SLUDGE SURROGATE DEVELOPMENT AND VALIDATION USING CAKING FILTRATION PARAMETERS FOR A RADIOACTIVE SODIUM BEARING WASTE DERIVED SLUDGE AT THE IDAHO NATIONAL ENIGINEERING AND ENVIRONMENTAL LABORATORY

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ABSTRACT

The U.S. Department of Energy is conducting remediation of eleven underground **high-level nuclear waste** storage tanks at the Idaho National and Engineering Laboratory. This will eventually result in one of the 300,000-gallon capacity tanks, accumulating over **70 tons of hazardous and radioactive sludge**. To close this tank in an environmentally compliant manner to meet a state of Idaho/DOE legally binding agreement, the sludge has to be removed, treated, and disposed by 2012. To develop, test, and verify the design of sludge transporting, mixing, and drying processes necessary to accomplish these tasks, a highly representative **surrogate** for the sludge is paramount. Justification for developing a representative solid surrogate, and its corresponding chemical preparation procedure, is provided by economic factors and safety issues associated with personnel exposure to hazardous chemicals and radiation, and the high capital costs of radioactive material processing equipment and facilities.

To ensure a high quality surrogate that accurately represents the unique chemical and physical properties of the actual toxic sludge, the present INEEL contractor has achitectured a novel and broad **simulation** strategy. This strategy includes the preparation of a solid **surrogate** in a manner similar to that which caused the actual waste sludge (e.g., **metathesis synthesis**), and also involves a surrogate validation procedure that includes a statistical comparison of surrogate-to-real-sludge properties.

The innovative strategy the INEEL contractor is presently deploying to ensure a representative and validated **solid surrogate,** is described to highlight the unique approach taken, in comparison to traditional solid surrogate preparations. Specifically, this strategy was pursued to ensure that test results arrived at using the solid surrogate would be transferable, and thus, scale-up tests with the surrogate could take place with high confidence that subsequent implementation of actual treatment equipment and procedures would follow directly without the typical unforeseen problems that arise after having used a poorly designed and unrepresentative surrogate. The strategy has applicability throughout the nuclear and hazardous waste industry. This is a work-in-progress that will not be completed until June 2004; however, currently available data from analyzing and testing the surrogate and actual waste **sludges** are presented. Included are data from **constant pressure filtration** studies.

INTRODUCTION

The Idaho National Engineering and Environmental Laboratory (INEEL) was involved in reprocessing spent nuclear (SNF) fuel at the Idaho Nuclear Technology and Engineering Center (INTEC) for the Department of Energy (DOE) nuclear power and weapons program for over 40 years. Those activities resulted in the generation of High Level Radioactive wastes (HLW) until termination of reprocessing activities 1990. The liquid HLW (first cycle raffinate) and other radioactive liquid wastes were often combined in the same tanks at the INTEC Tank Farm because of similarities in composition, regardless of regulatory classification. Between 1964 and 2000, all of the liquid HLW mixture was thermally calcined into ~ 4400 cubic meters of oxide solids for safer interim storage in stainless steel enclosed bins. Solid bottoms from the tanks were not removed and calcined at that time, and more than 900,000 gallons of additional radioactive liquid and solids were introduced into the tanks as a result of subsequent decontamination, and other operations activities.

The additional wastes introduced into the underground storage tanks at the INTEC Tank Farm, were not HLW. Solids and liquids were introduced, and additional solids formed resulting from metathesis reactions, time sensitive transformations, and thermal and radiolytic reactions occurring in the tanks. They resulted from years of decontamination and reprocessing activities (solvent recovery operations) involving the sodium salts of hydroxides and carbonates. These wastes were subsequently referred to as Sodium Bearing Waste (SBW) due to their relatively

high dissolved sodium ion concentration (i.e., 1.6 to 2.3 M). The liquid SBW is presently stored in 3 of the eleven 300,00 gallon underground storage tanks at INTEC (numbered WM-180 through WM-190) and all the sludge heels in the remaining 8 tanks have been or will be flushed to a fourth tank (WM-187). This fourth tank in turn will be eventually evaporated, resulting in over 70 tons of solid sludge (dry basis). The sludge will require, like the liquid volume of SBW, removal, treatment, and disposal on a schedule to meet a high priority INEEL tank closure milestone in 2012.

As a consequence of the regulatory mandate, characterization of the Tank Farm liquids and solids has become a priority and been given appropriate resources necessary to develop surrogate Tank Farm liquids and solids. These surrogate development activities are necessary so that representative recipes can be formulated for the large volumes of surrogates required to develop, test, and eventually design one of several promising SBW retrieval, treatment and disposal options. Testing potential handling and treatment processes with a surrogate solid is highly preferential to working with the actual wastes since they contain radionuclides contributing to a nominal 5 R/g field on contact.

SURROGATE PREPARATION STRATEGY

Non-Hazardous surrogates have traditionally been used to test treatment process for hazardous and/or radioactive wastes. 'First generation' solid surrogates are typically prepared by combining available solid chemical reagents and minerals, so that the overall elemental analysis of the surrogate approximates the elemental make-up of the solid waste. This method can be successful, but one-to-one element matching alone (between the surrogate and actual waste solid) does not typically result in a surrogate with similar chemical composition, chemical properties, or physical properties, to those of the actual solid waste. As such, waste solid-, and sludge surrogates prepared in such a manner do not provide a reliable design feature essential for meaningful testing of proposed full-scale processes involving real solid wastes.

A large fraction of the SBW solids existing in the Tank Farm, were formed in the tanks as multiple solutions containing a varying concentration of suspended solids and dissolved cations and anions were introduced, and precipitated, attached to existing precipitates, or combined in metathesis reactions to form solids, which subsequently precipitated, respectively. It is reasonable to presume that a solid surrogate prepared in a similar manner would produce a solid with similar chemical and physical characteristics to that of the actual waste solid. Further, preparing a surrogate in this manner allows the formulation to be devoid of hazardous constituents and radionuclides. This method of using metathesis reactions to generate solid surrogates produces a surrogate herein referred to as 'second generation' surrogates. The approach and rationale is briefly described below.

Surrogate Formulation via a Metathesis Approach

The INTEC Tank Farm sludge is a complex mixture of particles with largely unknown chemical composition. The small size of the particles, the conditions under which the sludges were formed, and the large range of elements present, make duplicating the sludge a difficult and uncertain task. The Savannah River Technical Site (SRTC) took early (and wholly inadequate) sludge analytical data from two INEEL tanks and produced a 'first generation' formulation for a surrogate sludge by simply adding and mixing various minerals and chemicals that gave a close element balance and particle size. Since initial INEEL analyses of the tank sludge did not identify any of the mineral matter, it did not reveal the true nature of the solids. Subsequent analyses revealed some of this mineral matter phases present and other physical and chemical features of the sludge, providing incentive to modify the solid surrogate formulation using metathesis reactions.

The underlying objective is to produce a non-hazardous solid surrogate with chemical and physical properties closely matching those of the Tank Farm solid wastes, and provide a simple procedure for reproducing the surrogate. Metathesis synthesis involves the provoked reaction of cations and anions in aqueous solutions for the purpose of forming insoluble solids (i.e., precipitates). This was accomplished by preparing an aqueous acidic solution of known soluble tank compounds and then, subsequently adding solutions containing ions and compounds, that when mixed with the first solution cause solids to form. This approach was used to produce surrogate solids for the cold filtration tests described further in this paper. The following recipe for making the 'second generation' solid surrogate is provided immediately following. The procedure and recipe are for generating ca. 100 grams of solid (dry weight) and initially

requires the preparation of three aqueous solutions, as indicated. Recipe amounts indicated for each reagent were obtained based on analyses of unwashed solids from the WM-186 tank, pulled over the last two years. Chemicals used were reagent grade from Aldrich, and the water was de-ionized.

2nd Generation INEEL Tank Sludge Surrogate-Metathesis Recipe

Solution 1	**Amount added to make 100 g solid**
$Al(NO_3)_3 \cdot 9H_2O$	124 g
$ZrO(NO_3)_2 \cdot H_2O$	20 g
$Ca(NO_3)_2 \cdot 4H_2O$	11.6 g
$Fe(NO_3)_2 \cdot 9H_2O$	11.6 g
$Mn(NO_3)_2 \cdot H_2O$	2.6 g
$Mg(NO_3)_2 \cdot 6H_2O$	8 g
$SnCl_2 . 2H_2O$	8 g
NaF	0.8 g
HNO_3 (70 wt. %)	25 ml

Solution 2	**Amount added to make 100 g solid**
27% SiO_2 in 14% NaOH	68 ml

Solution 3	**Amount added to make 100 g solid**
H_2SO_4 (95 – 98 wt. %)	2.4 ml
H_3PO_4 (85 wt. %)	10.4 ml

The above three solutions were prepared with water added, as necessary to dissolve the compounds in the respective solutions. Solution 1 was mixed in an 8-L or 12-L 3-neck round-bottom flask and heated to 50 ºC. Over a period ranging from ½ hour to 1 hour, Solutions 2 and 3 were simultaneously added to the round-bottom flask containing Solution 1. All additions were made as the original flask solution was constantly agitated with air aspiration or by using a magnetic stirrer.

Precipitates (i.e., the sludge surrogate) formed immediately, and stirring was discontinued upon complete addition of all chemical solutions. The mixture was allowed to stand over night before being filtered under vacuum in a Buchner apparatus using Watman # 40 filter paper. Portions of the solid simulant were rinsed with water for subsequent analyses. The bulk of the solid surrogate was not rinsed, and was subsequently used in various tests to determine its physical properties. Those tests include measuring the cake resistance to filtration by determining the compressibility under various constant pressure filtration conditions.

Numerous analytical techniques were employed to determine the elemental compositions of the surrogate and actual waste solids, as well as chemical phases present, thermal properties, bulk and micro-structures, ions present, degree of crystallinity, radionuclides, and the particle size distribution. These data are largely not presented here due to space limitations, but will be forthcoming is subsequent reports and publications.

Selected Results

SBW solids characterized by TEM were first washed with either water or HNO_3. As shown in various micrographs, the solids range from below a discernable size, to around 200 nanometers in length. The solids exhibit hard agglomerates of sub-micron rock-shaped particles. In several areas, fiber-shaped particles were also found. Selected area electron diffraction (SAD) patterns from these agglomerates suggest that they are amorphous. The main elements in these agglomerates identified by energy dispersive detectors (EDS) are Al, Si, Zr, P, K and O. The relative amount of these elements varies from one area to the other in a sub-micron scale as indicated by an EDS spectrum from a typical amorphous area. Minor elements such as Na, Ca, Fe, Cr, Ni, Ti, Sn, Mg, Cu, Zn, Nb, Ag, Ru, S and N were also detected in various areas.

Even though the SBW solids are mainly amorphous, many sub-micron crystalline particles were found. Zirconium oxide, aluminum oxide, Gibbsite (aluminum hydroxide), Mg-Al spinel, and titanium oxide are some of the crystalline phases identified in these samples. The image of a spinel ($MgAl_2O_4$) crystal was also discovered. In a few areas, nano-sized silicon oxide particles were also identified.

Based on the results from TEM characterization, the following conclusions were drawn:

- The matrix of the solids consists of agglomerates of sub-micron rock-shaped amorphous particles. Fiber-shaped amorphous particles are also found in some areas.
- EDS reveals that these amorphous agglomerates have Al, Si, Zr, P, K, and O as the major constituents.
- Size, geometry, and chemical composition of the agglomerates vary from one place to another on a sub-micron scale.
- Minor elements such as Na, Ca, Fe, Cr, Ni, Ti, Sn, Mg, Cu, Zn, Nb, Ag, Ru, S and N were found in various areas.
- Crystalline particles identified in this study are: zirconium oxide, aluminum oxide, Gibbsite (aluminum hydroxide), Mg-Al spinel, and titanium oxide.
- Agglomerates of very tiny SiO_2 particles (10-20 nm, non-crystalline) were found in a couple areas.

Preliminary TEM analyses on the solid surrogate indicate similar structure and mineral phases present. The micrographs taken of the actual and surrogate solids can then be qualitatively and semi-quantitatively compared. Noted similarities provide support of the overall metathesis formation of a solid surrogate for SBW tank sludge wastes.

SURROGATE AND ACTUAL SOLID SLUDGE COMPARISON STRATEGY

Figure 1 depicts a flowchart revealing the strategy for both chemical and physical based testing and comparisons. The flowchart shows the various physical property and chemical analytical activity pathways that lead to direct comparisons between the actual and surrogate sludges. The flowchart symbols representing the properties and analysis indicated are listed below. Even though the chart indicates a once-through comparison, this is not expected to be the case. Actual tank solid analysis will provide feed-back for changes in the surrogate preparation process, and iterative comparisons will be made until the desired degree of likeness for a chosen set of properties and solid characteristics is obtained.

α = Specific Cake Resistance
η = Cake Compressibility
ρ_P = Particle Density
ρ_B = Bulk Density
ρ_S = Slurry Density
SV = Settling Velocity
μ_S = Slurry Viscosity
τ = Shear Stress
du/dx = sheer rate
UDS = Undissolved Solids
TDS = Total Dissolved Solids
PSD = Particle Size Distribution
DSC = Digital Scanning Calorimetry
TGA = Thermogravimetric Analysis
XRD = X-Ray Diffraction
TEM = Transmission Electron Microscopy
SEM = Scanning Electron Microscopy
EXAFS = Extended X-Ray Absorption Fine Structure

CAKE FILTRATION STUDIES

The objective of the constant pressure cake filtration studies was to determine the de-watering features of the solid surrogate and the SBW solids by determining two key filtration properties: the specific cake resistance and the cake compressibility. For this evaluation, all tests were conducted with a bench-scale constant pressure filtration apparatus (see Fig. 2) and the surrogate utilized was a 2nd generation- metathesis prepared solid surrogate. Following the initial screening test to system-check the bench-scale filtration system, filtration experiments were performed to determine the key filter parameters of cake specific resistance and compressibility as derived and defined below. Tests were also conducted on the surrogate and SBW sludges to determine the settling rate of the solids, the particle size distribution (PSD) of solids, the mass of undissolved solids (UDS) in the sludge, the mass of total dissolved solids (TDS) in the filtrate, and the density and viscosity of the sludges and filtrate solutions.

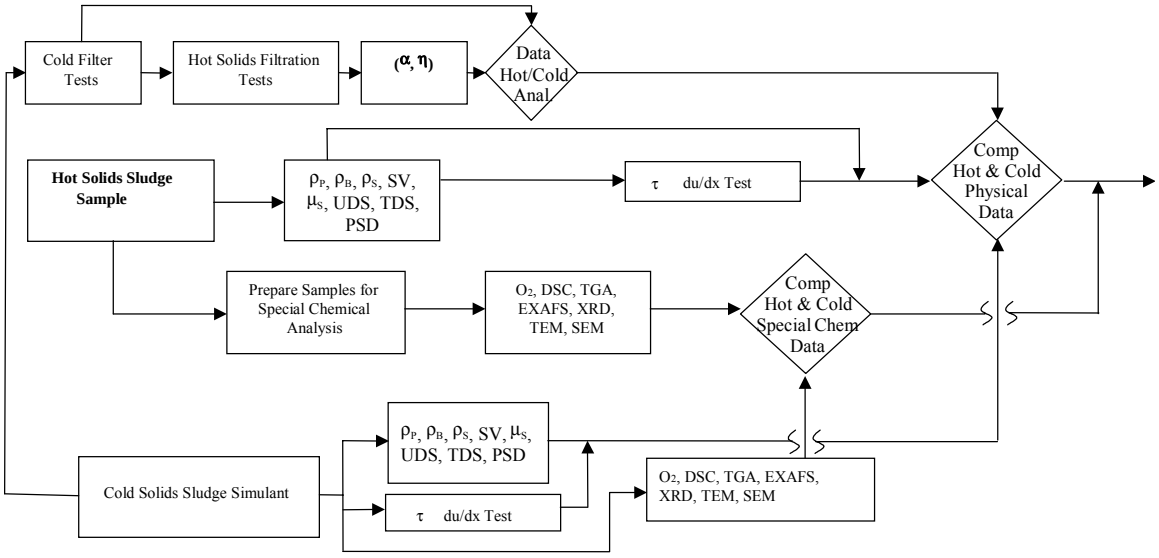

Fig. 1 Surrogate validation strategy

Water in the system can be described as:

- Free water or interstitial water, which exists between the sludge particles, but is not bound to the particles.
- Surface water, which is loosely bound chemically or physically to the surface of the sludge particles.
- Water of hydration, which is formally part of the chemical make-up of the chemical species present**(1)**.

The free water content may represent the largest fraction in the SBW sludge. The liquid moves freely between the individual sludge particles, it is not adsorbed by them, not bound to them, and is not significantly influenced by capillary forces. This type of liquid can be separated mechanically, for example, by centrifugal forces or filtration. However, the surface, and hydration water will likely remain in the filter cake, post filtration.

A small-scale filtration test was conducted under constant pressure, at a constant rate, or under simultaneous variable pressure and variable rate conditions. The constant pressure test used for this evaluation was selected because of its relative simplicity, low amount of material needed, and ease of data interpretation as required for determining and comparing the specific cake resistance and compressibility of both the solid surrogate and SBW sludge.

Cake filtration, as a solid/liquid separation process, is widely used in both the chemical and process industries. Despite its simplicity and long history of development, filtration is not easily described like some other transport unit operations, such as heat transfer, mass transfer, fluid mixing, and fluid transport. For these latter operations, properties are well defined and predictable. However, in the case of filtration, solids can have widely varying properties in addition to size distribution, that depend on conditioning and processing. For example, particle size and shape can change with treatment, aging, flocculation, pH, and pumping. For these reasons, filtration and other

solid/sludge waste processing technologies are difficult to understand, and are very underrated engineering disciplines.

Filtration performance is affected by a series of parameters, some of which are related to the suspended solid or flocculent properties of the sludge feed. An optimization of the filtration operation implies a systematic analysis of each important parameter. Noted 'Father of Filtration', F. M. Tiller of the University of Houston stated that: "Experiment is a necessary part of any filtration design procedure, and average filtration resistances are noticeably affected by sludge concentration, rate of change of applied stresses, and internal shear forces. Even under carefully controlled conditions, it is difficult to measure resistance within ±10%. Caution and judgment are essential to interpret and make use of filtration data correctly"**(2)**.

The most commonly used analysis for measuring the de-liquoring rates of sludges is the specific resistance to filtration (SRF) test. **(3,4,5,6)** The SRF test is a laboratory procedure that measures the rates at which sludges will de-liquor under pressure or vacuum. The test is based on an analysis of pressure drop for flow through a porous medium (i.e., the filter cake). The theoretical description of filtration identifies the SRF as the proportionality factor between the amount of cake solids deposited in the cake and the total flow resistance of the cake. As expected the SRF, as briefly derived below, is related to cake permeability.

In cake filtration, the sludge to be treated is dispersed in a liquid medium, whereafter it is brought into contact with a filter medium with openings smaller than the diameters of most of the particles present in the sludge. A cake is formed above the filter medium, which subsequently provides filtering, and the cake thickness increases with time. The cake structure may undergo changes as a result of cake compression caused by the sludge flow. In turn, this change in cake structure may dynamically affect filtration performance **(7).**

If the cake from the sludge filtration contains a wide range of particle sizes, there will be a tendency for the cake to behave like one composed of its finer particles than one composed of its coarser particles. Sludges containing fine particles are extremely difficult to separate because they form highly compressible cakes. While the majority of the particles are retained to form a cake, a small amount of finer ones may penetrate into the cake. The permeability of a cake depends on the extent of the compression to which it is subjected, as well as the amount of fines retained within the cake. Fine particle retention can contribute significantly to the decrease of cake permeability and may significantly effect the performance of cake filtration even if the amount of fines are small **(8)**.

Cake Filtration Theory

Liquid flow through porous media is the common characteristic of filtration processes. As the slurry liquid passes around the surface of the solid particles trapped on a porous medium (a frit or the filter cake), friction between the liquid and the solid particles being collected on the filtration medium creates a pressure drop over the length of the medium, resulting in a reduction in flow through the medium. A basic flow equation – Darcy's Law **(9) -** provides a fundamental relation between this pressure drop and the liquid flow through both the cake and the filter medium.

$$q = dV/dt = k\,(A\,p)/(\mu\,L) \qquad \text{(Eq. 1)}$$

or

$$q = dv/dt = p/(\mu\,R) \qquad \text{(Eq. 2)}$$

Where q is the volumetric flow rate of the filtrate; V, the total liquid filtrate volume collected at time, *t; t*, the time since the start of filtration; k, the cake permeability (assumed constant here, but not so in reality); A, the cross-sectional area of the collected solid (also equal to the surface area of the filter medium); p, the pressure drop across the collected cake *and* the filter medium; L, the porous cake depth; μ, the liquid filtrate viscosity; R, the sum of the resistances of the cake, R_c, and the resistance of the filter medium, R_m , (also equal to L/k); v , the filtrate volume collected at time, t (i.e., V) per unit area of filtration (i.e., A).

Both the solid filter cake resting on a filter medium and the medium itself contribute to the various resistances during constant pressure filtration. Starting with equation (2) and using the defined resistance identities of equations (4) and (5) below, the following resistance model of cake filtration is obtainable:

$dv/dt = p/\mu\ (\alpha\ C\ V/A + R_m) = p/\mu\ (R_c + R_m)$ (Eq. 3)
Where $R = R_c + R_m$ and (Eq. 4)
$R_c = (\alpha\ C\ V)/A = \alpha_{av}\ C\ v = \alpha_{av}\ w_c$ (Eq. 5)

α is the specific resistance of filtration (SRF) for the filter cake in units of m/kg; C, the slurry concentration expressed as the mass of dry cake per unit volume of filtrate (kg/m^3); R_c and R_m are the cake and filter medium resistances, respectively (1/m); and $w_c = Cv$, the total mass of dry cake solids per unit area of filter surface (kg/m^2).

Inspection of equation (3) reveals a linear relationship between the rate of filtration and the total volume of filtrate collected. In order to obtain this v vs. t relationship for constant pressure filtration, Tiller **(10,11)** recommends using the following equations, as derived from equation (3)

$pdt/\mu dv = p/(\mu\ q) = \alpha_{av}\ C\ v + R_m$ (Eq. 6)
$pt/\mu v = p/(\mu\ q_{av}) = (\alpha_{av}/2)\ C\ v + R_m$ (Eq. 7)

Since $R_c = \alpha_{av}\ C\ v$

$R = p/\mu\ q = R_c + R_m$ (Eq. 8)
$p/(\mu\ q_{av}) = \frac{1}{2}\ R_c + R_m$ (Eq. 9)

Where $q = dv/dt$, the instantaneous rate, and $q_{av} = v/t$, the average rate over the entire filtration cycle. Since equations (6) and (7) are of linear form, a plot of q versus v (w_c) provides a curve whose slope is related directly to the particular cake SRF (or α_{av}), as well as a y intercept that is representative of the resistance of the filter medium. As will be discussed in detail later, graphical interpretations of equations (6) to (7), designated as filtration models I and II by Teller, are provided in **Fig. 3**. However, experimental data are frequently not precise, and undoubtedly any points on both the $p/\mu q$ and $p/\mu q_{av}$ plots will probably deviate from that of exact straight lines. Since the slope of the equation (6) is twice that of the equation (7), Tiller **(10,11)** advised plotting both lines to reach a compromise on both the slope and intercept.

The greater the SRF, the greater the time required for filtration. To determine the effect of a change in the applied filtration pressure for a particular sludge, at least three different constant pressure tests were conducted, and for each case, SRF (or α_{av}) was determined. Based on reference **(12)**, plotting the natural log of α (*Ln* α*) versus Ln p* also results in an approximate straight line. The straight line indicates that equation (10) as proposed by Sperry, and given below, is consistent with numerous documented experiments with sludge cake filtration. Sperry's results indicate that α_0 and n are empirical constants specific for a particular sludge, and the slope of the line, as generated by the Ln-Ln plot described above, is the compressibility of the cake, n. This value varies from 0 for a rigid, incompressible cake, to n>1 for a super-compactable cake. Values of n used to classify the cake compressibility are listed in **Table I**.

$\alpha_{av} = \alpha_0 * (p)^n$ (Eq. 10)

Table I Cake compressibility classifications

Incompressible	n = 0
Moderately compressible	n ~ 0.5-0.6
Highly compressible	n ~ 0.7-0.8
Super compressible	n>1

Cake compressibility is influenced by numerous factors such as the particle size distribution, the particle shape, and their aggregation **(5,6)**. In the case of low or moderate cake compressibility, higher filtration pressure leads to higher filtration rates- a desired result, if filtration is a critical processing step. On the other hand, highly compressible cakes can greatly increase filtering time since increasing the pressure may not accelerate de-liquoring.

Experimental Apparatus and Procedure

The test apparatus, illustrated in **Fig. 2**, comprises a 600-ml clear filtration cylinder, a filtrate collection vessel, a pressurized air supply, an air heater, a pressure regulator, and a mass flow meter. The upper part of the filtration cylinder consists of double-wall plastic pipe, 20 cm high, with an inside diameter of 6.4 cm. The filter cup is 5 cm high, with an inside diameter that gradually decreases from 6.4 to 3.2 cm and a cylinder height above the filtration area of 1.2 cm. A filter cup housed the filter solids, the filter medium, and the filter medium support, which was fabricated for these tests.

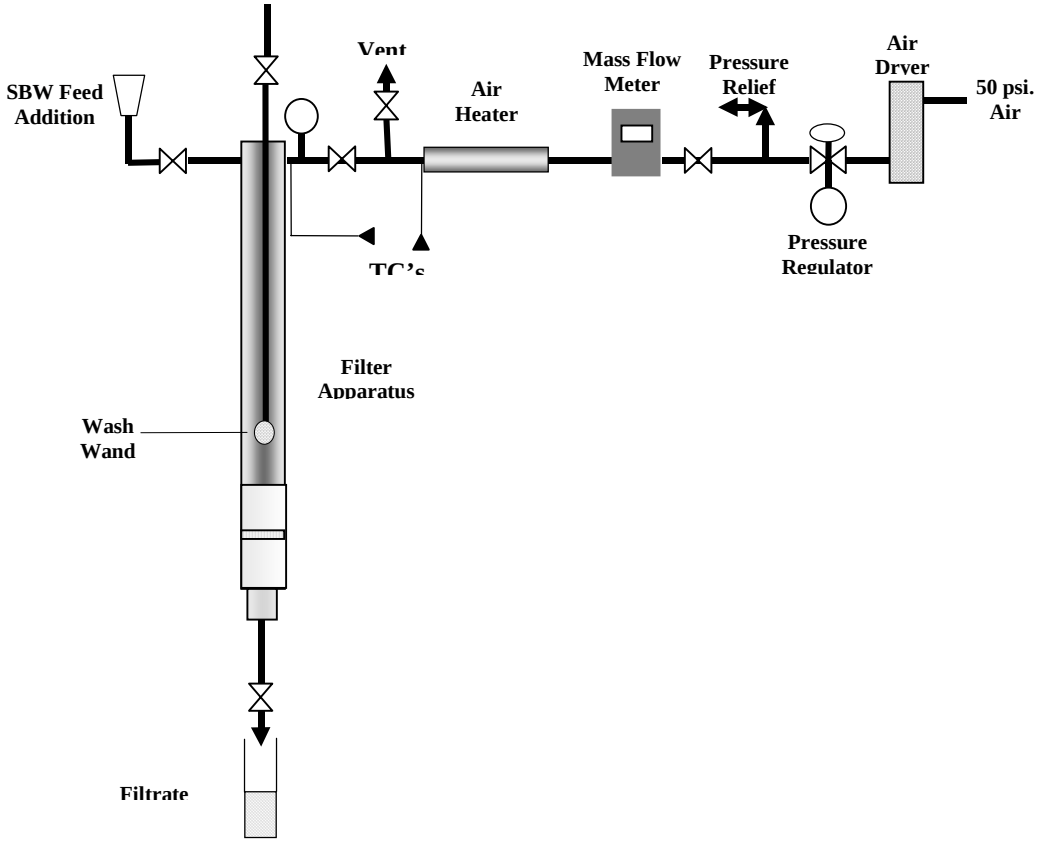

Fig. 2 Bench scale Cconstant pressure filtration apparatus

The filter cup was sandwiched between the upper cylinder section and the lower receiving part by a screw connection. The lower receiving part of the filtration cylinder was used to collect and release filtrate. Connections between the upper cylinder, the filter cup, and the receiving part were sealed with Viton O-rings to prevent leakage. An air supply of up to 80°C and 50 psig, as well as feed and wash water inlets were connected to the top of the filtration cylinder. Filter medium cloths made of polyvinylidene fluoride (PVDF) – Kynar, polypropylene sulfide (PPS) – Ryton were used and they contained mean pore sizes around 2.9, 5.5, and 11.5 μ, respectively. The filtration cylinder can be assembled and disassembled remotely (and was for the test involving SBW solids), and the entire test apparatus can be operated with hot cell manipulators. Two identical test systems were constructed for surrogate and SBW sludges, respectively, to avoid contamination.

Compressed air was introduced into the filter test vessel immediately after a predetermined amount of either the surrogate or SBW sludge slurry was added to the feed vessel, and each experiment was carried out at a constant

pressure. Filtrate was collected in a receiver equipped with an electronic balance. The filtration time and mass of the filtrate were continuously recorded by a data acquisition system until filtration was complete. When the filtrate flow ceased, air pressure was stopped and the filter-cup with cake was removed and weighed. The mass of filtered solids was measured after oven drying at 100-105°C.

Test Sample Preparation and Description

Constant pressure filtration experiments using the surrogate were conducted to determine the filtered cake properties (e.g., SRF, n) the surrogate and compare them with the corresponding properties of the cake formed by the radioactive SBW sludge.

A high-solid content slurry of surrogate**(13)** was mixed with a diluted liquid surrogate (representative of the tank liquids)**(14,15)**. Detailed chemical composition is not reported here, however, some of its properties are listed in **Table II.**

Table II Properties of the SBW slurry surrogate

pH		Settled Solid Volume %		Slurry UDS (g/liter)			Liquid TDS (g/liter)	
0.2 ~ 0.7		35		27.5			98	
Filtrate Density ((g/ml)/°C)				Filtrate Viscosity (cp/°C)				
1.09/17	1.08/20	1.075/22	1.07/23	1.32/17	1.29/19	1.245/21	1.205/23	1.155/25

The SBW sludge samples were collected and transferred to a remote analytical laboratory at INTEC. Because the received actual sludge samples have relatively high acid content (2.39 M) and high liquid density (1.28 g/ml @ 33°C), each of the samples for the filtration test were modified by mixing 30 ml of the SBW sludge with 45 ml of water. The mixed samples were allowed to stabilize for a minimum of two days before testing. At this time the settled SBW sludge layer constituted approximately 50% of the sample bottle volume. At this point, approximately 35 ml of supernate was removed, and 40 ml samples were used to minimize the sample size for the filtration test. Properties of the modified SBW sludge slurry (post decant) are listed in **Table III**.

Table III Properties of the modified radioactive sludge slurry (decant)

pH		Settled Solid Volume %		Slurry UDS (g/liter)		Liquid TDS (g/liter)	
~0		N/A		30		105	
Filtrate Density ((g/ml)/°C)				Filtrate Viscosity (cp/°C)			
1.122 (31.7)	1.12 (32.7)	1.11 (33.7)	1.1 (34.5)	1.01 (31.7)	0.987 (32.7)	0.96 (33.7)	0.947 (34.2)

A Horiba Instrument Model LA-300 was utilized to measure the particle size distribution (PSD) on the surrogate solids and the modified SBW solids. The surrogate sample was sonicated prior to use in the filter tests in order to better match their size to that of the SBW solids. The resulting size was 13.98 μm (SD = +/- 13.6 μm), and with a density of 2130 kg/m^3. In contrast, the average diameter of the modified SBW solids was 7.68 μm (SD = 5.25 μm).

The settling rate of a solid is usually a function of concentration. To obtain settling rates, samples of the surrogate and SBW solids were shaken in a 12 mm diameter glass column and the height of the solids layer was monitored overtime, respectively. The solids settled slowly and the un-decanted modified slurries were used for the measurements. **Table IV** provides the calculated values of the liquid-solid interface for both slurries. For the surrogate, it took approximately two days to settle; however, it took 5 days for the modified SBW slurry to settle completely.

Table IV Comparison of SBW slurry Ssettling rates

Surrogate		Modified Hot Sludge Slurry	
Time (hr)	Interface Velocity (mm/hr)	Time (hr)	Interface Velocity (mm/hr)
1.4	----	2.5	----
2.1	48	5	2.26
5.4	9.5	21.25	0.35
9.8	5	25.5	0.68
25	3.4	29.25	0.75
47	1.4	117	0.32

Results and Discussion

For constant pressure filtration studies reported in the literature, volume (or mass) vs. time are the data obtained. Many slurry filtration data display anomalies associated with the initial stages of filtration, even though their overall character is parabolic. Anomalies in the initial stages of filtration may be the result of a slow buildup of pressure drop across the cake, or error in determining the initial start time and corresponding filtrate volume **(3,10)**. The formation of the first particle bridge is a delicate process. A collapse of these structures induced by a high-pressure load at the beginning of cake formation may cause severe medium clogging and blinding. However, a slowly increasing pressure might permit the formation of stable structures. Once the solids bridge the pores of the filter medium, pressure drop across the cake begins to increase concomitantly with cake development.

For data that fit both constant pressure filtration models I and II (equations (6)-(7)), initial timing of the filtrate mass (or volume) reading does not affect, theoretically, the slope of the standard plot or the calculated SRF. In order to obtain consistent results, data collection may be delayed for 10 seconds or longer, as long as the system is under constant pressure, and the time and filtrate mass (volume) readings are matched pairs **(10)**.

SBW Slurry Surrogate Test Results

Laboratory filtration tests usually yield the SRF (or α) data via the slope of the line generated when plotting q versus w_c, which are then usable in process design, scale-up calculations, and simulant validation.

Table V summarizes the filtration results obtained from 28 constant pressure filtration runs on three filter mediums, with various amounts of SBW slurry simulant. SRFs were calculated using both instantaneous rate (model I) and average rate (model II) over the entire filtration cycle. An example of filtration data (at 49 psi) that fit the standard models are presented in **Fig. 3**, and as evident by the figure the data fits both models well. As indicated by the theory-based equations, the slope of the $pt/\mu v$ plotted line is approximately half of the slope of $pdt/\mu dv$ (or $p/\mu v$) line. The wet cake thicknesses were at approximately 3.0, 3.5 and 5.5 mm for 30, 40 and 60 ml samples; and the equivalent total dry cake mass (UDS+TDS) was determined at approximately 0.7, 1.04 and 1.77 g, respectively. After washing the filter cake to remove the dissolved solids, the amount of UDS in each of the bone dry filter cakes was estimated at approximately 81% of the original cake mass. Because of sample variation, each dry cake needs to be collected and its mass verified individually.

The initial SRF determined for the SBW slurry surrogate ranged from 1.00×10^{13} to 1.17×10^{13} m/kg at 30 psig and 49 psig (Test Set 1). However, the SRF measurements of the same slurry surrogate gradually reduced to between 7.18×10^{12} and 8.42×10^{12} m/kg (Test Set 6) under identical test pressure, two weeks later. This observed decrease of SRF was probably due to sample aging, i.e., the fine particles agglomerated over the duration.

Table V SRF summary for the surrogate

Test Set: 1						
Sample Size: 30 ml	Filter Medium: PVDF, Mean Pore Size: 5.5µm					
Model	I			II		
Pressure (psi)	30	40	49	30	40	49
α_{av} (m/kg)*E-12	10.2	10	11.7	8.98	11.36	11.4
	10.6	11.6		10.58	10.28	
Test Set: 2						
Sample Size: 30 ml	Filter Medium: PPS, Mean Pore Size: 2.9µm					
Model	I			II		
Pressure (psi)	30	40	49	30	40	49
α_{av} (m/kg)*E-12	8.86	10.7	11.3	9.28	9.86	10.2
	8.87	10.	10.8	8.86	10.3	10.94
Test Set: 3						
Sample Size: 40 ml	Filter Medium: PVDF, Mean Pore Size: 11.5µm					
Model	I			II		
Pressure (psi)	30	40	49	30	40	49
α_{av} (m/kg)*E-12	9.56	10.5	11.2	9.64	10.24	10.38
	8.86	10.4	11.7	8.52	10.24	10.8
Test Set: 4						
Sample Size: 40 ml	Filter Medium: PVDF, Mean Pore Size: 5.5µm					
Model	I			II		
Pressure (psi)	30	40	49	30	40	49
α_{av} (m/kg)*E-12	9.77	10.4	11.2	9.28	10.14	10.82
		9.36	10.7		9.16	10.78
Test Set: 5						
Sample Size: 40 ml	Filter Medium: PPS, Mean Pore Size: 2.9µm					
Model	I			II		
Pressure (psig)	30	40	49	30	40	49
α_{av} (m/kg)*E-12	7.94	8.92	9.23	8.1	8.6	9.12
Test Set: 6						
Sample Size: 60 ml	Filter Medium: PPS, Mean Pore Size: 2.9µm					
Model	I			II		
Pressure (psig)	30	40	49	30	40	49
α_{av} (m/kg)*E-12	7.18	8.15	8.42	7.16	8.04	8.16

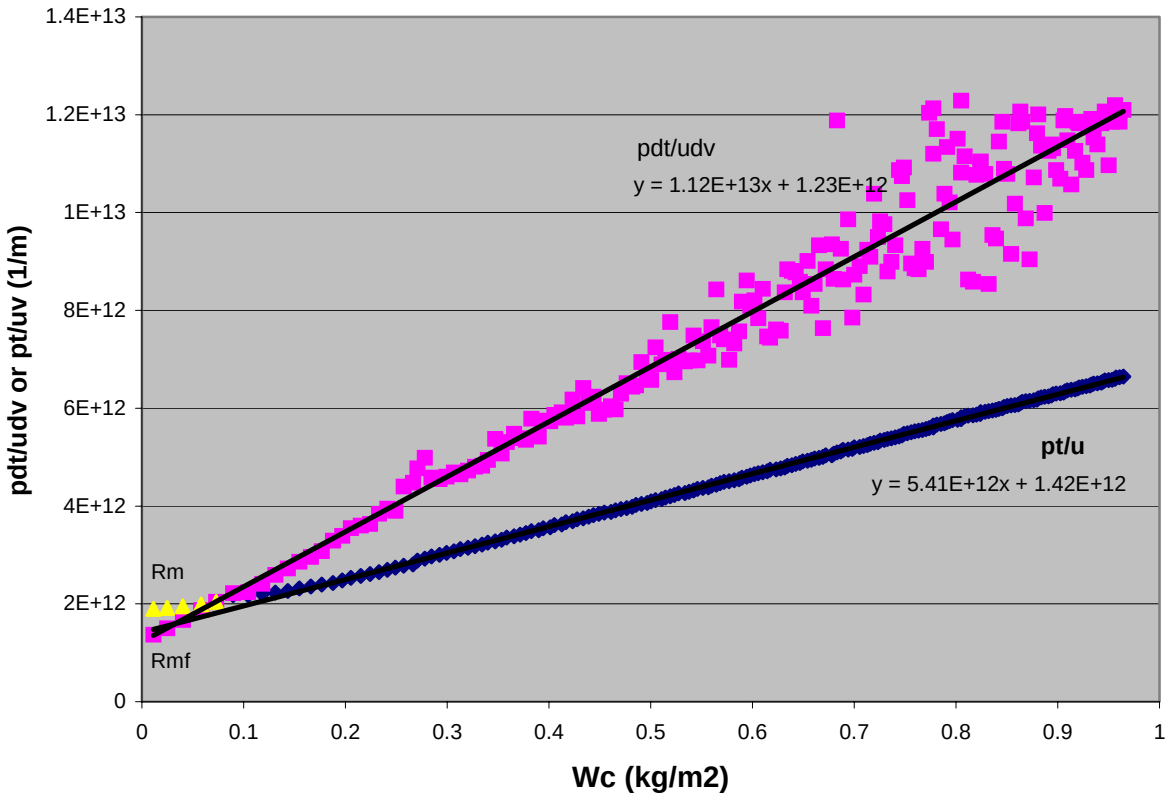

Fig. 3 Determination of cake filtration resistance in a constant pressure filtration run.

Table VI SRF summary of radioactive SBW slurry

Model	I			II		
Pressure (psig)	30	40	50	30	40	50
α_{av} (m/kg)*E-12	22.7	28.6	37.1	22.	27.2	38.4
	24.4	27.1	33.	24.2	26.8	32.2
	21.4	28.3	30.4	20.8	27.8	30.4
	22.4	26.6	31.7	21.	26.8	29.8
	19.8	23.7	29.8	20.8	22.6	30.4
	20.5		27.4	17.9		28.0
			31.1			29.0

Radioactive SBW Slurry Test Results

A total of 18 filtration tests were performed at the remote analytical laboratory (RAL) at INTEC. All tests were conducted by using the filter medium made of PVDF; at a mean pore size of 5.5 µm. Specific filtrate volume (m^3/m^2) was calculated by dividing the filtrate volume by the filter area. **Table VI** shows the derived values of the SRF for the SBW sludge using Models I and II. The wet cake thickness ranged between 8-10 mm for the 40 ml sample, and the equivalent total dry cake mass (UDS+TDS) was determined at 1.4-1.8 g. The total UDS was estimated at approximately 75% of the dry cake mass.

Comparison of SRF (α) and Cake Compressibility

Following the cake filtration tests carried out at different pressures, the parameter SRF (or α) was plotted as a function of the applied pressure, *p*. A useful expression for this purpose is only valid over a specified range of pressures and takes the form of equation (10). The results of the α vs. *p* relationship for both the surrogate and the

SBW sludge are shown in **Fig. 4**, illustrating the decrease in permeability associated with smaller particle sizes (SBW sludge) and higher applied pressures. In addition, the permeability (flow rate) similarly decreases when the particles are better dispersed. That is, the slower sedimentation velocity of the SBW sludge increases the SRF. Over the pressure range of this study, the SRF for the SBW sludge was within experimental error to that determined for the surrogate. Regardless, filtering the SBW slurries took approximately 2-3 times longer under the given conditions to filter, than the surrogate.

The filter cake collected from the 2nd generation surrogate has an average cake compressibility of 0.33(25), a low-to-moderate compressible filter cake. In contrast, the cake collected from the filtration of the actual radioactive sludge slurry (**Table VII**) has an average cake compressibility of 0.71(20), a moderate-to-highly compressible filter cake.

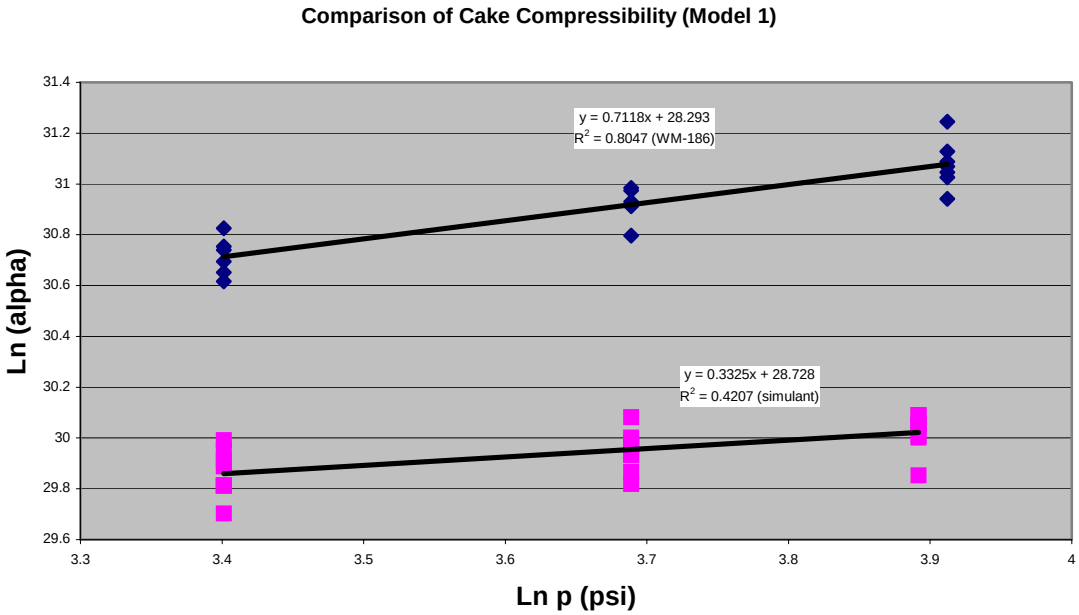

Fig. 4 Comparison of cake compressibility, Model I

Table VII Comparison of cake compressibility coefficients (Model I and II).

Model		I		II	
Waste Stream		WM-186 Slurry	Surrogate	WM-186 Slurry	Surrogate
n	mean	0.71	0.33	0.76	0.29
	Upper95%	0.9	0.5	0.98	0.45
	Lower95%	0.53	0.16	0.54	0.14

Comparison of the SBW sludge results to those of the surrogate, as shown in Fig. 4, Table VII, and Table VIII, show that the surrogate is a reasonably close match to the SBW sludge. There are many potential reasons for the dissimilarities, as there are many inherent differences between the surrogate and the SBW solids. The surrogate has only 8 metallic (or metalloid) cationic species and 6 anionic species added, whereas the SBW sludge has about 80% of the elements of the Periodic Chart, not to mention the higher density elements and numerous radionuclides present in the SBW sludge, but not in the surrogate. In addition, the SBW sludge has had years in which the chemical species could transform through radiolytic reactions, and other kinetically slow, but thermodynamically favorable reactions like oxide formation from hydrated species. Further, the tests using the SBW sludges were conducted at higher temperatures (in the hot cell) without closely matching the particle sizes of the surrogate. Subsequent tests with the surrogate are being conducted to better match the experimental conditions used for the WM-186 SBW sludge, and ultrasonic conditioning of the surrogate is being used to duplicate the particle sizes of the SBW sludges. It is worthy to note that the particle size distribution (PSD) of the surrogate (as prepared and not further conditioned) is within the range exhibited by the variance shown for all of the Tank Farm sludges, i.e., the

PSD ranges from 5 – 6 microns for SBW sludges in some of the tanks to over 12 – 13 microns in some of the other tanks, with significant contributions from particle sizes ranging to 200 microns.

TABLE VIII Summary of Solids Characteristics

Property	SBW Solids	Surrogate Solids
Radioactivity	ca. 5 R/g	No
Hazardous	DOT, RCRA, NRC	No
Ave. Particle Size (μ)	ca. 8 (WM-186)	ca. 13
Dry Density (g/ml)	Not Determined	2.06(1)
Wet Density (g/ml) (no free liquids, ca. wt. 75% water)	1.25	1.25(10)
Dynamic Viscosity	Psuedoplastic	Psuedoplastic
Compressibility	0.71(20)	0.33(25)
Settling	Flocculation/Sedimentation followed by Zone Compression	Flocculation/Sedimentation followed by Zone Compression

CONCLUSION

Developing surrogates that realistically behave as the hazardous and/or radioactive materials they are intended to replace in testing, such as the waste streams from the DOE and nuclear industry, is of paramount importance if appropriate treatment technologies are to be successfully developed and tested within an acceptable safety and economic envelope. Waste sludges created in nuclear waste storage tanks have some inherently unique properties apart from other wastes, yet they may not be specifically unique so as to preclude the development of a representative surrogate. It is highly unlikely that a representative surrogate can be made by the simple mixing of solid chemicals obtained 'off the shelf' when complex chemical and physical processes were operative during the time the waste solids were formed. However, generating a surrogate by partially reproducing the conditions similar to those that were operative during the generation of an actual waste can result in a surrogate that has remarkably close chemical and physical behavior. The metathesis synthesis reported herein appears to produce a surrogate with chemical phases and physical properties closely approximating those exhibited by the waste sludges present in the Tank Farm tanks.

As indicated by the preliminary results presented in this paper, comparison of the metathesis prepared surrogate and SBW waste sludges under constant pressure filtration test conditions, provides an early indication of the iterative nature of the process for aligning the properties of the surrogate with those of the actual wastes. Using this approach to determine the chemical and physical properties of actual wastes may appear to be costly and time-consuming (and in fact are), it is a more economically viable option than integrated testing with actual wastes, particularly when the wastes are radioactive. Further, the rigorous surrogate development method briefly discussed herein will help provide reliable processing data leading to successful and cost-effective waste technology deployment. To the contrary, poorly assumed and simple solids surrogate representation in the cold development phase will inevitably result in inadequate full-scale design and operation: hence cost prohibitive retrofits and reworks. As proven by documented waste processing case histories, such financial setbacks are not an option available to project engineering managers responsible for successfully meeting high-profile waste treatment and disposal milestones across the DOE complex.

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