

**Waste Tank Organic Safety Project
Organic Concentration Mechanisms Task
FY 1994 Progress Report**

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Summary and Conclusions

The Pacific Northwest Laboratory (PNL),^(a) Waste Tank Organic Safety Project is conducting research to support Westinghouse Hanford Company's (WHC) Waste Tank Safety Program, sponsored by the U.S. Department of Energy's Tank Farm Project Office. The goal of PNL's program is to provide a scientific basis for analyzing organics in Hanford's underground storage tanks (USTs) and for determining whether they are at concentrations that pose a potentially unsafe condition. Part of this research is directed toward determining what organic concentrations are safe by conducting research on organic aging mechanisms and waste energetics to assess the conditions necessary to produce an uncontrolled energy release in tanks due to reactions between the organics and the nitrate and nitrate salts in the tank wastes. The objective of the Organic Concentration Mechanisms Task is to assess the degree of localized enrichment of organics to be expected in the USTs due to concentration mechanisms.

This report describes the progress of research conducted in FY 1994 on two concentration mechanisms of interest to the tank safety project: 1) permeation of a separate organic liquid phase into the interstitial spaces of the tank solids during the draining of free liquid from the tanks; and 2) concentration of organics on the surfaces of the solids due to adsorption.

Three experiments were conducted to investigate permeation of air and solvent into a sludge simulant that is representative of single-shell tank sludge.

The first experiment, investigating air permeation into the sludge, was conducted to evaluate test methods and obtain preliminary data on the desaturation of the solids. The results of the experiment indicate that a sludge layer that is 2.4 m in thickness would remain saturated even after all free supernate has been removed from above the sludge layer using a drain located at the bottom of the sludge. Instead, as more supernate is removed, the sludge consolidates to a volume equal to about 60% of its initial volume to maintain saturation. The remaining water in the sludge after steady state is achieved would account for about 26 wt% of the sludge.

The second experiment investigated permeation of the sludge by a 50 vol% tributyl phosphate (TBP) in dodecane solvent mixture. The sludge interstitial liquids were conditioned to approximate the pH and salt strength of the supernate in Tank C-103. The results of the experiment indicate that a sludge layer that is 3.5 m or more in thickness would become desaturated in supernate after all free supernate has been removed from above the sludge layer using a drain located at the bottom of the sludge. Instead, as more supernate is removed, a portion of the supernate in the sludge is displaced by the solvent. In this experiment, the data also indicates that the volume of the sludge located 5 m above the bottom of the sludge layer would consolidate to about 67% of its initial volume and that 13% of the final volume would consist of solvent.

The third experiment is similar to the second experiment except the sludge is conditioned to contain soluble salts at a pH > 12 and interstitial liquid salt strength 10 times that in the previous

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experiment. Results to date suggest that permeation occurred at a much lower value than in the previous experiment with 70 vol% of the initial sample drained as supernate at conditions representative of sludge 2.3 m above a drain.

The permeation behavior of air and solvent into the sludge simulant can be explained by the properties of the fluid pairs (air/supernate and solvent supernate) and the sludge.

One important fluid property is the interfacial tension between the supernate and either the solvent or air. In general, the greater the interfacial tension between two fluids, the more difficult it will be for the air or solvent to displace the supernate during dewatering of the sludge. The interfacial tension of the air/supernate fluid pair is on the order of 70 mN/m whereas the air/solvent interfacial tension will be much lower ranging from 7 mN/m to 45 mN/m depending on the solvent. The interfacial tension of supernate and solvent consisting of 50% TBP in dodecane was not measured but is expected to be near the lower end of this range. For example, the interfacial tension between TBP and water is 7.4 mN/m to 8 mN/m whereas the interfacial tension between TBP saturated water and air is 42.1 mN/m.

The ability of either air or solvent to displace supernate in a porous solid also depends on the properties of the solid. In general, it is easier for air or solvent to displace supernate in a relatively coarse material such as sand, as opposed to a material such as silt. The sludge simulant has a particle size distribution closer to that of silt that can maintain saturated conditions at heights of more than 3 m above a drain.

Another property of the sludge in the USTs is that it is not fully consolidated due to the colloidal behavior of the sludge particles and will shrink as it is drained. This allows the sludge to maintain saturation as supernate is drained until enough contact between adjacent particles occur to form a rigid, porous matrix.

Research conducted on the adsorption mechanism has been limited primarily to the development of test methods. Preliminary evaluation of the surface areas of saltcake and sludge simulants indicate that saltcake has too low a surface area ($0.39 \text{ m}^2/\text{g}$) to achieve significant adsorption of organics on its surfaces. Sludge simulant containing only insoluble salts had a surface area of up to $149 \text{ m}^2/\text{g}$, which would be sufficient to achieve significant adsorption.

Test methods for conducting adsorption of organics on the sludge simulant are being developed. Sodium salts of ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) will be evaluated in the first set of experiments using gibbsite and goethite as the solids. Both of these minerals have been identified in waste samples from the single-shell tanks. The results of ongoing experiments with these materials will be reported in the FY 1995 progress report for this task.

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Introduction

The Pacific Northwest Laboratory (PNL), Waste Tank Organic Safety Project is conducting research to support Westinghouse Hanford Company's (WHC) Waste Tank Safety Program. This work is sponsored by the U.S. Department of Energy's Tank Farm Project Office. The goal of PNL's project is to provide a scientific basis for analyzing organics in the Hanford Site's underground storage tanks (USTs), and for determining whether the organics in the tanks are at concentrations that pose a potentially unsafe condition. Part of this research is to determine what organic concentrations are safe by conducting research on organic aging mechanisms and waste energetics to assess the conditions necessary to produce an uncontrolled energy release in tanks due to reactions between the organics and the nitrate and nitrate salts in the tank wastes. The objective of the Organic Concentration Mechanisms Task is to assess the degree of localized enrichment of organics expected in the USTs resulting from concentration mechanisms.

In FY 1992, PNL conducted an initial evaluation of physical and chemical processes that could lead to significant localized concentrations of organic waste constituents in the USTs (Gerber et al. 1992). Four of the concentration mechanisms evaluated in the study were identified for further study:

1. Permeation of a separate organic liquid phase into the interstitial spaces of the tank solids during the draining of free liquid from the tanks.
2. Concentration of organics on the surfaces of the solids caused by adsorption.
3. Phase separation of organics from a high ionic strength aqueous solution into a solid or organic phase in a mechanism referred to as salting out.
4. Degradation of organic resins.

Research was initiated in late FY 1993 to evaluate the surface area and particulate size distribution of single-shell tank (SST) sludge and saltcake simulants, used for this task. The objective of the research performed in FY 1994 was to develop test methods for investigating the permeation and adsorption mechanisms using sludge and saltcake simulants and to obtain preliminary data on the significance of these mechanisms.

Progress of research conducted in FY 1994 for the Organic Concentration Mechanisms Task is described in this report. Research was conducted and reported for only the first two of the four mechanisms identified for further study: 1) permeation of solids by a separate organic layer, and 2) sorption of organics onto the surfaces of sludge solids.

Permeation of Solids by a Separate Organic Layer

The permeation of a separate organic liquid phase into the tank sludge is a potentially significant partitioning mechanism. Many of the SSTs have been, or are currently in the process of being drained of free liquids by pumping supernate from the bottom of the tanks. Some of these tanks contain(ed) a separate organic layer, such as the Purex solvent composed of tributyl phosphate (TBP) and normal paraffinic hydrocarbons (NPH [C_{10} to C_{14}]), floating on the surface of the supernate in the tanks. As the tanks are drained, the solvent eventually comes into contact with the tank solids and has an opportunity to permeate into the solids as the dewatering continues. The remaining drained solids may contain a mixture of both organic and aqueous phases depending on the ability of the organic to displace the aqueous phase. Since the porosities of particulate solids typically range from about 20% to 60% of their bulk volume, the organic phase could occupy a significant fraction of the solid phase.

Ideally, the sludge layer in the tanks maintains its shape, as shown in Figure 1(a), while the supernate is drained from the bottom of the tank, maintaining a flat, horizontal surface for the organic phase to contact. But in fact, some solids nearest the pump are removed along with the liquid during draining, creating a depression on the sludge surface around the pump [see Figure 1(b)], which provides a direct path for free supernate and solvent to drain from the sludge surface to the pump. In addition, however, the surface of the sludge fractures immediately after the free supernate is removed because the sludge begins to consolidate. These cracks provide areas for isolated pockets of solvent to be trapped at or near the surface during draining.

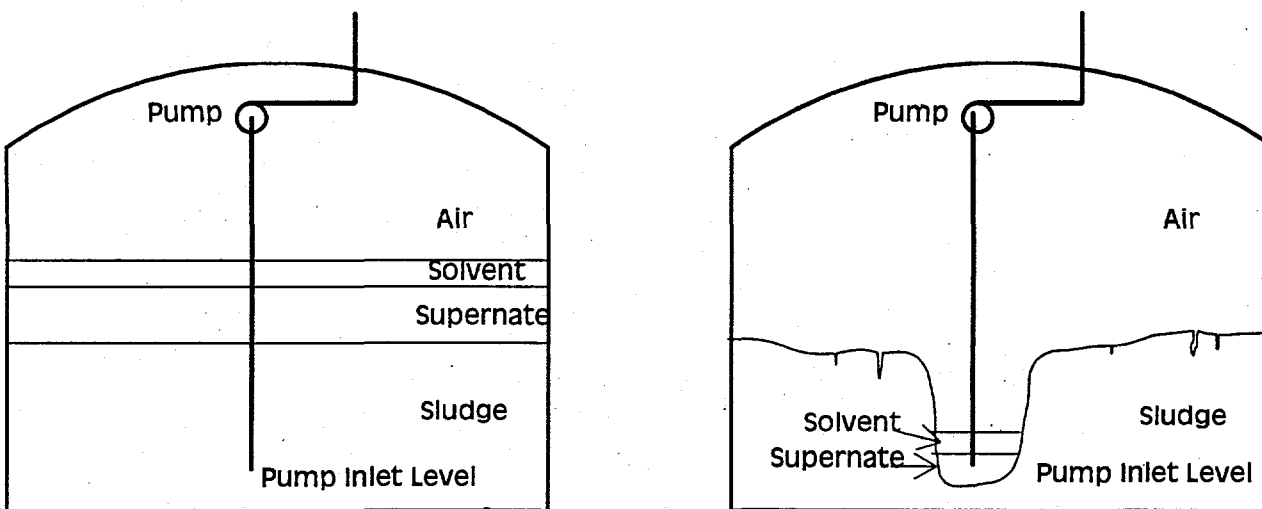


Figure 1. (a) Ideal Profile of Sludge and Liquids in Tank. (b) Profile of Drained Tank

Mechanism for Solvent Permeation

The permeation behavior of a solvent into a porous material saturated with supernate is very similar to that between air and supernate. The principle differences are these inherent in the properties of the air and solvent and the added pressure applied against the water in the porous material due to the height of the solvent above the supernate phase in the solid.

Figure 2 shows a typical moisture profile for water in a porous solid resting in a pool of water. The total specific energy potential (energy available to do work per unit mass) at any point in the solid above the water level in the pool is defined by Freeze and Cherry (1979) as

$$\Phi = gz/g_c + (P_i - P_a)/(\rho) \quad (1)$$

where Φ = total potential (ft-lb_{force}/lb_{mass}), (or just ft by equating unit weight and mass).

g = gravity (32.17 ft/sec²)

z = height above a reference point of zero matric potential

g_c = gravitational constant (32.7 ft-lb_{mass}/lb_{force}-sec²)

P = pressure measured at a point in the solid (either hydraulic or tension pressure)

P_0 = reference pressure at height $z = 0$

ρ = density of the fluid.

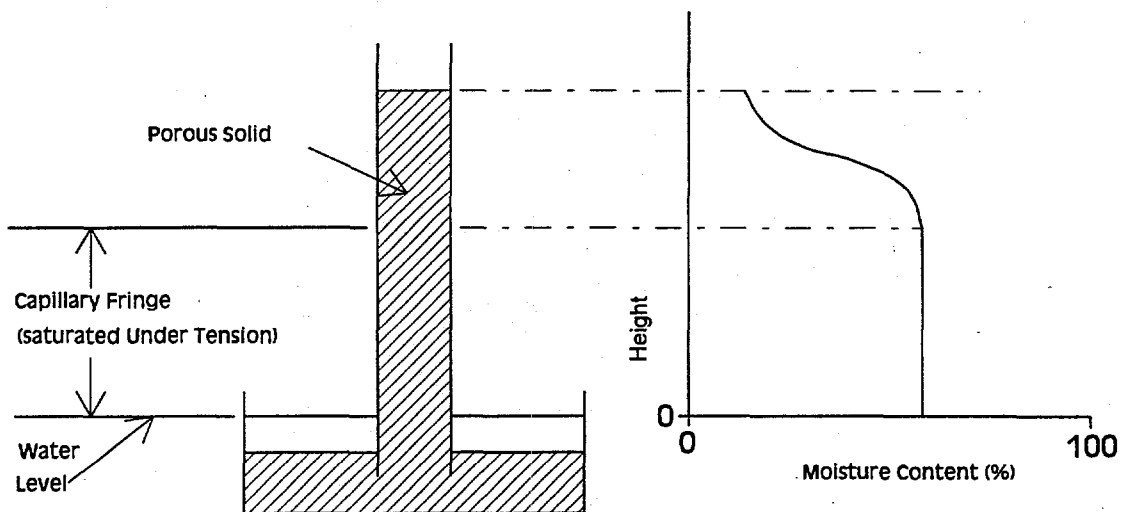


Figure 2. Moisture Profile of a Porous Solid in a Pool of Water

The first term on the right of equation (1) is the gravitational potential due to the elevation of the point of interest above a reference point, such as the pump inlet in a UST. The second term, the matric potential due to the tension exerted on the liquid in the pores due to its surface tension, has a negative value (i.e., a measure of the pull of the surface tension against gravity as water undergoes a capillary rise). Other terms associated with energy potential, such as chemical energy, are not considered.

The absolute value of the term $(P_1 - P_a)$ represents the capillary pressure of the supernate at the air/supernate interface. The value of the capillary pressure above which air can enter the pores of the solid is called the air entry pressure (bubbling pressure) of the supernate for that particular material. The capillary pressure is also the pressure that would be measured by a manometer if the reference pressure for the manometer is same as the air pressure.

The height of the capillary rise (in which all pores remain saturated under tension) can be related to matric potential at equilibrium using equation (1) and by setting the total energy potential to zero. As the capillary pressure increases (the matric potential becomes more negative) at points above the capillary fringe, air enters the pores and displaces a portion of the capillary water and the porous material becomes progressively less saturated at equilibrium as shown in Figure 2. Eventually, at very high capillary pressure, it reaches a residual saturation level where the remaining water is immobilized along the solid surfaces.

As previously discussed, the behavior of an air/supernate system and a solvent/supernate system are essentially the same if the depth of the solvent is negligible. For a solvent/supernate system, the solvent entry pressure can be equated to the air entry pressure (i.e., that capillary pressure above which the solvent would enter the pores of the solid). The difference between the values of the solvent entry pressure and the air entry pressure is largely due to differences in values of the interfacial tension for the solvent/supernate fluid pair and the air/supernate fluid pair. The capillary rise for supernate in an oil/supernate system is less than that for an air/supernate system because the interfacial tension of the fluid pair in the former system is lower. Values for surface tension of selected liquids are listed in Table 1.

Table 1. Interfacial Tension of Various Fluid Pairs

Fluid Pair	Interfacial Tension (mN/m)	Reference
Air/water	70.79	Lenhard and Parker (1988)
Air/dodecane	24.9	Riddick and Bunger (1970)
Air/Soltrol	24.23	Lenhard and Parker (1988)
Soltrol/water	44.21	Lenhard and Parker (1988)
Air/TBP	27.59	Burger (1984)
Air/water-saturated TBP	42.1	Burger (1984)
Air/TBP saturated Water	35.6	Burger (1984)
TBP/water	7.4 - 8.0	Burger (1984)
TBP/5M HNO ₃ (Aq)	8.7	Burger (1984)
Air/8.9M HNO ₃ (Aq)	68.3	Dean (1973)
Air/2.8M HNO ₃ (Aq)	70.9	Dean (1973)
Air/7.0M NaNO ₃ (Aq)	80.3	Dean (1973)
Air/5.0M NaOH (aq)	83.1	Dean (1973)

Several things can be inferred from the surface tensions of various pairs. First, it is generally assumed that the surface tension of a pair of immiscible liquids (water/dodecane) is approximately the difference of the air/liquid surface tensions of the two liquids). However, it can be seen that an organic such as TBP, which is sparingly soluble in water (0.39 g/L) and nitric acid (0.82 g/L in 5.2M HNO₃), produces a significantly reduced surface tension of the liquid pair compared to the air liquid values. However, the solubility of TBP in salt solutions is decreased due to salting out, which may make the behavior of the TBP/aqueous solution pair more like a truly immiscible pair. The presence of other polar solvents in the TBP could offset this, though, because most polar solvents in water reduce the air/liquid surface tension (Dean 1973). The presence of salts also appears to increase the surface tension of the aqueous solution/air pair. It may be inferred from these values that it is possible that the oil will displace the water in the solids relatively easily but that air may not be able to displace the water in the solids.

The physical properties of the sludge solids are also important because they also affect the magnitude of the capillary rise for any fluid pair. The magnitude of the capillary rise in tank sludge is important because it determines whether the sludge height above the inlet pump is greater than the capillary rise leading to conditions of desaturation in respect to air or solvent.

Figure 3 shows that the capillary rise can range from a few centimeters for relatively coarse material to as much as 5 m for very fine material (clay particle diameters range from 1 to 20 μm). The type of solid is also important if the supernate contains organic constituents that can adsorb on the particle surfaces and reduce their hydrophilic character.

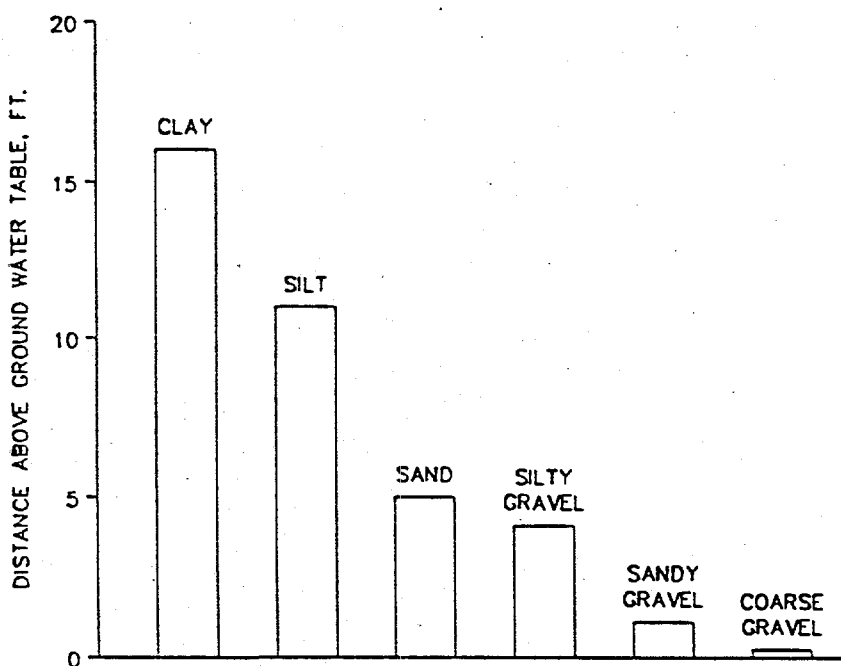


Figure 3. Capillary Rise for Various Soils

Another property of the sludge in the USTs is that it is not fully consolidated due to the colloidal behavior of the sludge particles and will shrink as it is drained, maintaining saturation as supernate is drained until enough contact between adjacent particles occur to form a rigid, porous matrix.

Test Methods

The following sections describe the preparation of simulants, experimental apparatus, and procedures used in conducting solvent permeation tests.

Preparation of Materials

The simulant used in this study is very similar in composition to one that was used by Elmore, Colton, and Jones (1992) to investigate the effects of thermal aging on chemical speciation in the sludge simulant. Their recipe represents an average of SST compositions for tanks that have been previously characterized. Table 2 shows the composition of the simulant used by Elmore et al. (1992).

The recipe used in this research is described in the Appendix. It differed from that for the earlier simulant because container A of the recipe was raised to a pH of 12 following the addition of the chemicals, and the combined mixture of the three containers (step 5) was neutralized to a pH of 10 by bubbling CO₂ through the solution before washing. These modifications were done in order to cause the aluminum species to remain dissolved until all containers were mixed and to produce carbonate compounds. Also, the silicon was added in the form of Na₂SiO₃ instead of a 30% SiO₂ solution to avoid adding silica in colloidal form. The stock solution used in this study was not analyzed for chemical composition, but should be similar to the composition of the insoluble solids used in the aging studies shown in Table 2.

Table 2. Composition of Simulated SST Insoluble Solids Used in Aging Studies (Elmore, Colton, and Jones 1992)

Component	Dry Wt %
AlOOH, Al(OH) ₃	38
BiPO ₄	10
FeOOH, FePO ₄	15
SiO ₂	17
Organic Salts	2
Na ₂ SO ₄	2
Ce(OH) ₃	2
Ca(OH) ₂	1
Cr ₂ O ₃ , Cr(OH) ₃	1
Na ₂ O, NaOH	1
La(OH) ₃	1
Oxides, hydroxides, phosphates (< 1% each of Pb, Mg, Ag, Zn, Mn, Zr, Sr) and water of Hydration	10

A sufficient quantity of simulated saltcake with the composition shown in Table 3 was added to the wet insoluble solids to produce a stock solution consisting of 45% saltcake and 55% sludge slurry. Most of the saltcake appeared to dissolve in the slurry; however, the exact quantity was not determined.

Table 3. Composition of Simulated SST Salt Cake

Component	Dry Wt %
NaNO ₃	75.2
NaNO ₂	4.8
Na ₂ SO ₄	2.4
Na ₂ CO ₃	4.3
NaAlO ₂	4.3
Na ₃ PO ₄	4.6
NaOH	4.4
Total	100.0

A stock solution of supernate simulant with the composition shown in Table 4 was also prepared for these experiments. This solution was used at full strength or diluted by a factor of 10 and neutralized to a pH of 10 as described in the procedure.

Table 4. Composition of Supernate Simulant

Component	<u>M</u>
NaNO ₃	2.94
NaAlO ₂	0.46
NaNO ₂	0.20
Na ₂ SO ₄	0.05
NaHCO ₃	0.60
KNO ₃	0.08
Na ₃ PO ₄	0.01
NaF	0.01
NaOH	1.26
Total	5.64

Properties of Sludge Simulant

A nitrogen adsorption isotherm was obtained using the Brunauer, Emmett, and Teller (BET) method, for an archived sludge simulant sample based on the same recipe, to provide an indication of the surface areas of the sludge and salt material. Approximately 1 g of sludge, or 5 g of saltcake, prepared as shown in Table 5, was placed in a sample holder of a Micromeritics ASAP 2000 chemisorption system and further degassed under a vacuum at 100°C. This was necessary to ensure that the sample surface was free of all volatile material. The nitrogen isotherm was obtained at 25°C and

Table 5. Description of Simulant Samples Analyzed for Surface Area

Sample No.	Method of Preparation	Surface Area (m ² /g)
1A	SST simulant saltcake: simulant supernatant dried at 60°C.	0.39
1B	SST simulant solids (decant-dry): decanted solids evaporated to dryness at 60°C (approximately 45% saltcake, 65% insoluble solids).	30
1C	SST simulant solids (filter-dry): solids filtered to near dryness and then dried at 60°C.	74
1D	SST simulant solids (decant-dry-wash-dry): decanted solids dried at 60°C, then washed in three stages, followed by drying at 60°C.	126
1E	SST simulant solids decant-wash-filter-dry): decanted solids washed using three stages of mixing with an equal volume of distilled water and filtered. Filtered solids dried at 60°C.	149

the data for BET surface area calculated automatically. Table 5 summarizes the surface area data obtained for samples. It can be seen from data that the insoluble sludge samples that were washed (samples 1D, 1E) had relatively high surface areas ranging from 78 m²/g to 155 m²/g. By comparison, the salt cake sample had surface areas of 0.39 m²/g. The low saltcake surface areas are not totally unexpected, considering the tendency of the nitrate and nitrite to form relatively large crystals. The values obtained for the saltcake simulant would be consistent with crystals about 1 μm to 10 μm in diameter.

A particle size distribution for samples of the sludge simulant was obtained using a Microtrac full-range particle analyzer. The simulant was analyzed 5 times and the data averaged. The particle size distribution is shown in Figure 4, which illustrates that the SST simulant had a bimodal in distribution with an average particle size of 7.84 μm, but with local maximum concentrations at about 1.3 μm and 15 μm.

The particle size distribution for the simulant is fairly similar to that of an actual tank waste sample presented by Elmore et al. (1992), except the actual waste tank sample did not show a pronounced peak at 1.3 μm. The difference is probably a result of differences in composition and because the actual sample had aged for many years.

Experimental Apparatus

The experimental apparatus used to conduct the solvent permeation experiments is shown in Figure 5. The apparatus is based on the tension table design used to measure water retention in soils (Carter 1993). This apparatus is also referred to as a hanging water column in some references. The filter consisted of a standard two-piece 47-mm microfilter and a supported plain 0.1-μm nylon filter

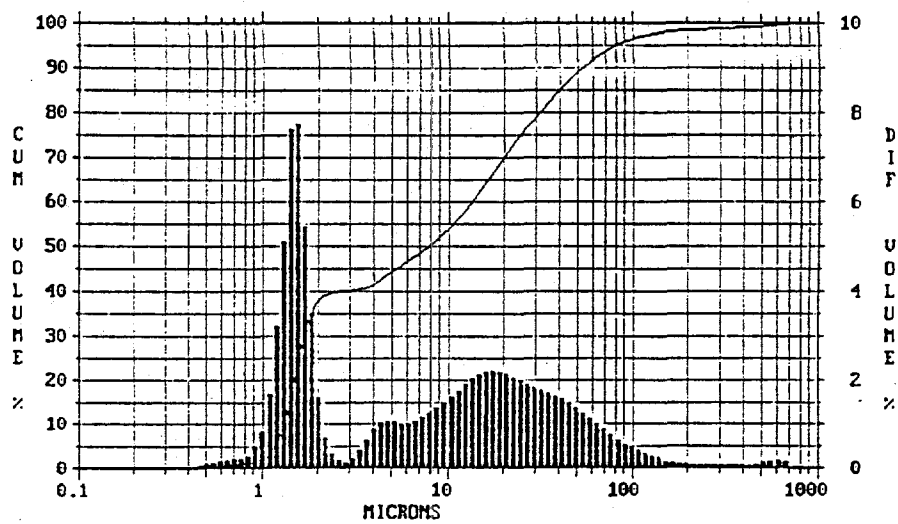


Figure 4. Particle Size Distribution of SST Simulant Solids

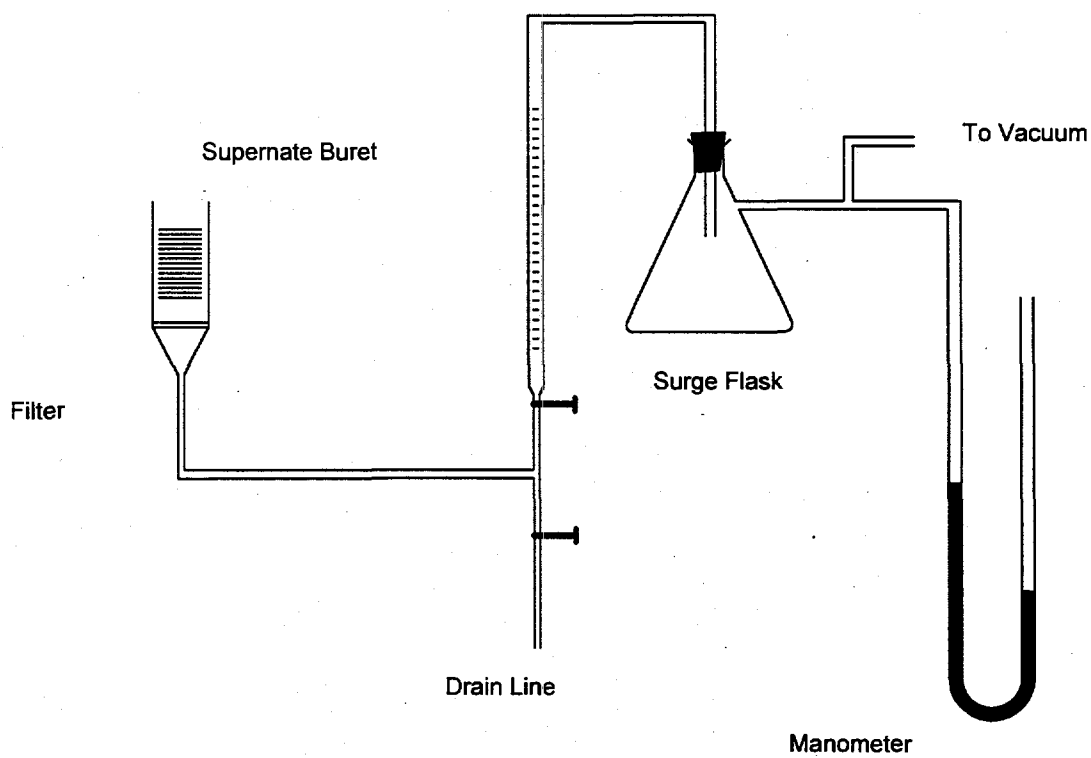


Figure 5. Diagram of Experimental Apparatus for Solvent Permeation Experiments

membrane to retain the sludge simulant and solvent. The nylon filter membrane is a hydrophilic material that serves as a porous barrier to the solvent. The graduated scale on the outside of the filter was used to measure sludge volume at the beginning of the experiment.

The matric potential at the filter is established by applying a vacuum to the bottom of the filter. The vacuum can be correlated to an equivalent height of supernate above the pump inlet in the sludge in a SST. Water displacement is measured in the buret, with a correction applied to account for differences in the height of the supernate in the buret and the average height of the sample.

Experimental Procedure

Three experiments were conducted in FY 1994 to develop test methods and to obtain preliminary data for solvent permeation into the sludge simulant. The first experiment was conducted without solvent to determine the adequacy of the apparatus and test methods and to obtain data on a air/supernate system, which was used to interpret the other tests.

In the air/supernate system, the system was first backfilled to the buret and the bottom of the filter with full-strength supernate to serve as an incompressible fluid between the filter and the buret. Sludge simulant was mixed thoroughly before being added to the filter to resuspend the settled solid. The sludge was dewatered by applying a vacuum to the bottom of the filter. The sludge simulant settled at a relatively fast rate during dewatering, producing a temporary, distinct free supernate phase above the solids. When the last of the free supernate was removed from the surface, the volume of the sludge was measured. The vacuum was adjusted to the desired value and supernate removal measurements were recorded over a period of time using the buret. The measurements were continued until the rate of supernate removed was less than 0.05 ml/day. Then the total amount of supernate drained was recorded, the vacuum reset to a higher value, and measurements taken as before.

At the completion of the experiment, the sludge sample was removed from the filter and weighed, and the final volume of the sludge was determined by displacement of water in a graduated 100 ml beaker. The sample was next dried for 24 hr at 105 °C and weighed. Then it was rinsed using deionized water to remove soluble salts, dried again for 24 hr and reweighed.

The other two experiments were conducted using a solvent mixture containing 50% (by volume) TBP in dodecane. Prior to conducting these experiments, the solvent and supernate of the desired strength and pH were mixed and stirred for at least 3 days to equilibrate the two phases before separating them for the experiment. The equilibrated supernate was then mixed in equal volumes with the sludge simulant for over 24 hr to allow any dissolved organics to adsorb onto the solids. The apparatus was then backfilled with unequilibrated supernate of the desired strength and pH, and the sludge was added to the filter. When the free supernate in the filter approached the level of the settled solids, as previously described, an additional volume of equilibrated supernate equal to the volume of settled solids was added to the filter, and twenty ml of solvent was then layered on top of the supernate. Sample dewatering continued until the solvent/supernate interface contacted the entire surface of the settled solids. The sludge volume was recorded and the experiment conducted as described for the previous experiment. At the completion of the experiment, displacement measurements were made as in the previous experiment. In addition, a portion of the sample of sludge simulant was extracted with methylene chloride to extract any dodecane and TBP present and the extract analyzed using gas chromatography-mass spectrometry (GC-MS).

The main difference between the second and third experiments was the strength of the supernate used. The second experiment was conducted using a 10X dilution of the supernate adjusted to a pH of 10. This solution was made to approximate the Tank C-103 supernate composition. Tank C-103 is known to contain a separate organic layer floating on supernate that, in turn, overlies a sludge layer. Table 6 compares the composition of the dilute supernate simulant and the supernate in Tank C-103 (Pool 1994). While the individual salts are at different values for the two supernates, the total ionic strength, which directly affects the solubility of the solvent, is nearly the same.

Table 6. Comparison of Supernate Simulant and Tank C-103 Aqueous Phase

Component	Supernate Simulant (10X Dilution)	Tank C-103 Aqueous Phase
	<u>M</u>	<u>M</u>
NaNO ₃	0.294	0.036
NaAlO ₂	0.046	---
NaNO ₂	0.020	0.464
Na ₂ SO ₄	0.005	0.043
NaHCO ₃	0.060	---
KNO ₃	0.008	---
Na ₃ PO ₄	0.001	0.023
NaF	0.001	0.054
NaOH	(pH 10)	(pH=10)
Total	0.564	0.631

Experimental Results

The following sections describe the results of the solvent permeation experiments conducted in FY 1994.

Air/Supernate System

The air/supernate experiment was conducted to obtain supernate desaturation data as a function of matric potential using the SST sludge simulant. One purpose of this experiment was to verify the adequacy of the microfilter system using a 0.1- μ m nylon filter membrane, and to gain operating experience with the system before investigating a purex solvent/supernate system. Another purpose of the experiment was to obtain data on the expected behavior of the sludge as the capillary pressure was increased and to determine whether air entered the sludge.

In general the microfilter system worked satisfactorily for the air/water system. However, the sludge had a tendency to shear as it consolidated during the initial stages of dewatering. The shearing action created a cylinder of sludge about the diameter of the filter membrane surface, as evidenced by the observance of a circular crack on the surface of the sludge. The cylinder of sludge was surrounded by sludge that was resting on the shoulder of the microfilter, where its diameter increased from about 42 mm to about 75 mm. This separation created a potential for the sludge surrounding the cylinder to lose a connective path to the filter and thus cease to desaturate. Connectivity was restored during the experiments by periodically healing the crack. Once the sludge had decreased to

about 78% of its initial volume, it was sufficiently stiff so that the sludge could be pushed away from the shoulder using a spatula. While this appeared to halt the effects of the shoulder, it was no longer possible to quantitatively monitor further shrinkage of the sludge and final volume had to be determined after retrieving the sample from the microfilter. At the beginning of the experiment (after the sludge was first dewatered), the approximate volume of the sludge was 76 ml. The vacuum was then applied in three steps to the sample over a period of approximately 175 hr. The last step was maintained for only 36 hr, but supernate removal was only 1.06 ml over that period. The vacuum values correspond to matric potential of (0.59 m, 1.7 m, and 2.4 m). The total volume of liquid withdrawn from the sample was 27.5 ml. The final volume of the sample was 45 ml. The difference between the volume of liquid withdrawn (27.5 ml) and sample volume change due to shrinkage (31 ml) is within the accuracy of the sample volume measurements. These measurements indicate that air did not permeate the sludge.

After completion of the experiment, sample weight measurements were made before and after drying and following rinsing to remove soluble salts. The wet and dry sample weights were 61 g and 45 g, respectively, indicating a final water content of 26 wt%. The dried sample weight following rinsing was 20 g. The salt content of the sample was well above that associated with the interstitial liquid indicating that the sample retained most of its inventory of saltcake during the experiments. It was also noted that the sample continued to show evidence of shrinking during drying but before rinsing, because its final bulk volume after drying and grinding was approximately 30 ml.

Solvent/Dilute Supernate Experiment

The second experiment was conducted to evaluate the permeation of an SST sludge simulant with solvent under conditions comparable to those recently characterized for Tank C-103 (see Table 6). The solvent was 50% (by volume) TBP in dodecane. The supernate simulant was a 10X dilution (adjusted to a pH of 10) of the SST supernate simulant stock solution prepared earlier. This dilution and pH approximate the electrolytic strength and pH found in Tank C-103 as shown in Table 6. The microfilter was modified for this experiment to eliminate the shoulder on the reservoir.

Table 7 lists the various values of matric potential evaluated, the time spent at each step, and the amount of supernate withdrawn at equilibrium. Equilibrium was defined as the point in time when the volume of supernate removed was less than 0.5 ml/day or 300 hr. The last matric potential value was not taken to equilibrium, which was estimated to be about 0.75 ml greater at 300 hr.

Observations of the sludge sample during the steps up to a matric potential of -3 suggest that all of the supernate withdrawn was accounted for by a similar decrease in the sludge volume due to consolidation. This is supported by the fact that equilibrium was reached after about 100 hr. For steps evaluated from 11.3 ft to 16.2 ft, the time to reach equilibrium increased to 300 hr with about 0.25 ml/day of supernate being removed at termination. The total volume withdrawn over 100 hr for these steps was also found to be greater than for the previous steps.

During the initial consolidation of the sludge, the sample initially fractured, as expected, producing vertical cracks exposing solvent to the membrane. The sample adhered to the filter reservoir walls, however, and eventually formed a horizontal crack as the sample further consolidated.

**Table 7. Matric Potential Steps Evaluated in Solvent Permeation Experiment
Using 10X Diluted Supernate**

Matric Potential, m (supernate)	Time, hr	Supernate Volume Drained, ml
-0.4	89	3.12
-0.8	115	1.27
-1.8	101	2.12
-2.5	67	0.93
-3.0	98	1.17
-3.5	331	3.11
-4.3	301	3.20
-5.0	201	2.26

At the conclusion of the experiment, the free solvent was recovered from the filter system and the volume of the sludge sample was measured by displacement in water. During sample removal from the filter, it was apparent that the horizontal cracking may have resulted in the loss of a connective path for the supernate to drain from the upper portion of the sample and the sample resting on the filter. The solvent recovered from the filter system accounted for all but 3 ml of the solvent added at the beginning. This suggests an upper limit of 3 ml of solvent permeated into the sludge, and would account for about 13% of the final sludge volume of 23.5 ml. The initial sludge volume at the time the solvent contacted the sludge surface was 35 ml, which indicates a volume decrease of 11.5 ml due to consolidation during the experiment. Total supernate removed from the sample was 15 ml and exceeded the sludge volume decrease change by 3.5 ml.

Based on the above results, it appears that solvent did permeate the sludge and that it likely began during dewatering to occur at a matric potential of -11.3 ft. It also appears that further consolidation occurred during dewatering at steps of higher vacuum as the matric material was made more negative, accounting for about 65% of the supernate removed while solvent permeation was taking place.

Solvent/Supernate System

The third experiment is being conducted using full-strength supernate, because the earlier test results using air and full-strength supernate suggested that the soluble salts would be retained in the sludge and would likely increase the average particle size of the sample. The test was conducted in the same manner as the previous experiment except that the inside of the microfilter reservoir was first sprayed with dry teflon lubricant to reduce adhesion of the sludge to the reservoir walls. This lubricant consists of tetrafluoroethylene telomer (TFE) solids, 1,1-dichloro-1-fluoroethane, and isopropanol. The latter two agents have a low boiling point and flash rapidly. The total sludge sample was only 60% of the volume of the sludge sample in the second test. Also the first vacuum setting shown in Table 7 was much higher than that in the second test. Some of the teflon lubricant showed a tendency to pull away from the reservoir wall when the sludge was first added, and the sample adhered to the reservoir walls. The bulk of the sample also pulled away from the wall leaving a thin annulus of sludge on the wall. The bulk sample continued to consolidate without forming any vertical cracks, but the sludge on the wall developed a checking pattern as it consolidated.

Table 8 lists the two values of matric potential evaluated to date, the time spent at each step, and the amount of supernate withdrawn at equilibrium. The criteria for equilibrium was the same as in the second test.

Table 8. Matric Potential Steps Evaluated in Solvent Permeation Experiment Using Full-Strength Supernate

Matric Potential, m (supernate)	Time, hr	Supernate Volume Drained, ml
-1.8	310	11.8
-2.2	336	3.61

The initial volume of the sludge at the beginning of the experiment was 22 ml. It can be seen that the supernate removed to date accounts for about 70% of the initial sample volume. This suggests that permeation of the sludge by solvent has occurred at less negative matric potential values than occurred during the previous experiment.

Observations made during these steps showed consolidation of the sludge as was expected. In this case, however, the sludge pulled away from the walls of the filter reservoir, leaving only a small amount of sludge on them. There were no fractures in the top of the sludge monolith that pulled away from the walls.

Sorption of Organics Onto the Surfaces of Sludge Solids

Sorption refers to preferential partitioning of organics between an aqueous liquid and the surface of solids in equilibrium with the liquid, due to chemical interaction between the organics and the solid surface. Adsorption involves a number of mechanisms including ion exchange, physical adsorption due to Van der Waals forces of attraction, specific adsorption involving the formation of partially covalent bonds between organic anions and the solids constituents, and chemisorption due to chemical reactions between the organic and the solids. In addition, the organics adsorbed onto the surface can attract other organics in solution to form admicelles, thus increasing the total concentration of organics on the surfaces.

The maximum amount of total organic carbon (TOC) in the tank saltcake and sludge due to sorption depends on the specific surface area of the solids, the surface area on the solids occupied by organic molecules at maximum packing, and the number of carbons in the organic compounds. Gerber et al. (1992) discussed these factors and showed that a C_{10} carboxylic acid occupying a cross-sectional area of 0.22 nm^2 would achieve a concentration of $7.5 \times 10^{-6} \text{ mole/m}^2$ or $9 \times 10^{-4} \text{ g carbon/m}^2$. Thus 100% coverage of the surfaces of solids possessing a surface area of 56 m^2 by a C_{10} carboxylic acid could produce a 5% TOC in the solids (dry wt basis). The sorption of a second layer of carboxylic acid to form admicelles would reduce the surface area requirement by a factor of up to 2.

The surface area data presented in Table 5 clearly indicates that the saltcake in the USTs has too low a specific surface area to produce a significant enrichment of organic by sorption. Surface area for the SST sludge simulant indicates that it possesses enough surface area to produce significant TOC concentrations due to the high specific surface areas of the insoluble solids in the sludge. The greatest potential for relatively high TOC levels in the solids can be achieved if the solids in the sludge consist only of insoluble solids (no saltcake). These TOC levels may be significant even if only a fraction of the surface sorbs organics because of the large surface area involved.

The amount of sorption on a solid also depends on a number of factors affecting the degree of attraction between the organics and the surface. The pH of the aqueous phase in the USTs, which ranges from 9 to > 14 under conventional assumptions, should produce a surface with a significant net negative charge that would repel organic anions such as EDTA and citric acid. However, the total concentration of dissolved ions ranges as high as $10M$ in sodium-based salts. This high electrolyte strength is expected to cause significant deviation from ideal liquid and surface behavior. For example, the single ion activity coefficient for sodium increases from a low of about 0.7 (at an ionic strength of about 0.7 M) to 1.1 (at an ionic strength of 5M) with the most rapid increase occurring above 2.0 M (Roy et al. 1987). Non-ideal behavior of the liquid and solid phases may produce a charge reversal on the surface. Alternatively, the increase in ionic strength of the solution may result in an effective zero net charge on the solid surfaces due to shielding effects at the surface. Under these conditions, physical adsorption may become an important mechanism for concentrating organics on the surfaces. The behavior of the chelating agents in a high ionic strength can also affect the tendency for adsorption. Finally, the solids species can have a dramatic effect on sorption. For example, goethite and gibbsite, both of which have been identified in SST tank sludge samples at significant concentrations, are known to have high surface areas and good sorption characteristics.

Test Methods

The following sections describe the materials and experimental procedures used in conducting sorption experiments.

Materials Selection

Initial tests are being conducted using reagent-grade high-surface area gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) with a surface area of $1250 \text{ m}^2/\text{g}$, and goethite ($\text{FeO}[\text{OH}]$) with a surface area of $50 \text{ m}^2/\text{g}$. These compounds were selected because they have good sorption properties and are known to be stable species in the tanks and the SST sludge simulant. The simulant also has a high aluminum and iron content, which could be in the form of gibbsite and goethite and account for the high surface area measured for the simulant.

^{14}C -EDTA and ^{14}C -NTA were selected as the organic compounds to be initially tested. EDTA was selected because it was added to the tanks in large quantities and is representative of compounds in the tanks with both carboxylic acid and amine functionality. NTA was selected because it was also added to the tanks and the data can be compared to that obtained in an earlier study.

Sodium nitrate is added in the initial experiments to produce the desired electrolyte strength. The solutions are adjusted to the desired pH using sodium hydroxide solution.

Experimental Procedure

All experiments are conducted using the batch adsorption method. A series of conditions are evaluated for each organic/solid pair. The series consist of stirred suspensions at individual pHs for an experimental combination of solid, adsorbate, ionic strength, and solid to solution ratio. Time course sampling of each suspension are conducted for a period of 1-4 weeks to ensure equilibrium. Adjustments in pH are made as necessary to counteract the buffering effect of the solids.

Supernate samples are analyzed by first filtering them through a $0.1\text{-}\mu\text{m}$ filter and analyzing the filtrate with a ^{14}C scintillation counter. Inorganic carbon analysis are conducted for some experiments to quantify formation of carbonate species formation due to degradation of the organics and adsorption of CO_2 from the atmosphere.

At this time, experiments have been initiated to investigate this mechanism, but there are no results. These results will be incorporated in the FY 1995 Progress Report for this task.

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Appendix

Recipe for Preparing SST Simulant Insoluble Solids

1. Add 600 ml H₂O and 143.35 g Al(NO₃)₃·9H₂O to a 4 L beaker (container A) and stir 1 hr. While stirring add:

2.31 g Ca(NO₃)₂·4H₂O
0.30 g Pb(NO₃)₂
0.80 g Mg(NO₃)₂·6H₂O
0.04 g AgNO₃
0.14 g Zn(NO₃)₂·6H₂O
0.09 g Zr(O)(NO₃)₂·2H₂O
0.36 g Ce(NO₃)₃·6H₂O
14.73 g Fe(NO₃)₃·9H₂O
0.95 g Cr(NO₃)₃·9H₂O

Stir 1 hr, then adjust pH to 12.0 with 25% NaOH

2. Add 100 ml H₂O to a 100 ml beaker (container B) and dissolve 0.21 g KMnO₄. Add 0.20 g Mn(NO₃)₂ dissolved in 2 ml H₂O, while stirring vigorously.
3. Add well-stirred contents of container B to container A.
4. Add 400 ml H₂O to a 1-L Beaker (container C) and add:

13.6 g Fe(NO₃)₃·9H₂O
1.48 g Cr(NO₃)₃·9H₂O
0.98 g La(NO₃)₃·6H₂O

Stir 1 hr. Then dissolve 0.21 g Mn(NO₃)₂ in 2 ml H₂O and add to container C while stirring. Mix 10 min. While mixing, add 3.45 g 85% H₃PO₄ and stir until it is dissolved. Add 7.82 g Bi(NO₃)₃·5H₂O (forming a precipitate) and mix 10 min. While mixing add:

10.09 g Na₃PO₄
2.07 g Ce(NO₃)₃·6H₂O
0.49 g Zr(O)(NO₃)₂·H₂O

Stir 1 hr and then adjust pH to 10 with 25% NaOH. While stirring add:

0.38 g Ni(NO₃)₂·6H₂O
0.09 g Sr(NO₃)₂

Stir 1 hr and then adjust to pH 10.0.

5. Add contents of container C to container A. Bubble CO_2 gas through mixture to reduce pH to 10. Wash the precipitate in container A by adding pH 10.0 H_2O solution to the container to make 3.5 L and mix. Let the contents settle overnight and decant the clear liquid. Repeat the washing 2 more times.

6. Add:

0.17 g NaF
1.42 g K_2SO_4
17.06 Na_2SiO_3 (silicon equivalent to 27.99 g 30% SiO_2)

to container A and mix.

Add 75.78 g of salt cake simulant whose composition is:

<u>Component</u>	<u>Dry Wt %</u>
NaNO_3	75.2
NaNO_2	4.8
Na_2SO_4	2.4
Na_2CO_3	4.3
NaAlO_2	4.3
Na_3PO_4	4.6
NaOH	4.4

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