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Comparison of Oxalic Acid Cleaning Results at SRS and Hanford and the Impact on Enhanced Chemical Cleaning Deployment

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ABSTRACT

Waste tanks must be rendered clean enough to satisfy very rigorous tank closure requirements. During bulk waste removal, most of the radioactive sludge and salt waste is removed from the waste tank. The waste residue on the tank walls and interior components and the waste heel at the bottom of the tank must be removed prior to tank closure to render the tank clean enough to meet the regulatory requirement for tank closure.

Oxalic acid has been used within the DOE complex to clean residual materials from carbon steel tanks with varying degrees of success. Oxalic acid cleaning will be implemented at both the Savannah River Site and Hanford to clean tanks and serves as the core cleaning technology in the process known as Enhanced Chemical Cleaning. Enhanced Chemical Cleaning also employs a process that decomposes the spent oxalic acid solutions.

The oxalic acid cleaning campaigns that have been performed at the two sites dating back to the 1980's are compared. The differences in the waste characteristics, oxalic acid concentrations, flushing, available infrastructure and execution of the campaigns are discussed along with the impact on the effectiveness of the process. The lessons learned from these campaigns that are being incorporated into the project for Enhanced Chemical Cleaning are also explored.

INTRODUCTION

SRS stores waste in 49 High Level Waste (HLW) tanks. The old style waste tanks, those without full secondary containment, must be closed by 2022 per the Federal Facilities Agreement (FFA) and the waste dispositioned by 2028. The strategy for preparing tanks for closure at SRS currently consists of two mechanical cleaning methods and one oxalic acid chemical cleaning method.

Oxalic acid cleaning of tanks was successfully demonstrated through the cleaning of Tank 16 in the early 1980's. Tanks 5 and 6 were cleaned using large batches of concentrated oxalic acid similar to the Tank 16 cleaning campaign. This method is also planned for Tank 7. This process is referred to as bulk oxalic acid cleaning. Although the application of this process has been

determined to be acceptable for Tanks 5, 6 and 7 as documented in Liquid Waste System Plan revision 15 [1], it results in hundreds of thousands of gallons of spent acid that must be handled. The spent acid forms oxalates that are anticipated to create evaporator foaming and scaling problems, increase the volume of water required to wash the sludge, and increase the volume of Saltstone grout that is produced. For these reasons, the bulk process cannot be accommodated in the liquid waste system flowsheet over the long term and is therefore not planned for any additional tanks after Tank 7.

Enhanced Chemical Cleaning is based on adapting proven techniques from the commercial reactor and steam-generating industries to the cleaning of the SRS and Hanford carbon steel waste tanks. A dilute acid stream dissolves residual waste and etches steel surfaces to clean tank internals. The oxalates in the acid stream are then destroyed using a proprietary process developed by AREVA. The dissolved metals and associated radionuclides precipitate out and are transferred to a sludge tank. Concentrated oxalic acid or oxalic acid crystals regenerate the acid cleaning stream for reuse. Since this process can be utilized with minimal impacts on tank space and downstream processes, the tank cleaning can continue until the residual waste has been removed.

Although bulk oxalic acid cleaning will not be employed long term at SRS, the data and information collected from the dissolution of sludge heels with bulk oxalic acid will be used to develop the dissolution process of Enhanced Chemical Cleaning. Waste characteristics, available infrastructure, deployment methods and acid concentrations of past bulk oxalic acid cleaning campaigns are evaluated for application to Enhanced Chemical Cleaning for both SRS and Hanford.

DISCUSSION

Both SRS and Hanford have used oxalic acid to clean waste tanks. SRS has the most experience with oxalic acid with four campaigns in Tanks 16, 24, 5 and 6. Hanford used oxalic acid in Tank C-106.

Tank 16

Tank 16 was cleaned with oxalic acid in the 1980's. About 1,400 gallons (5300 liters) of sludge remained in Tank 16 after bulk waste removal was complete. The cleaning campaign consisted of two water washes, three acid strikes and a final water rinse. The water washes consisted of 60,000 to 70,000 gallons (227,000 to 265,000 liters) of water added with 5 rotary spray jets at 90°C. The oxalic acid strikes were completed as shown in the attached table. The water was sprayed in at 90°C and 3 slurry pumps were used for mixing. The pumps were also re-located near the areas of the largest deposits. [2]

Table I. Tank 16 Oxalic Acid Strikes

Oxalic Acid	Strike 1	Strike 2	Strike 3
Gallons seal water (liters)	22,937 (86,826)	27,220 (103,039)	20,307 (76,870)
Gallons water added (liters)	41,596 (157,458) [sprayed at 90°C]	46,477 (175,935) [sprayed at 90°C]	5,797 (21,944) [sprayed at 90°C]
Gallons oxalic acid added (liters)	12,611 [4 wt%] (47,738)	9,865 [4 wt%] (37,343)	50,545 [4 wt%] (191,334)
Final% acid (does not include seal water)	4 wt% added, diluted with water to 1 wt%	4 wt% added, diluted with water to 1 wt%	4 wt%
# of pumps	3	3	3
hours of operation	40	45	48
temperature	66	59	62

Tank 24

Zeolite removal by oxalic acid dissolution was attempted in Tank 24 in 1985. The zeolite had undergone a chemical reaction in the concentrated caustic solution that would have required more oxalic acid to dissolve the material than originally planned. Two oxalic acid strikes were completed with an in-tank neutralization and water wash between the strikes. Two slurry pumps provided the mixing as shown in Table II. [3]

Table II. Tank 24 Oxalic Acid Strikes

Oxalic Acid	Strike 1	Strike 2
Gallons water added (liters)	12,000 [added at 80°C] (45,425)	0
Gallons oxalic acid added (liters)	22,500 [8 wt% added at 80°C] (85,172)	23,500 [8 wt%] (88,957)
Final % acid (does not include seal water)	5 wt %	8 wt%
# of pumps	2	2
hours of operation	72	72

Tank 5

An oxalic acid cleaning campaign was conducted in Tank 5 during 2008. The campaign consisted of two oxalic acid strikes, an oxalic acid spray wash and a water wash. The oxalic acid strikes were completed as shown in the attached table. Mixing was only used in the first strike. The style of mixer pump used in this application did not add water from seal bearings. The oxalic acid was added at 60°C. Temperature in the tank was not recorded. [4]

Table III. Tank 5 Oxalic Acid Strikes

Oxalic Acid	Strike 1	Strike 2	Spray Wash
Gallons water added (liters)	43,177 (163,443)	0	10,000 (37,854)
Gallons oxalic acid added (liters)	67,468 [8 wt%] (255,394)	13,760 [8 wt%] (52,087)	9,645 [8 wt%] (36,510)
Final % acid (does not include seal water)	8 wt% added, diluted with water to 4 wt%	8 wt%	4 wt%
# of pumps	2	0	0
hours of operation	90	0	0

Tank 6

An oxalic acid cleaning campaign was also conducted for Tank 6 in tandem with Tank 5 in 2008. The Tank 6 campaign consisted of two oxalic acid strikes, an oxalic acid spray wash and a water wash. The oxalic acid strikes were completed as shown in the attached table. Mixing was only used in the first strike. The style of mixer pump used in this application did not add water from seal bearings. The oxalic acid was added at 60°C. Temperature in the tank was not recorded. [5]

Table IV. Tank 6 Oxalic Acid Strikes

Oxalic Acid	Strike 1	Strike 2	Spray Wash
Gallons water added (liters)	0	0	10,000 (37,854)
Gallons oxalic acid added (liters)	110,830 [8 wt%] (419,537)	28,881 [8 wt%] (109,326)	9,650[8 wt%] (36,529)
Final% acid (does not include seal water)	8 wt%	8 wt%	4 wt%
# of pumps	2	0	0
hours of operation	100	0	0

Tank C-106 (Hanford)

C-106 is a 530,000 gallon (2,006,000 liter) single shell tank that contained a heel of 18,000 gallons (68,000 liters) of sludge solids. An oxalic acid and modified sluicing campaign was conducted for Tank C-106 in 2003. The campaign consisted of six oxalic acid strikes with a modified sluicing operation after the third, fourth and fifth oxalic acid strikes. The oxalic acid strikes were completed as shown in the attached table. The first through fifth oxalic acid strikes were re-circulated with a mixer-eductor. The remaining sludge heel after this campaign was 4,117 gallons (15,600 liters). [6]

Table V. Tank C-106 Oxalic Acid Strikes

Oxalic Acid	Strike 1	Strike 2	Strike 3	Strike 4	Strike 5	Strike 6
Gallons water added (liters)	579 (2,192)	1,343 (5,084)	1,021 (3,865)	1,960 (7,419)	908 (3,437)	315 (1,192)
Gallons oxalic acid added (liters)	15,803 (59,821)	25,957 (98,258)	31,686 (119,945)	31,772 (120,270)	15,632 (59,174)	21,169 (80,133)
Final % acid (does not include sluice water)	8 wt%	8 wt%	8 wt%	8 wt%	8 wt%	8 wt%
Gallons sluice water added (liters)			56160 (212,588)	46,472 (175,916)	59,228 (224,202)	83,501 (316,086)

Comparison and Contrast

Tank 16 was the most successful bulk oxalic acid cleaning campaign. Some of the attributes contributing to this success included removing soluble salts, using unsaturated oxalic acid solution, vigorous mixing, and large amounts of water for washing. The soluble salts were removed by copious pre-washing. This allowed the oxalic acid to have the maximum capacity to dissolve the radioactive and non-radioactive metal oxides and hydroxides. During dissolution, the oxalic acid concentration was kept below solubility limits, even as the pH increased through dissolution. The moles of oxalic acid used per gallon of sludge were greater than any subsequent oxalic acid campaign as shown in Table VI.

Table VI. Ratio of oxalic acid quantity to sludge volume for each tank

Tank	Tank 16	Tank 5	Tank 6	Tank 24	Tank C-106
Moles oxalic acid/gallon of sludge	341	88	84	14	27
Moles oxalic acid/liter of sludge	1,291	333	318	53	102

Mixing was vigorous throughout all of the campaign. The final water wash used a feed and bleed technique with mixing to remove as much of the suspended solids as possible. Tank 16 was left with less than an estimated 50 gallons (190 liters) of sludge.

Tank 24 was the only high aluminum heel removal attempted with oxalic acid at SRS. Data indicated that the original form of the zeolite assumed was incorrect. Three times more oxalic acid would have been required to remove the heel than originally planned. The first wash showed complete reaction of the oxalic acid. The second wash did not completely consume the oxalic acid, probably due to more densely packed solids remaining in the tank. This oxalic acid campaign was only marginally successful. The key lesson from this campaign was the need to understand the chemical form of the heel solids in defining the approach to chemical cleaning.

Tank C-106 at Hanford also contained a high aluminum heel. The oxalic acid in the last strike was not entirely consumed as indicated by low pH readings. More vigorous mixing of the oxalic acid and sludge solids might have enabled more dissolution of the sludge solids.

Tanks 5 and 6 were recently cleaned with oxalic acid. These tanks contained heels with high concentrations of iron, similar to Tank 16. The planning for this campaign included a process model, simulant run, and real waste test. The actual results from both of these operations are compared to the process model, simulant run and real waste test. Only one oxalic acid strike was performed in the simulant and real waste tests.

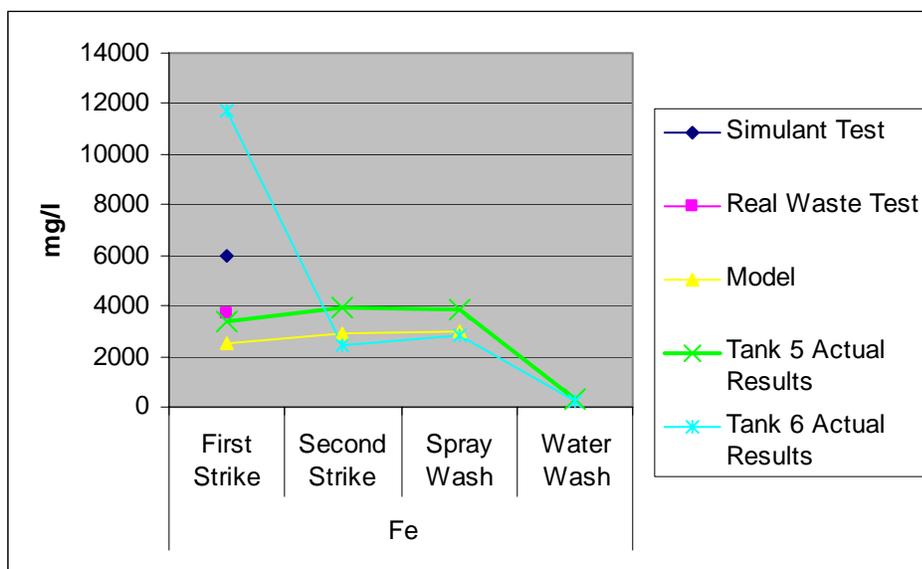


Figure 1. Comparison of Tank 5 and 6 iron concentrations to test results

Figure 1 shows the iron concentrations by sample analysis in each strike. The concentration is reported versus quantity removed, which has been discussed in other reports. Evaluation of concentration provides more insight into the dissolution behavior during ECC, which will use many strikes of dilute oxalic acid.

The key difference between Tanks 5 and 6 on the first strike was the strength of oxalic acid. The oxalic acid concentration for Tank 6 was 8 wt% versus 4 wt% for Tank 5, due to water dilution to operate the mixer pumps. The higher oxalic acid concentration resulted in a higher iron

concentration in the strike. The simulant tests, real waste tests and models were all completed using 8 wt%.

Mixing was only used in Tanks 5 and 6 on the first strike. There is a clear difference between the Tank 6 iron concentration in the first strike with mixing and the expected results from the real waste test, simulant test and modeling. The Tank 5 iron concentration in the first strike with 4 wt% was similar to that predicted from the real waste test and modeling for 8 wt%, showing a trade-off between oxalic acid concentration and mixing. The subsequent strikes for both Tanks 5 and 6 matched the model prediction. The iron concentration continued to increase from the second strike to the spray wash during each of the oxalic acid strikes showing that iron dissolution was not complete. The water wash did not contain any oxalic acid and the low iron concentrations reflect that fact.

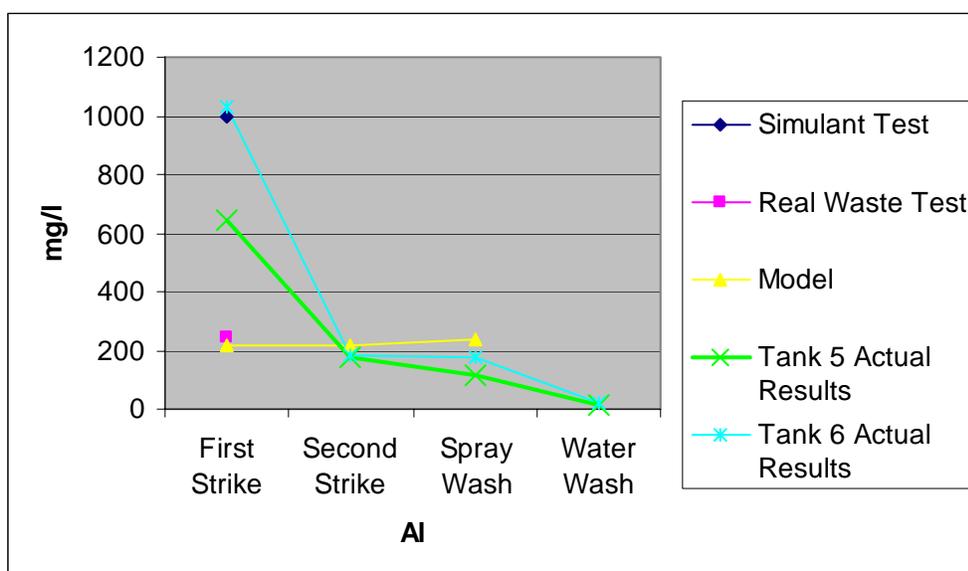


Figure 2. Comparison of Tank 5 and 6 aluminum concentrations to test results

The Tank 6 aluminum concentration matched the simulant test concentration in the first strike. The Tank 5 aluminum concentration at 4 wt% oxalic acid was between the simulant test and the real waste test concentrations.

The impact of mixing can also be seen with the aluminum concentrations in the first strike. There is a clear difference between the Tank 6 aluminum concentration in the first strike with mixing and the expected results from the real waste test and modeling. The Tank 5 aluminum concentration in the first strike with 4 wt% was higher than that predicted from the real waste test and modeling for 8 wt%, again demonstrating the advantage of mixing. Some of the benefits of mixing were probably achieved in the simulant test, since the results matched the Tank 6 results very well. The subsequent strikes for both Tanks 5 and 6 matched the model prediction. The aluminum concentration had not decreased significantly from the second strike to the spray wash during each of the oxalic acid strikes showing that dissolution was not complete. The water wash did not contain any oxalic acid and the low aluminum concentrations reflect that fact.

Therefore the big difference between the first and second strikes in aluminum concentration for both tanks was due to mixing.

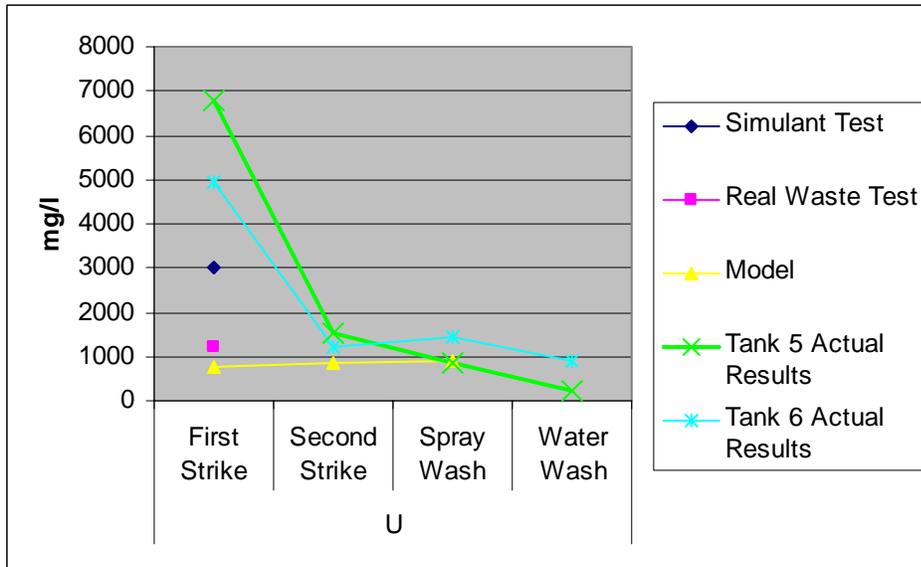


Figure 3. Comparison of Tank 5 and 6 uranium concentrations to test results

The uranium concentrations for the first strike greatly exceeded the prediction by any of the tests and models run. The significant difference between the first strike and the subsequent strikes was probably again due to mixing, as reflected in both the iron and aluminum dissolution analyses. The lower Tank 6 uranium concentration versus the Tank 5 uranium concentration on the first strike cannot be easily explained, unless the amount of uranium in Tank 6 was significantly less than Tank 5. No samples were taken of Tank 6 solids to confirm this hypothesis.

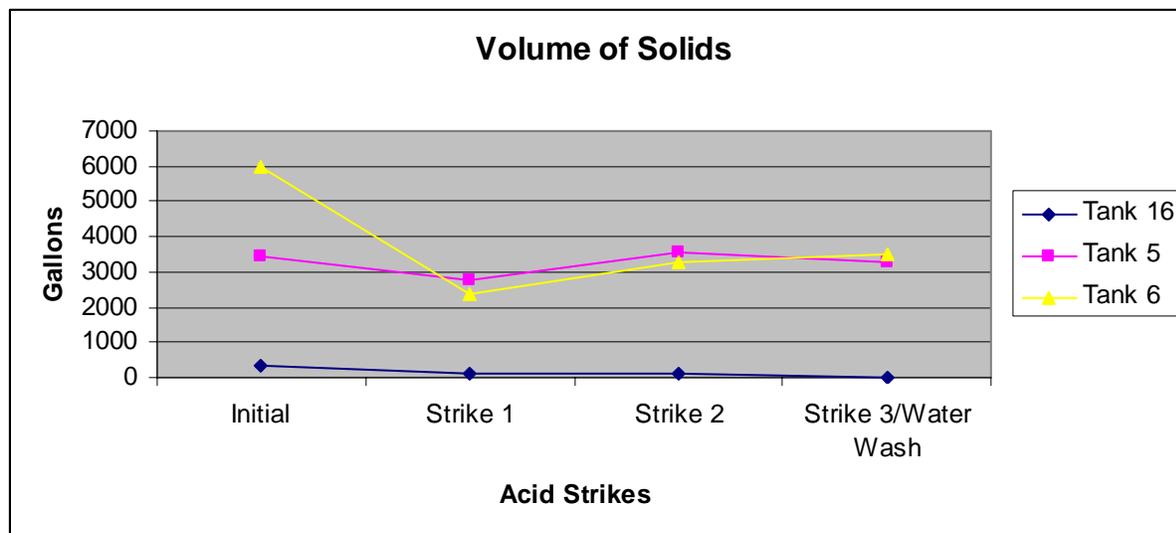


Figure 4. Solids volume after each strike

For the three oxalic acid campaigns on the iron rich sludge heels, mixing was a key feature of the first oxalic acid strike. In all of these campaigns, a decrease in solids remaining in the tank was observed after the first strike. In the subsequent strikes for Tanks 5 and 6, a high strength oxalic acid strike combined with a lack of mixing contributed to the formation of oxalates that were not removed from the tank in the transfers. Therefore the volume of solids increased in the subsequent strikes.

The volume of solids in Tank 24 decreased from 10,000 gallons (37,800 liters) to about 6,400 gallons (24,200 liters) of zeolite. Although the moles of oxalic acid per gallon of sludge heel were the lowest of the campaigns discussed, mixing during the transfer probably enabled some undissolved solids to be removed from the tank. The volume of solids in Tank C-106 decreased from 18,000 gallons (68,000 liters) to 4117 gallons (15,600 liters).

Application to Enhanced Chemical Cleaning

The data from these oxalic acid campaigns can be applied to Enhanced Chemical Cleaning. Dilute oxalic acid will be used to dissolve the sludge metals. While the concentration of metals in each batch is expected to be less than the campaigns explained here, the reuse of water will allow multiple batches of oxalic acid to be used in the tank, with some ability to optimize the amount and strength of the oxalic acid. Mixing will be used to enhance the dissolution of solids and promote the transfer of undissolved particles from the tank.

CONCLUSION

Successful completion of the chemical cleaning step is expected to render the tank clean and thus strongly support meeting the tank closure requirements, both the potential dose or groundwater concentration limits and the removal to the Maximum Extent Practical requirement. Lessons learned from past oxalic acid cleaning campaigns are applied to development of the Enhanced

Chemical Cleaning process. An effective cleaning solution must have free oxalic acid ions to react and the capacity to dissolve the newly created oxalates, favoring the dilute chemistry of Enhanced Chemical Cleaning. While there are physical limitations, keeping the temperature high and the pH low improved dissolution while also minimizing re-precipitation. Mixing is critical to facilitate mass transfer and promote dissolution and suspend undissolved solids so that they can be transferred out. Repeated strikes of oxalic acid aid in removing the more soluble metal ions and allowing dissolution of the less soluble radionuclides.

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Appendix I. Data from Tanks 5, 6, 16 and 24 Oxalic Acid Comparisons

	Tank 16	Tank 5	Tank 6	Tank 24
Heel Volume	700	3453	5984	11000
				Calculated for Tank 16 assuming sludge contains 30% liquid. Tank 24 contained zeolite.
Water Wash #1				
Seal water	31093			
Sprayed	63015			
Total gallons	94108			
# of mixing pumps	3			
hours of mixing	83, 70, 42			
temperature, C	49			
Sludge Heel Volume, gal	420			
Water Wash #2				
Seal water	23853			
Sprayed	70125			
Total gallons	93978	45000	45000	
# of pumps	3			
hours of operation	57, 51, 58			
temperature	51			
Sludge Heel Volume, gal	360	3453	5984	11,000
Oxalic Acid Strike #1				
Seal water	22937			
Water added	41596 (sprayed at 90 C)	43177		12000 (added at 80C)
oxalic acid added	12611 (4 wt%)	67468 (8wt%)	110830 (8 wt%)	22500 (8 wt%) added at 80 C
Final % acid (does not include seal water)	4 wt% added, diluted with water to 1 wt%	8 wt% added, diluted with water to 4 wt%	8 wt%	5 wt%
# of pumps	3	2	2	2
hours of operation	47, 47, 38	90	97, 101	72
temperature	66			
Component Concentrations				Total volume sampled
Na, mg/l		3636	3000	8142
k	1860	912	nd	3596
C2O4, mg/l	4488	22800	44363	25608
Fe, mg/l	952	3385	11745	224
Al, mg/l	108	644	1031	22410
U, mg/l		6784	4943	
Cs, mCi/l	0.6	77	25	3.04
Sr, mCi/l	60	1409	1050	0.04
Pu-238, mCi/l	0.21	0.006	0.05	
Pu-239, mCi/l		0.03	0.06	
Sludge Heel Volume, gal	116	2750	2393	13000
Oxalic Acid Strike #2				
Seal water	27220			
Water added	46477 (sprayed at 90 C)			
oxalic acid added	9865 (4 wt%)	13760 (8 wt%)	28881 (8 wt%)	23500 (8wt%)
Final % acid (does not include seal water)	4 wt% added, diluted with water to 1 wt%	8 wt%	8 wt%	8 wt% Does not include seal water
# of pumps	3	0	0	2
hours of operation	46, 46, 44	0	0	72
temperature	59			
Component Concentrations				
Na, mg/l		1163	918	13915
NO3, mg/l	372	nd	nd	2790
C2O4, mg/l	4224	49100	51000	77752
Fe, mg/l	616	3935	2450	448
Al, mg/l	89.1	179	185	3645
U, mg/l		1550	1231	
Cs, mCi/l	0.3	29	7	7.6
Sr, mCi/l	43	441	255	0.1
Pu-238, mCi/l	0.15	0.009	0.005	
Pu-239, mCi/l	nd	0.03	0.008	
Sludge Heel Volume, gal	93	3570	3250	
Oxalic Acid Strike #3				
Seal water	20307			
Water added	5797 (90 C)	10000	10000	
oxalic acid added	50545 (4 wt%)	9645 (8 wt%)	9650 (8 wt%)	
Final % acid (does not include seal water)	4 wt%	4 wt%	4 wt%	
# of pumps	3	3	0	
hours of operation	48, 48, 48	0	0	
temperature	62			
Component Concentrations (total volume sampled)				
Na, mg/l		404	804	
NO3, mg/l	186	nd	nd	
C2O4, mg/l	27280	24000	24600	
Fe, mg/l	4256	3848	2864	
Al, mg/l	159.3	118	176	
U, mg/l		851	1426	
Cs, mCi/l	0.1	11	4.5	
Sr, mCi/l	64	254	150	
Pu-238, mCi/l	0.24	0.003	0.005	
Pu-239, mCi/l		0.014	0.007	
Sludge Heel Volume, gal	122	not measured	not measured	
Final Water Wash				
gallons	112446	99230	114935	
# of mixing pumps	3	1	2	Tank 6 SMP's shut down halfway through transfer
hours of mixing	106, 128, 134	72	?	
temperature, C	65			
Component Concentrations (total volume sampled)				
Na, mg/l	not measured	404	644	
NO3, mg/l	not measured	nd	nd	
C2O4, mg/l	not measured	1000	1884	
Fe, mg/l	not measured	289	210	
Al, mg/l	not measured	11	21	
U, mg/l	not measured	218	887	
Cs, mCi/l	not measured	1.7	2	
Sr, mCi/l	not measured	27	9.3	
Pu-238, mCi/l	not measured	nd	0.001	
Pu-239, mCi/l	not measured	0.0008	0.002	
Sludge Heel Volume, gal	17	3282	3488	