.81E-11	9.30E-10	2.84E-10	1.05E-09
19.000	6.09E-12	5.13E-12	4.20E-11	1.02E-10	1.04E-09
47.000	1.50E-12	2.58E-12	9.26E-12	1.29E-10	3.80E-10
90.000	1.11E-12	1.82E-12	4.49E-12	1.27E-10	1.58E-10

Time (d)	PH	eH (mV)
0.083	10.8	365.0
0.292	10.9	172.0
1.000	10.8	175.0
2.000	10.8	209.0
3.000	10.4	202.0
4.000	10.5	237.0
5.000	10.6	203.0
19.000	11.0	130.0
47.000	11.2	375.0
90.000	11.1	388.0

Table 4. T Grout replicate A neat grout ANS 16.1 data.

Time (d)	Sr (mg/L)	Al (mg/L)	Ca (mg/L)	Si (mg/L)	NO_3^- (mg/L)
0.083	0.073	0.028	14.097	0.625	0.019
0.292	0.086	0.051	15.697	0.489	0.019
1.000	0.182	0.174	36.784	1.421	0.028
2.000	0.187	0.220	47.850	1.782	0.038
3.000	0.147	0.186	40.863	1.722	0.038
4.000	0.100	0.184	16.329	1.676	0.029
5.000	0.118	0.209	30.554	1.925	0.019
19.000	0.975	0.611	208.154	3.825	1.010
47.000	0.564	0.639	95.820	4.554	1.010
90.000	0.664	0.757	82.308	4.463	0.820

			De (cm^2/s)		
Time (d)	Sr	Al	Ca	Si	NO_3^-
0.083	4.33E-11	4.22E-14	4.89E-11	5.04E-12	2.75E-12
0.292	7.82E-11	1.83E-13	7.93E-11	4.01E-12	3.58E-12
1.000	1.04E-10	6.29E-13	1.30E-10	1.01E-11	2.31E-12
2.000	1.35E-10	1.25E-12	2.69E-10	1.96E-11	5.22E-12
3.000	1.43E-10	1.52E-12	3.35E-10	3.10E-11	8.87E-12
4.000	9.26E-11	2.07E-12	7.51E-11	4.14E-11	7.28E-12
5.000	1.66E-10	3.44E-12	3.39E-10	7.02E-11	4.04E-12
19.000	1.40E-10	3.65E-13	1.94E-10	3.41E-12	1.40E-10
47.000	3.40E-11	2.89E-13	2.98E-11	3.52E-12	1.01E-10
90.000	4.23E-11	3.65E-13	1.98E-11	3.05E-12	6.03E-11

Time (d)	PH	eH (mV)
0.083	11.0	329.0
0.292	11.0	146.0
1.000	11.0	121.0
2.000	10.9	154.0
3.000	10.3	158.0
4.000	10.8	166.0
5.000	11.1	131.0
19.000	11.1	66.0
47.000	11.0	367.0
90.000	11.4	346.0

Table 5. T Grout replicate B neat grout ANS 16.1 data.

Time (d)	Sr (mg/L)	Al (mg/L)	Ca (mg/L)	Si (mg/L)	NO_3^- (mg/L)
0.083	0.073	0.027	15.806	0.733	0.019
0.292	0.073	0.050	5.825	0.470	0.029
1.000	0.191	0.169	38.283	1.211	0.028
2.000	0.191	0.210	49.536	1.503	0.018
3.000	0.146	0.191	37.910	1.548	0.038
4.000	0.082	0.174	10.897	1.539	0.029
5.000	0.127	0.182	30.473	1.656	0.039
19.000	0.866	0.593	160.838	3.359	0.910
47.000	0.592	0.629	95.092	3.999	1.010
90.000	0.592	0.793	52.029	4.718	0.820

Time (d)	De (cm^2/s) Sr	Al	Ca	Si	NO_3^-
0.083	4.33E-11	3.91E-14	6.16E-11	6.92E-12	2.75E-12
0.292	5.64E-11	1.76E-13	1.09E-11	3.72E-12	8.31E-12
1.000	1.15E-10	5.97E-13	1.41E-10	7.35E-12	2.31E-12
2.000	1.42E-10	1.13E-12	2.89E-10	1.39E-11	1.17E-12
3.000	1.41E-10	1.59E-12	2.88E-10	2.51E-11	8.87E-12
4.000	6.24E-11	1.85E-12	3.35E-11	3.49E-11	7.28E-12
5.000	1.93E-10	2.63E-12	3.35E-10	5.20E-11	1.69E-11
19.000	1.11E-10	3.45E-13	1.16E-10	2.66E-12	1.14E-10
47.000	3.75E-11	2.80E-13	2.93E-11	2.70E-12	1.01E-10
90.000	3.37E-11	4.01E-13	7.94E-12	3.38E-12	6.03E-11

Time (d)	pH	eH (mV)
0.083	11.0	324.0
0.292	10.5	141.0
1.000	11.0	124.0
2.000	11.1	165.0
3.000	10.6	150.0
4.000	9.6	190.0
5.000	11.1	193.0
19.000	11.1	83.0
47.000	11.1	379.0
90.000	11.4	373.0

Table 6. T Grout replicate C neat grout ANS 16.1 data.

Time (d)	Sr (mg/L)	Al (mg/L)	Ca (mg/L)	Si (mg/L)	NO_3- (mg/L)
0.083	0.073	0.023	15.676	0.760	0.019
0.292	0.105	0.059	23.057	0.474	0.009
1.000	0.182	0.164	34.892	1.160	0.028
2.000	0.191	0.201	48.875	1.393	0.028
3.000	0.164	0.219	37.748	1.548	0.038
4.000	0.137	0.200	32.921	1.474	0.029
5.000	0.109	0.183	28.913	1.565	0.028
19.000	0.556	0.582	92.503	3.068	1.010
47.000	0.601	0.630	96.322	3.726	1.110
90.000	0.601	0.730	76.777	4.263	1.020

Time (d)	De (cm^2/s) Sr	Al	Ca	Si	NO_3-
0.083	4.330E-11	2.860E-14	6.060E-11	7.440E-12	2.750E-12
0.292	1.170E-10	2.450E-13	1.710E-10	3.770E-12	7.990E-13
1.000	1.040E-10	5.570E-13	1.170E-10	6.750E-12	2.310E-12
2.000	1.420E-10	1.040E-12	2.820E-10	1.200E-11	2.840E-12
3.000	1.770E-10	2.090E-12	2.840E-10	2.510E-11	8.870E-12
4.000	1.730E-10	2.450E-12	3.060E-10	3.200E-11	7.280E-12
5.000	1.420E-10	2.670E-12	3.020E-10	4.660E-11	8.750E-12
19.000	4.560E-11	3.310E-13	3.830E-11	2.210E-12	1.400E-10
47.000	3.850E-11	2.810E-13	3.010E-11	2.350E-12	1.230E-10
90.000	3.470E-11	3.400E-13	1.720E-11	2.770E-12	9.330E-11

Time (d)	pH	eH (mV)
0.083	11.0	322.0
0.292	11.1	129.0
1.000	11.0	133.0
2.000	11.2	145.0
3.000	10.5	143.0
4.000	11.0	153.0
5.000	11.1	126.0
19.000	11.1	83.0
47.000	11.1	380.0
90.000	11.3	361.0

Table 7. E Grout replicate A neat grout ANS 16.1 data.

Time (d)	Sr (mg/L)	Al (mg/L)	Ca (mg/L)	Si (mg/L)	NO_3^- (mg/L)
0.083	0.020	0.027	1.103	1.138	0.385
0.292	0.005	0.005	0.759	0.024	0.415
1.000	0.005	0.010	1.358	0.034	0.480
2.000	0.001	0.018	1.190	0.052	0.450
3.000	0.001	0.018	1.386	0.047	0.482
4.000	0.001	0.019	1.289	0.029	0.500
5.000	0.001	0.009	1.459	0.021	0.444
19.000	0.010	0.027	3.362	0.056	2.990
47.000	0.018	0.036	4.967	0.094	4.190
90.000	0.027	0.035	6.276	0.103	2.090

Time (d)	De (cm^2/s)				
	Sr	Al	Ca	Si	NO_3^-
0.083	4.90E-12	1.31E-13	2.82E-10	1.53E-11	1.69E-09
0.292	3.99E-13	5.88E-15	1.74E-10	8.87E-15	2.56E-09
1.000	1.19E-13	7.05E-15	1.65E-10	5.27E-15	1.02E-09
2.000	5.80E-15	2.79E-14	1.56E-10	1.52E-14	1.10E-09
3.000	9.85E-15	4.74E-14	3.60E-10	2.12E-14	2.15E-09
4.000	1.39E-14	7.46E-14	4.38E-10	1.13E-14	3.25E-09
5.000	1.79E-14	2.15E-14	7.21E-10	7.67E-15	3.30E-09
19.000	2.21E-14	2.39E-15	4.76E-11	6.74E-16	1.85E-09
47.000	5.21E-14	3.07E-15	7.50E-11	1.37E-15	2.63E-09
90.000	1.05E-13	2.62E-15	1.08E-10	1.48E-15	5.92E-10

Time (d)	pH	eH (mV)
0.083	10.2	269.0
0.292	9.6	174.0
1.000	9.8	176.0
2.000	10.3	193.0
3.000	9.8	212.0
4.000	10.8	214.0
5.000	8.7	207.0
19.000	10.2	122.0
47.000	10.7	339.0
90.000	10.7	360.0

Table 8. E Grout replicate B neat grout ANS 16.1 data.

Time (d)	Sr (mg/L)	Al (mg/L)	Ca (mg/L)	Si (mg/L)	NO_3^- (mg/L)
0.083	0.010	0.113	0.964	1.150	0.395
0.292	0.005	0.005	0.732	0.023	0.405
1.000	0.005	0.005	1.313	0.022	0.450
2.000	0.001	0.009	1.338	0.046	0.460
3.000	0.010	0.001	1.094	0.037	0.482
4.000	0.010	0.009	1.044	0.048	0.520
5.000	0.100	0.009	0.985	0.003	0.414
19.000	0.010	0.001	3.252	0.030	2.790
47.000	0.009	0.001	4.379	0.029	3.890
90.000	0.018	0.001	5.226	0.029	1.790

			De (cm^2/s)		
Time (d)	Sr	Al	Ca	Si	NO_3^-
0.083	1.21E-12	2.31E-12	2.15E-10	1.56E-11	1.78E-09
0.292	3.99E-13	5.88E-15	1.61E-10	8.15E-15	2.43E-09
1.000	1.19E-13	1.75E-15	1.55E-10	2.22E-15	8.95E-10
2.000	5.80E-15	6.98E-15	1.97E-10	1.20E-14	1.15E-09
3.000	9.85E-13	1.47E-16	2.26E-10	1.32E-14	2.15E-09
4.000	1.39E-12	1.67E-14	2.86E-10	3.10E-14	3.52E-09
5.000	1.79E-10	2.15E-14	3.30E-10	1.56E-16	2.87E-09
19.000	2.21E-14	3.30E-18	4.44E-11	1.93E-16	1.61E-09
47.000	1.30E-14	2.39E-18	5.84E-11	1.30E-16	2.27E-09
90.000	4.69E-14	2.15E-18	7.48E-11	1.17E-16	4.34E-10

Time (d)	pH	eH (mV)
0.083	10.2	266.0
0.292	9.8	172.0
1.000	9.8	175.0
2.000	10.3	189.0
3.000	9.8	208.0
4.000	10.3	226.0
5.000	10.1	177.0
19.000	10.2	123.0
47.000	10.6	336.0
90.000	10.6	375.0

Table 9. E Grout replicate C neat grout ANS 16.1 data.

Time (d)	Sr (mg/L)	Al (mg/L)	Ca (mg/L)	Si (mg/L)	NO_3^- (mg/L)
0.083	0.019	0.007	1.072	1.170	0.400
0.292	0.005	0.009	0.548	0.034	0.412
1.000	0.005	0.010	1.303	0.025	0.460
2.000	0.001	0.072	1.335	0.164	0.450
3.000	0.010	0.010	1.031	0.151	0.498
4.000	0.010	0.010	0.925	0.003	0.500
5.000	0.100	0.019	0.967	0.012	0.444
19.000	0.010	0.001	3.434	0.048	2.890
47.000	0.009	0.001	4.261	0.029	4.090
90.000	0.027	0.009	5.344	0.020	2.090

Time			De (cm^2/s)		
(d)	Sr	Al	Ca	Si	NO_3^-
0.083	4.39E-12	8.84E-15	2.64E-10	1.62E-11	1.82E-09
0.292	3.99E-13	1.90E-14	9.05E-11	1.77E-14	2.52E-09
1.000	1.19E-13	7.05E-15	1.52E-10	2.86E-15	9.35E-10
2.000	5.80E-15	4.47E-13	1.97E-10	1.52E-13	1.10E-09
3.000	9.85E-13	1.47E-14	2.01E-10	2.18E-13	2.29E-09
4.000	1.39E-12	2.07E-14	2.28E-10	1.21E-16	3.25E-09
5.000	1.79E-10	9.62E-14	3.21E-10	2.50E-15	3.30E-09
19.000	2.21E-14	3.30E-18	4.96E-11	4.94E-16	1.73E-09
47.000	1.30E-14	2.39E-18	5.53E-11	1.30E-16	2.51E-09
90.000	1.05E-13	1.73E-16	7.83E-11	5.59E-17	5.92E-10

Time (d)	pH	eH (mV)
0.083	10.2	276.0
0.292	9.9	172.0
1.000	9.6	185.0
2.000	10.4	145.0
3.000	9.6	210.0
4.000	10.8	202.0
5.000	10.3	171.0
19.000	10.3	123.0
47.000	10.8	332.0
90.000	10.7	378.0

Table 10. C75 Grout replicate A neat grout ANS 16.1 data.

Time (d)	Sr (mg/L)	Al (mg/L)	Ca (mg/L)	Si (mg/L)	NO_3^- (mg/L)
0.083	0.040	0.010	2.910	0.070	0.047
0.292	0.020	0.010	2.280	0.020	0.038
1.000	0.110	0.080	7.510	0.450	0.038
2.000	0.110	0.100	11.050	0.600	0.029
3.000	0.120	0.130	12.190	0.820	0.048
4.000	0.100	0.140	12.480	0.850	0.038
5.000	0.130	0.190	14.050	1.320	0.047
19.000	0.910	0.950	68.500	8.300	0.820
47.000	0.640	0.730	43.640	10.020	1.010
90.000	0.500	0.600	30.000	6.020	0.590

			De (cm^2/s)		
Time (d)	Sr	Al	Ca	Si	NO_3^-
0.083	2.53E-11	1.17E-14	5.59E-12	4.21E-13	3.26E-11
0.292	8.24E-12	1.52E-14	4.46E-12	4.46E-14	2.77E-11
1.000	7.39E-11	2.89E-13	1.45E-11	6.75E-12	8.25E-12
2.000	9.10E-11	5.58E-13	3.87E-11	1.48E-11	5.92E-12
3.000	1.85E-10	1.59E-12	7.98E-11	4.69E-11	2.76E-11
4.000	1.82E-10	2.60E-12	1.18E-10	7.10E-11	2.43E-11
5.000	3.94E-10	6.21E-12	1.93E-10	2.19E-10	4.80E-11
19.000	2.38E-10	1.91E-12	5.65E-11	1.08E-10	1.80E-10
47.000	8.51E-11	8.17E-13	1.66E-11	1.14E-10	1.99E-10
90.000	1.02E-10	1.08E-12	1.54E-11	8.07E-11	1.33E-10

Time (d)	pH	eH (mV)
0.083	10.7	310.0
0.292	11.0	235.0
1.000	10.9	185.0
2.000	11.6	213.0
3.000	11.1	190.0
4.000	11.0	199.0
5.000	10.9	203.0
19.000	10.6	210.0
47.000	10.8	292.0
90.000	10.9	301.0

Table 11. C75 Grout replicate B neat grout ANS 16.1 data.

Time (d)	Sr (mg/L)	Al (mg/L)	Ca (mg/L)	Si (mg/L)	NO_3^- (mg/L)
0.083	0.040	0.020	4.200	0.100	0.037
0.292	0.020	0.040	1.490	0.020	0.047
1.000	0.110	0.090	10.270	0.550	0.038
2.000	0.110	0.110	11.470	0.660	0.028
3.000	0.100	0.130	11.960	0.720	0.028
4.000	0.130	0.190	15.290	1.160	0.037
5.000	0.140	0.220	15.200	1.400	0.047
19.000	0.980	0.920	70.350	8.200	0.920
47.000	0.620	0.810	42.630	9.670	1.110
90.000	0.450	0.580	31.120	6.360	0.820

			De (cm^2/s)		
Time (d)	Sr	Al	Ca	Si	NO_3^-
0.083	2.53E-11	4.67E-14	1.17E-11	8.60E-13	2.02E-11
0.292	8.24E-12	2.43E-13	1.90E-12	4.46E-14	4.25E-11
1.000	7.39E-11	3.66E-13	2.71E-11	1.01E-11	8.25E-12
2.000	9.10E-11	6.74E-13	4.17E-11	1.79E-11	5.53E-12
3.000	1.29E-10	1.59E-12	7.69E-11	3.62E-11	9.39E-12
4.000	3.06E-10	4.82E-12	1.76E-10	1.33E-10	2.30E-11
5.000	4.58E-10	8.30E-12	2.27E-10	2.46E-10	4.80E-11
19.000	2.75E-10	1.79E-12	5.96E-11	1.05E-10	2.25E-10
47.000	8.00E-11	1.00E-12	1.58E-11	1.06E-10	2.39E-10
90.000	8.29E-11	1.01E-12	1.66E-11	9.00E-11	2.57E-10

Time (d)	pH	eH (mV)
0.083	10.7	311.0
0.292	10.7	237.0
1.000	11.2	172.0
2.000	10.5	198.0
3.000	10.9	192.0
4.000	10.4	195.0
5.000	10.8	206.0
19.000	11.2	198.0
47.000	10.9	284.0
90.000	10.9	312.0

Table 12. C75 Grout replicate C neat grout ANS 16.1 data.

Time (d)	Sr (mg/L)	Al (mg/L)	Ca (mg/L)	Si (mg/L)	NO_3^- (mg/L)
0.083	0.070	0.020	6.330	0.150	0.047
0.292	0.030	0.010	3.440	0.050	0.038
1.000	0.090	0.050	7.770	0.320	0.047
2.000	0.140	0.130	13.460	0.830	0.028
3.000	0.170	0.200	17.930	1.270	0.028
4.000	0.130	0.170	15.890	1.080	0.038
5.000	0.110	0.140	12.630	1.020	0.047
19.000	0.950	0.940	66.750	7.880	0.820
47.000	0.630	0.760	44.110	9.740	1.010
90.000	0.470	0.550	29.160	6.130	0.910

Time (d)	De (cm^2/s)				
	Sr	Al	Ca	Si	NO_3^-
0.083	7.75E-11	4.67E-14	2.66E-11	1.93E-12	3.26E-11
0.292	1.86E-11	1.52E-14	1.02E-11	2.81E-13	2.77E-11
1.000	4.99E-11	1.13E-13	1.55E-11	3.41E-12	1.27E-11
2.000	1.49E-10	9.38E-13	5.69E-11	2.83E-11	5.53E-12
3.000	3.71E-10	3.79E-12	1.72E-10	1.12E-10	9.39E-12
4.000	3.06E-10	3.87E-12	1.91E-10	1.15E-10	2.43E-11
5.000	2.80E-10	3.35E-12	1.55E-10	1.32E-10	4.80E-11
19.000	5.19E-10	3.72E-12	1.07E-10	1.93E-10	3.59E-10
47.000	8.26E-11	8.85E-13	1.70E-11	1.07E-10	1.99E-10
90.000	9.06E-11	9.13E-13	1.46E-11	8.39E-11	3.14E-10

Time (d)	pH	eH (mV)
0.083	10.5	313.0
0.292	10.9	229.0
1.000	10.8	180.0
2.000	10.3	200.0
3.000	10.9	186.0
4.000	10.7	189.0
5.000	11.0	214.0
19.000	10.6	223.0
47.000	10.6	262.0
90.000	10.8	296.0

Table 13. S Grout replicate A neat grout ANS 16.1 data.

Time (d)	Sr (mg/L)	Al (mg/L)	Ca (mg/L)	Si (mg/L)	NO_3^- (mg/L)
0.083	0.010	0.040	0.060	0.910	0.038
0.292	0.160	0.120	2.720	0.220	0.028
1.000	0.170	0.340	10.260	1.090	0.038
2.000	0.110	0.200	6.910	0.720	0.028
3.000	0.160	0.540	12.400	1.980	0.019
4.000	0.100	0.380	10.390	1.630	0.028
5.000	0.090	0.290	8.470	1.450	0.010
19.000	0.680	1.510	46.430	7.630	0.820
47.000	0.340	1.140	13.110	7.480	1.400
90.000	0.170	0.590	7.500	4.400	0.720

Time (d)			De (cm^2/s)		
	Sr	Al	Ca	Si	NO_3^-
0.083	1.14E-12	2.40E-14	6.66E-15	1.21E-10	1.56E-11
0.292	3.87E-10	2.81E-13	1.79E-11	9.32E-12	1.10E-11
1.000	1.30E-10	6.72E-13	7.50E-11	6.83E-11	6.04E-12
2.000	6.62E-11	2.86E-13	4.21E-11	3.65E-11	4.04E-12
3.000	2.41E-10	3.53E-12	2.32E-10	4.70E-10	3.14E-12
4.000	1.31E-10	2.45E-12	2.28E-10	4.47E-10	9.67E-12
5.000	1.38E-10	1.86E-12	1.96E-10	4.53E-10	1.58E-12
19.000	9.71E-11	6.21E-13	7.25E-11	1.56E-10	1.32E-10
47.000	1.75E-11	2.55E-13	4.20E-12	1.08E-10	2.78E-10
90.000	8.66E-12	1.34E-13	2.69E-12	7.38E-11	1.44E-10

Time (d)	pH	eH (mV)
0.083	10.4	300.0
0.292	10.6	222.0
1.000	10.1	202.0
2.000	10.3	203.0
3.000	11.0	200.0
4.000	9.8	205.0
5.000	10.5	212.0
19.000	10.8	226.0
47.000	10.5	205.0
90.000	10.9	224.0

Table 14. S Grout replicate B neat grout ANS 16.1 data.

Time (d)	Sr (mg/L)	Al (mg/L)	Ca (mg/L)	Si (mg/L)	NO_3^- (mg/L)
0.083	0.060	0.030	2.850	0.120	0.038
0.292	0.020	0.020	1.290	0.030	0.028
1.000	0.110	0.011	6.100	1.090	0.037
2.000	0.130	0.140	8.250	0.640	0.028
3.000	0.200	0.440	14.550	1.930	0.019
4.000	0.120	0.250	10.470	1.160	0.028
5.000	0.090	0.200	7.450	1.030	0.010
19.000	0.690	1.150	41.390	7.740	1.020
47.000	0.340	1.230	12.100	6.960	1.590
90.000	0.180	0.570	7.600	4.500	0.820

Time (d)	De (cm^2/s) Sr	Al	Ca	Si	NO_3^-
0.083	4.16E-11	1.33E-14	1.50E-11	2.12E-12	1.56E-11
0.292	6.03E-12	7.80E-15	4.01E-12	1.72E-13	1.10E-11
1.000	5.37E-11	7.00E-16	2.67E-11	6.83E-11	5.72E-12
2.000	9.38E-11	1.40E-13	6.03E-11	2.88E-11	4.04E-12
3.000	3.75E-10	2.35E-12	3.18E-10	4.45E-10	3.14E-12
4.000	1.91E-10	1.07E-12	2.31E-10	2.28E-10	9.67E-12
5.000	1.38E-10	8.80E-13	1.51E-10	2.30E-10	1.58E-12
19.000	1.00E-10	3.60E-13	5.76E-11	1.60E-10	2.04E-10
47.000	1.75E-11	2.97E-13	3.57E-12	9.37E-11	3.57E-10
90.000	9.71E-12	1.26E-13	2.77E-12	7.71E-11	1.87E-10

Time (d)	pH	eH (mV)
0.083	10.2	301.0
0.292	11.0	205.0
1.000	10.0	228.0
2.000	10.1	198.0
3.000	10.5	210.0
4.000	10.0	201.0
5.000	10.7	199.0
19.000	10.9	203.0
47.000	10.6	223.0
90.000	10.8	232.0

Table 15. S Grout replicate C neat grout ANS 16.1 data.

Time (d)	Sr (mg/L)	Al (mg/L)	Ca (mg/L)	Si (mg/L)	NO_3^- (mg/L)
0.083	0.080	0.060	3.360	0.190	0.037
0.292	0.060	0.010	1.660	0.040	0.028
1.000	0.140	0.340	7.510	0.460	0.038
2.000	0.250	0.440	15.740	1.830	0.028
3.000	0.130	0.220	9.710	1.020	0.019
4.000	0.150	0.380	12.580	1.790	0.028
5.000	0.130	0.340	10.460	1.640	0.019
19.000	0.680	1.440	46.140	7.580	1.020
47.000	0.330	1.240	11.960	7.070	1.500
90.000	0.160	0.560	7.400	4.600	0.820

			De (cm^2/s)		
Time (d)	Sr	Al	Ca	Si	NO_3^-
0.083	7.38E-11	5.39E-14	2.09E-11	5.34E-12	1.47E-11
0.292	5.42E-11	1.94E-15	6.64E-12	3.07E-13	1.10E-11
1.000	8.83E-11	6.72E-13	4.05E-11	1.21E-11	6.04E-12
2.000	3.44E-10	1.38E-12	2.19E-10	2.37E-10	4.04E-12
3.000	1.59E-10	5.87E-13	1.41E-10	1.25E-10	3.14E-12
4.000	2.98E-10	2.45E-12	3.34E-10	5.38E-10	9.67E-12
5.000	2.89E-10	2.55E-12	2.98E-10	5.82E-10	5.70E-12
19.000	9.71E-11	5.63E-13	7.17E-11	1.54E-10	2.04E-10
47.000	1.65E-11	3.02E-13	3.48E-12	9.68E-11	3.16E-10
90.000	7.68E-12	1.21E-13	2.62E-12	8.07E-11	1.87E-10

Time (d)	pH	eH (mV)
0.083	10.6	297.0
0.292	10.1	216.0
1.000	9.8	232.0
2.000	10.2	192.0
3.000	10.9	206.0
4.000	9.5	195.0
5.000	10.2	211.0
19.000	11.0	207.0
47.000	10.6	197.0
90.000	10.9	211.0

Appendix D

Cement Chemistry and Durability

Appendix D

Cement Chemistry and Durability

Introduction

The purpose of this review is to describe the chemical properties of cementitious grout systems, discuss their expected change with time, and use this information to estimate the solubility limits of contaminants of potential concern found in the Idaho National Engineering and Environmental Laboratory (INEEL) Subsurface Disposal Area (SDA).

The in situ grouting technology is a method to stabilize and encapsulate buried waste such as that found at the SDA. Many different grout materials may be used for this application and may have a very broad range of compositions and properties. Examples include grout materials based on silicone, or phosphate, or iron oxide-sulfate, or paraffin or others. The specific grout material would be selected to meet the requirements of a specific application. Cementitious grout materials and their derivatives are discussed in the following paragraphs. They include a very broad range of materials having a very broad range of properties. They share the common characteristic of belonging within the same chemical family as the well known Portland cements and they are often a derivative of one of the Portland cements. The in situ grouting application mixes the anhydrous cementitious grout material with water and injects this mixture into the waste site at high pressure. The result is a hydrous grout material in intimate contact with the waste materials and whose chemical properties may affect the buried waste components.

The chemical properties of the grout material may affect, and be affected, by the chemical properties of the waste site ground water and waste materials. The acid-base character (pH) and oxidation-reduction potential (eH) are two chemical properties, which are particularly important for estimating the behavior of grout materials in the waste site chemical environment. Changes in pH and/or eH can affect the dissolution/precipitation of mineral material and the dissolution/evolution of gasses and also the adsorption/desorption of aqueous species.

PH is defined as the negative logarithm of the hydrogen ion activity and is a measure of the acid versus base properties of an aqueous system. The pH can affect the solubility of the grout and waste materials by altering the chemical speciation of a particular material in aqueous solution. The eH is the electrical potential required for moving electron(s) between oxidized and reduced species in an aqueous solution and is expressed in volts. eH is important for estimating the behavior of elements, which can exist in more than one oxidation state, such as technetium, chromium, plutonium, neptunium, and americium. Elements such as technetium and chromium are very insoluble in reducing conditions, but become very soluble in a more oxidized environment. Some elements can exist in as many as four oxidation states. Each oxidation state has a different solubility because the oxidation state (and pH) affects the speciation of the element in aqueous solution.

Chemical Properties of Cement

Cement grout is an engineered material, which usually has an anhydrous bulk composition of about 60 to 65 percent lime (CaO) and 21 to 24 percent silica (SiO2) with less than about 15 percent total of alumina (Al2O3), iron oxide (Fe2O3), magnesia (MgO) and sulphate (SO4). Several variations of the cement compositions have been developed for certain applications, for example sulfate resistant varieties, quick set varieties, expanding varieties for demolition application, varieties for oil field applications and many others. The composition may also be modified by adding various substances, both organic and inorganic, to optimize a particular set of properties for various applications. Inorganic materials used to modify the composition include fly ashs, silica fumes, blast furnace slags, and various natural pozzolans.

After one year at ambient temperatures, a typical Portland cement material will be made up of 95 to 98 percent of hydrated compounds and will, based on engineering experience, remain unchanged within the next 100 to 200 years (Atkins and Glasser, 1992) to perhaps thousands of years as found in ancients cements (Atkins et al,1991). The grout after set and cure will consists of a liquid and a solid material. The liquid is an aqueous phase consisting of water and dissolved species. The water is located in the pore space. The pore space makes up about 20 to 30 volume percent of the set material and has a pore size generally <2um, both pore volume and size depends primarily on the initial water-cement ratio. The porosity generally decreases with age (Atkins and Glasser, 1992). The solid material is composed primarily of cement matrix gel (referred to in the cement literature as "CSH"), a hydrated, amorphous material composed of lime (CaO), and silica (SiO2) as well as water (H2O). Additional phases may include lesser amounts of portlandite (Ca(OH)2) and smaller amounts of other phases such as ettrihngite [(Ca3Al(OH)6*12H2O)]2(SO4)3*2H2O, and hydrogarnet (Ca3Al2(OH)12-Ca3Al2Si(OH)8 and others (Atkins and Glasser, 1992). In the cases where fly ashs, silica fumes, or blast furnace slags are added to Portland cement, the amount of portlandite is reduced or eliminated by chemical reaction during the set and cure process and other phases, such as gehlinite hydrate (Ca2AlSiO4(OH)3 and others, may be produced.

PH, Acid-Base Properties

The cement materials are somewhat soluble in water and control the pH of the water in the intergranular space within the waste form monolith. The most soluble materials produce the pH of the intergranular solution at a given time. The pH will change with time, becoming lower in successive steps, as each of the pH controlling phases is removed in turn by some processes such as dissolution or chemical reaction. In the case of Portland cement, small amounts of sodium and/or potassium hydroxide may cause the initial pH values to be very high, in excess of 13. These hydroxides are very water soluble, therefore the pH drops to lower values as they dissolve and are leached from the system. The portlandite, Ca(OH)2, component of Portland cement maintains the pH of the intergranular solution at about 12.5 as long as any portlandite remains in the cement matrix. If portlandite is depleted or is initially not present as is the case in many blended grouts, dissolution of the cement matrix gel, CSH, controls the pH of the intergranular solution. As the CSH ages and changes composition slightly, the pH may decrease to about eleven.(Abrojano and Johnson, 1990) or 10.5 (Krupka and Serne 1998) The pH will remain at these values as long as CSH remains in the waste form matrix. Cement grouts "buffer" the pH for long periods of time because CSH is the dominate material, greater that about seventy percent of the total cementitious material. The pH will remain approximately constant as long as a portion of the CHS remains in chemical contact with the remainder of the system.. If the cement matrix gel is totally removed or isolated by some process, residual phases or reaction products, particularly calcite, or the ambient environment will control the pH of the system. In the case of the SDA, ground water pH is about 7.2 at present, (Hull and Pace 2000) and is controlled by chemical reactions among calcite (CaCO3) and carbon dioxide (CO2) and ground water

The cement matrix gel may be removed from the system by several mechanisms. These include simple dissolution, crystallization and chemical reaction.

Dissolution is unlikely to remove significant quantities of the cement matrix because the results of American Nuclear Society (ANS)/ANSI 16.1 leach test show (see Section 3.6 in the body of the report) that several tens of thousands of years are required to remove one percent of the major components, given the water infiltration rate (8.5 cm/year) at the SDA. The ANS/ANSI 16.1 leach tests provide conservative estimates because the procedure uses distilled water and frequent leachate replacement. Similar conclusions were reached by Alkorn et al, (1989) and also Alcorn et al (1990) who showed that Portland type-V grout waste repository seals, 0.5 m thick, would have worst case performance life time of several tens of thousands of years.

Crystallization of cement matrix gel would be unlikely to significantly affect pH values in time periods less than several thousand years. Crystallization of cement matrix gel would cause it to become a crystalline material. and would therefore have different properties. The cement matrix gel is an amorphous to slightly ordered material capable of showing a diffuse, poorly defined x-ray diffraction pattern similar to the mineral tobermorite. The cement matrix gel is thermodynamically unstable with respect to well crystallized materials, such as tobermorite, which have a similar bulk composition. The pH produced by a semicrystalline tobermorite is 11 (Atkins et al, 1990). If the matrix crystallizes, the pH will be somewhat lower. Experimental studies measuring pH versus time have shown that both Portland type V cement and type V cement modified with blast furnace slag or fly ash require about 500,000 to 1,000,000 years for the pH to decline to 10 (Atkinson, et al 1990).

The cement matrix gel can also be affected by reaction with other chemical species within the waste site environment such as sulfate (SO4) and carbon dioxide (CO2). In this case the pH controlling phases are removed from the system by chemical reaction. The rate of these degradation reactions is controlled by the rate of diffusion of sulfate, carbon dioxide and related species into the cement matrix from the surrounding environment. Potential sulfate-cement reaction products include gypsum (CaSO4) and ettringite Ca6Al2(SO4)3(OH)12*26H2O. A minor amount of gypsum is an additive to certain grout materials and minor itteringite is a common cement phase. Typical SDA ground water does not have a high sulfate content and is not saturated in gypsum, (Hull and Pace 2000). Compared to typical grout materials the chemical potential of sulphate in SDA ground water is not high and is not expected to have a significant affect on in situ grouting grout materials. Carbon dioxide is an important component in the SDA geochemical system and locally comprises up to ten percent of the soil gas. In the case of the in situ grouting materials, the diffusion rate of carbon dioxide and related species, as well as sulfate, will be no greater than the rate of diffusion of the nitrate measured using laboratory in situ grouting samples and the ANS/ANSI 16.1 diffusion measurement procedure. Computer model estimates of the rate of carbon dioxide penetration of cement waste form materials indicate about 7 cm of the outer repository wall could be penetrated in 300 years (Keum et al 1997), assuming a CO2 aqueous source saturated with calcite and an effective diffusion coefficient of 4.1x10-4 m2/year. The measured effective diffusion coefficients for nitrate in the in situ grouting grout materials are about 1.2x10-6m2/year or about 100 times smaller than that used in the computer simulation model. The SDA ground water is saturated in calcite at a pH of about 7.2 (Hull and Pace 2000). The 7.2 pH is the limiting value in the case of complete alteration of the cement matrix to calcite and silica (opal)

EH

The oxidation state of in situ grouting grout materials control the eH environment within the intergranular pore solutions within the in situ grouting monolith in a fashion similar to the pH (Atkins and Glasser, 1992). Portland cement and similar cementitious materials are manufactured by heating, in air, mixtures of calcite, clay and other materials to temperatures somewhat above the beginning of melting of the calcined ingredients. Air is "oxidizing" compared to many environments and the relatively oxidizing character of air present in the high temperature kilns during the cement manufacturing processes is inherited by the finished cement product. eH measurements of typical Portland cements range from 0 to about 100 mV (Atkins and Glasser 1992). Blast furnace slags have an oxidation-reduction character exactly opposite that of Portland cement. Blast furnace slag is a by-product of the iron and steel manufacturing processes. Like Portland cement, iron and steel are also produced at high temperature, above the beginning of melting of the oxide as well as metallic constituents. Unlike Portland cement, the manufacture of iron and steel produces very reducing conditions, much more so than is found in most environments. Blast furnace slag is a glassy material containing one to two percent of dissolved sulphur and also iron and manganese (Atkins and Glasser,1992), all of which are in a chemically reduced form. The reduced chemical species impose and maintain the very strongly reducing conditions of the original iron and steel making process when used as a hydraulic cement material. The eH of the intergranular pore fluid in blast furnace slag cements is typically about -300 mV. (Atkins and Glasser,1992) The oxidizing capacity of a grout material to control eH can be measured by an electro-titration method (Atkins and Glasser,1992). The development of the eH value of grout materials produced by blends between Portland cement and blast furnace slag is time dependent, with lesser quantities of slag requiring longer time periods to produce the low eH, reducing conditions. For example, cement-blast furnace slag blends containing more than 70% slag produced reducing conditions within one month where as the data suggested that a 50% blend would probably require more than 18 months. The time dependence of the eH reduction is thought to be due to the slow reaction rate of blast furnace slag. (Atkins and Glasser,1992) In the natural environment, the grout materials would become oxidized over time and eventually loose their eH controlling properties. There are virtually no quantitative data to estimate the time period that grout materials would control the eH of their intergranular pore solutions. The oxidation rate would probably be comparable to the rate of diffusions of oxidizing chemical species into the treated waste material.

In Situ Grouting Bench Test Results

The in situ grouting bench tests have measured the pH, eH and many other properties of five potential grout candidates and the affect on the in situ grouting properties when mixed with nitrate salts (12 weight percent), SDA soils (fifty weight percent) and simulated series 743 organic sludge from the Rocky Flats Plant (nine weight percent). The results are presented in detail in Appendix C and Appendix D and discussed in Section ---of the Final Report. The grout materials include:

TECT

TECT is a pozzolanic cementitious grout with proprietary additives (Grant et al. 2000). The average pH of five through forty three day ANS/ANDI 16.1 leach periods is 11.2 (Appendix C). Similar measurements with added nitrate salts: 11.7, with added organic sludge: 11.6, with added SDA soil:11.6 (Appendix D). The average eH values are 241 mV (Appendix C) for the neat material and is virtually constant for all interference mixtures at 410 mV.

U.S. Grout (Ultra Fine Grout)

U.S. Fine grout (American Petroleum Institute [API] Type H) is a pozzolanic material (Grant at al. 2000). The average pH of five through forty three day ANS/ANDI 16.1 leach periods is 11 (Appendix C). Similar measurements with added nitrate salts: 11.3, with added organic sludge: 11.5, with added SDA soil:11.6 (Appendix D). The average eH values are 241 mV (Appendix C) for the neat material. It is virtually constant for all interference mixtures at 410 mV.

Enviro-Blend

Enviro-Blend is a proprietary cementitious grout containing phosphorous. The average pH of five through forty three day ANS/ANDI 16.1 leach periods is 10.3 (Appendix C). Similar measurements with added nitrate salts: 10.8, with added organic sludge: 10.2, with added SDA soil:10.8 (Appendix D). The average eH values are 254 mV (Appendix C) for the neat material. eH is virtually constant for all interference mixtures at 408 mV.

GMENT-12

GMENT-12 is a derivative of the Tank Closure Grout (Westinghouse Savannah River Company [WSRC] 1997) developed at the Savannah River site to stabilize waste remnants in storage tanks. It is formulated with over 50 weight percent Type V cement (ASTM C150), about nine weight percent ground blast furnace slag and lesser silica fume and thirty percent water plus various additives. (Grant et al. 2000). The average pH of five through forty three day ANS/ANDI 16.1 leach periods is 10.8 (Appendix C). Similar measurements with added nitrate salts: 11.4, with added organic sludge: 11.6, with added SDA soil:11.0 (Appendix D). The average eH values are 247 mV (Appendix C) for the neat material. eH is virtually constant for all interference mixtures at 410 mV.

Salt Stone

Salt Stone was developed at the Savanna River Site to stabilize nitrate salt waste streams and associated radioactive contaminants. (WSRC 1992 and 1994) It is formulated from a mixture of Class F fly ash and grade 120 blast furnace slag in equal proportions together with 3.3 weight percent Portland Type II cement (ASTM C150) and 41.3 weight percent water (Grant et al. 2000). The average pH of five through forty three day ANS/ANDI 16.1 leach periods is 10.7 (Appendix C). Similar measurements with added nitrate salts: 10.9, with added organic sludge: 10.5, with added SDA soil:11.3 (Appendix D). The average eH values are 212 mV (Appendix C) for the neat material. eH is virtually constant for all interference mixtures at 411 mV.

Recommended pH and eH Values

A single recommended pH value for contaminate solubility estimates is eleven. The results of the bench testing indicate that all the tested grout formulations behave similar to blended cements and have pH values less than 12.5, indicating an absence of the phase portlandite. TECT, GMENT-12, SALT TONE, and U.S. Grout are very similar to one another and have pH values in the range 10.7 to 11.7 including neat grout samples as well as the mixtures of grout and interference material. Of these, GMENT-12 and Saltstone may have systematically slightly lower pH values by about 0.4 units, but the variation in the data is too great to demonstrate this conclusively. The pH of neat Enviro-Blend and mixtures of this grout with interference materials range from 10.3 (neat) to 10.8 (INEL soil and nitrate salts). These values are about 0.8 units less than TECT and U.S. Grout and are greater than the scatter in the data.

The single value recommended for modeling purposes is pH 11, a reasonable representative of the grout formulations being considered and consistent with the long-term pH boundary of 11 (Atkins and Glasser, 1992) or 10.5 (Krupka and Serne 1998) imposed by cement matrix gel on the intergranular matrix pore solutions.

Three eH values are suggested for contaminant solubility estimates. These are: –300 mV, a representative value for blast furnace slag (Atkins and Glasser, 1992); 0 mV, a representative value for Portland cements and similar grout materials (Atkins and Glasser, 1992); and 500 mV, a representative value for SDA ground water (Eric Miller, personal communication, 2002). The blast furnace slag represents the long term eH boundary for reducing materials such as SALT STONE and GMENT-12. The eH value for Portland cement is a reasonable estimate for grout formulations which do not contain chemically reducing materials such as sulfur and/or ferrous iron.

The measured eH data of the grout formulations and their mixture with interference materials are difficult to interpret. It is suggested that they not be used for contaminant solubility estimates. The average values for all measurement of neat grout samples are virtually identical at 241 to 254 mV, except for SALT STONE, which is 212 mV and is not significantly different from the other samples. Individual measurements for a given sample may vary by up to 100 mV. The eH values for all grout-interference mixtures is very constant at about 410 mV with very little scatter in the data. All the measured eH values are very oxidizing compared to most environments and above the values expected by pure Portland cement (0 to 100 mV, Atkins and Glasser 1992). Saltstone and GMENT-12 both contain blast furnace slag and are potentially very reducing. Blast furnace slag typically has eH values of about –300 mV although several months may be needed for the necessary chemical reactions to take place, (Atkins and Glasser 1992). The eH measurements were made on the leachate from the ANS/ANSI16.1 leach tests using the ASTM 1498-93 standard procedure. The leachate itself has very little capacity to preserve the eH of the intergranular pore solutions. Other factors, such as oxygen from air, may have changed the apparent eH value. The eH imposed by the neat grouts is significantly less than the same grouts mixed with interference materials, about 210 mV for neat grouts versus about 410 mV for grouts mixed with interference materials. It is suggested that some common factor, such as air entrainment during blending of the cement- interference mixture samples, together with very slow chemical reaction rates in the grouts containing reducing materials may have resulted in little or no eH reaction and reduction during the sample leach period. Given the uncertainty in the measured eH data, three eH values are given for the contaminant solubility estimates to provide a reasonable set of values for comparison

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Appendix E

Grout with Interferences American Nuclear Society 16.1 Individual Sample Data

Appendix E

Grout with Interferences American Nuclear Society 16.1 Individual Sample Data

Table 1. U Grout with 9% Organic Sludge - Strontium American Nuclear Society (ANS) 16.1 Data.

Time		Sr (mg/L)				
(d)	Sample 1	Sample 2	Sample 3			
0.083	0.010	0.010	0.010			
0.292	0.010	0.010	0.020			
1.000	0.080	0.080	0.110			
2.000	0.110	0.090	0.120			
3.000	0.110	0.130	0.120			
4.000	0.060	0.050	0.060			
5.000	0.050	0.040	0.040			
19.000	0.230	0.270	0.260			
47.000	0.150	0.160	0.140			
90.000	0.190	0.150	0.130			
Time		De (cm^2/s)			Leach Index (LI)	
(d)	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
0.083	1.46E-12	1.46E-12	1.46E-12	11.8	11.8	11.8
0.292	1.90E-12	1.90E-12	7.62E-12	11.7	11.7	11.1
1.000	3.61E-11	3.61E-11	6.83E-11	10.4	10.4	10.2
2.000	8.41E-11	5.58E-11	9.96E-11	10.1	10.3	10.0
3.000	1.43E-10	2.01E-10	1.69E-10	9.8	9.7	9.8
4.000	5.99E-11	4.16E-11	5.99E-11	10.2	10.4	10.2
5.000	5.35E-11	3.42E-11	3.42E-11	10.3	10.5	10.5
19.000	1.40E-11	1.92E-11	1.79E-11	10.9	10.7	10.7
47.000	4.30E-12	4.88E-12	3.76E-12	11.4	11.3	11.4
90.000	6.21E-12	3.87E-12	2.93E-12	11.2	11.4	11.5
Time		PH			eH (mV)	
(d)	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
0.083	10.3	10.2	10.3	323.0	322.1	398.0
0.292	10.6	10.5	10.6	382.1	375.5	384.2
1.000	11.4	11.2	11.2	402.4	395.0	388.5
2.000	11.2	11.0	11.8	403.0	421.0	401.2
3.000	11.0	11.1	11.0	412.3	422.0	412.0
4.000	11.1	11.1	11.1	416.8	404.1	420.1
5.000	11.0	11.0	10.9	411.0	398.0	412.0
19.000	11.6	11.6	11.3	412.0	403.0	421.0
47.000	11.3	10.2	10.9	412.0	423.0	432.0
90.000	11.7	11.8	11.7	414.8	412.6	421.5

Table 2. U Grout with 12% Nitrate Salt - Strontium ANS 16.1 Data.

	Sr (mg/L)		
Time (d)	Sample 1	Sample 2	Sample 3
0.083	0.010	0.010	0.010
0.292	0.010	0.010	0.010
1.000	0.020	0.020	0.020
2.000	0.040	0.020	0.030
3.000	0.050	0.020	0.040
4.000	0.020	0.010	0.020
5.000	0.030	0.010	0.010
19.000	0.130	0.120	0.130
47.000	0.080	0.060	0.070
90.000	0.060	0.140	0.130

	De (cm^2/s)			Leach Index (LI)		
Time (d)	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
0.083	1.36E-12	1.36E-12	1.36E-12	11.9	11.9	11.9
0.292	1.77E-12	1.77E-12	1.77E-12	11.8	11.8	11.8
1.000	5.27E-13	5.27E-13	5.27E-13	12.3	12.3	12.3
2.000	1.03E-11	2.60E-12	5.81E-12	11.0	11.6	11.2
3.000	2.75E-11	4.41E-12	1.76E-11	10.6	11.4	10.8
4.000	6.21E-12	1.55E-12	6.21E-12	11.2	11.8	11.2
5.000	1.79E-11	2.00E-12	2.00E-12	10.7	11.7	11.7
19.000	4.14E-12	3.57E-12	4.14E-12	11.4	11.4	11.4
47.000	1.14E-12	6.42E-13	8.74E-13	11.9	12.2	12.1
90.000	5.78E-13	3.13E-12	2.69E-12	12.2	11.5	11.6

Time	PH			eH (mV)		
(d)	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
0.083	10.0	10.3	10.2	398.0	376.2	388.1
0.292	8.9	10.0	10.1	376.4	398.4	396.5
1.000	10.3	10.4	9.8	398.2	402.6	429.8
2.000	11.0	11.1	11.1	411.0	403.0	422.6
3.000	10.8	10.8	10.6	399.0	400.2	412.0
4.000	10.9	10.8	11.2	406.9	403.2	403.5
5.000	11.0	11.1	11.0	409.0	411.0	423.0
19.000	11.3	11.4	11.3	399.2	410.0	412.0
47.000	11.5	11.4	11.6	405.0	413.8	399.8
90.000	11.4	11.6	11.5	407.2	405.2	408.3

Table 3. U Grout with 50% INEEL Soil - Strontium ANS 16.1 Data.

Time (d)	Sr (mg/L) Sample 1	Sample 2	Sample 3			
0.083	0.010	0.010	0.010			
0.292	0.010	0.010	0.010			
1.000	0.040	0.070	0.060			
2.000	0.080	0.080	0.070			
3.000	0.040	0.070	0.100			
4.000	0.030	0.050	0.050			
5.000	0.020	0.040	0.020			
19.000	0.080	0.050	0.120			
47.000	0.050	0.070	0.080			
90.000	0.060	0.060	0.020			
Time (d)	De (cm^2/s) Sample 1	Sample 2	Sample 3	Leach Index (LI) Sample 1	Sample 2	Sample 3
0.083	1.13E-12	1.13E-12	1.13E-12	11.9	11.9	11.9
0.292	1.48E-12	1.48E-12	1.48E-12	11.8	11.8	11.8
1.000	7.03E-12	2.16E-11	1.58E-11	11.2	10.7	10.8
2.000	3.47E-11	3.47E-11	2.66E-11	10.5	10.5	10.6
3.000	1.47E-11	4.51E-11	9.21E-11	10.8	10.3	10.0
4.000	1.17E-11	3.24E-11	3.24E-11	10.9	10.5	10.5
5.000	6.67E-12	2.67E-11	6.67E-12	11.2	10.6	11.2
19.000	1.32E-12	5.16E-13	2.95E-12	11.9	12.3	11.5
47.000	3.73E-13	7.31E-13	9.56E-13	12.4	12.1	12.0
90.000	4.83E-13	4.83E-13	5.37E-14	12.3	12.3	13.3
Time (d)	pH Sample 1	Sample 2	Sample 3	eH (mV) Sample 1	Sample 2	Sample 3
0.083	10.5	10.2	10.1	388.5	389.2	366.1
0.292	10.3	10.2	10.2	376.0	402.1	398.5
1.000	11.0	11.2	11.2	412.0	413.0	411.5
2.000	11.1	11.2	11.2	400.0	412.0	405.3
3.000	10.2	10.1	9.8	398.2	411.0	416.0
4.000	11.0	11.0	11.0	399.5	399.5	423.1
5.000	11.3	11.4	11.3	402.6	407.8	407.4
19.000	11.3	11.4	11.5	399.0	413.0	412.0
47.000	11.7	11.5	11.6	423.0	413.0	401.6
90.000	11.6	11.5	11.8	412.0	412.8	415.9

Table 4. T Grout with 9% Organic Sludge - Strontium ANS 16.1 Data.

Time (d)	Sr (mg/L) Sample 1	Sample 2	Sample 3			
0.083	0.040	0.040	0.030			
0.292	0.010	0.020	0.010			
1.000	0.080	0.170	0.060			
2.000	0.080	0.140	0.090			
3.000	0.100	0.100	0.080			
4.000	0.060	0.140	0.070			
5.000	0.060	0.110	0.040			
19.000	0.690	0.750	0.730			
47.000	0.710	0.680	0.770			
90.000	1.350	1.450	1.390			
Time (d)	**De (cm^2/s) Sample 1**	**Sample 2**	**Sample 3**	**Leach Index (LI) Sample 1**	**Sample 2**	**Sample 3**
0.083	1.37E-11	1.37E-11	7.67E-12	10.9	10.9	11.1
0.292	1.12E-12	4.46E-12	1.12E-12	12.0	11.4	12.0
1.000	2.13E-11	9.59E-11	1.20E-11	10.7	10.0	10.9
2.000	2.62E-11	8.00E-11	3.31E-11	10.6	10.1	10.5
3.000	6.95E-11	6.95E-11	4.45E-11	10.2	10.2	10.4
4.000	3.52E-11	1.91E-10	4.78E-11	10.5	9.7	10.3
5.000	4.53E-11	1.52E-10	2.02E-11	10.3	9.8	10.7
19.000	7.42E-11	8.74E-11	8.29E-11	10.1	10.1	10.1
47.000	5.67E-11	5.20E-11	6.68E-11	10.2	10.3	10.2
90.000	1.85E-10	2.12E-10	1.95E-10	9.7	9.7	9.7
Time (d)	**pH Sample 1**	**Sample 2**	**Sample 3**	**eH (mV) Sample 1**	**Sample 2**	**Sample 3**
0.083	10.5	10.5	10.5	398.0	376.2	347.8
0.292	10.1	10.2	10.2	382.1	376.5	386.2
1.000	11.1	11.0	11.1	403.0	421.6	388.5
2.000	11.1	11.1	11.3	400.2	412.0	401.2
3.000	11.0	11.0	10.8	412.3	422.0	412.0
4.000	10.9	10.9	10.9	421.0	404.1	416.2
5.000	11.0	11.5	11.4	411.0	426.0	412.0
19.000	11.8	11.8	11.8	409.0	412.0	421.0
47.000	11.6	11.7	11.5	399.8	416.3	405.0
90.000	11.9	11.8	11.9	407.8	412.7	415.6

Table 5. T Grout with 12% Nitrate Salt - Strontium ANS 16.1 Data.

Time (d)	Sr (mg/L) Sample 1	Sample 2	Sample 3
0.083	0.020	0.020	0.010
0.292	0.010	0.020	0.020
1.000	0.050	0.040	0.110
2.000	0.070	0.080	0.160
3.000	0.100	0.100	0.100
4.000	0.050	0.070	0.120
5.000	0.080	0.040	0.110
19.000	0.880	0.210	1.180
47.000	0.600	0.900	0.800
90.000	0.330	0.340	0.710

Time (d)	De (cm^2/s) Sample 1	Sample 2	Sample 3	Leach Index (LI) Sample 1	Sample 2	Sample 3
0.083	3.42E-12	3.42E-12	8.56E-13	11.5	11.5	12.1
0.292	1.12E-12	4.46E-12	4.46E-12	12.0	11.4	11.4
1.000	8.28E-12	5.31E-12	4.01E-11	11.1	11.3	10.4
2.000	2.62E-11	8.00E-11	3.31E-11	10.6	10.1	10.5
3.000	6.95E-11	6.95E-11	6.95E-11	10.2	10.2	10.2
4.000	3.52E-11	1.91E-10	4.78E-11	10.5	9.7	10.3
5.000	8.06E-11	2.02E-11	1.52E-10	10.1	10.7	9.8
19.000	1.21E-10	6.90E-12	2.17E-10	9.9	11.2	9.7
47.000	4.05E-11	9.11E-11	7.21E-11	10.4	10.0	10.1
90.000	1.10E-11	1.17E-11	5.11E-11	11.0	10.9	10.3

Time (d)	pH Sample 1	Sample 2	Sample 3	eH (mV) Sample 1	Sample 2	Sample 3
0.083	10.2	10.2	10.6	398.0	376.2	347.8
0.292	10.5	10.5	10.4	376.6	398.1	396.4
1.000	11.0	11.2	11.2	398.2	402.6	441.2
2.000	11.1	11.0	11.1	411.0	393.0	396.2
3.000	11.4	11.2	11.3	399.0	403.0	421.2
4.000	11.2	11.0	11.1	407.1	402.3	403.5
5.000	11.6	11.4	11.5	410.5	411.0	423.0
19.000	12.0	12.0	11.7	399.2	412.0	403.0
47.000	11.9	11.5	11.6	400.0	401.0	396.0
90.000	11.9	11.7	11.9	205.8	412.7	412.9

Table 6. T Grout with 50% INEEL Soil - Strontium ANS 16.1 Data.

Time (d)	Sr (mg/L) Sample 1	Sample 2	Sample 3			
0.083	0.020	0.020	0.030			
0.292	0.010	0.020	0.020			
1.000	0.070	0.050	0.080			
2.000	0.110	0.070	0.120			
3.000	0.840	1.020	1.030			
4.000	0.060	0.040	0.070			
5.000	0.050	0.030	0.050			
19.000	0.500	0.420	0.560			
47.000	0.490	0.510	0.400			
90.000	0.570	0.440	0.190			
Time (d)	De (cm^2/s) Sample 1	Sample 2	Sample 3	Leach Index (LI) Sample 1	Sample 2	Sample 3
0.083	3.42E-12	3.42E-12	7.67E-12	11.5	11.5	11.1
0.292	1.12E-12	4.46E-12	4.46E-12	12.0	11.4	11.4
1.000	1.62E-11	8.28E-12	2.13E-11	10.8	11.1	10.7
2.000	2.00E-11	2.62E-11	1.04E-10	10.7	10.6	10.0
3.000	4.90E-09	7.22E-09	7.37E-09	8.3	8.1	8.1
4.000	2.44E-11	4.78E-11	1.41E-10	10.6	10.3	9.9
5.000	3.14E-11	1.13E-11	3.14E-11	10.5	10.9	10.5
19.000	3.88E-11	2.74E-11	4.88E-11	10.4	10.6	10.3
47.000	2.71E-11	2.93E-11	1.80E-11	10.6	10.5	10.7
90.000	3.29E-11	1.96E-11	3.64E-12	10.5	10.7	11.4
Time (d)	pH Sample 1	Sample 2	Sample 3	eH (mV) Sample 1	Sample 2	Sample 3
0.083	10.2	10.2	10.1	366.5	381.2	376.5
0.292	10.2	10.5	10.4	376.0	402.2	398.5
1.000	11.1	11.1	11.0	401.6	423.0	412.6
2.000	11.4	11.4	11.4	399.8	403.6	402.0
3.000	11.0	11.0	11.0	398.2	411.0	416.0
4.000	10.8	11.0	10.9	400.0	399.5	423.1
5.000	11.0	11.3	11.4	402.6	402.8	407.8
19.000	11.9	11.8	11.6	415.6	411.2	411.0
47.000	11.6	11.8	11.5	415.6	423.5	412.8
90.000	11.8	11.5	11.7	421.5	413.7	412.0

Table 7. E Grout with 9% Organic Sludge - Strontium ANS 16.1 Data.

Time (d)	Sr (mg/L) Sample 1	Sample 2	Sample 3
0.083	0.010	0.010	0.010
0.292	0.010	0.010	0.010
1.000	0.010	0.010	0.010
2.000	0.010	0.010	0.010
3.000	0.010	0.020	0.020
4.000	0.010	0.020	0.030
5.000	0.010	0.010	0.010
19.000	0.010	0.010	0.010
47.000	0.100	0.120	0.110
90.000	0.030	0.020	0.020

Time (d)	De (cm^2/s) Sample 1	Sample 2	Sample 3	Leach Index (LI) Sample 1	Sample 2	Sample 3
0.083	1.31E-12	1.31E-12	1.31E-12	11.9	11.9	11.9
0.292	1.71E-12	1.71E-12	1.71E-12	11.8	11.8	11.8
1.000	5.08E-13	5.08E-13	5.08E-13	12.3	12.3	12.3
2.000	6.26E-13	6.26E-13	6.26E-13	12.2	12.2	12.2
3.000	1.06E-12	4.29E-12	4.29E-12	12.0	11.4	11.4
4.000	1.50E-12	6.04E-12	1.35E-11	11.8	11.2	10.9
5.000	1.93E-12	1.93E-12	1.93E-12	11.7	11.7	11.7
19.000	2.38E-14	2.38E-14	2.38E-14	13.6	13.6	13.6
47.000	1.72E-12	2.50E-12	2.10E-12	11.8	11.6	11.7
90.000	1.40E-13	6.26E-14	6.26E-14	12.9	13.2	13.2

Time (d)	pH Sample 1	Sample 2	Sample 3	eH (mV) Sample 1	Sample 2	Sample 3
0.083	7.9	8.8	8.8	325.6	333.8	356.4
0.292	8.5	7.8	7.7	366.5	378.6	398.6
1.000	9.5	8.4	9.8	398.0	376.2	388.1
2.000	9.9	9.9	9.7	376.4	398.4	396.5
3.000	10.5	10.5	10.4	398.2	402.6	441.2
4.000	10.2	10.3	10.4	411.0	403.0	421.6
5.000	10.0	10.1	10.1	399.2	409.0	412.0
19.000	9.7	10.5	10.0	397.0	399.8	416.3
47.000	10.1	10.3	10.2	407.1	402.3	403.5
90.000	10.2	10.7	10.5	406.4	412.6	417.8

Table 8. E Grout with 12% Nitrate Salt - Strontium ANS 16.1 Data.

Time (d)	Sr (mg/L) Sample 1	Sample 2	Sample 3			
0.083	0.020	0.010	0.010			
0.292	0.010	0.010	0.010			
1.000	0.010	0.010	0.010			
2.000	0.010	0.010	0.010			
3.000	0.010	0.010	0.010			
4.000	0.020	0.010	0.020			
5.000	0.020	0.020	0.010			
19.000	0.010	0.010	0.010			
47.000	0.120	0.140	0.150			
90.000	0.010	0.010	0.010			
Time (d)	De (cm^2/s) Sample 1	Sample 2	Sample 3	Leach Index (LI) Sample 1	Sample 2	Sample 3
0.083	4.76E-12	1.19E-12	1.19E-12	11.3	11.9	11.9
0.292	1.55E-12	1.55E-12	1.55E-12	11.8	11.8	11.8
1.000	4.62E-13	4.62E-13	4.62E-13	12.3	12.3	12.3
2.000	5.69E-13	5.69E-13	5.69E-13	12.2	12.2	12.2
3.000	9.66E-13	9.66E-13	9.66E-13	12.0	12.0	12.0
4.000	1.36E-12	5.44E-12	1.22E-11	11.9	11.3	10.9
5.000	7.01E-12	7.01E-12	1.75E-12	11.2	11.2	11.8
19.000	2.17E-14	2.17E-14	2.17E-14	13.7	13.7	13.7
47.000	2.24E-12	3.08E-12	3.52E-12	11.6	11.5	11.5
90.000	1.41E-14	1.41E-14	1.41E-14	13.9	13.9	13.9
Time (d)	pH Sample 1	Sample 2	Sample 3	eH (mV) Sample 1	Sample 2	Sample 3
0.083	7.6	7.6	8.0	382.1	376.5	386.2
0.292	8.7	8.5	8.0	393.0	396.2	388.5
1.000	8.9	7.7	9.2	403.0	421.2	401.2
2.000	9.2	9.1	9.6	412.3	422.0	412.0
3.000	9.6	10.0	10.0	402.4	402.7	414.0
4.000	10.1	10.2	10.4	412.0	403.0	421.0
5.000	10.6	10.6	10.3	401.0	396.0	405.0
19.000	11.0	11.0	11.1	421.0	404.1	416.2
47.000	10.8	10.6	10.9	411.0	426.0	412.0
90.000	10.6	10.8	10.7	411.6	412.3	411.9

Table 9. E Grout with 50% INEEL Soil - Strontium ANS 16.1 Data.

Time (d)	Sr (mg/L) Sample 1	Sample 2	Sample 3
0.083	0.010	0.010	0.010
0.292	0.010	0.010	0.010
1.000	0.010	0.010	0.010
2.000	0.010	0.010	0.010
3.000	0.010	0.010	0.010
4.000	0.020	0.020	0.010
5.000	0.010	0.010	0.010
19.000	0.010	0.010	0.010
47.000	0.010	0.010	0.010
90.000	0.010	0.010	0.010

Time (d)	De (cm^2/s) Sample 1	Sample 2	Sample 3	Leach Index (LI) Sample 1	Sample 2	Sample 3
0.083	9.72E-13	9.72E-13	9.72E-13	12.0	12.0	12.0
0.292	1.27E-12	1.27E-12	1.27E-12	11.9	11.9	11.9
1.000	3.77E-13	3.77E-13	3.77E-13	12.4	12.4	12.4
2.000	4.65E-13	4.65E-13	4.65E-13	12.3	12.3	12.3
3.000	7.90E-13	7.90E-13	7.90E-13	12.1	12.1	12.1
4.000	4.42E-12	4.42E-12	1.11E-12	11.4	11.4	12.0
5.000	1.43E-12	1.43E-12	1.43E-12	11.8	11.8	11.8
19.000	1.77E-14	1.77E-14	1.77E-14	13.8	13.8	13.8
47.000	1.28E-14	1.28E-14	1.28E-14	13.9	13.9	13.9
90.000	1.15E-14	1.15E-14	1.15E-14	13.9	13.9	13.9

Time (d)	PH Sample 1	Sample 2	Sample 3	eH (mV) Sample 1	Sample 2	Sample 3
0.083	10.5	9.4	9.9	398.2	389.0	376.6
0.292	10.0	10.0	9.9	399.8	389.2	364.1
1.000	9.8	10.0	10.2	416.8	403.6	405.5
2.000	10.0	10.4	10.3	376.0	402.1	398.5
3.000	10.4	10.6	10.6	415.6	411.2	411.0
4.000	10.7	10.5	10.6	402.6	402.6	407.5
5.000	10.6	10.6	10.6	412.0	413.0	411.5
19.000	11.0	11.0	11.1	417.3	413.0	412.0
47.000	10.9	10.8	10.8	409.0	411.0	423.0
90.000	10.8	10.9	10.8	411.7	412.7	416.0

Table 10. C75 Grout with 9% Organic Sludge - Strontium ANS 16.1 Data.

Time (d)	Sr (mg/L) Sample 1	Sample 2	Sample 3
0.083	0.020	0.030	0.010
0.292	0.030	0.020	0.020
1.000	0.080	0.050	0.090
2.000	0.180	0.160	0.150
3.000	0.100	0.120	0.170
4.000	0.070	0.140	0.140
5.000	0.070	0.050	0.060
19.000	0.660	0.680	0.670
47.000	0.310	0.320	0.330
90.000	0.440	0.420	0.290

Time (d)	De (cm^2/s) Sample 1	Sample 2	Sample 3	Leach Index (LI) Sample 1	Sample 2	Sample 3
0.083	6.64E-12	1.49E-11	1.65E-12	11.2	10.8	11.8
0.292	1.94E-11	8.66E-12	8.66E-12	10.7	11.1	11.1
1.000	4.12E-11	1.61E-11	5.18E-11	10.4	10.8	10.3
2.000	2.57E-10	2.04E-10	1.79E-10	9.6	9.7	9.7
3.000	1.34E-10	1.93E-10	3.90E-10	9.9	9.7	9.4
4.000	9.29E-11	3.73E-10	3.73E-10	10.0	9.4	9.4
5.000	1.20E-10	6.10E-11	8.78E-11	9.9	10.2	10.1
19.000	1.31E-10	1.40E-10	1.36E-10	9.9	9.9	9.9
47.000	2.09E-11	2.23E-11	2.37E-11	10.7	10.7	10.6
90.000	3.81E-11	3.47E-11	1.65E-11	10.4	10.5	10.8

Time (d)	pH Sample 1	Sample 2	Sample 3	eH (mV) Sample 1	Sample 2	Sample 3
0.083	9.7	9.6	9.6	336.5	354.8	346.7
0.292	10.0	10.3	10.2	398.6	377.5	386.0
1.000	10.7	10.7	10.7	402.5	396.2	402.3
2.000	10.8	10.9	10.9	412.0	421.2	401.2
3.000	10.6	10.5	10.6	407.8	422.0	412.0
4.000	11.8	11.8	11.6	421.0	404.1	415.8
5.000	11.6	11.4	11.9	404.6	426.0	412.0
19.000	11.5	11.4	11.7	413.6	403.0	422.6
47.000	11.4	11.4	11.6	405.0	413.0	402.8
90.000	11.6	11.7	11.6	404.6	405.8	416.7

Table 11. C75 Grout with 12% Nitrate Salt - Strontium ANS 16.1 Data.

Time (d)	Sample 1	Sr (mg/L) Sample 2	Sample 3			
0.083	0.010	0.010	0.010			
0.292	0.020	0.020	0.010			
1.000	0.040	0.040	0.040			
2.000	0.050	0.060	0.060			
3.000	0.027	0.030	0.040			
4.000	0.040	0.020	0.030			
5.000	0.030	0.030	0.040			
19.000	0.080	0.290	0.290			
47.000	0.160	0.180	0.200			
90.000	0.320	0.280	0.280			
		De (cm^2/s)			Leach Index (LI)	
Time (d)	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
0.083	1.54E-12	1.54E-12	1.54E-12	11.8	11.8	11.8
0.292	8.10E-12	8.10E-12	2.01E-12	11.1	11.1	11.7
1.000	9.60E-12	9.60E-12	9.60E-12	11.0	11.0	11.0
2.000	1.85E-11	2.66E-11	2.66E-11	10.7	10.6	10.6
3.000	9.16E-12	1.13E-11	2.01E-11	11.0	10.9	10.7
4.000	8.66E-11	3.47E-10	3.47E-10	10.1	9.5	9.5
5.000	2.05E-11	2.05E-11	3.64E-11	10.7	10.7	10.4
19.000	1.80E-12	2.36E-11	2.36E-11	11.7	10.6	10.6
47.000	5.21E-12	6.57E-12	8.17E-12	11.3	11.2	11.1
90.000	1.88E-11	1.44E-11	1.44E-11	10.7	10.8	10.8
Time		pH			eH (mV)	
(d)	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
0.083	9.9	10.0	9.9	398.0	376.2	347.8
0.292	9.8	9.6	9.8	382.1	375.5	384.2
1.000	11.8	11.7	11.7	398.2	402.6	441.2
2.000	10.9	10.8	10.9	411.0	403.7	421.6
3.000	11.0	11.0	11.3	399.0	400.8	412.0
4.000	10.7	10.5	10.6	407.1	402.9	403.9
5.000	11.2	11.2	11.1	409.0	411.0	423.0
19.000	11.5	11.6	11.5	399.2	409.0	412.0
47.000	11.4	11.2	11.4	412.0	403.0	421.0
90.000	11.5	11.5	11.8	404.9	415.6	411.8

Table 12. C75 Grout with 50% INEEL Soil - Strontium ANS 16.1 Data.

	Sr (mg/L)		
Time (d)	Sample 1	Sample 2	Sample 3
0.083	0.020	0.020	0.030
0.292	0.020	0.020	0.030
1.000	0.110	0.110	0.080
2.000	0.100	0.120	0.080
3.000	0.100	0.100	0.140
4.000	0.050	0.080	0.040
5.000	0.040	0.060	0.050
19.000	0.630	0.630	0.190
47.000	0.430	0.320	0.300
90.000	0.330	0.330	0.330

	De (cm^2/s)			Leach Index (LI)		
Time (d)	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
0.083	5.00E-12	5.00E-12	1.12E-11	11.3	11.3	11.0
0.292	6.52E-12	6.52E-12	1.46E-11	11.2	11.2	10.8
1.000	5.87E-11	5.87E-11	3.09E-11	10.2	10.2	10.5
2.000	5.91E-11	8.54E-11	3.80E-11	10.2	10.1	10.4
3.000	1.00E-10	1.00E-10	1.98E-10	10.0	10.0	9.7
4.000	2.27E-11	5.71E-12	1.28E-11	10.6	11.2	10.9
5.000	2.93E-11	6.60E-11	4.57E-11	10.5	10.2	10.3
19.000	8.99E-11	8.99E-11	8.16E-12	10.0	10.0	11.1
47.000	3.02E-11	1.68E-11	1.47E-11	10.5	10.8	10.8
90.000	1.60E-11	1.60E-11	1.60E-11	10.8	10.8	10.8

	pH			eH (mV)		
Time (d)	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
0.083	9.9	10.0	10.0	376.1	376.2	388.1
0.292	9.9	10.2	10.2	376.0	412.8	398.5
1.000	12.0	12.0	12.0	412.0	413.0	421.0
2.000	10.7	10.6	10.6	400.6	403.6	402.0
3.000	10.7	10.6	10.5	398.2	411.0	417.8
4.000	10.7	10.6	10.6	399.8	413.2	422.4
5.000	10.9	11.0	11.0	402.6	402.6	407.4
19.000	11.7	11.6	11.6	417.9	411.2	411.0
47.000	11.0	11.4	11.3	415.8	412.6	399.5
90.000	11.3	11.4	11.5	421.0	413.0	415.0

Table 13. S Grout with 9% Organic Sludge - Strontium ANS 16.1 Data.

Time (d)	Sr (mg/L) Sample 1	Sample 2	Sample 3
0.083	0.040	0.060	0.020
0.292	0.050	0.050	0.070
1.000	0.130	0.130	0.080
2.000	0.150	0.120	0.110
3.000	0.120	0.110	0.100
4.000	0.080	0.090	0.080
5.000	0.070	0.050	0.060
19.000	0.390	0.320	0.440
47.000	0.250	0.220	0.260
90.000	0.340	0.340	0.390

Time		De (cm^2/s)			Leach Index (LI)	
(d)	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
0.083	1.96E-11	4.41E-11	4.90E-12	10.7	10.4	11.3
0.292	3.99E-11	3.99E-11	7.82E-11	10.4	10.4	10.1
1.000	7.97E-11	7.97E-11	3.04E-11	10.1	10.1	10.5
2.000	1.31E-10	8.41E-11	7.11E-11	9.9	10.1	10.1
3.000	1.43E-10	1.21E-10	9.85E-11	9.8	9.9	10.0
4.000	8.94E-11	1.13E-10	8.94E-11	10.0	9.9	10.0
5.000	8.82E-11	4.50E-11	6.49E-11	10.1	10.3	10.2
19.000	3.38E-11	2.28E-11	4.31E-11	10.5	10.6	10.4
47.000	1.01E-11	7.82E-12	1.09E-11	11.0	11.1	11.0
90.000	1.68E-11	1.68E-11	2.20E-11	10.8	10.8	10.7

Time		pH			eH (mV)	
(d)	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
0.083	9.0	9.1	8.9	345.0	340.0	378.7
0.292	8.9	8.9	9.0	382.6	377.0	393.0
1.000	10.6	10.5	9.9	393.0	396.2	388.5
2.000	10.8	10.8	10.8	403.0	413.0	403.6
3.000	10.7	10.8	10.6	411.0	405.8	412.0
4.000	10.4	10.4	10.3	422.0	406.7	416.3
5.000	10.3	10.2	10.3	411.0	423.0	412.0
19.000	10.9	10.2	10.2	412.0	404.6	421.0
47.000	10.6	10.4	10.1	401.0	401.4	405.9
90.000	10.8	10.9	10.8	401.5	412.6	414.8

Table 14. S Grout with 12% Nitrate Salt - Strontium ANS 16.1 Data.

Time		Sr (mg/L)	
(d)	Sample 1	Sample 2	Sample 3
0.083	0.020	0.020	0.020
0.292	0.070	0.040	0.060
1.000	0.140	0.080	0.070
2.000	0.190	0.110	0.120
3.000	0.100	0.130	0.120
4.000	0.100	0.100	0.090
5.000	0.080	0.060	0.050
19.000	0.500	0.440	0.210
47.000	0.380	0.300	0.310
90.000	0.420	0.450	0.500

Time		De (cm^2/s)			Leach Index (LI)	
(d)	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
0.083	4.58E-12	4.58E-12	4.58E-12	11.3	11.3	11.3
0.292	7.29E-11	2.37E-11	5.35E-11	10.1	10.6	10.3
1.000	8.70E-11	2.83E-11	2.17E-11	10.1	10.5	10.7
2.000	1.23E-10	7.87E-11	6.62E-11	9.9	10.1	10.2
3.000	9.25E-11	1.57E-10	1.34E-10	10.0	9.8	9.9
4.000	1.30E-10	1.30E-10	1.05E-10	9.9	9.9	10.0
5.000	1.07E-10	6.04E-11	4.19E-11	10.0	10.2	10.4
19.000	5.18E-11	4.01E-11	9.18E-12	10.3	10.4	11.0
47.000	2.16E-11	1.35E-11	1.44E-11	10.7	10.9	10.8
90.000	2.38E-11	2.73E-11	3.37E-11	10.6	10.6	10.5

Time		pH			eH (mV)	
(d)	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
0.083	9.6	9.7	9.6	402.0	370.6	399.0
0.292	10.0	10.0	9.8	378.5	399.7	396.8
1.000	10.5	10.5	10.6	400.2	404.9	433.2
2.000	10.5	10.5	10.2	411.5	402.5	421.6
3.000	10.6	10.7	10.7	399.0	400.2	412.0
4.000	10.8	10.8	10.7	407.1	416.4	403.5
5.000	10.5	10.5	10.5	409.8	411.0	402.3
19.000	11.4	11.6	11.5	402.6	409.9	412.0
47.000	10.6	10.7	10.5	412.6	419.7	422.0
90.000	10.9	10.9	10.9	403.2	405.1	412.4

Table 15. S Grout with 50% INEEL Soil - Strontium ANS 16.1 Data.

Time (d)	Sr (mg/L) Sample 1	Sample 2	Sample 3
0.083	0.050	0.050	0.070
0.292	0.030	0.020	0.020
1.000	0.070	0.060	0.080
2.000	0.070	0.060	0.070
3.000	0.100	0.110	0.120
4.000	0.100	0.100	0.100
5.000	0.080	0.070	0.070
19.000	0.480	0.460	0.490
47.000	0.260	0.280	0.280
90.000	0.180	0.410	0.360

Time (d)	De (cm^2/s) Sample 1	Sample 2	Sample 3	Leach Index (LI) Sample 1	Sample 2	Sample 3
0.083	2.45E-11	2.45E-11	4.82E-11	10.6	10.6	10.3
0.292	1.15E-11	5.11E-12	5.11E-12	10.9	11.3	11.3
1.000	1.87E-11	1.37E-11	2.44E-11	10.7	10.9	10.6
2.000	1.69E-10	5.69E-11	6.74E-11	9.8	10.2	10.2
3.000	7.98E-11	9.66E-11	1.14E-10	10.1	10.0	9.9
4.000	1.12E-10	1.12E-10	1.12E-10	10.0	10.0	10.0
5.000	9.24E-11	7.09E-11	7.09E-11	10.0	10.1	10.1
19.000	4.12E-11	3.78E-11	4.29E-11	10.4	10.4	10.4
47.000	8.74E-12	1.01E-11	1.01E-11	11.1	11.0	11.0
90.000	3.78E-12	1.96E-11	1.51E-11	11.4	10.7	10.8

Time (d)	pH Sample 1	Sample 2	Sample 3	eH (mV) Sample 1	Sample 2	Sample 3
0.083	10.0	9.9	10.0	376.7	398.7	366.8
0.292	10.0	9.8	10.0	376.0	403.0	399.0
1.000	10.7	10.6	10.4	415.0	403.6	404.5
2.000	10.6	10.7	10.5	377.0	402.1	402.0
3.000	10.9	11.1	11.1	416.5	411.2	411.0
4.000	10.8	10.9	10.9	403.5	412.0	407.5
5.000	10.7	10.7	10.7	412.0	402.7	413.0
19.000	11.7	11.7	11.6	418.0	414.0	419.0
47.000	11.3	11.2	11.4	409.0	411.0	416.9
90.000	11.3	11.6	11.7	406.5	404.3	408.4

Appendix F

Carbon Additive to Reduce Migration of Volatile Organic Compounds

Appendix F

Carbon Additive to Reduce Migration of Volatile Organic Compounds

Scope and Objectives

This report addresses the feasibility of using powdered-activated carbon (PAC) as an additive to a barrier grout wall to reduce the migration of carbon tetrachloride (CCl_4), perchloroethylene (PCE), trichloroethane (TCA), and trichloroethylene (TCE). The report addresses the following four topics:

- PAC potential to effectively remove CT, PCE, TCA, and TCE volatile organic compounds (VOCs) from the vapor phase
- Postulated effect of PAC as a grout additive
- Postulated grout PAC concentration needed to accomplish positive effects
- Anticipated long-term waste form stability.

PAC Potential to Effectively Remove CT, PCE, TCA, and TCE Contaminants from the Vapor Phase

The potential effectiveness for activated carbon to treat vapor contaminated with CT, PCE, TCA, and TCE is a complicated undertaking and requires (at a minimum) examination of:

- Each component vapor phase and water vapor concentration.
- The equilibrium adsorption relationship for each material in the vapor phase and activated carbon (called an adsorption isotherm).
- A multicomponent model to accurately predict how the components interact and the expected sorption capacity of each compound at equilibrium.
- A dynamic model to relate mass transfer from the diffusing gas into the carbon, used to determine the time needed to remove the vapors and how much contact is needed with the activated carbon.

To assess PAC potential, the adsorptive capacity for the contaminant on activated carbon could be compared to components that are currently removed from the gas phase with carbon. Nyer et al. (1996) present carbon adsorption capacity information for five compounds that are effectively treated:

Table 1. Adsorption Capacity (pounds compound per 100 pounds activated carbon).

Compound	At 10 ppm_v	At 100 ppm_v
Benzene	13	19
Carbon Tetrachloride	20	33
Methylene Chloride	1.3	2.7
Toluene	21	27
Trichloroethylene	19	33

Benzene and toluene are components of petroleum products; they are commonly removed from the gas phase with activated carbon as a result of remediation efforts. This comparative information indicates that at a concentration of 10-ppmv, CT and TCE adsorption is similar to toluene and considerably greater than for benzene. At 100-ppmv, CT and TCE adsorb better than both toluene and benzene. These data indicate that powdered activated carbon potential for removing CT and TCE is quite good.

Information is needed for PCE and TCA to compare with the other compounds. Isotherm data were not available for all the components on the same activated carbon, but information is available for TCE and PCE on BPL activated carbon (Crittenden, et al., 1989). They demonstrate an isotherm of a single component that covers a wide range of equilibrium concentrations can used be used to define the activated carbon adsorption performance (toluene was used in their study). This isotherm can be used to predict the gas phase adsorption of TCE and PCE using the Dubinin-Radushkevich (D-R) equation [see appendix for the equation and brief discussion]. Using the D-R equation, the TCE and PCE isotherms of Crittenden et al (1989), and the molecular weights, liquid densities, and vapor pressures of TCE, PCE, CT and TCA, the adsorption isotherms for CT and TCA were predicted.

The experimental PCE and TCE isotherms indicate that PCE is considerably more adsorbable than TCE. Since TCE is effectively removed from the gas phase, PCE should have an even greater adsorption capacity on activated carbon. The projected isotherms for CT and TCA are nearly identical, with both projecting greater ability to sorb than TCE. From Table 1, CT was projected to sorb slightly better than TCE at the lower concentration and about the same at the higher concentration—the same trends can be observed with the projected isotherms. These data all indicate that activated carbon adsorption can effectively remove all four volatile organic contaminants from the vapor phase.

Multi-component adsorption equilibrium modeling and the dynamic mass transfer modeling required to evaluate CT, PCE, TCA, and TCE mixtures is beyond the scope of this project, largely because of the extensive computer programming and modeling requirements. Literature information can be used to assist in determining how multi-component equilibrium adsorption will be affected by additional components and with water vapor present. When both TCE and PCE are present (Crittenden, et al., 1989), the presence of the other lowers the equilibrium loading of the other component on the adsorbent. The presence of TCE reduces the amount of PCE the carbon can adsorb and the PCE reduces the amount of TCE adsorbed. Since the PCE is the more strongly adsorbed component, the amount of TCE adsorbed would be more adversely affected by PCE than the PCE adsorption when the vapor phase concentrations are the same. Water vapor has the same negative effect on sorption as does a competing organic compound (Nyer et al. 1996 and Crittenden et al. 1989). When the gas phase concentration of the TCE in these studies was high (> 4,000 ppmv), the reduction in amount adsorbed was small; when the TCE concentration was small, an 85% reduction was observed.

Literature information provides insight into the dynamic sorption of multiple contaminants in an adsorption column treating air stripper off-gas (Mueller and DiToro, 1993). Considering the breakthrough curves of CT, PCE, TCA, and TCE, TCA exited the column slightly ahead of CT, which was immediately followed by TCE. PCE broke through the adsorber last. Using the isotherms above, the compound with the greatest amount adsorbed at a particular concentration (PCE) is expected to breakthrough last. TCE was expected to breakthrough the adsorber first. Mass transfer must also play an important role in the process. TCE diffusivity in the gas phase (8.3 x 10-2 cm^2/s) is greater than that for TCA and CT (both are 8.0 x 10-2 cm^2/s) and is likely to cause it to adsorb faster on the carbon. Since TCA and CT sorption is not substantially greater than that of TCE, that energy of sorption difference may not have been substantial enough to displace the TCE. An additional complicating factor is the difference in gas concentrations of the different species. Even though PCE diffusivity is smaller than the other components, its adsorption equilibrium capacity is considerably greater than the other components. This substantial difference in adsorption strength is the main reason its breakthrough is last.

Except for the last component in the gas stream to exit the adsorption column, PCE in this case, each component is displaced from the activated carbon. Immediately after component breakthrough, the effluent concentration continues its breakthrough and the effluent concentration is greater than the influent concentration. To prevent these higher concentrations in the effluent than in the influent, adsorber operation would have to be terminated prior to the weakest materials breaking through the adsorber. Dynamic modeling and the pilot study demonstrate that complete removal, within detection limits, is possible with TCA likely to breakthrough the column first. Estimates of the adsorption cycle run time are very important for the control of treated gas concentrations.

Postulated Effect of PAC as a Grout Additive

The literature is sparse on the addition of materials to prevent the gas phase migration of organic compounds by sorption. The literature relates to contaminant sorption from the aqueous phase, or more accurately to the prevention of leaching from the solid into the aqueous phase. Organophillic clays and activated carbon have been tested. The activated carbon results are discussed to indicate its potential as an additive to the grout, keeping in mind that liquid phase application was tested and not the gas phase.

One study evaluated PAC for the adsorption of phenol, aniline and naphthalene (Hebatpuria, et al.; 1999a & b). In their research, sand was contaminated with phenol and allowed to age, and then PAC was added as a percentage of the sand weight, and the cement and water added to this mix. Leaching tests were performed on the solidified/stabilized soil using both the Toxicity Characteristic Leaching Procedure (TCLP) and the American Nuclear Society (ANS) 16.1 test. PAC dramatically reduced the leaching of phenol and aniline (Hebatpuria, et al.; 1999b), indicating significant potential in reducing leached contaminant concentrations to acceptable concentrations. The inability of PAC to reduce naphthalene leaching is a concern. It should be recognized that naphthalene did not leach significantly during the TCLP test (sample without PAC leached 1.3% of the naphthalene, whereas for phenol and aniline the values were 65% and 26% respectively); PAC didn't dramatically reduce the amount of leaching that occurred. A more detailed study of phenol adsorption determined that phenol sorption appeared irreversible (Hebatpuria, et al.; 1999a). Phenol desorption is a concern, since mixing cement with activated carbon increases the pH of the mix to above 12; phenol has a pKa of 10, so at this pH the phenol becomes phenate anion which is substantially less adsorbable. Mixing the phenol contaminated sand, water, and cement simultaneously did not adversely affect adsorption, so the adsorption process is rapid and isn't adversely affected by the pH swing during the hydration of the cement. Changes in crystallization of the cement mixture was noted when PAC was present, probably from an accelerated hydration of the cement and less formation of Ca(OH)2 gels.

PAC was added to sand and the mixture evaluated as a permeable-barrier media to remove benzene from groundwater (Rael et al. 1995). Several sorptive additives were evaluated, with PAC performing best and therefore studied more extensively. A column test with an empty-bed-contact-time of 350 minutes and 3% PAC removed 40-mg/L of benzene to less than its detection limit, with the PAC use rate slightly better than predicted in adsorption isotherm tests. This study does indicate that a classic breakthrough curve does develop and nearly theoretical carbon use is obtained with a fluid flowing through a permeable barrier.

Postulated Grout PAC Concentration Needed to Accomplish Positive Effects

The PAC concentration to be added will depend upon:

- VOC concentrations in the vapor phase,
- mass of waste material encapsulated by the grout,

- propensity of the VOCs to sorb onto the PAC,
- rate at which the each VOC diffuses into the barrier,
- ability of each VOC to sorb onto grout, soil and other materials present in the waste cell,
- ability of other reactions to degrade and destroy each VOC,
- presence of water within the cell and its affect on vapor phase concentration and adsorption to PAC.

Other than the mass of the material trapped by the barrier grout wall and the ability of the VOCs to sorb, the other factors require assumptions that could vary by at least an order of magnitude. In an effort to estimate the barrier ability to sorb VOCs, the following assumptions were made:

- VOC concentration in the vapor phase can be calculated:
  - At equilibrium
  - Without water present
  - Using the fugacity approach (Mackay, 1979)
- All VOC movement results from a concentration gradient from the vapor phase concentration calculated in the waste cell; these concentrations at the barrier wall are assumed to remain constant. [In other words, within the main cell, diffusion is not restricted and the vapor phase concentration will be immediately replaced as the VOCs diffuse into the barrier wall and is sorbed in the PAC. Actually the contaminant concentration adjacent to the barrier would decrease; additional time would be required to replace the VOCs, and therefore this estimate is conservative.]
- The sorption mass transfer zone is 5 cm with the concentration decreasing from the main cell VOC concentration to zero using Fick's law of diffusion.
- VOC diffusivity is substantially less than the gas phase diffusivity. TCE diffusivity in soil with a porosity of 0.29 was measured to be 2.5 x 10-4 cm^2/s while the gas phase diffusivity is 8.3 x 10-2 cm^2/s (Hutter et al. 1992). Other VOC diffusivity values will be adjusted proportionately to the TCE values.
- The interior surface of the PAC is not blocked by the grout; i.e. all the adsorptive capacity of the PAC can be used.
- Internal diffusion is much faster than the diffusion of VOCs to the external PAC surface; therefore, the PAC reaches equilibrium rapidly.
- Maximum amount of PAC is 0.053-g/cm^3 in the barrier wall; the value could be greater but this in line with the values used by Hebatpuria et al. (1999 a,b).
- VOCs do not sorb on nonPAC materials; even though VOCs are likely to sorb on the other materials, therefore this will overestimate the quantity of material going to the barrier wall.
- No VOC destruction mechanisms are present.

- Barrier thickness is 3-ft.

Fugacity calculations using assumption (1) resulted in the following equilibrium gas phase concentrations:

Table 2. Gas phase VOC concentrations.

Compound	Concentration g/L
CT	0.490
PCE	0.023
TCA	0.001
TCE	0.081

The projected vapor phase concentration of CT is greatest, followed by TCE; PCE is significant and TCA is small. The flux of each component into the barrier was determined based on Table 2 and assumptions (2), (3), and (4). The total flux is estimated at 2.9 x 10-4 g/day/cm^2.

Multi-component modeling of the equilibrium situation is beyond the scope of this report and because the uncertainties are not likely to aid the estimates. TCE adsorbs the least of the compounds and CT was found to breakthrough a column treating air stripper off-gas before CT (Mueller and DiToro, 1993). The solid phase loading at these high influent concentrations is about 0.6-gVOC/gPAC based on the D-R equation and assumptions (5) and (6). This high loading is near the maximum amount that can be sorbed on the PAC and therefore would depend upon the PAC.

Using this information and assumptions (7) through (10), the barrier would be expected to last 30 years before VOCs started to breakthrough the barrier. This may not be satisfactory, but many assumptions could easily be varied by an order-of-magnitude.

- For instance, instead of using pure VOCs in equilibrium with the gas phase to determine the concentrations in Table 2, the gas phase concentrations would be reduced by a factor greater than 10 by including water. The reduced VOC transport rate would be countered with a reduced equilibrium concentration on the PAC resulting from lower VOC concentrations (about a 20% reduction in capacity) and water vapor competing for space. It is unlikely that these two considerations would reduce PAC capacity for the VOCs by 90%; therefore the life expectancy of the PAC barrier would increase.
- The VOC diffusion rate within the barrier and within the main cell could be substantially smaller. This could result from a smaller solid phase porosity or VOC sorption on the solid matrix—the overall effect would reduce the VOC transport to the PAC barrier.

Anticipated Long-Term PAC Stability in Grout

The PAC and sorbed VOCs should be quite stable, with chemical degradation and/or biological activity having little effect on the PAC. Reactions could cause VOC degradation, but they would not be expected to occur either. VOC desorption could occur if a high concentration of a competing organic compound were exposed to the barrier or if the barrier temperature were increased substantially; again, this would not be expected.

The main concern would be the constant influx of VOCs from the main cell. Once the PAC capacity is completely exhausted with the weakest adsorbing contaminant, TCE, the continuing inflow of the mixture of contaminants would permit PCE to displace TCE. High TCE concentrations could then diffuse from the barrier to the surrounding area, with all but the most strongly adsorbed material eventually being displaced from the adsorbent.

Summary

Addition of PAC to the exterior barrier confining the bulk of the waste could reduce the target VOC concentrations to very low concentrations. Using several conservative assumptions, this barrier is expected to be effective for approximately 30 years. After that time, the weakest adsorbed VOCs could be displaced by a more strongly adsorbed VOCs, and the displaced VOCs would enter the vapor phase outside the cell. While the 30-year life may not appear good, there are two main reasons to think this may be underestimated by a factor of 10 to 100:

- The equilibrium vapor phase concentrations are very high. Including water in the estimates would reduce these values by at least an order of magnitude. Sorption of the VOCs to the solid matrix within the cell could also reduce these concentrations by an order of magnitude. Both these effects would drastically reduce the amount of VOCs being transported to the barrier and the PAC. Vapor phase VOC concentrations need to be determined for the main cell design.
- Effective diffusivities of the VOCs in the main cell and within the barrier may greatly reduce the transport of VOCs. The values used were deduced from gas phase values and correspond to transport in soils with 29% porosity. If the main cell and the barrier porosities are smaller and if the materials are retarded in their movement by constant sorption/desorption on the solid matrix, the amount of VOCs transported to the barrier and the PAC would be substantially reduced. Effective VOC diffusivities need to be experimentally determined for the main cell and barrier wall materials.

There is one main reason why the estimate could be optimistic: The matrix surrounding the PAC could block access to the activated carbon microspore surface area and prevent sorption from occurring. This would drastically reduce the sorptive capacity of the PAC and prevent VOC sorption. PAC needs to be imbedded into the barrier matrix and adsorption equilibrium studies determined.

Dubinin-Radushkevich (D-R) Equation

$$q = \left[\frac{W_o \rho_l}{MW \cdot 10^{-6}}\right] \exp\left[\frac{-B}{\beta^2}\left(RT \ln \frac{P_s}{P}\right)^2\right] \quad (1)$$

Where:

q = the solid phase concentration of the VOCs (μmol/g carbon);

W_o = the maximum adsorption space of the adsorbent (cm^3/g);

B = the microporosity constant (mol^2/cal^2);

ρ_l = liquid density of the pure VOCs (g/cm^3);

MW = the VOC molecular weight;

β = the affinity coefficient of the VOCs (dimensionless);

P_s = VOC vapor pressure (mmHg);

P = partial pressure of VOCs (mmHg);

R = gas law constant (1.986-cal/mol/^{o}K); and

T = the temperature (^{o}K).

This equation can be used to estimate an adsorption isotherm for a compound adsorbed onto an adsorbent from the gas phase. To use this equation, an adsorption isotherm has to be determined over a wide range of concentrations for a single chemical – referred to as the characteristic curve for that particular adsorbent. The characteristic curve and the reference compound molecular weight, liquid density, and vapor pressure are used to define the Wo and B. The β is an additional correction factor needed to predict another compound isotherm (for the reference compound β is 1). β depends on a compound molar volume, parachor, or polarizability relative to that of the reference compound; while all are claimed to work, different situations result in one working better for certain families of compounds. The D-R equation was used to predict the CT and TCA adsorption data, with both the TCE and PCE data used to generate the characteristic curve with molar volumes used to calculate the β.

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Appendix G

Evaluation of Void Space in a Pit

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Evaluation of Void Space in a Pit

Based on a rough order of magnitude for estimating purposes, the total available voids in the pit are estimated by analysis. For the organic drums there is only about 15% voids, for the inorganic there could be as high as 33% voids, for the nitrate salts 33%, for the boxes 70-80%, for the combustible drums 40-70% voids, and for the surrounding soils 40-50% voids(including bridging effects). Now looking at the test plan (Grant) table2 "volume fractions of buried transuranic waste" the combustible drums are about .536, the organic sludges are about .059, and nitrate is .043 and the inorganic is .124, and the boxes full of asphalt/metal/cinder blocks and wood are about .238. If the soil is about 50% and the waste about 50% then the available voids can be estimated as follows (the volume percent of the pit times the volume percent of the waste times the estimated void volume in the waste or soil type).

Estimated void volume where V is the volume of the pit:

- Soil .5x .5 = .25V
- organic .059x.5x.15 = .004V
- inorganic .124x.5x.33 = .020V
- nitrate .043x.5x.33 = .007V
- combustibles .5x.5x.7 = .17V
- other boxes etc. .5x.2x.7 = .07V
- Total voids = 0.521V

Now, allowing for some grout returns (look at the Loomis 1996 data for TECT), the amount of return is 50 gal for a pit, which is on a total pit volume basis: (11/18) x 1,615 gal or .05V. Since most of these returns are neat grout, this .05V can be added to the .521V above to give a total expected grout injected of 0.571V.

Now, finally, accounting for some compaction of soil around the pit due to the grouting action (conveniently say .029V) we get 0.6V. In other words, 60% of the volume of the pit is the amount of voids expected in the pit.

Appendix H

Grouting Pit Construction Details

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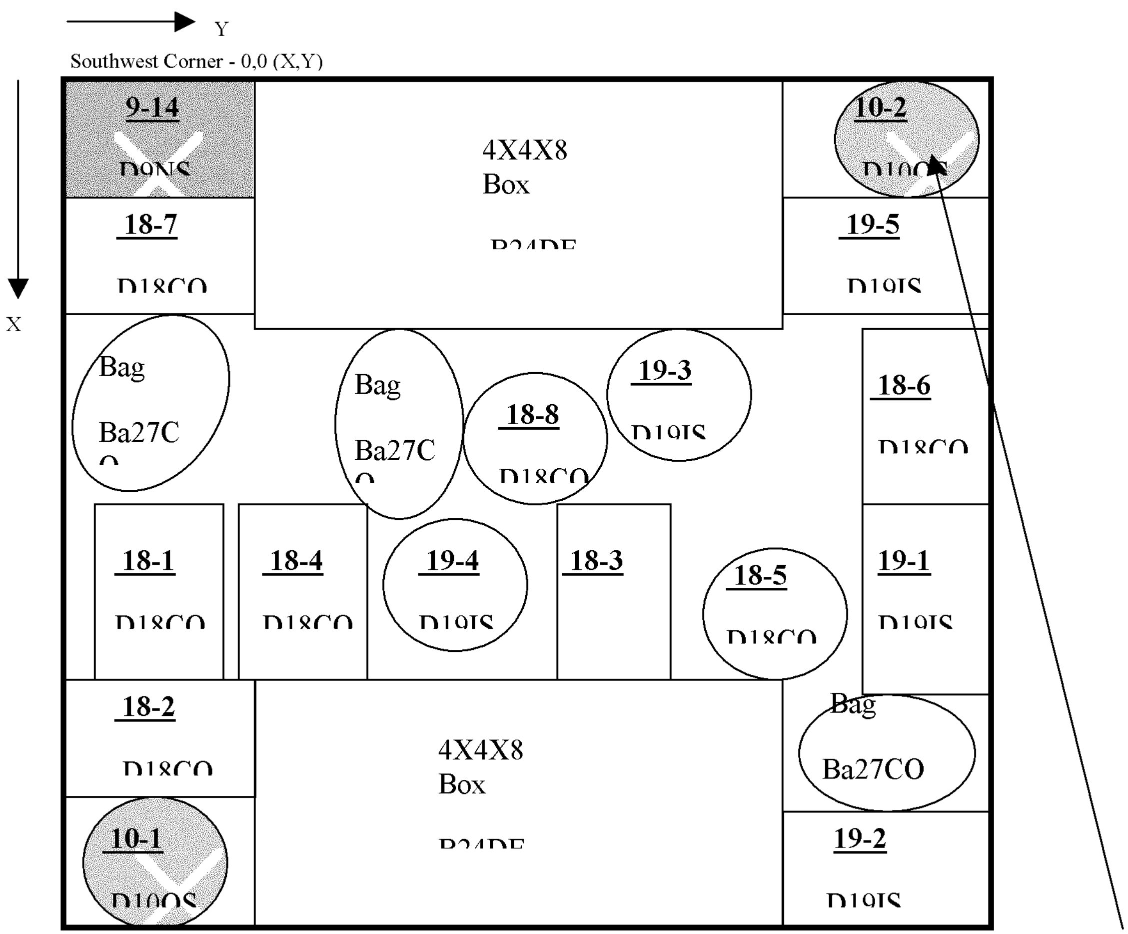
Grouting Pit Construction Details

As-Built for LAYER 1, 0-2 FT., Includes Numbers for Surrogate Waste Forms

North



DRUMS
D18CO =8
D19IS = 5
D10OS= 2, Metal
D9NS= 1, Metal
TOTAL = 16

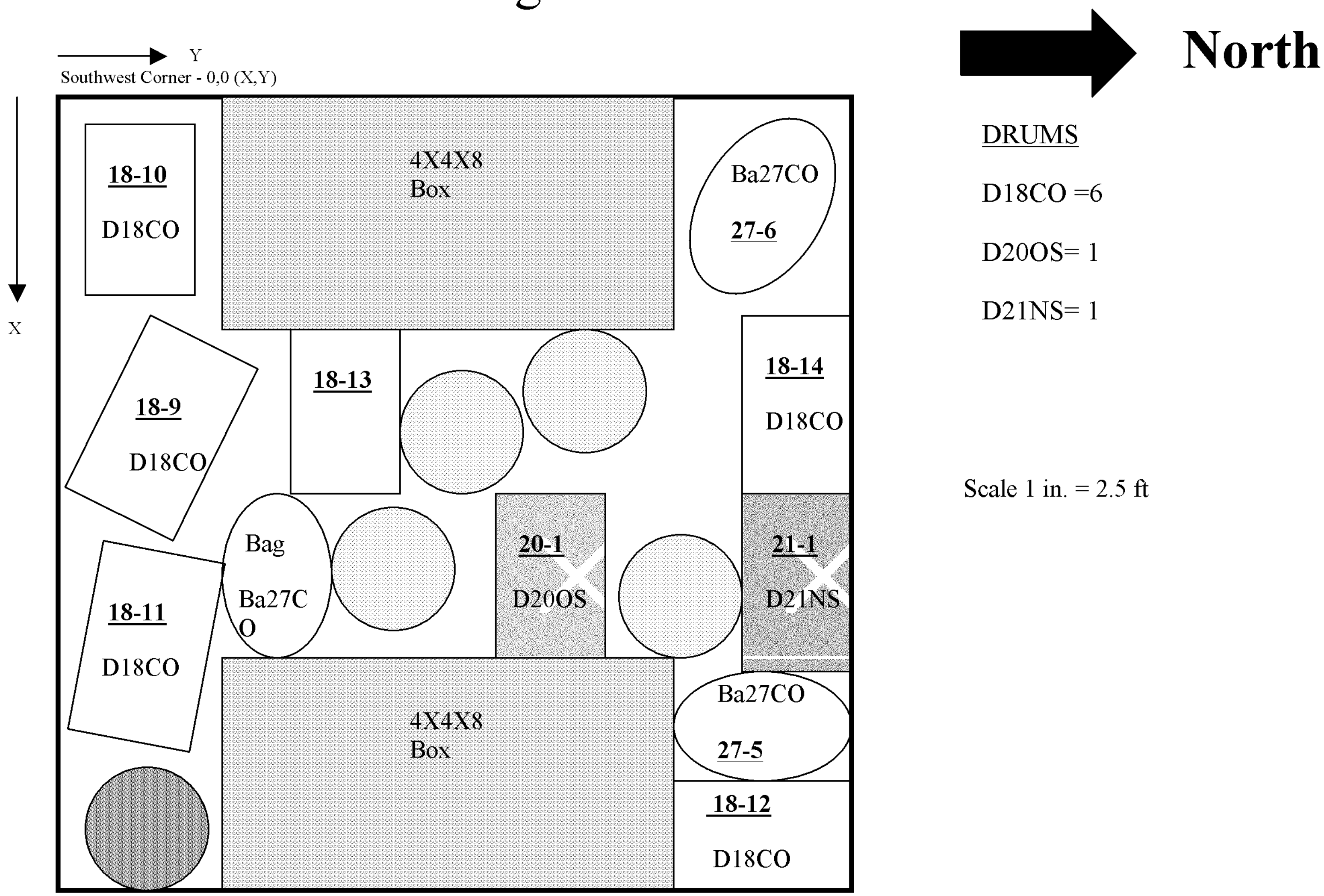
BOXES
Ba27CO = 3
B24DE=2

Scale 1 in. = 2.5 ft

CO-Combustibles
IS-Inorganic Sludge
OS- Organic Sludge
NS- Nitrate Salt
DE-Debris
D-Drum
Ba-Bag
B-Box
#=Mix Number

Drum 10-2 was installed in a Vertical Position instead of horizontal

As Built for LAYER 2, 0-4 FT., Includes Numbers for Surrogate Waste Forms



DRUMS

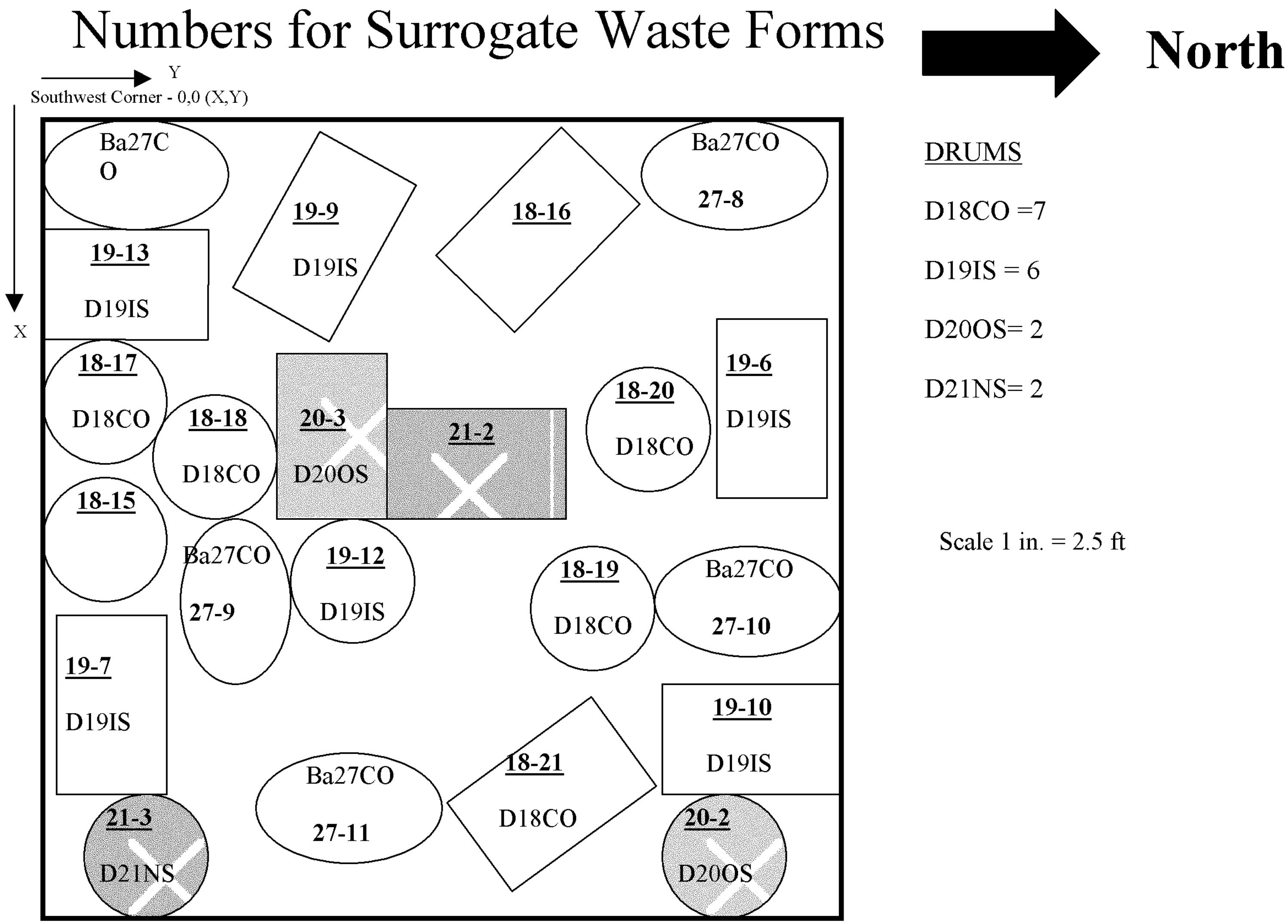
D18CO =6

D20OS= 1

D21NS= 1

Scale 1 in. = 2.5 ft

As-Built for LAYER 3, 0-6 FT., Includes Numbers for Surrogate Waste Forms



DRUMS

D18CO =7

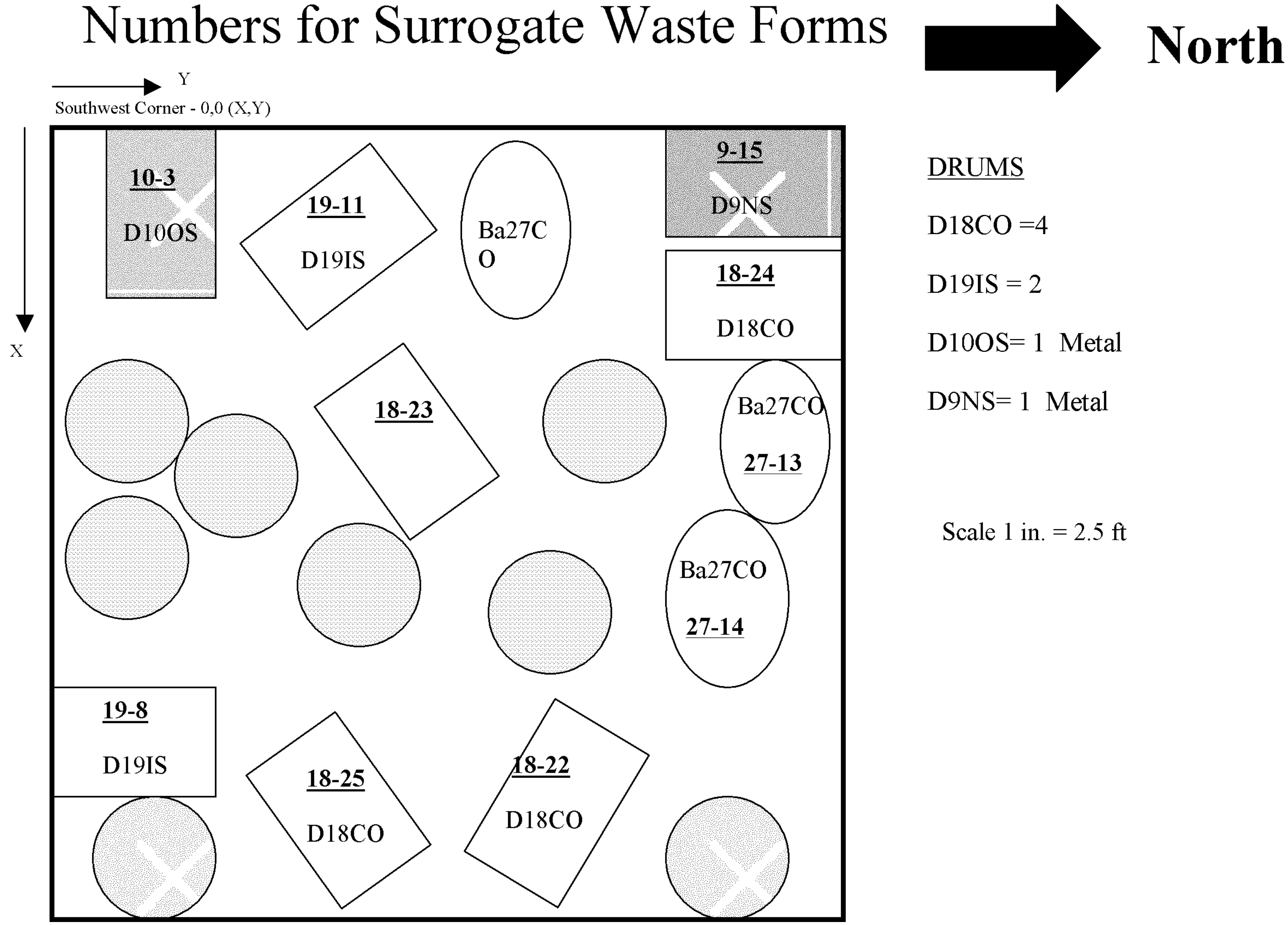
D19IS = 6

D20OS= 2

D21NS= 2

Scale 1 in. = 2.5 ft

As-Built for LAYER 4, 0-8 FT., Includes Numbers for Surrogate Waste Forms



DRUMS

D18CO =4

D19IS = 2

D10OS= 1 Metal

D9NS= 1 Metal

Scale 1 in. = 2.5 ft