Final Report

U.S. Department of Energy

Numerical Modeling of Mixing of Chemically Reacting, Non-Newtonian Slurry for Tank Waste Retrieval

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3. Executive Summary

Fifty-four million gallons of wastes containing 180-million curies of radioactivity are stored in single (SSTs)- and double-shell underground tanks (DSTs) at the U.S. Department of Energy's Hanford Site in eastern Washington (Gephart and Lundgren 1997). They are a multiphase, multicomponent, high-ionic strength, and highly basic mixture of liquids, solids, and, in some cases, gases. Mixer pumps will be installed in twenty-eight 4,000-m^3 DSTs to stir radioactive sludge/saltcake and supernatant liquid (and possibly a solvent) so the waste can be retrieved from the tanks for subsequent treatment and disposal. During the retrieval operation, complex interactions occur between waste mixing, chemical reactions, and rheology. Thus, decisions made about waste retrieval must account for these complex interactions.

To satisfy this need, we developed the non-Newtonian reactive transport computer simulation code ARIEL, which couples chemical reactions, multiphase hydrodynamics and transport, and non-Newtonian/Newtonian waste rheology under this EMSP Project 65371. Integrating chemistry and fluid mechanics into one computer framework holds a great promise for addressing the complex phenomena of tank waste retrieval. This approach is very new and is used only for groundwater, river, and accidental fire simulations (Yeh and Tripathi 1989; Steefel and Lichter 1994; Steefel and Lasage 1994; Gran and Magnussen 1996; Yabusaki et al. 1998).

ARIEL was intended for idealized waste conditions and represents the first major step in our systematic approach to develop a scientific waste retrieval assessment capability. ARIEL can determine tank waste processing operational parameters such as how and how much waste can

be retrieved from the tanks. Its applications demonstrated that ARIEL is applicable to idealized tank waste conditions—pure crystal solids, no agglomerates, fast and simple kinetics, and simple non-Newtonian rheology.

To make scientifically defensible decisions for waste retrieval, we must develop an assessment methodology that can evaluate realistic tank conditions: multiple solid phases with different particle sizes, hydrates, chemical properties, and effects on rheology. Unwanted chemical reactions and associated rheology changes could make these waste retrieval operations impossible. Thus, the next step would be to build upon ARIEL to systematically expand its capability to address hydrates, agglomerated solids, colloidal formations, liquid and slurry viscosities, and variable solution densities. With this future expansion of predictive capabilities of the combined chemistry, rheology and waste mixing simulation, The ARIEL could address the potentially crippling waste retrieval issues associated with hydrated mineral formations.

4. Research Objectives

4.1 Research Objectives

In the U.S. Department of Energy (DOE) complex, 100 million gallons of radioactive and chemical wastes from plutonium production are stored in 281 underground storage tanks. Retrieval of the wastes from the tanks is the first step in its ultimate treatment and disposal. Because billions of dollars are being spent on this effort, waste retrieval demands a strong scientific basis for its successful completion. As will be discussed in Section 4.2, complex interactions among waste chemical reactions, rheology, and mixing of solid and liquid tank waste (and possibly with a solvent) will occur in DSTs during the waste retrieval (mixer pump) operations.

The ultimate goal of this study was to develop the ability to simulate the complex chemical and rheological changes that occur in the waste during processing for retrieval. This capability would serve as a scientific assessment tool allowing a priori evaluation of the consequences of proposed waste retrieval operations.

Hanford tank waste is a multiphase, multicomponent, high-ionic strength, and highly basic mixture of liquids and solids. Wastes stored in the 4,000-m^3 DSTs will be mixed by 300-hp mixer pumps that inject high-speed (18.3 m/s) jets to stir up the sludge and supernatant liquid for retrieval. During waste retrieval operations, complex interactions occur among waste mixing, chemical reactions, and associated rheology. Thus, to determine safe and cost-effective operational parameters for waste retrieval, decisions must rely on new scientific knowledge to account for physical mixing of multiphase flows, chemical reactions, and waste rheology.

To satisfy this need, we integrated a computational fluid dynamics code with state-of-the-art equilibrium and kinetic chemical models and non-Newtonian rheology (Onishi et al. 1999). This development is unique and holds great promise for addressing the complex phenomena of tank waste retrieval.

The current model is, however, applicable only to idealized tank waste conditions—solids are crystals, not hydrates; kinetic rates are fast; the slurry has simple rheology; and the water mass is constant. Thus, this idealized reactive transport model, ARIEL could provide a basis for addressing potentially crippling waste retrieval issues associated with hydrated mineral formation by systematically expanding its modeling capabilities.

4.2 Tank Waste Characteristics to be Accounted for in the Waste Retrieval Assessment Tool

To achieve final waste disposal, the waste must be removed (retrieved) from the tanks. These wastes are highly basic (pH of 10–14), have high salt content, and are chemically and physically very complex. Solids, salt cakes, sludges, liquids, and vapors often coexist in the same tank. Even the sludges alone have varieties of solids with a widely varying chemical and physical characteristics (Onishi et al. 1996), as shown in Figure 4.1.

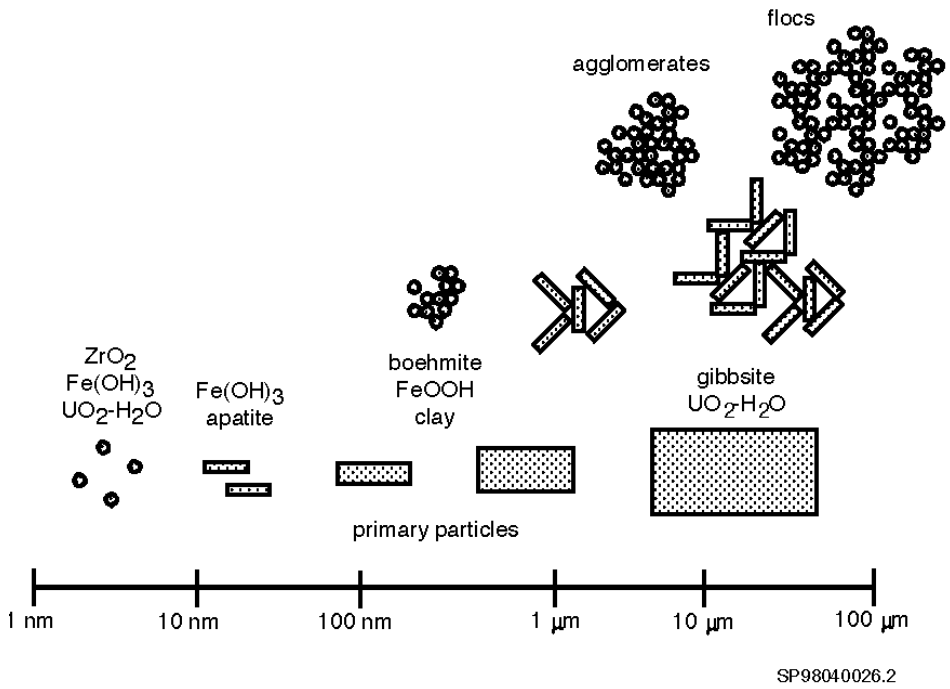

Figure 4.1. Some primary particle and agglomerate sizes and shapes in sludge

The wastes stored in 28 of the 4,000-m^3 DSTs at the Hanford Site will be retrieved by installing one or two high-powered rotating mixer pumps that inject 18-m/s jets to stir up the sludge/saltcake and supernatant liquid in the tank, blending them into a slurry that will be pumped from the tank to a waste treatment facility, as shown in Figure 4.2 (Onishi et al. 2000). In some cases, solvents (e.g., water or sodium hydroxide solution) will be added to dissolve and thus reduce the amount of solids, decrease the density and viscosity of the solution, and make the waste easier to mix, retrieve, and transfer (through pipelines) to other tanks or to the treatment facility.

When a sludge is mixed with supernatant liquid and solvent in the tank, physical and chemical changes occur. Dilution alone changes important physical properties. This change can be observed from rheological measurements of wastes in DST 241-SY-102 at Hanford (Onishi et al. 1996). As shown in Figure 4.3, the original sludge is non-Newtonian, while the sludge diluted by 48 wt% of supernatant liquid is Newtonian. Thus, when the sludge is withdrawn to

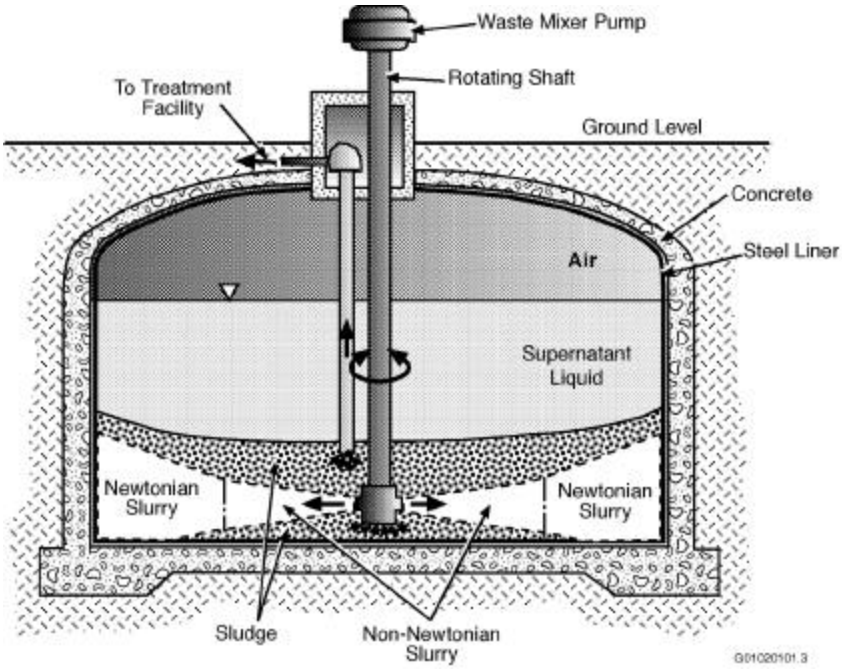

Figure 4.2. Double-shell tank pump jet mixing

the mixer pump near the tank bottom and is injected back into the sludge layer, the jet is a non-Newtonian flow. The jet entrains the supernatant fluid as it penetrates and mixes with the sludge layer. The resulting slurry becomes a Newtonian flow with significantly reduced viscosity and shear stress.

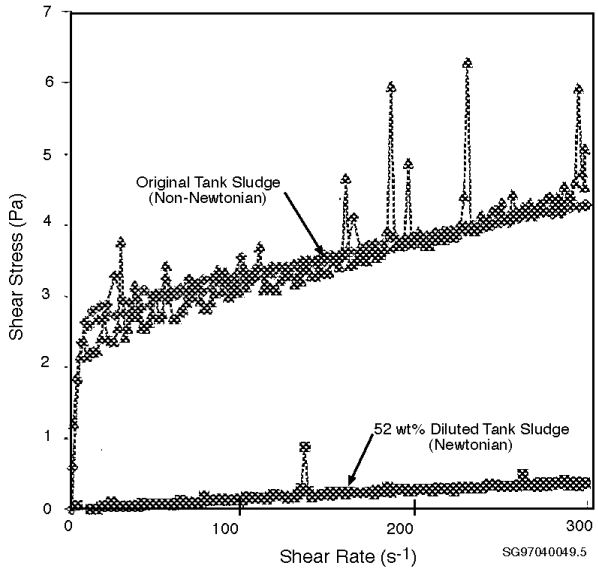

Figure 4.3. Constitutive relationship between shear stress and shear rate of Tank 241-SY-102 Newtonian and non-Newtonian Wastes (Onishi et al. 1996)

Aqueous and chemical reactions and solid dissolution and/or precipitation will occur in response to changing conditions during mixing. The dissolution and precipitation change solid and aqueous chemical compositions and thus affect physical properties (e.g., densities of supernatant liquid and sludge), rheology (e.g., viscosity and yield stress/strength), and flow conditions (e.g., drags behind solid particles). These changes, in turn, affect the slurry mixing, solids resuspension, and settling of tank wastes.

Unwanted chemical reactions and associated rheology changes could make these waste retrieval operations impossible. At Hanford, aluminum-containing precipitates represent one of the largest fractions of material present. Aluminum solids may be composed of the larger gibbsite ($Al(OH)_3$) particles or smaller boehmite (AlOOH) particles, depending on tank waste conditions. Boehmite can also form a gel with significantly higher viscosity, as shown in Figure 4.4 (Rector and Bunker 1995).

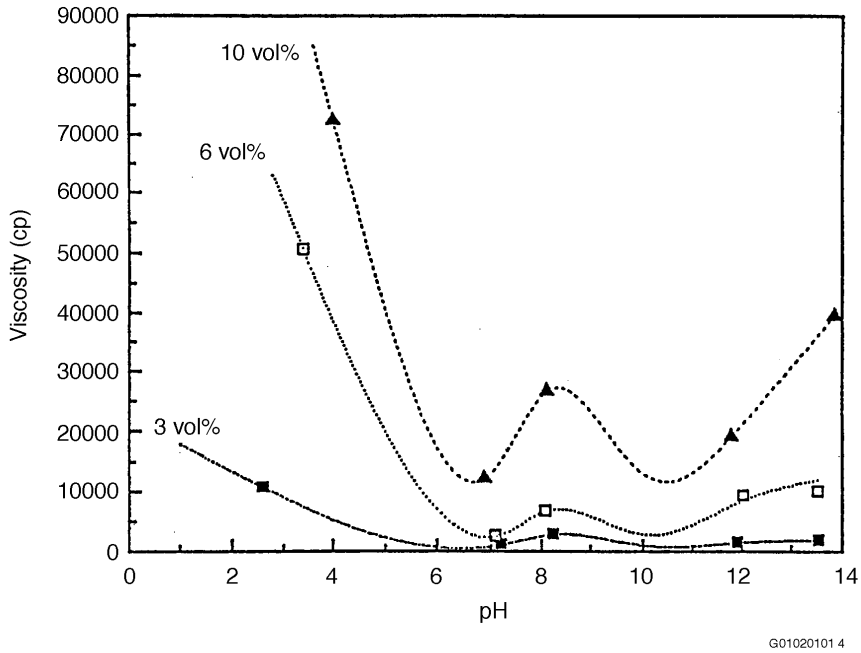

Figure 4.4. Viscosity of boehmite in 1 M $NaNO_3$ as a function of pH and solid loading at shear rate of 11.5 s^{-1}

During pump jet mixing, tank waste may experience complex rheological changes. Figure 4.5 shows a jet penetrating into sludge that is initially non-Newtonian (see the top image in the figure). As the waste is being mixed, the slurry becomes Newtonian (middle image), as Figure 4.5 indicates. However, if chemical conditions and solid concentrations are such that boehmite and its aggregates form even locally, the waste becomes a gel (bottom image) and the tank waste can neither be removed from the tank nor transferred into treatment facilities through pipelines. Since the waste retrieval is the first step for tank waste remediation, not being able to remove waste from underground tanks has severe consequence to DOE's tank waste remediation program. Thus, it is important to investigate chemical reactions, rheology, and mixing processes with their interactions.

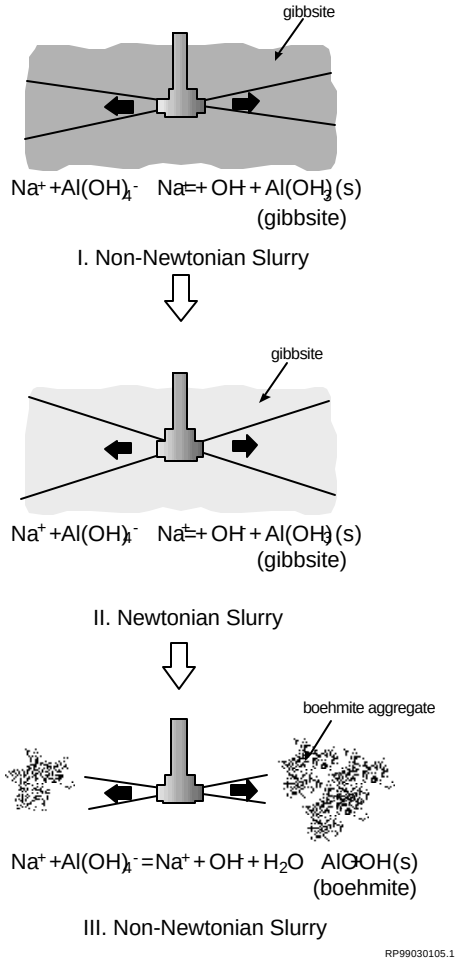

Figure 4.5. Pump jet mixing of waste having gibbsite and boehmite reactions

Another example that shows the critical importance of chemical changes on waste rheology and thus waste retrieval and pipeline transfer is related to trisodium phosphate hydrates, which can make waste retrieval impossible, as discussed previously.

Even without the dramatic changes caused by formations of boehmite and trisodium phosphate hydrate, changes from a non-Newtonian to Newtonian slurry affect how the jet spreads, mixes, and erodes the sludge. If Equation (4.1) for the erosion of fine sediment (silt and clay) is indicative of sludge erosion (Krone 1962), a Newtonian slurry can be more easily removed from the tank than a non-Newtonian slurry with a given shear stress acting on it (see Figure 4.6). This difference between Newtonian and non-Newtonian mixing has also been found from numerical mixing experiments (Ten et al. 1996, 1997, 1998). Moreover, the amount of sludge retrieved from the tank bottom is linearly proportional to the shear stress, indicating the importance of accurately evaluating jet mixing processes and shear stresses of both Newtonian and non-Newtonian slurries for waste retrieval.

$$S = E\left(\frac{\tau}{\tau_c} - 1\right) \tag{4.1}$$

where

E = erodability coefficient

S = amount of solid eroded per unit bottom surface area per unit time

τ and τ_c = shear stress and critical shear stress (yield stress) for erosion.

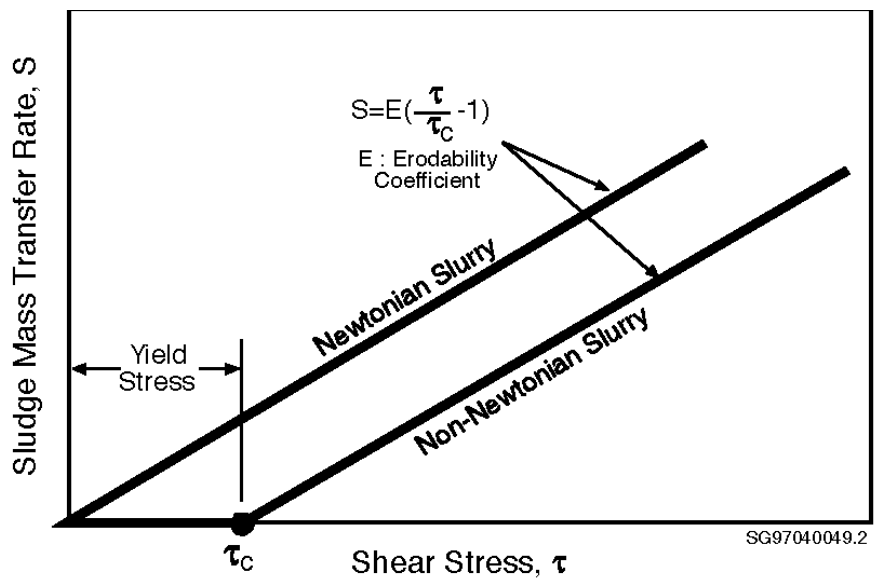

Figure 4.6. Sludge Mass Transfer Rate Versus Shear Stress

To summarize, during mixing aqueous reactions and solids dissolution and precipitation will change the amount of solids and the aqueous chemical compositions and affect the physical properties and rheology of the waste. These changes, in turn, affect slurry mixing, solid erosion, and settling. A capability is needed to account for these multiple reactions.

5.0 Methods and Results

5.1 Work Performed at Pacific Northwest National Laboratory

5.1.1. Waste retrieval assessment approach

Under this project, Pacific Northwest National Laboratory (PNNL) adapted a new reactive transport approach (Gran and Magnussen 1996; Yabusaki et al. 1998) to develop an integrated chemical reactions, hydrodynamic transport, and changing waste rheology by combining the state-of-the-art-equilibrium chemical reaction code, GMIN (Felmy 1995), a kinetic chemical reaction model, a time-dependent, three-dimensional computer program, TEMPEST (Trent and Eyler 1994), and formulations for tank waste physical property/rheology (Mahoney and Trent 1995) into one computer program, ARIEL (Onishi et al. 1999). The ARIEL code explicitly

accounts for interactions of aqueous chemical reactions, adsorption/desorption, and dissolution/ precipitation under high ionic-strength conditions and associated rheology changes.

ARIEL was intended for idealized waste conditions and represents the first major step in our systematic approach to developing a scientific waste retrieval assessment capability that can determine tank waste processing operational parameters under realistic tank waste conditions such as how and how much waste can be retrieved from the tanks. Its current limitations include

- no hydrates
- crystal solids but not agglomerated solids
- no colloidal formations
- fast (equilibrium) kinetic reactions (e.g., $NaNO_2$, $NaNO_3$), but not slow kinetics (e.g., AlOOH)
- slurry viscosities controlled by solid volume fractions and strain rate not by chemical species
- constant solution density and viscosity for hydrodynamic calculations that are not affected by aqueous chemical species
- constant liquid water mass with no accounting for water mass changes due to chemical reactions (e.g., AlOOH – $Al(OH)_3$ and $Na_3PO_4 \bullet n\ H_2O$)
- relatively coarse grid used due to requirements of large computation time, especially for simulating chemical reactions.

Nonetheless, it is a state-of-the-art non-Newtonian reactive transport computer code that is fundamentally applicable to a time-varying, three-dimensional hydrothermal field with multi-phase, multicomponent, high ionic-strength, and highly basic chemical conditions.

5.1.2 Non-Newtonian reactive transport computer code, ARIEL

The waste retrieval assessment methodology, ARIEL developed under this EMSP project is a time-dependent, three-dimensional computer code that can simulate fluid mechanics, equilibrium and kinetic chemical reactions, and rheology, all coupled (Onishi et al. 1999).

Fluid dynamics

The fluid mechanics portion of the assessment methodology solves three-dimensional, time-dependent equations of flow, turbulence, heat, and mass (solids, liquids, and gas) transport. It uses integral forms of the following fundamental conservation laws applied in a finite volume formulation (Trent and Eyler 1994), as shown below:

- Conservation of mass (continuity)

$$\frac{M}{Mt} \int_{cv} \rho dV + \int_{cs} \rho U_s dA_s = 0 \tag{5.1}$$

- Conservation of momentum (Newton's second law)

$$\frac{\partial}{\partial t}\int_{cv} \rho U_r dV + \int_{cs} \left[\rho U_r U_s + \mathbf{j}_{\mu s}\right] dA_s = S_\mu + F_r \tag{5.2}$$

- Conservation of energy (first law of thermodynamics)

$$\frac{\partial}{\partial t}\int_{cv} \rho e dV + \int_{cs} \left[\rho U_s h + \mathbf{j}_{qs}\right] dA_s = S_q \tag{5.3}$$

- Conservation of turbulent kinetic energy, k

$$\frac{\partial}{\partial t}\int_{cv} \rho k dV + \int_{cs} \left[\rho U_s k + \mathbf{j}_{ks}\right] dA_s = S_k \tag{5.4}$$

- Conservation of turbulent kinetic energy dissipation

$$\frac{\partial}{\partial t}\int_{cv} \rho \varepsilon dV + \int_{cs} \left[\rho U_s \varepsilon + \mathbf{j}_{\varepsilon s}\right] dA_s = S_\varepsilon \tag{5.5}$$

- Conservation of mass constituents (solid, liquid and gas), C_i

$$\frac{\partial}{\partial t}\int_{cv} \rho C_i dV + \int_{cs} \left[\rho (U_s + U_i) C_i + \mathbf{j}_{C_i s}\right] dA_s = S_{C_i} \tag{5.6}$$

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; j_{xs} = diffusive flux (gradient function) 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; S_{C_i} = source term for i^{th} mass constituent; S_k = source term for turbulent kinetic energy, S_μ = source term for momentum, S_q = source term for thermal energy; S_ε = source term for dissipation of turbulent kinetic energy; U_r = velocity component in the rth coordinate direction; U_i = settling or rising velocity of ith constituent; t = time; V = volume; ε = turbulent kinetic energy dissipation; and ρ = density.

We incorporated various viscosity models of non-Newtonian and Newtonian fluids as a function of the strain rate and solid concentration to calculate the shear stress. The sludge viscosity is used in viscous terms of the Navier-Stokes equation (Equation. 5.2), whereas yield

strength is treated as a force that resists the shear and normal stresses of a fluid flow (Onishi and Trent 1999).

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 (Pitzer 1991) in the aqueous phase modeling. The governing equations to minimize the Gibbs free energy subject to the mass and charge balance are

$$G = \sum_{j=1}^{ns} \mu_j n_j \tag{5.7}$$

subject to

$$\sum_{j=1}^{ns} A_{ij} n_j = b_i \qquad i = 1, p \tag{5.8}$$

$$\sum_{j=1}^{nas} z_j n_j = 0 \tag{5.9}$$

$$n_j \geq 0 \quad \text{for all } j \tag{5.10}$$

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

$$\frac{d[C_{si}]}{dt} = \left\{k_{i1} + k_{i2}[C_{si}]\right\}\left\{1 - \frac{Q_i}{K_i}\right\} \tag{5.11}$$

$$\frac{d[C_{wj}]}{dt} = a_{ij} \frac{d[C_{si}]}{dt} \tag{5.12}$$

where $[C_{si}]$ = molality of solid i, k_{i1} = solid i's reaction rate, which is independent of the solid concentration, k_{i2} = solid i's reaction rate, which is dependent on the solid concentration, Q_i = the activity product, K_i = an equilibrium constant, $[C_{wj}]$ = molality of aqueous species j, and a_{ij} = the number of moles of aqueous species j, produced from precipitation/dissolution of one mole of solid i. ARIEL calculates Qi/Ki in Eq. (5.11) under the equilibrium chemistry calculation to determine the deviation of the actual aqueous condition from the final equilibrium condition.

5.1.3 Model testing work performed at PNNL

PNNL developed a non-Newtonian reactive transport computer program coupling chemical reactions, non-Newtonian rheology, and hydrodynamics for waste retrieval assessment. With this newly developed non-Newtonian simulation code, ARIEL, we studied non-Newtonian waste sludge erosion and waste chemistry, rheology, and mixing interactions through mathematical modeling.

We then examined mobilization and settling of erosion-resisting tank wastes by simulating: 1) solid deposition and accumulation in a tank, 2) jet injection into tank sludge, and 3) sludge pump jet mixing. The computer evaluation indicated that the slurry pump jets rapidly burrow into the sludge bank, collapsing the overhanging sludge layer but eroding only those portions of the sludge where the shear and normal stresses are greater than or equal to the sludge's yield strength. For sludge and saltcake with a yield strength of 200 Pa (representative of Hanford DST low-activity waste saltcake [e.g., Tanks 241-AN-104 and -AN-105]) and 1,000 Pa (representative of Hanford DST high-activity waste sludge [e.g., Tanks 241-AZ-101 and –AZ-102]), simulation results are shown in Figure 3.7. As shown on the left side of the figure, the jet injected by the pump is strong enough to penetrate through the entire length of the weaker sludge (200-Pa yield strength). Its lateral spread is still rather limited because the sludge resists being mobilized by the weaker jet-induced velocity at the peripherals of the jet. With greater sludge strengths of 1,000 Pa, the jet did not penetrate through the entire sludge length (right plot of Figure 3.7). With the sludge having a yield strength of 3,000 Pa, the mixer pump mobilized no sludge. These tests showed that the mobilization/immobilization of solids is controlled directly by the sludge yield strength, which changes its value with solids volume fraction, strain rate, and solid chemical terms. Moreover, the sludge erosion is mostly due to normal stress, not much by shear stress; thus in situ or laboratory measurements should be taken of the sludge's strength in resisting the combined forces of normal and shear stresses.

The ARIEL computer code, developed under this EMSP Project 65371, was then applied to actual Hanford DST 241-AZ-102 waste to determine how much solids would be mobilized. This evaluation for the W-211 Project and a waste feed delivery planning project were needed to determine whether two 300-hp rotating mixer pumps were needed, and if so, how much sludge with 1,650 Pa yield strength could be retrieved by the two pumps. (The W-211 Project at Hanford is installing 300-hp mixer pumps in 10 DSTs that are first in line for waste retrieval.)

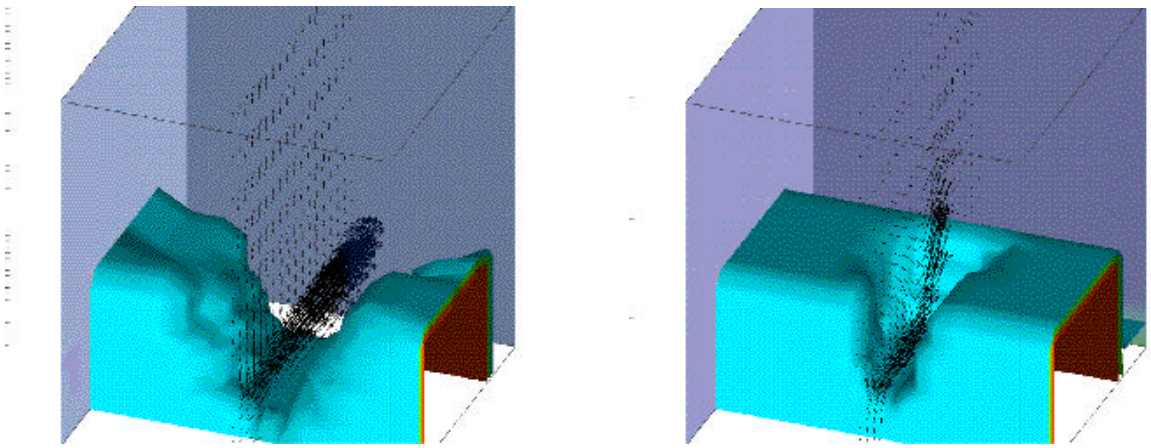

Figure 5.1. Three-dimensional distributions of predicted velocity and erosion pattern of the sludge with yield strengths of 200 and 1,000 Pa at one simulation hour

The ARIEL code, simulating three-dimensional AZ-102 pump jet mixing, predicted that 50% of the sludge would be eroded by the mixer pump jets and that suspended solids would be uniformly distributed throughout the tank, except for the portion where sludge was not mobilized, as shown in Figure 5.2. The figure shows one of the 22 airlift circulators and heating coils. ARIEL thus provided useful information on retrieval design and waste feed delivery planning.

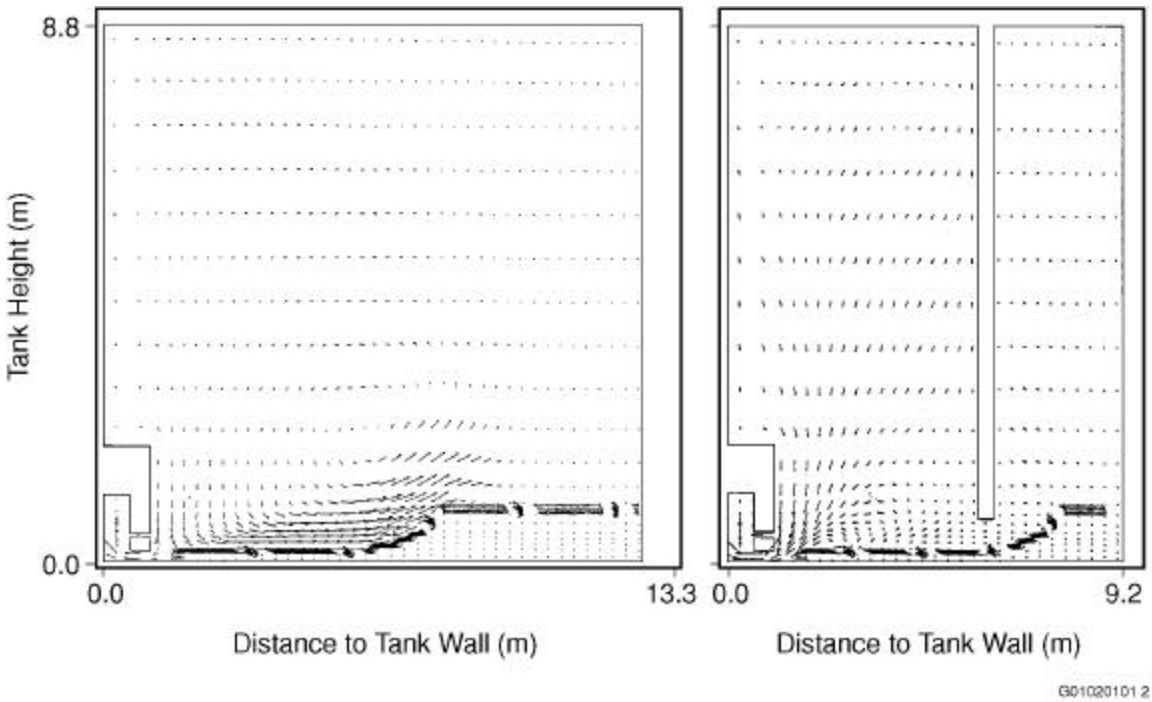

Figure 5.2. Predicted distributions of predicted velocity and solid concentrations for Hanford DST 241-AZ-102 at two simulation hours

The main limitation of ARIEL is that its rheology (yield strength in this application) is not correlated with chemical conditions, while actual tank waste rheology is clearly affected by chemical conditions beside the physical conditions (Onishi et al. 2000).

In another application, we tested this interactive behavior with an axisymmetric pump jet to mix the salt cake overlain by water. Because approximately half of Hanford DST waste consists of sodium nitrate and nitrite, we considered their chemical reactions. In addition, these chemical reactions do not involve hydration, and their kinetic reactions are relatively fast. Thus, six aqueous species (Na^+, NO_2^-, NO_3^-, $NaNO_2$(aq), $NaNO_3$(aq), and H_2O) and three solids [$NaNO_2$(s), $NaNO_3$(s), and nonreactive solids representing nondissolvable solids] were examined. The non-Newtonian viscosity was assigned to be a function of solid volume fraction and strain rate. The axisymmetric model predicted that, as water penetrated into and mixed with the saltcake, $NaNO_2$(s) and $NaNO_3$(s) would be dissolved and only the nonreactive solids remained as solids. As these solids dissolved, viscosity of the saltcake decreased and the total amounts of Na^+, NO_2^-, NO_3^-, $NaNO_2$(aq), $NaNO_3$(aq) in the solution increased. These changes are shown in Figure 3.9 (left plot) for $NaNO_3$(s) concentrations predicted at 20 simulation seconds. As the simulation time progressed, all $NaNO_2$(s) and $NaNO_3$(s) eventually dissolved. There was a mass balance error of several percent, and we identified this problem caused by the repeated use of expected liquid density to convert aqueous chemical species concentration between molality and kg/m^3 at every computational cell at every time step of the entire simulation time. This clearly illustrates the importance of calculating accurate solution density as a part of the simulation, and we plan to address solution density in the proposed study.

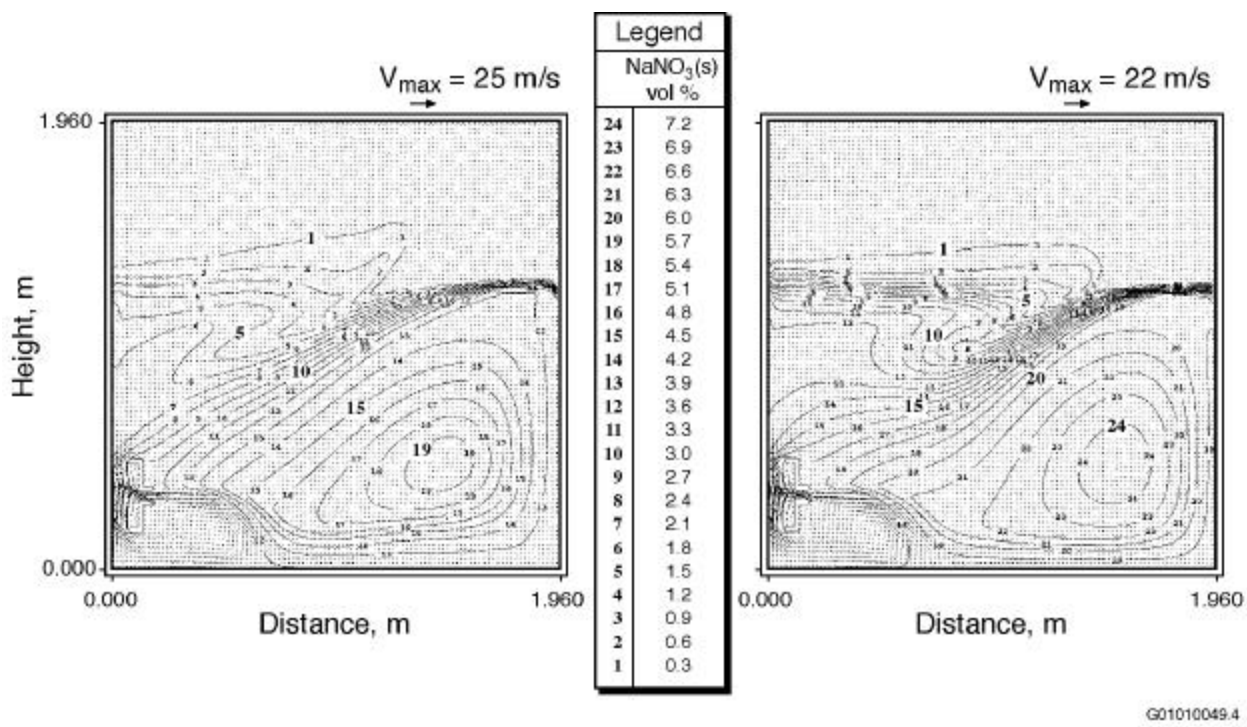

Figure 5.3. Predicted $NaNO_3$(s) concentrations (vol%) at 20 simulation seconds with (left plot) and without (right plot) chemical reactions

Without the chemical reactions (Figure 5.3, right), solid concentration changes are due solely to mixing. Thus, accounting for the chemical reactions, the mixer pump will encounter a smaller amount of solids with less sludge/saltcake viscosity to mobilize. This results in improved efficiency. This simple numerical test reveals the importance of accounting for the chemical reactions and associated rheology changes to determine the effectiveness of mixer pumps to mobilize the sludge. Adding water to low-activity waste tanks (e.g., the AN tanks) is currently the base retrieval operation process.

We also compared the behavior of non-Newtonian and Newtonian mixing with chemical reactions assuming that waste viscosity was a function of the solid concentration but not dependent on strain rate for the Newtonian case. As shown in Figure 5.4, the simulation indicates that non-Newtonian slurry generally mixes less than Newtonian. PNNL's EMSP project team supplied the time-varying computed velocity field to the University of Minnesota project team for their detailed mixing analysis, which confirmed PNNL's finding, as is discussed later in Section 5.2. However, in some instances, non-Newtonian mixing is more extensive, revealing the very complex nature of chemically active non-Newtonian slurry mixing phenomena.

ARIEL showed that it can simulate chemically reactive waste mixing if waste conditions are simple, e.g., solids are crystals. ARIEL's limitations in these tests are that viscosity of the solution and slurry and solution density are not related to chemical species.

The ARIEL code was tested in a Hanford DST to determine how much water (added as a solvent to the tank) would dissolve and mix saltcake with two 300-hp mixer pumps. The viscosity of this tank waste varies seven orders of magnitude from saltcake to supernatant liquid. We incorporated a non-Newtonian rheology model in the code, as shown in Figure 5.5. This figure presents measured viscosity values and our tank-specific rheology model with the following formulation of the viscosity as a function of solids concentration and strain rate:

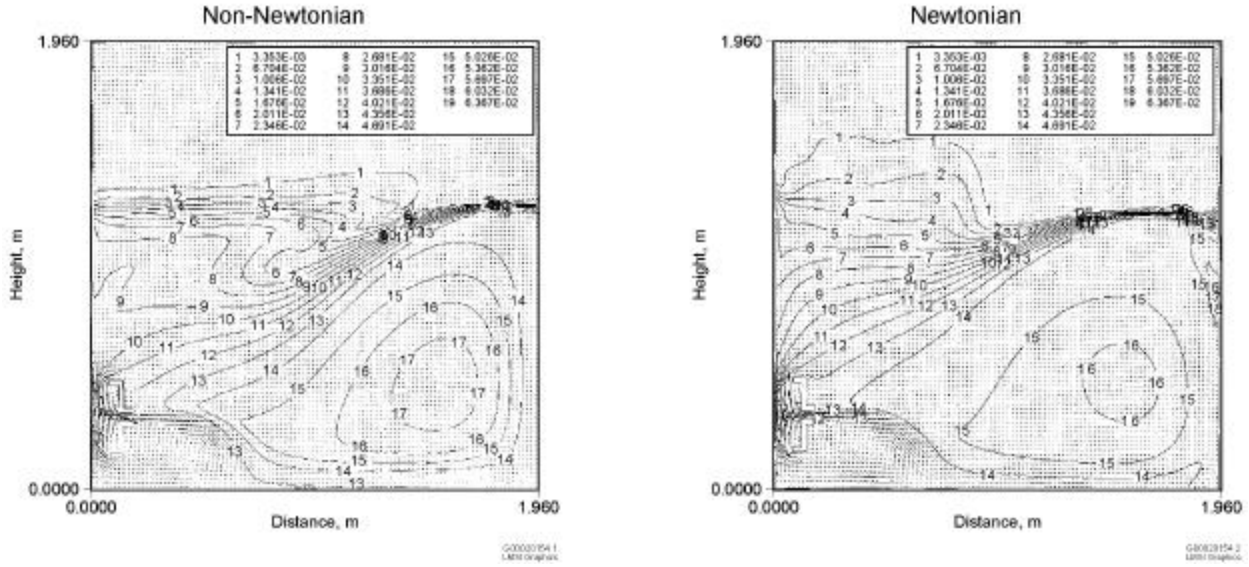

Figure. 5.4. Predicted $NaNO_3(s)$ distributions for 2-D non-Newtonian (left) and Newtonian (right) cases with chemical reactions at 20 simulation seconds

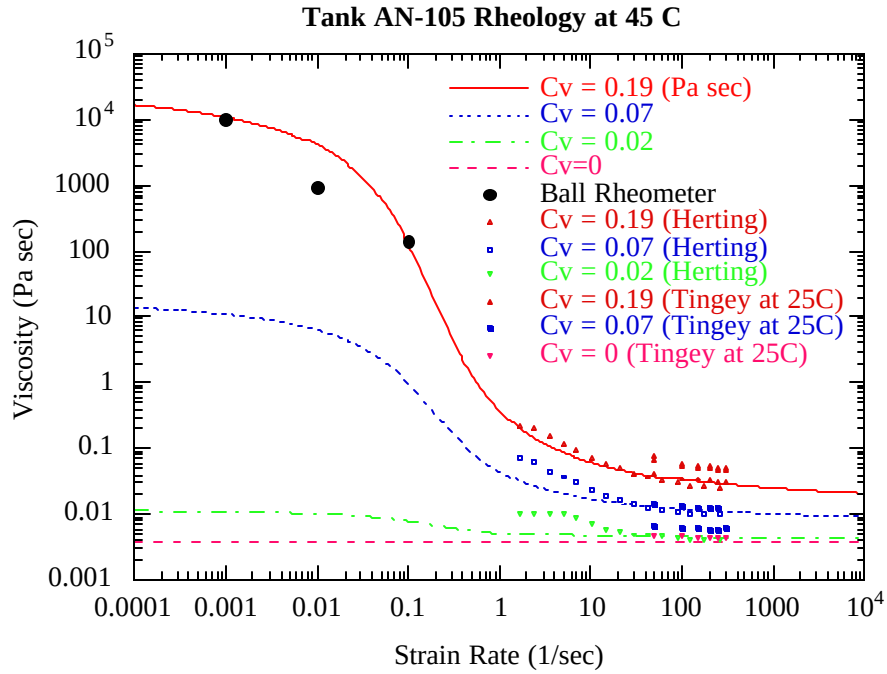

Figure 5.5. Viscosity measurements and rheology model for a Hanford DST 241-AN tank

$$\mu(\dot{\gamma}, C_v) = \mu_N \exp\left(A(\beta)\left\{1 + a_1\left[1 - \frac{2}{\pi}\arctan\left(a_2 \ln \lambda\dot{\gamma} + a_3\right)\right]\right\}\right)$$

where

$$A(\beta) = \frac{a_4\,\beta(1+4\beta)}{1 - a_5\,\beta\left(1 - 2\beta + a_6\,\beta^2\right)}, \text{ and } \beta = \frac{C_v}{C_{vm}}$$

and

a_i:	=	constants
C_v:	=	solid volume fraction
C_{vm}:	=	maximum solid volume fraction
μ:	=	viscosity (in Pas-sec)
μ_N	=	viscosity of the liquid
λ:	=	time constant of the fluid.

The saltcake in these tanks has a yield strength of 100–200 Pa, which is also being simulated in this tank model.

Chemical reactions simulated in this case are Na–OH–$Al(OH)_4$–CO_3–SO_4–NO_2–NO_3–$NaNO_2$(aq)–$NaNO_3$(aq)–H_2O with solids of $Na_2CO_3 \cdot H_2O$, Na_2SO_4, and $Al(OH)_3$. Most of the $Na_2CO_3 \cdot H_2O$(s) and Na_2SO_4(s) are expected to be dissolved with water, based on experiments and our chemical modeling. The model setup is shown in Figure 5.6, and the simulation result for $Na_2CO_3 \cdot H_2O$(s) at a very early time (10 simulation seconds) is shown in Figure 5.7.

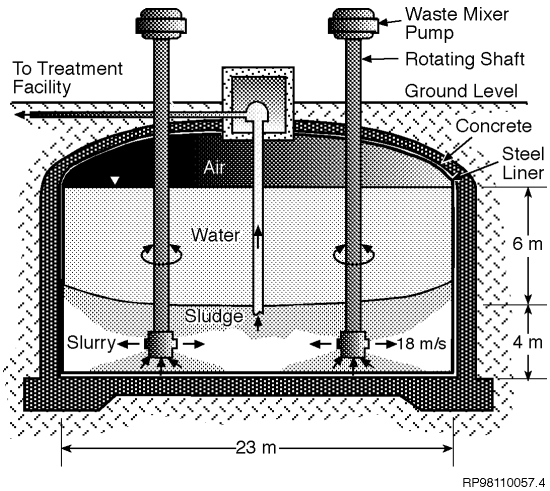

Figure 5.6. Hanford AN tank pump jet model

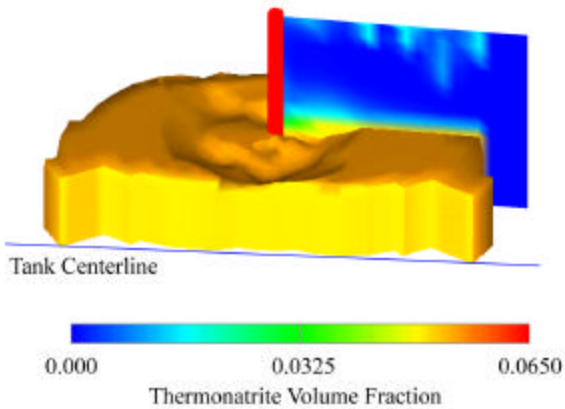

Figure 5.7. $Na_2CO_3 \cdot H_2O(s)$ concentrations

This test case deals with more realistic waste conditions. Although ARIEL started to simulate this case, it clearly shows its current limitations—its inability to handle the following situation: 1) $Na_2CO_3 \cdot H_2O(s)$ is a hydrate and as it dissolves, the water will be released to the solution, 2) $Na_2CO_3 \cdot H_2O(s)$ may form $Na_2CO_3 \cdot 10H_2O(s)$ as it mixes with water, thus, significantly reducing sludge and solid densities and increasing solid size, 3) $Na_2SO_4(s)$ may form $Na_2SO_4 \cdot 10H_2O(s)$, affecting both sludge property (density and viscosity), and solution density by changing the amount of water in solution, 4) these hydrates may form agglomerates and gels, 5) these chemical reactions may occur at first locally in small scale and may eventually spread to the whole tank (see detailed mixing analysis discussed in Section 4.2), 6) their kinetic rates may not be in the same time scale as the hydrodynamic time scale, and 7) the solution density is affected by the aqueous chemical species and concentrations.

Overcoming these limitations is a formidable scientific and technical task requiring a systematic and comprehensive approach. One approach would be to systematically expand the current ARIEL's capability to address these shortcomings, so that it can evaluate more realistic waste conditions and changes.

PNNL developed the non-Newtonian reactive transport computer code as a tool to examine interactive chemical and hydrodynamic mechanisms that control waste mixing in Hanford tanks. This testing indicates the usefulness of the non-Newtonian reactive transport code, ARIEL, for ideal waste conditions, and its potential to evaluate waste retrieval. However, as shown in the three-dimensional (Figures 5.6 and 5.7) case, it also shows the current limitations to handle realistic waste conditions, especially dealing with hydrates and their associated complexity. Thus, ARIEL needs to be systematically expanded to handle non-ideal, more realistic waste conditions, including hydration.

5.2 Work performed at University of Minnesota

During this grant period, we have studied the effects of mixing in thermal convection, shear deformation in solid-state inclusions with different rheologies, and mixing in waste tanks. Besides refining the techniques for the field approach in passive mixing (Ten et al. 1996, 1997) we have further developed a particle-line method consisting of particles linked together in a line (Figure 5.8). It is a LaGrangian-based method using passive particles that are connected by fourth-order bicubic splines and dynamically distributed at each time step. We have used up to one million tracers per line and ten lines for obtaining high-resolution fine features encountered

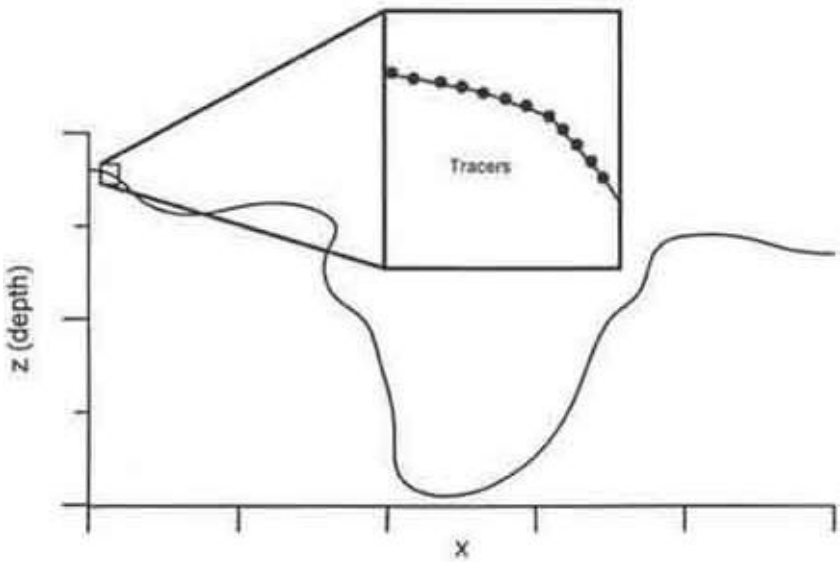

Figure 5.8. Schematic of line approach. Velocity field advects the particles passively; up to a million particles were used to ensure accuracy; dynamic update of each line occurs adaptively.

in mixing with a resolution that is equivalent to a grid configuration of 500,000 x 500,000 equally spaced points (Ten et al. 1998, 1999; Yuen et al. 2000). One of these articles (Ten et al. 1999) appeared electronically with several movies in *Electronic Geosciences* and is also available for downloading on http://bobby.msi.umn.edu/mixing.

Figures 5.9 and 5.10 show the dynamics of mixing in both global and local perspectives. The zoom-in view of Figure 5.10 reveals the complexity of the stretching and folding processes in mixing, which can shed light on mixing in nuclear waste. Our finding of the multiplicity of spatial scales from the global to the very fine shear-band structures suggests that local mixing may take place in certain regions where chemical reactions and rheological transitions would also occur. Thus retrieval operation decision making must account for the interactions of chemical reactions and physical mixing induced by non-Newtonian rheology accurately.

We also analyzed by spectral analysis of the velocity field (Figure 5.11) the difference between Newtonian and non-Newtonian mixing (Ten et al. 2001) and developed an analytical method for looking at folding and stretching events in shear flow (Figures 5.12 and 5.13). We

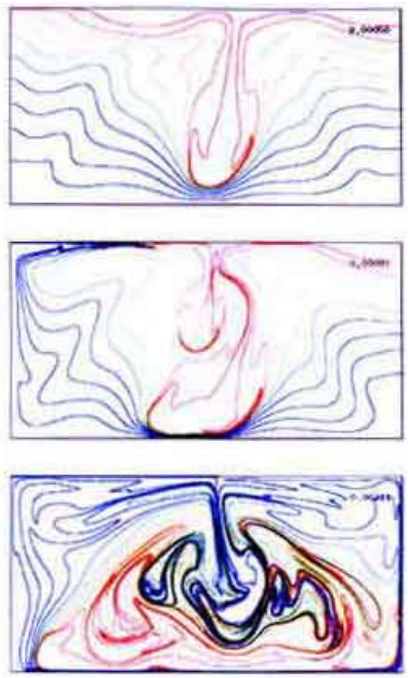

Figure 5.9. A sequence of shots portraying the mixing of passive tracers by the method of lines. There are one million particles per line, and 10 lines have been deployed.

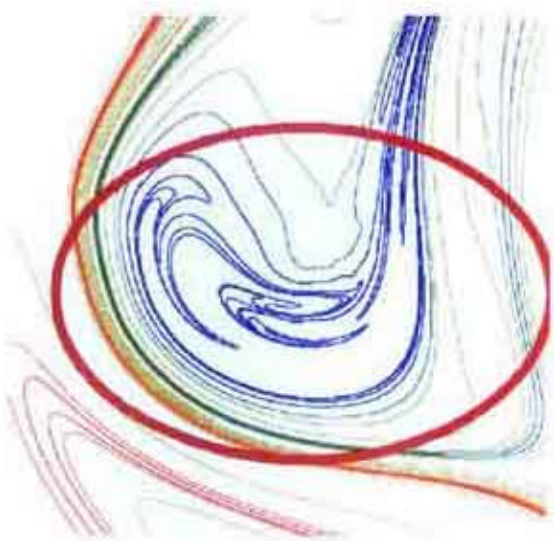

Figure 5.10. Zoom in of Figure 5.9. The encircled area is around 1/70 of the original domain. Note the occurrence of material filaments being continuously stretched and folded by means of the horseshoe transformation as mixing induces smaller-scale structures.

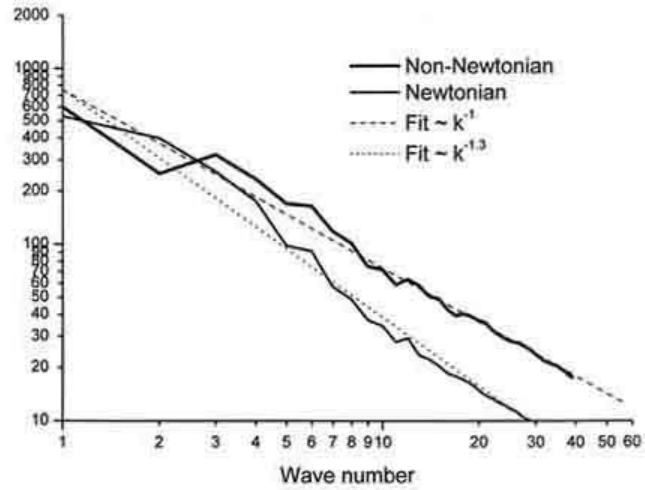

Figure 5.11. Time-averaged horizontal spectra of velocity profiles along middle depth

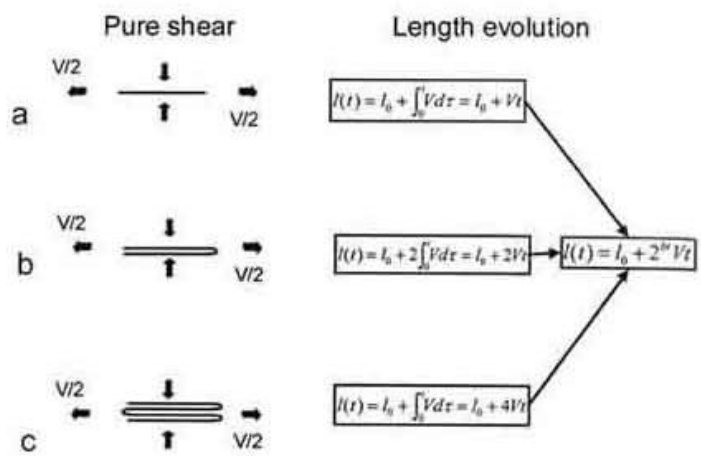

Figure 5.12. Modes of stretching in pure shear: a) line grows proportionally to V*dt; b) folded line grows proportionally to 2V*dt; c) a double-folded line grows proportionally to 4V*dt

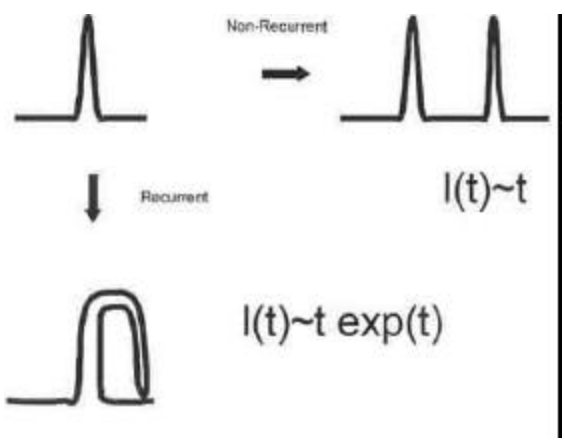

Figure 5.13. Mixing of Newtonian tank waste sludge by a constant-velocity jet portrayed with passive particles

also developed a method for calculating the length of each line undergoing recurrent stretching and folding events (Figure 5.14). Measuring the relative length of the stretched lines can throw considerable light on the overall mixing process. The longer the line, the more it has been mixed and stretched. Yuen et al. (2001) also recently developed a 2-D wavelet transform method for examining mixing processes by decomposing the mixed fields into various scales (Figure 5.15).

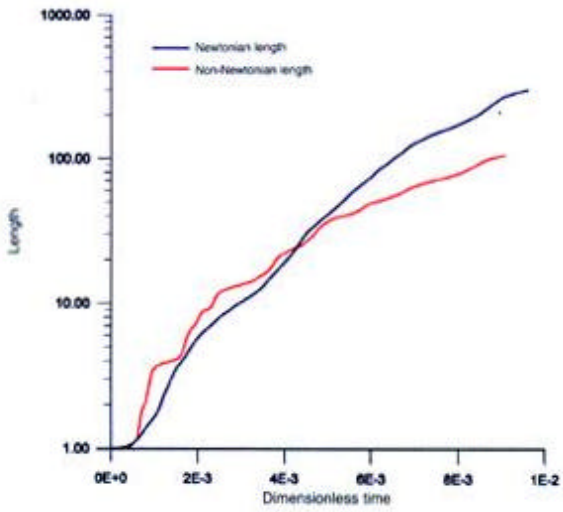

Figure 5.14 A comparison of the length of stretched lines as a function of time caused by mixing and stretching in Newtonian (blue) and non-Newtonian (red). The lines being compared are taken from the middle line for each rheological case.

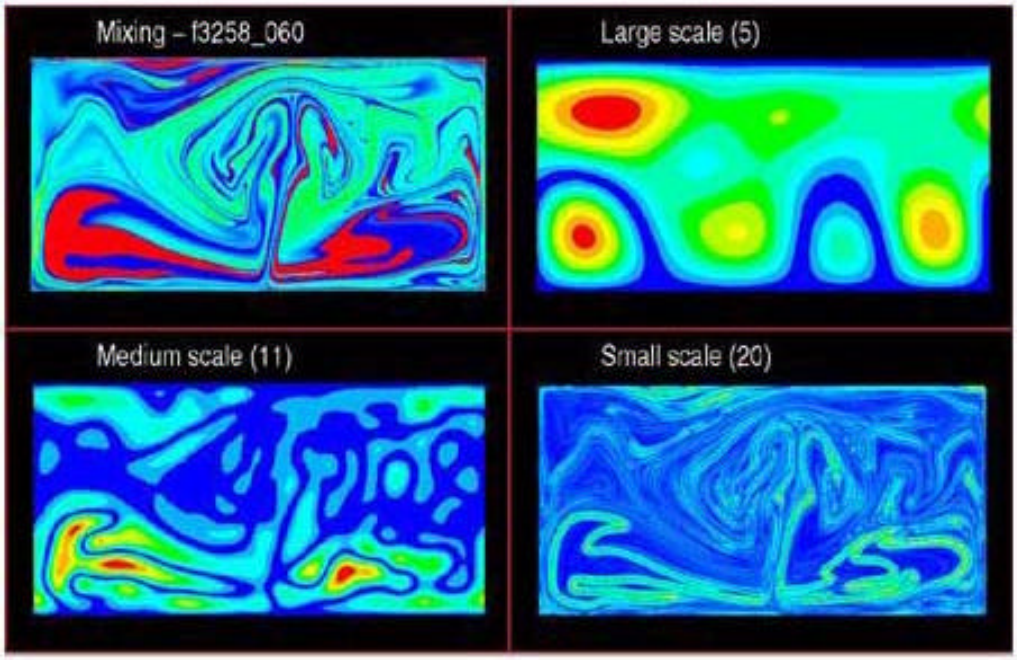

Figure 5.15. Different scales of 2D mixing in non-Newtonian rheology portrayed by 2D Gaussian wavelet transforms. We display the original field of mixing (upper-left panel) along with the wavelet decompression of the field into three different length scales.

In mixing liquids and sludge we employed the 2-D velocity fields from Onishi and Wells (2001) and studied mixing with particles for both Newtonian and non-Newtonian rheology (Figures 5.16 and 5.17). These movies show again that non-Newtonian flows mix less efficiently than Newtonian flows. Movies of the mixing for both types of rheologies can be found on our web site: http://www.msi.umn.edu/~cathy/pnnlproposal/figures.html.

In the realm of matrix inclusions, which is relevant for deformation between materials with different rheologies, we carried out two-dimensional investigation of time-dependent deformation behavior of an inclusion and its dependence on the ambient rheology under simple shear (Ten and Yuen 1999). We used the level-set method (Sethian 1999) for monitoring the deformation of the inclusion with developing shear motions. The results of numerical modeling (Ten and Yuen 1999) show that a key factor of structural appearance is the contrast between effective viscosity and inclusion to the solid matrix. The high contrast is found to inhibit stretching of the inclusion. Results of this work can be applied to mixing in materials with different material properties.

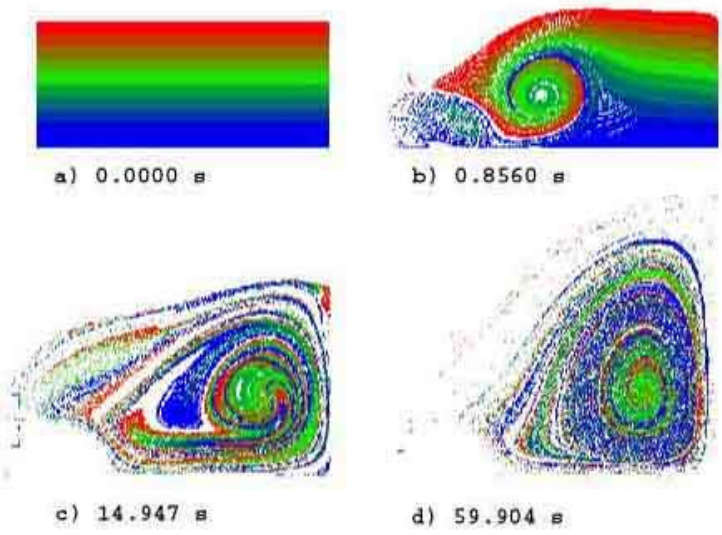

Figure 5.16. Mixing of Newtonian tank waste sludge by a constant velocity jet portrayed with passive particles

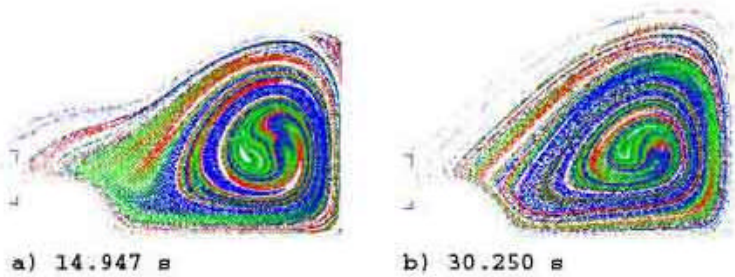

Figure 5.17. Mixing of non-Newtonian tank waste sludge with a constant velocity jet portrayed with passive particles. Initial configuration of particles is the same as in Figures 5.3 and 5.4.

6. Relevance, Impact, and Technology Transfer

With estimated costs ranging from tens to hundreds of billions of dollars, retrieval and solidification of a large volume of radioactive and chemical wastes is one of the greatest problems facing DOE. Fifty-four million gallons of this waste is stored in 177 underground tanks at the Hanford Site in Washington State (Gephart and Lundgren 1997).

A basic retrieval process is mixing chemically reactive, non-Newtonian, tank wastes with solvents (e.g., water and NaOH solution) in DSTs to mobilize and dissolve tank waste solids within the tank or pipeline for the retrieval and pipeline transfer operations. These tank wastes will experience complex interactions of aqueous and solid chemical reactions, rheology, and non-Newtonian and Newtonian slurry mixing, as discussed in Section 4.2.

It is a formidable and challenging scientific and technical task to account for the chemical and physical interactions in the decision-making process for retrieval safety and operations. Because in situ tank and laboratory experiments are impossible to perform for a wide range of tank conditions prior to actual tank waste mixing, we need new computational tools to determine the safety and design/operational parameters for waste processing activities in a timely and cost-effective manner.

As discussed in Section 5.1, under this EMSP Project (#65371), PNNL successfully developed a non-Newtonian reactive transport computer code, ARIEL, to assess waste retrieval under idealized conditions. As illustrated in Section 5.1.3, The ARIEL computer code was applied to actual Hanford DST 241-AZ-102 waste to determine how much solids would be mobilized to determine whether two 300-hp rotating mixer pumps were needed, and if so, how much sludge with 1,650 Pa yield strength could be retrieved by the two pumps. (The W-211 Project at Hanford is installing 300-hp mixer pumps in 10 DSTs that are first in line for waste retrieval.) The ARIEL code, simulating three-dimensional AZ-102 pump jet mixing, predicted that 50% of the sludge would be eroded by the mixer pump jets and that suspended solids would be uniformly distributed throughout the tank, except for the portion where sludge was not mobilized. ARIEL thus provided useful information on retrieval design and waste feed delivery planning.

This ARIEL code was also used to determine whether two 300-hp mixer pumps could mix very viscous (over 1,000-Pa-s viscosity at a low strain rate) saltcake with added water (as a solvent) The viscosity of this tank waste varies seven orders of magnitude from saltcake to supernatant liquid. With a non-Newtonian rheology model in the code and yield strength of 100 Pa incorporated in the model, the tank mixing simulation predicted that two mixer pumps could totally mobilize the saltcake and fully mix it with water, thus, providing information needed for the waste retrieval design and planning.

The two- and three-dimensional model testings of waste retrieval also illustrate the importance of accounting for the interactions among waste chemical reactions, rheology changes and waste mixing to evaluate the tank waste retrieval. These testings indicate the usefulness of the non-Newtonian reactive transport code, ARIEL, for ideal waste conditions, and its potential to evaluate waste retrieval. However, it also shows the current limitations to handle realistic waste conditions, especially dealing with hydrates and their associated complexity. Thus, this

study provide the needed basis for systematically expanding waste retrieval assessment capabilities to handle non-ideal, more realistic waste conditions, including hydration.

7. Project Productivity

The joint team of University of Minnesota and PNNL successfully achieved the project goals by (i) developing the coupled reactive transport code for waste retrieval assessment, and (ii) evaluating the non-Newtonian mixing processes in detail.

8. Personnel Supported

The following personnel were supported by this project:

Minnesota Supercomputer Institute, University of Minnesota:

Dr. D.A. Yuen, professor, Geophysics and Scientific Computation
Dr. A.A. Ten, post-doc, Geophysics and Scientific Computation
Ms. C.A. Hier, graduate student, Geophysics and Scientific Computation

PNNL

Dr. Y. Onishi at Fluid and computation group
Dr. J.R. Rustad at Environmental Molecular Science Laboratory
Mr. B.E. Wells at Fluid and Computational Science Group
Dr. D.S. Trent at Fluid and Computational Science Group
Mr. T.E. Michener at Fluid and Computational Science Group
Dr. A.R. Felmy at Environmental Molecular Science Laboratory.

9. Publications

Ten AA and DA Yuen. 1999. Time-dependent formation of mantled inclusion structures for different rheologies under a simple shear. *Earth Plane. Sci. Lett.,* Vol. 165, pp. 25-35.

Ten AA, DA Yuen, and YY Podladchikov. 1999. Visualization and analysis of mixing dynamical properties in convecting systems with different rheologies. *Electronic Geosciences*, Vol. 4, p. 2.

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New Millennium, pp. 403-462, E Boschi, G Ekstrom and A Morelli, eds. Editrice Compositori, Bologna, Italy.

Onishi Y and DS Trent. March 1999. "Mobilization Modeling of Erosion-Resisting Radioactive Tank Waste." *Proceedings of the Rheology in the Mineral Industry II*. Kahuku, Oahu, Hawaii. United Engineering Foundation, New York, pp. 45-56.

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*, San Francisco.

Onishi Y and BE Wells. 2001. "Chemically active non-Newtonian tank waste mixing." Proceedings of 4th International Conference on Multiphase Flow, New Orleans, LA, May 27 – June 1, 2001.

http://www.msi.umn.edu/~cathy/pnnlproposal/figures.html.

10. Interactions

Co-Principal Investigator, Dr. Onishi at PNNL participated a Tank Focus Area workshop (in 1999), an EMSP workshop (in 2000) and a Tank Focus Area meeting (in 2001) on waste retrieval and pretreatment.

This project was jointly performed by University of Minnesota lead by Professor Yuen and PNNL led by Dr. Onishi. Dr. Yuen's graduate student, Catherine Hier worked on some parts of this project at PNNL for summers of 2000 and 2001, as a part of her on-going Ph.D. thesis work.

11. Transitions

The AREIL computer code developed under this project was used for the Hanford's W-211 Project to evaluate the retrieval design and operation decisions, and waste feed delivery planning, as described in Section 5.1.3.

12. Patents

No patent was generated under this project.

13. Future Work

The waste retrieval assessment code, ARIEL was intended for idealized waste conditions for mixing of chemically active waste with a solvent (water), and was successfully tested. It represents the first major step in our systematic approach to developing a scientific waste retrieval assessment capability that can determine tank waste processing operational parameters

under realistic tank waste conditions such as how and how much waste can be retrieved from the tank's realistic waste conditions. Its current limitations include

- no hydrates
- crystal solids but not agglomerated solids
- no colloidal formations
- fast (equilibrium) kinetic reactions (e.g., $NaNO_2$, $NaNO_3$), but not slow kinetics (e.g., AlOOH)
- slurry viscosities controlled by solid volume fractions and strain rate not by chemical species
- constant solution density and viscosity for hydrodynamic calculations that are not affected by aqueous chemical species
- constant liquid water mass with no accounting for water mass changes due to chemical reactions (e.g., AlOOH – $Al(OH)_3$ and $Na_3PO_4 \bullet n\ H_2O$)
- relatively coarse grid used due to requirements of large computation time, especially for simulating chemical reactions.

Thus, the ARIEL code must be systematically expanded its capability to overcome these limitations to be able to cover more realistic tank waste conditions.

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15. Feedback

None.

16. Appendices

None.

17. Quantities/Packaging

None.