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Pacific Northwest
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Operated by Battelle for the
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Reactive Transport Modeling Approach and Its Initial Saltcake Dilution Chemical Modeling

Y. Onishi

November 2002

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RL01830

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Summary

During waste retrieval operations, chemical reactions, waste property changes, and waste movements/mixing interact. Thus, to be accurate, a waste process assessment methodology must account for these physical and chemical waste characteristics and mechanisms. This study was performed by Pacific Northwest National Laboratory (PNNL) to provide suggestions to Florida International and Mississippi State Universities for their column tests and modeling as a part of their efforts to investigate Hanford Tank S-112's saltwell pumping. In addition, PNNL used the GMIN code for chemical modeling of S-112 saltcake dilution with 50% and 100% water as the first step in evaluating the feasibility of the reactive transport code ARIEL as a waste retrieval assessment methodology. The chemical modeling predicted the S-112 saltcake chemistry reasonably well, predicting that about 63% of the saltcake would be dissolved at 50% dilution with water, and 100% would be dissolved at 100% dilution. Although it is too early to conclude the usefulness of this reactive transport modeling approach, it is worth further evaluating its applicability to the waste retrieval processes.

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1.0 Introduction

This document is the final report of the Hydrodynamic Modeling subtask under Task 3, Saltcake Dissolution, of the U.S. Department of Energy (DOE) Tanks Focus Area (TFA) Technical Response B554, "Tank Waste Chemistry during Preparation, Processing, and Transport." The overall objective of Technical Response B554 was to obtain fundamental understanding of the processes involved in dissolution and transport of waste materials from storage tanks to processing steps for final waste treatment.

Saltcake dissolution studies are important for evaluating the effects of chemistry on feed preparation; retrieval, transport, and receipt operations; and their downstream processes. Aqueous reactions, solids dissolution, and precipitation will occur during these tank waste retrieval and pretreatment processes. Furthermore, dissolution and precipitation change the amount of solids and the aqueous chemical compositions and affect the physical properties (e.g., densities of supernatant liquid and sludge/saltcake) and rheology (e.g., viscosity and yield stress/strength) of the waste. These waste properties, in turn, affect waste transport and mixing, resulting in further changes in waste chemistry during these waste processes. To obtain an accurate assessment, a waste process assessment methodology must account for the following physical and chemical waste characteristics and mechanisms:

- Multiphase (solid, liquid and possibly gas) flow mixing
- Non-Newtonian sludge/saltcake waste with high viscosity and yield strength
- Newtonian waste slurry and solutions
- Multicomponent systems dominated by $Na\text{-}NO_2^-\text{-}NO_3^-\text{-}CO_3^{2-}\text{-}SO_4^{2-}\text{-}Al(OH)_4^-\text{-}OH^-$
- High ionic-strength solutions
- High solid content, often dominated by $NaNO_2(s)$, $NaNO_3(s)$, $Na_2CO_3{\cdot}H_2O(s)$, $Na_2SO_4(s)$, $Al(OH)_3(s)$, and $NaAlO_2(s)$
- Very basic solution (pH=10~14).

Under Task 3, the Florida International (FIU) and Mississippi State (MSU) Universities conducted column experiments and chemical modeling with the Environmental Simulation Program (ESP) code to evaluate Hanford single-shell tank (SST) 241-S-112 (S-112) waste retrieval. The objective of the Hydrodynamic Modeling subtask was to provide the fluid dynamics expertise and modeling needed to supplement chemical equilibrium and kinetic models for developing a predictive capability for the S-112 dissolution process. Specifically, Pacific Northwest National Laboratory (PNNL) was to provide technical advice, consulting, and support to the TFA team, including:

- input on modeling approaches
- input on lab- and pilot-scale test definition and design
- advice to the TFA team on tests and modeling that build on and complement the S112 project-funded activities
- advice on principal factors that need to be considered in the test design and modeling
- support to MSU on formulating a simple model and interpreting results from those calculations.

PNNL also conducted preliminary chemical simulations using the GMIN code (Felmy 1995), which employs Gibbs free energy minimization and Pitzer equations (Harvie et al. 1987; Pitzer 1991).

This study was originally intended for two years but, because of the overall TFA program changes, was conducted for only one year. Thus, this final report describes the first-year study results.

2.0 Tank Waste Retrieval and Its Assessment Approach

2.1 Single- and Double-Shell Tank Waste Retrieval

The baseline retrieval approach of saltcake waste from Hanford SSTs is saltwell pumping. This approach adds water to the tank to dissolve the saltcake and pumps the resulting liquid out of the tank (Herting and Bechtold 2002). Figure 2.1 illustrates saltwell pumping in Tank S-112, indicating water added above the saltcake layers and removing the resulting liquid (combination of water, dissolved solids, and original interstitial waste solution) from around the bottom of the center of the tank.

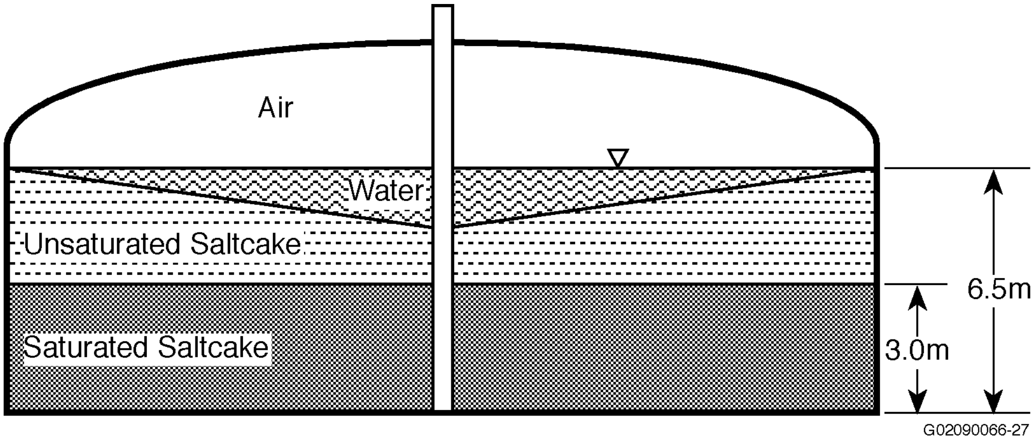

Figure 2.1. Saltwell Pumping of Hanford Single-Shell Tank S-112

For Hanford's saltcake double-shell tanks (DSTs), the baseline retrieval approach has the following five steps (Orme et al. 2001):

Step 1. Remove supernatant liquid waste from a DST and transfer it through a pipeline using in-line dilution with water
Step 2. Add water to the tank
Step 3. Mix the saltcake waste and water with mixer pumps to dissolve soluble solids
Step 4. Let undissolved solids settle to the tank bottom
Step 5. Remove the resulting supernatant liquid waste from the tank.

To perform Step 3, one or two 300-hp mixer pumps would be installed in the tank to mix the saltcake with water and dissolve much of solids. Figure 2.2 shows Tank 241-AN-105 (AN-105) waste retrieval conditions.

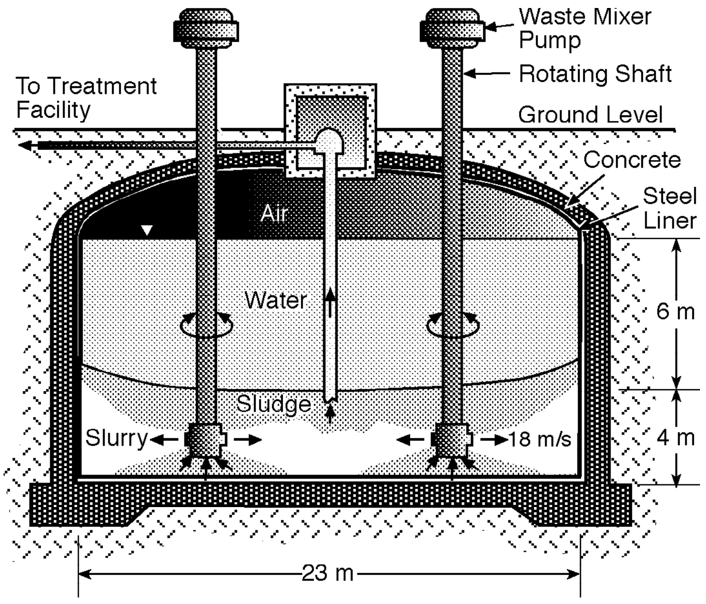

Figure 2.2. Pump Jet Mixing of Hanford Double-Shell-Tank AN-105

2.2 Four Modeling Approaches for Saltwell Pumping

Four approaches were evaluated for simulating solids dissolution and water migration in SSTs. The first approach was to develop empirical models based on measured tank waste flow movements and measured or predicted chemical reactions. This approach could produce relatively simple models for predicting saltwell pumping phenomena. Its shortcoming is that the applicability is limited to the conditions under which these models are developed.

The second approach was to implement mathematical expressions of groundwater parameters (e.g., porosity, permeability, diffusivity) and the resulting waste property (e.g., waste density and viscosity) affected by the saltcake dissolution in conventional subsurface (vadose and groundwater) computer codes. These mathematical expressions can be obtained by conducting in situ measurements or experiments correlating these property changes with chemical reactions. Currently there are many subsurface models in both the public and private domains.

The third approach was to use subsurface-water, reactive transport computer codes. These codes simulate coupled chemical reactions and subsurface flow (with Darcy's law). The reactive models include those developed by Yeh and Tripathi (1989), Yabusaki and White (Yabusaki et al. 1998), and Steefel (Steefel and Lasaga 1994). Some of these codes were applied to tank waste movements outside the tanks. These subsurface-water, reactive transport codes could handle dry and wet saltcake layers in the tank like those in a subsurface flow. This approach appears sound; however, many of these codes do not change the subsurface-water parameters to reflect the solid dissolution and other chemical reactions. The resource needs for the computer simulation can also be very intensive.

The fourth approach was to use the hydrodynamic (surface water), reactive transport code ARIEL (Onishi et al. 1999). This approach couples chemical reactions, waste properties, and chemical reactions. Unlike the subsurface-water reactive transport codes, hydrodynamics solves the Navier-Stokes and Continuity equations. But its applicability to a dry saltcake layer is very limited. The computation requirements can be even more intense than the subsurface-water, reactor transport codes.

3.0 Suggestions for S-112 Column Test

MSU's bench-scale column tests and FIU's small [3-inch (2.5-cm) diameter, 1-ft (0.3-m) long] and pilot-scale [1-ft (0.3-m) diameter, 8-ft (2.4-m) long] column tests are expected to:

- Gain a better understanding of liquid migration in an SST during saltcake dissolution with water
- Develop a predictive modeling capability for SST saltcake dissolution and liquid migration.

PNNL provided information and suggestions for FIU column tests in April 2002. The following general steps were suggested:

1. Select one publicly available generic vadose and groundwater (or a combined vadose/groundwater) model or a model specifically developed for tank waste (e.g., a model by Handy [1975])
2. Estimate ranges of expected waste properties (e.g., porosity, density, hydraulic conductivity)
3. Simulate water movements over expected ranges with the selected model
4. Develop a column test plan based on the model results; for instance,
    a. the length of the experiment
    b. the data needed for
        - understanding the phenomena
        - model input
        - model validation
    c. the instrumentation and its performance requirements (size, sensitivity, accuracy, etc.) based on the model results
    d. strategic placement of the instruments to capture the phenomena in time and space
    e. the frequency of measurements
5. Conduct the experiments
6. Analyze and identify the chemical and flow processes occurring in the test column
7. Compare the experimental and model results, and develop better mathematical formulations for waste property (e.g., porosity, permeability)
8. Modify the model to include these new formulations.
9. Run the modified model to reproduce the column test results to
    a. develop and improve the tank waste model
    b. obtain a better understanding of chemical and flow phenomena.
10. Repeat Steps 4 through 9 for various tests for different conditions and columns.

The following sections contain more specific information and suggestions that were provided in April 2002.

3.1 Test Column Sizes

FIU has planned to conduct tests with a 3-inch diameter, 1-ft long column and a 6-inch diameter 1-ft long column for bench-scale tests, and a 1-ft diameter, 8-ft long column for pilot-scale tests. PNNL suggested using a much larger (several feet) diameter, but shorter (1 ~ 2 ft long) column for the pilot-scale test. The reasons are discussed in the following paragraphs.

The actual SST flow phenomena are expected to be three-dimensional if water is sprinkled or sprayed over the entire waste surface, but the narrow columns force the flows to be one-dimensional. When the water is sprinkled/sprayed in an SST, it is expected to run not only vertically downward, but also horizontally, like an overland runoff flow during and after a rainfall. These water movements produce both vertical and horizontal channels to create preferential pathways, rather than water (now containing some dissolved solids) moving downward as a porous media flow.

With the bench-scale tests, one can evaluate 1) how water dissolves solids, moves vertically and produces vertical channels, collapses some of the remaining saltcake layer, plugs the pore spaces due to possible solid precipitation, and transports and redeposits solids; and 2) saltcake collapse. With better understanding of these mostly one-dimensional processes from the bench-scale tests, one can then develop mathematical expressions for porosity and hydraulic conductivity (or permeability). These expressions can then be incorporated into available subsurface (vadose and groundwater) models.

With a large-diameter (for example, 8-ft diameter and 2-ft long) pilot-scale column test, one could observe large-scale horizontal movements of water. FIU could then compare these observed, three-dimensional phenomena with the one-dimensional models developed under the bench-scale tests. With a better understanding of the three-dimensional flow movements gained from the pilot-scale tests, one could expand the mathematical expressions of porosity and permeability developed under the one-dimensional bench scale tests to more realistic three-dimensional SST water/liquid waste flow conditions. The expanded subsurface models could then be further tested against data obtained under various pilot-scale tests.

3.2 Flow Measurements

The hydraulic properties (porosity, permeability, and capillarity) of tank saltcake have been studied for almost 30 years. Handy (1975) describes measurements using a simulated saltcake. He also described producing a crystalline pack in cookbook-type steps. FIU should measure time-and space-varying hydraulic properties (e.g., porosity, channelization, saltcake collapse) by measuring distributions of water (liquid), solids and pressure during the experiments. Liquid and solid distributions could be measured in various ways, including X-ray scanning, neutron scanning, time domain reflectometry (TDR), and nuclear magnetic resonance (NMR). In some cases, the liquid could be doped to enhance its detection. The pressure could be measured by tensiometer to measure the negative pressure in an unsaturated flow (vadose) region. Piezoelectric crystals could be used to obtain the weight for solids to determine the saltcake layer collapse. Conductivity/permeability could be obtained by a commonly performed pump test duruing the pilot-scale tests.

3.3 Porosity of the Saltcake

One of the key physical parameters affected by the solids dissolution and controlling the liquid waste movements in SSTs is the porosity of the saltcake and sludge. Although the porosities were not estimated specifically for SST S-112, some studies have been conducted to determine both the actual porosity and the drainable porosity of SST waste during saltwell pumping. For saltcakes, the actual porosity of the saltcake may vary from 0.273 to 0.613 with an average of 0.39.[a] The drainable porosity of the SST saltcake varies from 0.13 to 0.47 with an average of 0.25. The drainable porosity is the volume fraction of the liquid that has drained. Because not all of the interstitial liquid would be drained (pumped out), the drainable porosity would be smaller than the actual porosity in the sludge. The bench- and pilot-scale test conditions could be adjusted to match some of these porosity values prior to sprinkling/spraying water.

Simmons (1995, 1996) evaluated the porosity of various SST wastes to determine moisture distributions in the saltcake and sludge as well as saltwell pumping efficiency. Simmons also reported the porosities (both actual and drainable) of the saltcake in SSTs BY-104, BY-106, BY-108, BY-110, S-102, and U-107.[a] These results are shown in Figures 3.1 and 3.2 as the number of occurrences of a specific porosity value. The actual porosity of these six SSTs averaged 0.386 (Figure 3.1) while the drainable porosity averaged 0.243 (Figure 3.2); thus the average difference between actual and drainable porosity for the saltcake is 0.143 (0.386 – 0.243).

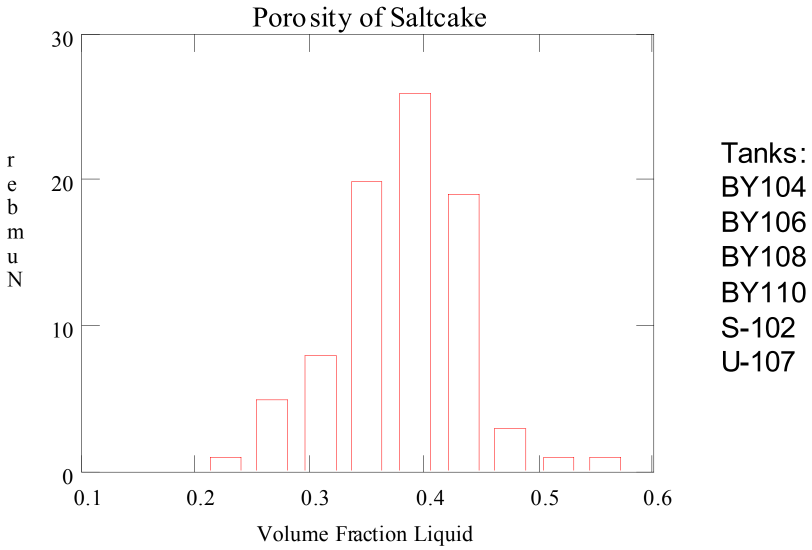

Figure 3.1. Porosity of Saltcake Waste for Six SSTs (volume fraction liquid equals porosity for saturated waste)[a]

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[a] Simmons CS. 1998. “Drainage of Analytes.” February 24, 1998 memo to Organic Waste Tank Safety Managers, Pacific Northwest National Laboratory, Richland, WA.

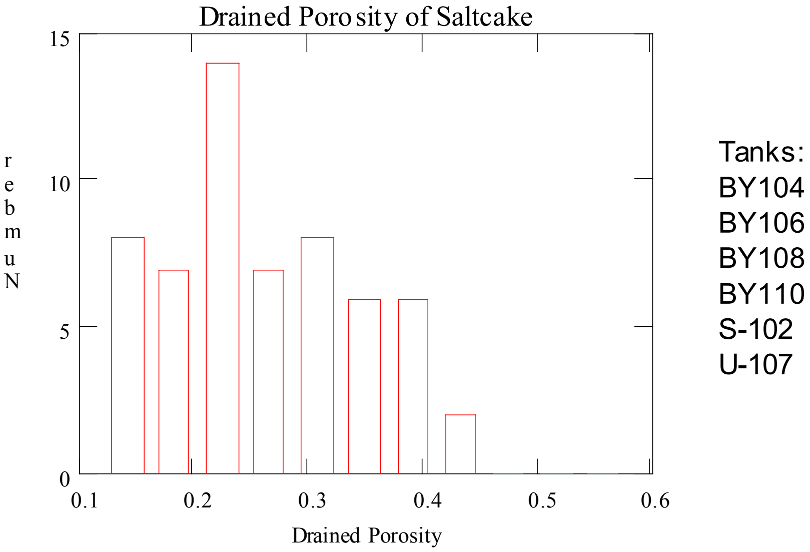

Figure 3.2. Drainable Porosity of Saltcake Waste
(the volume fraction of liquid that has drained)[(a)]

Simmons also reported the actual porosity of sludge in these six tanks. As shown in Figure 3.3, the average porosity of the sludge of these six SSTs is 0.494, and a porosity of 0.4 ~ 0.55 contains about 60% of the all porosity values. Simmons' study indicates that the porosity of the sludge, on average, is greater than that of the saltcake by 0.11 (0.494 – 0.386).

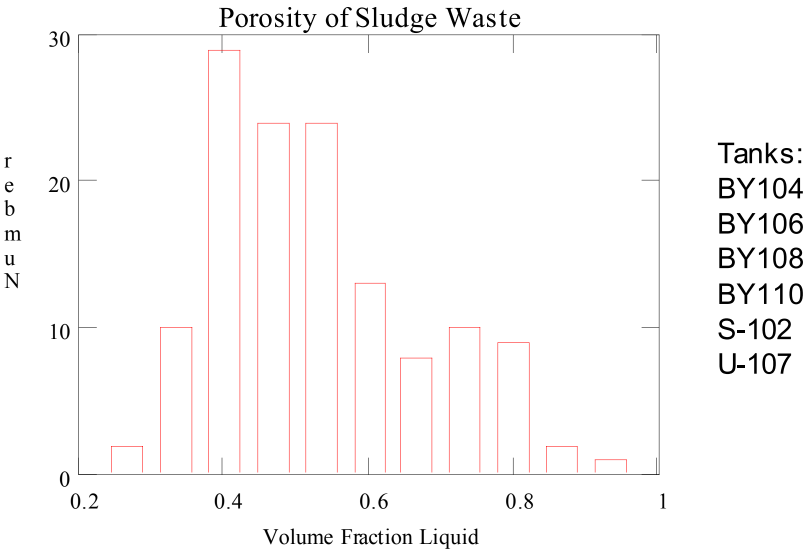

Figure 3.3. Porosity of Sludge Waste for Six SSTs
(volume fraction liquid = porosity for saturated waste)[(a)]

(a) Simmons CS. 1998. "Drainage of Analytes." February 24, 1998 memo to Organic Waste Tank Safety Managers, Pacific Northwest National Laboratory, Richland, WA.

Simmons (1998) and DeWeese (1988) also evaluated many more BY and TX SST tanks. The estimated drainable porosities for 22 BY and TX tanks are presented in Table 3.1. Group 1 tanks represent waste with a very slow decline of interstitial solution levels, while Group 2 tanks are those with much faster liquid level decline during saltwell pumping. The drainable porosity varies from 0.13 to 0.45, with an average of 0.30. As stated above, not all interstitial solution would be drained (pumped out); thus the actual porosity would be greater than the drainable porosity. Simmons (1998) estimated that the actual porosities of Groups 1 and 2 tank wastes are 0.43 and 0.455, respectively. As indicated in Figures 3.1 and 3.2, the difference between the actual and drainable porosities of the saltcake is estimated to be 0.143. Thus, the actual porosities of Groups 1 and 2 may be estimated as 0.473 (0.33 + 0.143) and 0.443 (0.30 + 0.143) respectively, if one assumes that the actual and drainable porosity difference (0.143) for the saltcake also holds for these cases. These estimates (0.473 and 0.443) are close to the values (0.43 and 0.455) obtained by Simmons, which indicates that these porosity evaluations are probably valid.

Fort (2000) also evaluated drainable porosity for the saltcake and sludge of tanks BX-107, BX-112, C-102, C-107, C-110, T-107, TY-101, and TY-105. He reported that the drainable porosity of the SST sludge waste varies from 0.07 to 0.2, averaging 0.15, and the drainable porosity of the SST saltcake varies from 0.13 to 0.47 with an average of 0.25. Using 0.143 as the difference between the actual and drainable porosities, the actual porosity of the saltcake may vary from 0.273 to 0.613 with an average of 0.393, very close to the 0.386 shown in Table 3.1. Thus Simmons'(a) results are basically consistent with Fort (2000), DeWeese (1988), and Simmons' later analyses (Simmons 1998).

(a) Simmons CS. 1998. "Drainage of Analytes." February 24, 1998 memo to Organic Waste Tank Safety Managers, Pacific Northwest National Laboratory, Richland, WA.

Table 3.1. Estimated Drainable Porosity of Some BY and TX SSTs (Simmons 1998)

Tanks	Drainable porosity
Group 1	
241-BY-104	0.34
241-BY-107	0.32
241-BY-108	0.23
241-BY-110	0.42
241-BY-111	0.37
241-BY-112	0.38
241-TX-102	0.36
241-TX-103	0.25
241-TX-106	0.41
241-TX-108	0.13
241-TX-109	0.45
241-TX-118	0.35
Group 1 Average	0.33
Group 2	
241-BY-101	0.19
241-TX-105	0.30
241-TX-110	0.32
241-TX-111	0.18
241-TX-112	0.17
241-TX-113	0.35
241-TX-114	0.33
241-TX-115	0.25
241-TX-116	0.27
241-TX-117	0.27
Group 2 Average	0.26
Overall Average	0.30

4.0 Waste Process Assessment Code, ARIEL

During waste retrieval operations, complex interactions will occur among chemical reactions, waste property changes, and waste flow/mixing. Thus, as stated in Section 1, a waste process assessment methodology must couple the following physical and chemical waste characteristics and mechanisms to obtain an accurate assessment:

- Multiphase (solid, liquid and possibly gas) flow mixing
- Non-Newtonian sludge/saltcake waste with high viscosity and yield strength
- Newtonian waste slurry and solutions
- Multi-component systems dominated by $Na\text{-}NO_2^-\text{-}NO_3^-\text{-}CO_3^{2-}\text{-}SO_4^{2-}\text{-}Al(OH)_4^-\text{-}OH^-$
- High ionic-strength solutions
- High solid content, often dominated by $NaNO_2(s)$, $NaNO_3(s)$, $Na_2CO_3{\cdot}H_2O(s)$, $Na_2SO_4(s)$, $Al(OH)_3(s)$, and $NaAlO_2(s)$
- Very basic solution (pH=10~14).

To satisfy this need, the waste retrieval and waste process assessment code ARIEL was developed (Onishi et al. 1999). It is a time-dependent, three-dimensional code that combines the equilibrium chemical reaction code GMIN (Felmy 1995) with the Pitzer equations, a kinetic chemical reaction model, and the hydrodynamic TEMPEST code (Trent and Eyler 1994). Thus, the ARIEL code explicitly accounts for interactions of aqueous chemical reactions, dissolution/precipitation under high ionic-strength conditions, and associated rheology changes while simulating tank waste movements. The following is a description of the ARIEL waste retrieval and process assessment methodology.

Fluid dynamics: The fluid mechanics portion of the code solves three-dimensional, time-dependent equations of flow, turbulence, heat, and mass (solids, liquids, and gas) transport. It uses integral forms of the fundamental conservation laws applied in a finite volume formulation. The governing equations of computational fluid dynamics are shown below:

- Conservation of mass (continuity)

$$\frac{\alpha}{\alpha t}\int_{cv} \rho dV + \int_{cs} \rho U_s dA_s = 0 \qquad (4.1)$$

- Conservation of momentum (Newton's second law)

$$\frac{\alpha}{\alpha t}\int_{cv} \rho U_r dV + \int_{cs} (\rho U_r U_s + \mathbf{j}_{\mu s}) dA_s = \dot{S}_\mu + F_r \qquad (4.2)$$

- Conservation of energy (first law of thermodynamics)

$$\frac{\alpha}{\alpha t}\int_{cv} \rho_{edV} + \int_{cs} (\rho_{U_s h} + j_{qs}) dA_s = \dot{S}_a \qquad (4.3)$$

- Conservation of turbulent kinetic energy, k

$$\frac{\alpha}{\alpha t}\int_{cv}\rho k dV+\int_{cs}(\rho U_s k+\mathbf{j}_{ks})dA_s=\dot{S}_k \tag{4.4}$$

- Conservation of turbulent kinetic energy dissipation

$$\frac{\alpha}{\alpha t}\int_{cv}\rho\varepsilon dV+\int_{cs}(\rho U_s\varepsilon+\mathbf{j}_{\varepsilon s})dA_s=\dot{S}_\varepsilon \tag{4.5}$$

- Conservation of mass constituents, C_i

$$\frac{\alpha}{\alpha t}\int_{cv}\rho C_i dV+\int_{cs}\left(\rho(U_s+U_i)C_i+\mathbf{j}_{C_i s}\right)dA_s=\dot{S}_{C_i} \tag{4.6}$$

where A_s = area in the s coordinate direction; C_I = mass concentration of ith constituent; cs and cv = control surface and volume, respectively; e = internal energy; F_r = force component in the rth coordinate direction; g_r = gravitational component in the rth coordinate direction; h = enthalpy; $\mathbf{j}_{xs}$ = diffusive flux for conserved quantity, x, in the s coordinate direction (μ and q as x are momentum and heat); k = turbulent kinetic energy; r = tensor coordinate index; r = 1, 2, 3, s = tensor summation index (used as a free index); s = 1, 2, 3; $\dot{S}_{C_i}$ = source term for ith mass constituent; $\dot{S}_k$ = source term for turbulent kinetic energy, $\dot{S}_\mu$ = source term for momentum, $\dot{S}_q$ = source term for thermal energy; $\dot{S}_\varepsilon$ = source term for dissipation of turbulent kinetic energy; U_r = velocity component in the rth coordinate direction; U_i = slip velocity of ith constituent; t = time; V = volume; ε = turbulent kinetic energy dissipation; and ρ = density.

Equilibrium chemistry: The GMIN code (Felmy 1995) was incorporated into ARIEL to calculate chemical equilibrium (Onishi et al. 1999). This equilibrium chemistry submodel minimizes the Gibbs free energy to simulate fast aqueous chemical reactions. It can also calculate chemical equilibrium for solid, solid solution, gas, and adsorption phases. Because much of the tank waste exists under high ionic-strength conditions, the excess solution free energy is modeled by the Pitzer equations (Harvie et al. 1987) in the aqueous phase modeling. Equations (4.7 through 4.10) are the governing equations to minimize the Gibbs free energy subject to the mass and charge balance:

$$G=\sum_{j=1}^{ns}\mu_j n_j \tag{4.7}$$

subject to

$$\sum_{j=1}^{ns}A_{ij}n_j=b_i \qquad i=1,\ldots.p \tag{4.8}$$

$$\sum_{j=1}^{nas} z_j n_j = 0 \tag{4.9}$$

$$n_j \geq 0 \qquad \text{for all j} \tag{4.10}$$

where G is the Gibbs free energy, μ_j is the chemical potential of species j, n_j is the number of moles of species j, ns is the total number of the chemical species in the system, A_{ij} is the number of moles of component i in one mole of species j, b_i is the number of moles of each component i, p is the number of linearly independent mass balance constraints, z_j is the charge of species j, and nas is the number of aqueous species.

Kinetic chemistry: The kinetic chemistry in ARIEL simulates kinetic reactions of precipitation/dissolution. We used the following rate law (Steefel and Lasaga 1994) for the solid, i, and associated aqueous species, j:

$$\frac{d[C_{si}]}{dt} = \{k_{i1} + k_{i2}[C_{si}]\}\{1 - \frac{Q_i}{K_i}\} \tag{4.11}$$

$$\frac{d[C_{wj}]}{dt} = a_{ij}\frac{d[C_{si}]}{dt} \tag{4.12}$$

where a_{ij} is the number of moles of aqueous species j, produced from precipitation/dissolution of one mole of solid i; $[C_{si}]$ is molality of solid i; $[C_{wj}]$ is molality of aqueous species j; K_i is an equilibrium constant; k_{i1} is solid i's reaction rate, which is independent of the solid surface; k_{i2} is solid i's reaction rate, which is dependent on the amount of the solid surface area; and Q_i is the activity product. ARIEL calculates Q_i/K_i in Eq. 4.11 under the equilibrium chemistry calculation to determine how far the actual aqueous chemistry is from the final equilibrium conditions.

5.0 Hanford Tank S-112 Chemical Modeling

The four approaches suggested to predict saltwell pumping are described in Section 2.2. FIU and MSU were to pursue either the first (using the totally empirical models) or second (with partially empirical models for waste and subsurface model properties) approach for S-112 saltwell pumping. The third approach (subsurface-water, reactive transport modeling) had been attempted previously at PNNL for a S-112 waste retrieval assessment. Thus, only the fourth approach had not been tested for the S-112 saltwell pumping case. The hydrodynamic, reactive transport code ARIEL fits the requirements of the fourth approach because it combines chemical reactions, fluid dynamics, and waste rheology. ARIEL was tested previously under some simple tank waste conditions. PNNL applied the predictive capability of the GMIN code, the chemical model built into the ARIEL code, to predict the S-112 waste solubility as a first step for testing its modeling capability for the S-112 saltwell pumping conditions.

5.1 Current Tank Waste Chemistry

Before S-112 waste chemical reactions with water were evaluated, it was required to reproduce the current S-112 waste chemical conditions with the GMIN code. Because S-112's interstitial solution in the saltcake was expected to be in an equilibrium condition with solids in the saltcake, it was necessary to first identify the solids that control the waste solution chemistry to determine the aqueous chemistry of the interstitial solution. Tank S-112 saltcake (solids and interstitial solution) mostly contains Al, Cl, F, Cr, K, Na, P, S, Si, inorganic carbon, and organic carbon based on the Hanford TWINS database. Thus, the liquid waste probably contains $Al(OH)_4^-$, Cl^-, F^-, OH^-, NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^{2-}. The elements in the S-112 interstitial solution within the saltcake are shown in Table 5.1.

We selected the following species for the interstitial solution to perform the chemical reaction modeling: $Al(OH)_4^-$, $Cr(OH)_4^-$, Na^+, CO_3^{2-}, $H_2SiO_4^{2-}$, NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}, F^- and OH^-, $NaNO_3$(aq), and $NaNO_2$(aq). The estimated (from TWINS data) molalities of the aqueous species of the S-112 interstitial solution are also presented in Table 5.1.

Herting and Bechtold (2002) identified S-112 solids in approximate relative order of abundance: $NaNO_3$(s) >>$Na_2CO_3{\cdot}H_2O$(s) >anhydrous $Na_2CO_3{\cdot}H_2O$(s) >$Na_6CO_3(SO_4)_2$ (burkeite) >>$Na_3PO_4{\cdot}12H_2O$(s) and unidentified phases of Na-S-rich phase, an Al-rich phase with no association with Si or Cr, and a trace phase containing U-Cr-Mn-Fe. We selected the following as possible solids in the S-112 saltcake: $NaNO_3$(s), $NaNO_2$(s), sodium carbonate monohydrate [$Na_2CO_3{\cdot}H_2O$(s)], $Na_3PO_4{\cdot}12H_2O$(s), NaF(s), and SiO_2(am). We did not include anhydrous $Na_2CO_3{\cdot}H_2O$(s) and $Na_6CO_3(SO_4)_2$ because we did not have their thermodynamic data in the database. However, because sodium nitrate makes up most of the saltcake (about 95% of the saltcake taken from Core 291) (Herting and Bechtold 2002), inclusion of the first two main solids adequately represents the dissolution of the solids with water. Sodium oxalate and solids bearing U, Cr, Mn, and Fe were treated here as undissolvable solids and thus were not modeled for possible dissolution or precipitation. These solids have very low solubility limits, as evidenced by very low or below detection levels of aqueous concentrations of species associated with these solids in the interstitial solution. Thus, this assumption was judged to be reasonable.

Table 5.1. Chemical Compositions and Their Concentrations for S-112 Supernatant Liquid (estimated from the TWINS database)

Compound	Measured Concentration µg/g	Selected Aqueous Species	Measured or Estimated Concentration (M)
Al	36,867	$Al(OH)_4^-$	1.795
Cr	13,800	$Cr(OH)_4^-$	0.349
K	5,280	K^+	0.061
Na	238,000	Na^+	11.953$^{(a)}$
TIC$^{(b)}$ (as CO^3)	5,993	CO_3^{2-}	0.263
Si	1,877	$H_2SiO_4^{2-}$	0.002
Cl	7,057	Cl^-	0.261
		NO_2^-	1.174
		NO_3^-	3.570
		SO_4^{2-}	0.125
		PO_4^{3-}	0.104
		OH^-	3.767

(a) Reduced from 13.606 M to satisfy the charge balance.
(b) Total inorganic carbon.

We used GMIN to first examine whether solids dissolution and precipitation would occur by imposing only one of monohydrate sodium carbonate [$Na_2CO_3 \cdot H_2O(s)$], $NaNO_2(s)$, $NaNO_3(s)$, $Na_3PO_4 \cdot 12H_2O(s)$, NaF(s), and $SiO_2(am)$ exists with the S-112 interstitial solution. If they did not dissolve into the solution, we judged these solids and the solution to be in equilibrium conditions. The following are chemical simulation results for each of these potential solids with the solution of S-112 saltcake.

Table 5.2 summarizes how much solids are dissolved into or precipitated from the solution to reach the solubility limits of each of the nine solids tested with the GMIN code. The chemical model thus predicted $NaNO_3(s)$, $Na_2CO_3 \cdot H_2O(s)$, $Na_3PO_4 \cdot 12H_2O(s)$, and NaF(s) in order of abundance (in molality).

After selecting these four solids, we tested their potential chemical reactions with the GMIN code by modeling them with the S-112 interstitial solution. This ensured that these solids and the solution used in the GMIN code could reproduce the measured concentrations of aqueous chemical species and solids in Tank S-112. The predicted conditions of interstitial solution and solids in the saltcake are presented in Figures 5.1 and 5.2, together with measured (or estimated from measured) data. Only the total concentrations of Na^+, NO_3^-, and NO_3^- were reported in the TWINS database, while the model predicted Na^+, NO_3^-, $NaNO_3(aq)$, NO_3^-, and $NaNO_2(aq)$ concentrations separately.

Table 5.2. Summary of Solids Testing by GMIN

Solid	Molality Dissolved	Presence among S-112 Solids
$NaNO_2$(s)	5.37	No
$NaNO_3$(s)	0.32	Yes
NaF(s)	0.05[(a)]	Yes
$Na_2CO_3 \cdot H_2O$(s)	0.58	Yes
$Na_3PO_4 \cdot 12H_2O$	0.33	Yes
SiO_2(am)	1.85	No
(a) Precipitated.		

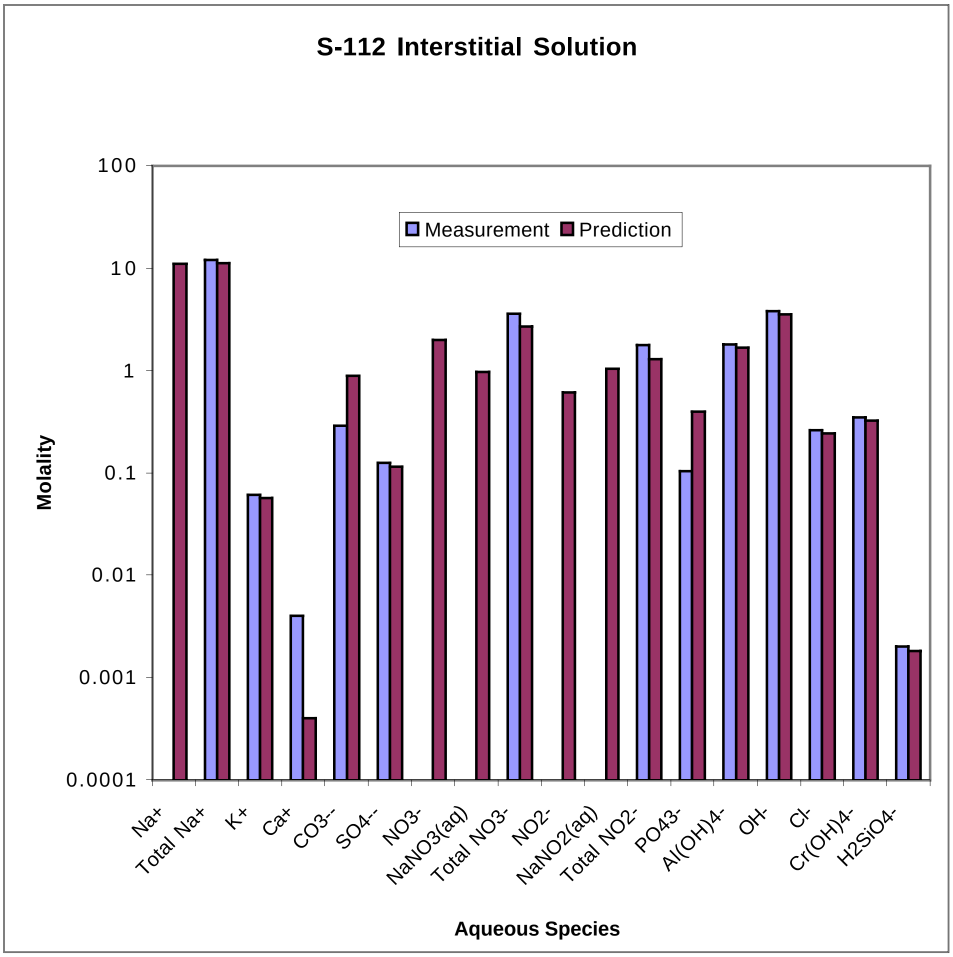

Figure 5.1. Comparison of Measured and Predicted Aqueous Species of an Interstitial Solution of S-112 Saltcake

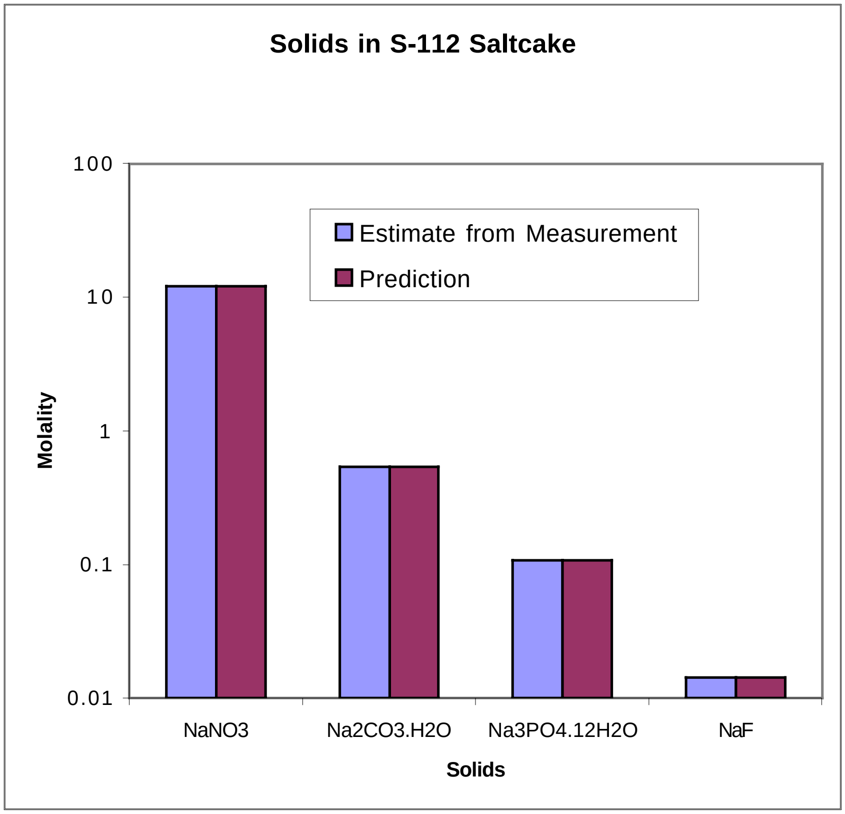

Figure 5.2. Predicted and Estimated (based on measurements) Solids in the S-112 Saltcake

5.2 Saltwell Pumping

5.2.1 In-Tank Dilution of S-112 Saltcake with Water

We simulated chemical reactions due to saltcake dilution with 50 vol% water (1 volume part saltcake and 0.5 volume part water). We used the equilibrium condition predicted above as the original S-211 saltcake condition for the subsequent dissolution modeling. Figure 5.3 shows the model predictions (shown as “dilution with chemical reactions”), as well as the original solid amounts in the saltcake (“original saltcake”) and corresponding solid amount if the saltcake was diluted but no solids dissolved (“dilution without chemical reaction”). As shown in this figure, 63% of the $NaNO_3$(s) was dissolved in this case. All other solids were totally dissolved. Thus, the S-112 saltcake is very soluble with water. Herting (2002) reported that in his dilution experiments 50% of the saltcake was dissolved with 50% dilution with water. Thus, the model prediction slightly overestimated saltcake solubility but agreed reasonably well, considering that TWINS database values were used for this assessment and not accounting for harder-to-dissolve solids in the modeling.

When the saltcake was diluted by 100 vol% water (1:1 volume ratio of saltcake and water), the chemical modeling predicted that all solids were dissolved, as shown in Figure 5.4. Herting (2002) reported that over 90% of the saltcake was dissolved at this dilution ratio.

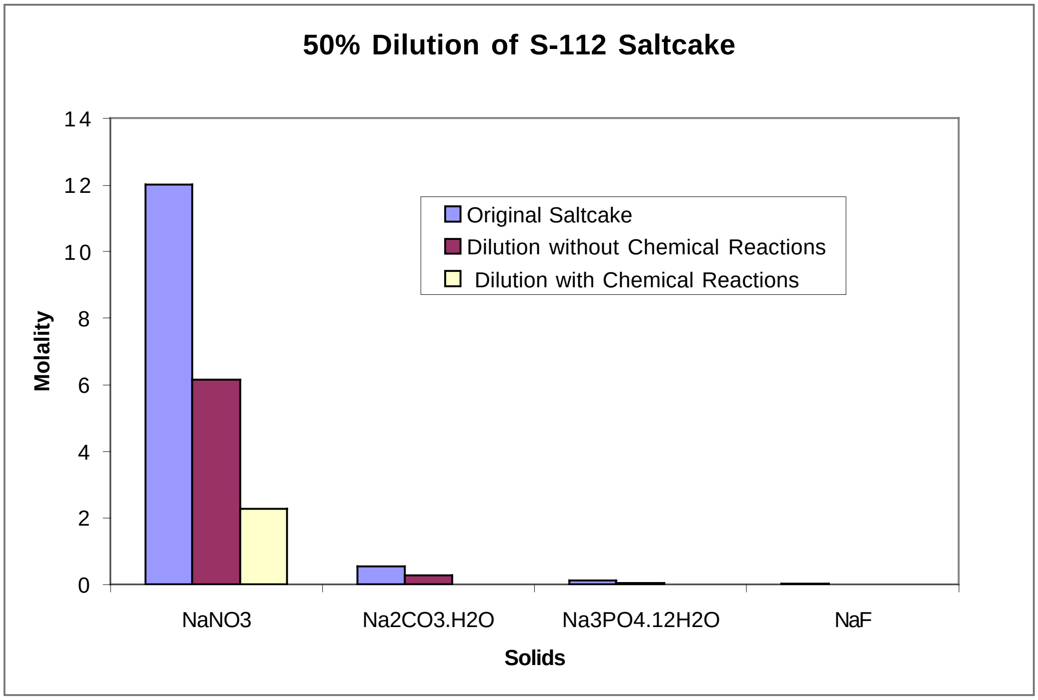

Figure 5.3. Predicted Solids after 50% Dilution of S-112 Saltcake by Water

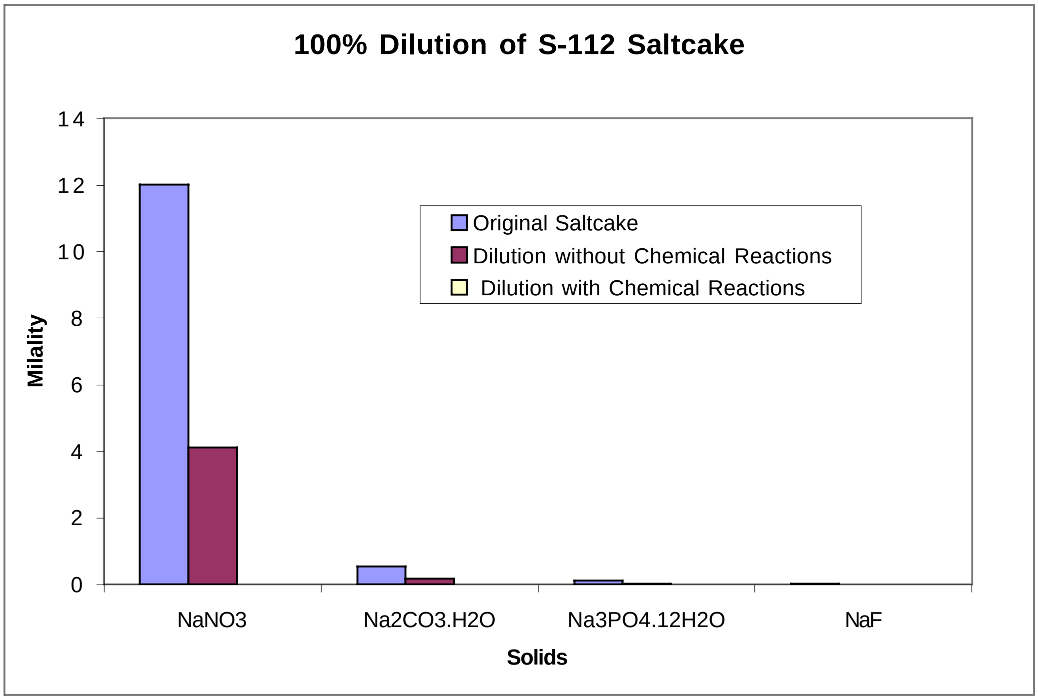

Figure 5.4. Predicted Solids after 100% Dilution of S-112 Saltcake by Water

5.2.2 Saltwell Pumping

Section 5.2.1 demonstrates that the GMIN code, built in as the equilibrium portion of the reactive transport code ARIEL, shows the reasonable predictions of the waste chemistry of S-112 saltcake and its dilution with water. The ARIEL code could then be tested by applying it to the S-112 saltwell pumping case, as shown below. However, due to the termination of this two-year study at the end of the first year, further model evaluation was not conducted.

Because the ARIEL code can simulate up to nine aqueous species, we planned to select H_2O, Na^+, CO_3^{2-}, NO_3^-, NO_2^-, PO_4^{3-}, F^- OH^-, and $NaNO_3$(aq) as aqueous species. We planned to select fine solids $NaNO_3$(s), $Na_2CO_3 \cdot H_2O$(s), $Na_3PO_4 \cdot 12H_2O$(s), and NaF(s) and one nonreactive solid representing unidentified phases of a Na-S-rich phase, an Al-rich phase, and U-, Cr-, Mn-, and Fe-bearing solids. With these selected chemical species as modeled constituents, ARIEL could possibly simulate waste chemistry and property changes and transport and mixing of water, original interstitial solution, and dissolved solids during saltwell pumping of Tank S-112.

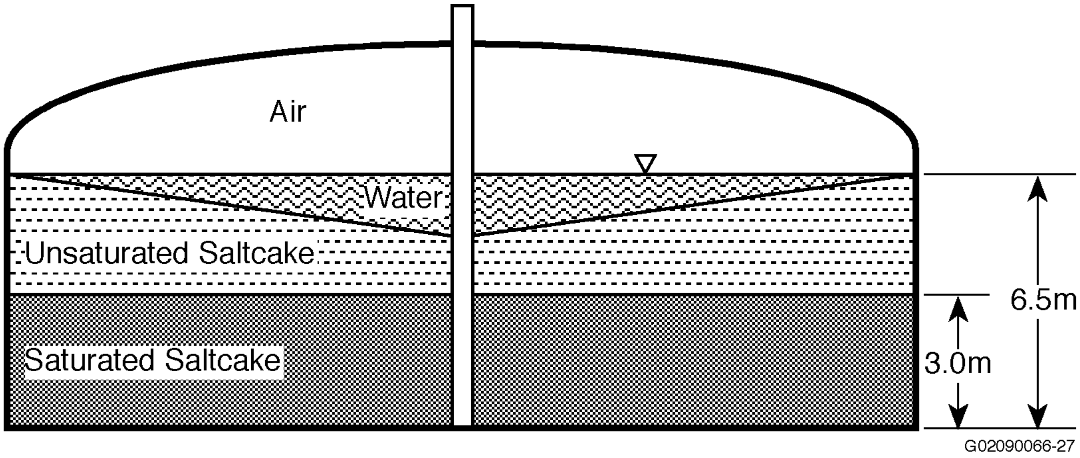

Figure 5.5. S-211 Saltwell Pumping Model Setup

6.0 Summary and Conclusions

During waste retrieval operations, chemical reactions, waste property changes, and waste movements/mixing interact. Thus, to be accurate, a waste process assessment methodology must account for all these physical and chemical waste characteristics and mechanisms. Four possible approaches were investigated: 1) the totally empirical models correlating these interactions, 2) subsurface-water codes imbedded with mathematical expressions empirically correlating the waste property and subsurface-flow parameters to the chemical reactions, 3) subsurface-water, reactive transport codes, and 4) hydrodynamic, reactive transport codes.

This study provided suggestions to FIU and MSU column tests and simulation modeling to investigate Tank S-112's saltwell pumping for the development of either the first or the second approach. In addition, PNNL initiated GMIN chemical modeling of S-112 saltcake dilution with 50% and 100% water as the first step toward evaluating the feasibility of applying the reactive transport code ARIEL. The ARIEL code was perfectly suited to the fourth approach. The chemical modeling predicted the S-112 saltcake chemistry reasonably well, predicting that about 63% of the saltcake would be dissolved at 50% dilution with water, and 100% would be dissolved at 100% dilution. Although it is too early to conclude the usefulness of this reactive transport modeling approach, it is worth further evaluating its applicability to the waste retrieval processes.

7.0 References

DeWeese GC. 1988. *Observed Porosity of Single-Shell Tank Waste Salt Cakes and Sludges.* WHC-SD-WM-TI-328, Westinghouse Hanford Company, Richland, WA.

Felmy AR. 1995. "GMIN, A Computerized Chemical Equilibrium Program Using a Constrained Minimization of the Gibbs Energy: Summary Report." *Chemical Equilibrium and Reaction Models*. Soil Science Society of America, Special Publication 42.

Felmy AR, DA Dixon, JR Rustad, MJ Mason, and LM Onishi. 1998. "The Hydrolysis and Carbonate Complexation of Strontium and Calcium in Aqueous Solution. Use of Molecular Modeling Calculations in the Development of Aqueous Thermodynamic Models." *J. Chem. Thermodynamics*, 30, 000-000, Article No. c1980376.

Fort LA. 2000. *Updated Pumpable Liquid Volume Estimates and Jet Pump Durations for Interim Stabilization of Remaining Single-Shell Tanks*. HNF-2978 Rev. 2, CH2MHILL Hanford Group, Inc., Richland, WA.

Handy LL. 1975. *Flow Properties of Salt Cake for Interstitial Liquid Removal/Immobilization Development Program*. AHR-C-6, Atlantic Richfield Hanford Company, Richland, WA.

Harvie CE, JP Greenberg, and JH Weare. 1987. "A Chemical Equilibrium Algorithm for Highly Non-Ideal Multiphase Systems: Free Energy Minimization." *Geochemica et Cosmochimica Acta*, 51, 1045–1057.

Herting DL and DB Bechtold. 2002. *Tank 241-S-112 Saltcake Dissolution Laboratory Test Report*. RPP-10984 Rev. 0, Fluor Hanford Company, Richland, WA.

Onishi Y, DS Trent, TE Michener, JE Van Beek, and CA Rieck. July 1999. "Simulation of Radioactive Tank Waste Mixing with Chemical Reactions." FEDSM99-7786, *Proceedings of 3rd ASME/JSME Joint Fluids Engineering Conference*. ASME/JSME, San Francisco.

Orme RM, DJ Geniesse, and GT MacLean. 2001. *Generalized Feed Delivery Descriptions and Tank Specific Flowsheets*. RPP-8218 Rev. 0, Ch2MHILL Hanford Group, Inc., Richland, WA.

Pitzer KS. 1991. *Activity Coefficients in Electrolyte Solutions*. CRC Press, Boca Raton, FL.

Simmons CS. 1995. *A Simplified Model of Salt cake Moisture Distribution*. PNL-10803, Pacific Northwest National Laboratory, Richland, WA.

Simmons CS. 1996. *Modeling Water Retention of Sludge Simulants and Actual Saltcake Tank Wastes*. PNL-10831, Pacific Northwest National Laboratory, Richland, WA.

Simmons CS. 1998. *Dryout Modeling in Support of the Organic Tank Safety Project*. PNL-11935, Pacific Northwest National Laboratory, Richland, WA.

Steefel CL and AC Lasaga. 1994. "A Coupled Model for Transport of Multiple Chemical Species and Kinetic Precipitation/Dissolution Reactions with Application to Reactive Flow in Single Phase Hydrothermal Systems," *American Journal of Science*, Vol. 294, pp. 529-592.

Trent DS and LL Eyler. 1994. *TEMPEST: A Computer Program for Three-Dimensional Time-Dependent Computational Fluid Dynamics*. PNL-8857 Vol. 1, Pacific Northwest National Laboratory, Richland, WA.

Yabusaki SB, CI Steefel, and BD Wood. 1998. “Multidimensional Multispecies Reactive Transport in Nonuniform Velocity Fields: Code Verification Using an Advective Reactive Streamtube Approach.” *Journal of Contaminant Hydrology*, Vol. 30, pp. 299-331.

Yeh GT and VS Tripathi. 1989. “A Critical Evaluation of Recent Developments in Hydrogeochemical Transport Models of Reactive Multichemical Components.” *Water Resources Research*, Vol. 25 (1), pp. 93-108.

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