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Status and Progress in Sludge Washing: A Pivotal Pretreatment Method

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STATUS AND PROGRESS IN SLUDGE WASHING: A PIVOTAL PRETREATMENT METHOD

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ABSTRACT

Separation of the bulk soluble chemical salts from the insoluble metal hydroxides and radionuclides is central to the strategy of disposing Hanford tank waste. Sludge washing and caustic leaching have been selected as the primary methods for processing the 230 million L (61,000,000 gal) of Hanford tank waste. These processes are very similar to those selected for processing waste at the West Valley site in New York and the Savannah River Site in South Carolina. The purpose of sludge washing is to dissolve and remove the soluble salts in the waste. Leaching of the insoluble solids with caustic will be used to dissolve aluminum hydroxide and chromium hydroxide, and convert insoluble bismuth phosphate to soluble phosphate. The waste will be separated into a high-level solids fraction and a liquid fraction that can be disposed of as low-level waste after cesium removal. The washing and leaching operations involve batchwise mixing, settling, and decanting within the existing underground storage tanks.

PROCESSING PLANS

The waste will be retrieved from the single-shell underground storage tanks with as much blending as possible. The retrieved waste will be accumulated in million-gallon underground storage tanks to a volume of approximately 1 million L (300,000 gal) of settled solids. The waste sludge will be processed through a series of leaches using 3-molar caustic, followed by inhibited water washing. Because methods for retrieving single-shell waste are still being developed, early sludge washing will be performed on selected double-shell tank waste with limited blending.

The first sludge to be washed is the neutralized current acid waste (NCAW) that was generated during the first solvent extraction cycle in the plutonium-uranium extraction (PUREX) process. The radionuclide inventory consists of fission products (primarily Cs-137 and Sr-90) with significant amounts of transuranic elements. With the exception of Cs-137, the fission products have low solubility in the alkaline solution and are present in the solid phase. Transuranic compounds as well as aluminum, iron, and zirconium compounds are also present as solids. Soluble components consist of nitrate, nitrite, hydroxide, carbonate, aluminate, and sodium ions.

The NCAW is stored in two 3.8 million-L (1 million-gal) tanks. Both tanks will be decanted using a floating suction pump down to a level of 30 cm (12 in.) above the sludge, or until the suspended solids concentration in the pump discharge exceeds 100 ppm. The first wash water will consist of 3 million L (800,000 gal) of dilute liquid waste, which will be mixed for 7 to 10 days using 300-HP mixer pumps. The contents of both tanks will be combined, mixed with mixer pumps for 7 to 10 days, and allowed to settle for 1 month. The solids will be washed once more with 2.3 million L (600,000 gal) of water and decanted.

It is estimated that washing the two tanks together will remove 97% of the soluble salts while only 0.4% of the insoluble solids will be carried over with the supernatant. A total of 10.2 million L (2.7 million gal) of supernatant solutions are generated, but these will be concentrated by evaporation to 3.8 million L (1 million gal). Thus, the two tanks containing NCAW will become one tank containing washed sludge ready for vitrification and one tank filled with solution ready for cesium removal.

The above outline plan was initiated as the "AZ-101 Sludge Washing Process Test," began when the airlift circulator operation in the tank was terminated on August 4, 1993. The next phase is to install a decanting pump, a control system, and instrumentation, then decant the supernatant to another storage tank. The final phase is to install and test two, 300-HP vertical centrifugal mixing pumps.

Airlift Circulator Operation

Every tank at the Hanford Site designed to contain PUREX high-level waste contains 22 airlift circulators. These circulators mix the tank contents to prevent insoluble solids from settling. If the solids settle and compact, the possibility exists that the high-heat-generating solids can cause steam to form in the sludge layer. Trapped steam might accumulate until it is released suddenly, resulting in a burp or steam bump. Such an event has the potential of adverse consequences due to overpressurizing the tank, thus causing potential airborne release of small quantities of radionuclides. In the case of a large burp, the physical damage may influence the integrity of the tank structure.

In-tank washing or leaching of insoluble solids requires that the solids be allowed to settle so that the solutions can be separated by decantation. This requires that airlift circulator operation be discontinued during the settling period. There was concern that a steam bump could occur during the settling period. Therefore, a computer model was developed to simulate the tank dynamics,[1] and a process test was carried out to determine if a bump could occur in the tank with the highest heat-generating rate.[2]

The test consisted of turning off the airflow to all the circulators in tank AZ-101. The temperature readings from the many thermocouples permanently installed in and around the tank were monitored and recorded. It was found that the average temperature of the solution increased about 11 °F, from 136 to 147 °F. The average sludge temperature increased about 13 °F, from 141 to 154 °F, with a maximum temperature of 190 °F near the tank center when the annulus ventilation system was not operating. With the bubble point of the solution being about 220 °F at the waste surface and 260 °F at the bottom, the formation of steam was not possible. The results of the test agreed well with the predictions of the computer model discussed later in this report.

Decantation of Waste Tank AZ-101

To decant tank AZ-101, a decanting pump, instrumentation to measure suspended solids concentrations and the sludge interface level, and a control system were needed. These have been designed, procured, and fabricated for installation. The total system has been tested at the Sulzer Bingham Pump Co. facility in Portland, Oregon. A drawing of the tank with equipment and instrumentation and including the mixing pumps is shown in Figure 1.

The decanting pump is a modified vertical turbine pump with a floating suction intake. A flexible metal hose is attached to the intake at one end, and the stainless steel float is attached to the other end. A cable attached to the float controls the position of the float, and allows the float to be pulled up out of the waste. A load cell is used to measure and control the tension on the cable, and an encoder or resolver measures the unreeled cable length.

The pump operation is controlled by a Siemens Power Corporation programmable logic controller, with a remote operator station located outside the tank farm fence line. There is instrumentation to measure the pump discharge flow rate, the discharge liquid turbidity (calibrated in ppm suspended solids with a waste simulant), a tank turbidity profiler, and a buoyancy liquid level monitor. This instrumentation will be wired into the controller so that the pump can be automatically switched between recycle back to the tank and transfer out of the tank or turned off. The position of the diverter valve or on-off status of the pump will be based on discharge flow and turbidity as well as tank waste liquid level and sludge/liquid interface level.

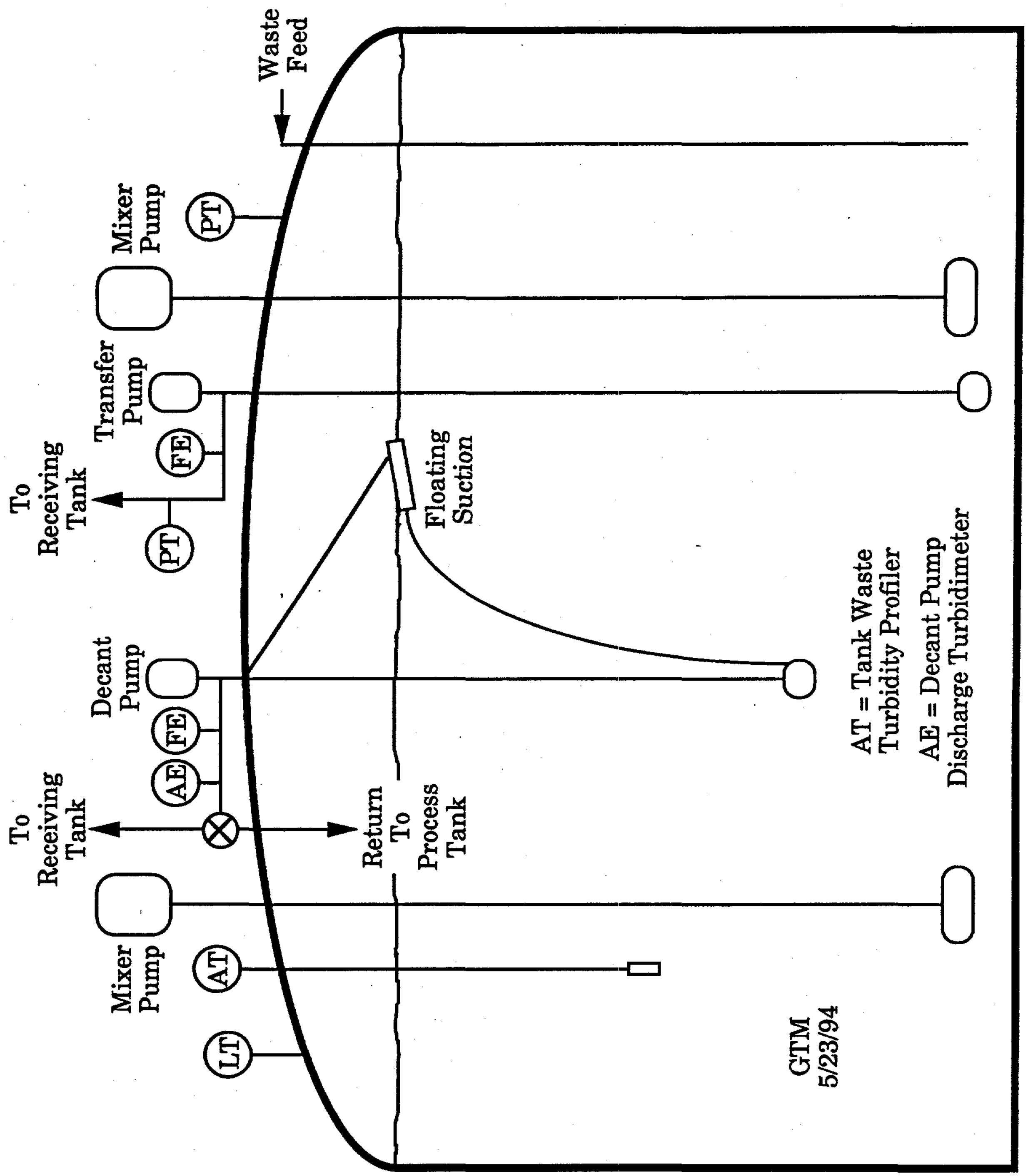
When the decant pump system is installed, tank AZ-101 will be decanted to about 0.3 m (1 ft) above the sludge layer. Then the tank will be refilled with a very dilute wastewater from another tank to reduce radiation exposure for the installation of two vertical centrifugal mixing pumps. This dilute waste will also be used for the first wash of the waste after the pumps become operational. The mixing pumps will be the first installed at the Hanford Site for the purpose of mobilizing and washing compacted waste sludge.

Future Test Plans

Following the testing of the mixing pumps, it is planned to decant a neighboring PUREX high-level waste tank (AZ-102) and pump the contents of tank AZ-101 to it. The combined sludge from the two tanks will then be washed and stored as feed for the future high-level waste vitrification plant. The washed sludge will also be available for laboratory or pilot-scale vitrification tests.

Also planned is a test of in-tank leaching and washing of single-shell tank waste that is scheduled for removal and transfer to a double-shell tank. This waste sludge contains a substantial amount of strontium-90 and large amounts of iron, aluminum, silicon, and phosphorus. It is an ideal waste to demonstrate the caustic dissolution of aluminum and methasis of phosphate to hydroxide. The waste will be sluiced from the single-shell tank C-106 into double-shell tank AY-102, which is in close proximity to tanks AZ-101 and AZ-102.

Figure 1. In-Tank Processing Equipment and Instruments.



LABORATORY STUDIES

Laboratory studies have been conducted with both simulated waste and real tank waste. These studies were designed to:

1. Evaluate the efficiency of washing and caustic leaching the waste to separate alkaline water soluble nonradioactive species from radioactive species

2. Determine the settling characteristics of simulated waste, including the effects of high-heat generation in the sludge and pumping the waste through mixing pumps.

These studies were conducted by the Pacific Northwest Laboratory for Westinghouse Hanford Company.

Leaching and Washing of Actual Waste

Samples of waste taken from several single-shell tanks were subjected to a series of water washes and alkaline leaches with sodium hydroxide solutions.[3] This was done to determine the solubility of aluminum, chromium, phosphate, and other species in 3 M OH^- solution and water.

Tables 1, 2, and 3 data indicate that much of the aluminum and phosphorus, and some of the chromium, can be leached out of tank waste with hot caustic soda solutions. The amount varies with each tank waste because the chemical composition varies from tank to tank. Overall, the majority of the aluminum and phosphorus compounds, and some of the trivalent chromium compounds, can be leached from the sludge with 3 M NaOH solution. Computer simulation of these processing experiments is discussed in a following section.

Settling and Washing of PUREX Waste Simulant

Experiments were conducted to determine the unhindered and hindered settling rates and supernatant clarity of a simulated PUREX waste.[4] The experiments were carried out in a 26-L (7-gal) tank, using 19 L (5 gal) of slurry. The experiments were also designed to measure the effect on settling of natural conduction caused by heat generation in the settled sludge, and to determine if a steam bump could occur. This was done by placing a spiral heating coil on the bottom of the tank. The effect on settling of pumping the slurry through a centrifugal pump was also studied.

Preparations were made to test various flocculants as settling aides, but the tests were not carried out because very clear settled solutions were obtained during the experiments without flocculants. Initial settling rates were found to be around 1 cm/h, and supernatant clarities were less than 10 nephelometric turbidity units.

TABLE I. Comparison of Laboratory and Computer Simulation Results for Tank B-110

Element	Feed slurry (ppm wt.)	Mixed wash (mMol/L)		Mixed leach (mMol/L)		Leached sludge (ppm wt.)		Total removed (%)	
		Lab	ESP	Lab	ESP	Lab	ESP	Lab	ESP
Am	0.012	0	1.2E-5	0	0	NA	0	0	100
Al	316	BD	0.1	BD	1.3	NA	3,710	≤53	47
B	--	--	--	--	--	--	--	--	--
Bi	6,330	BD	0	BD	0	NA	157,000	≤3	0
Ca	237	0.15	0.06	0.15	0.06	NA	5,360	19	8
Cr	234	0.12	0.09	0.67	1.0	NA	0	64	89
Cs	0.0045	NA	8E-5	NA	0	NA	0	97	100
Fe	5,540	0	0	0	0.01	NA	137,000	0	0
La	--	--	--	--	--	--	--	--	--
Mg	40	0	0.02	0	0.003	NA	944	0	5
Mn	--	--	--	--	--	--	--	--	--
Nd	--	--	--	--	--	--	--	--	--
Ni	--	--	--	--	--	--	--	--	--
P	4,740	34	36	5.4	0.09	NA	2,960	≥97	97
Pb	294	BD	0	BD	0.02	NA	7,250	≤27	1
Pu	--	--	--	--	--	--	--	--	--
Si	2,640	7.4	14	15.8	4.0	NA	11,500	74	80
Sn	--	--	--	--	--	--	--	--	--
Sr	61	BD	0.008	BD	0.07	NA	797	0	42
U	--	--	--	--	--	--	--	--	--
Zn	NA	BD	--	0.023	--	--	--	--	--

BD = below detection limit.
ESP = Environmental Simulation Program.
NA = not available.

TABLE II. Comparison of Laboratory and Computer Simulation Results for Tank C-109

Element	Feed slurry (ppm wt.)	Mixed wash (mMol/L)		Mixed leach (mMol/L)		Leached sludge (ppm wt.)		Total removed (%)	
		Lab	ESP	Lab	ESP	Lab	ESP	Lab	ESP
Am	--	--	--	--	--	--	--	--	--
Al	13,400	10.1	3.5	107	74	75,600	66,200	81	61
B	--	--	--	--	--	--	--	--	--
Bi	463	BD	0.001	BD	0.01	14,000	6,870	≤54	2
Ca	1,980	0.16	0.05	0.066	0.064	59,400	29,600	1	1
Cr	85	0.35	0.07	BD	0.3	416	0.002	85	92
Cs	--	--	--	--	--	--	--	--	--
Fe	2,260	0.52	34E-4	0.036	0.009	64,600	34,100	5	0.1
La	190	BD	0	BD	0	5,750	2,880	≤26	0
Mg	--	--	--	--	--	--	--	--	--
Mn	201	BD	6E-4	BD	0.23	6,080	2,210	≤5	24
Nd	241	0.0091	0.42	0.058	4E-5	4,880	0	33	100
Ni	2,920	0.42	0.04	BD	0.94	85,500	40,400	3	8
P	1,840	5.0	6.1	1.6	0.09	32,000	15,300	42	43
Pb	833	BD	0	0.49	0.002	14,800	12,600	≤42	0.3
Pu	0.90	NA	2E-7	NA	2E-9	NA	14	0	0
Si	1,320	0.52	0.44	1.6	1.3	33,600	16,900	16	15
Sn	--	--	--	--	--	--	--	--	--
Sr	34	BD	0.005	BD	0.07	102	60	≤25	80
U	2,300	BD	3E-5	BD	3E-5	54,200	27,100	≤55	0
Zn	--	--	--	--	--	--	--	--	--

BD = below detection limit.
ESP = Environmental Simulation Program.
NA = not available.

TABLE III. Comparison of Laboratory and Computer Simulation Results for Tank C-112

Element	Feed slurry (ppm wt.)	Wash liquids (mMol/L)		Leach liquids (mMol/L)		Leached sludge (ppm wt.)		Total removed (%)	
		Lab	ESP	Lab	ESP	Lab	ESP	Lab	ESP
Am	--	--	--	--	--	--	--	--	--
Al	1,130	4.0	3.4	6.73	1.6	1,940	5,260	85	47
B	208	BD	4.8	BD	0	2,410	0	≤9	100
Bi	188	BD	0.001	BD	0.01	2,180	1,600	≤73	5
Ca	2,620	0.16	0.08	BD	0.07	30,000	23,500	1	1
Cr	67	0.17	0.09	0.16	0.23	99	0	87	93
Cs	--	--	--	--	--	--	--	--	--
Fe	4,570	0.60	0	0.71	0.01	50,000	41,200	5	0
La	--	--	--	--	--	--	--	--	--
Mg	43	BD	0.06	BD	0	500	334	NA	14
Mn	40	BD	0	BD	0.17	457	2	≤21	89
Nd	704	0.19	1.2	0.13	0	6,350	0	22	100
Ni	1,810	0.67	0.05	BD	1.1	19,300	13,900	8	14
P	10,400	46	73	38	0	18,900	12,300	84	87
Pb	192	BD	0.0001	BD	0.003	2,210	1,710	≤24	1
Pu	--	--	--	--	--	--	--	--	--
Si	2,422	0.054	0.0005	2.5	3.2	24,800	16,400	11	23
Sn	147	BD	0.31	BD	0	1,690	0	NA	100
Sr	93	BD	0.004	BD	0.075	1,070	583	≤10	32
U	24,400	BD	0	BD	0	283,000	221,000	≤8	10
Zn	42	BD	0.16	0.063	0	329	0	≥31	100

BD = below detection limit.
ESP = Environmental Simulation Program.
NA = not available.

Heating the sludge layer increased the settling rate, presumably because the temperature of the solution was increased, thereby decreasing the viscosity and density. Washing the sludge with alkaline, inhibited water also resulted in higher settling rates, possibly again because of a decrease in density. The slurry was pumped through a centrifugal pump with the same impeller tip speed as planned mobilization mixing pumps. No effect was observed on the settling characteristics of the slurry.

The conclusions from the experiments with the PUREX simulant is that flocculants will not be needed to gravity separate tank waste insoluble solids and solutions. Neither radiological heating in the sludge layer nor water washing the sludges will adversely affect the separation. The effects of shearing the slurry through mixing pumps is not expected to affect the settling properties.

THERMODYNAMIC SIMULATION

To predict the results of full-scale leaching and washing of various mixtures or blends of tank waste, a method to simulate processing with computers is necessary. A licensed process simulator can calculate activity coefficients and, thus equilibrium concentrations, for mixtures of aqueous and nonaqueous solutions, solids, and vapors. This simulator, produced by OLI Systems and called Environmental Simulation Program (ESP), includes extensive data banks for aqueous, organic, solid, and vapor phase species. It is being used at the Hanford Site to simulate a wide variety of processing. Two examples are discussed in the following sections.

Leaching and Washing of Actual Waste

Waste samples are taken from Hanford Site storage tanks by coring the tanks in a manner similar to geological coring. These samples are analyzed in a variety of ways. As discussed earlier, they are also processed in the laboratory by leaching and washing to obtain data on the solubility and leachability of the various constituents. A large amount of very valuable data comes from these laboratory leaching and washing experiments. However, because the results are for a single tank waste and are experimental, it is not easy to extrapolate the results to waste mixtures.

The ESP is being used to simulate the leaching and washing experiments. In ESP, the extensive data banks are searched for all species that possibly exist in equilibrium with the input species. Semi-theoretical methods are then used to calculate activities and concentrations for all the species. If the results of the laboratory tests can be predicted with reasonable accuracy, then the results from processing mixtures of tank waste can likely be predicted.

Simulations have been completed of the first three tank waste leaching and washing experiments.[5] These simulations were for tanks B-110, C-109, and C-112. Comparisons between the laboratory results and ESP simulations are shown in Tables 1, 2, and 3. The ESP simulations, in general, agree well with the laboratory results.

Sludge Washing Process Test

As discussed earlier, a full-scale process test of sludge washing is in progress in Hanford Site tank AZ-101. In preparation for this test, an ESP simulation was run of the separation and combining of waste that will occur as part of the decanting and refilling of the tank. This simulation was valuable for assessing whether any safety problems could exist, and for determining phase material balances during processing.

COMPUTATIONAL FLUID DYNAMICS SIMULATION

To evaluate the effects on safety of performing various operations in Hanford Site double-shell waste storage tanks, a tool has been needed to simulate the transport phenomena in the tank systems. Of particular concern has been the effects of heat-generating radionuclides, which can cause steam generation and possible "bumping" of the tanks. This need has lead to the development of computational fluid dynamics (CFD) models to simulate waste tank dynamics and heat transfer. The GOTH computer code has been adapted to simulate the dynamics in a PUREX waste storage tank and ventilation system.[1]

Fluid Dynamics in Tank AZ-101

As discussed earlier, the operation of the airlift circulators in tank AZ-101 was discontinued as the initial step in the sludge washing process test. Before shutoff of the circulators, a CFD simulation was made of the tank waste and vapor space dynamics to determine if steam could accumulate in the sludge and then be released suddenly. For this to occur, the transfer of heat from the sludge to the ventilated air space above the tank would have to be slower if the airlift circulators were not operating. This, in turn, would mean that the rate of heat transfer from the sludge layer to the liquid surface is faster when the circulators are operating.

The simulation was designed to simulate the heat, mass, and momentum transfer in the liquid and vapor phases as a function of time. The initial conditions used were those measured in tank AZ-101 with the circulators on. The simulation was then run until near steady-state conditions were reached. GOTH solves for the local fluid velocity, pressure, and temperature in the liquid and vapor space of the tank.

The results indicated that the supernatant solution temperature would rise about 10 °F, but that the bubble point would not be reached anywhere in the tank after the circulators are shut off. The temperatures in the sludge layer varied, but again, the bubble point of the solution in the sludge was never reached. When the actual test was performed and the circulator operation was stopped, the temperature changes corresponded well to what was predicted by the CFD simulations.

Decantation of Tank AZ-101

There was concern that when tank AZ-101 was decanted, the temperature of the remaining sludge and solution might rise and possibly boil. This decanting process was simulated with the GOTH model to determine what temperatures are predicted to be reached. The results were that as long as some liquid covered the sludge there will be very little change in temperature.[6] This is because the force-ventilated vapor space remains well mixed, even when the tank is nearly empty. Thus, the rate of transfer of water vapor, and therefore latent heat, from the liquid surface to the vapor space remains relatively constant during decanting. The CFD model showed that most of the heat removal is through evaporation.

ENGINEERING EVALUATIONS

Although separation of metal hydroxide sludges traditionally has been performed by sedimentation because of the very small particle size, examination of other methods to accomplish the sludge washing process has recently been initiated. If a large radioactive processing facility is required it might make either economic or operational sense to perform this processing on a semi-continuous basis using centrifugal or filtration methods. A study has shown that it may be possible to use a crossflow filter for washing and separating the insoluble solids. This would be accomplished by continuously circulating waste slurry through the filter while adding water to it to maintain a constant suspended solids concentration.

The feasibility and efficiency of both the in-tank and crossflow filter processes needs to be demonstrated.

CONCLUSIONS

Sludge washing and leaching is central to the Hanford Site's approach to disposal of the tank waste. All experimental and analytical work done to date supports the feasibility of washing and leaching the tank waste currently stored at the Hanford Site using an in-tank process. An approach using computer simulation, physical simulant testing, and in-tank testing is being pursued and is providing validation of planning assumptions. By continuing to look at alternative methods it is expected that Hanford Site tank waste will be processed in the most cost-effective manner to allow disposal in accordance with legal commitments.

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