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Permeation of Tank C-103 Sludge Simulant by Organic Solvent

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Preface

This report (PNL-10412, Rev. 1) was revised from an earlier version issued in March 1995 to provide additional data not available at that time. The investigation of permeation of Tank C-103 sludge simulant by organic solvent was further pursued at the recommendation of the sponsor. The March report contained data that provided a lower bound on the amount of solvent that could permeate the tank sludge if the tank was interim stabilized without first removing the organic solvent phase from the free liquids above the sludge in the tank. The earlier results were based on parameters of a finer sludge and also a higher interfacial tension between the solvent and aqueous phases than were measured using actual waste. This revised report provides data on the permeation behavior under conditions of a sludge that is coarser than that in the tank and an interfacial tension equal to or less than that measured between these two phases in the tank. The upper bound of solvent permeating the coarse sludge simulant reported in this revised report is over 6 times greater than that obtained using the finer sludge reported in the March issue of this report.

Summary

The plan for stabilizing underground storage tanks calls for draining the supernate from the tanks; however, there is concern that draining the supernate from Tank C-103 will degrade safety in the tank. The sludge in Tank C-103 contains ranges in depth from 1 to 1.5 m and is covered by both an aqueous phase and a separate organic layer. The main concern is that draining the supernate will cause the solvent to permeate the sludge solids and provide a source of fuel for a fire on the surface of the drained sludge. The question of whether the solvent will permeate sludge that is 1 to 1.5 m deep after the tank is dewatered is the purpose of the tests conducted and described in this report.

Evaluation of the solvent permeation mechanism required the preparation of solvent, supernate, and sludge simulants based on the known chemistry of Tank C-103. Solvent and aqueous phase supernate simulants are based on the results of fiscal year 1994 sampling of the tank solvent and supernate. Sludge simulant is based on the chemical analyses of tank sludge samples retrieved in 1986.

Experiments were conducted with each simulant to evaluate solvent permeation under matrix potentials ranging from 0.8 m to 1.8 m of supernate. These values were selected because the depth of sludge in Tank C-103 varies from 0.9 to 1.5 m. The amount of solvent recovered for each experiment was recorded as well as the maximum amount of solvent that could be in the sludge based on solvent recovered from resuspended sludge and solvent not recovered. The wt% of water remaining in the sludge was also recorded for each experiment, which was determined by measuring the weight of the sludge after drying it and subtracting the maximum amount of solvent in the sludge.

The experimental results showed that solvent permeation would likely range between 0.5 wt% for fine particulate sludge (4.15 μm average particle diameter) in Tank C-103 sludge at a height of 0.8 m above the free liquid level in the tank following dewatering, to a maximum of 21.1 wt% in a coarse sludge (88.5 μm average particle diameter) and at a height of 1.5 m. The interfacial tension had a significant effect on the amount of solvent permeation in the fine particulate sludge with permeation achieving a concentration of 6 wt% with a solvent/supernate pair with a interfacial tension of < .1 dyne/cm for conditions representing a sludge height of 1.5 m. This effect did not appear for the coarse sludge.

The degree of permeation was found to be greater at greater heights of sludge, as was expected. However, the coarse sludge also demonstrated that significant solvent permeation will occur at sludge heights of 0.05 m (2 in.) or greater, even when this material is capped with finer material, if a crack occurs that penetrates through the upper layer of the finer material.

One issue that could not be resolved was whether solvent not recovered from the permeation experiments was still retained in the washed sludge. Attempts to remove residual solvent by trapping vapors during drying and by performing a Soxhlet extraction only recovered trace quantities of solvent. A chloroform extraction of a sample of unwashed sludge did appear to recover a greater percentage of solvent that had been recovered by rinsing with supernate.

A remaining uncertainty in interpreting the results of these experiments is whether different approaches for reducing the interfacial tension of the solvent supernate simulant pairs affects the

amount of permeation. Most likely this is an issue primarily with the fine sludge in the tank, because different constituents in the solvent and supernate could influence the wettability of the sludge particles for the solvent phase. Resolution of this uncertainty will require more detailed information on the organic compounds in both the solvent and supernate phases in Tank C-103, or a more exhaustive exploration of the effects of different additives to both fluids on both the interfacial tension and subsequent permeation of the fine sludge by solvent.

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Introduction

The sludge contained in Tank C-103 ranges in depth from 1 to 1.5 m and is covered by both an aqueous phase and a separate organic layer. The organic layer is primarily composed of tributyl phosphate (TBP) and normal paraffinic hydrocarbons (NPH) (C_{10} to C_{14}) floating on the surface of the aqueous supernate (free liquids) in the tanks. The plan for stabilizing underground storage tanks (USTs) calls for draining the supernate from the tanks; however, there is concern that draining the supernate from Tank C-103 will degrade safety in the tank. The main concern is that the solvent will permeate the sludge solids and provide a source of fuel for a fire on the surface of the drained sludge. Two questions need to be answered to address this concern: 1) Will the solvent permeate sludge that is 1 to 1.5 m deep if the tank is dewatered, and 2) will the entrained solvent burn on the surface if an ignition source is provided? This report describes only the tests conducted to determine whether the solvent will permeate the surface.

Background

Ideally, the sludge layer in a tank maintains its shape (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 (Figure 1[b]) that provides a direct path for free supernate and solvent to drain from the sludge surface to the pump. In addition, the surface of the sludge fractures immediately after the free supernate is removed because the sludge begins to consolidate. These cracks trap the solvent in isolated pockets 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 principal differences are those 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. This concept will be explained in this section.

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

$$\Phi = gz/g_c + (P_z - P_0)/(\rho) \quad (1)$$

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_z = pressure measured at height z 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 because of its interfacial tension, has a negative value (i.e., a measure of the pull of the interfacial 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 $(P_z - P_0)$ represents the capillary pressure of the supernate at height z . 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 at height z . The capillary pressure is also the pressure that would be measured by a manometer if the reference pressure for the manometer is the 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 solvent/supernate system and interfacial tension for the air/supernate system. The capillary rise for an oil/supernate system is less for air because the interfacial tension of the solvent is much closer to that of water than is air. Values for interfacial 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 interfacial tensions of various pairs. First, it is generally assumed that the interfacial tension of a pair of immiscible liquids (water/dodecane) is approximately the difference of the air/liquid interfacial 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 interfacial 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, however, because most polar solvents in water reduce the air/liquid interfacial tension (Dean 1973). The presence of salts also appears to increase the interfacial 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 oil in the solids.

The physical properties of the sludge solids are 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 respective 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 μ m). 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.

Preparation of Simulant Materials

Evaluation of the solvent permeation mechanism required the preparation of solvent, supernate, and sludge simulants based on the known chemistry of Tank C-103. Solvent and aqueous phase supernate simulants are based on the results of fiscal year 1994 sampling of the tank solvent and supernate (Pool and Bean 1994). Sludge simulant is based on the chemical analyses of tank sludge samples retrieved in 1986 (Weiss and Schull 1988). Both the solvent and supernate simulants were varied to evaluate interfacial tension.

Baseline Solvent Simulant

Solvent samples retrieved from Tank C-103 were analyzed by Pacific Northwest Laboratory (PNL)^(a) in December 1993, using gas chromatography/mass spectrometry (GC/MS) (Pool and Bean 1994). According to these results, the TBP, dibutylbutyl-phosphonate (DBBP), and NPH account for 64%, 2.6%, and 33.4% by weight, respectively, of the identified constituents in the organic phase. However, collectively these account for only 73.7 wt% of the organic phase. The remaining 26.3 wt% of the constituency is unknown. The known composition of the organic phase is shown in Table 2.

Table 2. Components Determined by GC/MS Analysis of the Organic Layer

Component	Retention Time, min.	Wt%	Relative Wt%
Dodecane	10.51	2.0	3.8
Alkane	10.74	0.2	0.3
Alkane	11.85	1.1	1.5
Tridecane	12.38	11.4	15.5
Alkane	13.23	0.5	0.6
Alkane	13.72	1.0	1.3
Tetradecane	14.17	6.0	8.1
Alkane	15.17	0.7	1.0
Pentadecane	15.84	0.9	1.2
DBBP	17.6	1.9	2.6
TBP	18.09	47.2	64.0
Total		73.7	100.0

(a) Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract number DE-AC06-76RLO 1830.

The relative quantities of dodecane, tridecane, tetradecane and pentadecane are consistent with commercially available NPH reported by Wilbourn (1977).

The baseline solvent simulant used in the permeation simulant was prepared consisted of the 64, 33.4, and 2.6 volume % of TBP, NPH, and DBBP. Dibutyl phosphate (DBP) was also added in several experiments discussed later. The specific gravity of the solvent was 0.909 and 0.902 with and without DBP added, respectively.

Baseline Aqueous Phase Simulant

Aqueous phase samples were also retrieved from Tank C-103 and analyzed by PNL in December 1993 (Pool and Bean 1994). Inorganic analysis included ion chromatography (IC) for anions, and inductively coupled plasma/atomic emission spectrometry (ICP/AES) for cations. Ammonia was analyzed using well-established ion selective electrode methodology according to procedure PNL-ALO-226 "Ammonia (N) in Aqueous Samples." Total organic carbon (TOC) and total inorganic carbon (TIC) were analyzed using the hot persulfate oxidation/coulometry detector method PNL-AALO-381 REV. 0 "Determination of TC, TOC, and TIC in Radioactive Liquids, Soils, and Sludges by Hot Persulfate Method." Table 3 shows the analysis of the aqueous phase from Tank C-103 for various analytes.

Table 3. Inorganic Analytes Found in Tank C-103 Aqueous Phase

ICP Elements	µg/g	IC - Anions	µg/g
P	2,350	F ⁻	1,100
Na	30,400	Cl ⁻	400
Ni	67	NO ₂ ⁻	23,000
Cd	0.8	NO ₃ ⁻	2,450
Ca	10	PO ₄ ³⁻	2,000
Ag	11	SO ₄ ²⁻	3,000
Cr	53	Ammonia	
Fe	3		215
K	300	TOC	
Mo	10		6700
U	1950	TIC	
Zr	280		4800

Table 4 shows the composition of the aqueous phase simulant that was used in the experiments. This table also shows, for comparison, the key analytes found in actual tank aqueous samples on a molar basis.

For most of the experiments (Exp. 1A, 1B, 1C, 2A, 2B, 2C, and 3B), the total sodium in the simulant was less than that in the actual waste. However, based on the TIC measured in the actual waste (Table 3), it is likely that the balance of sodium is a counterion to carbonate anions in the waste,

Table 4. Baseline Compositions of Aqueous Phase Simulants^(a)

Simulant Concentration Component	Simulant Concentration (mol/L)	Tank C-103 Concentration Constituent	Tank C-103 Concentration (mol/L)
NaNO ₂	0.50	NO ₃ ⁻	0.53
Na ₂ SO ₄	0.031	SO ₄ ⁻²	0.033
NaNO ₃	0.039	NO ₃ ⁻	0.042
Na ₂ HPO ₄	0.023	HPO ₄ ⁻²	0.023
NaF	0.053	F ⁻	0.062
NaCl	0.011	Cl ⁻	0.012
Na ₂ CO ₃	0.00 (0.101) ^(b)	TIC	—
NaHCO ₃	0.00 (0.286) ^(b)	TIC	—
NaOH	(pH 9.8)	OH ⁻	(pH 9.8)
Total Na	0.711 (1.20)	Total Na	1.23
Total TIC	0.00 (.486)	TIC	0.602

(a) Not including sodium added with organic acid salts.

(b) Values in parentheses added in several experiments.

supernate promoting salting out of organics, as well as altering the conditions for the agglomeration of aggregate particles, thereby affecting their size. Experiments 3A, 3C, and 3D did evaluate this variable using the values shown in parentheses in Table 4. The specific gravity of solvent equilibrated supernate with and without added carbonates was 1.07 and 1.05, respectively.

Adjustments Made to Solvent and Supernate Simulants to Lower Interfacial Tension

One difficulty in preparing the solvent and supernate simulants has been the selection of organic species to account for the TOC in the Tank C-103 supernate, and to achieve a low interfacial tension between the fluid pair. The TOC in the tank waste is significant in that some organics believed to be in the tank may interact with the solid phase particle surfaces, thereby altering their wettability by solvent. Also, the presence of small quantities of certain organics can significantly reduce the interfacial tension between the supernate and organic liquid phases. Both of these effects could promote permeation of the sludge by organics.

The aqueous phase in Tank C-103 has not been analyzed for organic species. Consequently, the organic species present can only be speculated. Possible sources for TOC in the aqueous phase are TBP, and its principal degradation product DBP, as well as a lesser quantity of monobutyl phosphate; organic acid salts resulting from degradation of NPH products (and butanol fragments from TBP); and complexants added to the tank along with their degradation products. Other possible volatile products from solvent degradation including alcohols, ketones, and aldehydes were not identified in the solvent recovered from Tank C-103 and were therefore excluded from this work.

Interfacial tension measurements were made for two samples containing solvent and supernate phases retrieved from Tank C-103. Interfacial tension values ranged from <1 to 2 dyne/cm. However,

the method used was not standard. In the standard method, a clean du Noüy ring (or platinum coupon) is immersed in the aqueous phase before adding the solvent phase. The platform containing the sample is slowly lowered until the ring encounters the interface level (from below it) and a measurement of the force applied on the ring due to interfacial tension is recorded. This method requires using separated phases for each measurement and would have required a separation step between measurements because of the small quantities of tank solvent and supernate samples available. The nonstandard method used involved placing the ring (coupon) in the solvent after it had been layered on top of the supernate and then raising the platform until the ring encountered the interface (from above it) and taking a measurement at the interface level. This latter method can give an incorrect value because the solvent precoats the ring, changing its wetting properties.

Several organic acid salts were added to supernate simulant in concentrations shown in Table 5. The nonstandard method was used to compare the interfacial tension of the different aqueous phase/organic phase combinations and for comparison to the data from actual waste solvent and supernate. A platinum coupon was used instead of a de Noüy Ring because it does not require corrections to the measured force as does the ring. Values using this method were determined from

Table 5. Interfacial Tension Measurements of Solvent/Supernate Simulant Pairs

Organic Acid Salts Added (adjusted to pH 9.8)	Total Supernate Organic Carbon, wt%	Interfacial Tension, dyne/cm	
		Coupon Pulled from Aqueous Phase	Coupon Pushed from Solvent Phase
None	0.00	8.59	8.07
None (Exp. 7)	0.00	9.23	8.37
Sodium formate	0.10		5.80
Sodium formate	0.50	9.25	8.91
Sodium succinate	0.50	9.81	8.80
Sodium octanoate	0.50	2.79	2.42
Sodium stearate/palmitate ^(a)	0.01	7.89	8.08
Na ₃ citrate	0.50	9.91	9.28
Na ₃ nitrilotriacetate	0.20	9.57	9.06
Na ₄ ethylenediamenetriacetate	0.50		3.26
Na ₄ ethylenediamenetriacetate	0.50		5.30
Acid salt simulant mixture ^a	0.55		4.15
Solvent Additive	Volume%	Interfacial Tension, dyne/cm	
		Coupon Pulled from Aqueous Phase	Coupon Pushed from solvent Phase
Dibutyl phosphate	9.1	2.95	2.05
	13.0	0.58	0.43
	16.7	<0.10	<0.10

(a) Approximately equal parts of each acid salt.

the average of four or more repeated insertions of the coupon, as was done on the actual waste samples. The standard procedure using the platinum coupon was also used to provide an indication of how representative the nonstandard method was. However, because the tests were done for the purposes of screening candidate organic additives, only one data point was obtained for each sample using the standard method.

The acid salt simulant mixture used in experiments 1A&B, 2A&B, and 2C was obtained by adding a quantity of sodium citrate, sodium EDTA (ethylenediaminetetraacetic acid), sodium octanoate, and sodium oxalate to the baseline supernate simulant to produce a concentration of 0.1 wt% TOC of each; and sufficient DBP to produce a concentration of 0.15 wt% TOC, for a total of 0.55 wt% TOC. Partitioning of a small portion of the TBP in the solvent was also expected to contribute to the TOC in the supernate.

The interfacial tension of the supernate containing the organics was 4.15 dyne/cm using the nonstandard method. This value also compares to a value of 8.07 dyne/cm obtained for the solvent and supernate that did not contain the organic salts.

Also shown in Table 5 are the effects of adding DBP to the solvent phase. These solvent mixtures were prepared by adding DBP to the baseline solvent in the amounts shown. It can be seen that DBP has a dramatic affect on the interfacial tension with 16.7% DBP producing an interfacial tension value that could not be detected. Its presence in the solvent phase could be responsible for much of the reduced interfacial tension measured using solvent and supernate from Tank C-103. Experiments using DBP as an additive to the solvent did not use any of the other added acid salts.

Sludge Simulant

Three sludge simulants were prepared based on chemical composition data (Table 6) for sludge samples retrieved from Tank C-103 in 1986 (Weiss and Schull 1988). The two simulants differed in their particle size distributions to bound the expected range of particle size distributions for Tank C-103. The particle diameter, in which 50% of the particles in the sample have smaller diameters, were reported for the tank sludge samples obtained in 1986 from two different locations within the tank. These values were 11.5 μm and 49.5 μm , even though their elemental compositions were very similar. A more recent sludge sample obtained from Tank C-103 had an average particle diameter of 35 μm .

Simulant 1 was prepared by combining a mixture of 25.8% solids in the proportions listed in Table 7 and 74.5% supernate simulant. After mixing the solid components with the aqueous phase solution, 1M NaOH solution was added until pH reached 12. The sludge was then stirred for 3 h and final pH was adjusted to 9.8 by adding 1M HNO₃. Because a significant amount of NaNO₃ was generated during the pH adjustment process, the supernate now contained more NaNO₃ than desired. Therefore, drainable supernate was removed by centrifuge and replaced with equal amounts of new aqueous phase solution. The viscous mixture was then stirred overnight. The resulting sludge was reddish brown in color and had a consistency similar to wet clay. The particle size distribution was determined using a Microtrac Full-Range Particle Analyzer and using a solids loading index of about 0.75. The particle size distribution is shown in Figure 4. The 50% volume particle diameter was 4.55 μm .

Table 6. Composition of 1986 Tank C-103 Sludge Samples

Constituent	Average Concentration ($\mu\text{mol/g}$)
Silicon	2513
Sodium	2196
Iron	1554
Aluminum	537
Calcium	277
Magnesium	255
Zirconium	135
Phosphorus	134
Nickel	49
Nitric Acid	45
Manganese	45
Potassium	36
Other	92

Table 7. Solids Used in Preparing Simulant 1

<u>Solid phase total = 25.8 wt% of sludge</u>		
Component	Wt%	Primary Particle Size, μm
$\text{Fe}(\text{OH})_3$	11.1%	0.01
SiO_2	10.1%	0.06
$\text{Al}(\text{OH})_3$	2.0%	0.250
AlOOH	0.7%	0.005
$\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$	1.9%	4.0
<u>Aqueous phase total = 74.2 wt% of sludge</u>		
Component	Simulant (mol/L)	Tank (mol/L)
NaNO_2	0.50	0.50
NaSO_4	0.031	0.031
NaNO_3	0.039	0.039
Na_2HPO_4	0.023	0.023
NaF	0.053	0.053
NaCl	0.011	0.011
NaOH	(pH 9.8)	(pH 9.8)

Figure 4. Particle Size Distribution for Sludge Simulant 1

The solids in Simulant 2 had approximately the same composition as shown in Table 8, but the primary particles were much larger to promote a coarser-grained sludge. Preparation was similar to that for Simulant 1 except that the aqueous phase initially mixed with the solids was a neutral solution without sodium nitrate. This was done to minimize the excess nitrate present during synthesis. The pH 12 solution was also stirred for 16 h before neutralization. The resulting sludge had a purplish hue and a coarse appearance with a consistency more like silt. Small discrete particle grains could be observed in the simulant. The particle size distribution for this simulant, obtained using a loading index of 0.87, is shown in Figure 5. The mean particle diameter (volume basis) was 15.78.

Simulant 3 was prepared using a composition that is similar to that used in previous simulants, but with the FeOOH and SiO_2 material prepared by grinding and dry sieving material to a 53-106 μm particle size range. The solids were added to the supernate at a pH of 9.8 and equilibrated on a shaking table for 24 h. A check of the pH after 24 h indicated no change in pH. Table 9 shows the composition of the sludge and supernate used in making the simulant. Figure 6 shows the particle size distribution for the new simulant, which has an average particle diameter of 88.3 μm (volume basis) at a loading index of 0.96. A second batch of Simulant 3 had an average particle diameter of 91.4 μm and a slightly different profile as shown in Figure 7. Differences are probably due to differences in grinding and screening methods used for each batch.

Table 8. Solids Used in Preparing Simulant 2

<u>Solid phase total = 25.9 wt% of sludge</u>		
Component	Wt%	Primary Particle Size, μm
FeOOH	10.5%	75-125
SiO ₂	11.3%	0.02
Al(OH) ₃	0.5%	7.5
AlOOH	1.5%	0.005
Ca ₁₀ (OH) ₂ (PO ₄) ₆	2.1%	0.004

<u>Aqueous phase total = 74.1 wt% of sludge</u>		
Component	Simulant (mol/L)	Tank (mol/L)
NaNO ₂	0.49	0.50
NaSO ₄	0.032	0.031
NaNO ₃	0.039	0.039
Na ₂ HPO ₄	0.023	0.023
NaF	0.053	0.053
NaCl	0.011	0.011
NaOH	(pH 9.8)	(pH 9.8)

Figure 5. Particle Size Distribution for Sludge Simulant 2

Table 9. Solids Used in Preparing Simulant 3

<u>Solid phase total = 25.8 wt% of sludge</u>		
Component	Wt%	Primary Particle Size, μm
$\text{Fe}(\text{OH})_3$	7.0%	75-106
$\text{Fe}(\text{OH})_3$	3.3%	53-75
SiO_2	7.0%	75-106
SiO_2	3.9%	53-75
$\text{Al}(\text{OH})_3$	1.9%	0.250
AlOOH	0.5%	0.005
$\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$	2.0%	4.0
<u>Aqueous phase total = 74.2 wt% of sludge</u>		
Component	Simulant (mol/L)	Tank (mol/L)
NaNO_2	0.48	0.50
NaSO_4	0.032	0.031
NaNO_3	0.040	0.039
Na_2HPO_4	0.021	0.023
NaF	0.053	0.053
NaCl	0.012	0.011
Na_2CO_3	0.101	
NaHCO_3	0.286	
NaOH	(pH 9.8)	(pH 9.8)

Figure 6. Particle Size Distribution for Sludge Simulant 3--First Batch

Figure 7. Particle Size Distribution for Sludge Simulant 3--Second Batch

Experimental Procedure

The experimental apparatus used to conduct the solvent permeation experiments is shown in Figure 8. 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. The filter consisted of a standard two-piece 47-mm microfilter and a supported plain 0.1- μm nylon filter membrane to retain the sludge simulant and 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. 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.

Figure 8. Diagram of Experimental Apparatus for Solvent Permeation Experiments

Before conducting an experiment, 25 mL of the solvent and 250 mL of the supernate simulants were combined in a capped jar and agitated on a shaker table at 240 rpm for 4 h and then separated. Approximately 40 to 70 mL of sludge simulant was added to 200 mL of equilibrated supernate, stirred for about 24 h, and then separated using a centrifuge. This step was done to pre-wet the solids with the organics in the supernate simulant. Approximately 50 mL of the supernate from the

centrifuge was used to backfill the apparatus from the buret to the bottom of the filter. The sludge was added to the filter reservoir and about 20 mL of supernate added on top of it. After the sludge had settled enough to create clear liquid on top, 20 mL of equilibrated solvent was layered onto the supernate in the reservoir. The system was dewatered at the desired vacuum level (corresponding to 0.05 to 1.5 m of supernate), using the buret to track the amount of supernate withdrawn. The buret reading and the volume of sludge in the reservoir at the point that the solvent first covered the surface of the sludge was recorded. The experiment was continued until the volume of supernate withdrawn in a 24-h period was less than 0.1 mL/day, or after 300 h. In those experiments in which solvent appeared below the filter frit, the experiment was terminated after about 48 h.

At the completion of the experiment, the system was shut down and free solvent poured from the reservoir. The sludge was removed from the reservoir into a 50 mL beaker and its volume measured by filling the beaker with supernate to a known volume; the difference between the known volume and the amount of supernate added equalled the displaced volume. The supernate was drained from the sludge into a separatory funnel. A second addition of supernate was added to the sludge to further rinse the surface and then drained into the separatory funnel. Solvent remaining on the filter membrane was rinsed off using supernate and added to the separatory funnel. The glass frit was rinsed by applying supernate to the top of the filter while it was under vacuum and the rinse water recovered and added to the separatory funnel. After about 2 h, the solvent was recovered from the separatory funnel. The sludge was resuspended in approximately 200 mL of supernate and allowed to settle for about 2 h in a separatory funnel to separate any free solvent from the sludge. This solvent is also recovered and measured. The quantity of solvent recovered by the different procedures were recorded individually.

Experimental Results

Experiments were divided into 2 sets: those using supernate with organic acid additives to reduce interfacial tension and those conducted using DBP added to the solvent phase to reduce interfacial tension.

Experimental Results Using Supernate with Organic Acids to Reduce Interfacial Tension

The first set of experiments were conducted using Simulants 1 and 2 to evaluate solvent permeation under matric potentials ranging from 0.8 m to 1.8 m of supernate, with the organic acid salt mixture, previously described, added to reduce interfacial tension. These matric potential values were selected because the depth of sludge in Tank C-103 varies from 0.9 to 1.5 m. Table 10 shows the amount of solvent recovered at the completion of each experiment, and the maximum amount of solvent that could be in the sludge based on solvent recovered from resuspended sludge and solvent not recovered. Also shown is the wt% of water remaining in the sludge at the conclusion of each experiment, which was determined by measuring the weight of the sludge after drying it and subtracting the weight of the maximum solvent content. The maximum solvent that could be in the sludge for tests 1A, 2A, and 2B less than 1 mL, which is considered to be within the accuracy expected for solvent loss under conditions of no permeation.

Table 10. Experiment Results of Permeation Evaluation of Sludge Simulants Using Supernate with Organic Acids to Reduce Interfacial Tension

Experiment	Simulant/matrix potential, (m Supernate)	Total solvent recovered, mL	Solvent recovered from sludge, mL	Final weight of sludge	Maximum wt% solvent in sludge	Wt% water in sludge
1A	Simulant 1 -0.9	19.26	0.06	34.4	2.0	73.1
1B	Simulant 1A -1.3	18.92	0	28.7	3.4	64.9
2A	Simulant 2 -0.8	19.825	Trace	29.3	0.5	65.2
2B	Simulant 2 -1.3	19.575	0.1	32.6	1.5	62.7
2C	Simulant 2A -1.8	18.53	0.0	51.238	2.6	60.0

Previous tests conducted using dodecane, 50 mL of a sludge simulant, and supernate used in earlier research (Gerber 1994) and at a vacuum corresponding to 0.75 m water showed that more than 19.1 mL of an initial quantity of 20 mL of solvent could be recovered by these procedures. These tests also showed that about 0.25 mL of solvent would be recovered during the first rinsing even though the test conditions precluded permeation of the organic. This quantity is attributed to the thin coating of solvent remaining on the sludge monolith following rinsing.

Experiments 1B and 2C showed indirect evidence of significant adsorption. Total of solvent not recovered was 1.08 and 1.47 mL, respectively, greater than that normally lost. Also, there is a trend of increasing solvent loss with increasing applied vacuum for both simulants. One difference that occurred in conducting experiments 1B and 2C was that some solvent passed through the filter membrane and it is possible that at least a portion of the solvent was not recovered from the glass frit supporting the filter membrane, although about 0.2 mL of solvent was recovered by washing the frit with supernate with the system under vacuum.

One interesting observation from the first set of experiments was that Simulant 2 had a lesser degree of permeation than Simulant 1 under similar conditions, even though it is a somewhat coarser material. There is no explanation for this trend at this time.

Experimental Results Using DBP in Solvent Phase to Reduce Interfacial Tension

The second set of experiments was conducted to investigate the effect of reducing interfacial tension on solvent permeation. The results of these experiments are summarized in Table 11.

Table 11. Experiment Results of Permeation Evaluation of Sludge Simulants Using DBP to Reduce Interfacial Tension

Experiment	Simulant/matrix potential, (m Supernate)	Dibutyl phosphate Vol%	Total solvent recovered, mL	Solvent recovered from sludge, mL	Final weight of sludge	Maximum wt% solvent in sludge	Wt% water in sludge
1C	Simulant 1A -1.5	16.7	17.81	0.05	33.6	6.0	67.4
3A	Simulant 3 ^(a) -1.5	0.00	18.67	7.64	40.7	21.13	33.9
3B	Simulant 3 -1.5	9.09	17.73	4.91	33.5	19.8	27.9
3C	Simulant 3A ^(a) -1.5	9.09	18.79	5.34	33.6	17.7	30.8
3D	Simulant 3A ^(a) -1.5	9.09	17.58	5.84	37.5	19.8	29.9

(a) Sodium carbonate and sodium bicarbonate added (see text).

Experiment 1C was conducted using 16.7% DBP in the solvent mixture and sludge Simulant 1, which had the smallest average particle size diameter. Because the interfacial tension between the solvent and supernate was <0.1 dyne/cm, the vacuum was raised in steps corresponding to 0.11 m, 0.15 m, 0.30 m, and 0.67 m of sludge height over a 137-h period. The solvent appeared below the filter at the last setting. It was not possible to ascertain the amount of solvent permeation at this time because of significant consolidation of the sludge. The vacuum was then increased to a value corresponding to 1.53 m of sludge height and maintained for 49 h. A total of 5.8 mL of solvent was collected from below the filter frit at the end of the experiment. As was the case with the first set of experiments using the fine sludge, very little solvent was actually recovered from the sludge but had to be inferred from the amount of solvent not recovered. It can be seen from a comparison of the results from this experiment with those shown in Table 10 that the reduced interfacial tension did produce a much greater amount of solvent that was not recovered, inferring greater solvent permeation. The total amount of solvent permeating the sludge was still relatively modest, although there was no way for knowing of certain whether steady state was fully achieved.

Experiments 3A, 3B, 3C, and 3D were all conducted using the sludge Simulant 3 to provide an upper bound on the effect of particle size and on solvent permeation. This sludge had 2 important characteristics that differed from the previous simulants. First, it did not appear to undergo significant consolidation during supernate removal. Second, it readily fell apart and gave up a significant quantity of solvent during the first washing, although, as before, there was still solvent unaccounted for at the end of each experiment, as shown in Table 11. Experiment 3A had the greatest amount of solvent permeation with a maximum of over 21 wt%. This experiment differed from the others in that there was no DBP added to the solvent so the interfacial tension was relatively high (8.59 dyne/cm). One problem that occurred in this experiment was when the sludge was added to the filter reservoir a significant quantity of very fine material layered on to the top because of settling differences and

disturbance of the sludge when supernate was added on top of it. The other experiments minimized this effect by not rinsing sludge remaining in a graduated cylinder, used to fill the reservoir with sludge, into the reservoir and by adding additional supernate drop-wise until there was enough present to minimize further disturbance of the sludge surface. One possible consequence of this fine layer of material was that it served as a cap preventing solvent permeation at matric potentials corresponding to sludge depths less than 1.5 m. Once the cap was breached, however, the solvent quickly entered the coarser sludge below and reached steady state. This behavior may have been due to consolidation of the upper layer of fine sludge, which may have created a crack.

Experiment 3B was conducted using solvent containing 9.09% DBP with the same sludge and procedure as experiment 3A, except that the supernate used to equilibrate the sludge did not contain the sodium carbonate and bicarbonate. The interfacial tension for the solvent supernate pair was about 2.0 dyne/cm. Also, the sludge was added in a manner that removed the fine material from the top of the sludge cake previously discussed. A vacuum corresponding to 0.05 m (2 in.) of sludge height was initially applied for about 16 h, during which about 2.0 mL of solvent appeared to permeate into the sample. The vacuum was then gradually increased to 0.30 m over about 4 h, during which an additional 2.2 mL of solvent appeared to permeate. The vacuum was reset to a value corresponding to about 0.46 m of equivalent sludge height over a 42-h period, at which time solvent appeared below the filter frit. Apparent solvent permeation was an additional 2.4 mL. Vacuum was finally set to a value corresponding to about 1.5 m of sludge height for about 41 h, at which time the experiment was concluded. An additional 1.5 mL of solvent was eventually recovered from below the filter frit. The maximum amount of solvent that permeated the sludge was comparable to that in the previous experiment in which no DBP was added. The fact that significant permeation occurred at matric potentials equal to 0.5 m of sludge depth suggests that solvent could accumulate in coarse sludge encountered near the bottom of a tank if it is exposed by a crack penetrating the finer material above it.

Experiments 3C and 3D were conducted as duplicates to one another using the second batch of the third sludge simulant, as well as identical supernate (containing carbonates) and solvent mixtures. These experiments were conducted in a single step corresponding to a sludge depth of 1.5 m and for a period of 47 h. The results of these experiments provide an indication of the variability of permeation with specific experiments, probably due to variations in the way the sludge settled in the filter reservoirs. However, these results, combined with those of experiments 3A and 3B, indicate that the permeation is definitely affected by the coarseness of the sludge particles and that the permeation of sludge Simulant 3 averages about 19.5 wt% with a standard deviation of 1.23 wt%.

Based on the limited data from these experiments there does not appear to be any influence of carbonate content or interfacial tension on the permeation of sludge Simulant 3 over the range of conditions evaluated. However, for Simulant 1, there appears to be a clear dependence of solvent permeation on the interfacial tension of the two fluids. One difference between these two sludges that may account for this difference is the tendency toward consolidation as water is removed from the sludge. In the case of the sludge Simulant 1, the sludge is consolidating toward very small pores as the sludge becomes more and more rigid. As the interfacial tension between the two fluids is reduced it is possible that the solvent can more readily displace supernate in the semi-rigid pores. This is supported by the final water contents of the sludges in Table 10, which show a consistent trend of greater consolidation and lower water content with increasing solvent permeation. However, the water content of the sludge in experiment 1C is significantly higher than that of experiment 1B, even though the solvent content is nearly twice as great.

Solvent Losses

As mentioned earlier, previous tests conducted using dodecane, 50 mL of a sludge simulant, and supernate used in earlier research (Gerber 1994) and at a vacuum corresponding to 0.75 m water showed that more than 14.1 mL of an initial quantity of 15 mL of solvent could be recovered by these procedures. This value is considered an upper limit because it was the recovery from the first test on recovery; later attempts had recoveries as high as 14.92 mL out of 15 mL added. These tests also showed that about 0.25 mL of solvent would be recovered during the first rinsing even though the test conditions precluded permeation of the organic. This quantity is attributed to the thin coating of solvent remaining on the sludge monolith following rinsing.

There were three other sources of solvent loss during recovery. The first source is a result of organic films left behind on the filter reservoir, beakers, and separatory funnels. Using the solvent recovery value for experiment 2A, this source would account for about 0.15 mL of solvent. The second source, which was not anticipated while conducting experiments 1A, 2A and 2B, was the possible dissolution of the TBP present in the solvent into the water (about 200 mL) used to resuspend the sludge to separate solvent. Subsequent experiments were modified to rinse the sludge and resuspend it using solvent equilibrated supernate. The fact that no solvent was recovered from the sludge in these experiments suggests that the solvent may be remaining, attached to the sludge particles even after resuspension. The third source was solvent loss in the filter frit in those cases where solvent permeated and collected below the filter frit and collected below the filter. Flushing of the filter frit by pulling supernate through it using vacuum recovered about 0.1 to 0.2 mL. Further flushing and back-flushing under higher vacuum did not increase recovery from the frit. It is believed that very little solvent actually collected in the frit based on two observations: 1) The frit possesses relatively low volume, and 2) permeation appeared to be localized to a few paths through the frit that presumably had the largest pores. Furthermore, in experiments conducted with DBP in the solvent, the filter frit was precoated with a thin layer of ferric oxide that had an average particle diameter of 2 μm . This precoat prevented permeation of the filter at matric potential corresponding to 1.5 m of sludge depth for experiments 3C and 3D, although permeation occurred for experiments 1C and 3B. In earlier tests of the ferric oxide precoat using the baseline solvent and organic acid salt modified supernate (interfacial tension = 4.15 dyne/cm) the precoat prevented permeation of the filter at vacuums up to 25 cm hg, whereas the 0.1 nylon membrane alone failed at about 12 cm hg vacuum, and produced a solvent loss of 0.475 mL if the frit was not rinsed to increase recovery. A portion of this loss is attributed to solvent permeating the precoat solids.

Two attempts were made to recover solvent from the washed solids with little success. The first method for recovering solvent from washed sludge was a Soxhlet extraction of the washed sludge from experiment 1C, using 300 mL of methylene chloride. Analysis of the methylene chloride following evaporative concentration to 1 mL produced a total of 0.032 mg NPH, 0.75 mg DBBP and 18 mg of TBP. The relative abundance of NPH to TBP raises considerable doubt regarding the adequacy of the method considering the TBP/NPH ratio is about 2 in the solvent.

The second method was by using a cold trap at 0°C followed by a second cold trap at -40°C to condense volatile organics and water vapors from the washed sludge from experiment 3A that was heated to dryness under a 1 m torr vacuum. The sample flask became incandescent during heating, however. Total liquid collected equalled 8.45 g, which accounted for all but 0.4 g of the weight loss of the sludge sample (16.2 g dry weight). A GC/MS analysis of the recovered liquids identified 0.332 mg of NPH and 0.027 mg of TBP. The low recovery of TBP relative to NPH (TBP/NPH ratio

= .08 as opposed to about 2.0 in the original solvent) suggests that the TBP may have pyrolyzed with the phosphate remaining on the sample. A second attempt at this method using washed sludge from experiment 3B recovered a liquid total equal to 13.61 g, which accounted for all but 1.28 g of the weight loss of the sludge sample (17.2 g dry weight). A GC/MS analysis of the recovered liquids identified 40 mg of NPH and 2.25 mg of TBP. Although both of these attempts demonstrated that solvent was remaining in the sludge it appears that it may only be a trace amount. The upper limit on the amount of solvent in the washed sludge is suggested to be 0.4 g to 1.28 g based on the amount of material not recovered. Neither of these quantities would account for the solvent losses for these experiments.

A 0.625 g sample of unwashed sludge from experiment 3B was also extracted three times with 3 mL of chloroform and analyzed using GC/MS. A total of 26 mg NPH, 57 mg of TBP and 2 mg of DBBP were recovered from the sample. The sample was not analyzed for DBP, which accounted for about 9% of the solvent. These totals, when prorated to the total sample, equate to 4.56 g of solvent or about 4.95 mL. Correcting for DBP that should have been present would produce a total of about 5.44 mL of solvent compared to recovery of 4.91 mL using 2 rinses as shown in Table 11. One concern with these results was that the sample was not analyzed for about 1 month after it was taken and may have experienced some evaporation prior to analysis.

Conclusions and Recommendations

The experiments conducted in this project were intended to provide a bounding estimate of the amount of solvent that could permeate the Tank C-103 sludge base on the use of supernate, solvent and sludge simulants that were based on the known physical and chemical characteristics. To provide a conservative estimate of the degree of solvent permeation from a safety perspective, the maximum amount of solvent was determined, which includes solvent recovered from the sludge following an experiment as well as quantity of solvent that could not be recovered and was presumed to be in the permeated sludge. These tests primarily investigated the magnitude of the solvent/supernate interfacial tension, sludge particle size distribution, and matric potential as the three most important parameters affecting the amount of permeation.

The experimental results showed that solvent permeation would likely range between 0.5 wt% for fine particulate sludge (4.15 μm average particle diameter), in Tank C-103 sludge at a height of 0.8 m above the free liquid level in the tank following dewatering, to a maximum of 21.1 wt% in a coarse sludge (88.5 μm average particle diameter) and at a height of 1.5 m. The interfacial tension had a significant effect on the amount of solvent permeation in the fine particulate sludge with permeation achieving a concentration of 6 wt% with a solvent/supernate pair with a interfacial tension of < .1 dyne/cm for conditions representing a sludge height of 1.5 m. This effect did not appear for the coarse sludge.

The degree of permeation was found to be greater at greater heights of sludge as was expected. However, the coarse sludge also demonstrated that significant solvent permeation will occur at sludge heights of 0.05 m (2 in.) or greater even though this material is capped with finer material if a crack occurs that penetrates through the upper layer of the finer material.

One unresolved issue was whether solvent that was not recovered from the permeation experiments was still retained in the washed sludge. Attempts to remove residual solvent by trapping vapors during drying and by performing a Soxhlet extraction only recovered trace quantities of solvent. A chloroform extraction of a sample of unwashed sludge did appear to recover a greater percentage of solvent than was recovered by rinsing with supernate.

A remaining uncertainty in interpreting the results of these experiments is whether different approaches for reducing the interfacial tension of the solvent supernate simulant pairs affects the amount of permeation. Most likely this is an issue primarily limited to the fine sludge in the tank because different constituents in the solvent and supernate could influence the wettability of the sludge particles for the solvent phase. Resolution of this uncertainty will require more detailed information on the organic compounds in both the solvent and supernate phases in Tank C-103, or a more exhaustive exploration of the effects of different additives to both fluids on both the interfacial tension and subsequent permeation of the fine sludge by solvent.

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