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Low Temperature Aluminum Dissolution Of Sludge Waste

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ABSTRACT

High Level Waste (HLW) at the Savannah River Site (SRS) is currently stored in aging underground storage tanks. This waste is a complex mixture of insoluble solids, referred to as sludge, and soluble salts. Continued long-term storage of these radioactive wastes poses an environmental risk. The sludge is currently being stabilized in the Defense Waste Processing Facility (DWPF) through a vitrification process immobilizing the waste in a borosilicate glass matrix for long-term storage in a federal repository. Without additional treatment, the existing volume of sludge would produce nearly 8000 canisters of vitrified waste.

Aluminum compounds, along with other non-radioactive components, represent a significant portion of the sludge mass currently planned for vitrification processing in DWPF. Removing the aluminum from the waste stream reduces the volume of sludge requiring vitrification and improves production rates. Treating the sludge with a concentrated sodium hydroxide (caustic) solution at elevated temperatures (>90°C) to remove aluminum is part of an overall sludge mass reduction effort to reduce the number of vitrified canisters, shorten the life cycle for the HLW system, and reduce the risk associated with the long term storage of radioactive wastes at SRS.

A projected reduction of nearly 900 canisters will be achieved by performing aluminum dissolution on six targeted sludge batches; however, a project to develop and install equipment will not be ready for operation until 2013. The associated upgrades necessary to implement a high temperature process in existing facilities are costly and present many technical challenges. Efforts to better understand the characteristics of the sludge mass and dissolution kinetics are warranted to overcome these challenges. Opportunities to further reduce the amount of vitrified waste and increase production rates should also be pursued.

Sludge staged in Tank 51 as the next sludge batch for feed to DWPF consisted primarily of radioactive wastes containing a very high aluminum concentration. Based on initial laboratory testing and previous sludge characterization, aluminum in this sludge could be dissolved at low temperature (no more than 65°C) in a concentrated caustic solution. The amount of aluminum predicted to dissolve under these conditions ranged from 25% to 80%. An opportunity existed to remove a significant amount of aluminum prior to vitrification in DWPF and increase the level of understanding of the effects of caustic dissolution of aluminum at lower temperatures.

This paper presents the results of a real waste laboratory demonstration and full-scale implementation of a low temperature aluminum dissolution process which should be considered as a viable means to reduce radioactive sludge mass and reduce the amount of waste to be vitrified.

INTRODUCTION

History

The Savannah River Site (SRS), owned by the United States Department of Energy (DOE), began operations in the early 1950's. The primary mission of the site was to recover uranium and plutonium for defense purposes. In the past, SRS fabricated and irradiated aluminum clad fuel assemblies and targets. These were dissolved in the two

chemical separation facilities to recover the uranium, plutonium and other radioactive isotopes of interest. The remaining materials, consisting of fission products and dissolved metals, were discarded as waste. This waste is currently stored in large underground storage tanks waiting final disposition processing. Continued long-term storage of these radioactive wastes poses an environmental risk.

Over the years, the separation processes generated over 450 million liters of liquid high-level radioactive waste (HLW). This acidic waste stream was neutralized with sodium hydroxide to prevent corrosion of the carbon steel waste tanks. Neutralization of the waste causes the formation of insoluble precipitates (sludge) that settle to the bottom of the SRS HLW tanks and a supernatant liquid consisting of sodium salts. The volume of sludge generated since SRS started operations is estimated to be about 11.4 million liters of settled sludge, about 8% of the total SRS waste inventory. The sludge contains about 7.5 million TBq (203,000,000 Curies) of radioactivity or 48% of the total SRS waste inventory.

Sludge consists of stable and radioactive fission products, actinide elements, and other elements added in the separation processes. The principle insoluble constituents of sludge are the oxides and hydroxides of iron, aluminum and manganese. As the waste ages and cools, these insoluble components settle to the tank bottom. Sludge layers accumulated in SRS tanks vary from a tenth of a meter to over 2 meters thick.

One of the current missions of the site is to dispose of the waste through solidification. The disposition pathway for the sludge is through a vitrification process that immobilizes the waste in a borosilicate glass matrix for long-term storage in a federal repository. At the Defense Waste Processing Facility (DWPF), sludge is mixed with waste from other processes, blended with glass frit, and melted to vitrify it into glass. The molten glass is poured into stainless steel canisters where it solidifies as it cools, immobilizing the radioactive waste within the glass structure. DWPF has been in operation vitrifying sludge since 1996 and has produced over 2000 canisters of glass.

The cost of disposal of the sludge is significantly higher than the cost of disposal of the salt solution. A can of vitrified waste costs about $1,000,000 to produce and disposition at a permanent federal facility. The can holds about 750 kg of sludge as oxides. Therefore, even modest reductions in the mass of waste disposed in canisters of glass results in significant cost savings.

Starting in 2005, a year long effort was conducted to update the sludge batch planning baseline in terms of the mass of sludge insoluble solids in the tank farm. This effort resulted in an increase in the projected amount of sludge that would require treatment and vitrification that was significant enough to prompt investigation of mitigation options. Three mitigation paths were developed. The first was to establish a team to resurrect the old baseline process for aluminum dissolution. The baseline process for aluminum dissolution (called the standard aluminum dissolution process in this paper) required a dedicated HLW tank, equipment upgrades and an updated technical baseline. It was apparent that this process could not be brought online until 2013 at the earliest. The second mitigation path was to investigate ways to improve waste loading using frit optimization and the third was to look into improved melter technologies, both of which are ongoing.

The possibility of removing aluminum from the sludge during in-situ waste removal, by adding caustic and allowing the tanks to heat up using decay heat and waste energy from the slurry pumps was considered, but the facility upgrades that would be needed in the old style tanks that were being decommissioned were not economically practical and the expected effectiveness of the aluminum removal was fairly low.

In the meantime, the team working on the standard aluminum dissolution process charted data from the full scale demonstration of aluminum dissolution conducted during the early 1980s. It was recognized that a significant amount of aluminum was dissolved during the caustic addition phase of the demonstration, even before the tank heating with steam spargers was initiated.

Consideration of this data resulted in recognizing that by using higher concentrations of caustic and extended treatment times, the aluminum dissolution could be conducted at lower temperatures but with some reduction in effectiveness. Further investigations into sludge mass reduction options continued to point to the need for some type of lowered temperature, minimal facility cost process. The sludge collected in Tank 51 provided a unique

opportunity to both remove aluminum using the low temperature process and to collect data to be used in support of the development of the standard aluminum dissolution process.

Problem Statement

The purpose of the sludge mass reduction program is to minimize the number of canisters of vitrified glass produced. The program plans to remove aluminum from the sludge solids by caustic treatment. The aluminum will then be dispositioned as part of the salt solution waste treatment processes. The savings in canisters of vitrified glass are due to the higher waste loadings possible without the aluminum, the faster processing rates possible without the aluminum and the reduction in the total mass of solids which have to be vitrified.

SLUDGE CHARACTERIZATION

The sludge in Tank 51 is the result of separations preformed using a process to treat assemblies made with enriched uranium. Sludge from this process is significantly higher in aluminum than sludge made from other processes. In addition, the sludge characteristically is slow to settle and exhibits a high yield stress as a function of weight percent insoluble solids. Tank 51 initially contained about 188,000 kg of insoluble solids of which 25 weight percent was aluminum. The tank contained sufficient supernatant so that when the contents were fully blended, the overall weight percent of insoluble solids was about 9 percent. In addition, soluble salts contributed about 6 percent to the total weight, for combined total solids of about 15 weight percent. This concentration is at the upper end of what can be transferred to the DWPF feed tank due to the high yield stress.

The characteristically high yield stress as a function of insoluble solids in this sludge is believed to be the result of the form of aluminum in the sludge. This aluminum was formed by precipitation following neutralization of an initially acidic solution. Aluminum precipitate from acidic solutions is known to exhibit a small particle size and to be gelatinously in nature. This is in contrast to aluminum precipitated from caustic solution which tends to have a larger particle size and to be readily filterable. The two forms are typically characterized as aluminum monohydrate and aluminum trihydrate. The aluminum monohydrate form exhibits the high yield stress and poor settling, as well as limited solubility at low temperatures and caustic concentrations. The aluminum trihydrate form is readily soluble in moderate temperatures and caustic. The actual forms of the aluminum compounds in the sludge are not pure and are composed of a wide range of specific surface areas. Aluminum monohydrate would typically have a high specific surface area and aluminum trihydrate would typically have a lower one. The actual sludges are composed of these forms as well as atypical forms with higher or lower specific surface area than expected. This causes a smearing of the characteristics behavior of the sludge by type in terms of rheology, settling, and solubility.

Therefore, characterization of the sludge has to include specific measurements of the response of the solids under dissolution conditions. The characterization performed on a 3 liter sample of sludge slurry to establish the optimum caustic treatment conditions for low temperature dissolution is described later in the document.

PROCESS FLOWSHEET

The form of the aluminum directly influences aluminum solubility and dissolution rate. Dissolution of the aluminum trihydrate form of aluminum involves the following reaction:

$$Al(OH)_{3(s)} + NaOH \rightarrow NaAlO_2 + 2H_2O$$

The aluminum monohydrate form of aluminum dissolves according to the reaction:

$$AlOOH_{(s)} + NaOH \rightarrow NaAlO_2 + H_2O$$

In each case, sodium hydroxide is consumed to form sodium aluminate, a readily soluble salt.

However, existing data contains a large amount of uncertainty regarding the form of aluminum compounds in the high aluminum sludge waste. Further complicating any prediction of reaction rates includes physical factors that affect the diffusion of reactants and products from the solids surface. The parameters that directly affect diffusion in the liquid phase to the solid surface include:

- particle surface area,
- bulk liquid phase properties, and
- diffusion layer thickness, which is controlled by liquid phase velocity relative to the particle surface.

The process flowsheet needed to be developed with minimal physical characterization data. By focusing on the desired result, dissolving as much aluminum as practical, a few key parameters need to be determined, which include the total capacity needed for the liquid phase after dissolution, minimum process temperature, estimation of the fraction of aluminum dissolved at process temperature, and the time required.

The dissolution conditions chosen for Low Temperature Aluminum Dissolution (LTAD) allow for the dissolution of up to 80% of the aluminum and for dissolved aluminum to remain completely soluble at 30°C for long-term storage of the supernate. Storage of decanted supernate from aluminum dissolution requires a sufficient margin below saturation of aluminum. At the nominal 50% dissolution of aluminum, the free hydroxide ion concentration will be adequate to maintain aluminum in solution, but additional caustic needs to be added to the storage tank, Tank 11, if more aluminum dissolves.

Table I shows the initial composition in the process tank, Tank 51, and storage tank, Tank 11. A starting concentration of 4.3 M after addition of 50% NaOH solution would result in a post-dissolution condition that meets the process conditions outlined earlier. This results in a molar ratio of hydroxide to aluminum of about 5 to 1.

Table I: Initial Process Conditions

	Tank 51	**Tank 11**
Liquid Volume (L)	1,862,000	59,800
Insoluble solids Volume of Sludge (L)	78,400	14,000
Insoluble Solids (kg)	188,000	34,000
wt% Insoluble Solids	9.31	-
Al in Insoluble Solids (wt% of dry insoluble solids)	25.3	-
Specific Gravity	1.026	1.034
pH	-	10.8
Liquid Phase Concentration in M:		
Na^+	1.08	0.38
NO_2^-	0.46	0.23
NO_3^-	0.24	0.12
OH^-	0.057	< 0.01
Cl^-	0.00073	< 0.0007
SO_4^-	0.023	0.012
F^-	0.0020	-
CO_3^{-2}	0.12	-
AlO_2^-	0.021	0.0005*
$C_2O_4^{-2}$	0.0045	-
PO_4^{-3}	0.0009	-
K^+	0.0031	-

* Estimated value

Aluminum dissolution was performed in a full-scale demonstration in 1982 by adding 50 wt% NaOH to the process tank, Tank 42. Steam heating was used to hold the slurry temperature at 85°C for three to five days while slurrying continuously. The NaOH was added in sufficient quantity to provide a minimum initial ratio of 3 moles of free hydroxide per mole of acid soluble aluminum and to provide a final liquid phase free hydroxide molarity of 3. The actual conditions during dissolution varied from these initial conditions due to a variety of operational issues, but roughly approximated these conditions. This full-scale dissolution demonstration provided an initial indication that substantial aluminum will dissolve at lower temperatures than used in the demonstration.

During the full-scale demonstration, a total of 394,000 liters of 50-wt% sodium hydroxide and 447,000 liters of dissolved salt solution were added to 473,000 liters of high aluminum sludge. Initial dissolving conditions were 1.3 M $N0_3^-$, 0.28 M $N0_2^-$, and 3.64 M OH^-. The tank was heated from 63 to 83°C in 38 hours with steam spargers (2700 kg/hr) and was continuously agitated. Thereafter, a steam flow of 450 kg/hr was used to maintain tank temperatures between 83 and 85°C. After five days of digestion, sample analyses indicated that approximately 80% of the total aluminum in the sludge had dissolved.[1] During caustic addition to the process tank, the temperature maintained between 60°C and 70°C and about 50% of the aluminum dissolved during the 4 weeks needed to add the NaOH.

Further support for a lower process temperature was demonstrated in bench scale tests. Laboratory tests of aluminum trihydrate dissolution indicate that aluminum trihydrate dissolves rapidly at 65°C, i.e., in less than a day.[2] Additional testing with Tank 12 sludge at 60°C shows most of the aluminum dissolved in 10 days.[3] The fraction of aluminum trihydrate in Tank 12 is expected to be similar to the composition in Tank 11.

In each of the tests, a substantial fraction of the aluminum dissolves at temperatures between 60°C and 70°C, leaving a much slower dissolving fraction. The total fraction of the slower dissolving fraction dissolved was estimated by using a dissolution model developed for SRS waste. Equation (1) shows a kinetic model developed for dissolving aluminum from sludge that is based on dissolution test data, in tank demonstration data, and literature data.[4]

$$t = \frac{\alpha\, F(wf,\alpha)}{(2\times 10^{15})\sqrt{C_{OH}^0}} e^{\frac{14800}{T}} \qquad \text{(Eq. 1)}$$

where:

t = Dissolution time, hr

$$F(wf,\alpha) = \frac{1}{\sqrt{\alpha(\alpha\text{-}1)}} \mathrm{Ln}\left|\frac{(\sqrt{\alpha}-\sqrt{\alpha-1})(\sqrt{\alpha\text{-}1+wf}+\sqrt{\alpha-1})}{(\sqrt{\alpha}+\sqrt{\alpha-1})(\sqrt{\alpha\text{-}1+wf}-\sqrt{\alpha-1})}\right|$$

α = Mole ratio at initial conditions of free OH ion in the liquid phase relative to Al in the solid phase, dimensionless

C_{OH}^0 = Initial liquid phase concentration of free OH ion in molal units, gmol/kg water

T = Dissolution operating temperature, K

wf = Weight fraction of initial Al remaining in solids at the conclusion of the dissolution process, dimensionless

The rate equation is based on a number of simplifying assumptions, including:

- Sufficient solids and liquid mixing is provided,
- The dissolution endpoint composition is selected such that the solubility limit does not influence the dissolution rate at the dissolution operating temperature,
- The change in liquid phase water mass is negligible over the dissolution time period,
- The operating temperature is constant over the dissolution time period, and
- The liquid phase sodium hydroxide activity is approximately proportional to the molal concentration of free hydroxide ion in solution.

The rate equation is applicable for hydroxide ion concentrations less than 6.8 M. A shift in reaction order occurs above this concentration and the rate equation would be expected to over-estimate times to dissolve aluminum while the liquid phase is at free hydroxide ion concentration greater than 6.8 M.

The rate equation shows that the dissolution rate approximately changes by an order of magnitude for each decade change in temperature. Considering that test data shows dissolution of the fast dissolving fraction of aluminum occurs within as little as 1 day at 65°C, a minimum practical temperature of 55°C was chosen to provide conservatism in the event that higher temperatures became difficult to achieve. The time needed to dissolve most of the faster dissolving aluminum at the minimum temperature was estimated to take 3 weeks.

Figure 1 shows the dissolution process and aluminum balance.

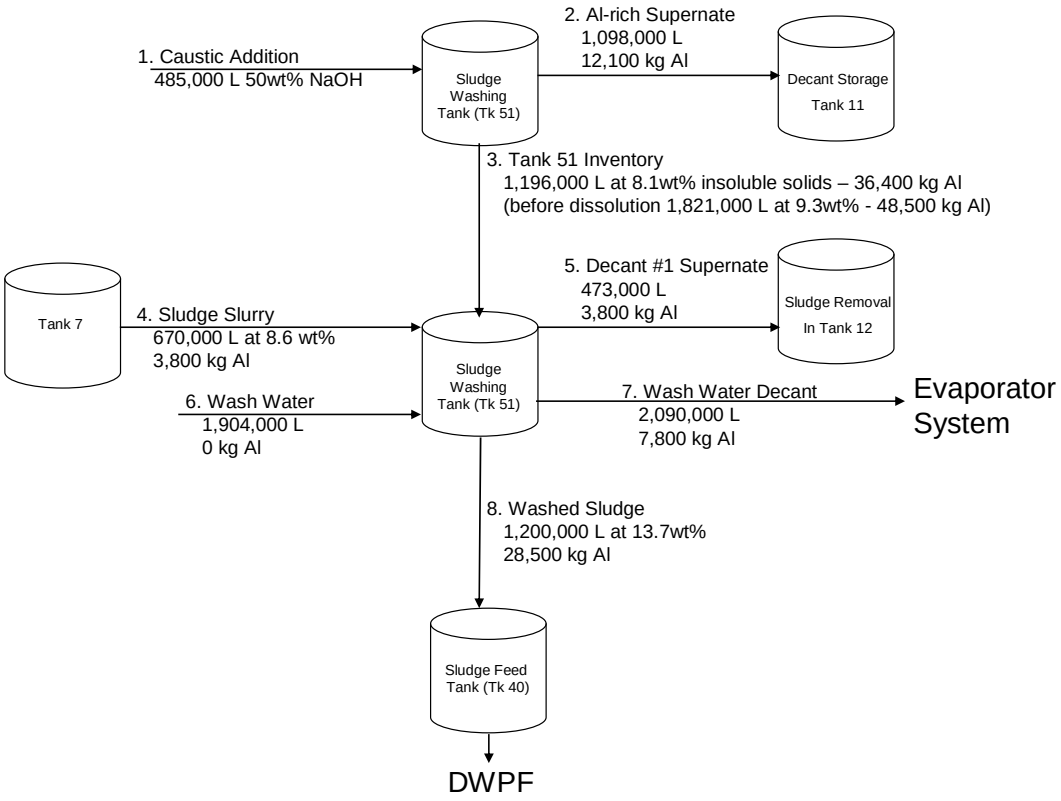

Figure 1. Aluminum Balance for Aluminum Dissolution in Tank 51.

LABORATORY DEMONSTRATION

Before the process was to be performed in Tank 51, a small-scale demonstration in the Savannah River National Laboratory (SRNL) Shielded Cells Facility using a 3-L sludge slurry sample was performed to verify the processing parameters and confirm the extent of aluminum removal. The aluminum dissolved sludge would also be used to determine potential downstream impacts and allow technical issue resolution prior to the start of the sludge batch processing. The potential downstream impacts to be assessed included the sludge batch washing and concentration process, and the DWPF Chemical Process Cell (CPC) and melter processing envelopes. Demonstration conditions to replicate those expected for Tank 51 and DWPF nominal conditions were established.

A 3-L sample of sludge slurry from Tank 51 was delivered to SRNL on May 31, 2007. A full characterization of both sludge solids and liquid supernate was performed to establish the initial conditions for several materials of concern.[5] A portion of the sludge slurry was passed through a 0.45µ filter to obtain the supernate. The characterization of the analytes of concern from the filtered supernate is shown in Table II. Iron concentration is of concern as it is a poison for fissile material. Uranium and plutonium are of concern to prevent material consolidation through dissolution and subsequent reprecipitation of fissile material. Dissolution to an appreciable extent of any of these materials is undesirable.

Table II. Tank 51 Supernate Characterization.

Analyte	Units	Average
Na	M	1.05
Al	M	0.013
Fe	mg/L	<7.6
U-238	mg/L	0.15
Pu-239	mg/L	<0.016

The demonstration was initiated on August 29, 2007. The 3-L demonstration system is shown in ***Figure 2***, and was configured in cell #2. The system configuration consisted of a large poly bottle to simulate Tank 51 in a thermally controlled water bath. A ported cap was fit to the poly bottle to provide for temperature measurement, sample withdrawal, vapor space monitoring and equipment insertion. A paddle agitator was inserted into the bottle to provide mixing for the slurry.

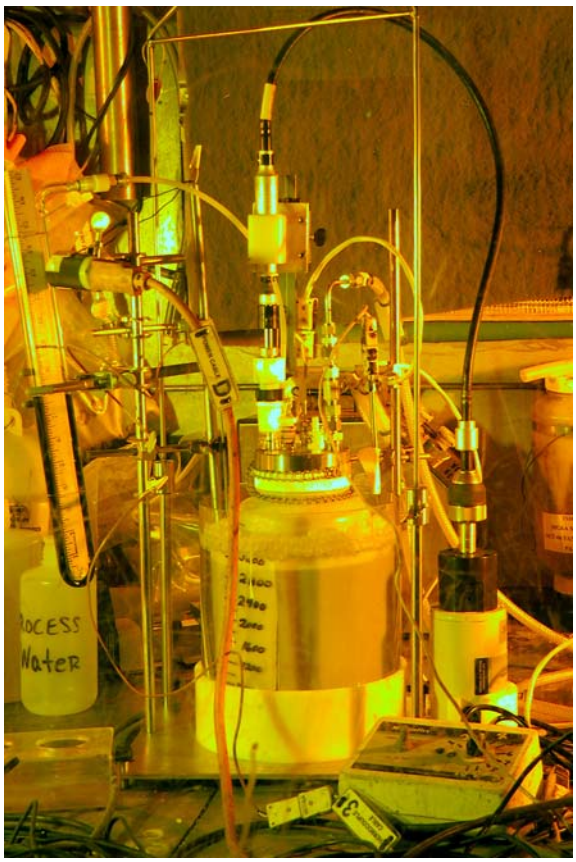

Figure 2. Small-scale demonstration equipment in shielded cells.

Approximately 2.48 liters of sludge slurry were used for the demonstration. This amount was required to provide ~1 liter of washed sludge for the evaluation of the impact on DWPF processing based on the assumption that 50% of the aluminum in the sludge dissolves. The aluminum dissolution demonstration added a volume of 662 mL of ~19 M NaOH, equivalent to the amount estimated in the flowsheet material balance and dissolution assumptions. The

amount added was targeted to achieve a 5:1 molar ratio of hydroxide to aluminum and a starting concentration of ~4.3 M hydroxide or greater in the slurry. The slurry was heated to 55 °C and mixed for 21 days to dissolve aluminum from the sludge solids. Small samples of the slurry were obtained every other day (except over weekends) to determine the amount of aluminum dissolved versus time. Samples were pulled and immediately filtered through a 0.45µ filter to remove the sludge solids and stop any further dissolution. The filtrate from the periodic samples were diluted in acid and sent for analysis.

The samples obtained during the aluminum dissolution were analyzed for Al, Cr, Fe, Mn, Na, Pu, and U.[5] The decanted supernate and the total dried solids of the sludge slurry at the completion of the aluminum dissolution test were analyzed in the same manner as the initial sludge sample: the total dried solids of the sludge were dissolved by two methods and the dissolved solids analyzed for Na, Al, and other metal ions, U and Pu isotopes, and Hg; the supernate was analyzed for Na, Al, and other metal ions, free hydroxide, common anions, carbonate, Hg, and U and Pu isotopes.

The analytical results for the periodic samples are given in Table III. The percent aluminum dissolved represents an estimate of the amount of aluminum dissolved out of the sludge solids based on a material balance calculation. The amount of aluminum dissolved from the sludge and the amount of aluminum removed from the sludge slurry may not be the same value, and would depend on the amount of solution decanted from the sludge and the effectiveness of sludge washing.

Table III. Periodic Sample Results for Aluminum Dissolution.

Sample No. (hours)	Al (M)	Estimated Percent Al Dissolved	U-238 (mg/L)	Pu-239 (mg/L)
Initial	0.010	0	0.12	<0.012
1 (1 hr)	0.012	0.3	2.45	0.31
2 (42 hrs)	0.081	9	2.79	0.032
3 (89 hrs)	0.13	15	3.37	0.031
4 (143 hrs)	0.17	20	3.36	0.090
5 (189 hrs)	0.19	23	3.49	0.026
6 (259 hrs)	0.24	29	3.73	0.045
7 (308 hrs)	0.26	32	3.61	<0.008
8 (358 hrs)	0.28	35	3.45	0.043
9 (400 hrs)	0.30	37	3.54	0.037
10 (453 hrs)	0.32	38	3.39	0.042
11 (495 hrs)	0.33	40	3.33	0.037

After completion of the aluminum dissolution step the temperature was lowered to 35 °C and the mixer was turned off. The sludge was maintained at 35 °C and allowed to settle undisturbed for 3 weeks. After approximately 300 hours (12.5 days) the sludge reached the final settled level and settled no further over the remaining 200 hours. The settling rate of the post aluminum dissolution sludge appeared to be within the expected settling rates observed with a previous Tank 51 sludge sample from July 2005.

The aluminum rich supernate was decanted to another bottle and set aside to replicate expected storage conditions. The supernate was adjusted to match the final hydroxide concentration anticipated in Tank 11 during storage. The decanted supernate was maintained at the cell's ambient temperature and was monitored over the course of several weeks to observe for any reformation of solids. No precipitation of aluminum occurred. A small sample of the

remaining sludge slurry was obtained for characterization. The remaining sludge slurry was then washed in preparation for simulated DWPF processing.

PROCESS IMPLEMENTATION

Setup/Initial Conditions

The activities that are required to execute LTAD process are performed routinely by the operating personnel. Due to the low operational complexity of the LTAD process, an operating plan was developed utilizing normal transfer and operating procedures in accordance with Tank Farm requirements.[6] The plan did not require that a manual be prepared or that a special procedure be used simplifying the process execution.

The low temperature aluminum dissolution treatment of the Tank 51 sludge consisted of the following sequence. Approximately 488,000 liters of concentrated caustic solution was added to Tank 51 in 21 days via tanker truck unloading. The temperature increased to a maximum 64°C and the contents of the tank mixed for 50 days. Operational issues prevented mixing for a 12 day period in December. Mixing was then suspended and the sludge allowed to gravity settle for 3 to 4 weeks. Following settling, the supernatant containing dissolved aluminum will be decanted out of Tank 51 and stored in Tank 11 until future processing as salt waste. Settling is not complete at the time of this paper.

Prior to caustic addition, the cold chemical addition connectors will be replaced and the Tank 51 cooling coils will be shut off to allow the internal temperature to increase. Also, slurry pumps were operated to provide a basis to declare Tank 51 a mixed tank.

Caustic Addition

About 488,000 liters of 50 wt. % sodium hydroxide was transported by approximately 43 tanker trucks carrying an approximate volume of 11,400 liters each. The caustic was systematically unloaded into HPT-7 and HPT-8. Only one tanker truck was unloaded at a time. The estimated time to unload a tanker truck was approximately 3 hours including one hour for setup, one hour for unloading and one hour to disconnect the tanker. A maximum of 4 tanker trucks were unloaded each day depending on operational efficiency. The transfers from HDB-8 to Tank 51 alternated between HPT-7 and HPT-8 to minimize total volume transfer time. The time to transfer the total volume of caustic to Tank 51 via HPT-7 and 8 was 21 days.

The first phase of caustic transfer was staged at HDB-8. The contents of the tankers were transferred into the pump tanks by pressurizing the tankers using an on-board vendor air supply. The new cold chemical addition connectors featured a two-inch female cam and groove connection. The new connections were verified by the vendor to be compatible with the tanker trucks. The tankers were pressurized in the range of 15-20 psig. The transfer equipment included a chemical hose and a flush rig (distribution manifolds).

The 50 wt. % sodium hydroxide starts to freeze at 12˚C to 13˚C (53 to 55ºF). The NaOH was heated prior to loading into the tanker trucks. The tanker trucks were insulated to minimize the heat loss during transit. The caustic, once in HPT-7 or HPT-8, was pumped into Tank 51 using underground transfer lines. While the time that the caustic was stored in the pump tanks was minimized, the transfer lines are underground and beneath the frost cap which helps maintain the temperature of the caustic at an acceptable level above 13ºC. The actual transfer duration from the pump tank to Tank 51 is short enough to avoid the likelihood of freezing in the transfer lines.

During the caustic addition, the slurry pumps were run in approximately 8 hour shifts after the addition of every 6 to 9 tankers in order to increase Tank 51 temperature and promote mixing/dissolution. Midway through the caustic addition, slurry pumps were operated, as available, to increase the Tank 51 temperature to approximately 65ºC or above (maximum allowable temperature was 75ºC per corrosion control program). Although a temperature of 65ºC to 70ºC was desired, a lower temperature was acceptable.

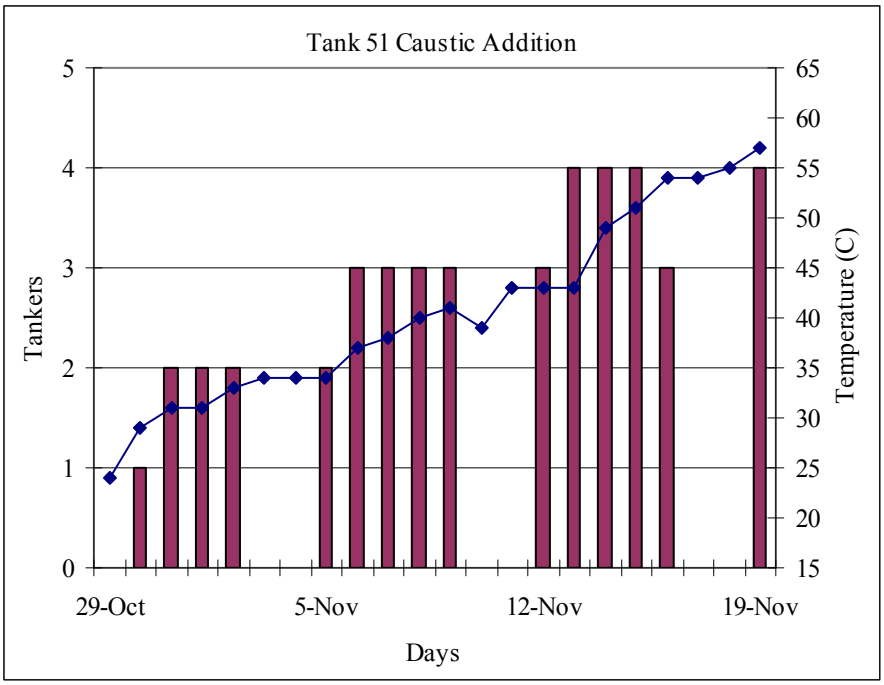

Figure 3. Caustic additions to Tank 51 and sludge slurry temperature.

Mixing

Once all of the caustic was added to Tank 51, operation of the installed slurry pumps continued intermittently for approximately 50 days in order to mix the tank. Pump run hours were minimized by only running the minimum number of pumps necessary to heat the tank to 65ºC to 70ºC, maintain that elevated temperature, and to mix the sludge. As few as two of the four slurry pumps were used in pairs, alternating turns, to maximize mixing/dissolution and to minimize the run time on individual pumps. Operational problems with two of the pumps prevented alternating as planned for most of the mixing time. In addition, a 12-day pump outage prevented any mixing during the outage in December.

Pump operational problems included mechanic problems with one pump that required several weeks to repair and excessive bearing water leakage with another. The slurry pumps use pressurized water to cool the bearings on the pump shaft. The mechanical seal at the bottom of the shaft, which is inside the tank, purposely leaks at a very low rate. As the seals wear out, the leak rate increases. At the normal leak rate, the effect of dilution and increasing tank level are insignificant.

Dip samples were taken periodically during the caustic addition and mixing/dissolution process in order to trend the effectiveness of the dissolution process. Once all of the caustic was added to Tank 51, the Tank51 slurry pumps operated intermittently for approximately 50 days in order to mix the tank and to achieve or maintain the desired temperature range.

75-ml dip samples were taken and analyzed about every three days during mixing to monitor the progress of the aluminum dissolution process. This sample frequency allowed determination of the amount of mixing/dissolution that has taken place and enabled management to respond to the actual tank conditions (i.e. if mixing/dissolution occurs more rapidly than predicted, then terminate mixing early and proceed with settlement). Once a rate of dissolution curve was established from Tank 51 samples (e.g. after 12 to 15 days of mixing/dissolution), the sample frequency may be decreased. Sample results are given in Table IV.

Table IV. Periodic Sample Results During Caustic Addition and Mixing.

Sample No. (hours)	Al (M)	Estimated Percent Al Dissolved
Initial	0.021	0
11/8/07	0.042	6%
11/15/07	0.064	9%
11/20/07	0.13	18%
11/23/07	0.16	22%
11/26/07	0.19	26%
11/29/07	0.23	32%
12/02/07	0.23	32%
12/05/07	0.28	39%
12/10/07	0.32	45%
12/22/07*	0.33	46%

* sample after 12 days without mixing.

Settling

After completion of mixing, the waste will be allowed to settle. Turbidity readings will be taken approximately every five days to monitor the settling of the sludge. Settling is expected to take up to twenty-two days. The amount of time between completion of mixing and the start of decanting the supernatant should be maximized to allow the maximum amount of aluminum to be transferred to Tank 11. However, the combined settling time and time required to transfer to Tank 11 must be less than the quiescent time requirements for periodic mixing of Tank 51.

During the settling phase, turbidity readings will be taken every five days to monitor the sludge settling and to establish a minimum of 24 inches of separation between the sludge level and the jet suction. Settling is expected to take up to twenty-two days.

Decant

Once the settling phase has completed in Tank 51, the aluminum-rich supernatant will be transferred to Tank 11 using a jet. The separation distance between settled sludge height and the transfer jet suction must be greater than or equal to 24 inches if the sludge sounding was conducted between the waste influent line discharge and the transfer jet.

Subsequent to transferring the supernatant from Tank 51 to Tank 11, the final sample of the aluminum-rich supernatant in Tank 11 will be obtained and analyzed to determine the effectiveness of the aluminum dissolution process. This sample will be used to determine the amount of aluminum dissolved and transferred to Tank 11, establish a solubility composition, and establish a corrosion control baseline.

The final sample will be a 600 ml slurried sample of the remaining contents of Tank 51 after decant to Tank 11 is complete. This sample will be used for a study of the effects of caustic treatment on sludge properties such as particle size and rheology as well as validation of the efficacy of the dissolution process.

RESULTS

Figure 4 shows the tank temperature achieved during caustic addition as well as during mixing. The tank temperature reached 57ºC by the end of caustic addition, adequate to promote dissolution, prior to the end of caustic addition to Tank 51. During dissolution, the temperature of the sludge slurry fluctuated between 57ºC and 64ºC. During the 12 days without mixing in December, the temperature curve shows a distinct separation in temperature between an upper and lower layer. The sludge solids were settling during this time. The sludge layer retains heat better due to better thermal insolating properties of the sludge in addition to the natural heat source from most of the radioactivity in the solids. The tank temperature became relatively uniform after the pumps returned to service.

Figure 4 also shows the progress of dissolving the aluminum. No samples were taken during the pump outage in December. Operational issues prevented any samples after the pump outage until after the start of the settling phase. Sampling of the final slurry after the liquid decant to Tank 11 will confirm the amount of aluminum dissolved from the sludge. Figure 4 also shows the results of Equation 1 for a dissolution temperature of 60ºC and 70ºC and actual dissolution conditions. The dissolution rate model appears to predict dissolution rates lower than observed at 60ºC. The constant ($2x10^{15}$) was fit to a limited dataset and may need to be refined with this new dataset.

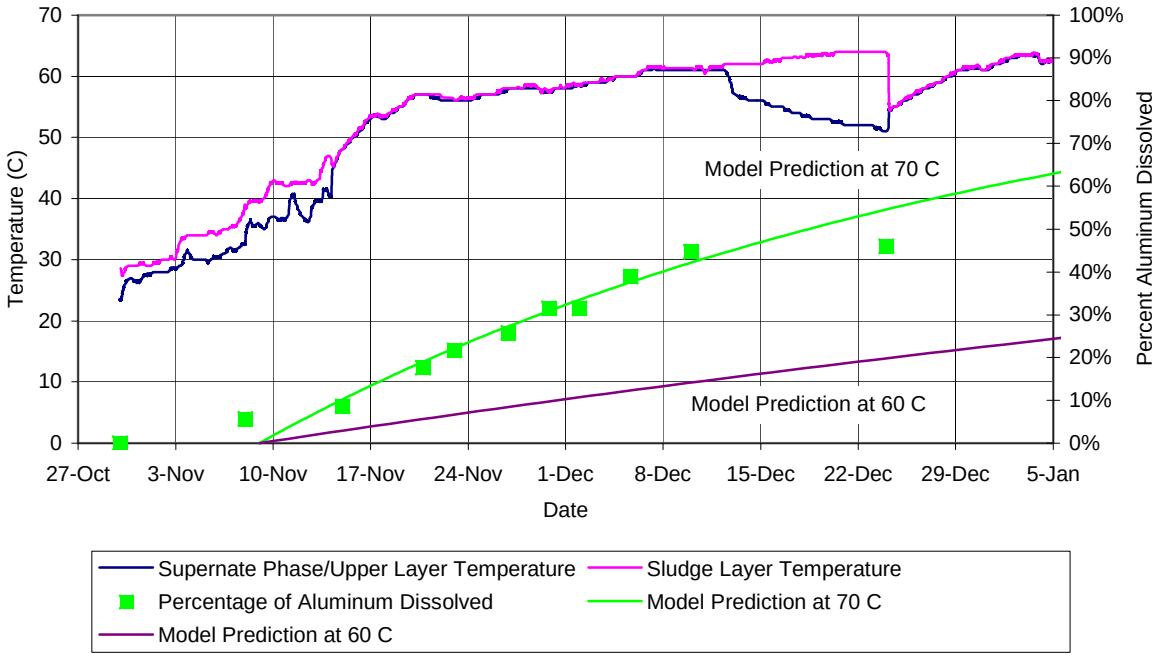

Figure 4. Extent of Dissolution with Tank Temperature.

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