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DOUBLE SHELL SLURRY PROCESS TEST EVALUATION

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INTRODUCTION

Reduction in volume of Hanford radioactive liquid waste is accomplished by evaporation-crystallization. Evaporation of dilute liquid waste produces a slurry of salts and concentrated liquor. The solids in the slurry are allowed to settle in single shell tanks forming a drainable salt cake and a clear supernatant. The supernatant is recycled for additional volume reduction by evaporation or partial neutralization. Eventually, the aluminum concentration in the concentrated liquid approaches a maximum. Further concentration will cause sodium aluminate solids to precipitate and produce a salt cake not acceptable for storage in single shell tanks (Reference 4).

Accepted disposition of this residual liquid for the interim period is storage in double shell tanks. Since recycle of this material for additional processing is not planned, there is no technical basis for avoiding precipitation of aluminum solids in double shell tanks. This allows additional concentration of the liquids to obtain further volume reduction and production of a double shell slurry material.

This report discusses the results of a plant demonstration of the double shell slurry process which was conducted April 25 to 28, 1977. It details the operating experience obtained during the course of the three day run. The characteristics of the product are also discussed.

SUMMARY

Approximately 274,000 gallons of double shell slurry were produced from 365,000 gallons of Hanford Defense Residual Liquor. The volume reduction obtained was 25 per cent. No operating problems were attributed to the double shell slurry process.

Process control was maintained near the proper zone in the early part of the run. However, the feed was underconcentrated in the latter part of the run. This underconcentration was due to heat transfer surface fouling not caused by the double shell slurry process.

Hydroxide concentrations of the product samples ranged from 2.1 to 5.9 Molar. The aluminum to caustic ratio varied from 0.33 to 1.07. The solids were primarily sodium nitrate, carbonate, aluminate, and nitrite. All samples were totally water soluble.

The double shell slurry product increased in volume by 19,000 gallons from April to October 1977. It appears that the growth is caused by organic chelating agents that were in the feed materials. Laboratory studies are continuing to determine the mechanism of this growth.

The double shell process is an acceptable volume reduction technique for interim storage of uncomplexed wastes. Studies should continue to verify the complexant growth interaction and any control technology available. A second demonstration should be run with noncomplexed waste when double shell tanks become available in 200 East area. This will provide verification that the noncomplexed double shell slurry is stable.

DISCUSSION

The bases for conducting a plant demonstration of the double shell slurry process was to demonstrate at least a 10 per cent volume reduction; equipment operability; process control; acceptable pump vibrations; ability to distribute the slurry to the slurry receiver; ability of the slurry to dissipate radiogenic heat; and solubility of the product salts in the laboratory (Reference 1). In addition, the physical and chemical characteristics of the slurry product were of major interest. Each of these points is discussed below.

Volume Reduction

An average volume reduction of 25 per cent was achieved for the test. Approximately 365,000 gallons of Hanford Defense Residual Liquor (HDRL) was reduced to 274,000 gallons of double shell slurry. A plot of the feed tank volume (241-102-SY) versus the slurry tank volume (241-101-SY) during the course of the run is nearly linear (Figure 1). This implies a constant volume reduction throughout the test. This volume reduction was determined to be 25 per cent based on the slope of a least squares straight line approximation.

Condensate Contamination

All the condensate produced during the short three-day run was routed to 103-S due to high levels of radionuclides above discharge limits. This may have been due to the short length of the run or it may be characteristic of the process. There is some evidence that the complexant in the feed material has an adverse effect on the ion exchange cleanup system. Provision for the collection of process condensate and subsequent recycle should be made during any double shell slurry process run.

Equipment Operability

No significant equipment problems were apparent during the run. Some minor instrumentation problems occurred but did not require terminating the process test.

The PB-1 recirculation pump amperage is proportional to the power required to maintain recirculation of the slurry in the evaporator system. An increase in the pump amperage would indicate an increase in the work required to maintain slurry recirculation. As is seen from a plot of the pump amperage for the entire run, the amperage averaged about 132 amperes (Figure 2). This compares to a normal operating range of 125-130 amperes and is not considered to be a significant variation.

No problems were encountered in transporting the slurry to the slurry receiver. Slurry flows ranged from 45 to 75 gallons per minute during the run. The slurry pump discharge pressure remained well within normal operating ranges at the beginning of the test. After about 12 hours of operation, the slurry transfer pressure transducer failed. Efforts to restore operation were unsuccessful. In lieu of the pressure measurements, the slurry flow versus the slurry pump (PB-2) amperage and slurry flow versus slurry pump revolutions per minute were plotted. Since the electric current requirement is analogous to fluid flow rate in hydraulic systems, these plots serve as an indication of the slurry transport operation. No significant variations were observed in the curves resulting from these plots. This indicates that slurry line pluggage problems were not encountered during the run.

The response of the feed and slurry flowmeters appeared to be erratic during the run. An engineering study (Reference 2) determined that the flow measurements were inaccurate and that the flowmeters were damaged in some way. It was later determined that the teflon liners were damaged during installation due to a design-assembly problem. The designs were adjusted, and new flowmeters have since been installed.

Fouling of the reboiler heat transfer surface was observed near the end of the test. It was later determined that the temperature difference between the evaporator body and evaporator room air had exceeded the operating specification (Reference 3). The evaporator room temperature had cooled more than 20°F below the process temperature. Similar temperature differences during past operations were observed to lead to similar fouling of the heat transfer surface. It was concluded that the fouling was not a result of the double shell slurry process test, but was caused by the temperature difference.

Double Shell Slurry Process Control

A boiling temperature-absolute pressure curve was determined for the process test based on analysis of feed samples (Reference 5). This was based on a laboratory boildown and analysis of an actual feed sample (Reference 8). The control diagram is given in Figure 3. The feed analysis is given

in Table 1. In the early stages of the process test, temperature control was maintained fairly close to the desired set point. The temperature was held within $\pm 2^{\circ}\text{F}$ of the control point for the first 25 hours of the test (Figure 4). However, as the test progressed, heat transfer surface fouling prevented addition of enough heat to maintain the required temperature. The temperature then dropped sharply, until at the conclusion of the run the evaporator process temperature was 12°F below the control point. Despite this significant drift in control temperature, an average 25 per cent volume reduction was maintained during the run. It was concluded that the feed was non-homogeneous and became more dilute as the test proceeded. The history of the feed specific gravity (Figure 5) and the results of the product sample analysis both support this hypothesis.

The specific gravity of the slurry averaged 1.72 and went as high as 1.79 during the course of the run (Figure 5). A plugged dip tube resulted in one erroneous reading of 1.9. The decrease in feed concentration toward the end of the run is apparent in the gradual and then somewhat sharp drop in feed specific gravity. The general trend of the slurry specific gravity follows that of the feed specific gravity quite closely.

Eight product samples were taken over a five month period to provide a comprehensive evaluation of the double shell slurry. The sodium hydroxide concentration ranged from 2.1 molar to 5.95 molar (Reference 6). This concentration is considerably less than the 8 molar hydroxide limitation proposed for limiting general corrosion and preventing stress corrosion cracking in the steel double-shell tanks. A plot of the sodium aluminate versus caustic concentration verifies the effect of the temperature control problem (Figure 6). The temperature deviation from the desired control point corresponds to a specific product hydroxide concentration (Figure 7). Hydroxide concentrations ranging from 6.5 molar to 1.1 molar should have been produced during the test. This variation in caustic concentration may account for the variation in the composition of the samples obtained from Tank 241-SY-101.

If the temperature of the boiling slurry could have been maintained near the control point as the feed became more dilute, a higher volume reduction could have been obtained for the latter part of the run. More heat would have been transferred to the slurry thereby increasing the boiloff rate. The volume reduction would have then increased, leading to production of a more concentrated double shell slurry with less variation in the product composition.

Concrete wall temperatures were monitored during the double-shell slurry test to ensure that excess thermal stresses did not develop in the steel liner and concrete structure. Transfer of slurry into Tank 241-SY-101 caused the internal temperature of the tank wetted by solution to increase at least 94°F . The tank concrete wall temperatures (Figure 8) did not exceed the 30°F per foot that was determined as the maximum allowable temperature gradient (Reference 10).

Operability of the temperature - pressure control scheme was demonstrated. With proper control of the process temperature and pressure, double shell slurry of a specified composition and acceptable specific gravity can be produced. The plant test also demonstrated that the double shell slurry process can be controlled within established specifications and standards.

PRODUCT CHARACTERIZATION

One of the main objectives of the process test was to produce an aluminum supersaturated slurry. A decrease in the aluminum concentration as the supersaturation slowly precipitated was expected. This decrease should be evident as an aluminum/caustic ratio decrease as a function of time.

A series of nine samples were taken of the initial double shell slurry. The samples taken varied considerably in texture and liquid content. Most of the samples were a muddy brown color. All appeared to be very thixotropic. The samples were held at the corresponding tank temperature for a period of time before any solids were separated from the supernate. The supernate analyses are summarized in Table II. Analyses of the solid portions are included in Table III (Reference 6).

Liquid Phase Characteristics

The aluminum to caustic ratio (a/c) of the liquid phase of the samples varied from 0.33 to 1.07 in an apparent random fashion. The variation in the process control described earlier could easily account for this variation. However, no aluminum supersaturation was apparent in most of the samples. One sample taken on June 24, 1977, had concentrations which indicated that the feed (Table I) had been concentrated 25 per cent, and that the resultant aluminum supersaturation was relieved. Four of the nine samples were clear solutions at tank temperature. Five had sufficient solids for separation and analysis.

Solid Phase Characteristics

Five samples were analyzed for solid compositions. The solids were primarily sodium nitrate with smaller amounts of sodium carbonate, sodium aluminate, and sodium nitrite. The solids were virtually totally soluble, with less than 5 per cent insoluble in each case. The chemical compositions of the solids are summarized in Table III.

No large amounts of sodium aluminate were precipitated in these samples, as the liquid analysis indicates. The solids in the samples consisted of big crystals surrounded with a large number of fine crystals.

Slurry levels taken at different radial positions in Tank 241-SY-101 showed the slurry to be uniformly distributed. Measurements indicated levels ranging from 106.25 to 109.5 inches with one measurement of 97.75 inches.

The tank contents were photographed on July 21, 1977, and again in April 1978. There is evidence of crust formation over all the tank surface in the most recent test photographs.

Thermal Characteristics

The heat transfer characteristics of the double shell slurry are comparable to solids and solutions stored in other Hanford Tank Farms. The temperature of the slurry declined steadily upon completion of the process test (Figure 9). From the steady state temperature profiles and the analysis of the radionuclide concentrations, an estimate of the thermal conductivity of the double shell slurry product was determined. A value of 0.35-0.4 BTU/hr. ft. °F was estimated with a heat generation rate of 0.05 BTU/hr/gallon.

Volume Increases

From April 29 to October 31, 1977, the slurry level in 101-SY increased 7 percent from 100.05 inches to 106.95 inches (Figure 10). This represents an increase in volume of about 19,000 gallons. An inadvertent liquid addition on April 30 contributed about 0.8 inches (2200 gallons) to this volume expansion. The remaining 6.1 inches represent an average volume increase of about 100 gallons per day. A laboratory program has been initiated to evaluate several mechanisms proposed to explain this phenomena (Reference 8). Preliminary studies indicate that the growth mechanism is related to organic complexant contamination in the process material. Provided the organic contamination can be isolated as the cause, then the continuing growth would not be expected to occur in every double shell slurry run. However, until the growth mechanism is defined and the extent of the growth identified, general process application to complexed materials is not recommended.

RECOMMENDATIONS

It appears that the concentration of Hanford Defense Residual Liquor into the double shell slurry region can be accomplished by proper temperature-pressure control similar to standard evaporation crystallization. No large scale problems are expected with equipment or instrumentation during application of the double shell slurry process. Condensate may have to be stored and later reevaporated.

The growth of the double shell slurry in 241-SY-101 raises questions about the long-term stability of the material. Preliminary laboratory studies indicate that the growth is caused by the organic complexant present in the double shell slurry. Until this is verified, the double shell slurry process should not be applied routinely to complexed materials. Laboratory studies indicate no apparent growth of double shell materials that have no complexant components.

When new double shell tanks become available in 200 East area, a second process run of noncomplexed feed should be completed. The volumetric stability of this noncomplexed double shell slurry can then be demonstrated. If the volume is stable after a three-month period, routine double shell slurry processing of noncomplexed feeds can begin.

Studies which determine the mechanism of the complexed slurry growth will continue. These will determine the critical concentration of the organic complexant. The results of this study may affect final volumes of Hanford Defense Residual Liquor that must be stored for the interim period. Processes to reduce the volume of complexed materials are under study at this time.

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TABLE I
FEED SOLUTION ANALYSIS

	<u>CTL</u>		<u>AL</u>	
Density	1.469		1.532	
H ₂ O		39.8%		49.9%
NaAlO ₂	1.84M	10.3%	1.08M	5.8%
NaOH	2.98M	8.1%	3.05M	8.0%
NaNO ₂	2.66M	12.5%	2.78M	12.5%
NaNO ₃	3.04M	17.6%	2.40M	13.3%
Na ₂ CO ₃	0.798M	5.8%		
				<u>89.5%</u>
Total		94.1%		
A/C	0.62		0.35	
Pu	3.06 x 10 ⁻⁵ g/l			
⁸⁹⁺⁹⁰ Sr	1.65 x 10 ⁴ μCi/l		1.01 x 10 ⁴ μCi/l	
¹³⁷ Cs	6.82 x 10 ⁵ μCi/l		8.08 x 10 ⁵ μCi/l	

TABLE II
SUPERNATE SAMPLE ANALYSIS

	----- Date Sampled -----								
	4/28	6/7	6/10	6/29	7/6	7/15	9/20	9/23	9/26
Density	1.39	1.56	1.66	1.53	1.57	1.58	1.55	1.52	1.50
H ₂ O, %	36.9	34.9	40.2	40.7	43.2	43.1	36.4	43.7	
NaAlO ₂ M	2.46	1.78	1.47	1.98	2.28	1.89	2.02	0.97	1.91
NaOH M	3.92	3.44	3.30	5.95	2.13	2.93	4.44	1.46	4.10
NaNO ₂ M	4.74	2.36	3.63	2.08	3.19	2.30	3.93	2.53	1.82
NaNO ₃ M	3.26	4.28	3.33	3.11	4.21	2.44	3.78	1.98	2.02
Na ₂ CO ₃ M	0.12	0.42	0.15	0.24	0.20	0.12	0.14	0.08	0.15
⁸⁹⁺⁹⁰ Sr μ Ci/l	6.54x 10 ³	81.3	2.53x 10 ³	3.43x 10 ³	2.97x 10 ³	1.78x 10 ³	1.22x 10 ³	2.67x 10 ³	4.84x 10 ³
¹³⁷ Cs Ci/l	1.03	0.76	0.68	0.81	0.97	0.66	0.86	0.91	0.99
A/C Ratio	0.63	0.52	0.45	0.33	1.07	0.65	0.45	0.66	0.47

TABLE 3
SOLIDS ANALYSIS

	----- Date Sampled -----				
	6/10/77	7/6/77	7/15/77	9/20/77	9/23/77
NaAlO ₂ %	5%	5%	0%	0%	0%
NaOH %	1%	14%	11%	7%	9.5%
NaNO ₂ %	4%	9%	26%	0%	44.2%
NaNO ₃ %	64%	40%	54%	0%	43.2%
Na ₂ CO ₃ · H ₂ O %	27%	32%	9%	93%	3%
⁸⁹⁺⁹⁰ Sr	16 µCi/g	12 µCi/g	2 µCi/g	6.3 µCi/g	1.02 µCi/g
¹³⁷ Cs	9200 µCi/g	3600 µCi/g	0	409 µCi/g	141 µCi/g

FIGURE 1

FEED VS SLURRY VOLUME

FIGURE 2

FIGURE 3

MAXIMUM BOILING TEMPERATURES FOR DOUBLE SHELL SLURRY

FIGURE 4

TEMPERATURE DEVIATION FROM CONTROL POINT VS TIME

FIGURE 5

FEED Sp. G. AND SLURRY Sp. G. VS TIME

FIGURE 6

ALUMINUM, HYDROXIDE CONCENTRATIONS OF DOUBLE SHELL SLURRY LIQUID PHASE,
WITH DAYS NOTED

FIGURE 7

TANK CONCRETE WALL TEMPERATURE GRADIENT (INSIDE TO OUTSIDE)

FIGURE 3

DEVIATION FROM CONTROL POINT AND RESULTANT OH⁻ CONCENTRATION

FIGURE 9

FIGURE 10

TANK 101SY LIQUID LEVEL (INCHES) VS TIME