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Stabilization of In-Tank Residual Wastes and External-Tank Soil Contamination for the Hanford Tank Closure Program: Applications to the AX Tank Farm

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**Stabilization of In-Tank Residual Wastes and External-Tank Soil
Contamination for the Hanford Tank Closure Program: Applications to
the AX Tank Farm**

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EXECUTIVE SUMMARY

Technical support for the Hanford Tank Closure Program focused on evaluation of concepts for immobilization of residual contaminants in the Hanford AX tanks and underlying soils, and identification of cost-effective approaches to improve long-term performance of AX tank farm closure systems. Project objectives are to develop materials or engineered systems that would significantly reduce the radionuclide transport to the groundwater from AX tanks containing residual waste. We pursued several studies that, if implemented, would help achieve these goals. They include: (1) tank fill design to reduce water infiltration and potential interaction with residual waste; (2) development of in-tank getter materials that would specifically sorb or sequester radionuclides; (3) evaluation of grout emplacement under and around the tanks to prevent waste leakage during waste retrieval or to minimize water infiltration beneath the tanks; (4) development of getters that will chemically fix specific radionuclides in soils under tanks; and (5) geochemical and hydrologic modeling of waste-water-soil-grout interactions. These studies differ in scope from the reducing grout tank fill employed at the Savannah River Site in that our strategy improves upon tank fill design by providing redundancy in the barriers to radionuclide migration and by modification the hydrogeochemistry external to the tanks.

The tank fill design consists of six layers of different materials, including cementitious grout, gravel, and asphalt cement. The material cost for the tank fill was estimated to be about \$400K per tank. Other costs related to the handling and disposal of contaminated soil and equipment are not included in this estimate. The tank skirt, a vertical cutoff wall around the exterior of each tank or possibly around the four-tank AX complex (\$4-8M), is proposed to be constructed to a minimum depth of 60 ft. below the ground surface. Two options are proposed for the location of the barrier: 1) jet grouting a barrier about 4 ft. from the tank wall followed by permeation grouting between the jet grouted barrier and the tank wall; and 2) a barrier at a standoff of approximately 10 ft. composed of two barriers jet grouted and 4 ft. apart followed by permeation grouting the soil between to form a cut off wall. The cost of tank skirts are estimated to be between \$1-2M if constructed around each tank, and they increase linearly if constructed around the 4-tank AX complex. Both tank fill and skirt use current emplacement methodologies.

Numerical simulation has been performed to evaluate the hydrologic behavior in the vicinity of a tank with and without jet-grouted vertical skirts. The amount of groundwater percolating directly beneath the tank can be decreased with increasing skirt lengths. A cost-performance analysis showed that a skirt length of 10-15 ft. beneath the tank is optimal for reducing the amounts of percolating water beneath the tanks. This corresponds to a depth for a coarse pebbly layer with high hydraulic conductivity. Overall, the vertical skirt will improve long-term waste stability by isolating it from reaction with groundwater.

Vertical fluid flow and 1D transport of highly soluble and relatively insoluble radionuclides through a single fracture or through multiple fractures in tank fill were calculated using standard diffusive transport equations. Adding getters would retard highly soluble radionuclides (e.g., Tc) migration over the period of regulatory concern for single cracks and they would slow its instantaneous release in highly fractured tank fill. Addition of getters for sparingly soluble radionuclides (e.g., U) appears to be of little value, even in a highly fractured matrix, although the addition of non or slightly radioactive components (e.g., depleted U) might limit radionuclide mobility by its incorporation in other U minerals.

The getter materials, used primarily in an in-tank and conceivably in the soil-moisture environments, were evaluated for their effectiveness in reducing the solution concentrations and mobility of radionuclides under various conditions. Magnetite, bone char and reducing grout were tested for their ability to retard ^{99}Tc and U species. More than 50% of the ^{99}Tc in alkaline solutions has been sequestered by bone char, and there is up to 90% sorption from deionized water. However, without further tests to fully characterize sequestration mechanisms, getter performance cannot be accurately predicted. With reducing grout, however, Tc will be remobilized if the site becomes oxidizing. The stability and gettering effectiveness of goethite, Portland cement, and hydroxyapatite when used as an additive to tank fill, skirt and under tank barrier materials were evaluated with a geochemical modeling code, REACT. The combination of goethite and Portland cement appears to effectively reduce the total amount of Am, Eu, Np, Pu and U, but they show no effect on Se retention. However, experimental results show a significant Se reduction in the presence of the getter materials.

An assessment was made regarding the feasibility of using directional drilling to emplace a close-coupled barrier beneath the SSTs thus preventing waste leakage during retrieval operations. A survey was sent to contractors claiming experience in directional drilling or jet grouting. A field scale demonstration at a cold test site is recommended to satisfy questions regarding specific performance requirements, such as drilling accuracy grout emplacement efficiency, barrier integrity verification, environmental and safety concerns, and costs, especially at the Hanford site. Emplacement of a close-coupled barrier immediately beneath and adjacent to SSTs seems to be technically feasible.

In conclusion, we have developed an improved tank closure strategy, which incorporates a multilayered tank fill, vertical and horizontal barriers, and development of radionuclide getters. While more costly and complex than the monolithic pours proposed for closure of Savannah River Site waste tanks, this strategy addresses likely cracking of tank grout, reoxidation and leaching of residual waste, and, ultimately, migration of radionuclides to the surrounding soils and groundwater. By anticipating these phenomena, radionuclide migration will be limited over the regulatory lifetime of the waste tanks. Getter applications are somewhat limited because of our poor understanding of retardation mechanisms and availability of good geochemical data. On the other hand, current civil engineering practices are quite sufficient to fill Hanford tanks and to emplace close-coupled barriers around them, although a "cold" field demonstration is highly desirable.

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1.0 Introduction

Waste tank closure at Hanford is not a simple proposition. There are many short- and long-term technical and engineering issues that must be addressed in order to minimize public risk (e.g., from radionuclides) and to satisfy legal and regulatory requirements (e.g., Tri-Party Agreement, Ecology et al., 1989). Our overall support of the Hanford Tank Closure Program is focused on evaluation of concepts for immobilization of residual contaminants in the Hanford AX tanks and underlying soils, and identification of cost-effective approaches to improve long-term performance of AX tank farm closure systems. The Waste Immobilization Technology Development program was initiated by Sandia National Laboratories in FY97 to develop materials or design engineered systems that would significantly reduce the transport of radionuclides to the groundwater from tanks which have been sluiced and contain only residual waste (Balsley et al., 1998).

The proposed strategies for immobilization of residual waste in tanks and in previously contaminated soils, and improved closure systems for the AX tanks and AX tank farm, includes: (1) emplacement of cementitious grouts and/or other materials in the tank to reduce water infiltration ponding in the tank and potential interaction with residual waste; (2) development of getter materials that, when added either prior to or as a component of tank fill, would specifically sorb or sequester radionuclides; (3) emplacement of grout barriers under and around the tanks to prevent waste leakage during waste retrieval or to minimize infiltration of rainwater directly beneath the tanks; (4) injection of minerals into contaminated soils surrounding tanks (or possibly as a component of the grout barriers) that will chemically fix specific radionuclides; and (5) combined geochemical and hydrologic modeling of soil-grout-waste-water interactions.

Solidification and stabilization technology is currently being used to treat a wide variety of hazardous and nuclear wastes, and includes the use of cementitious grout. In fact, two tanks at the Savannah River Site (17F and 20F) have been filled with a reducing grout, followed by monolithic pours of conventional grouts after waste retrieval, although they have not officially been closed (Caldwell, 1997). This simple and cheap tank closure strategy was considered along with other innovative designs using engineered materials to fill AX tanks after waste retrieval. While the design concept of a multilayered tank fill for a typical Hanford single shell tank (SST)

is more complex and costly than the SRS design, it also ensures structural support for the tank. However, in contrast to SRS tank fill design, it minimizes the possibility of cracks extending completely through the tank fill. This, in turn, minimizes water infiltration into the tank and interaction with residual waste and decreases post-closure leaching and transport of radionuclides. The latter involves the addition of specific minerals or sequestering materials that have the ability to enhance immobilization of radionuclides (getters).

The concept of a low-permeability jet-grouted, vertical skirt surrounding an underground waste storage SST was evaluated with the idea that it might affect local infiltration paths in the soil under and near a tank. Diversion of the flow of water (e.g., rainfall or spills) past the external tank wall might reduce vertical waste transport underneath the tank, lateral incursion of water into the tank, and provide structural support for the tank wall. Materials selection was limited to cementitious materials because of its historical longevity, cost, and ease of installation. Numerical simulations have been performed to evaluate the hydrologic behavior in the vicinity of a Hanford waste tank with or without jet-grouted vertical skirts. Multiple infiltration scenarios and vertical skirt lengths were evaluated using a two dimensional, radially symmetric model.

Sequestration or stabilization of selected radionuclide waste species, including Tc, Se, U, and some actinides, was evaluated for two separate environments, both tanks and soils. The geo- and chemical processes that occur as the various dissolved and solid components of residual waste (sludge and sluicing fluid) interacts with grout, grout plus additives, soils, or soils plus additives was addressed by laboratory experimental tests and computer modeling. The performance of selected getters in immobilizing (e.g., sorbing and precipitating) radionuclides was documented by laboratory tests and reaction path modeling under the representative in-situ tank or ex-situ soil conditions. For example, interactions of dilute tank fluid with soil clays and groundwater were simulated with the equilibrium-based computer code, REACT (Bethke, 1998), to predict the release of radionuclides and their impact on groundwater quality with or without the presence of a getter(s). Although the matter of placing getters in contaminated soils was not explicitly dealt with in this report, the concept of jet grouting could be applied to the problem of placing finely divided getter materials as well as to the matter of stabilizing the soil by injecting Portland cement.

2.0 Tank Fill Design and Performance

2.1. Introduction

Design and evaluation is needed to assure that the tank fill materials will fulfill the required functions. These functions are structural support of the tank roof, limitation of water infiltration, prevention of leaching and transport of water. The most important factors to consider are the hydrologic conductivity and mechanical integrity of a layered, cementitious grout backfill structure, as well as construction materials, overall cost, and emplacement methodology. While recognizing the structural support that a tank fill design must provide, our primary concern for a multilayered design is hydrology. The fill is intended to minimize water infiltration to the bottom of the tank and preclude undue wetting of the residual waste. The structural integrity of the layered backfill is also important because grout fractures dramatically enhance hydrologic conductivity (preferred path for water migration) in a tank filled with cementitious materials. Those issues that affect hydrologic conductivity and mechanical stability of the layered tank fill include fill material durability, layer or grout composition, structural properties of grout and fill, and chemical reactivity of fill materials and layers with residual waste. Cost will be addressed with the caveat that expenses increase dramatically when working in a radiologically contaminated environment. Other related issues that also were considered include:

(1) The construction sequence may have an important impact on the tank structural stability. For example, construction of a vertical skirt or a horizontal, close-coupled barrier may involve the use of high pressure jet grouting near the SST wall or base. An assessment of structural stability must be made prior to initiating jet grouting next to the tank wall. If the close-coupled barrier is placed prior to removal of the waste, hydrostatic pressure of the tank waste will provide additional stability to the tank wall, which may be very important to prevent tank wall failure. If tank fill is placed prior to the cut off wall, this will also provide stability for the tank wall.

(2) The mechanical integrity of the vertical barrier is important to verify, as it will ultimately control the migration of radionuclides through this barrier. Considerable confidence in its long-term integrity will be gained by installation of the standoff barrier outlined later. However, verifying the integrity of this barrier will pose a difficult task and is beyond the scope of this report.

(3) Cement-based grouts proposed for use as structural fill inside the tank form rigid materials when they are cured. These materials typically exhibit shrinkage, which causes shrinkage induced cracking. In conventional concrete slab construction these cracks are spaced 15 to 30 ft. (4.5 to 9.1 m) apart. Considerable experience is available with mixtures designed to compensate for shrinkage. It may be reasonable to design grout mixes used for tank fill with shrinkage compensating additives to eliminate shrinkage cracking.

(4) The tank wall/fill interface is an area of particular concern in designing the tank fill materials. Rigid cement-based materials are not likely to adhere to the steel tank wall liner and a separation is anticipated. A layer of asphalt cement is specifically intended to seal the tank wall/fill interface. The material selected will be installed hot and will stiffen as it cools. The viscosity will be selected so that even after cooling the material will flow under stress. This viscoelastic property is anticipated to seal any openings that may develop above or below the asphalt layer.

(5) Open graded granular layers are proposed for two locations in the tank fill. These layers will allow adjacent materials to penetrate into the void space of the granular layer to some extent. This is desirable for two reasons. First, if soft or liquid materials remain after placing a layer, the void space will accommodate these materials and relieve any pressure and would prevent their movement. Second, the infiltration of one layer into another will serve to stabilize the interface between materials.

(6) The tank filling operations will displace vapor occupying the tank headspace at the time filling is initiated. Previous studies have indicated that high-efficiency particulate air (HEPA) filtration systems would be required to minimize radiological emissions (Skelly et al., 1996). This aspect has not been fully evaluated in this study.

2.2. Tank Fill

There are three specific functions that the tank fill is designed to provide. They are:

- (1) Stabilization of residual waste materials left in the bottom of the tank following removal operations. These wastes are assumed (via TPA) not to exceed 360 ft.³ (~2700 gal.), and represents 1% of the existing volume of SST waste when allocated equally to each SST by area.

- (2) Structural support of the tank dome and filling the void volume of the tank. This volume is estimated to be 6436 yd³ (4920 m³).
- (3) Isolation of residual tank waste and sealing of the tank fill-tank wall interface to prevent surface water infiltration from reaching the stabilized waste layer at the bottom of the tank.

The tank fill is constructed in several layers of different materials to enhance its ability to provide required performance characteristics. These layers are identified as Layers 1 through 6, although the materials in some of these layers are identical to other layers as described below. The tank fill concept is illustrated in Figure 2.1. This drawing is conceptual and is not drawn to scale.

Layer 1: Grout stabilized residual waste.

The first layer is designed to stabilize the residual waste in the tank bottom. First, getters will be added in a dry powdered form and then the waste will be solidified by blowing a layer of dry powdered Portland cement in on top of the getter layer. Alternatively, mixing the waste and the first rise of grout may be desirable. In this case, the dry Portland cement would be omitted and grout could be mixed with the residual waste by a modified jet grouting technique or multipoint injection grouting, a patented process used at Oak Ridge National Laboratories (ORNL) for demonstration of stabilization of Gunite and Associated Tanks (GAAT) (Spence and Kauschinger, 1997). These two methods are similar, and both should be considered for further evaluation in regard to Hanford tank waste stabilization. Significant development of these techniques will undoubtedly be necessary to successfully apply them at Hanford tanks and they will depend on the specific characteristics of the residual waste in the AX tanks. The specific grout to be used must be designed so that it includes a suite of getter materials that are selected based on the specific radionuclide species to be stabilized. The grout mixture must be designed to exhibit acceptable pumping characteristics and physical properties of the hardened grout. Compressive strength in the range of 250 to 500 psi (1723 to 3447 KPa) is sufficient to support estimated overburden loads and is achievable with conventional grout mixtures. The materials will be a rigid solid when cured, and there will be no free water following cement hydration. Jet grouting for this specific application should accomplish delivery of the grout to the tank bottom and achieve mixing with residual materials on the tank bottom. The multipoint injection method has been demonstrated in an experiment at a Savannah River site (Spence and Kauschinger,

1997). However, the mixing process discussed here is based upon the report of experience at SRS. The selection of getters and sludge desiccating agents are discussed in Section 4 of this report.

The grout will be composed of sand, cement, flyash, bentonite and admixtures to enhance mixing, pumpability or viscosity, redox state, and to control the rate of hardening. Availability of these materials and recommendations for sources have been detailed previously (Skelly et al., 1996). Heat generated during hydration reactions will have to be estimated and a determination made of time required for heat dissipation and development of layer thickness to be placed.

The estimated volume of residual waste is less than 360 ft³ (~10 m³) according to TPA milestone M-45-00. The volume of grout in this layer will depend on the degree of dilution desired in the mixing process, and ultimately upon NRC incidental waste criteria that are being proposed for use during SST closure (see Cochran & Shyr, 1998). Assuming 5:1 dilution yields a volume of about 67 yd³ (50 m³) of grout. Layer 1 will be approximately 0.4 ft. (0.1 m) in thickness, although its volume could be increased, if necessary, to achieve concentration limits for Class C low-level waste as set out in 10 CFR part 61 or to facilitate mixing and emplacement.

Layer 2: Granular Fill.

A layer of granular fill will be placed on top of the layer 1 grout mixed with residual waste. This layer consists of rigid rock particles in the size range of 100 percent passing the 1 inch and 100 percent retained on the 1/2 inch sieve. The rock will be limestone, which should be chemically compatible with the alkaline waste solutions remaining in the tanks. Acidic rock (e.g., basalt) should not be used in this layer due to the highly alkaline (and reactive) environment inside the tanks. The purpose of this layer is to: (i) accommodate any deformation of layer 1, (ii) relieve any fluid pressures generated due to load imposed deformation of layer 1, (iii) provide sufficient void space to accommodate layer 1 materials without influencing other fill materials, (iv) provide a capillary break in the tank fill structure. The final several inches of the granular layer will be composed of sand sized material to block the voids and prevent the layer from becoming filled with grout in the subsequent layer.

Specifications for the aggregate will be similar to those routinely used for highway construction in order to assure durability in handling and placing the materials. The aggregate will be placed by use of a centrifugal thrower mechanism that slings the rock around the interior

of the tank (Skelly et al., 1996). This device has been previously evaluated at Hanford and found to accomplish distribution of the material. The filling apparatus is designed to be installed in a 42 inch diameter riser (Gilbert et al., 1985). Other in-tank hardware that interferes with the distribution of rock would have to be removed. Previously, proposals were made to cut through this hardware and let it fall to the bottom of the tank. The removal of in-tank hardware should be completed after the construction of layer 1 so as to minimize disturbance of residual waste and to preserve the integrity of the SST.

Layer 3: Grout Fill

The third layer will be a grout mixture that is self-leveling, as the underlying granular fill surface may be uneven. It will be introduced by pumping the mixture into the tank. Candidate materials include the cold cap grout mixture proposed by the Corps of Engineers (cement, sand and fly ash; Skelly et al., 1996) and void fill grout mixtures (cement, sand, fly ash, bentonite) routinely used in civil engineering and mining applications. Grout will be mixed in the same portable batch plant used for mixing layer 1 grout and pumped into the tank by means of pipes inserted through existing riser penetrations. Grout will be placed in lifts allowing for heat dissipation before placing subsequent layers. This aspect must be studied during grout mix design to determine the rate of heat production and the thickness of layers that may be used without causing concrete distress due to thermal effects.

The grout will constitute the largest component of the tank fill material. The thickness of layer 3 will be approximately 22.5 ft. (6.9 m), which will require 100,000 ft³ (2800 m³) of grout. Lift thickness will be developed based on heat of hydration characteristics of the grout mixture.

Layer 4: Asphalt Cement Sealing Layer

An asphalt cement layer is intended to function as a positive seal that will penetrate any cracks that develop in the grout layers above and below the asphalt cement layer, as well as the space between the tank fill materials and the tank wall/liner system. Irregularities in the sidewall tank liner due to deterioration of the steel liner should also be sealed by asphalt cement flowing into those spaces. In order to achieve this effect the asphalt cement grade must be selected to provide a viscosity that will allow the material to move under pressure. The specific selection of a grade will require some laboratory experiments to provide a basis for design of the asphalt cement material. It is anticipated that soft asphalt cement will provide the desired properties.

The volume is estimated to be 8836 ft³, based on an initial layer thickness of 2 ft. (0.6 m). This thickness will decrease when the asphalt cement layer is placed under pressure and flows into voids left at the tank wall interface and any cracking that develops in the layer beneath the asphalt cement layer.

Layer 5: Granular Fill.

The same material used for layer 2 will be placed on top of the asphalt cement layer. The purpose is to allow the asphalt cement to infiltrate the void space forming a seal as the aggregate is pressed into the asphalt cement layer by overburden pressures as the remaining tank volume is filled above. The granular material will provide a stable load-bearing framework to relieve the pressure on the asphalt cement from overburden loads and form a rigid sealing layer. As long as there is pressure on the asphalt cement it will tend to flow. The goal is to have the granular fill penetrate all the way through the asphalt cement layer and rest on the grout below (layer 3) thus transferring the overburden load to the grout. By the time this occurs, the asphalt will form a seal between the tank fill and the tank wall, as well as in cracks or openings that may form in the grout layer above or below the asphalt cement layer. Materials and construction procedures for this layer of granular fill are identical to those discussed above.

Layer 6: Grout Fill

The grout previously described for layer 3 is used to fill the remaining void space above the granular layer. As this process proceeds the granular layer will penetrate into the asphalt cement layer. Each successive grout layer should induce some additional consolidation until the granular layer is resting on the underlying grout layer and the asphalt cement fills the void space in the granular layer and seals the tank fill/wall interface. The grout is identical to the layer 3 grout and is intended to fill the remaining space up to the dome roof. Several grout injections will be required to fill the space between the grout surface and the tank dome in order to allow heat of hydration to dissipate and for grout settlement as the asphalt cement and granular layer interact. If desired, the final lifts of this layer could be composed of a higher strength grout or concrete to serve as an intruder barrier (c.f., SRS tank fill, Calwell, 1997).

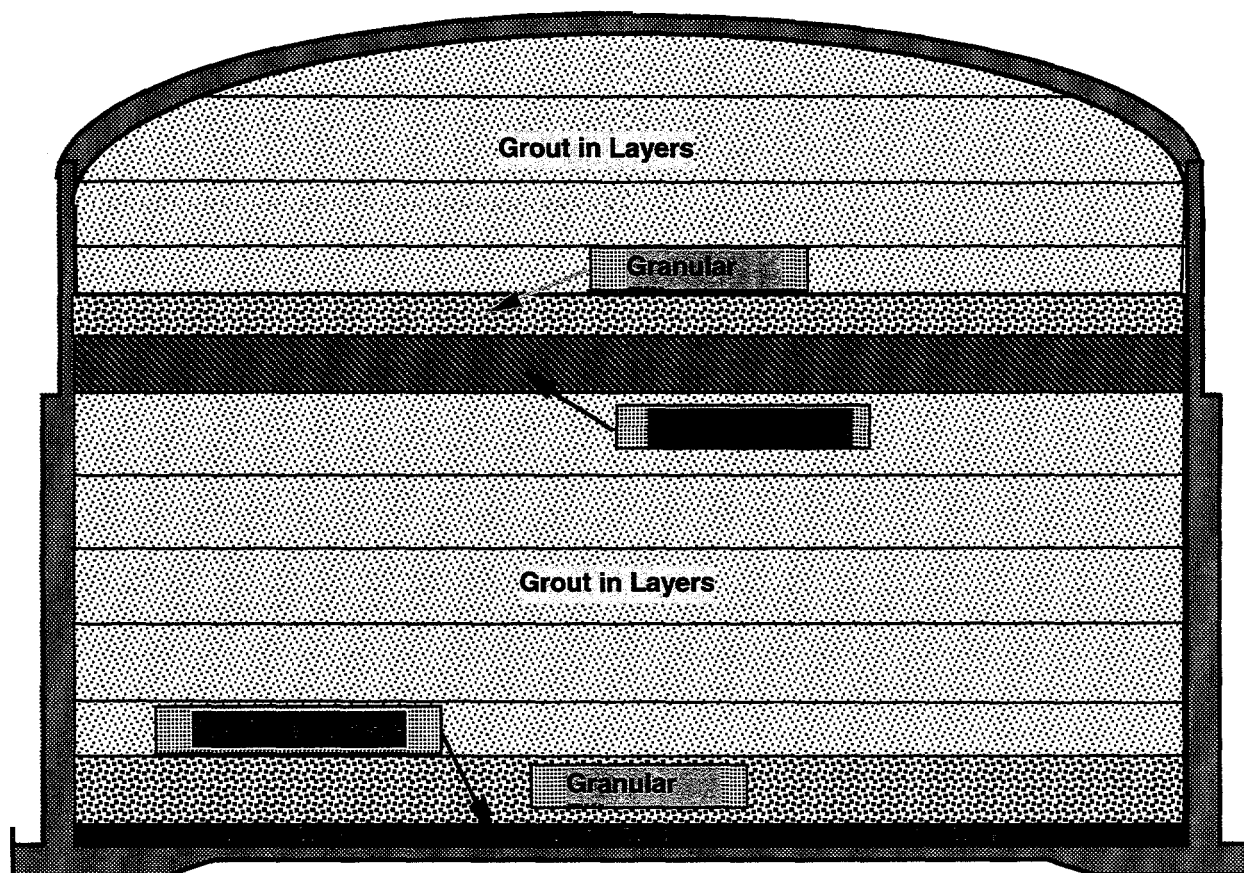


Figure 2.1. Tank Fill Concept.

2.3. Costs of Tank Fill

The grout will be prepared in a portable grout mix plant with a capacity of 150 yd³/hr (115 m³/hr) costing about \$415,000 (Skelly et al., 1996). The plant configuration would include computerized batch controls, scales, a dust collection system, silos for cement, flyash, and aggregate bin, a water heater for cold weather operation, a 10 yd³ (7.6 m³) capacity mixer, and a holding hopper. A concrete pump capable of delivering 150 yd³/hr (115 m³/hr) through 600 ft. (183 m) of pumpline will cost approximately \$250,000. The pumpline represents an additional cost of \$15,000 and replacement is required every 100,000 to 200,000 yd³ (76,152,900 m³) (Skelly et al., 1996). The same grout mixing and pumping equipment may be used for the Layer 3 and 6 grout materials discussed below. Due to the relatively small thickness, self-leveling will

not be a reliable method for distribution of the material uniformly around the tank floor. The mixing device used will have to provide for adequate distribution of the grout (Skelly et al., 1996; Kline et al., 1995).

Costs for Layer 1 grout were estimated previously (Skelly et al., 1996) and indicate grout layer material costs at about \$50/yd³ (\$65.4/m³). These costs are reasonable for the Layer 1 grout, except that additional costs will be incurred for the getter materials to be included in the grout mixture as well as the requirement for injection of the grout to mix it with residual wastes in the bottom of the tank. The effect, if any, of the getter materials on physical characteristics of the grout are unknown. The same equipment can be used for preparation of all grout materials used in the tank stabilization program. It is estimated the Layer 2 thickness will be 3 ft. (0.9 m), which indicates a quantity of approximately 491 yd³ (375 m³) of gravel will be required. Typical costs for this material are about \$15 per ton, depending on hauling distance that is required. Cost data developed specifically for the Layer 3 Grout for the Hanford Site in a previous study are shown in Table 2.1 below. Cost of asphalt cement for Layer 4 depends on the grade and whether the material has been modified by the addition of polymers. At this time it is not certain what grade will be specified or whether modification will be desirable. Therefore, costs are estimated to be \$150 per ton using average values. The 2 ft. thickness will require about 275 tons of asphalt cement at an estimated cost of \$41,250.

Layer 4 will be placed by heating the asphalt cement and pumping the hot material into the tank. This will require a hot-oil heater, pump and line for introducing the asphalt into the tank. A hot-oil heater with a pump would cost approximately \$150,000 for a portable 35,000 gallon (132 m³) tank. The details of distributing the material in order to develop a uniform thickness will require additional development. Cooling time and procedures will have to be estimated based on pumping temperatures and ventilation in the tank. Layer 5 granular materials and construction procedures for this layer of granular fill are identical to those discussed above. Costs and methods of construction for the Layer 6 grout were discussed above and are no different for this layer.

Table 2.1. Materials Cost Estimate*

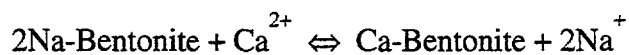
Layer	Material	Unit Cost (\$/yd ³)	Volume (yd ³)	Total (\$K/tank)	4 Tank Total (\$K)
1	Injected grout	\$100	70	\$7.0	28.0
2	Granular fill	\$22	491	\$10.8	\$43.2
3	Grout	\$50	3757	\$187.9	\$751.4
4	Asphalt	\$150	328	\$49.2	\$196.8
5	Granular fill	\$22	491	\$10.8	\$43.2
6	Grout	\$50	2620	\$131.0	\$524.0
All	Total		7757	\$396.7	1585.8

* Based on dollar value of 1996.

2.4. Chemical Stability of Bentonite

Bentonite-grout mixes are proposed as a component of the overall sealing package. The proximity of Portland cement and bentonite raises two questions. In the short term, ion exchange reactions will occur between the interlayer Na⁺ on the clay and the Ca²⁺ ions derived from the portlandite [Ca(OH)₂] in the cement. Over longer times, the clays themselves could deteriorate in the highly alkaline environment established by the cement.

To a coarse approximation, the extent of Na-Ca exchange can be evaluated using tabulated equilibrium constants (Fletcher and Sposito, 1989):



$$\text{and } [\text{Na}^{+}]^2 / [\text{Ca}^{2+}] = 1.48$$

If [Ca²⁺] is fixed at 0.021 molar by the solubility of Ca(OH)₂ then [Na⁺] should be about 0.18 molar. Because limestone/shale mixes are calcined to prepare Portland cements, the Na content of cement pore waters range from 0.06 to 0.18 molar (Berner, 1987). Thus, it is unlikely that

placing these waters in contact with the bentonite is going to result in large amounts of Ca being exchanged onto the clays or, more importantly, out of the cement phases.

Of somewhat greater concern is the chemical stability of the bentonite in the high pH environment established by the cement. To address this issue, samples of bentonite and portlandite were mixed in two fluids, deionized water and a 1% Double Shell Slurry Feed mixed with deionized water (DSSF; see Kupfer et al., 1997). The 1% value was selected because after the tanks have been cleaned, very little residual waste will remain relative to the amount of Portland cement grout to be emplaced. In bulk, this is probably still a great overtest, but there is some concern regarding the fate of materials near the interfaces where the proportion of waste to grout could be somewhat higher. "Normal" testing was carried out at room temperature and "accelerated" tests were carried out at 90°C. Sample splits were taken and analyzed by powder X-ray diffraction after 3 days, 25 days and 127 days. XRD patterns for those samples are shown in Figures 2.2-2.5, where SM refers to starting material. Phases identified by XRD include bentonite, feldspar, cristobalite, calcite, montmorillonite, and portlandite; CSH refers to an amorphous, variable composition, calcium-silicate-hydrate phase commonly found in cement.

Table 2.2 Chemical composition of 7 Molar DSSF simulant (based on [Na]).

Component	Molarity
NaNO ₃	1.162
KNO ₃	0.196
KOH	0.749
Na ₂ SO ₄	0.008
Na ₂ HPO ₄ ·H ₂ O	0.014
NaOH	3.885
Al(NO ₃) ₃ ·9H ₂ O	0.721
Na ₂ CO ₃	0.147
NaCl	0.102
NaNO ₂	1.512

Figure 2.2 XRD patterns for bentonite and portlandite in deionized water at 90°C.

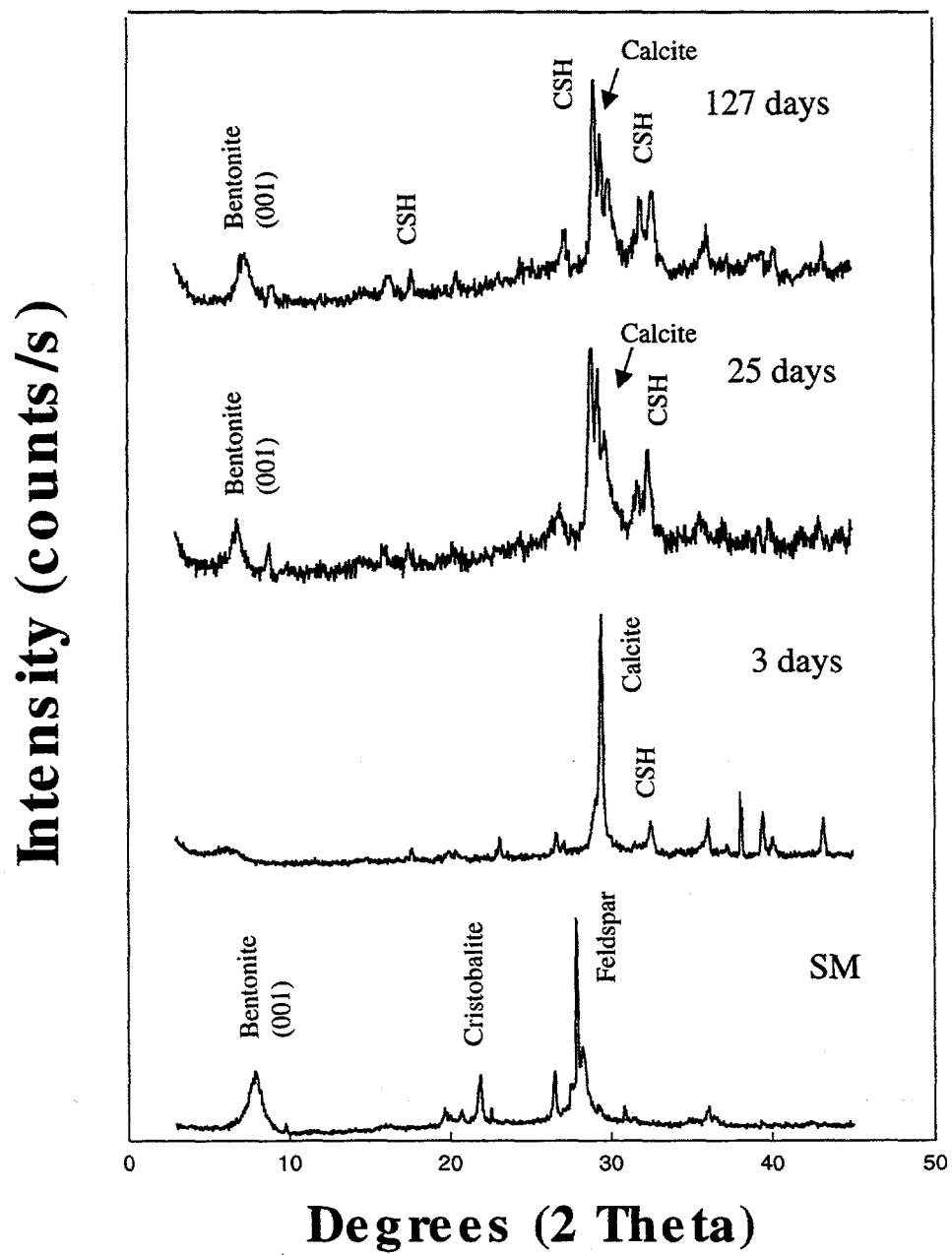


Figure 2.3. XRD patterns for bentonite and portlandite in deionized water at 23°C.

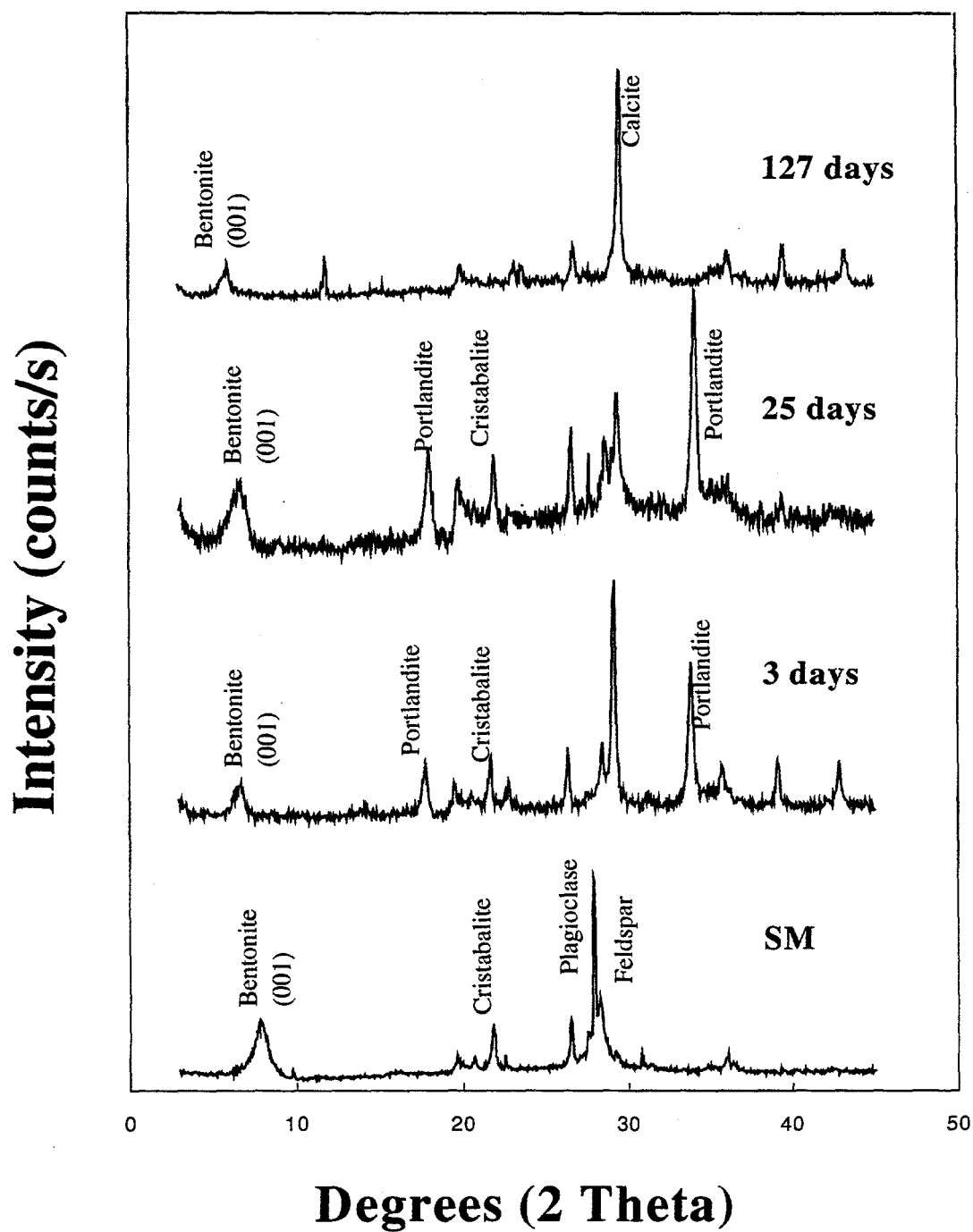


Figure 2.4. XRD patterns for bentonite and portlandite in a 1% DSSF solution at 90°C.

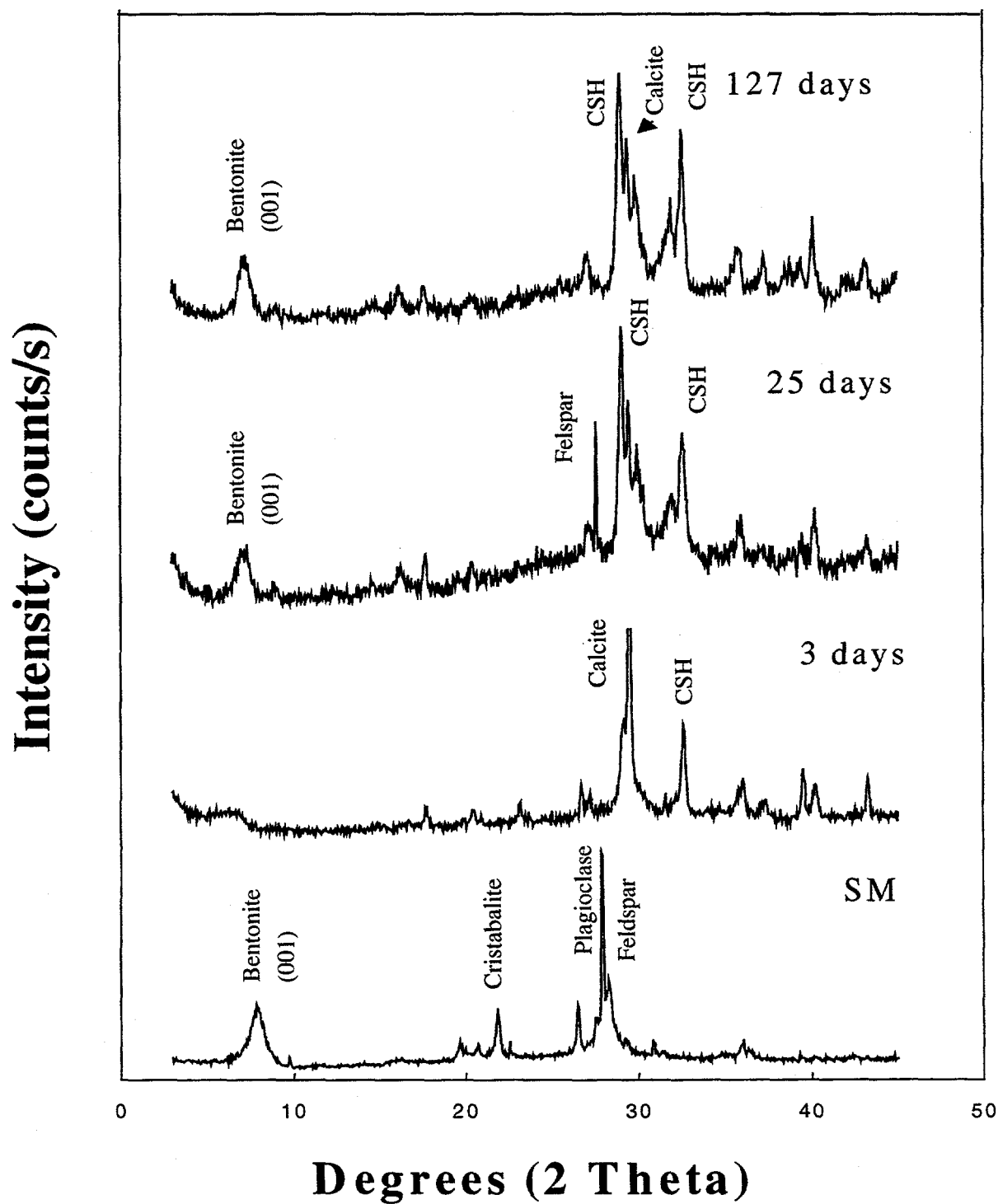
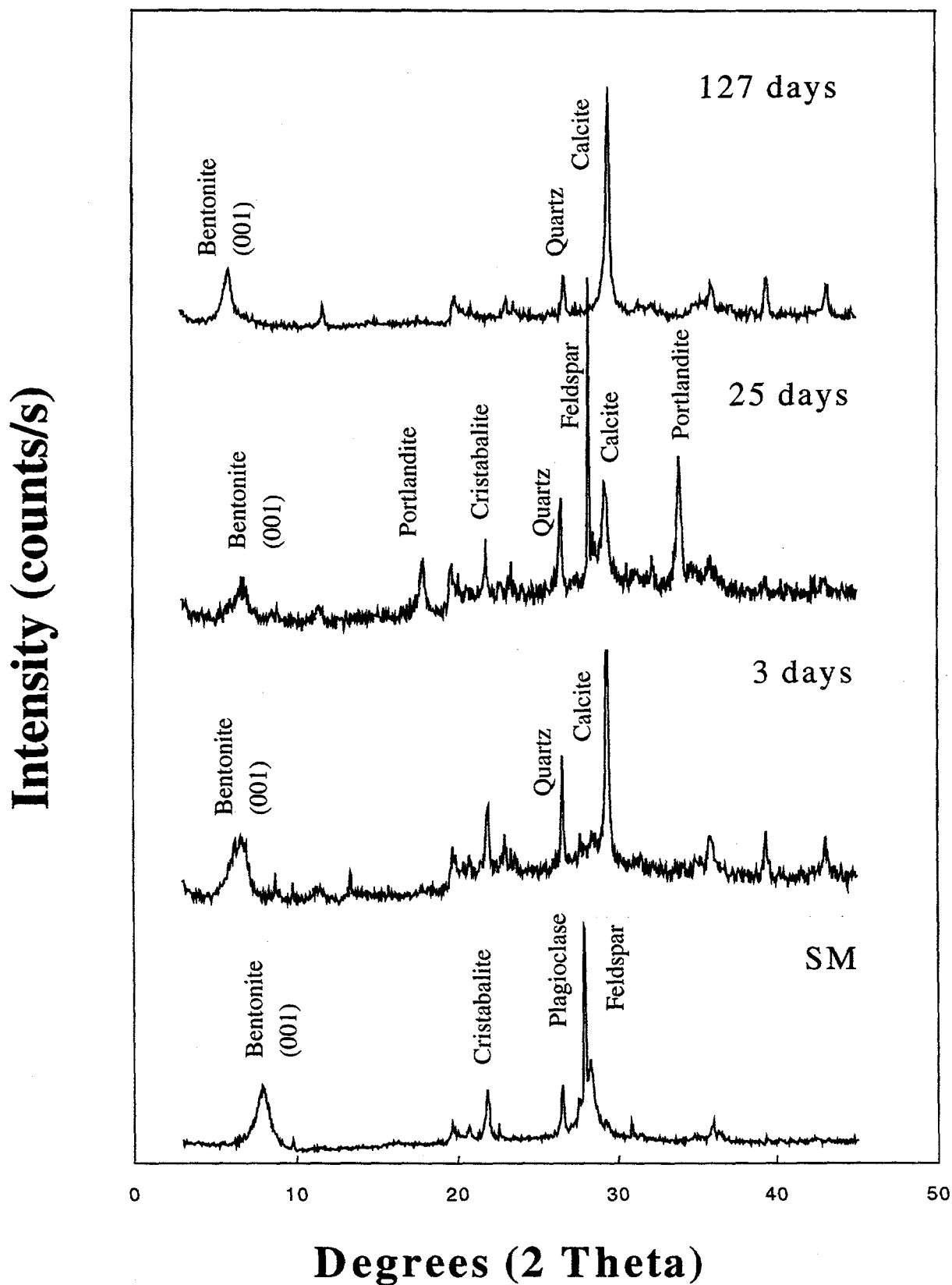


Figure 2.5. XRD patterns for bentonite and portlandite in a 1% DSSF solution at 23°C.



Several aspects of these test results are worthy of discussion. Feldspar $[(\text{Na},\text{K},\text{Ca})(\text{Al},\text{Si})_3\text{O}_8]$ peaks (between 27.5° to 28.5°) disappear immediately, probably because these particles settled to the bottom of the experiment. The main cristobalite (SiO_2) peak (at 21.9°) also disappears, as would be expected since this poorly crystallized form of silica is readily soluble in a mildly basic fluid. Occasionally a large calcite peak appears due to interactions between $\text{Ca}(\text{OH})_2$ and CO_2 from the air. Carbonation (e.g. calcite formation) is typically noted in ancient cements where it may form a surface layer that seals the structure. In any case, it is unlikely to play a large role in the bentonite seals simply because air *should* never have ready access to the bentonite-concrete seal. If it does, then the seal has already failed and the consequences of carbonation are moot unless it can be shown that the process reseals the cracks, perhaps by a volume expansion process. Finally, although it is much diminished, the main montmorillonite (Na,Ca-expandable clay) peak (11° - 12°) is visible in all the runs. However, in the accelerated tests the appearance of new peaks between 28° and 30° suggests the growth of various calcium silicate hydrates (CHS). In short, the accelerated tests provide some indication of deterioration that did not develop for the same solution and solid composition at room temperature.

On a longer time scale, the literature also contains descriptions of the clay rich aggregate particles in Roman concretes (Roy and Langton, 1989, Roy and Langton, 1980). Although interactions occurred at the interface between the cement and the aggregate, the bulk material does not seem seriously degraded. Taken together with our results, one can reasonably conclude that some of the bentonite will act as a pozzolana but some fraction may also survive indefinitely. Without further work it is not possible to fully quantify the transformation process.

3.0 Skirt Design and Performance

3.1. Introduction

The hydrologic behavior near an underground waste-storage tank can significantly impact waste isolation at the Hanford Site's Tank farms. Infiltration and percolation of water through the vadose zone can leach waste emanating from the tanks toward the water table. Caggiano et al. (1996) suggested several sources and pathways for contaminant transport to the water table at the Hanford site, many of which would be aggravated by significant amounts of groundwater

that contacted the waste and subsequently increased mobilization rates. Therefore, to reduce the contact between percolating water and waste in the vicinity of a tank, a cementitious, jet-grouted, vertical skirt as been proposed to serve as a protective "shield" around the waste tanks.

A vertical cutoff wall could be constructed around the exterior of each tank or possibly around the whole four-tank AX complex. Its main purposes would be to: (1) prevent fluids moving from the tank to the soil or the reverse path; (2) divert fluid collection on top of the tank away from the waste; and (3) provide structural support for the tank. Standard construction procedures are proposed for use in constructing this cutoff wall, with redundancy incorporated to raise the confidence in the integrity of the cutoff wall. This barrier may be installed as a close-coupled barrier next to the tank wall, (see objective #2) or at some standoff distance from the tank wall. In modeling the behavior of surface water, it is generally assumed the vertical skirt is close coupled, leaving no untreated soil between the barrier and the tank wall. From the standpoint of constructing the barrier, some questions must be considered before proceeding. The use of jet grouting to construct the barrier is clearly one of the most practical methods available. This involves inserting a pipe in the borehole and pumping a grout material through the pipe to a jet-grouting head, which rotates and mixes the surrounding soils and grout. This is accomplished under considerable pressure (several thousand psi). When the barrier is constructed next to the tank, it will be necessary to assess the impact of these grouting pressures on the stability of the tank wall prior to commencing construction. It is anticipated at this time the vertical skirt around the tanks will be installed prior to initiating waste retrieval operations, in order to provide additional reduction in the potential for release of waste during the retrieval operations. An analysis of the pressures on tank integrity is needed.

3.2. Construction.

A hole would be drilled and then a high-pressure jet-grouting head would be lowered to the desired depth. Air and cement-based grout would then be injected through the jet-grouting head at approximately 6000 lb/in² (4.1×10^4 KPa). Air and cement grout would be thoroughly mixed with the soil in a column approximately 3 to 6 ft. (1 to 2 m) in diameter. A seal would be achieved by overlapping the cylinders in the soil/grout columns. Approximately 80 to 85 percent of the soil impacted by the jet would be combined with the grout to form the barrier, while the remaining 15 to 20 percent of the soil volume would be pumped to the surface as the barrier was

formed (Treat et al., 1995). Since this material is assumed to be contaminated, drillers' health and safety issues as well as disposal of waste (including equipment) in support of the jet-grouting task will need to be addressed.

The vertical skirt or barrier will be constructed to a minimum depth of 60 ft. (15.2 m) below the ground surface, which will place the bottom of the barrier 10 ft (3 m) below the tank bottom. Hydrologic studies are needed to evaluate the benefits of extending the barrier farther, e.g., to depths of 120 m below the surface. A cost-benefit analysis regarding an appropriate depth for the vertical barrier is discussed later in this report.

The second issue is the location of the barrier. Two concepts were considered here. The first option is a close coupled barrier made by jet grouting a barrier approximately 4 ft. (1.2 m) from the tank wall followed by permeation grouting between the jet grouted barrier and the tank wall. The second option is a barrier at standoff of approximately 10 ft. (3 m) composed of two barriers jet grouted and 4 ft. (1.2 m) apart followed by permeation grouting the soil between to form a cut off wall. The greatest uncertainty in the use of jet grouting is the integrity of the barrier. The columns of jet grouted soil must overlap to form a positive cutoff and it is difficult to verify the integrity of the barrier once completed unless there is field testing of the barrier.

Materials for use in jet grouting are conventional cement based grout materials with combinations of additives and admixtures to provide the necessary viscosity, pumping and flow characteristics. A mix design will be based on the soils and pumping equipment used to make the installation. It is also possible to incorporate getter materials in the grout mixture to stabilize radionuclides in contact with the grout.

Costs of jet grouting vary depending on the organization contacted. These costs are considered to be construction costs and do not purport to represent costs of health and safety provisions that will be essential to installation in the vicinity of the AX tank farm. The measures required for health and safety and the disposal of soil wastes generated will be additional to the estimates below, especially when drilling in contaminated soils. The impact of depth on costs is not significant for the depths involved in this project (i.e., less than 120 feet). The estimated costs range from \$20 per ft.² (\$215 per m²) for a single jet grout cut off wall to \$80 per ft.² (\$861 per m²) for the double close-coupled barrier. These costs increase to \$100 per ft.² (\$1076 per m²) for the three lines of barrier at a standoff of 10 ft. (3 m). The thickness of the barrier will be

determined by the nature of the soils and the specific grouting mixture and injection pressures used.

Table 3.1 below summarizes cost estimates (in millions of dollars) computed for the vertical skirt. The rates used for the estimates were \$80 per ft.² (\$861 per m²) for the two lines of grout close coupled around each individual tank as illustrated in Figure 3.1. This sort of barrier was then estimated by computing cost to surround all four tanks with a single barrier composed of two lines of grout. The standoff concept was then estimated at \$100 per ft.² (\$1076 per m²) for placing around the 4 tanks in the AX Tank Farm. The economics of surrounding the 4-Tank AX farm complex with a vertical wall needed to be evaluated relative to individual tanks. This is illustrated in Figure 3.2. It is not practical to use the standoff concept for individual tanks located as close as the AX tanks are situated. Similarly, it is not practical to use the two lines of grout to surround the entire 4-tank complex. It was assumed in computing these estimates that the grout barriers are made up of 4 ft. (1.2 m) diameter columns when completed. Unless containment and preservation of contaminated soils near AX tanks are a major concern, it is apparent that using close-coupled barriers is more economical.

Table 3.1. Cost (\$M) for Vertical Skirt Construction.

Depth ft. (m)	Close Coupled (2 lines)	Close Coupled (2 lines)	Standoff (3 lines)
	@ \$80/ft. ² (\$861 m ²)	@ \$80/ft. ² (\$861 m ²)	@ \$100/ft. ² (\$1076 m ²)
	Single tank	4 tanks	4 tanks
60 (18.3)	\$1.3 M	\$5.2 M	\$8.2 M
80 (24.4)	\$1.8 M	\$7.0 M	\$11.0 M
100 (30.5)	\$2.2 M	\$8.8 M	\$13.7 M
120 (36.6)	\$2.6 M	\$10.5 M	\$16.4 M

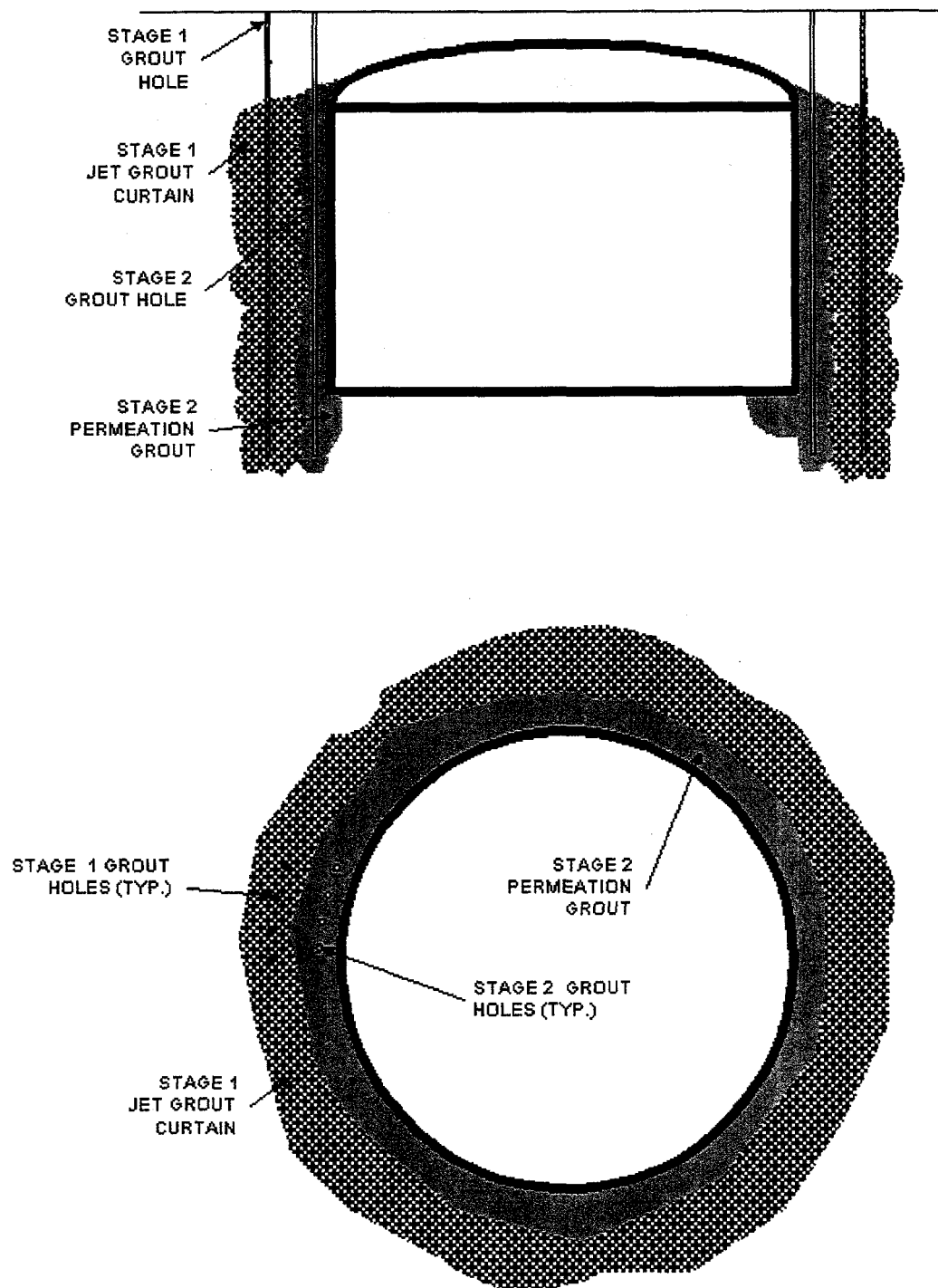


Figure 3.1. Close-Coupled Vertical Barrier around Individual Tanks.

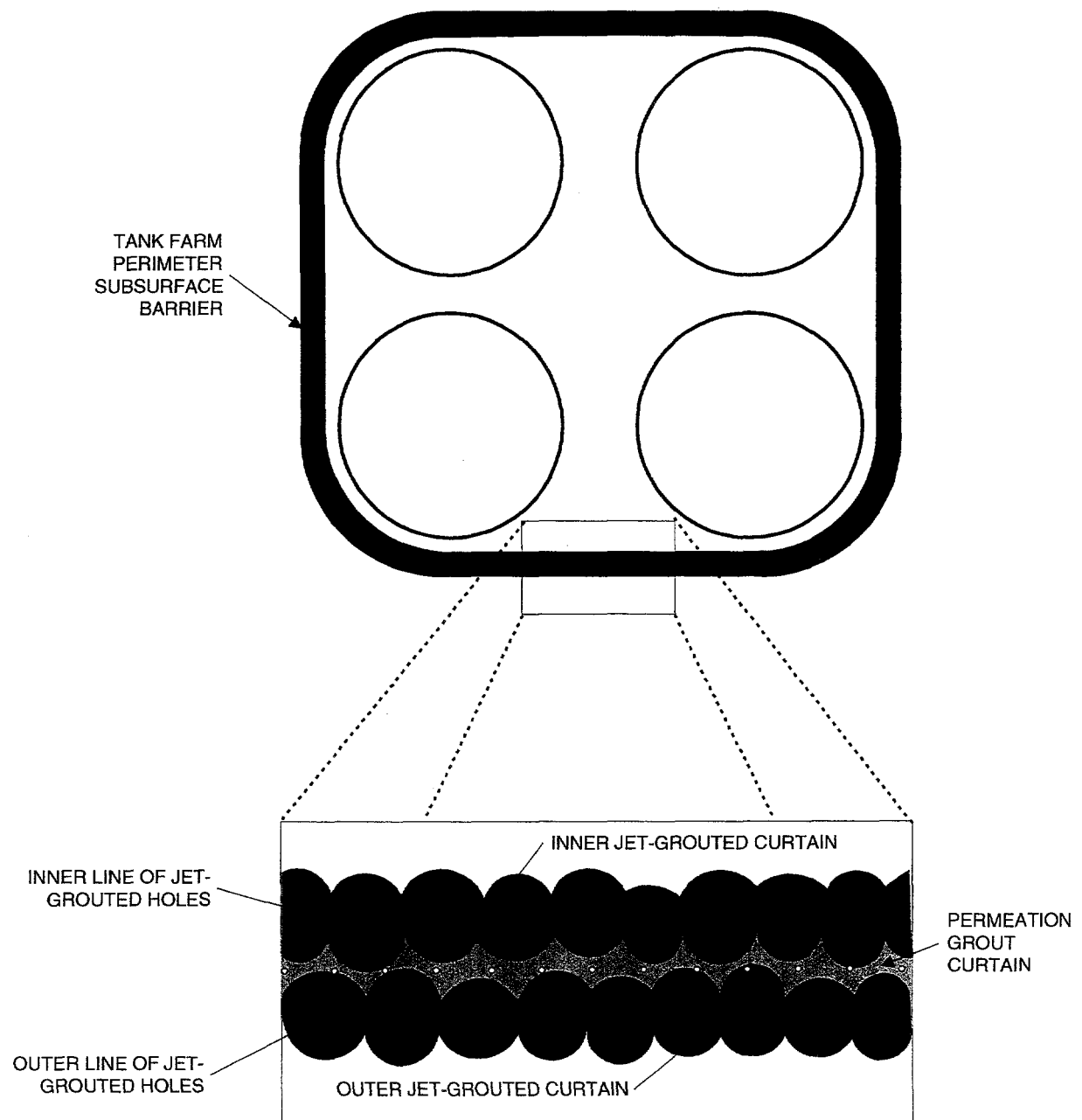


Figure 3.2. Standoff Vertical Barrier Constructed Around the AX Farm.

3.3. Hydrologic Analysis of a Hanford Tank with a Vertical Skirt

3.3.1. Introduction

The design and construction of a cementitious vertical skirt around SSTs have been discussed in section 3.5. Here, we evaluate their hydrologic benefits. Figure 3.3 shows a conceptual sketch of a vertical skirt surrounding a single waste-storage tank (the skirt can also be applied to an entire farm of tanks). The jet-grouted skirt is primarily intended to divert the flow of groundwater past the base of the tank and slow the infiltration of the groundwater through the external tank wall. The skirt can be extended past the base of the tank to further divert groundwater from passing directly beneath the tank. The skirt could also serve as structural support for the sidewall of the tank.

As a first step in understanding the impact of a vertical skirt on the performance of a Hanford waste tank, the hydrology around a single waste tank with varying skirt lengths is evaluated. Two different infiltration rates are used with four different skirt lengths. Groundwater flow patterns around the tank are compared among the simulations, and diversion capacities beneath the waste tank are evaluated. A cost evaluation for the construction of the vertical skirt is presented, along with recommendations for optimal skirt length and future work.

3.3.2. Numerical Approach

The numerical code TOUGH2 (Pruess, 1987; 1991) is used in the numerical simulations of groundwater flow around an underground storage tank with vertical skirts. TOUGH2 uses an integral finite difference method to solve for simultaneous transport of heat, gas, and liquid in porous and fractured media. One-, two-, and three-dimensional systems can be modeled with non-uniform elements. TOUGH2 has been used extensively in applications involving environmental remediation, nuclear waste management, and subsurface hydrology (Pruess, 1995). For the purposes of this study, only the single-phase, isothermal solver is invoked (EOS9: Richards' equation), which assumes a passive gas phase at a constant ambient pressure and temperature.

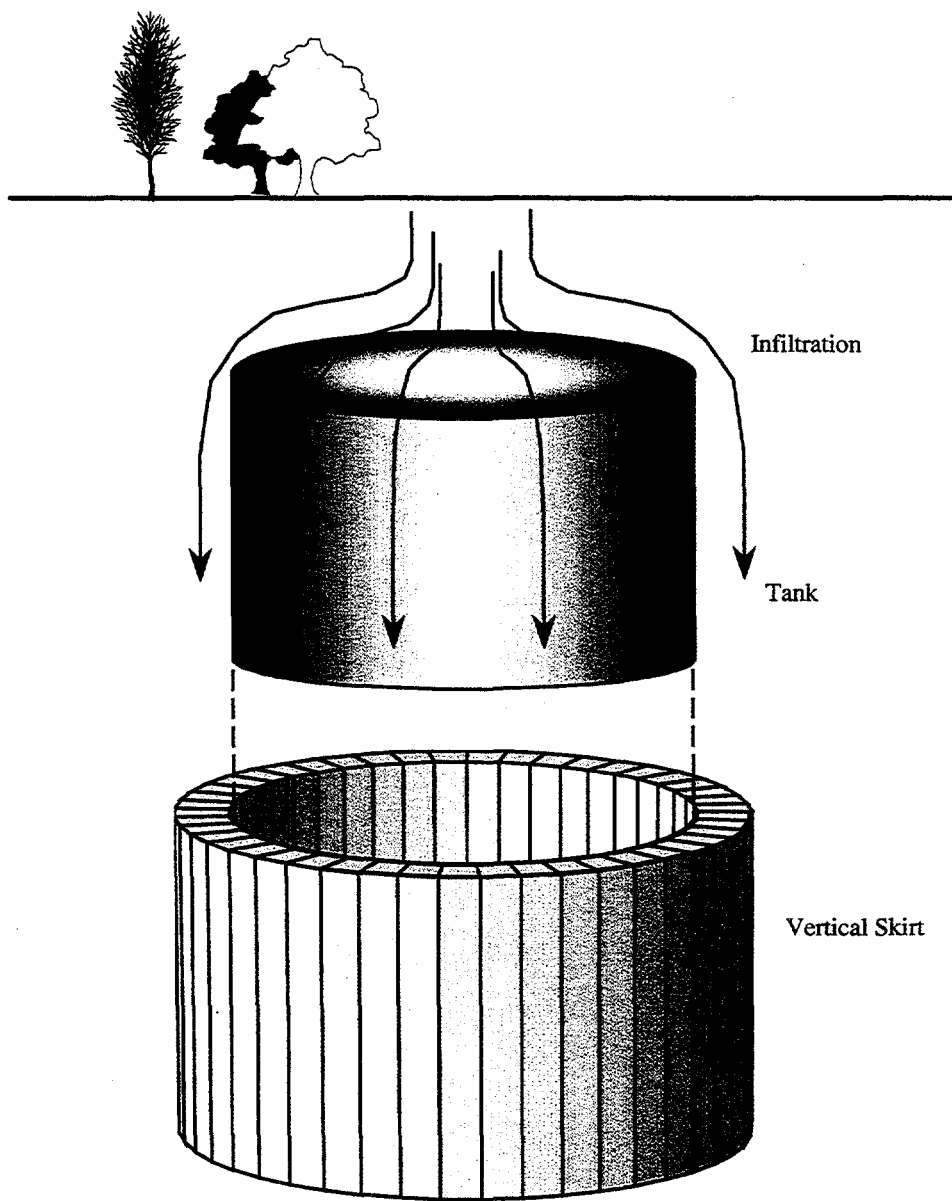


Figure 3.3. Conceptual sketch of a cementitious, jet-grouted, vertical skirt surrounding a Hanford underground waste tank.

A two-dimensional, radially symmetric region with a single waste-storage tank is assumed for the analysis. Figure 3.4 shows a plan view and a side view of the model domain. The model is bordered on the left by the vertical centerline of the tank, and the right boundary of the model is at a radial distance of 32 m from the centerline, sufficiently far to avoid boundary effects on the flow pattern near the tank. No flow conditions across the lateral boundaries are assumed. The water table at the bottom of the model is 64 m below the surface of the model and is maintained at a constant liquid saturation of one. The depth of the water table and the stratigraphy shown in Figure 3.4 are adapted from Ward et al. (1997). The location of the tank is shown in bold in Figure 3.4 and has a height of 14 m and a radius of 11 m. The tank is surrounded by a coarse backfill material and rests on top of a silty sand layer. Below this are alternating layers of unconsolidated silt, sand, and gravel, which overlie semi-consolidated sediments of the Ringold Formation. The hydrologic properties of the six alternating layers used in this model are adapted from Ward et al. (1997) and are shown in Table 3.2. The Brooks-Corey model (1966) for capillary pressure and relative permeability are used in the numerical simulations:

$$P_c = -\frac{P_t}{S_e^{1/\lambda}} \quad (1)$$

$$k_{rl} = S_e^{(2+3\lambda)/\lambda} \quad (2)$$

$$S_e = \frac{S_l - S_{lr}}{1 - S_{gr} - S_{lr}} \quad (3)$$

where P_c is capillary pressure (Pa), P_t is the threshold or air-entry pressure (Pa), S_e is the effective liquid saturation defined in Equation (3), λ is a pore-size distribution parameter, k_{rl} is the relative permeability of the liquid, S_l is the liquid saturation, S_{lr} is the residual liquid saturation, and S_{gr} is the residual gas saturation (assumed zero). The parameters in Equations (1)–(3) are given in Table 3.2.

The numerical grid is comprised of 51 rows and 22 columns for a total of 1,122 elements. The rows and columns are spaced non-uniformly with more refinement in the vicinity of the tank and at interfaces between stratigraphic layers. A constant mass flow is applied to the top row of elements to simulate constant infiltration rates of 0.5 and 100 mm/year (Ward et al., 1997). Because the vertical cross-sectional areas of the elements in this radial model increase with

increasing radial distance, the mass flow rates are varied accordingly to maintain the prescribed infiltration rates over each column of elements. To simulate the hydrologic effects of a vertical skirt that extends beyond the base of the tank, horizontal connections between selected elements beneath the outer rim of the tank are removed. For example, the bold vertical line that extends beneath the base of the tank shown in Figure 3.4 indicates the location of connections that would be removed if a 2 m vertical skirt were simulated.

For each of the two infiltration scenarios considered (0.5 and 100 mm/year), four skirt lengths (as measured from the base of the tank) are simulated: 0 (no skirt), 2, 4, and 6 m. All eight simulations are run to steady state. Liquid saturations and mass flows are then recorded and compared among the different simulations.

3.3.3. Results and Discussion

The liquid saturations and percolation fluxes for the 0.5 and 100 mm/year infiltration scenarios without vertical skirts are shown in Figure 3.5. The liquid saturations are indicated by the shades of grayscale in each plot, darker being wetter and lighter being drier. In general, the coarse layers such as the backfill and pebbly sand are drier, while the finer layers such as silt have higher liquid saturations. In addition, the higher infiltration case yields higher liquid saturations everywhere. In both cases, the infiltrating water is diverted around the waste tank and is shed around the outer wall of the tank. The percolation flux past the outer wall of the tank is nearly six times greater than the applied infiltration, commensurate with the findings of Ward et al. (1997), who reported a 3-5 times increase in percolation past the base of their two-dimensional Cartesian tank due to shedding. Upon closer inspection, the flow past the base of the tank is seen to migrate toward drier regions directly beneath the tank. This behavior is considered adverse to waste isolation if contaminants have seeped through the bottom of the tank.

The impact of vertical skirts extending beyond the base of the tank on hydrology near the tank is shown in Figure 3.6 for an infiltration rate of 0.5 mm/year. The view is expanded near the vicinity of the tank to allow better visualization of the flow vectors for each of the four vertical skirt lengths considered. As the skirts get longer (denoted in Figure 3.6 by solid vertical lines), the amount of groundwater flow percolating directly beneath the tank is decreased.

Table 3.2. Hydrologic properties used in Hanford simulations (from Ward et al., 1997).

Soil Type	Porosity ¹	Residual Saturation ²	Threshold Pressure ³ (Pa)	Pore-Size Parameter ³	Radial Permeability (m ²)	Vertical Permeability (m ²)
Backfill	0.259	0.00	901	1.838	1.21×10^{-12}	1.21×10^{-12}
Silty Sand	0.427	0.20	833	0.644	1.17×10^{-12}	7.54×10^{-13}
Pebbly Sand	0.508	0.008	47.4	0.239	1.62×10^{-10}	5.39×10^{-11}
Early Palouse	0.509	0.00	8950	1.0	2.74×10^{-13}	1.37×10^{-13}
Upper Ringold	0.418	0.081	810	0.953	3.53×10^{-13}	1.76×10^{-13}
Middle Ringold	0.422	0.081	691	0.952	3.68×10^{-12}	1.84×10^{-12}

¹Porosity is assumed equal to saturated moisture content (residual gas saturation is 0).

²Residual saturation is equal to residual moisture content divided by porosity.

³Used in Brooks-Corey model (1966) for capillary pressure and relative permeability.

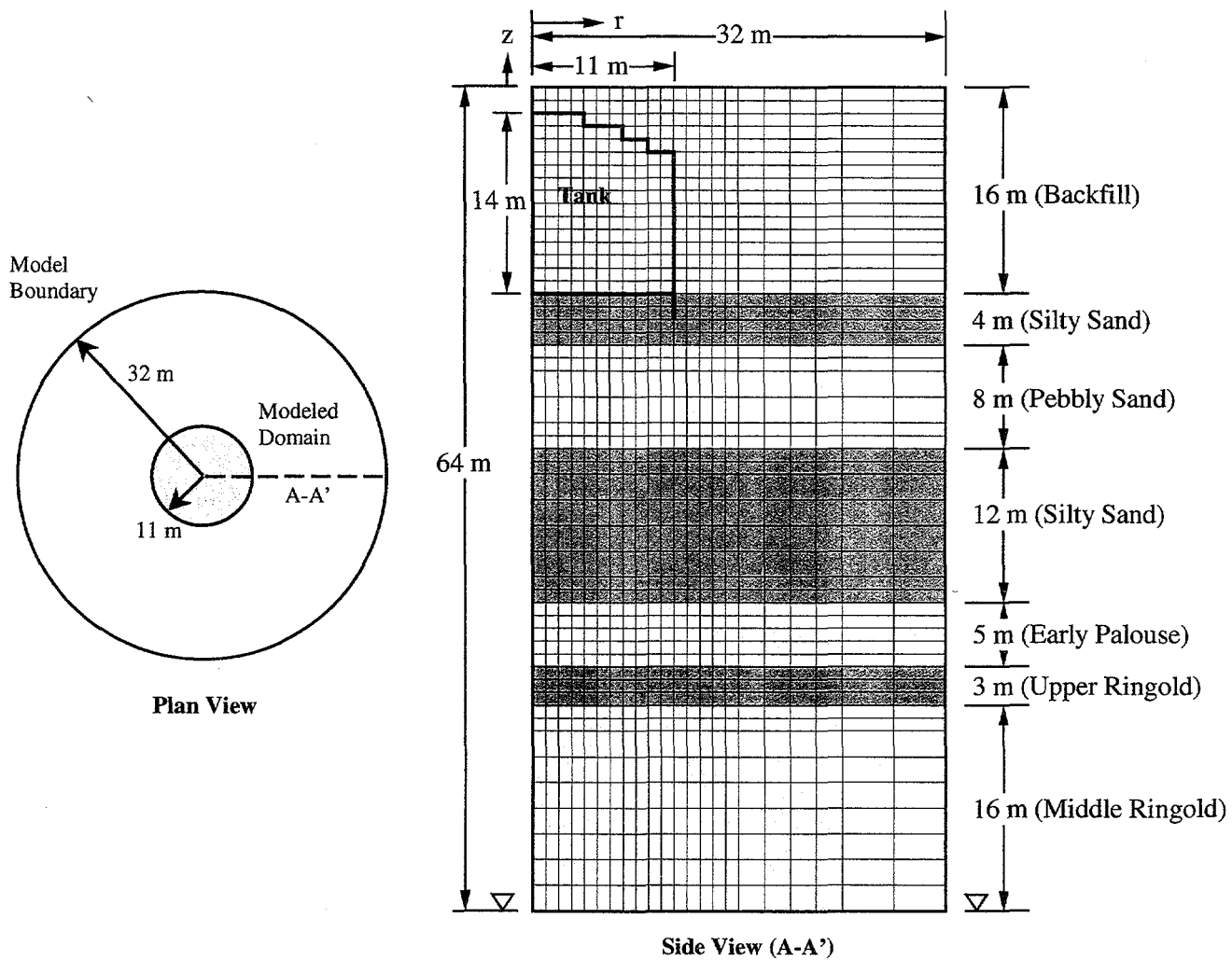


Figure 3.4. Model domain and numerical grid used in TOUGH2 simulations.

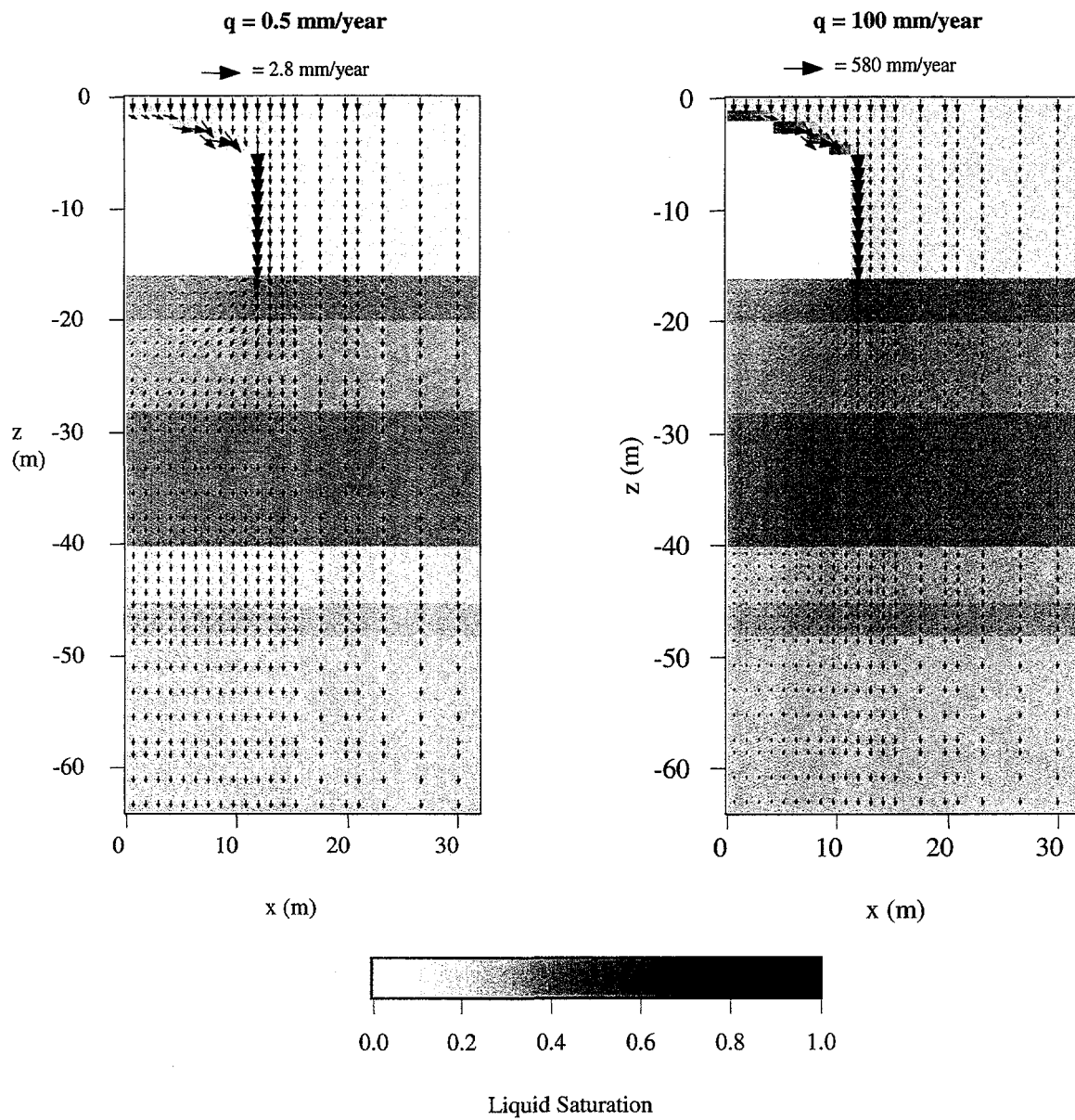


Figure 3.5. Simulated liquid saturations and percolation fluxes for the two infiltration scenarios (0.5 and 100 mm/year) with no vertical skirt.

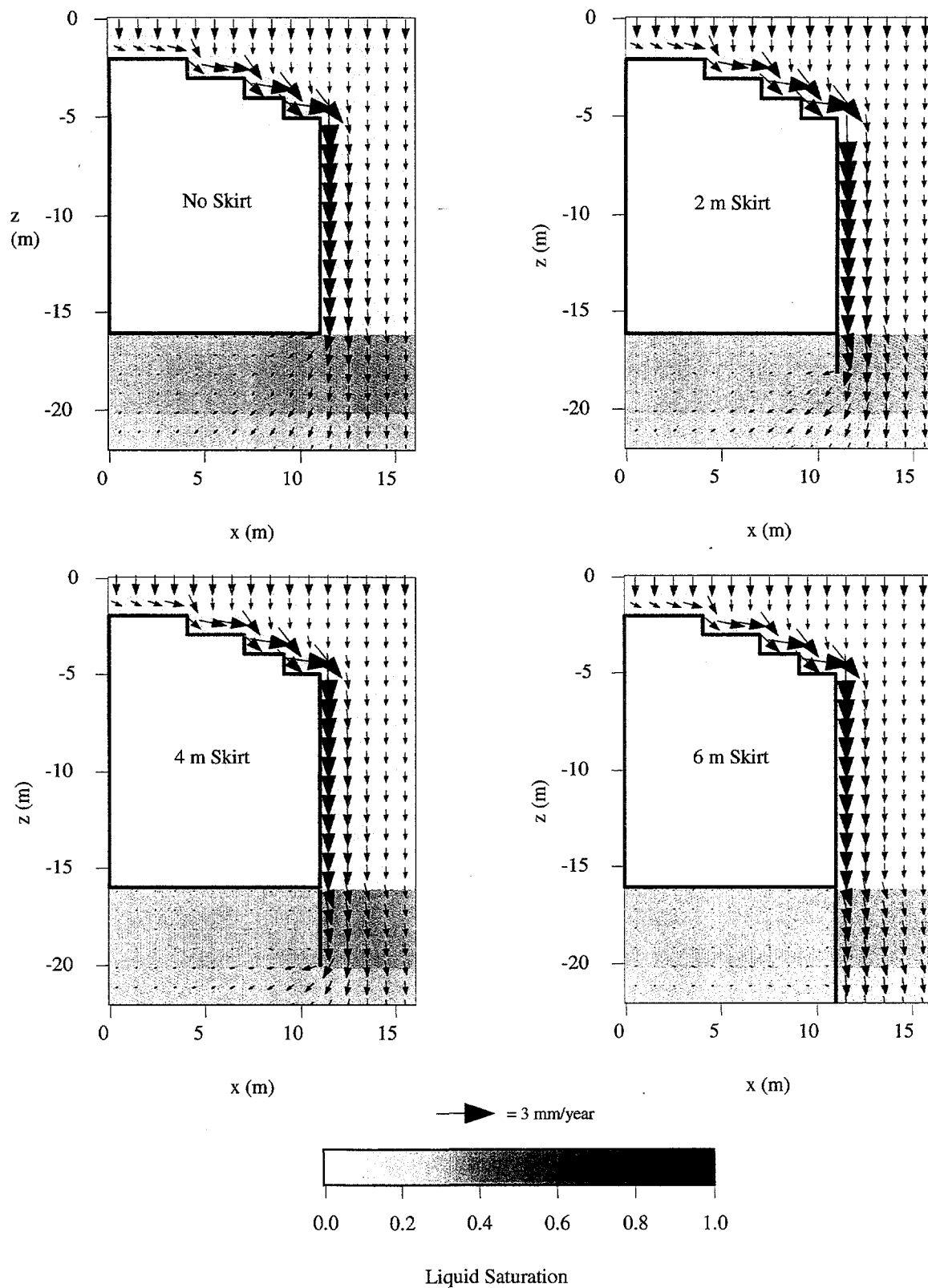


Figure 3.6. Simulated liquid saturations and percolation fluxes for different skirt lengths and an infiltration rate of 0.5 mm/year.

Groundwater shed around the tank cannot move laterally back toward the bottom of the tank until the flux is past the vertical skirt. This results in slightly lower liquid saturations beneath the tank and potentially less mobilization of waste beneath the tank. Figure 3.7 shows similar results for an infiltration rate of 100 mm/year, except that the liquid saturations are generally higher.

Figure 3.6 and Figure 3.7 present a qualitative description of the effects of vertical skirts on groundwater flow past a waste tank. Quantitative analyses can be performed by comparing the amount of mass flow beneath the tank to the infiltrating mass introduced above. Figure 3.8 plots the ratio of the downward mass flow from a distance four meters beneath the base of the tank to the surface. Infiltration is shown as a function of radial distance from the tank centerline (a ratio of one indicates that the downward mass flow is equal to the infiltration at a given location). Results of both infiltration rates and all four vertical skirt lengths are shown. The 4 m distance used in Figure 3.8 is arbitrarily chosen, but it allows a quantitative comparison of the flux distribution beneath the tank. Directly beneath the center of the tank at $r = 0$ m, the ratio of downward flow to infiltration is zero for all cases. As the radial distance increases, more downward flow occurs past the 4 m distance beneath the tank for simulations with no skirt and a 2 m skirt. For the simulations using a 4 m skirt and a 6 m skirt, the downward flow remains zero until the radial distance exceeds the radius of the waste tank (11 m). At this location, the ratio of downward flow to infiltration jumps significantly due to shedding around the waste tank. As the radial distance increases past 20 m, the downward flow is equal to the applied infiltration in all cases (recall that the outer boundary model is at 32 m).

The diversion capacity of the vertical skirts can also be evaluated as a function of depth beneath the tank. The downward flux beneath the tank is integrated in a region bounded by the radius of the tank and divided by the total infiltration directly above the tank. This ratio (labeled as fraction of infiltration flowing beneath the tank) is calculated as a function of depth beneath the tank for all cases and is plotted in Figure 3.9. The ratio of downward percolation to infiltration within the tank radius generally increases as the distance beneath the tank increases. As the distance increases, more liquid is allowed to migrate beneath the tank, increasing the ratio plotted in Figure 3.9. A quantitative comparison among the different skirt lengths can also be made. For example, at a distance of 6 m beneath the tank, the no-skirt simulation allows over 60% of the infiltration above the tank to flow beneath the tank for the 0.5 mm/year scenario. The 4 m and 2 m skirt simulations allow approximately 50% and 40%, respectively, and the 6 m skirt

simulation does not allow any downward flow at a distance of 6 m beneath the tank. The 100 mm/year simulations show similar trends, but the fraction of water flowing directly beneath the tank is less in all cases. A plausible explanation is that the ratio of capillary driven lateral spreading to gravity-driven downward flow is smaller when infiltration rates are increased.

Figure 3.9 also shows that a jump in improvement exists between the 4 m and 6 m skirt simulations that is disproportionate with the other simulations, especially at greater depths. One possible explanation is that the 6 m skirt simulation extends into the pebbly sand layer. Because this layer is extremely coarse, the capillary forces required to move water laterally are small in this layer. Thus, water that is shed into this layer by the 6 m skirt tends to proceed downward rather than laterally beneath the skirt. This postulation, if true, provides incentive to extend the skirt into the pebbly sand region beneath the silty sand layer. The feasibility of such an extension will depend on the depth of the layers and the cost of the skirt materials and injection process.

Figure 3.10 shows the percent improvement over the no-skirt conditions as a function of depth beneath the base of the tank. The percent improvement indicates the percent of infiltration that is diverted from beneath the base of the tank in excess of that diverted without a skirt. This quantity was calculated by simply taking the difference in the values of the curves shown in Figure 3.9 as a function of depth. For each of the three skirt lengths evaluated, the percent improvement increases rapidly with depth until the depth equals the skirt length, at which point the percent improvement gradually decreases as more water flows around the skirt and beneath the tank.

The cost of jet-grouting a single-walled vertical barrier around a Hanford waste tank can range from \$20 per square foot (Rumer and Mitchell, 1995; p. 205) to \$100 per square foot (estimate from a jet-grouting contractor in Denver, CO). These costs typically do not include waste disposal, grouting materials, and other contingencies, and they may rise significantly in contaminated soils from past leaks and spills (e.g., AX-102 and AX-104). Figure 3.10 shows plots of cost and percent improvement as a function of skirt length. The costs are plotted using two extreme estimates of cost per square foot of jet grouting and range can be as high as \$1.6 million for a 6 m skirt. The bottom two plots in Figure 3.11 show the percent improvement for the 0.5 and 100 mm/year infiltration simulations. Because the percent improvement is evaluated

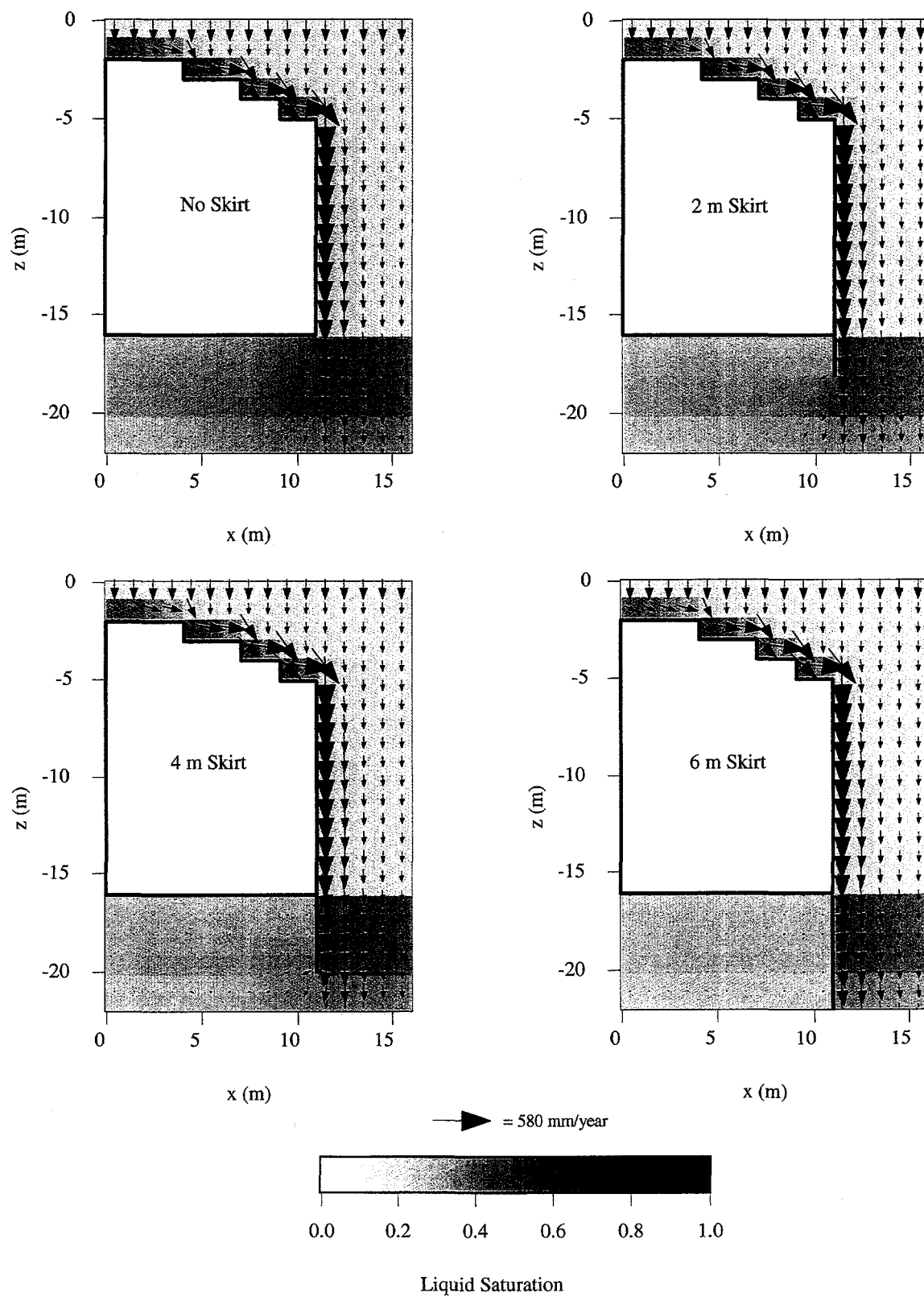


Figure 3.7. Simulated liquid saturations and percolation fluxes for different skirt lengths and an infiltration rate of 100 mm/year.

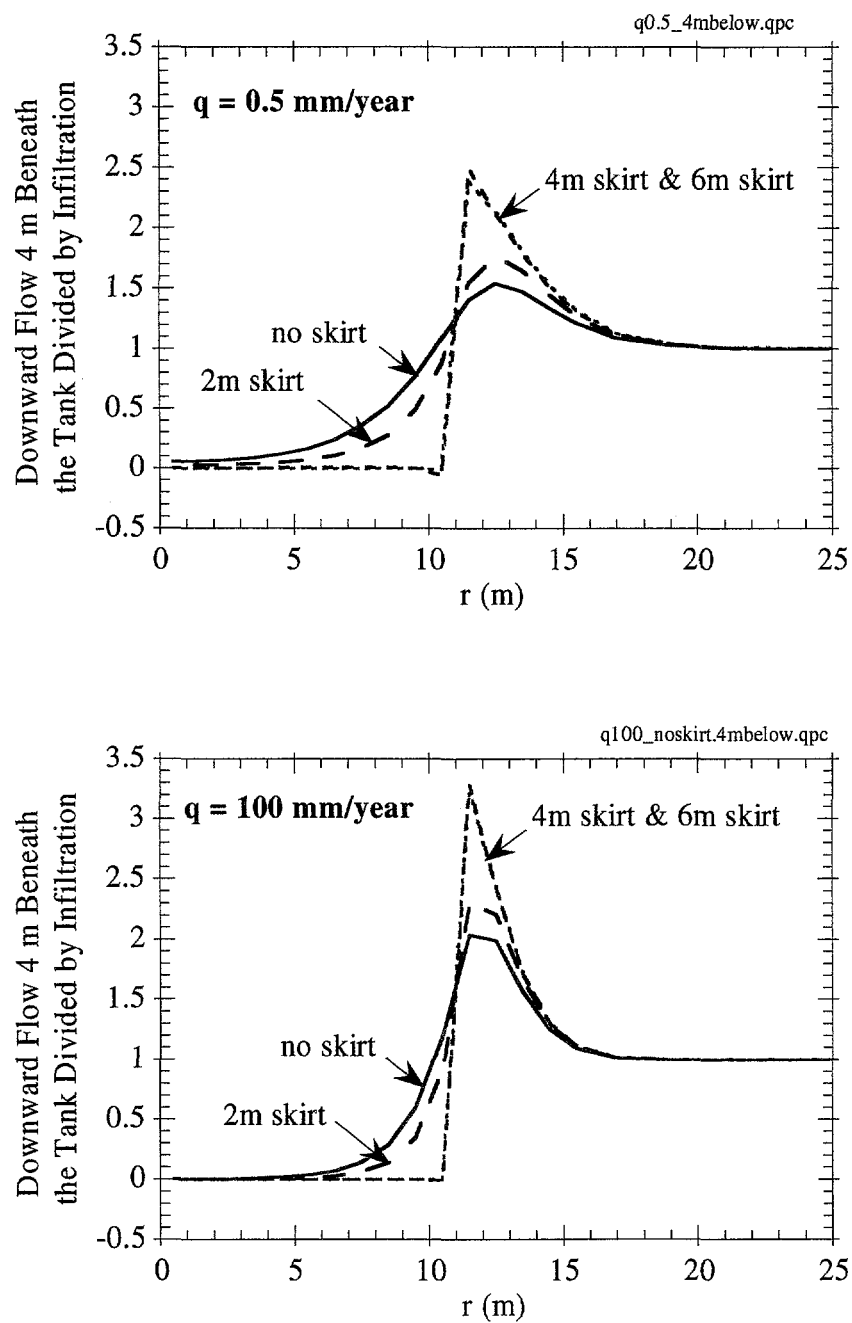


Figure 3.8. Downward flow four meters beneath the base of the tank divided by surface infiltration plotted as a function of radial distance for two different infiltration rates.

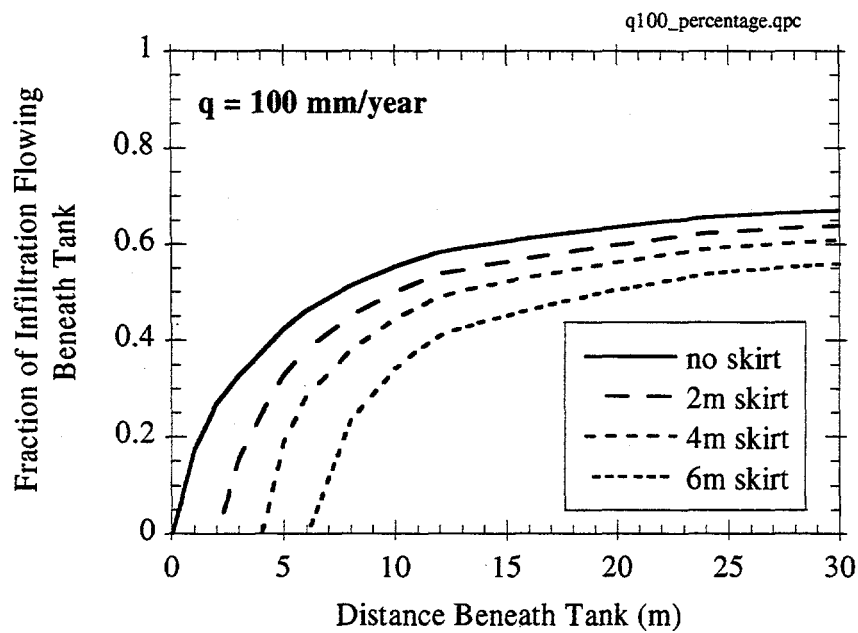
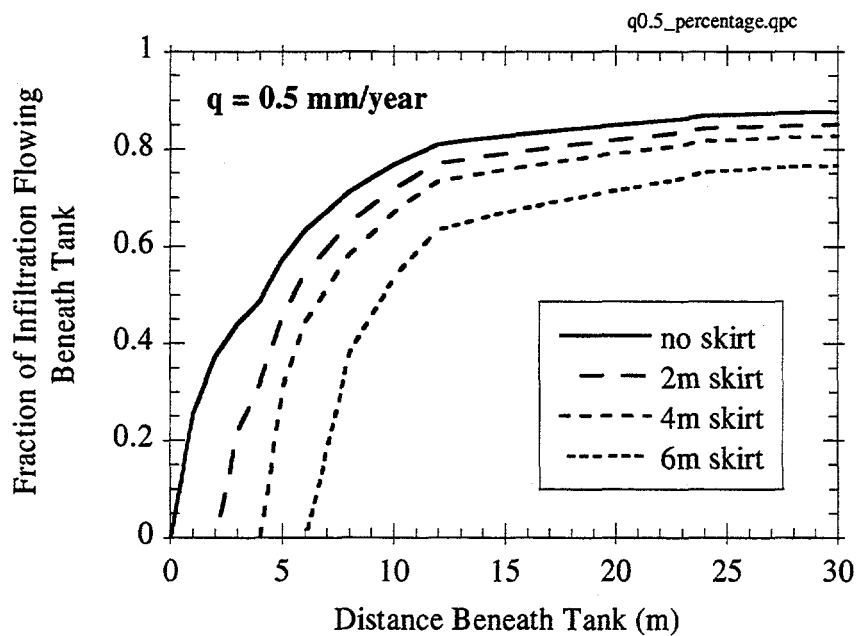


Figure 3.9. Total downward flow beneath the tank (bounded by the radius of the tank) divided by the infiltration above the tank plotted as a function of depth for two different infiltration rates.

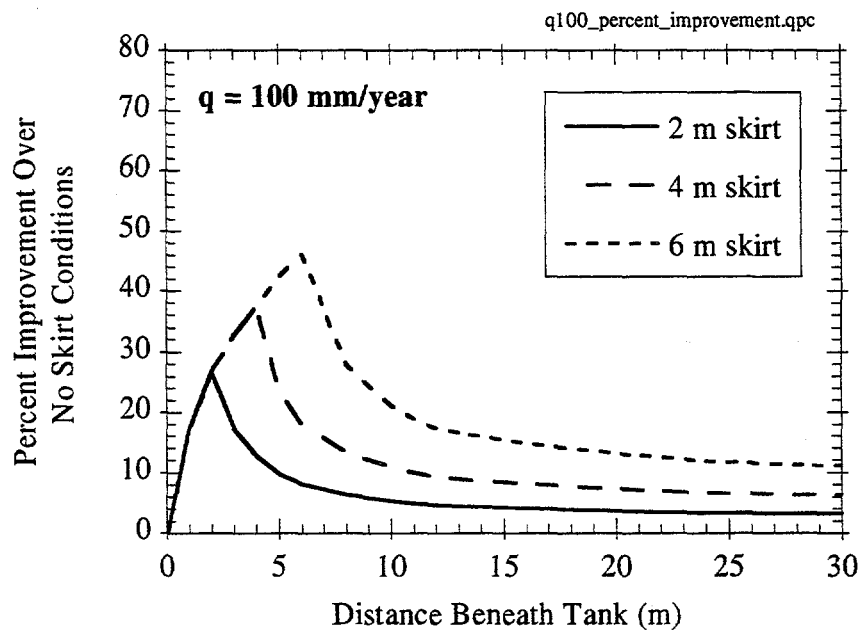
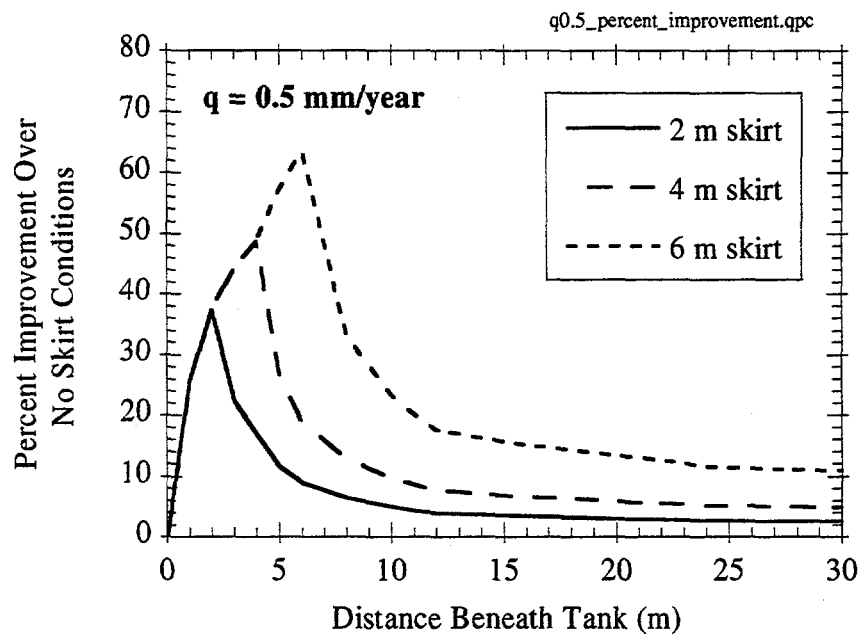


Figure 3.10. Percent improvement over no skirt conditions for different skirt lengths and infiltration rates as a function of depth using plots in Figure 3.9.

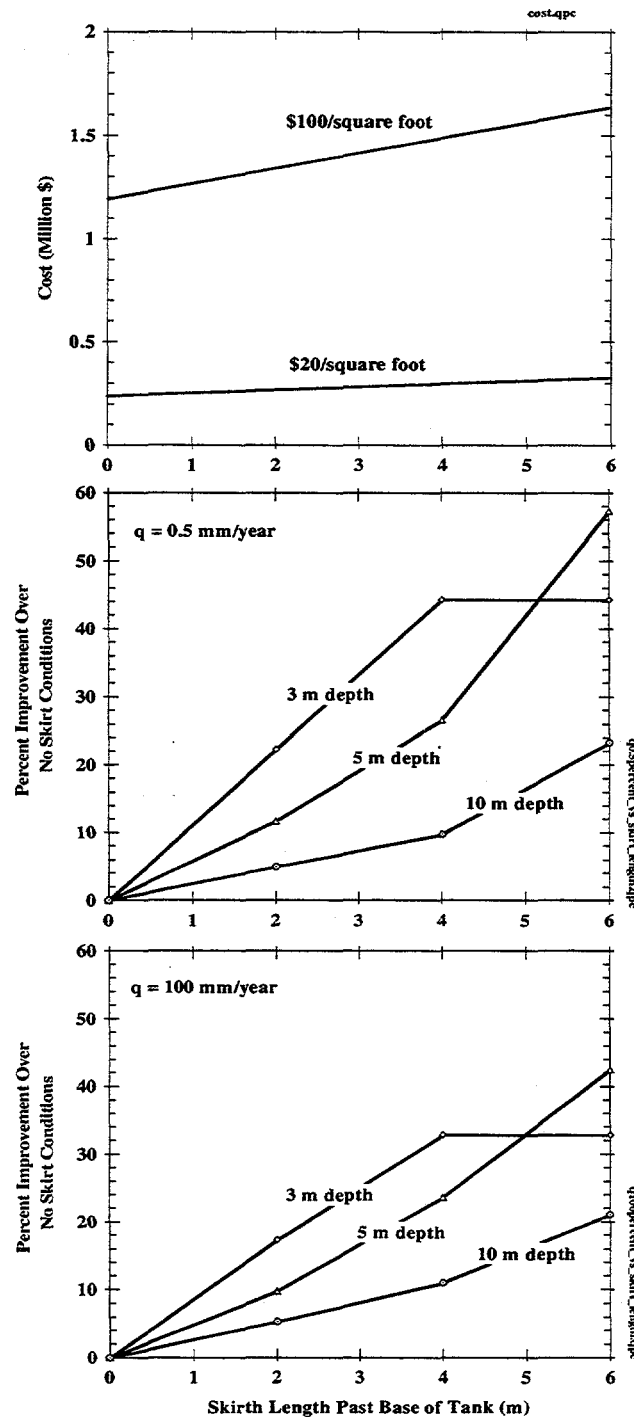


Figure 3.11. Cost and percent improvement over no-skirt conditions as a function of skirt length. The curves in the bottom two plots are also a function of the location (evaluated at 3, 5, and 10 m) beneath the base of the tank.

at a specific location beneath the base of the tank, three locations (3, 5, and 10 m) have been reported for comparison. At 3 m beneath the base of the tank, the percent improvement plateaus when the skirt is longer than 3 m. For skirt lengths greater than 3 m, the amount of flow at 3 m beneath the base of the tank remains the same. At 5 m and 10 m beneath the base of the tank, the rate of improvement increases as the skirt length increases, especially between the 4 m and 6 m skirt lengths. The increased performance of extending a skirt into the pebbly sand region may justify the increased cost; however, more rigorous analyses of contaminant transport need to be performed to obtain more meaningful metrics for performance evaluations.

3.3.4. Summary and Recommendations

Numerical simulations have been performed to evaluate the hydrologic behavior in the vicinity of a Hanford waste tank with and without jet-grouted vertical skirts. The numerical code TOUGH2 (SNL v. 3.1.2) was used to simulate two infiltration scenarios (0.5 and 100 mm/year) and four vertical skirt lengths (0, 2, 4, and 6 m beneath the base of the tank) in a two-dimensional, radially symmetric model. Results show that the amount of groundwater percolating directly beneath the tank can be decreased with increasing skirt lengths. For a given skirt length, the amount of percolation beneath the tank increases with depth. This has implications for radionuclides that might be leached out of a tank bottom as well as any pre-existing sediment that may already exist beneath a tank. Results also indicate that increased infiltration rates reduce the amount of percolation directly beneath the tank relative to the infiltration above the tank. This feature, however, may be misleading since the absolute amount of downward percolation beneath the tank may still be higher than that resulting from lower infiltration simulations. From a performance perspective, reduced amounts of percolating water beneath the waste tank may potentially improve waste isolation by allowing less waste to become mobilized. Therefore, we recommend that vertical skirts be implemented for the Hanford waste tanks and that the length of the skirt be extended beyond the base of the tank. When economically feasible, the skirt should be extended into the pebbly sand region that underlies the silty sand region beneath the tank. In addition, the following recommendations for future work are made to improve our understanding of the role of vertical skirts in waste isolation at the Hanford site:

- Perform realistic contaminant transport simulations using the established flow fields presented in this paper (e.g., on regulatory time scale). Use contaminant breakthrough curves at the water table and travel times as a more meaningful metric for performance of vertical skirts.
- Perform hydrologic simulations of multiple tanks, which will require three-dimensional models. Investigate behavior of a jet-grouted vertical skirt that surrounds the entire tank farm. Include contaminant transport simulations of multiple-tank model.
- Incorporate model of contaminant transport through fractured tank fill to provide a source term for the hydrologic models. Include stochastic characterization of fracture properties and features.

3.4. Effect of Cracks in the Tank Fill

Last year's annual report (Balsley et al., 1998) demonstrated a significant fluid carrying capacity for even a small crack that extended completely through the seal package and into the soil beneath the tank. To evaluate the impact of such a feature, models were developed on the premise that the flow through the crack was rapid enough to effectively keep the dissolved concentration of a radionuclide at zero on the crack surface. The other premise was that radionuclides were released through a single crack. That is, no horizontal flow paths were assumed to exist through the waste. If horizontal flow through the waste did occur then soluble constituents such as Tc would be released after the first few pore volumes of fluid had passed, and the release other constituents would be governed by the flux of water times the solubility of the principal phases containing them.

When one has a radionuclide such as Tc for which no solid sinks are identified, the only factor limiting its release would be the transport rate to the crack surface (after which it is immediately transported to the soil column below the tank). In the absence of lateral flow paths diffusion is the mechanism whereby this transport occurs. In one dimension the concentration that develops by diffusive transport from an infinite half space to a zero value boundary is given by (Crank, 1979):

$$C/C_0 = \text{erfc}\{x/2(Dt)^{1/2}\}, \quad \text{where}$$

x is the distance from the crack face,

D is the diffusion coefficient,

t is the elapsed time and

C/C_0 is the ratio of the concentration after time t at position x relative to the initial concentration.

Concentration profiles given by this formula have a sigmoidal shape but it works out that (within about 15%) at $C/C_0 = 0.5$ then the material present on the crack side of the half way point just about offsets the material missing from the far side of the half way point. Thus, it is common practice to characterize the removal of material from such a sink by treating it as a step function with the reaction front positioned at the locality given by the $C/C_0 = 0.5$. The other mathematical oddity involved in this analysis is that $\text{erfc}(0.5)$ is just about 0.5 (actually 0.47950...). Thus, so long as we are close to this value it is a reasonable approximation to use the approximation that $\text{erfc}(X) = X$. This results in:

$$0.5 = x/2(Dt)^{1/2} \text{ producing the well known formula}$$

$$x = (Dt)^{1/2}.$$

Using a value for D typical of saturated soils ($10^{-6} \text{ cm}^2/\text{sec}$) results in the following positions for the depletion front as a function of time.

Table 3.3. Depletion Front Position for a Soluble Radionuclide (e.g., Tc)

Time (years)	Position (cm)
1	5.6
10	17.7
100	56
1000	177
10000	560

At the other end of the spectrum lies releases from a sparingly soluble radionuclide for which most of the material resides in a solid phase. Again the model assumes that flow down the crack keeps the concentration on the crack surface effectively at zero. However, in contrast to the previous model, the solubility of the solid rather than the bulk content of the residue now controls the aqueous concentration within the source material. To model this situation, a depletion front is assumed to move through the source material. Near the front, the source material solubility is assumed to fix the aqueous concentration of the radionuclide. On the downstream side of the front the solid source material is assumed to have dissolved completely and the concentration gradient decreases linearly between the depletion front and the crack surface. The reaction front position is then given by:

$$x = (2DtC_1/C_s)^{1/2}$$

where $D (=10^{-6} \text{ cm}^2/\text{sec})$, and D and t are as defined before, C_s = concentration in the solid, and C_1 = liquid concentration as established by the solubility of the solid. (If the concentration at the crack surface were not zero, then this term is the difference between the solubility of the solid and the concentration on the crack surface.)

The release of uranium was modeled with the following parameters. Colton (1994) obtained an estimate of the range of sludge U contents from the tabulation. This resulted in an estimate of 10^{-1} to 10^{-3} moles U per kilogram. A number of authors have estimated the solubility of uranium in grout pore fluids. Since the mass of grout used to fill the tanks will greatly exceed that of the sludge the pore fluid chemistry of the grout will dictate the solubility of the U even in the sludge. Uranium values obtained from the literature range from 10^{-7} to 10^{-8} molar while a measured value is $10^{-6.5}$ after just a week of treatment (c.f., Section 4.2.3 and Table 4.3b). Using these parameters it is possible to calculate a range of reaction front positions (Table 3.4).

The contrast between Tables 3.3 and 3.4 is of considerable significance in planning tank closure strategies. In time frames commensurate with the statutory framework for tank closure, it is obvious that even a single crack could remove a large fraction of the Tc inventory from a tank. However, this mobilization is still far less extreme than the slug release assumed by many performance assessment (PA) calculations. To achieve a slug release would require an

interconnecting latticework of cracks and numerous lateral flow paths through the sludge. It is also obvious that adding a Tc getter could have a large impact on an overall PA calculation.

Table 3.4. Depletion Front Position for a Sparingly Soluble Radionuclide (e.g., U)

Time (years)	Maximum (cm)	Minimum (cm)
1	0.079	0.025
10	0.25	0.079
100	0.79	0.25
1000	2.50	1.26
10000	7.92	2.51

In contrast to Tc, an extensive latticework of cracks with spacings of less than to a meter would be required to release a significant fraction of the U. If this existed, then an appropriate source term would be the water flux times the solubility. Furthermore, there is clearly a possibility of incorporating trace amounts of other actinides in many uranium U minerals (Burns et al., 1997). Thus, coprecipitation with the uranophane-like phases that will form when waste and grout come in contact is a distinct possibility for the other actinides present in waste solutions or moderately soluble solids in the sludge. The fractional releases of U could then also be applied to other actinides since dissolution of the U host mineral(s) would be a prerequisite to their release. Adding a uranium getter, however, would seem to be of little use. However, adding depleted uranium could help to qualify a tank for closure that otherwise would fail based on the release of an actinide that had coprecipitated in the uranium minerals.

Some mathematical aspects of the two equations are also of importance in constructing performance assessment models. In the case of Tc, the *fraction* of the inventory released per unit time does not depend on the amount (e.g. concentration) initially present in the tank. In a P.A. calculation, the Tc flux out of the tank would, thus, scale linearly with the tank inventory. In the case of uranium, this is not the case. Here the fraction released scales with the inverse square root of the uranium content of the sludge.

In conclusion, adding getters would appear to be beneficial for highly soluble radionuclides since even a single crack could release much of the inventory in the period of regulatory concern. Secondly, instantaneous release of even highly soluble radionuclide can only be justified if it can be shown that mass is highly fractured throughout. Finally, for sparingly soluble radionuclides getters seem to be of little use but adding significant amounts of non or slightly radioactive components with a similar chemistry and low solubility may have a significant benefit.

4.0 Getter Development

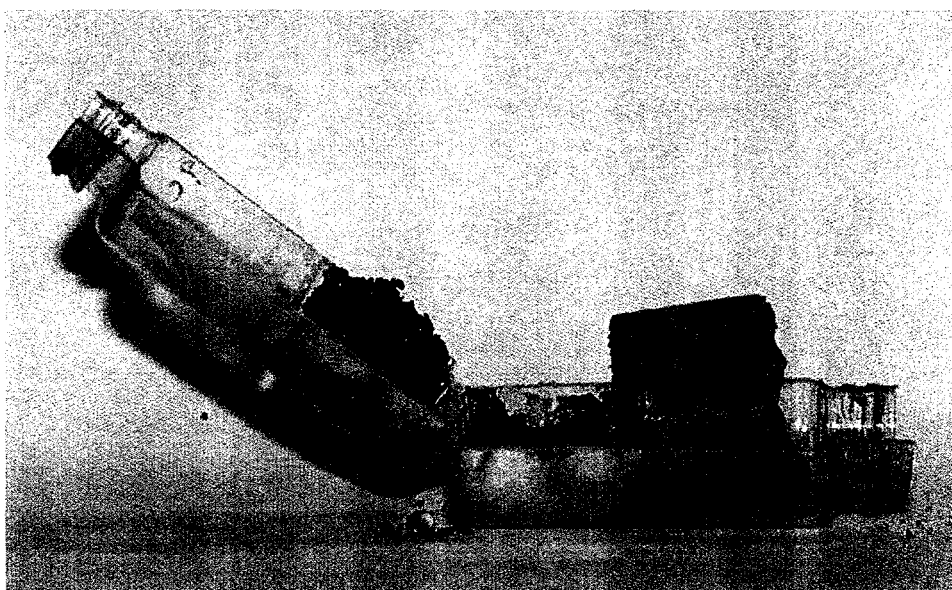
4.1. Sludge Desiccation

Much of the residue left after retrieval operations will be an inch thick layer of semisolid paste on the tank bottom. (Note: There will be both intra- and inter-tank heterogeneities in sludge thickness, texture, and composition.) Prior to filling the tank, it is highly desirable to desiccate and solidify this material. But, if the residue needs to be mixed with a significant volume of tank fill material in order to comply with NRC criteria for incidental waste classification, *this procedure should not be implemented.* Both cost and material compatibility considerations suggest that blowing in several inches of dry Portland cement powder on top of the residual sludge might accomplish this. However, concerns were voiced about the ability of the dry powder to wick up the fluid and stabilize the residual waste. Alternatively, a layer of granular getter material such as bone char could be used to mix with, or react with the residual damp sludge; this is discussed in Section 4.2.

To demonstrate the feasibility of using dry Portland cement as a desiccating agent, a 2.2 cm thick layer of artificial sludge (iron hydroxide precipitated in a concentrated sodium nitrate-hydroxide-nitrite fluid) with the consistency of wet cement was placed in a 2.5 cm diameter clear plastic bottle. Then, 2.6 cm of dry Portland cement was poured into the bottle and the bottle was capped. Within two hours, a dark discoloration indicative of a wetting front had migrated upward for a distance of 1 cm from the cement-sludge interface. After a total elapsed time of 6 hours the front had moved upward an additional 0.5 cm, after which no further movement upward was noted. Fluid uptake in an experiment where superplasticizer was mixed with the sludge prior to adding cement produced essentially the same result.

After several days the sludge pulled away from the glass in a few places and it appeared that some desiccation cracks developed in the sludge (none were observed in the cement). After that, the only change was the slow precipitation of additional whitish solids on the bottle wall. After 5 months it was no longer possible to observe the sludge, so the experiment was disassembled. The upper 1 cm of the cement in the bottle was only loosely cohesive and could be removed with gentle agitation from a spatula. Below that, however, the cement had set to form a hard plug. Sawing the bottle open lengthwise revealed that the sludge below the plug was entirely dry and fractured as a brittle substance (see Figure 4.1).

Figure 4.1 Cutaway view of Portland cement overlain as a powder over synthetic DSSF fluid and sludge; cement is now set and 'sludge' is dry and friable.



In general, it was concluded that initial wetting of the cement powder was not a problem. Furthermore, Portland cement powder is a sufficiently strong desiccating agent that it should completely dry the sludge it is in contact with. Other experiments with just DSSF fluid and Portland cement suggest that a week will be sufficient for cement hydration. Thus, dry Portland cement should provide a cost-effective method of stabilizing sludges.

4.2. Tc Getter Development

4.2.1. Introduction and Rationale

Work has focused on the selection and preliminary laboratory testing of potential getter materials for application in Hanford tank bottom environments after the tank has been drained, sluiced, and contains only residual sludge and rinse-dissolution fluids. Test parameters also included environments relevant to the soil environment under Hanford tanks (e.g., mineral assemblage and groundwater composition). Task objectives were to effectively sorb, or to significantly reduce the concentrations and mobility of ^{99}Tc (as pertechnetate) and U species. Rather than developing a comprehensive understanding of a particular gettering mechanism, these tests were empirical in nature because of limitations in budget and time. That is, by simulating Tc sorption in environments that were relevant to AX tank farm conditions, we hoped to be able to demonstrate that there were, indeed, getters that should work at Hanford. Laboratory tests have focused on the potential getter materials magnetite, bone char, and reducing grout, all of which possibly could immobilize residual pertechnetate and uranium species in solution. Species immobilization can occur either by sorption, precipitation, or oxidation/reduction processes. Although limited work to date has not been specific in determining which immobilization mechanisms or long-term processes are occurring, resultant data are tabulated using a K_d formalism in order to facilitate comparisons with other batch K_d studies in the literature. The test environments consisted of either highly alkaline, dilute DSSF-type fluids, or water which span the range of fluids found in and below Hanford tanks. Following getter sorption evaluations, limited short-term desorption tests in "fresh" leachate fluids were also conducted.

The majority of our laboratory studies have concentrated on the getter immobilization (effectiveness) of pertechnetate anions onto commercially available bone char. Bone char is essentially pyrolyzed cow bones consisting predominantly of a mixture of calcium hydroxyapatite and about 30% by weight of carbon compounds. To date, empirical sorptive results for pertechnetate onto bone char getter have been quite promising under relevant solution test conditions. These initial, encouraging laboratory results warrant further detailed mechanistic studies, so that parallel geochemical modeling studies on long-term performance and tank fill design efforts can incorporate these results for overall optimization of getter performance and

system design. In addition, we have also conducted several preliminary lab tests to evaluate the sorptive effectiveness of reducing grouts for U, Tc, Se, and Re (serving as a Tc surrogate for nonradioactive testing).

4.2.2. Experimental Description

For most of the tests conducted, getter sorptive-effectiveness was determined by using a modified "batch K_d -type" of experiment. The radioactive tracer was micro-pipetted into 20 ml of test solution, then swirled to homogenize it. Test solutions were placed in 40 ml. polycarbonate, Nalgene screw-cap containers. The getter material solid was added to the test solution, allowed to settle, and usually not subsequently stirred or agitated. This is representative and relevant to an "in-tank" environment, e.g., the potential addition of getter material to a large, near-empty Hanford tank. With one exception, the material was not stirred. Small aliquots of the test solution were taken as a function of time, including prior to getter addition and up to 30-50 days after addition. The liquid aliquots were filtered through a nylon, or later Teflon in-syringe type filter. The solution aliquot would then be added to a liquid scintillation cocktail, and the amount of tracer material, ^{99}Tc , as pertechnetate anion, or ^{232}U , remaining in solution, was determined by beta decay scintillation counting. Summary details on all test materials and procedures follow.

We used several test solutions to be representative of residual fluids in a Hanford tank after waste retrieval, where residual sludges are sluiced out with either water or dilute sodium hydroxide solution (some sludge dissolution may also occur). We presumed the initial composition of the tank fluid was similar to DSSF fluid; we used DSSF-7 solution (Kupfer, 1997). Following emptying, sluicing, and dissolution steps, the remaining in-tank fluid would be DSSF diluted with either water or NaOH. As such, we used the following test solutions:

DSSF-7:water solution, in the ratio of 1:10 and 1:100 (measured pH of 12.8 and 12.0).

DSSF-7:0.1 M NaOH solution in the ratio of 1:10 and 1:100 (measured pH of 12.9 and 12.7),
100% 0.1 M NaOH. (pH of 13)

100% deionized water. (pH of 5.7)

The water was intended, on first approximation, to be representative of the soil-moisture fluid below a Hanford tank. Bubbling either nitrogen or argon through the liquid prior to first use

initially deoxygenated all test solutions. No subsequent oxygen control of the test solutions was performed after getter addition; no oxygen control of in-tank fluids is anticipated.

We used the tracer material, ^{99}Tc , as pertechnetate anion, TcO_4^- (Tc^{+7}). For our tests, we used ^{99}Tc concentrations of 0.1, 0.5, 1, 5, and 20 ppm in solution (1 ppm in solution equals $\sim 10^{-5}\text{M}$). The lower concentrations are probably credible for in-tank solutions, the 20 ppm level was for a parametric overtest (Serne and Wood, 1990). In conjunction with a limited reducing grout test study, we also used ^{232}U tracer. In order to get the overall test solution to 50 ppm U, we added 50 ppm of "stable" ^{238}U , as $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. For nonradioactive tests with reducing grout, we used 50 ppm of Se and 50 ppm of Re.

Three potential getter materials were tested. Magnetite and bone char were tested for pertechnetate sorption. A reducing grout cementitious mix and bone char were tested for both ^{232}U and ^{99}Tc . Magnetite, $[\text{FeO} \cdot \text{Fe}_2\text{O}_3]$, was selected as a potential getter since it was anticipated that its FeO component could be oxidized in solution, thereby reducing the very mobile Tc^{+7} to the less mobile Tc^{+4} species, TcO_2 . Autoradiographic studies indicated that Tc could be sorbed onto dark minerals in a granitic rock. Natural magnetite was obtained in Tijeras Canyon, Albuquerque, New Mexico (adjacent to Sandia), by passing a strong magnet through the upper layers of sand in the arroyo. The magnetite was further isolated by several water washings with magnetic separations, to minimize the major impurity, silica sand. The purified magnetite was then ground in an Al_2O_3 shatter box and sieved to pass through a 100 mesh (150 μm) screen. We used the $\leq 150\text{ }\mu\text{m}$ material.

Bone char, essentially pyrolyzed cow bones, was found by Anderson (1998) to be a relatively effective column-sorbent material for very dilute waste groundwater streams containing As, Am, Cs, Se, Tc, Pu, and U. Consequently, it was added to this test program in order to evaluate its getter effectiveness in highly alkaline, dilute DSSF solutions that are relevant to Hanford tanks. The bone char used, Tigg Type MRM, was obtained from Anderson (Anderson, 1998b; the supplier is Tigg Corporation, Heber Springs, AZ). It was used in two particle sizes, granular (as received, predominantly 1.2-1.5 mm), and ground and sieved to pass through a 100 mesh (150 μm) screen.

For in-tank application, it is presumed that a large amount of sorptive getter material would be added (blown or pumped in as a dry powder) to mix with and sorb any residual liquid. For

example, if a 3-cm amount of residual liquid and/or damp sludge remained in a waste tank, we propose that approximately a 6-cm- thick layer of solid getter be added, to sorb and contain the liquid, as well as to chemically and physically sorb the residual pertechnetate and other radioactive species. This getter-solution dry paste could then serve as the first layer in a multi-layer tank-fill scheme as discussed earlier. As such, we primarily tested samples with a low solution to solid getter ratio. For magnetite, we used a 2:1 and 1:3 ml/gram ratio. For the bone char tests, we used a 2:1 and a (few) 20:1 ml/gram ratio. We also conducted "blank" sorption tests, where no getter materials were added. In all cases, there was adequate solution to sample remaining above the (settled) getter material. For an in-tank addition of getter material, a modified solution/solid ratio would be used so that no free liquid would remain prior to grouting.

Reducing grouts have achieved prominence in the waste management community as a way to immobilize Tc as well as other redox sensitive radionuclides (e.g., Cr, Se). They are, therefore, considered to be a potential Hanford single-shell tank fill material. For our tests, this reducing grout consisted of ordinary Portland cement to which Fe^{+2} and Mn^{+2} were added as reducing agents. When the Fe^{+2} , as $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, and Mn^{+2} , as $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, oxidize over time, they should reduce the U and Tc species to less mobile forms. In our tests, we used a 10:1 solution:grout (~50 ml:5 g) mix. Also, these tests were stirred-agitated periodically. Half of these tests contained about 50 ppm of U tracer, the other half, separately, contained 5 ppm of ^{99}Tc tracer.

The overall getter test program to date was conducted in three separate phases. In the first part (Phase I), we tested ^{99}Tc sorption (at 0.1 or 1 ppm) onto magnetite and bone char, in multiple tests solutions, for up to 30 days. Following these tests, the test containers were centrifuged, the original test solutions removed (as much as possible) and quantified, and fresh, similar test solution re-added, to leach or desorb the radionuclides present. The "refreshed" tests were then continued for another 14 days with periodic sampling in order to evaluate the extent and rate of desorption of the residual ^{99}Tc tracer.

Based on preliminary and positive sorption results (Phase I), the second set of tests was designed to focus on ^{99}Tc gettering by bone char under a variety of parametric test conditions. Pertechnetate sorption was tested as a function of:

- tracer concentration (0.5, 5, and 20 ppm ^{99}Tc);

- bone char particle size (ground and sieved $\leq 150 \mu\text{m}$ and "granular-as received");
- solution pH (about pH 12 dilute DSSF solutions and deionized water);
- liquid:solid ratio (20:1 vs. previous 2:1 ratio), with test mix agitated daily; and,
- temperature ($\sim 20^\circ\text{C}$ and 90°C ; terminated after 1 day due to experimental problems).

After 47 days of periodic sampling, these tests were converted to desorption tests, as described for Phase I tests, and continued for 7 more days.

Phase III tests consisted of a limited matrix of reducing grout tests for either ^{232}U or ^{99}Tc tracer sorption. After about 6 days of testing and sampling the reducing grout sorptive tests, we added 2 g of bone char to each test container and continued sampling for an additional 7 days. The purpose of this was to evaluate the sorptive or desorptive effects of the added bone char on the existing test system.

Early in the test program, unusual results were observed on some test blanks that caused us to investigate the influence of filter materials and fluid chemistry on the Tc analysis. The outcome of this investigation was that in deionized water, nylon filters sorbed 60 – 90% of the Tc. In the highly caustic simulated tank fluids, this figure dropped to around 10%. Teflon filters did not sorb Tc from any fluid, and so were used during the later stages of the study. Uranium sorption was noted on all filter types and particulate material is suspected. A more detailed discussion of the impact of filtration effects is included in the following sections.

4.2.3. Results and Discussion

Major results for the initial, Phase I pertechnetate sorption tests on magnetite and bone char are summarized in Table 4.1. Similarly, more detailed pertechnetate sorption test (Phase II) results with bone char are presented in Table 4.2. Phase III getter results for both U and Tc tracers with reducing grout and bone char are given in Table 4.3. Table 4.4 summarizes results for pertechnetate desorption on different sorbents, magnetite and bone char. All data presented in Tables 4.1, 4.2, 4.3 and 4.4. were corrected for sorption by filters, as measured by "blank" tests. These data tables illustrate the sorptive results with effects, if any, due to all tested variables.

Table 4.1. Tc Phase I Batch Sorption Results

Corrected for Nylon filter adsorption; filters assumed to adsorb a fixed percentage of the Tc in solution, regardless of concentration

Sample #	Test Fluid	Ratio	Tc conc. ppm	Sorbent, g	% sorbed after	Kd, ml/g	% sorbed after	Kd, ml/g	% sorbed after	Kd, ml/g
					2 days		14 days		30 days	
2A	DSSF:H ₂ O	1:10	0.104	Magnetite 9.9924	-1.40	-0.03	-0.59	-0.01	-0.48	-0.01
3A	DSSF:H ₂ O	1:10	1.07	59.9576	1.48	0.00	2.54	0.01	2.43	0.01
4A	DSSF:H ₂ O	1:100	0.104	9.9866	3.88	0.08	3.54	0.07	0.44	0.01
6A	H ₂ O *Uncorrected	—	1.07	59.9936	*86.42	*2.08	*93.98	*4.88	*92.93	*3.94
8A	DSSF: 0.1 M NaOH	1:10	0.104	10.0071	-1.10	-0.02	-0.34	-0.01	-0.65	-0.01
9A	DSSF: 0.1 M NaOH	1:10	1.07	59.9554	3.96	0.01	7.15	0.02	5.82	0.02
10A	DSSF: 0.1 M NaOH	1:100	0.104	9.9984	3.33	0.07	3.71	0.07	0.64	0.01
12A	0.1 M NaOH	—	1.07	60.0364	2.29	0.01	-1.00	0.00	-0.34	0.00
				Bone Char						
13A	DSSF:H ₂ O	1:10	0.104	9.9944	44.98	1.60	70.54	4.50	73.73	5.05
14A	DSSF:H ₂ O	1:10	1.07	9.9704	45.53	1.64	63.26	3.26	65.04	3.36
15A	DSSF: 0.1 M NaOH	1:10	0.104	9.9755	42.91	1.47	70.67	4.55	73.77	5.05
16A	DSSF: 0.1 M NaOH	1:10	1.07	10.0025	41.37	1.38	60.54	2.89	61.01	2.79
18	DSSF:H ₂ O	1:100	0.104	0	1.75		-2.76		0.67	
19	0.1 M NaOH	—	0.104	0	-0.04		-0.37		-1.23	

* Samples were shaken once, just after the 14-day sample was collected

Effect of filtering

Initial sample was not filtered upon collection; other samples were forced through a 0.2 µm nylon syringe filter. Filtered and unfiltered aliquots of samples 18 and 19 show that the filters absorb about 10% of the Tc. Thus, in those samples where sorption was 10% or less above, it is not clear whether sorption occurred onto the solid, the tube, or the filter.

Table 4.2. Tc Phase II Batch Sorption Results

Sample #	Test Fluid	Ratio	Tc conc. ppm	Sorbent, g	% sorbed after	Kd, ml/g	% sorbed after	Kd, ml/g	% sorbed after	Kd, ml/g	% sorbed after	Kd, ml/g
17	DSSF:H ₂ O	1:10	0.5	0 - Blank	1 day		2 days		14 days		32 days	47 days
20	DSSF: 0.1 M NaOH	1:100	0.5	0 - Blank			-0.72		0.44		-2.75	-6.39
21	H ₂ O	H ₂ O	0.5	0 - Blank			0.72		2.86		-1.36	-2.86
13B	DSSF:H ₂ O	1:10	0.5	9.9822			100.00		100.00		0.00	
14B	DSSF:H ₂ O	1:10	5.0	9.9898			45.76	1.64	64.09	3.34	67.78	69.97
15B	DSSF: 0.1 M NaOH	1:10	0.5	9.9836			42.97	1.47	57.46	2.51	59.09	60.19
16B	DSSF: 0.1 M NaOH	1:10	5.0	10.1403			44.41	1.56	63.86	3.29	67.82	70.40
22A	H ₂ O	H ₂ O	0.5	10.0019			42.34	1.41	54.75	2.23	55.31	55.88
22B	H ₂ O	H ₂ O	0.5	9.9875			81.38	8.47	91.58	20.00	94.64	96.11
23	DSSF:H ₂ O	1:10	20.0	9.9990			83.14	9.60	91.40	19.75	94.78	95.98
24	DSSF: 0.1 M NaOH	1:10	20.0	9.9992			38.73	1.25	54.69	2.28	55.96	57.20
25	DSSF:H ₂ O	1:10	5.0	10.0122			37.57	1.19	51.75	2.04	52.36	52.91
26	DSSF: 0.1 M NaOH	1:10	5.0	9.9997			61.88	3.16	61.23	2.97	61.44	62.50
27	DSSF:H ₂ O	1:10	5.0	1.0071			59.33	2.85	60.07	2.80	61.05	61.98
28	DSSF: 0.1 M NaOH	1:10	5.0	1.0097			12.51	2.65	9.78	1.93	6.48	5.73
29	DSSF:H ₂ O	1:10	5.0	1.0030			13.16	2.81	8.96	1.76	5.93	4.88
30	DSSF: 0.1 M NaOH	1:10	5.0	1.0186			-7.95	-1.43	—	—	—	—
							1.98	0.39	—	—	—	—

* Tests #27-30 vigorously shaken for 30 sec. Daily. Tests #29-30 conducted at 90 C, but terminated due to experimental problems.
Tests #25, 26, 29, 30 are granular-as received bone char; all others ground and sieved.

* **Nylon** filters sorb about 10-12 % of the Tc from alkaline solutions, and 60-100 % from deionized water solutions. **Teflon** filters do not sorb Tc.

Table 4.3. Phase III Tc Batch Sorption Results

Tc data *only* corrected for filter sorption Reducing Grout (cement), part A and bone char, part B

Sample #	Test Fluid	Ratio	Initial		Cement Sorbent, g	Initial results		1 hour results				1 day results				6 day results			
			conc., ppm			% sorbed	by filter	% sorbed	Kd*, ml/g	% sorbed	Conc., ppm U	Tc	Kd*, ml/g	% sorbed	Conc., ppm U	Tc	% sorbed	Conc., ppm U	Tc
			U	Tc															
			U	Tc															
31A	DSSF:H2O	1:10	50	5.7647		(0)		98.21	0.89	483		98.71	0.65	670		100.18	-0.09		
32A	DSSF:H2O	1:10	50	5.7872		(0)		98.69	0.66	662		98.20	0.90	480		99.97	0.02		
33A	DSSF:H2O	1:10	5	5.7976		-0.01		98.72		673		80.80		37		39.06	3.05		
34A	DSSF:H2O	1:10	5	5.8190		0.05		98.90	0.06	780		81.71		39		37.34	3.13		
35	DSSF:H2O	1:10	29	0	0	(0)		6.99	28.77			61.35	11.10			80.71	5.54		
36	DSSF:H2O	1:10	5	0	0	-0.04		-0.67		5.03		-0.47		5.02		-0.85	5.04		

After addition of Bone Char (on day7)

After addition of Bone Char (on day7)

Sample #	Test Fluid	Ratio	Initial conc., ppm		Sorbent, g	B-samples 1-day results				Teflon filters used			
			U	Tc		% sorbed	Conc., ppm U	Tc	B-samples 7-day results		Teflon filters used		
									Kd*, ml/g sorbed	%	Conc., ppm U	Tc	Kd*, ml/g
31B	DSSF:H2O	1:10	50	50	5.7647	100.01	-0.01	—	—	99.86	0.07	9583	—
32B	DSSF:H2O	1:10	50	50	5.7872	100.24	-0.12	—	—	99.86	0.07	9676	—
33B	DSSF:H2O	1:10	5	5	5.7976	36.48	3.18	5	5	22.88	3.86	4	—
34B	DSSF:H2O	1:10	5	5	5.8190	36.15	3.19	5	5	22.37	3.88	4	—
35	DSSF:H2O	1:10	29	29	0	80.55	5.58	—	—	83.57	4.72	—	—
36	DSSF:H2O	1:10	5	5	0	-1.83	5.09	—	—	0.01	5.00	—	—
										35 unfiltered 28.95 36 unfiltered 5.00			

All samples were filtered with **nylon** filters, except for the B-7day samples, which were filtered with teflon. Nylon adsorbs 10-12% Tc from the alkaline test solutions, **teflon** doesn't. Both appear to remove U is approximately equal amounts, but the initial, filtered, and the final, unfiltered values for U came out the same, suggesting that either the U changed chemical form during the experiment, or the filters aren't sorbing out U, but instead are filtering out a colloidal U mineral.

Table 4.4 Tc Batch Desorption Results

Corrected for filter sorption filters assumed to adsorb a fixed percentage of the Tc in solution, regardless of concentration
(filters assumed to adsorb a fixed percentage of the Tc in solution, regardless of concentration)

Sample #	Solution	Ratio	Initial Tc conc. ppm	Sorbent, g	Amount on Solid, at end adsorption expt., µg/g	~ 10 minutes after		1 day after		14 days after	
						adding fresh solution amount on solid, µg/g	conc. in liquid, µg/ml	adding fresh solution amount on solid, µg/g	conc. in liquid, µg/ml	adding fresh solution amount on solid, µg/g	conc. in liquid, µg/ml
2A	DSSF:H ₂ O	1:10	0.104	9.9924	-0.001	-0.003	0.009	-0.002		-0.002	0.009
3A	DSSF:H ₂ O	1:10	1.070	59.9576	0.008	0.000	0.332	0.006		-0.002	0.348
4A	DSSF:H ₂ O	1:100	0.104	9.9866	0.001	0.001	0.007	0.002		0.000	0.008
6A	H ₂ O	—	1.070	59.9936	0.322	0.322	0.024	0.323		0.218	0.261
8A	DSSF: 0.1 M NaOH	1:10	0.104								
9A	DSSF: 0.1 M NaOH	1:10	1.070	59.9554	0.019	0.009	0.323	0.016		0.009	0.337
10A	DSSF: 0.1 M NaOH	1:100	0.104								
12A	0.1 M NaOH	—	1.070	60.0364	-0.001	0.002	0.324	0.005		-0.004	0.336
13A	DSSF:H ₂ O	1:10	0.104	9.9944	0.145	0.119	0.017	0.117		0.106	0.022
14A	DSSF:H ₂ O	1:10	1.070	9.9704	1.317	0.986	0.217	0.919		0.851	0.275
15A	DSSF: 0.1 M NaOH	1:10	0.104	9.9755	0.145	0.124	0.014	0.121		0.108	0.021
16A	DSSF: 0.1 M NaOH	1:10	1.070	10.0025	1.223	0.893	0.226	0.890		0.765	0.286
					Filter type:	Nylon		Nylon			

Phase Two Tc Batch Desorption Results, corrected for filter sorption during initial loading (sorption) phase

(filters assumed to adsorb a fixed percentage of the Tc in solution, regardless of concentration)

Sample #	Solution	Ratio	Initial Tc conc. ppm	Bone Char Sorbent, g	Amount on Solid, at end adsorption expt., µg/g	~ 5 minutes after		2 days after		7 days after	
						adding fresh solution amount on solid, µg/g	conc. in liquid, µg/ml	adding fresh solution amount on solid, µg/g	conc. in liquid, µg/ml	adding fresh solution amount on solid, µg/g	conc. in liquid, µg/ml
13B	DSSF:H ₂ O	1:10	0.5	9.9822	0.64	0.50	0.09	0.47		0.47	0.11
14B	DSSF:H ₂ O	1:10	5.0	9.9898	5.44	3.59	1.24	3.52		3.47	1.29
15B	DSSF: 0.1 M NaOH	1:10	0.5	9.9836	0.64	0.52	0.09	0.49		0.49	0.10
16B	DSSF: 0.1 M NaOH	1:10	5.0	10.1403	4.97	3.23	1.28	3.14		3.05	1.35
22A	H ₂ O	H ₂ O	0.5	10.0019	0.91	0.90	0.01	0.90		0.89	0.01
22B	H ₂ O	H ₂ O	0.5	9.9875	0.92	0.90	0.01	0.89		0.89	0.02
23	DSSF:H ₂ O	1:10	20.0	9.9990	20.77	12.83	5.37	12.57		11.95	5.75
24	DSSF: 0.1 M NaOH	1:10	20.0	9.9992	19.15	11.89	5.35	11.73		11.73	5.41
25	DSSF:H ₂ O	1:10	5.0	10.0122	5.73	4.92	1.21	4.48		4.36	1.44
26	DSSF: 0.1 M NaOH	1:10	5.0	9.9997	5.66	4.75	1.26	4.47		4.27	1.46
27	DSSF:H ₂ O	1:10	5.0	1.0071	4.55	0.01	0.44	-0.63		-0.88	0.49
28	DSSF: 0.1 M NaOH	1:10	5.0	1.0097	3.92	0.03	0.42	-0.62		-0.73	0.46

Therefore, the observed experimental artifact of Tc sorption on nylon and Teflon syringe filters has been quantified and accounted for.

As indicated in Table 4.1, magnetite proved to be an ineffective getter sorptive material for pertechnetate anions in alkaline test solutions (DSSF:water and DSSF:NaOH solutions, pH ~12). The anticipated reduction of Tc^{+7} in pertechnetate to Tc^{+4} by the oxidation of Fe^{+2} did not occur; no sorption onto Fe_3O_4 was noted once filter effects were accounted for.

Results in Table 4.1 indicate that there is appreciable sorption of pertechnetate on the bone char getter material in alkaline test solutions, even after correcting for filtration effects. Tc sorption (corrected, taking nylon filter sorption into account) increased from about 41% - 45% after 2 days to about 61% - 74% after 30 days. Effective batch K_d values ranged from about 1.5 up to 5.1. Agitating the test mixtures once, after the 14-day sampling period, appeared to have a minimal effect. Initial data for test "blanks" #18 and #19, both filtered and unfiltered, indicated that the nylon filters absorb about 10% of the Tc. Thus, in those samples where initial (uncorrected) sorption was 10% or less, it is not clear whether sorption occurred onto the solid, the tube, or the filter. The corrected data in Table 4.1 take this into account. Based on the favorable technetium sorption onto bone char in these scoping Phase One tests, we expanded the appropriate test matrix in Phase Two.

The Phase II Tc batch sorption results presented in Table 4.2 provide a more comprehensive picture of the effectiveness of bone char as a getter. Tests #13B-#16B are near-replicates of the tests #13A-#16A in Phase One, except that the concentration of ^{99}Tc tracer was increased by a factor of 5. The percentage of Tc sorbed from alkaline solutions increased from about 42% to 70% after 47 days, with effective batch K_d values of 1.4 to 3.9. In addition, the test artifact of nylon filter sorption was eliminated; starting with the 32-day sampling period, non-sorbing Teflon syringe filters were used.

There was an apparent inverse correlation of Tc concentration with K_d in these data. Test K_d values in alkaline solutions were higher in test systems with 0.5 ppm of ^{99}Tc (tests #13B and #15B), compared to those with 5.0 ppm (tests #14B and #16B) and those with 20.0 ppm (tests #23 and #24). Secondly, in going from 0.5 to 20 ppm the effective K_d falls by about 50%. Tests #27-#28 provide further information relative to concentration effects. These tests used only 1 g

of bone char in 20 ml of solution; other tests used 10 g. The measured, effective batch K_d values for tests #27-#28 are 2X lower than similar tests #14B-#16B (with 10 g of bone char).

Apparently, the sorptive sites on the bone char are becoming saturated in the bone char-poor systems. As mentioned earlier, if bone char is used as a getter in emptied, sluiced-out waste tanks, much better technetium sorption could be obtained by using a large excess of the material, e.g., a 6-cm-high layer of solids added to a 3-cm-high layer of residual liquid.

The particle size of the bone char material also had a noticeable effect. Tests #25 and #26, with "granular-as received" material (1.2-1.5 mm), had moderately higher effective K_d values than the comparable tests #14B and #16B, with ground and sieved $\leq 150 \mu\text{m}$ material. Mechanistic interpretation as to why this occurred is not possible with the limited, available data. It would be easier and preferable to add granular bone char getter to an emptied, sluiced-out waste tank; grinding costs could be eliminated, dusting would be significantly reduced, and the getter sorptive capacity would be greater.

Bone char sorptive tests conducted in deionized water, tests #22A and #22B, had the highest measured K_d values after 47 days, 39.6 and 38.3, significantly greater than values measured in alkaline test solutions. Corrected results from "blank" test #21, also conducted in deionized water, as well as the same test sampled after 32 days using a Teflon filter, indicate that there is essentially zero Tc sorption without the bone char getter present. The deionized water test system is presumed, as described earlier, to be more relevant to soil moisture below (leaky) Hanford tanks. A potential application of bone char getter material could be its injection into the below-tank soil as a water slurry or possibly as a component of the grout barriers (Section 2), to sorb Tc as well as other leaked radioisotopes of U and Pu (Anderson, 1998) contained in the soil and groundwater.

Results from the Phase III tests with reducing grouts are somewhat more difficult to interpret, due to large quantities of solids in the solution plus complications in determining or sorting out applicable mechanisms of sorption. The preliminary, empirical results for U and Tc sorption are given in Table 4.3. Tests #31A and #32A indicate that essentially all of the U tracer had been removed from solution; sorption, precipitation, formation of colloids, or some combination of these mechanisms was increasing as a function of time. Blank test #35 also indicates that a lot of the removed U tracer may have been filtered out as a colloidal mineral. The calculated K_d values

shown in Table 4.3 should be used with caution, as the kinetics and mechanism(s) for removal of U solids are unknown. Addition of 2 g of bone char to tests #31A and #32A on day 7 had no noticeable impact on sorption or desorption of U tracer. It should be noted that the K_d 's shown in Table 4.3 may not be significant, as the solids are both soluble and reactive. Based on the blank results, precipitation probably took place in the uranium samples.

Several additional, nonradioactive experiments pertinent to effectiveness of reducing grout for redox sensitive species were also performed in conjunction with this program. An artificial reducing grout was made by mixing 0.4 grams of $MnCl_2 \cdot 4H_2O$, 0.4 grams of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, 5 g of dry powdered Portland cement, and 45 g of a stock solution that was 3% DSSF-7 and 50 ppm Re and Se. The sample was stirred for three days while the cement and water interacted, and while air slowly oxidized the Mn^{+2} and Fe^{+2} . The rationale behind this experimental approach was to: (1) create a loose slurry where the pore fluid could be readily sampled, and (2) investigate what happens when a normal near-surface oxidizing condition gains access to a reducing grout.

Analysis of this test fluid after three days and after the slurry had become a dark red brown (Fe had been oxidized) indicated that the pore fluids now contained only 0.2 ppm Se. Aging for 13 days produced a solution Se content of 0.59 ppm, and further accelerated aging for three days at 90° C raised the solution Se content to 0.64 ppm Se. No decrease in Re was observed in any experiment. This suggests that a coprecipitation of Se on ferric hydroxide is an effective method of immobilizing Se, but that neither the hydration of Portland cement or the precipitation of hydrous Fe^{+3} - Mn^{+4} oxides will provide sites for the immobilization of perrhenate, and by inference pertechnetate.

Results from Tc (pertechnetate) sorption tests #33A and #34A in the reducing grout are more interesting. After 1 hour of testing, almost the entire TcO_4^{-1} tracer had been removed from solution, presumably reduced to TcO_2 as the Fe^{+2} and Mn^{+2} in the reducing grout were oxidized. The amount of Tc in solution then increases as a function of time, up through 6 days, as the reducing grout obviously becomes less "reducing." On day 7, 2 grams of bone char were added to tests #33A and #34A. The bone char had no noticeable gettering effect in this grout system, the concentration of Tc in solution actually increased slightly over the next 7 days of testing, the effective Tc batch K_d values decreased to about 4. Again, further test data are required, and

should be obtained in the future, to resolve mechanistic sorption or nonsorption concerns in this environment. The bone char appears to function more effectively as a getter if it can be added to alkaline residual fluids before the reducing grout (potential tank fill material).

Table 4.4 lists available technetium desorption results obtained in Phase I and Phase II tests, with bone char getter materials. Desorption results are tabulated in units of $\mu\text{g/g}$ ($\sim\text{ppm}$) of Tc remaining on the solid sorbent and also in solution as a function of time. These values can be compared to the calculated values of $\mu\text{g/g}$ of Tc remaining on the getter at the end of the sorption of the tests, as well as compared to the initial value of Tc ppm in the test solution. As can be seen from the limited results, some Tc does desorb off of the bone char getter material when fresh solution is added. The majority of this Tc desorption occurs within the first 10 minutes, then continues at a much slower rate over the next 7 to 14 days. The smallest amount of initial (5 minute) Tc desorption occurred in the deionized water test system, tests #22A and #22B. The fact that at least a portion of the Tc can be released suggests an anion exchange removal process for Tc, and thus, that the K_d approach to tabulating these data may be useful.

4.2.4. Conclusions and Future Work

The stated test program objectives were to perform scoping tests to evaluate potential getter materials for ^{99}Tc (as pertechnetate) and U species under conditions that would simulate what might exist in and adjacent to one of the AX farm tanks. These materials should function effectively either in an in-tank environment, or conceivably in the soil-moisture environment below a Hanford waste tank. The getter materials magnetite, bone char, and reducing grout were tested in some detail during this programmatic time period. To date, preliminary results for magnetite were not promising for application in Hanford environments and have been terminated.

Detailed, sorptive results for pertechnetate onto bone char getter are quite promising under a variety of relevant test conditions. More than 50% of the ^{99}Tc in alkaline solution has been effectively gettered by bone char. There was a concentration effect upon measured, effective batch K_d values for pertechnetate. If bone char is to be used as a getter in emptied, sluiced-out Hanford waste tanks, the most effective technetium sorption could be obtained by using a large excess of the getter material. That is, a 6-cm-high layer of granular solids could be added (blown

in or otherwise distributed in dry form) to cover or sorb the 3-cm-high layer of residual, alkaline liquid and damp sludge, thereby eliminating any free liquid.

A reducing grout (gettering) material is being considered as a layered tank-fill component; this is being developed in a parallel work-scope segment of this Hanford Tanks Initiative - Waste Immobilization Technology Development Program. Preliminary test results indicate good sorptive effectiveness for U and Se, but a minimal sorptive capacity for bone char added after the reducing grout. The bone char appears to function more effectively as a getter if it is added to alkaline residual fluids before the reducing grout. Further, once oxidizing conditions are re-established a reducing grout seems likely to release its Tc, but neither is Se or U.

More than 90% of the ^{99}Tc in dilute water solutions was effectively sorbed by bone char getter. The deionized water test system is presumed, as described earlier, to be more relevant to soil moisture environments below (leaky) Hanford tanks. A potential application of bone char getter would be to inject or jet it into the below-tank soil as a water slurry. The possibility of stabilizing the soil at the same time using a mixture of Portland cement grout is attractive, but will require additional research in light of the negative impact Portland cement had on bone char sorption of Tc. In any case, it is also apparent that bone char could also be an effective getter for the actinides, specifically U and Pu (Anderson, 1998) contained in the soil and groundwater. Such subsurface getter injection needs to be coordinated with other engineering application efforts being conducted in this program.

Initial laboratory sorption and desorption test empirical results have been very encouraging. Bone char is easily obtainable, and a relatively inexpensive material (approximately \$2.25 a pound in FY98 dollars). It also was shown to be an effective getter sorbent for pertechnetate in Hanford tank-relevant alkaline solutions and even more effective in normal low salinity groundwaters. However, quantification of controlling mechanistic parameters for sorption, desorption, and long-term sequestration effectiveness, is lacking. This mechanistic information is required as input for modeling and design efforts being conducted as part of this Waste Immobilization Technology Development Project. As such, these initial, very promising results justify further detailed mechanistic laboratory studies. But, with our present level of understanding, the results will not support including specific K_d values in PA formalisms or long term predictive codes

5.0 In Soil Reactive Barrier Assessment

To assess the relative performance of getter materials that may be used as reactive barriers to mitigate subsurface migration of radionuclides near Hanford AX tanks, we conducted equilibrium-based reaction path computer modeling of tank waste fluids (DSSF plus contaminants), getters, soil minerals, and groundwater using REACT (Bethke, 1998). These calculations represent multiple reaction paths, ranging from direct interactions of contaminated DSSF fluids with soil minerals and groundwater to DSSF fluids that have reacted with getters placed in the tank or soil prior to their interaction with soil and groundwater. In addition, a series of tests involved a number of low ionic strength experiments was conducted to provide further basis for designing tank fill and barriers. It should be pointed out that the database in the code does not cover all minerals and species that are interested in this study. Further evaluation and addition of the thermodynamic database are necessary to improve these calculations, including the addition of kinetic models and data for sorption-desorption and dissolution-precipitation.

5.1. Modeling the Effects of Tank Getter Materials on Radionuclide Concentrations and Species Distribution in Soil Solutions

A series of tests were conducted with a geochemical computer code REACT to predict the mass transport and distribution of species for six radionuclides, Am, Eu, Np, Pu, Se and U, in the DSSF fluid after it mixes with soil beneath an AX tank. The DSSF fluid may react with in-tank getters prior to leakage or it may react directly with soil. Three reaction paths of DSSF with getters and soil are illustrated in Figure 5.1. The first (1) evaluates reaction of DSSF leaking directly into the ground and reacting with soil clays and groundwater. This serves as a reference for getter performance, especially related to radionuclide solubility, radionuclide sorption, or likely mineral stability. The second path (2) calculates the effects when one liter of the DSSF fluid is first reacted with 400 g goethite, 1,000 g Portland cement or 400 g hydroxyapatite. All are potential getters. The fluids from these reactions are then assumed to leak into soil and reacted with the soil clays and ten (10) liters of groundwater. The third reaction path (3) is when residuals from the reaction of DSSF and in-tank getters (path 2) interact with in-soil getters before they have a chance to react with soil clays and groundwater. The last path represents an engineered barrier placed beneath the tanks.

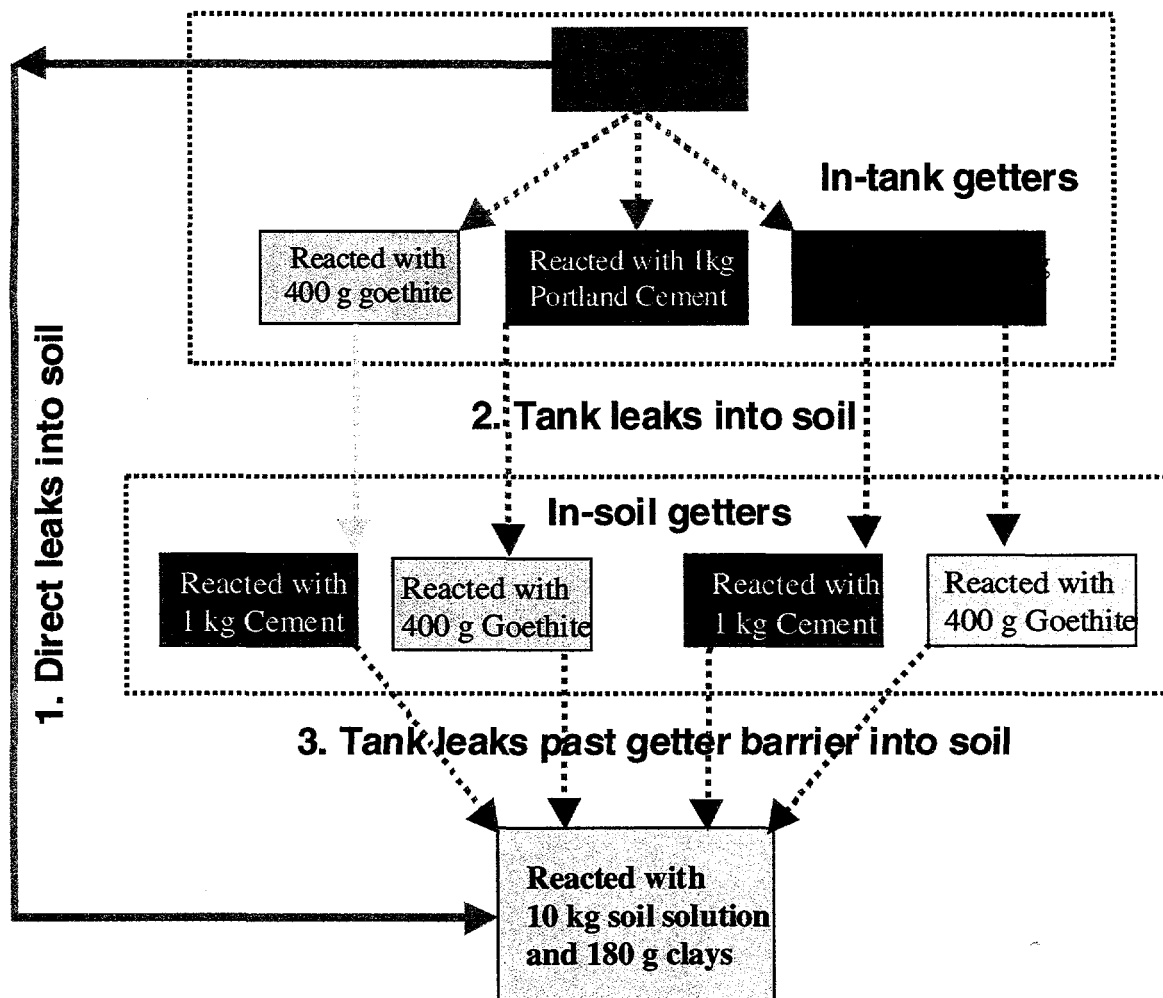


Figure 5.1. Multiple reaction paths of DSSF fluid with getters, soil clays, and groundwater used for geochemical modeling.

The composition of groundwater is from the reported uncontaminated water from a well at Hanford site (Well S3-25, PNNL-11385; Table 5.1). The clay fraction in the soil at Hanford site is about 10% of soil mass and only the clay fraction is assumed to react with the leaked fluid. The pH in the groundwater is 8.4 and this will be kept constant in the reactions occurring in soil.

The dominant minerals in the clay fraction are smectite ($\text{Ca}_{0.25} \text{Fe}_2 \text{Si}_{2.5} \text{Al}_{0.5} \text{O}_{10} (\text{OH})_2$), illite ($\text{K}_{0.64} \text{Na}_{0.02} \text{Ca}_{0.16} \text{Si}_{3.38} \text{Al}_{0.62} \text{Al}_{1.4} \text{Fe}_{0.39} \text{Mg}_{0.22} \text{O}_{10} (\text{OH})_2$) and vermiculate ($\text{Mg}_{2.36} \text{Fe}_{0.48} \text{Al}_{0.16} \text{Al}_{1.28} \text{Si}_{2.72} \text{O}_{10} (\text{OH})_2$). However, vermiculate is not included in the REACT database so its mass was added to the smectite during modeling. Quartz, although it is relatively inert, is the predominant mineral and may not be stable at high pHs. Thus, 80 g of quartz is included in the soil clays to react with the leaked tank fluid.

Table 5.1. Composition of Uncontaminated Groundwater at Hanford Site (Well S3-25)

Constituent	Concentration (mg/L)
pH	8.46 (unitless)
Cl^-	22
NO_3^-	1.7
SO_4^{2-}	108
Total Organic C	0.73
Total Alkalinity, as CO_3^{2-}	67.5
Al	0.14
B	0.05
Ba	0.069
Ca	67.5
Fe	3
K	3
Mg	16.4
Mn	0.046
Na	27.6
Si	16.2
Sr	0.28
^{99}Tc	0.004 $\mu\text{Ci/L}$
UO_2^{2+}	0.005

Figure 5.2 shows the effects of the three getters on retaining radionuclides by comparing the percents of the six elements leaking out of tanks after reactions with or without getters.

Considering the amount of radionuclide in the DSSF fluid as 100%, all of Am and Eu in the fluid are essentially removed from fluid and retained in the tank. Goethite dramatically reduces the amount of all of the elements, except U, leaking into soil (Figure 5.2).

However, a low U solubility (Figure 5.3) in groundwater was calculated when U in the groundwater is immobilized as solid (Figure 5.4). It is also noticed that the only mechanism for reducing in soluble Se is sorption onto goethite (Figures 5.2 and 5.3). The other two getters, hydroxyapatite and cement, do not adsorb in this simulation because we do not have the thermochemical database to calculate adsorption. Thus, soluble Se levels and the amounts of Se leached out in the fluids after reacting with apatite and cement are not changed as compared with that in the DSSF fluid (Figures 5.2 and 5.3). Except for Se, Portland cement is the most effective getter retaining the nuclides in the tanks (Figure 5.2). The cement removes nearly 100% of Am, Eu, and U, 90% of Np and 70% of Pu from DSSF fluid. Hydroxyapatite removes 70 and 97% of Pu and U, respectively, from DSSF fluid. However, it does not retain any Np and Se (Figure 5.2). After reaction with soil clay and groundwater, the soluble U concentration in the hydroxyapatite treatment is the highest among the goethite, cement and apatite treatments (Figure 5.3). This may be attributed to the formation of phosphate-uranium complexes, which are usually soluble, during the reaction of DSSF with hydroxyapatite. Evidence for this is seen in table 4.3b when 7 days exposure to bone char brings the U concentration up from below the detection limit to 0.07 ppm.

In summary, the reaction with single getter, goethite and cement can significantly reduce the amount of radionuclides leaching into groundwater and the soluble (therefore, labile) concentrations of these elements. Hydroxyapatite can also have the same effects for Am, Eu, and Pu, but not for Np and soluble U.

If the residuals of DSSF fluid that have reacted with their first getter are allowed to react with second getter, as described in the flowchart of Figure 5.1, before they are discharged into soil, the results indicated that five of the six radionuclides (except Se) in the DSSF solution are

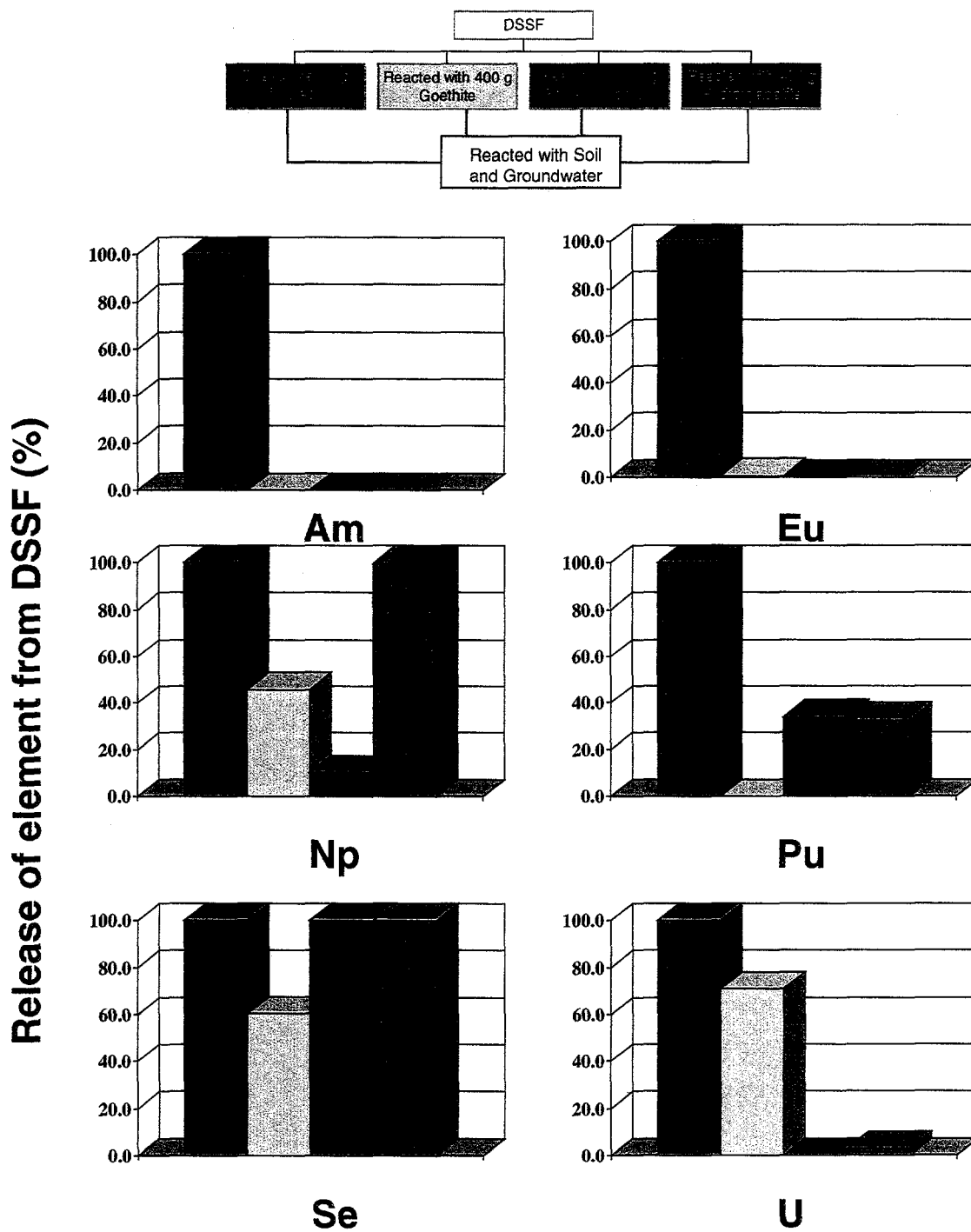


Figure 5.2. The percent of radionuclides in the DSSF fluid released into soil under various treatments.

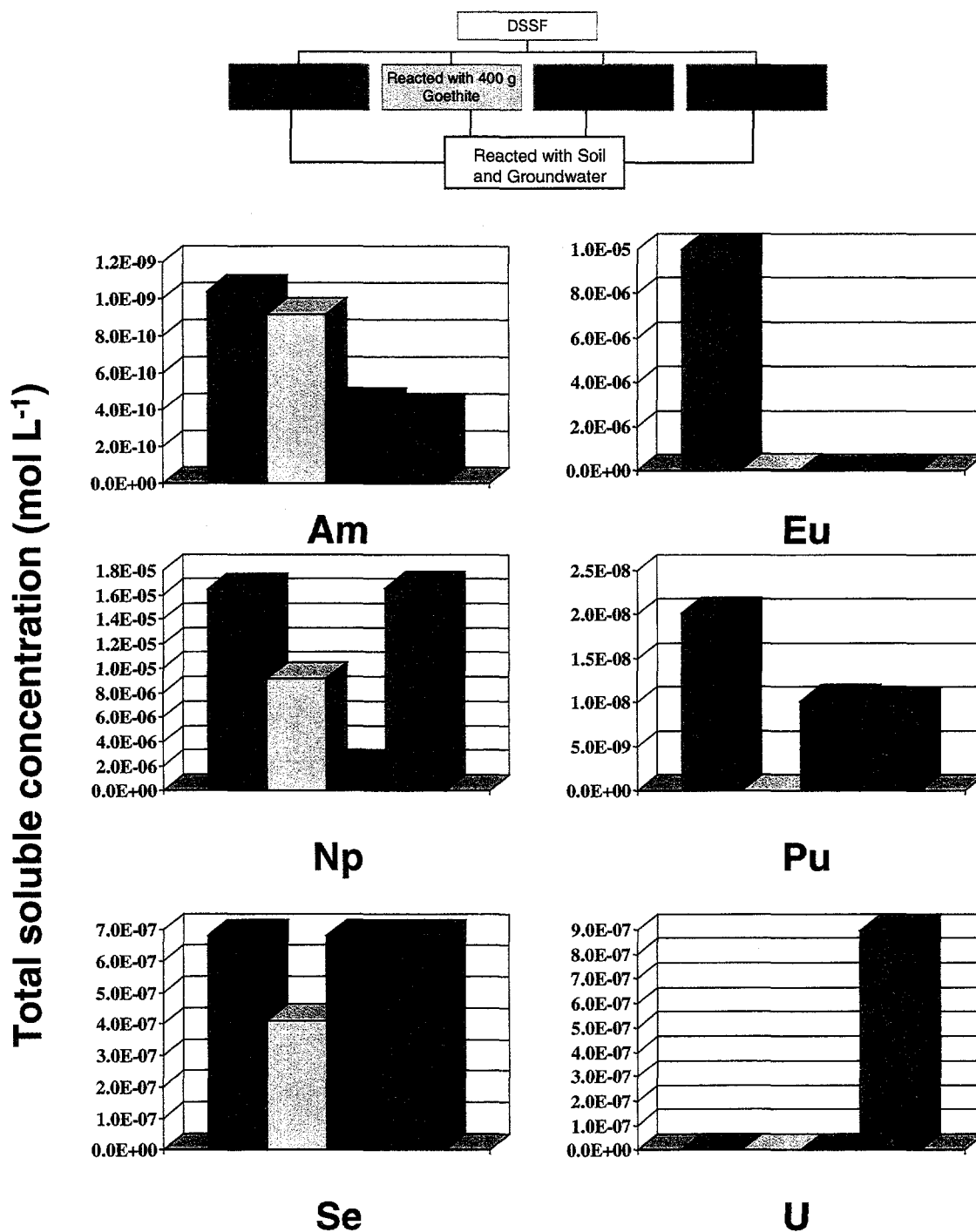


Figure 5.3. Effect of various getter materials on the soluble radionuclide concentration of waste tank residual suspensions released into soil.

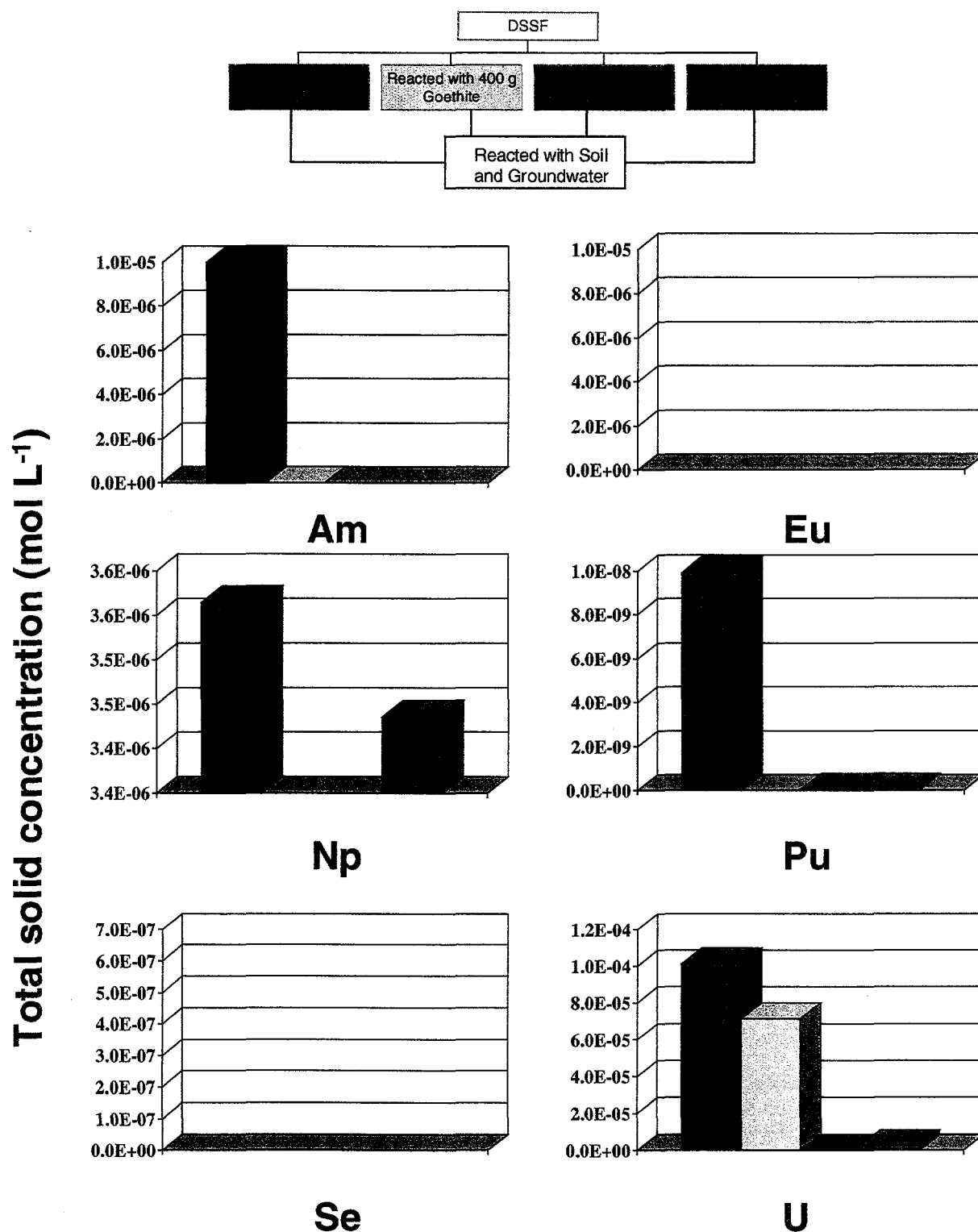


Figure 5.4. Effect of various getter materials on the formation solid from the nuclides in waste tank residual suspensions released into soil.

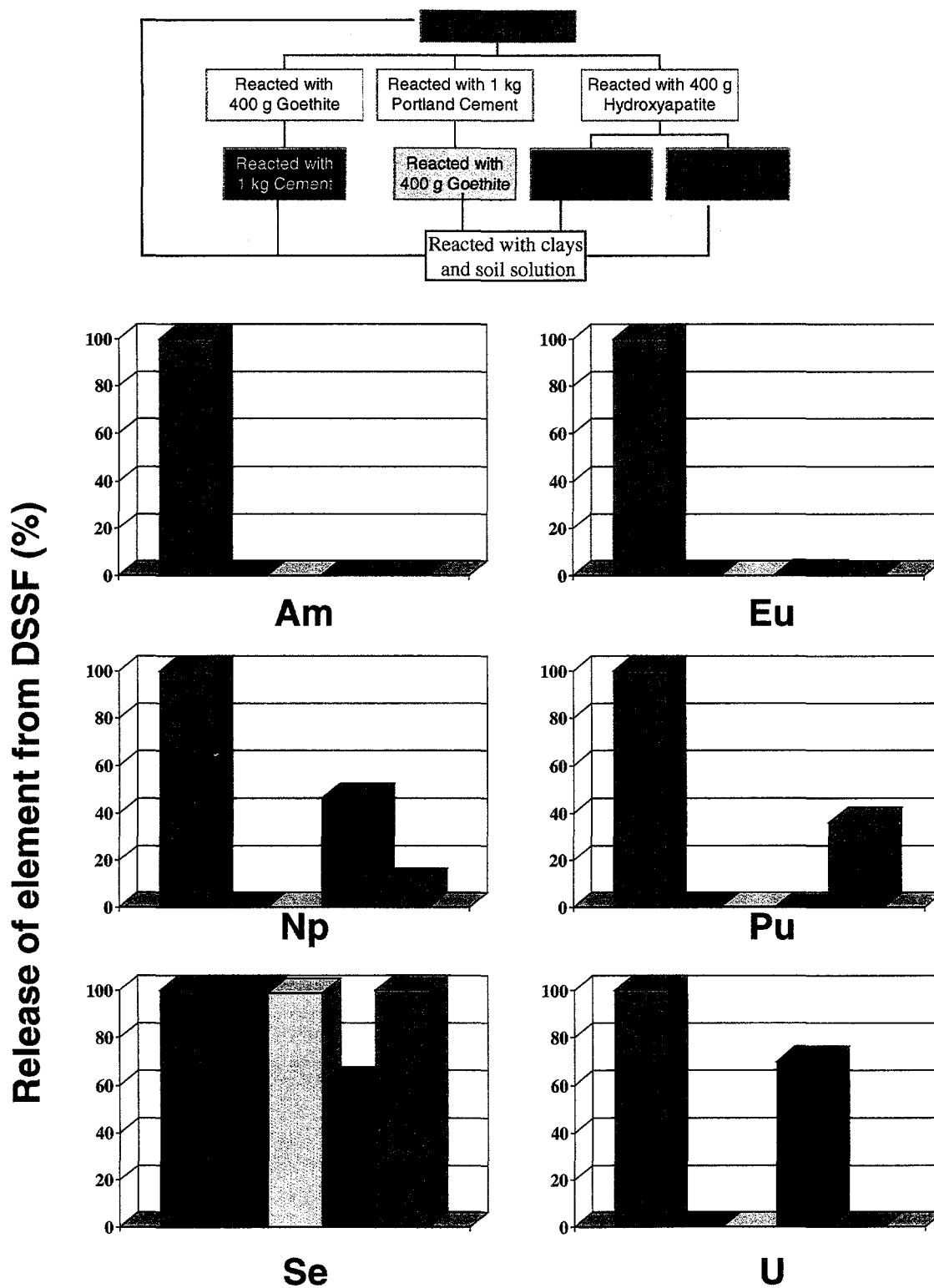


Figure 5.5. Effect of a double layer of getters in-tank and in-soil on release of radionuclides into soil

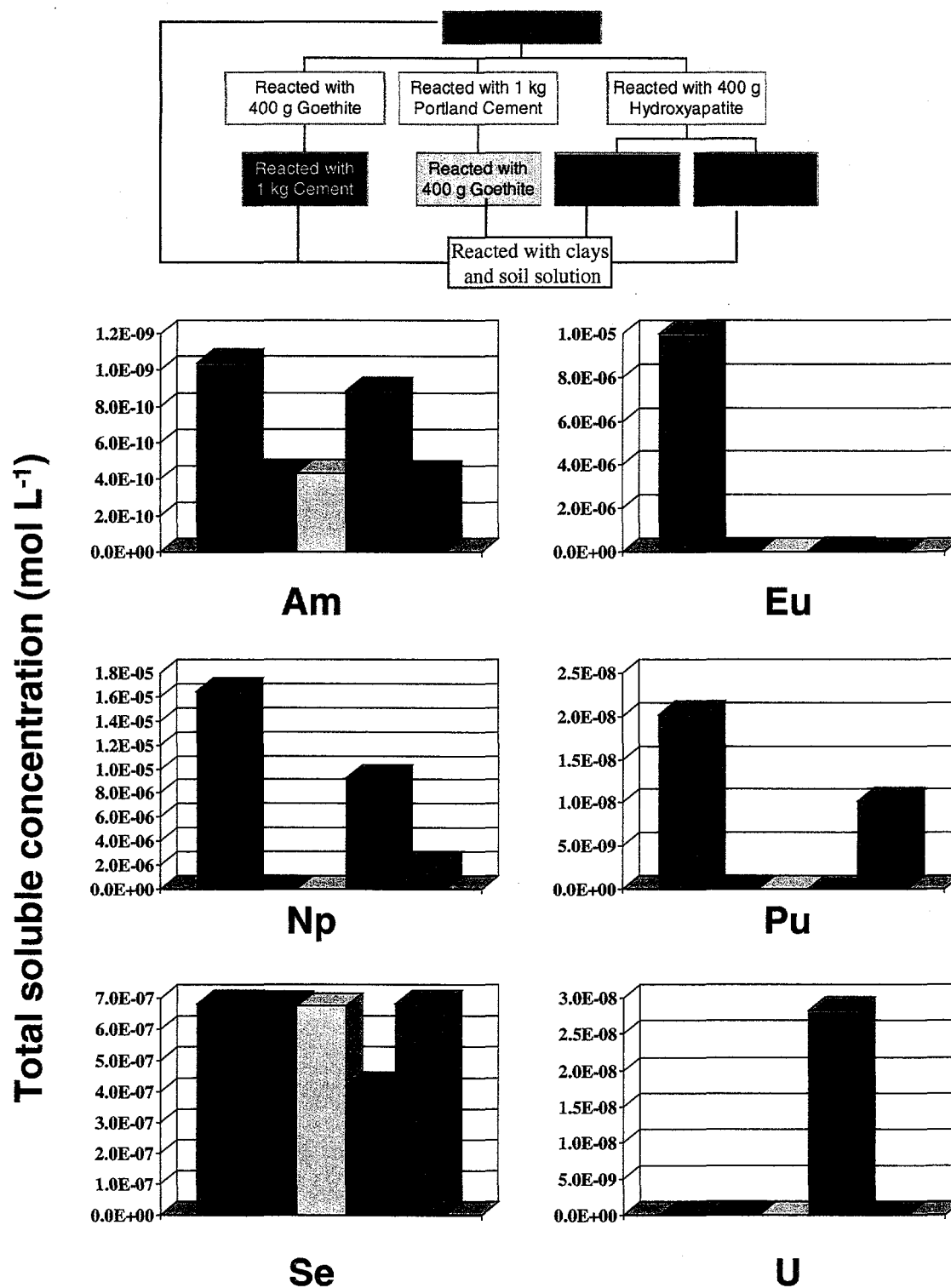


Figure 5.6. Effect of double of getters in-tank and in-soil on soluble radionuclide in soil groundwater.

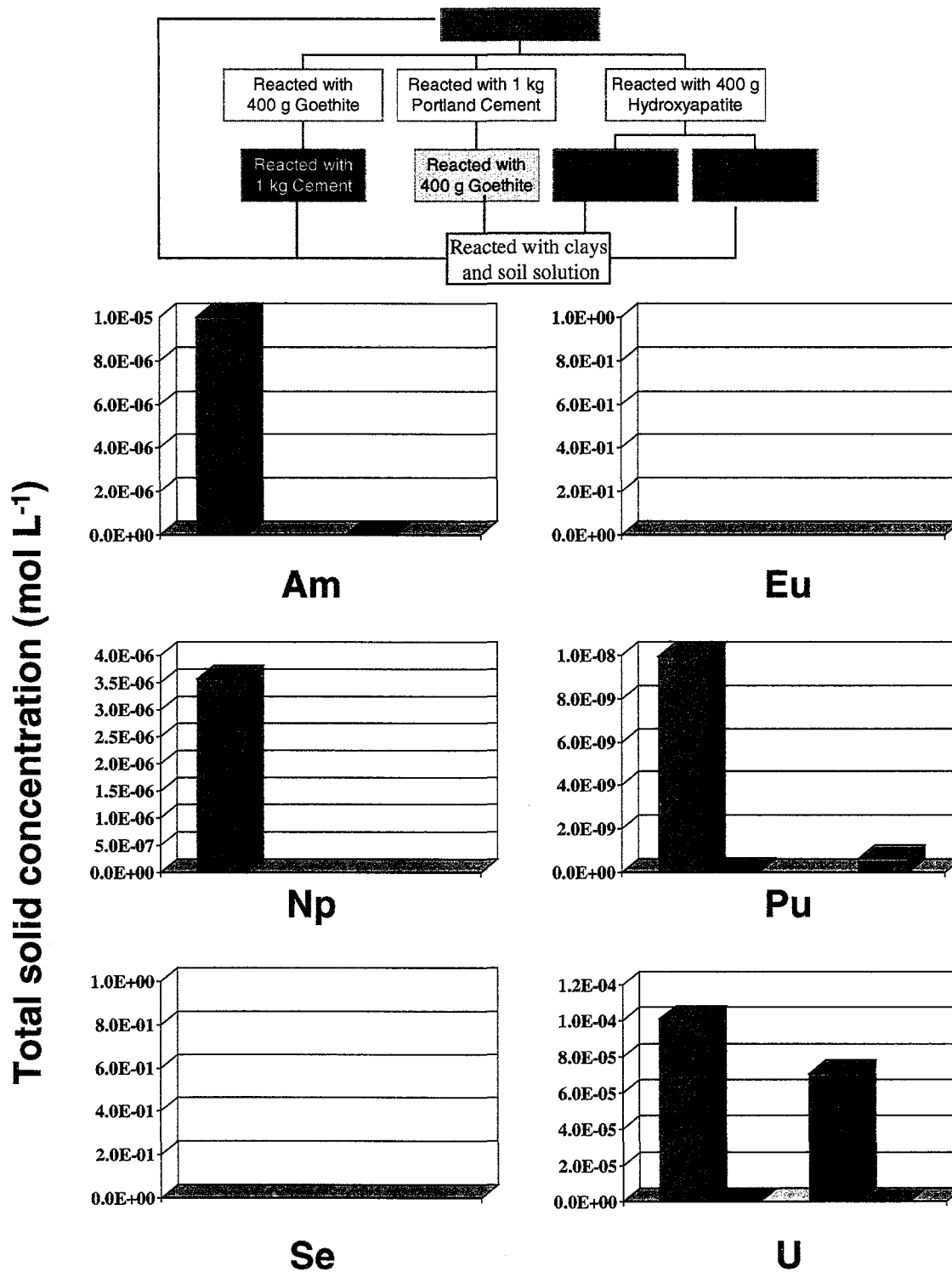


Figure 5.7. Effect of double layer of getters in-tank and in-soil on radionuclides in soil solids.

completely removed (Figure 5.5) in the reaction systems of goethite and cement. The soluble concentrations of the five elements in the groundwater are also minimized as compared with that of DSSF without reacting with getters (Figure 5.6). In contrast, removal of Np, Pu and U is not complete in the systems that are first reacted with hydroxyapatite and then reacted with goethite or cement, respectively (Figure 5.5). This results in relatively high soluble concentrations of Np, Pu and U in the groundwater (Figure 5.6). For Pu and U, the formation of solids in the reactions of tank residuals with soil clays and groundwater is only found in the systems that initially reacted with hydroxyapatite (Figure 5.7).

The results from thermochemical modeling suggest that goethite and cement are better candidates as the tank getters. However, the effectiveness of these two substances decreases when they are used alone. The removal of radionuclides can be effectively enhanced by combination of both goethite and cement application in the tank as a multiple-layer getters. Hydroxyapatite and hydroxyapatite mixed with goethite or cement are less effective in terms of solidification of Np, Pu and U and will result in higher soluble concentrations in the groundwater.

Selenium seems not to be affected by any treatment unless the last getter is goethite which lowers the solution pH and removes a fraction of selenium through adsorption (Figures 5.2 and 5.5). Unlike the other five radionuclides, selenite and selenate do not form any solid under those circumstances. Therefore, they stay either in the solutions or sorbed on the hydroxyl iron oxides' surfaces. In these studied reaction systems, pH is higher than 13 in most cases. At such high pH, the adsorption of any anion is limited because they can not compete with hydroxide and the goethite surfaces are negatively charged. In addition, we do not have the adsorption database other than that of goethite in this model.

It should also be pointed out that, laboratory work can not be simply replaced by computer modeling in which only chemical equilibrium is considered. Results from goethite-selenium interaction experiments conducted in the project indicate that the Se concentration is dramatically reduced in the aqueous phase. A possible mechanism might be that Se (mostly SeO_3) anion is covered by further precipitation of FeOOH on the growing goethite surface when the anion is physically sorbed at goethite surface. The computer modeling only provides a tool to predict relative, equilibrium-based reaction paths and distribution of species in a system and

can't include all factors (i.e., kinetics, wrong thermochemical data) that may affect the reactions and formation of reaction products.

The above discussions only qualitatively describe the possible results for the DSSF fluid reacting with getters following several assumed reaction paths. The mechanisms (e.g., the concentration of the major species and the masses of minerals involved in a specific reaction) used to calculate these results are briefly discussed in Appendix A. To obtain a more accurate modeling output, we need to expand the thermochemical database to include more adsorption complexes and minerals. The quality of thermodynamic data for reaction rates and mechanisms are critical in predicting the distribution of species, especially because fluid (and dissolved species) transfer in the tank or soil are often dependent upon changes in retardation mechanism or kinetics. Unfortunately, these data are limited, making laboratory measurements more valuable and complementary to modeling activities.

5.2. ReO_4^- Sorption Test

As a follow on to previous work ReO_4^- sorption measurements were carried out on a five materials: calcium monosulfate aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 13\text{H}_2\text{O}$), lignite (brown coal), Fe^{+3} -hydrotalcite, Fe^{+2} -hydrotalcite and Zn-hydrotalcite general formula $\text{M}_x^{2+} \text{M}_y^{3+} (\text{OH})_{2x+3y-nz} (\text{A}^{n-})_z \cdot m\text{H}_2\text{O}$. The experiment involved placing about 0.3 g of solid in 25 ml of deionized water spiked with Re as perrhenate. Three Re concentrations were used, 10 ppb, 1 Re and 0.1 ppb Re. Samples were equilibrated for more than a year (15 months) the fluids analyzed by ICP-mass spectroscopy. In some cases no sorption was observed but for all the materials there was at least one positive result (Table 5.2).

Given the small solution concentration changes involved and the analytic uncertainties, it is difficult to place much meaning on the K_d values for the first three materials. However, the change is clearly significant for the Zn-hydrotalcite. In addition, the fact that the K_d values are the quite similar over two orders of magnitude suggests that the removal mechanism is actually an ion exchange process. This suggested that tests at higher Re concentrations might be fruitful, but at 10 ppm Re, no sorption was observed. Thus, at that high concentration apparently all of

Table 5.2. Long-Term Experimental Re Kd value measurements

Material	K _d	Re concentration
Lignite	5.1	10 ppb
	2.4	1 ppb
Fe ⁺³ Hydrotalcite	5.0	10 ppb
Fe ⁺² Hydrotalcite	2.4	10 ppb
Zn Hydrotalcite	44	10 ppb
(SO ₄ ⁼ exchanged)	50	1 ppb
	56	0.1 ppb

the sorption sites have been swamped without removing any analytically detectable amount of Re. None the less, additional tests with tracer Tc and higher solid:liquid ratios are clearly warranted.

5.3. Effects of reducing grouts

Similar tests (using 10% DSSF7 rather than 3%) were then performed using 5 ppm TcO₄⁻ and 50 ppm UO₂²⁺ starting solutions. Samples were taken at 1 hour, 1 day and 7 days. As expected both U and Tc concentrations fell initially (to 0.6-0.9 ppm U and 0.05 - 0.06 ppm Tc). However, within a day the Tc value started to rise and after 7 days it had risen to half of its initial concentration. Over the same interval the U concentration continued to fall until it was no longer detectable (less than about 0.02 ppm).

In conclusion, it appears that a reducing grout can effectively immobilize Se and U even when oxygenated groundwaters gain access to a site. However, once a site becomes oxidizing the reduced Tc will be remobilized.

6.0 Feasibility Study on Using Directional Drilling to Emplace a Subsurface Barrier Beneath Hanford SSTs

6.1. Purpose

Another purpose of this project was to evaluate other potential field technologies that might be useful in the remediation of the SSTs at the Hanford Site in Washington. More specifically, we have assessed the current state-of-the-art capabilities of directional drilling as a means for emplacing a subsurface, close-coupled barrier beneath the single shell tanks (SSTs) at Hanford, WA.

6.2. Introduction

A primary survey was conducted to collect information regarding the feasibility of using directional drilling to emplace a barrier beneath the SSTs. The primary survey consisted of interfacing directly with companies working in the directional drilling field, as opposed to doing a secondary literature search at the library. A list of potential companies and associated points of contact (POC) was compiled with support from every available source. Each POC was given a summary of the purpose of the survey and asked for their respective inputs. It was immediately apparent that many of the companies were unfamiliar with the Hanford site and the DOE in general. In response to this a summary paper was drafted providing general information about the site, the project objective, and criteria for determining feasibility. All conversations with company representatives were fact finding as well as openings for suggestions, i.e., anything and everything discussed was open to suggestions. All suggestions were incorporated into the survey assessment.

The summary paper outlines the purpose and scope of the assessment, provides a description of the Hanford site and a list of criteria to be considered by each company when evaluating the feasibility and potential effectiveness of directional drilling for barrier installation. A copy of this report was mailed to each prospective company for interactive review. Refer to Appendix B for a copy of this summary report.

Appendix C contains a list of the companies that were contacted regarding the study. The companies range from environmental specialty companies, to grouting contractors to general

contractors. Many of the contractors were not qualified or were simply not interested. Only four companies appear both capable and interested in potentially being involved in a project of this magnitude in the DOE environment.

6.3. Technical Issues

A comprehensive assessment of the installation of a barrier beneath the SSTs at Hanford requires an evaluation of the following integral components of a subsurface barrier system:

1. Directional drilling methodology, including slanted and horizontal drilling techniques. All drilling methods will have to be precise and non-disruptive to the tanks so as to achieve a close-coupled barrier without causing leaks or enhancing existing waste contamination.
2. Emplacement methodology, including barrier material delivery and verification. A variety of techniques exist including jet and permeation grouting, cryogenic barriers, circulating air barriers (CAB), soil saws, slurry walls, vibratory beam, sheet piling, and pipe jacking from vertical caissons.
3. Choice of barrier materials, including emplacement, adhesion, and longevity issues. Barrier materials cover the range of commercially-developed cementitious grouts, and non-cementitious materials such as wax, and polymers. Depending upon the material, there are variations in how these grouts are emplaced, how well they bind to soil and existing tank structures, and how long they will last.
4. Monitoring methodology, including while-drilling and in-situ techniques. Post-emplacement barrier integrity will have to be monitored by a variety of techniques that measure changing subsurface chemical and radiologic environments. Current monitoring techniques include but are not limited to: thermomechanical and chemical sensors; electromagnetic and seismic imaging; and gas tracers.

Tremendous efforts and data collection regarding these four integral technologies has been completed in the last decade. Most data collectors agree that proper integration of these four technology components would result in emplacement of a successful barrier beneath the SSTs. However, there are legitimate unresolved questions regarding the drilling capabilities in the cohesionless, high porosity, cobbly soils at Hanford. In the past the primary drilling technique

employed in the tank farm areas has been cable tool drilling which does not represent state-of-the-art drilling capabilities. In addition, recent improvements in directional drilling have opened the door for further consideration of a subsurface barrier approach to assist in remediation of the SSTs.

As previously stated, there are numerous issues regarding construction of a barrier beneath the SSTs, but for the purpose of this study the subsurface access (drilling) technique was the focus. A variety of techniques are potentially applicable to accessing beneath the SSTs, but directional drilling is regarded as the most appropriate. In order to address the past criticisms of directional drilling the following technical issues are considered:

1. Depth and geometric (drilling radius) capability of directional drilling;
2. What type of fluid (air or water or both) is optimal for drilling;
3. How much fluid would be required;
4. How far would the fluid travel into the surrounding formation during drilling;
5. How is the drill bit steered and what is the accuracy in the site geologic conditions (no cohesion);
6. What is the spoils (drill cutting returns) volume associated with directional drilling technique;
7. What is the push/pull force (size), type, and footprint dimensions of the drill rig;
8. How will verification and monitoring be achieved.

6.4. Responses

Of the 24 companies considered, the following eight companies showed significant interest in addressing the Hanford SSTs:

- AGECE, Inc.;
- Schlumberger Environmental Technologies;
- Directed Technologies Drilling, Inc.;

- Mears, Inc.;
- Hayward Baker;
- Nicholson;
- A & L Underground, Inc.;
- Romonta (Flow-Tex).

Of these eight companies, only four (Schlumberger, Mears, Romonta, and A&L Underground) actually own and operate directional drilling rigs. Nicholson, Directed Technologies Drilling, Hayward Baker, and AGECE do not own or operate drill rigs, but still have potential for further consideration regarding this project. Nicholson and Hayward Baker are primarily grouting contractors, i.e., their primary business is soil improvement for foundations, tunnels, etc. Many of their projects require directional drilling efforts equal to or larger in scale than the Hanford SSTs. Nicholson and Hayward Baker typically subcontract and supervise directional drilling contractors to support projects of this nature. AGECE, Inc. is a small company with two employees that have a very strong understanding of the Hanford site, logistics, etc. resulting from a combined 30+ years of experience working at Hanford on environmental projects. Directed Technologies Drilling is very similar to AGECE.

6.5. Proposed Methods

Each of the companies responded to the summary report (Appendix B). The following is a synopsis of the proposals by the respondents.

AGECE, Inc. feels that directional drilling is possible at some Hanford tank farms. They recommend that tank farm operations conduct scaled and/or a full engineering field scale demonstration of directional drilling and barrier emplacement in a variety of geologic media. Including destructive examination to optimize the process and equipment and verify performance. AGECE is a small three person company with limited capabilities for managing a project of the magnitude of barrier installation beneath the SSTs; however, their pertinent knowledge and drilling experience would suggest a consultant role for the company.

Schlumberger Environmental Technologies proposed to drill with clay based fluids that will not leach into the formation (self-sealing), using a large-scale (300,000 lb. range) conventional directional drilling rig. The drill bit is steered with gyroscopes and accelerometers with an expected drilling accuracy of one meter or less. They would emplace a flexible tubing called 'coil tubing' in the drill holes. The coil tubing is then perforated at desired locations using controlled downhole charges to facilitate barrier material injection. This is a technology developed for the oil and gas production industry. In addition they would consider making many of their proprietary chemicals (grouts) available for use at the Hanford SSTs.

Directed Technologies Drilling, Inc. & MEARS, Inc. have proposed to team together on a project at Hanford. Conceptually they would use a relatively small directional drill unit (50,000 – 70,000 lb. class) minimizing drill fluid requirements and having a small foot print with automated rod handling to minimize crew contact with potentially contaminated drilling rods. The drill bit would be steered by an induced field with an anticipated accuracy of one meter or less. Drilling fluid used would be a clay based mud system that minimizes penetration of the mud into the formation. Horizontal wells would be installed from surface to surface and fractures would be propagated between wells and filled with grout material to form a continuous barrier. They also proposed to install horizontal wells beneath the SSTs after barrier installation to monitor the vadose zone above the barrier.

A & L Underground, Inc. proposed to use a 180,000 – 220,000 lb. drill rig to place directional drilled holes on 10 ft centers from surface to surface (start drilling on one side of tank farm and direct drill bit to surface on opposite side). They would then attach a cutter/grout bar to the parallel drill strings and pull the grout bar back through the plane between the two holes. The front or lead side of the bar has cutting ports, which are injecting a bentonite drilling mud to loosen soils and carry returns to the surface mud pit, while the back side of the bar has grout injection ports which fill the cavity cut by the bar as the bar progresses. If successful this methodology is self proving, i.e., the bar passes through the entire area to be grouted increasing the likelihood of a uniform barrier. It is noted that this concept has only been field tested at scales substantially smaller than the Hanford SSTs.

Realizing the problems that could occur due the cobbles at Hanford, a second method was proposed in the event that the cobbles were too large for the cutting bar method. This method

would require directional drilling of parallel holes three to five feet apart beneath the SSTs, grout injection at high pressure using jets to flood the formation filling the void space to form a barrier. This second method is more robust and proven but in theory is less efficient, requiring more drill holes and also is more difficult to verify integrity. Both methods require drilling from two sides of the tank farm to create a 'bathtub' effect with a minimum 6 inch thick barrier. In addition they proposed to install several horizontal wells below the barrier to monitor performance. The drill bit would be steered using a direct wireline with an anticipated accuracy of one meter or less.

Hayward Baker, Nicholson, and Romonta have not provided any specifics on how they would complete the project. However, each claims, and has case studies of, projects where grout materials were installed at scales comparable to the Hanford SSTs. The case studies are typically not environmental projects but instead are subway constructions, and under-river utility crossings.

6.6. Preliminary Observations

The number of companies capable of handling a barrier emplacement at the Hanford SSTs is very limited. Of the companies that are interested and capable, the proposed concepts are quite different. It is also noted that there is a noticeable disconnect between directional drilling companies and grout injection companies. This is unfortunate because the directional drilling companies do not have the expertise at material injection that the grouting companies have and vice-versa. Also it was noted that company responses to the technical issues such as drilling fluid volumes, spoils volumes, and verification methods were qualitative (assumption based) not quantitative in nature.

6.7. Recommendations

In order to validate the qualitative responses a field scale demonstration at a cold test site is recommended. The site should represent the geologic and geochemical conditions at the target SSTs area. A successful demonstration would quantify, i.e., provide answers to the unknowns.

More specifically, the demonstration should address the following specific performance requirements:

1. drilling system size, steering mechanism & 3-dimensional accuracy;
2. drilling fluid usage – volume and formation penetration distance;
3. spoils (drill cuttings) volume returned to surface;
4. equipment access requirements;
5. real time assessment of down hole contamination;
6. compatibility of barrier injection technology with directional drilling;
7. grout material(s);
8. barrier saturated hydraulic conductivity if an impermeable barrier, or treatment capacity if a reactive media barrier;
9. barrier integrity verification;
10. post monitoring method;
11. approximate cost/time requirements.

A demonstration answering these questions would provide sufficient data to perform a quantitative environmental risk reduction analysis and reasonable cost estimate of emplacement of a barrier beneath the SSTs at Hanford. A field scale demonstration should employ a grouting contractor in conjunction with a directional drilling company. This ensures comprehensive competency and optimum equipment for the two primary aspects of the demonstration:

- (a) directional drilling,
- (b) grout/barrier emplacement.

It is imperative that both aspects are demonstrated simultaneously to ensure compatibility.

In late September, 1998, a demonstration exhibiting a down hole real-time monitoring/logging tool is scheduled. The Principal Investigator for this demonstration (Cecelia Williams) is aware of this report and the recommendations. Cecelia has contracted A & L Underground to assist in this project. A & L Underground is fabricating a sub-assembly that will couple the logging tool with a directional drilling system. This demonstration will answer the majority of the questions posed in this report, with one exception, the integration of a directional drilling unit and grout injection system. This effort would require additional funding and planning. The knowledge gained from this September demonstration will provide the platform for a full-scale field demonstration of the entire system in FY 1999.

6.7. Conclusions Based on Evaluation Criteria

A brief report summarizing the Hanford Site conditions, assumptions and criteria for evaluating the technical feasibility of emplacing a subsurface barrier via directional drilling was given to interested companies. The following list is a summary of the criteria and corresponding conclusions based on respondent feedback.

(1) Are the physical characteristics of the surrounding soil amenable to directional drilling?

The soils are difficult and challenging, but the general consensus was that directional drilling is possible at the Hanford SSTs.

(2) Are the drilling lengths and depths (geometry) within the limitations of state-of-the-art directional drilling technology?

The drilling lengths and depths (geometries) are definitely achievable with state-of-the-art directional drilling technology. This is evidenced by case histories describing successful sub-river pipeline crossings, and tunnel installations of the scale required for emplacement of barriers beneath the Hanford SSTs.

(3) What is the three-dimensional accuracy of directional drilling in these soil conditions?

The general consensus among the directional drilling companies was an accuracy of 1 meter or less. It is noted that this estimate is not based on actual field testing, but on drillers' opinions.

- (4) What mechanism will be used to steer the drill bit (magnetic based systems will be interfered with by steel tanks), and how reliable is it?

A variety of steering mechanisms are available, each having a different basis of operation. A more thorough site investigation along with cost consideration would likely discern an optimum choice.

- (5) What barrier injection technology (jet or permeation grouting, etc.) is compatible with directional drilling to enable emplacement of a bottom barrier?

Jet or permeation grouting, and hydraulic fracturing were mentioned as possible injection technologies. Hydraulic fracturing appears very limited due to the cohesionless nature of the soil (less than ideal soil for fracture propagation); permeation grouting has potential but would be very difficult to assess barrier continuity or completeness; and finally jet grouting would provide the most robust, self-proving method but at the highest cost. A modification of jet grouting using a cutting bar was proposed by A & L Underground which has promise. Halliburton worked on a similar project called the horizontal soil saw in the 1995-1996 time frame. Halliburton had limited success with this technique primarily due to funding cuts and poor project management; consequently, resulting in an unfair evaluation of this concept's evaluation.

- (6) Is it possible to assess contamination type and levels down hole near the drill bit using real time analysis?

Yes, it is possible to assess contamination down-hole using real time analysis. Cecelia Williams and Randy Norman (both of Sandia National Laboratories) have contracted A&L Underground to conduct a test exhibiting such a concept using a Sandia National Laboratories developed tool. This demonstration is scheduled for late September, 1998. The results from this demonstration will provide a stepping stone for a future demonstration of emplacement of a barrier beneath the SSTs.

- (7) Assuming the drilling lubricant is air, what capability exists for filtering any potential return air/drill cuttings, thereby minimizing potential exposure to workers; and filtration of the drill cuttings has been demonstrated for vertical drilling projects of this nature. Worker exposure should be minimized and fully controlled.

Not evaluated in this report.

(8) If drilling is feasible what is a reasonable range of costs/linear ft. of directionally drilled hole?

It appears that directional drilling at Hanford is feasible, but the potential contractors are reluctant to attach a price tag to the task. Again, a more definitive answer to the costs would be found in a well planned, thorough demonstration.

(9) Are there any mechanisms available for isolating individual tanks, i.e., emplacement of a horizontal barrier beneath only an individual tank not an entire tank farm?

Yes, it is possible to emplace a barrier beneath individual tanks, but it would not be cost effective. The efforts required to access beneath the tank would be near the requirements for access beneath an entire tank farm. In other words, there is "economies of scale" resulting in tremendous cost savings inherent with emplacing a barrier beneath a tank farm rather than individual tanks.

7.0 Summary

Technical support for the Hanford Tank Closure Program is focused on evaluation of concepts for immobilization of residual contaminants in the Hanford AX tanks and underlying soils, and identification of cost-effective approaches to improve long-term performance of AX tank farm closure systems. Project objectives are to develop materials or design engineered systems that would significantly reduce the transport of radionuclides to the groundwater from SST tanks containing residual waste. FY98 activities include: (1) tank fill design, consisting of cementitious grouts and/or other materials to reduce water infiltration and potential interaction with residual waste; (2) development of getter materials that, when added to tank fill, would specifically sorb or sequester radionuclides; (3) evaluation of grout emplacement under and around the tanks to prevent waste leakage during waste retrieval or to minimize infiltration of rainwater directly beneath the tanks; (4) development of getters to inject into contaminated soils surrounding tanks that will chemically fix specific radionuclides; and (5) combined geochemical and hydrologic modeling of soil-grout-waste-water interactions.

The tank fill design consists of six layers of different materials constructed from the bottom to the top of the tank to enhance the ability to provide characteristics necessary to accomplish the

functions required. The cost for the tank fill (materials only) was estimated to be about \$400K per tank. The tank skirt, a vertical cutoff wall around the exterior of each tank or possibly around the four-tank AX complex, is proposed to be constructed to a minimum depth of 15 ft. below the bottom of the tank, based on hydrologic modeling and cost estimates. A vertical close-couples barrier could be located around each tank using jet grouting about 4 ft. from the tank wall followed by permeation grouting between the jet grouted barrier and the tank wall. Alternatively, it could be a standoff barrier about 10 ft. thick, composed of two barriers jet grouted and 4 ft. apart followed by permeation grouting the soil between to form a cut off wall. Tank skirts are estimated to be between \$1-2M if constructed around each tank. These costs increase to \$5-10M if constructed around the entire 4-tank AX complex.

Numerical simulations have been performed to evaluate the hydrologic behavior in the vicinity of a tank with and without jet-grouted vertical skirts. The amount of groundwater percolating directly beneath the tank can be decreased with increasing skirt lengths. This, in turn, improves waste isolation and decreases the potential for remobilization of residual waste in the soil immediately beneath the tanks. Therefore, the length of the skirt should be extended beyond the base of the tank, if economically feasible, into the pebbly sand layer that underlies the silty sand beneath the tank (at least 60 ft. deep). Also, vertical fluid flow and 1 dimensional transport of radionuclides, ranging from highly soluble ones to slightly soluble species, through a single fracture or through multiple fractures in tank fill was calculated using standard diffusive transport equations. For single cracks, adding getters would retard highly soluble radionuclides (e.g., Tc) migration over the period of regulatory concern. In addition, added getters would slow their migration in a fractured tank fill even in the event of an instantaneous release (PA scenario) through a dispersed, interconnected network of fractures. Finally, addition of getters for sparingly soluble radionuclides (e.g., U) seems to be of little use, even in a highly fractured matrix. Although adding significant amounts of non or slightly radioactive components (e.g., depleted U) with a similar chemistry and low solubility might limit radionuclide mobility by its incorporation in other U minerals.

A variety of likely getter materials, used in in-tank and in-soil environments, were evaluated for their effectiveness in reducing the mobility of selected, problematic radionuclides, including Tc, Se, and U (also analog for actinides). Magnetite, bone char and reducing grout were tested for their ability to retard ^{99}Tc and U species. More than 50% of the ^{99}Tc in alkaline solution has

been sequestered by bone char. In addition, bone char effectively sorbed 90% of the ^{99}Tc from groundwater. It was found that a reducing grout, a mixture of $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and Portland cement, can effectively immobilize Se and U even when oxygenated groundwaters gain access to a site. However, if the site becomes oxidizing the reduced Tc will be remobilized. Further, it was also demonstrated that neither the oxidation products of a reducing grout or the normal cement phases have any affinity for the TcO_4^- ion. Thus, a getter that is specific for pertechnetate will need to be added in addition to materials that would normally be used to close the tanks.

Reaction path modeling (REACT code) was used to evaluate the relative thermochemical stability and sorptive abilities of goethite, Portland cement, and hydroxyapatite relative to selected radionuclides in simulated tank fluids. These analyses were done when potential getters were added to the tank fill, skirt and under tank barrier materials. The combination of goethite and Portland cement appears to effectively reduce the total amount of nuclides released into groundwater and the concentrations of Am, Eu, Np, Pu and U in the soil solutions. These materials show no effect on selenium retention based on the modeling output. However, the results from experiments show a significant reduction in solution selenium in the presence of the getter materials. It is concluded that a combination of tank fill, a skirt and getter emplacement can greatly retard the release of radionuclides from a closed tank.

An assessment was made regarding the feasibility of using directional drilling to emplace a close-coupled barrier beneath the SSTs to prevent wastes from leaking during retrieval operations. This included a survey with companies working in the directional drilling or jet grouting fields. A field scale demonstration at a cold test side is recommended, and it would clarify specific performance requirements, such as drilling accuracy, grout emplacement efficiency, barrier integrity verification, environmental safety concerns, and costs. To date, directional drilling and grouting immediately beneath and adjacent to SSTs at Hanford seem to be within the realm of current industrial capabilities.

The needs for the future studies have also been discussed in detail in this report. We have identified potential topics for future work on waste immobilization and improved designs for AX tank farm closure systems. In response to the interest of potential sponsors, the topics listed in Appendix D cover a variety of follow on technical tasks, including performance evaluation

through lab experiments and modeling analyses, lab-scale feasibility studies, and field testing of engineered barriers. Some of these topics address critical needs for waste retrieval operations and immobilized LAW waste storage issues. We also included studies that would provide solutions to near-term problems, such as migration control of existing contamination through electrokinetics or reactive barriers, and tank leak control using close-coupled horizontal and/or vertical skirts around leak tanks. Getter studies will address waste migration and immobilization issues by quantifying their impact on radionuclide solubility and sorption data, which are used in near-field and far-field performance assessment.

Finally, this work was not performed in a vacuum, but is just one of several tank closure strategies presently being evaluated across the DOE complex. Savannah River has the most advanced program with several empty tanks already having been filled with a monolithic pour of Portland cement-based materials, but have not been "closed." They are awaiting final review and approval by the NRC. Our strategy is made more complex by several features that are specific to the AX tank farm, the Hanford site in general, the physical properties of grout.

First, the Hanford tanks are well above the water table in an arid environment. Thus it is likely that oxidizing conditions would be reestablished even if a tank were initially filled with a reducing grout. Consequently, we specifically developed Tc getters to function under oxidizing conditions. Thus, while much remains to be done to qualify the material, it is like that the first step in the actual placement process would be to blow in a layer of powdered bone char of comparable thickness to the layer of sludge remaining in the tank. Vadose zone capillary action and diffusion would then be sufficient to bring the dissolved Tc in contact with the getter and no later mixing would be necessary. One might also anticipate that to take full benefit of the getter it might be necessary to wait several weeks or months before proceeding with the next step.

The next step would be directed at immobilizing actinides. We anticipate dominantly oxidizing conditions in the waste, which generically are reflected in relatively high actinide mobilities. Rather than fighting this, we have again directed our efforts at developing getters, which are compatible with such a situation. In particular, we suggest that formation of abundant uranophane-like phases may coprecipitate other actinides dissolved in trace components in the waste fluids. To facilitate this, one would add (depleted) $\text{UO}_2(\text{NO}_3)_2$ either dissolved in a small amount of water or as a powder. During this stage, any components needed to form apatite

would also be added. To form apatite-like phases might require a second waiting period before proceeding.

Another site-specific variable requiring consideration is whether mixing with the overlying grout fill is necessary to satisfy legal limitations on bulk radionuclide volume and concentration. However, structural considerations may require that the base of the tank be solidified before the tank fill is added. This report demonstrates that this can be accomplished by blowing in a layer of dry Portland cement on top of the getters. If mixing is needed, or the layer on the tank bottom is so thin as to not present structural difficulties, then this step would be skipped and the filling of the tank would proceed. Our design did not explicitly evaluate the impact of risers, but presumably they would have to be cut off (and left on the bottom of the tank) before the bulk filling proceeded. Likewise, the timing of riser cutoff was not the focus of this study.

Our multilayered tank fill design is also more complex than that being considered at Savannah River because we believe that the impact of crack development in the tank fill must be addressed explicitly for the design to be generally accepted by the local regulatory community at Hanford. Even the most rudimentary modeling showed that even a single crack that penetrates completely through the tank fill could impact Tc releases significantly. In particular, our design incorporates both plastic layers and layers of alternating strength and weakness. Both types of layers are intended to minimize the probability that a crack could propagate all the way through down through the fill.

A final site-specific consideration is inclusion of a skirt in the overall closure design. This feature takes advantage of the long distance to the water table. It also acknowledges that whatever the integrity of the seal placed over the waste, there may be little we can do to remediate damage already done to the tank bottom underlying the waste. Rather than proposing directional drilling technologies be used to "pot" the tank farm in a huge monolith of concrete, (and possibly create a situation where a tank could eventually be sitting in a "pond"), we elected to leave the bottom open, but shielded it from the flux of passing groundwater by creating a "dead zone" under the tank.

To summarize, we have developed a closure strategy that is significantly more robust than merely creating a concrete monolith within the tank, and one which is intended to accommodate the likely long term environment of the Hanford tanks. In doing so, we have tried to take

advantage of well-established chemical and civil engineering practices. The notable exception is proposing the use of radionuclide getters. Here, there are few practical examples and so sequestration processes are not well understood so that an intensive and focused research will be needed before their performance envelopes can be established with certainty.

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Appendix A: Aqueous and Solid Chemical Speciation

The total release of nuclides to soil and the soluble and solid concentrations of those nuclides in the soil solution (see section of Assessment of Barrier Performance) were presented without specifying the species of those nuclides in the fluids and soil solutions. In Figure A.1 and A.2 we show the soluble and solid chemical forms, respectively, of the nuclides which remain in significant amounts (e.g., major, dissolved constituents of fluid) in the soil solutions after reacting with the potential getter and barrier materials. As illustrated in Figure 5.2, Am and Eu were essentially immobilized by the reactions of waste tank fluid (DSSF) with getter materials. This result in low concentrations of Am and Eu in the soil solutions (Figure 5.3). Therefore, the species of Am and Eu are not significant and not presented here. The soluble species of Np, Pu and U in the soil solutions vary in according with the reactions of the fluid with various getter materials. However, the solid species in the reacted fluids appear to be same as that in the fluid which is not reacted with getter materials, Figure A.2. It should be pointed out that some minor species are in such low concentrations in the calculated reaction paths that they are not represented in Figures A.1 and A.2.

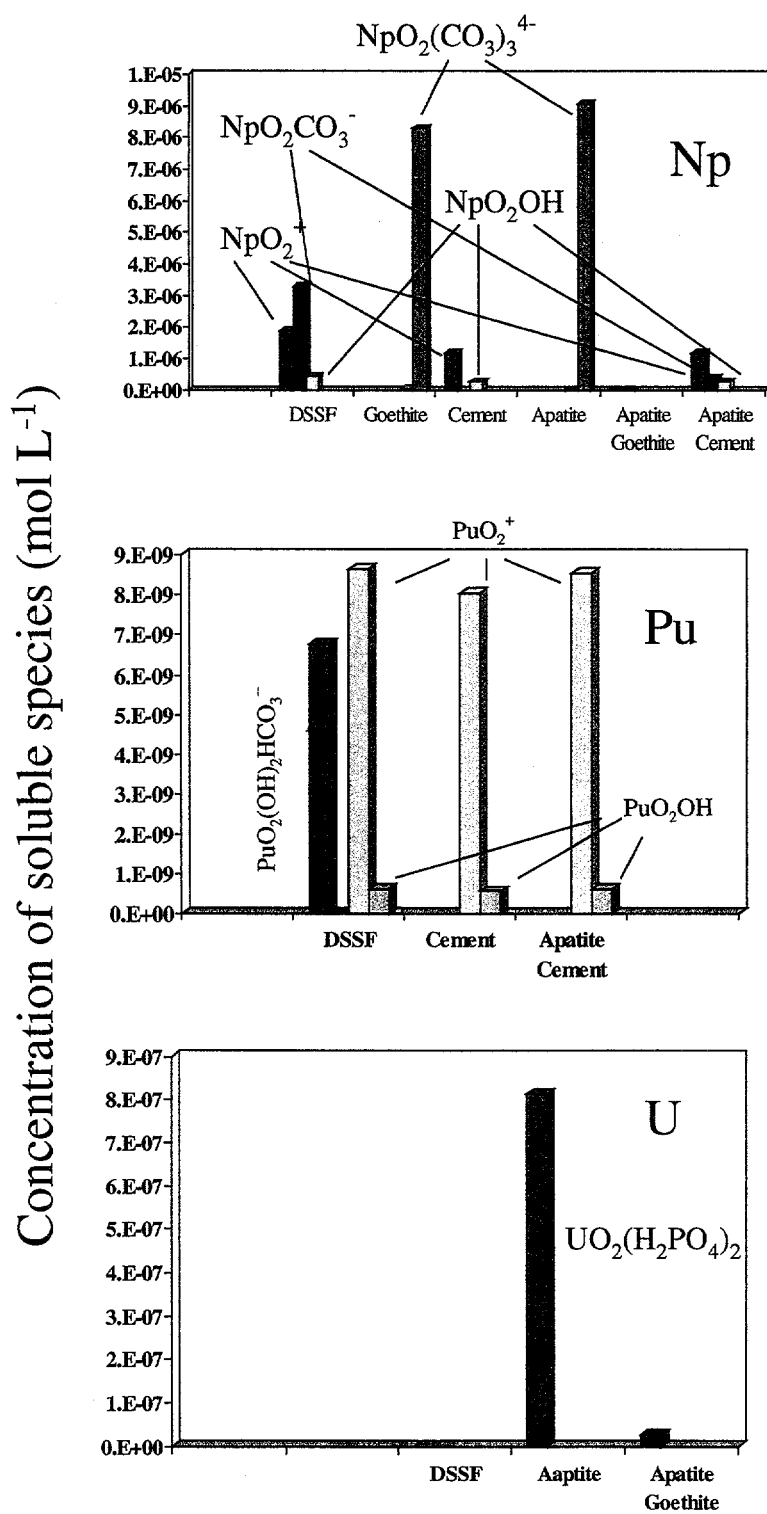


Figure A.1. The chemical forms of major soluble species of nuclides in the soil

Concentration of solid species (mol L⁻¹)

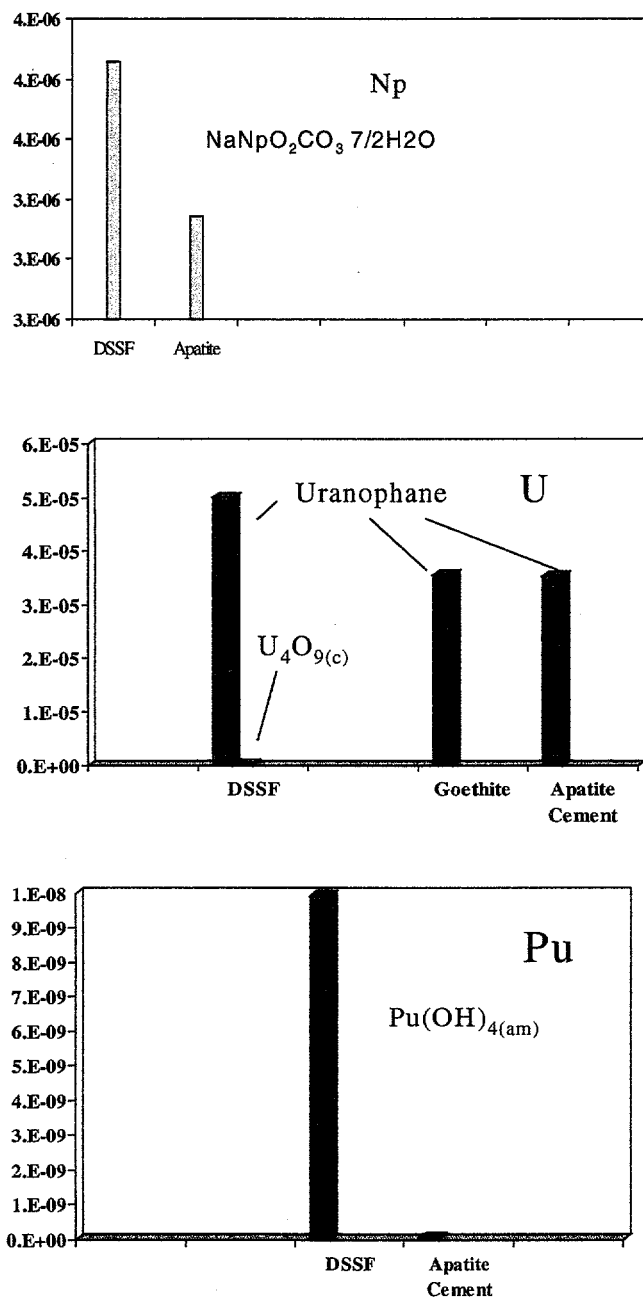


Figure A.2. The chemical forms of solid species of nuclides in the soil solutions.

Appendix B

FEASIBILITY OF ACCESSING SUBSURFACE BENEATH SSTs AT HANFORD USING DIRECTIONAL DRILLING

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Purpose

The sole purpose of this brief report is to summarize the site conditions and provide any additional assumptions and criteria necessary for directional drilling experts to determine whether or not it is feasible to directionally drill beneath a tank farm at the Hanford site. Directional drilling is being considered as an access method for emplacing a subterranean barrier beneath tank farms at the Hanford Site.

Introduction

Background

The Hanford Site is an approximately 560 square-mile Department of Energy (DOE) installation occupying a semiarid region in the Columbia River Basin in south-central Washington State. Since 1943 the area has been dedicated to the production of nuclear materials, electricity, diverse research, and waste management activities.

Irradiated fuel discharged from plutonium producing reactors was processed to recover uranium and plutonium. The processing resulted in the accumulation of a wide variety of radioactive and chemical waste. The majority of this waste has been stored in underground storage tanks located approximately 22 miles from the nearest residential community and at least 5 miles from the Columbia River. A total of 149 single shell tanks (SSTs) ranging in size from 55,000 to 1 million gallons were constructed to store the waste. The tanks are constructed of carbon steel, which provides the lining of a reinforced concrete shell. The tanks are below grade with at least 6 feet of cover providing radiation shielding.

Problem

The carbon steel liners used in the SSTs were not stress relieved after fabrication and consequently, the hot, alkaline radioactive waste mixture of liquid and sludge has induced stress-corrosion cracking of the steel over time. Many of the tanks are assumed leakers.

Solution

In order to mitigate continued leakage from the tanks, consideration is being given to the emplacement of a horizontal barrier beneath the tanks using directionally drilled emplacement holes. It is desired to have the barrier within close proximity to the bottom of the tanks to minimize the volume of potential contamination within the barrier. The 149 SSTs are located in 12 tank farms or clusters of tanks. Two mitigation options should be evaluated: 1) placement of a horizontal barrier beneath individual tanks if technically and economically feasible; or 2)

emplacement of a continuous barrier beneath a tank farm as opposed to an individual tank. It is also desired to emplace a material capable of confining leaking waste for only 20 years.

Representative Site Characteristics

To assist in evaluating the feasibility of emplacing a subsurface barrier by directionally drilling beneath a tank farm a representative site and corresponding assumptions are presented.

Geology/ Geotechnical

The stratigraphy for the first 100 ft. is composed primarily of sand with intermittent gravel/sand lenses and very small amounts of silt. The soil dry densities range from 110 to 130 pcf, porosity ranges are .25 to .35, angles of internal friction values range from 40 to 45 degrees, and cohesion values are all zero. Appendix B contains additional soil property information, geologist's stratigraphy logs, and tank farm elevations and layouts. Figures A.3-A.5 are pictures taken from soil excavations or outcrops in the various tank farm areas. Some areas have primarily sand, while other areas have poorly graded sand and gravel or larger cobble.

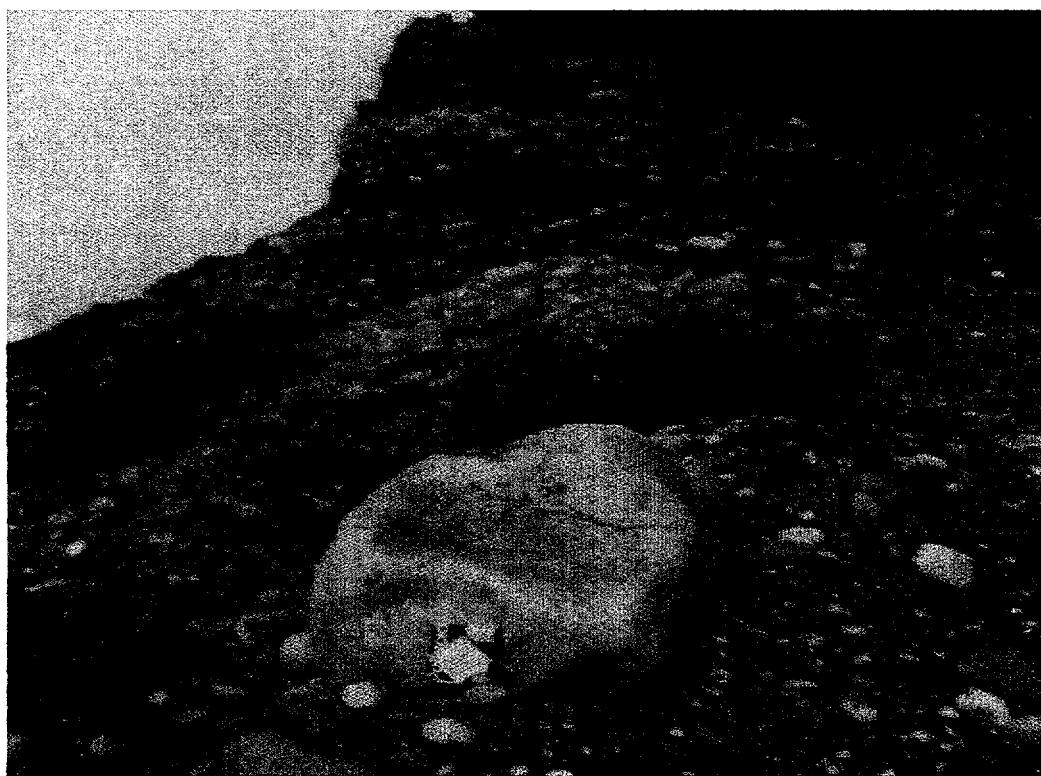


Figure A.3. Excavated pit exposing stratigraphy in heavy cobble region.



Figure A.4. Excavated pit exposing stratigraphy.



Figure A.5. Excavated pit exposing stratigraphy.

Geometry

Surface to surface directional drilling or some acceptable variation of that will require minimum approximate drilling lengths and depths as shown in Figure A.6. Figure A.7 exhibits a 2 X 2 tank farm (total of 4 tanks). This scenario represents the least difficult drilling configuration. Other tank farms are larger in area, having up to 12 tanks in one farm.

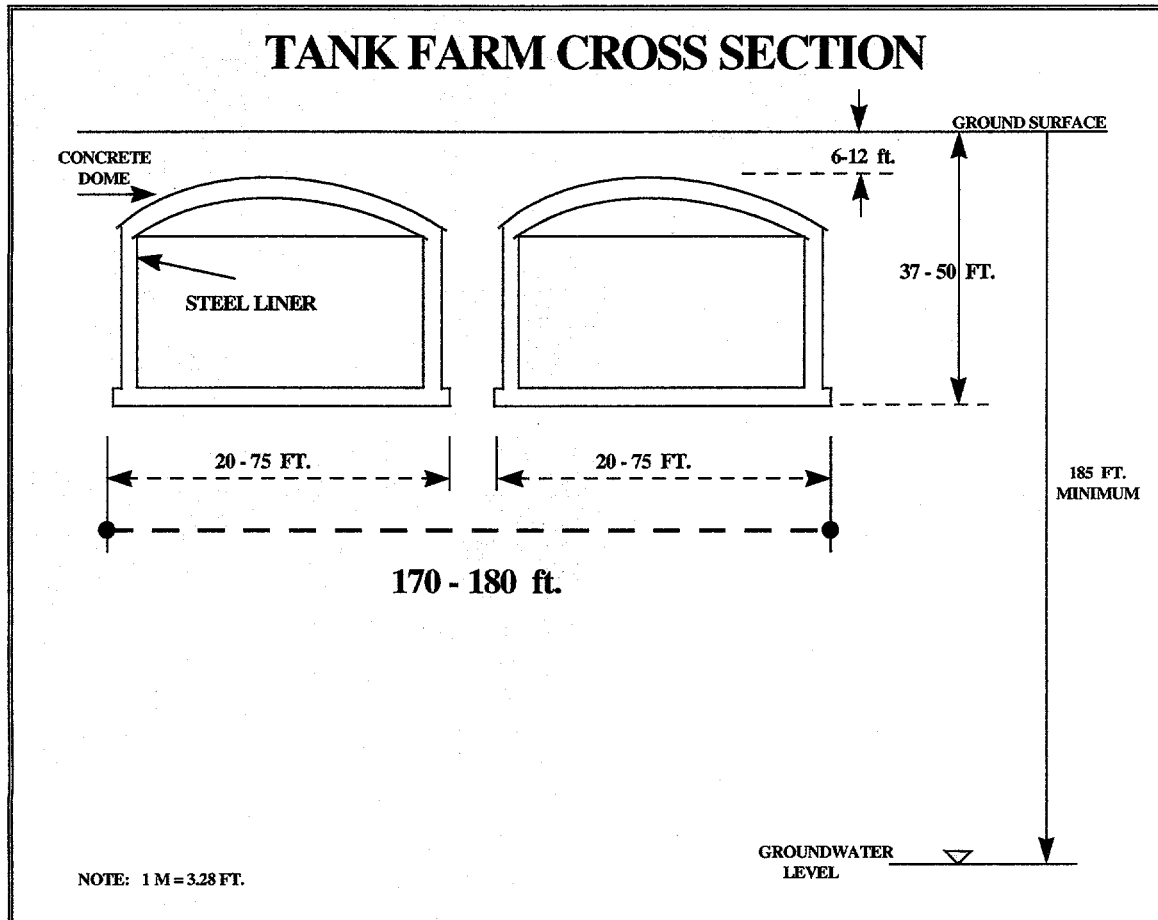


Figure A.6. Elevation view of four tank- tank farm and below ground surface points of interest.

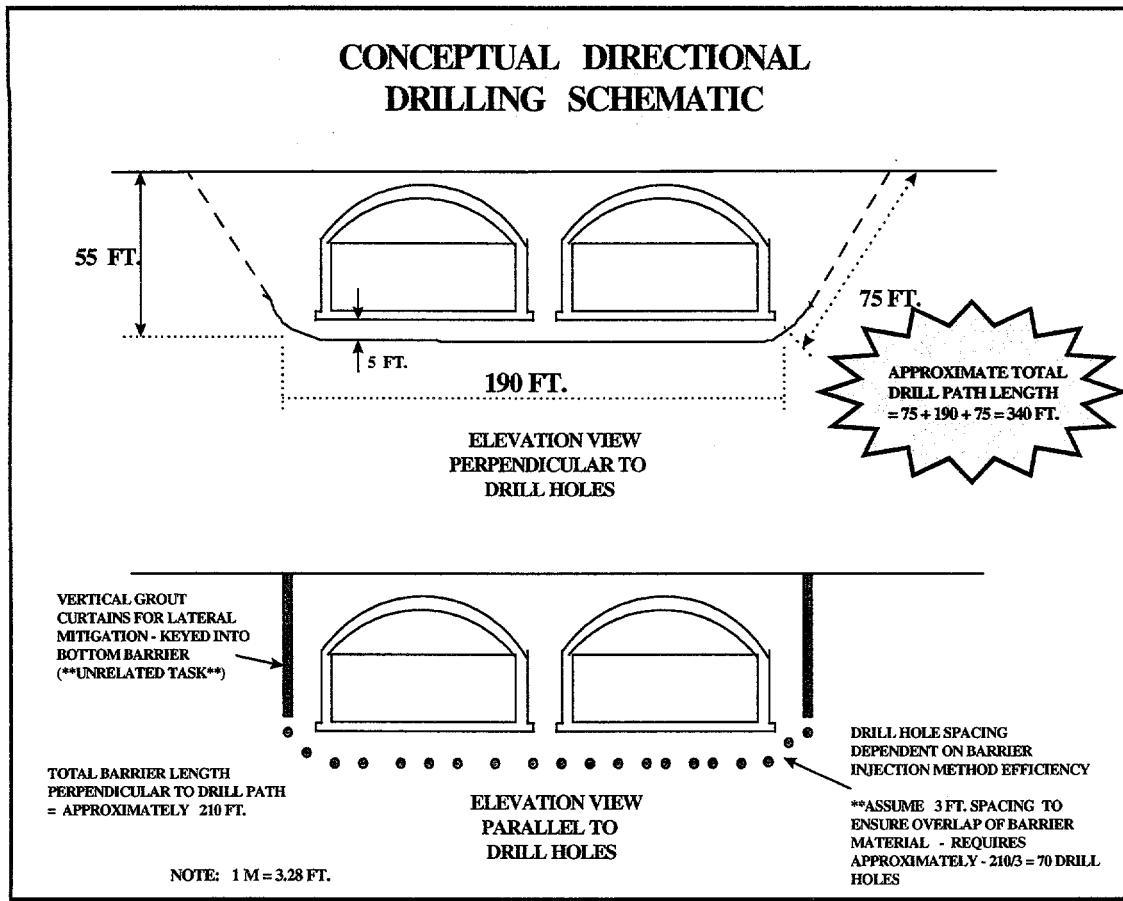


Figure A.7. Profile of conceptual directional drill geometry.

Waste Form

The potential to encounter contaminated soil during drilling operations is possible; therefore, knowledge of the waste characteristics is necessary. SST waste is classified as a mixed waste, i.e., contains both radioactive and hazardous waste. Chemical constituents are primarily sodium hydroxide, sodium salts of nitrate, nitrite, carbonate, aluminate, and phosphate; and hydrous oxides of aluminum, iron, and manganese. The radioactive components are primarily composed of fission products such as strontium-90, cesium-37 and actinide elements such as uranium, plutonium, thorium, and americium.

Summary of Evaluation Criteria

The following questions should be simultaneously considered when evaluating the feasibility and probable effectiveness of directionally drilling beneath a tank farm at the Hanford site:

- (1) Are the physical characteristics of the surrounding soil amenable to directional drilling?
- (2) Are the drilling lengths and depths (geometry) within the limitations of state-of-the-art directional drilling technology?
- (3) What is the three-dimensional accuracy of directional drilling in these soil conditions?

- (4) What mechanism will be used to steer the drill bit (magnetic based systems will be interfered with by steel tanks), and how reliable is it?
- (5) What barrier injection technology (jet or permeation grouting, etc.) is compatible with directional drilling to enable emplacement of a bottom barrier?
- (6) Is it possible to assess contamination type and levels down hole near the drill bit using real time analysis?
- (7) Assuming the drilling lubricant is air, what capability exists for filtering any potential return air/drill cuttings, thereby minimizing potential exposure to workers?
- (8) If drilling is feasible what is a reasonable range of costs/linear ft. of directionally drilled hole?
- (9) Are there any mechanisms available for isolating individual tanks, i.e., emplacement of a horizontal barrier beneath only an individual tank not an entire tank farm ?

Appendix C

CONTACT LIST

The following list is a partial summary of contacts to be made in completion of the technical feasibility assessment of subsurface barrier systems for the Hanford SSTs.

<u>Corporation</u>	<u>Agency Contact</u>
AGEC, Inc.	Steve Phillips (509) 943-2432
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Appendix D: Recommended Future Technical Activities (no prioritization)

Tank Fill

- **Tank Fill Performance Evaluation**
Tank fill accelerated degradation lab-scale experiment - multi-layer vs. monolith characterization and parameter value measurement and scaling for modeling analysis in 1.2.
- **Tank fill fracture-modeling analysis** - compare infiltration between multi-layer (Hanford/SNL) and monolith (SRS) tank fill.
- **Tank Fill Feasibility Study** - study the engineering/operational aspect of tank fill by considering the limited access and interference of ancillary equipment.

Vertical Skirt

- **Vertical Skirt Performance Evaluation**
Perform flow and transport analysis of radionuclide migration (with FEHM or T2VOC codes) to evaluate skirt performance when coupled with interim surface infiltration barrier or for long term infiltration control over entire AX Tank Farm complex
- **Vertical Skirt Emplacement Feasibility**
Evaluate emplacement feasibility of close-coupled vertical skirt (possibly with a horizontal barrier beneath a single tank) to stop current tank leak on the side or on the bottom of a tank

In Tank Getters

- **Validation and mechanistic studies** to quantify the impact of getters on K_d and/or solubility for use in performance assessment
- **Validation of FY98 'success'** for ^{99}Tc and ^{79}Se retention by bone char and reducing grout, respectively, coupled with detailed mechanistic understanding of sorption or precipitation for prediction of Tc and Se immobilization.
- **Laboratory evaluation of U immobilization** (as surrogate for actinides) on apatite or in reducing grouts; these tests would complement thermochemical (REACT) studies
- **Evaluate various reducing grouts**, including the one used by SRS, as a getter for Tc-99 in oxidizing environment
- **Deployment assessment** - assess the engineering aspect of deployment of in-tank getters, including emplacement and mixing.

In Soil Getters

- **Laboratory performance and mechanistic studies** to quantify the impact of getters on K_d and/or solubility
- **Evaluation of ^{99}Tc sorption on hydrotalcite, ^{79}Se sorption or precipitation on Fe-oxyhydroxides and hydrotalcite, and U sorption or precipitation onto apatite or other phosphates**, especially in the presence of competing ions in solution

- Deployment assessment - assess the engineering aspect of deployment of in-soil getters, including emplacement and mixing

Close-coupled Barrier and Reactive Barrier

- Field testing of close-coupled barrier emplacement - to evaluate the feasibility of using close-coupled barrier to contain retrieval leak.
- Field testing of reactive barrier emplacement - to evaluate the feasibility of using reactive barrier to reduce existing contamination migration through sorption.
- Field testing of impermeable infiltration barrier emplacement - to evaluate the feasibility of using infiltration barrier to control infiltration through existing plumes.

Electrokinetic Remediation of Contaminated Plumes

- Laboratory evaluation of SNL-patented electrokinetic remediation technique for Tc-99 removal from existing contamination soils; this technique has been tested for removal of chelated U species and should be suitable for removal of anionic pertechnetate species.

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