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Project Title: **Numerical Modeling of Mixing of Chemically Reacting, Non-Newtonian Slurry for Tank Waste Retrieval**

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

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(3) Research Objectives

The objectives of this study are to investigate interactions among chemical reactions, waste rheology, and slurry mixing occurring during the tank waste retrieval operation and to provide a scientific basis for the waste retrieval decision-making process. Specific objectives are to

- Evaluate numerical modeling of non-Newtonian waste with yield strength
- Examine reactive transport simulation of tank waste
- Conduct numerical modeling analysis of local and global mixing of non-Newtonian and Newtonian slurries coupled with the relevant chemical reactions and realistic rheology, which depends critically on the chemistry, strain rate, and slurry concentrations
- Develop easy-to-use interactive software with the collaborative visualization for monitoring the various flow regimes in nuclear waste tanks
- Provide the bases to develop an appropriate decision-making support tool based on scientifically justifiable analysis for tank-waste retrieval operation.

(4) Problem Statement

A major environmental remediation problem facing the U.S. Department of Energy is how to safely and cost-effectively dispose of 100 million gallons of highly radioactive wastes resulting from nuclear weapon production and stored in tanks (Gephart and Lundgren 1997). To achieve final disposal, the waste must be retrieved from the tanks. Many of the wastes will be retrieved by installing mixer pumps that inject high-speed jets to stir up the sludge and supernatant liquid in the tank, blending them into a slurry that will be pumped out of the tank into a waste treatment facility (Onishi et al. 1996a), as shown in Figure 1.

In some cases, diluents (e.g., water or sodium hydroxide) will be added to dissolve and thus reduce the amount of solids, increase the density and viscosity of the waste solution, and make the waste easier to mix, retrieve, and transfer (through pipelines) to other tanks or to the treatment facility.

Most of these tank wastes are highly basic, have high salt content, and are chemically and physically very complex. Solids, saltcakes, sludges, liquids, and gases often coexist in the same tank. The sludges alone have varieties of solids with widely differing chemical and physical characteristics (Onishi et al. 1996a). During the waste retrieval operation, complex interactions among the chemicals, associated slurry rheological changes, and non-Newtonian mixing occur in the tank. Unwanted chemical reactions and associated rheology changes can make these operations impossible; formations of boehmite and sodium phosphate hydrate plugged Hanford cross-site waste transfer pipelines during their initial waste retrieval and pipeline transfer operations.

Thus, to determine safe and cost-effective operational parameters for waste retrieval, decision-making support tools must account for these interactions. Pacific Northwest National Laboratory (PNNL) integrated the modeling of chemical reactions, hydrodynamics, and changing waste rheology into one computer program (Onishi et al. 1996b), while University of Minnesota (Ten et al. 1998) developed modeling capability on very detailed mixing of non-Newtonian slurry and its visualization. The university and IBM also jointly developed visualization techniques for simulation results. This three-year study by a multidisciplinary team of the University of Minnesota, PNNL, and IBM combines these

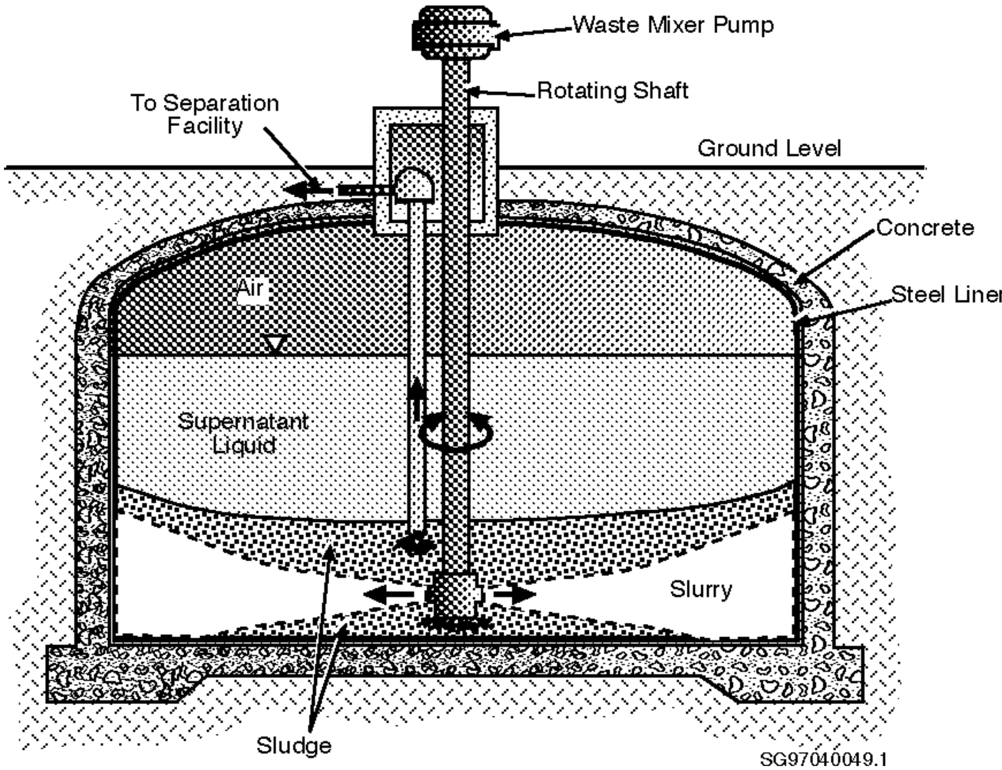

Figure 1. Pump Jet Mixing

modeling capabilities and investigates the interactions among waste chemistry, mixing, and rheology and non-Newtonian mixing processes; and supports a scientific basis for waste retrieval decision making with the use of numerical modeling.

(5) Research Progress and Implications

5.1 Evaluation of numerical modeling of non-Newtonian waste with yield strength – mobilization of tank waste

When sludge is mixed with supernatant liquid in the waste storage tank, mixing alone (even without chemical reactions) changes waste rheology, converting non-Newtonian sludge with yield strength to a Newtonian slurry of the sludge and supernatant liquid mixture. Figure 2 shows an example of 1) a non-Newtonian tank sludge stored in Tank 241-SY-102 at the Hanford Site and 2) Newtonian slurry resulting from the mixing of the sludge with the supernatant liquid at 1 part sludge and 0.5 part supernatant liquid (Onishi et al. 1996a). The change from non-Newtonian to Newtonian slurry affects how the slurry spreads and mixes (Ten et al. 1997). Because the amount of the sludge retrieved from the tank bottom is directly proportional to the ratio of hydrodynamic (normal and shear) stresses acting on the sludge and of its yield strength, it is important to account for the yield strength to accurately evaluate jet mixing processes and sludge mobilization for waste retrieval.

The TEMPEST code was modified to account for the yield strength (Onishi and Trent 1999). This modified code was tested for modeling mobilization of sludge with yield stress that resists being eroded by jet-induced flows (Onishi and Trent 1999). A series of tests was performed with and without the yield strength of the sludge under various conditions, including 1) solid settling and accumulation in a tank, 2) injection of a solvent (diluent) jet into the tank, and 3) a pump jet to mix the waste sludge.

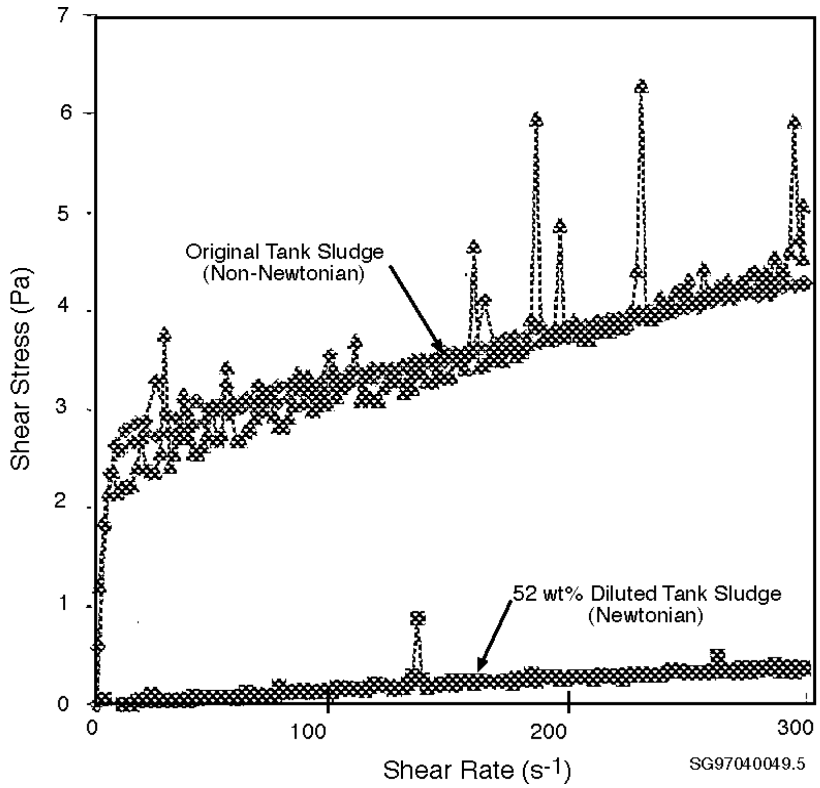

Figure 2. Rheologies of the Sludge and Slurry of Tank Waste (Onishi et al. 1996a)

In one of the test cases that examined whether the model would compute erosion and immobilization of sludge with various yield strengths, a pump installed in the rectangular waste tank mixes the contents of the tank. The non-Newtonian sludge was drawn up into the pump above the tank bottom and injected back into the sludge layer with a velocity of 18 m/s through an injection nozzle. When the original sludge has yield strength of 200 Pa, the 18-m/s slurry jet quickly burrows into the sludge in front of the injection nozzle. As the jet penetrates into the sludge, the non-Newtonian sludge is mixed and mobilized by the jet, eventually becoming Newtonian slurry. The jet injected by the pump is strong enough to penetrate through the entire sludge length in this case. Its lateral spread is rather limited because the sludge resists being mobilized by the weaker jet-induced velocity (and stress) at the peripherals of the jet.

For a given pump jet mixing condition, the simulation results confirmed that the extent of the sludge erosion depends on the yield strength of the sludge materials. Figure 3 shows the predicted sludge erosion patterns for yield strengths of 2,000 Pa. With this sludge strength, the jet did not penetrate through the entire sludge length. In cases with even greater yield strengths, no sludge was mobilized by the mixer pump.

These test results showed that the model simulated 1) solids being deposited and remaining on the tank bottom, while the sludge with these solids gained its yield strength as solid accumulated more on the tank bottom; and 2) the slurry pump jets burrowing into the sludge bank and eroding only portions of the sludge where the shear and normal stresses acting on the sludge are greater than or equal to the sludge's yield strength. These results confirm the importance of accounting for yield strength in non-Newtonian sludge mobilization to evaluate the tank waste retrieval operation: how much and how fast waste can be retrieved from the tanks, and how retrieval should be implemented.

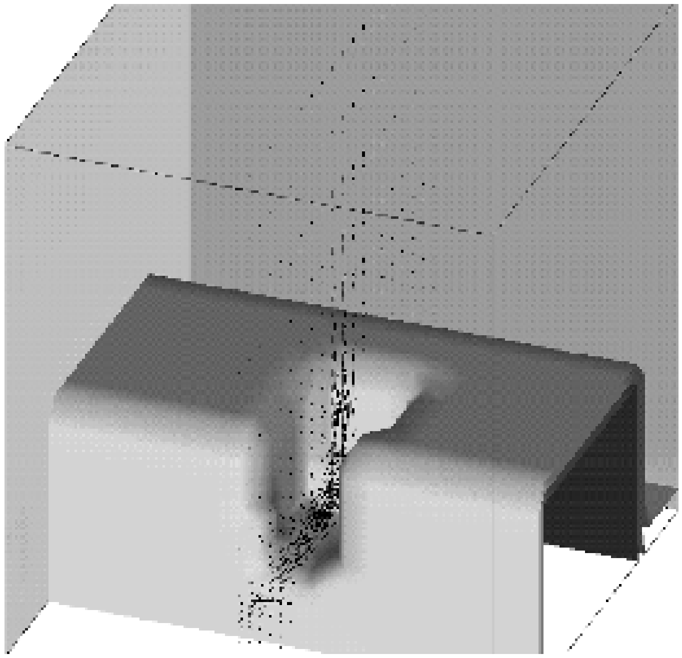

Figure 3. Three-Dimensional Distributions of Predicted Velocity and Erosion Patterns of Sludge with Yield Strength of 2,000 Pa

5.2 Examine reactive transport simulation of tank waste

To retrieve the tank waste, one or more pumps installed in a tank mix the sludge and supernatant liquid (and possibly a diluent, if it is added to the tank) to produce a slurry (see Figure 1). During the mixing, the waste undergoes aqueous and solid dissolution/precipitation reactions. The occurrence of solid dissolution/precipitation during waste retrieval was clearly predicted by the chemical modeling of Hanford double-shell Tank 241-SY-102, as shown in Figure 4 (Onishi and Hudson 1996). The predictions matched well with measured data on aqueous species (the uppermost figure) and solids (the middle figure) in the sludge. When the sludge is mixed with supernatant liquid in the same tank (e.g., say with the use of the pump jet mixing), most sodium solids are dissolved, while a small amount of gibbsite was precipitated. Dissolution of sodium solids changes the amount of the solids in the tank and affect the waste's physical properties and rheology (e.g., densities and viscosities of the resulting supernatant liquid and the slurry). Furthermore, if boehmite should be formed, instead of gibbsite, the slurry would have become effectively a non-Newtonian-like gel, which would be difficult to mix, and it would not be possible to retrieve this non-Newtonian waste from the tank.

Thus, the waste retrieval assessment must account for waste chemical reactions, mixing, and rheology changes simultaneously to provide a scientific basis for the waste retrieval decision-making process. To evaluate the coupled chemistry, mixing and associated rheology, the TEMPEST code is being run to simulate two-dimensional (axisymmentric) pump jet mixing of the tank waste with following chemical reactions:

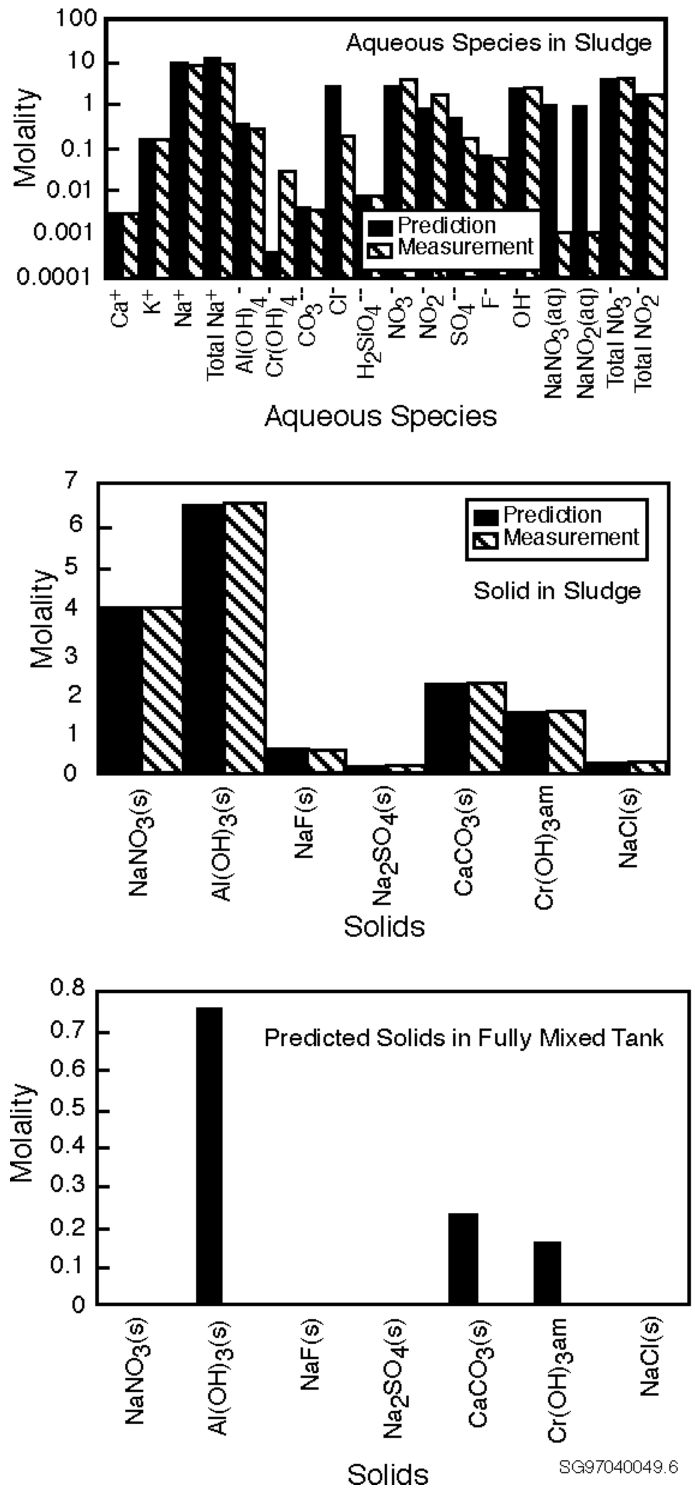

Figure 4. Chemical Changes before and after Hanford SY-102 Tank Waste Mixing (Onishi and Hudson 1996)

$$Na^{+} + NO^{-}_{3} = NaNO_{3}(aq)$$

$Na^{+} + NO^{-}_{2} = NaNO_{2}(aq)$
$Na^{+} + NO^{-}_{3} = NaNO_{3}(s)$
$Na^{+} + NO^{-}_{2} = NaNO_{2}(s)$
$Na^{+} + Al(OH)^{-}_{4} = Na^{+} + OH^{-} + Al(OH)_{3}(s)$.

In addition, more complex numerical modeling analysis is also being performed with three-dimensional pump jet mixing of tank waste (sludge consisting of solids and interstitial solution) and overlying water (as diluent to dissolve many solids), as shown in Figure 5. The chemical reactions considered for this case are

$Na^{+} + NO^{-}_{3} = NaNO_{3}(aq)$
$Na^{+} + NO^{-}_{2} = NaNO_{2}(aq)$
$Na^{+} + NO^{-}_{3} = NaNO_{3}(s)$
$Na^{+} + NO^{-}_{2} = NaNO_{2}(s)$
$Na^{+} + Al(OH)^{-}_{4} = Na^{+} + OH^{-} + Al(OH)_{3}(s)$
$2\ Na^{+} + CO_{3}^{2-} + H_{2}O = Na_{2}CO_{3}\bullet H_{2}O(s)$
$2\ Na^{+} + SO_{4}^{2-} = Na_{2}SO_{4}(s)$.

These axisymmetric and three-dimensional results will be carefully evaluated to examine interactions of chemical and hydrodynamic processes occurring during the waste retrieval operation.

It is especially critical to evaluate some local areas of unwanted chemical reactions not anticipated from small-scale laboratory experiments or coupled reactive slurry modeling by TEMPEST with coarse resolution. Thus, the hydrodynamic portion of the TEMPEST runs will be used to conduct numerical modeling analysis of local and global mixing of non-Newtonian and Newtonian slurries.

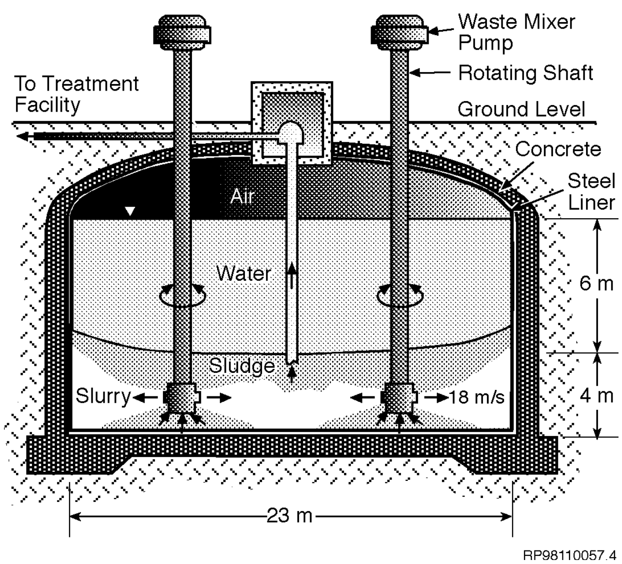

Figure 5. Pump Jet Mixing Model

The chemical evaluations include how and where the nucleation of unwanted solids (e.g., boehmite and sodium phosphate hydrate) may be dynamically induced in the waste tank. These reactions would make retrieval operation very difficult, if not impossible. The plugging of the 3.5-in.-diameter pipelines at Hanford Site is suspected to be the result of a combination of the chemical reactions of aluminum and phosphorus and resulting solid depositions as the wastes cooled off during pipeline transfer (Gephart and Lundgren 1997).

5.3. Numerical modeling analysis of local and global mixing of non-Newtonian and Newtonian slurries

Spatial resolution in mixing processes is an acute problem. We propose a line method akin to the contour dynamics technique used in meteorology. This is an extension of the particle method but with the particles redistributed on the line dynamically with each time step. We have used up to $5x10^5$ particles per line and 10 lines to investigate the dynamic and structural properties of mixing for both Newtonian and non-Newtonian temperature- dependent theological flows in a Cartesian two-dimensional geometry. The spatial structures and time history of the lines formed by the convective flow are different flow those produced in non-Newtonian convection, which tends to produce long-living horizontal structures. Efficient mixing would be inhibited by non-Newtonian rheology because of the decoupling nature of the shear layers formed.

We have examined how a key characteristic of the mixing process, the length of the material interface, would depend on the rheological differences. From mixing analysis, the Newtonian medium reveals a greater amount of stretching (by a factor of around 1000) than that of the non-Newtonian material (by a factor of 200). The rate of stretching is well fit by an exponential dependence with time, while the non-Newtonian rheology shows a power-law dependence with time in the stretching. Because of the nonlinear character of the rheology, the non-Newtonian medium offers a "natural" scale-dependent resistance to deformation, which prevents efficient mixing at smaller length scales. This result has important ramifications on mixing processes in nuclear waste tanks, because the chemistry can induce non-Newtonian character in the fluid medium. More can be found, with five visualizations available, on http://bobby.msi.umn.edu/mixing/.

We have also studied the effects of a moving heat source in the presence of temperature-dependent viscosity on mixing. We have found that the decoupling effects caused by the moving heat source would also make mixing of heterogeneities inefficient. This mechanism has the same cause as the non-Newtonian rheology described above.

The nonlinear dependence of temperature in the thermal conductivity of nuclear waste material can cause a radical change in the mode of heat transfer. We have investigated theoretically the nonlinear diffusion equation brought about the presence of a temperature-dependent thermal conductivity. Heat is found to be focused and locked in a mode with a compact local support. The speed of heat propagation is found to be finite, not "infinite," as in the case of the classical heat diffusion equation. We are studying both three-dimensional convection with variable thermal conductivity and one-dimensional advection-diffusion equation with a strongly temperature-dependent conductivity.

(6) Planned Activities

Remainder of FY 1999 and FY 2000: We plan to continue to simulate coupled chemistry and mixing for tank waste with the TEMPEST code. Using the predicted velocity field obtained by TEMPEST, we will perform detailed local and global mixing. We will examine differences of mixing scales and degrees of Newtonian and non-Newtonian slurries and their implications on chemical reactions and slurry rheological changes. We also plan to identify localized zones where dynamically induced nucleation of unwanted solids (e.g., boehmite and sodium phosphate hydrate) may occur. Probability distribution functions will also be used for the tracers. We will also conduct visualization of simulation results.

FY 2001: We plan to repeat the chemical (and possibly also coupled) modeling with FY-2000's detailed mixing results to evaluate global and localized chemical reactions and associated rheology changes. Comparing these results with the coupled mixing and chemistry modeling results by TEMPEST, we will use these new insights and findings to improve the scientific basis for developing retrieval operation decision-making support tools. In addition, we will perform visualization over MPP and production runs and interactive steering.

Through these analyses, we will evaluate the interactions among chemical reactions, hydrodynamic/transport processes, and waste rheology for the entire tank. These evaluations will help develop more scientifically defensive waste retrieval assessment tools. These modeling improvements will significantly reduce the uncertainties in

- Which and how much diluent (solvent) should be used
- Whether waste can be retrieved from a tank
- How much and in what physical/chemical forms the sludge can be removed
- How long the pump mixing and sludge sluicing should be performed
- Under what operating conditions the retrieved wastes can be transferred through a pipeline to separation and solidification facilities.

These improved chemically reactive, rheological, and flow modeling capabilities will also support determination of the safety, design, and operational conditions of waste pipeline transfer and subsequent separation activities to ensure the success of DOE's tank waste remediation efforts.

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