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ALTERNATIVE WASHING STRATEGY DURING IN-TANK PRECIPITATION PROCESSING (U)

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Summary

If late washing of precipitate is available, it is possible to modify the normal washing phase of the ITP process so that tank corrosion is prevented by inhibiting with sodium hydroxide rather than sodium nitrite. Hydroxide inhibition has numerous advantages to a hydroxide/nitrite flowsheet.[1] However, the rate of hydroxide depletion due to radiolysis and CO_2 absorption were uncertainties. Based on recent experiments and calculations:

- hydroxide consumption by radiolysis will be 0.01 molar per month during Tank 49 storage,
- hydroxide depletion due to CO_2 absorption will vary from 0.0006 to 0.025 molar per month for waste volumes between 50,000 and 1 million gallons and air flowrates between 100 and 200 cfm. A nominal rate of 0.006 molar/month (or less) is expected in Tank 49 after the first two ITP cycles have been completed.

A material balance for the ITP process based on hydroxide inhibition has been calculated and the potential savings have been estimated.

Introduction

Hydroxide ion in the washed precipitate slurry is consumed by two mechanisms during storage: (1) radiolysis, and (2) adsorption of atmospheric carbon dioxide. The precipitate undergoes radiolytic decomposition during storage, producing acidic products. The initial decomposition products and their relative production rates in alkaline solution are given by the following equation (per mole of KTPB that decomposes)[2]:

	$KBPh_4$	+ H_2O	+ OH^-	+ O_2	--- $Ph\text{-}H$	+ $Ph\text{-}Ph$ +
Moles:	1.0	0.60	1.47	0.67	1.73	0.40
	potassium tetraphenylborate				benzene	biphenyl

+ $Ph\text{-}O^-$	+ $Ph\text{-}B(O)_2^{2-}$	$+B(OH)_2O^-$	+ K^+
0.94	0.53	0.47	1.0
phenol	phenylboric acid	boric acid	

Radiolysis will consume about 7.5% of the precipitate per year by this reaction, corresponding to a hydroxide consumption rate of 0.003 molar/month. The initial decomposition products can also be broken down in reactions which consume more hydroxide ion and eventually produce carbonate.

All of the SRS waste tanks are equipped with active ventilation systems to prevent the buildup of flammable vapor mixtures. Hydroxide is depleted during the storage of alkaline waste solutions due to the absorption and reaction of carbon dioxide present in the air which passes through the waste tank. The rate of absorption of carbon dioxide has been previously measured for a variety of waste tanks including Tank 48 which contained the washed precipitate slurry from the 1983 In-Tank Demonstration.[3]

The most recent results from corrosion testing indicate that a minimum free hydroxide concentration of 1.5 molar is required to prevent corrosion in the ITP process up to 60°C.[4] Further corrosion testing could change this. The material balance given below assumes that a 20% excess of NaOH will be used as a safety margin above the required amount.

Rate of OH^- Depletion by Radiolysis

The rate of hydroxide depletion was measured on simulated slurries irradiated in a Co-60 source. The compositions of the simulated slurries (Table I) were similar to those expected in the ITP process with late washing. Specifically, the composition of the liquid phase was adjusted to reflect the high hydroxide concentration expected if NaOH is used as the only corrosion inhibitor. The slurries were irradiated in closed containers to doses of up to 320 megarads, simulating over two years of tank farm storage (Note: slurry containing 36 Ci of Cs-137 per gallon receives a dose of 145 megarads per year).

The changes in the free hydroxide concentration are shown in Figure 1 and the calculated rates are listed in Table II. In both slurries, there was a slight increase in free hydroxide during the first 50 Mrads of radiation dose. This was followed by a decline

TABLE I. Initial Composition of Simulated KTPB Slurries for Radiolysis Experiments

Component	Concentration in Liquid (molar) Low OH	High OH
Na^+	1.3	2.1
OH^-	1.1	1.9
NO_3^-	0.09	0.08
NO_2^-	0.04	0.03
SO_4^{2-}	0.01	0.01
CO_3^{2-}	0.009	0.008
KTPB	10 wt %	10 wt %

TABLE II. Rates of Hydroxide Depletion and Carbonate Accumulation

Initial Free OH- (M)	Loss of Free OH- (M/month)	Accumulation of Carbonate (M/month)
1.1	0.0115	0.0051
1.9	0.0128	0.0055

in the free hydroxide which was linear with dose. The rates of hydroxide depletion (after the initial increase) were similar for the two slurries. The average rate determined from these two experiments is 1.0×10^{-3} molar/Mrad or 0.012±.001 molar/month (for a slurry with 36 Ci of Cs-137/gal). This is similar to the previously reported rate of 0.01 molar/month at much lower hydroxide, nitrate, and nitrite concentrations.[2] There is a trend in the data from the three experiments which suggests that there may be a slight dependence in the rate of depletion on the initial free hydroxide concentration. This trend is not expected and is so small that it is likely due to experimental errors.

The rates of carbonate accumulation (Figure 2 and Table II) were very similar for the two slurries, although again the rate at the higher hydroxide concentration is slightly larger. The rate of carbonate accumulation for both slurries is slightly less than half of the rate of free hydroxide depletion as expected. Each mole of carbon dioxide formed will consume two moles of free hydroxide to form the carbonate ion. Since other hydroxide-consuming reactions are taking place at the same time, the rate of hydroxide depletion should be more than twice the carbonate accumulation rate.

Rate of OH^- Depletion by Carbon Dioxide Absorption

The hydroxide depletion rate in Tank 49 due to the absorption of atmospheric carbon dioxide has been calculated as a function of waste volume and air flowrate.[5] The following bases were used to calculate the hydroxide depletion rates as a function of waste volume and air flowrate: (1) the partial pressure of carbon dioxide in the air entering the tank is a constant 360 ppm (this is the

FIGURE 1. Loss of Free Hydroxide With Increasing Radiation Dose

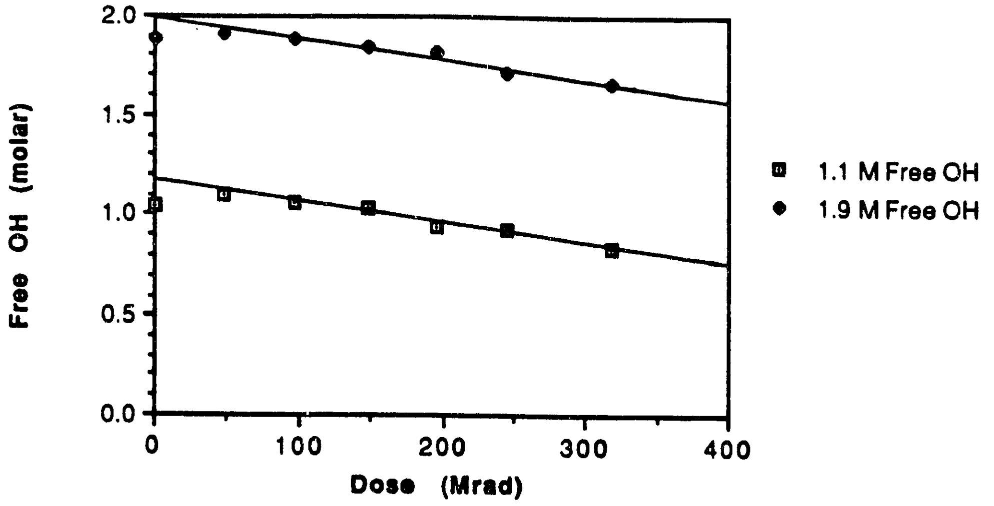
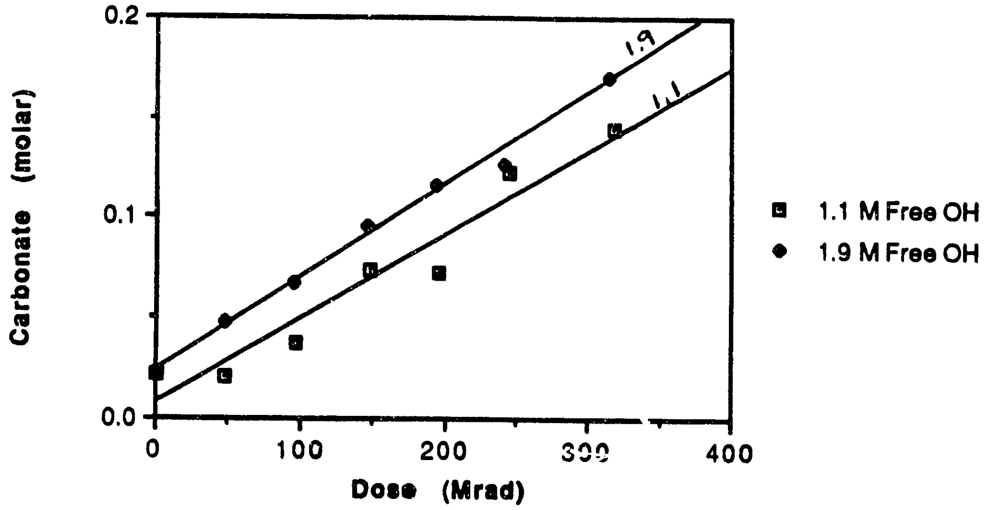


FIGURE 2. Accumulation of Carbonate with Increasing Radiation Dose



average of several measurements made in the SRS Tank Farm over a one year period), (2) the air temperature is a constant 50°C (anticipated high temperature for waste in Tank 49), (3) the fraction of carbon dioxide absorbed by the precipitate slurry is independent of the slurrry volume and the ventilation flowrate and has a value of 0.717, (4) one mole of carbon dioxide consumes two moles of hydroxide, (5) the volume of precipitate slurry ranges from 50,000 to 1,000,000 gallons, and (6) perfect mixing of air and nitrogen in the ventilation system with an air flowrate of between 100 and 200 cfm (total ventilation flowrate is higher due to the nitrogen purge gas). The calculated depletion rates are given in Table III. A graph of the depletion rate versus the volume of waste for three air flowrates (100, 150, and 200 cfm) is shown in Figure 3. The rate of absorption of carbon dioxide is constant for a given flowrate. However, because the volume of waste will be changing on a regular basis, the depletion rate on a unit volume basis will change. The rate increases if the volume of waste decreases. The depletion rate also increases with an increase in the purge air flowrate. This is a result of an increase in the carbon dioxide entering the tank and being absorbed into solution and reacting with hydroxide to form carbonate.

The expected ventilation rate in ITP is 500 cfm total flow, with 125 cfm of air inleakage and 375 cfm of nitrogen purge. After two cycles of ITP processing there should be at least 250,000 gallons of precipitate slurry in Tank 49. Under these conditions, the hydroxide consumption rate will be about 0.00013 molar/day or 0.004 molar per month.

Figure 3. Effect of Air Flowrate and Waste Volume on the Rate of Hydroxide Depletion Due to Carbon Dioxide Absorption

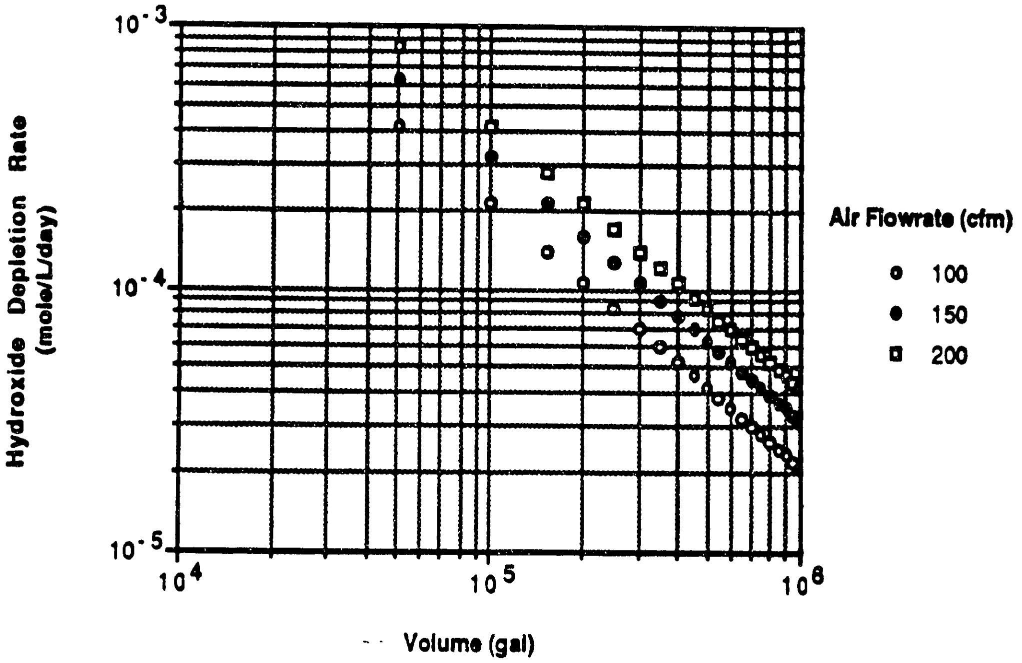


TABLE III. Tank 49 Hydroxide Depletion Rates

Air Temperature (°K)	Gas Density (L/mole)	[CO2] (atm)	Absorption Fraction
323	26.5	0.00036	0.717

Air Flowrate (cfm)	100	150	200
mole CO2 absorbed/day	3.97E+01	5.96E+01	7.94E+01
mole OH depleted/day	7.94E+01	1.19E+02	1.59E+02

Hydroxide Depletion Rate (mole/L/day)

Tank Volume (gal)	100 cfm	150 cfm	200 cfm
50000	4.20E-04	6.30E-04	8.39E-04
100000	2.10E-04	3.15E-04	4.20E-04
150000	1.40E-04	2.10E-04	2.80E-04
200000	1.05E-04	1.57E-04	2.10E-04
250000	8.39E-05	1.26E-04	1.68E-04
300000	7.00E-05	1.05E-04	1.40E-04
350000	6.00E-05	8.99E-05	1.20E-04
400000	5.25E-05	7.87E-05	1.05E-04
450000	4.66E-05	7.00E-05	9.33E-05
500000	4.20E-05	6.30E-05	8.39E-05
550000	3.82E-05	5.72E-05	7.63E-05
600000	3.50E-05	5.25E-05	7.00E-05
650000	3.23E-05	4.84E-05	6.46E-05
700000	3.00E-05	4.50E-05	6.00E-05
750000	2.80E-05	4.20E-05	5.60E-05
800000	2.62E-05	3.94E-05	5.25E-05
850000	2.47E-05	3.70E-05	4.94E-05
900000	2.33E-05	3.50E-05	4.66E-05
950000	2.21E-05	3.31E-05	4.42E-05
1000000	2.10E-05	3.15E-05	4.20E-05

Material Balance for the Hydroxide Flowsheet

In previous material balances for the ITP process, a combination of sodium hydroxide and sodium nitrite has always been used to meet corrosion inhibitor requirements for Tank 48 and Tank 49.[6] However, if the Late Wash Facility is constructed, a new approach to corrosion prevention in which only sodium hydroxide is used becomes feasible. Recent corrosion test results indicate that 1.5 molar free hydroxide is sufficient to prevent corrosion at low nitrate and nitrite levels for temperatures up to 70°C.[4] Thus, the new approach is based on maintaining a minimum of 1.8 molar hydroxide in Tanks 49 and 49 throughout the process cycle. The 20% excess over the requirement is a safety margin to avoid violations of Operational Safety Requirements. Washing in Tank 48 is reduced by almost half so the precipitate is stored in a "partially washed" condition. Washing is completed by the Late Washing process. Compared to the material balance using nitrite as the inhibitor (Late Wash flowsheet at 60°C),[6c] the hydroxide flowsheet has the following advantages:

- Volume of liquid to Saltstone is reduced by 1 million gallons per year (-12%),
- NaTPB requirements are reduced by 33,000 gal/yr (-10%),
- 50% NaOH requirements are increased by 17,000 gal/yr (+12%) (this is the total for Tk 48, Tk 49, Tk 22, and Late Washing)
- Sodium nitrite requirements are reduced by 48,000 gal/yr (-100%),
- ITP cycle time is reduced by 14 days (-11%).

This material balance is based on the same assumptions that were used in the nitrite flowsheet.[6c] Late Washing is assumed to reprecipitate Cs and K before washing. A 15-fold reduction in soluble salts is required in Late Washing, which is slightly less than in the nitrite flowsheet (16-fold reduction). The spent late washwater is inhibited to 1.2 M NaOH before it is transferred to Tank 22 (same as nitrite flowsheet). The maximum tank temperatures were assumed to be 55°C in Tank 48 although the inhibitor requirements for 70°C are met. Both material balances are based on average salt composition and on emptying one salt tank per year (three ITP cycles per year; nine ITP batches per year).

The washing endpoint in Tank 48 is based on several considerations. These include:

1. rate of radiolytic conversion of nitrate into nitrite (assumed to be complete within two years)[7]
2. rate of radiolytic destruction of nitrite (G=0.3 molecules/100 eV, 36 Ci of Cs-137/gal, 2 years of storage)[7]
3. feed specification for nitrite (<0.18 molar) to Late Washing and to DWPF (<0.01 molar).[8]
4. rate of consumption of free hydroxide in Tank 49 (0.016 molar/month, 36 Ci of Cs-137/gal, 2 years storage)

When radiolytic conversion of nitrate to nitrite, destruction of nitrite, and batch additions to Tank 49 are considered, the net result must be a nitrite concentration that does not exceed the washing capabilities of Late Washing. To accomplish this, Tank 48 washing must reduce the sum of the nitrate and nitrite concentrations to less than 0.25 molar.

The free hydroxide concentration must be maintained above 1.8 molar for corrosion inhibition in Tank 48 and Tank 49. A complication in Tank 49 is the depletion of free hydroxide by radiolysis and absorption of carbon dioxide from the ventilation air. To avoid having to add hydroxide inhibitor to Tank 49, enough excess NaOH is left in the washed precipitate in Tank 48 so that hydroxide depletion during two years of storage is accommodated. The hydroxide depletion rate is assumed to be 0.16 molar/month, or 0.38 molar during two years of storage. Thus, the last NaOH addition to Tank 48 during washing is sized so that the free hydroxide concentration is 2.18 molar at the end of washing.

A process flow diagram for the ITP process with Late Washing is shown in Figure 4. It is similar to previous material balances[6c] except that no sodium nitrite is added to Tank 48. The batch volumes for a cycle are shown in Table IV. The concentrations of the major components in these solutions are listed in Table V. The composition of the washed precipitate at various stages in Tank 49 and Late Washing is shown in Table VI. Table VII shows the sequence of inhibitor additions and the composition of the washed precipitate during Tank 48 washing. Table VIII lists the process steps and timing.

Quality Assurance

The new data and calculations reported for hydroxide depletion, carbonate accumulation, and material balance are recorded in Laboratory Notebook #WSRC-RP-92-132, pp 132-148. Calculations of the absorption of carbon dioxide are recorded in laboratory notebook #WSRC-NB-91-151, pp 156-159. Sodium tetraphenylborate used in the preparation of slurries was obtained from AFF, Inc. and was not purified before use. All other chemicals used to make slurries were prepared from reagent grade chemicals. Analyses for free hydroxide and carbonate were performed by the SRTC Analytical Development Section as routine samples. This work was carried out in accordance with the following program plan: D. D. Walker, "Late Washing Program Plan (U)," SRT-LWP-92-092, Rev.1, June 15, 1992.

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FIGURE 4. Process Flow Diagram for the ITP Process

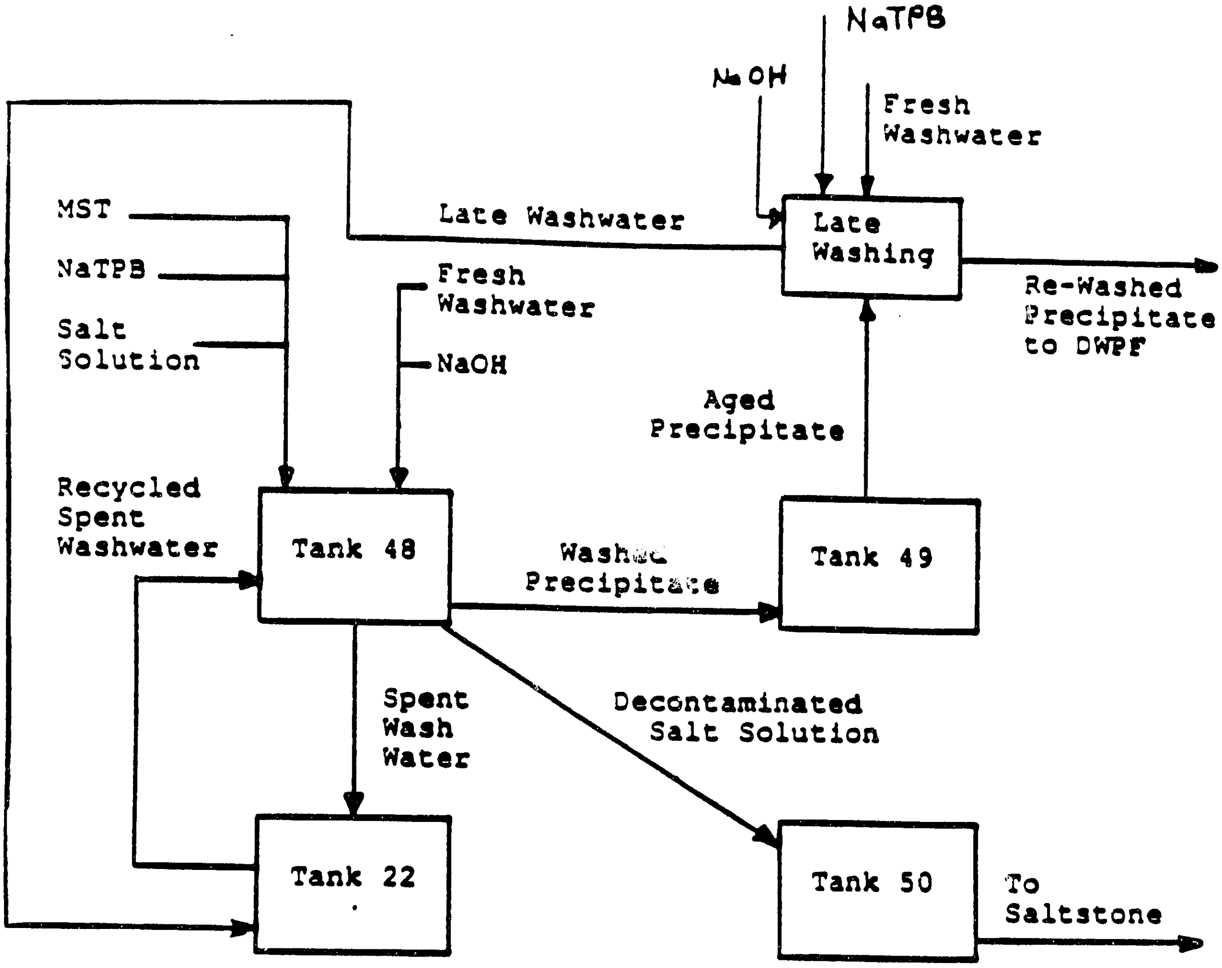

TABLE IV. Process Volumes for the Hydroxide Flowsheet

Component	Volume (kgal)		
	Batch #1	Batch #2	Batch #3
Heel		54.4	90.5
Salt solution	630	630	630
Recycled washwater	90	90	90
Late washwater	89	89	89
STPB	36.3	25.1	25.1
MST	2.0	0	0
Flush water	1	1	1
Total batch volume:	848	835	835
10 wt % slurry:			
before washing:	54.4	90.5	125.2
after washing:			120.7
Filtrate (to Tk 50):	794	799	800
Filtrate total per cycle:			2,393
	Solids (kg)		
KTPB	16,700	33,700	50,000
STPB	8,000	8,000	8,000
MST	1,000	1,000	1,000

TABLE V. Stream Compositions for the Hydroxide Flowsheet

Component	Concentration (molar)			
	Salt Sol'n	Recycled Washwater	Late Washwater	Filtrate (to Tk 50)
Na^+	6.3	3.84	2.06	5.44
OH^-	1.72	2.44	1.80	1.76
NO_3^-	2.42	0.72	0.00033	1.91
NO_2^-	0.89	0.27	0.051	0.71
TPB^-	0.0	0.01	0.004	0.0018
Cs-137 (Ci/L)	0.7	0.000005	0.0038	0.000003

TABLE VI. Composition of Concentrated Precipitate

Component	Concentration (molar)		
	To Tk 49	After 2 yrs	After Late Washing
K$^+$	0.0	0.050	0.0
Na$^+$	2.54	2.54	0.18
OH$^-$	2.16	1.78	0.126
NO$_3^-$	0.175	0.03-.001	0.002-.0007
NO$_2^-$	0.065	0.15	0.010
Cs-137 (Ci/L)			
soluble:	--	1.7	--
solid:	11.3	9.6	11.3
		Concentration (g/L)	
KTPB	109.4	93.0	109.4
CsTPB	1.16	.99	1.16
MST	2.38	2.38	2.38

TABLE VII. Corrosion Inhibitor Additions During Tank 48 Washing

		Concentration (molar)			Volume (kgal)	
Stage	Na+	OH-	NO3-	NO2-	Step	Total
Initial	5.44	1.76	1.91	0.71	0	0
End 1st filtration	3.50	1.13*	1.22	0.46	50	50
Add 12,000 gal NaOH	5.05	2.91	1.11	0.41	12	62
End 2nd filtration	3.13	1.79	0.68	0.25	55	117
Add 12,000 gal NaOH	4.71	3.50	0.61	0.23	12	129
End 3rd filtration	2.46	1.80	0.32	0.12	75	204
Add 12,000 gal NaOH	4.11	3.52	0.28	0.11	12	216
End 4th filtration	2.54	2.16	0.175	0.065	55	271

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*The first washing stage is terminated when the nitrate concentration approaches 1.2 molar, which is 20% above the OSR limit of 1.0 molar for OH$^-$/NO$_2^-$ inhibition. When the nitrate concentration drops below 1.2 molar, corrosion inhibition is based on the 1.5 molar OH$^-$ minimum.

TABLE VIII. Hydroxide Flowsheet Process Timing

Step	Action	Volume (gal)	Rate (gpm)	Time (hr)	Subtotal (days)
	Batch #1				
1	Set up supernate transfers			1.0	
2	Transfer salt solution	630,000	75	140.0	
3	Shut down transfer			1.0	5.9
4	Set up dilution water transfer			1.0	
5	Transfer dilution water	179,000	100	29.8	
6	Shut down transfer			1.0	1.3
7	Set up NaTPB transfer			1.0	
8	Transfer NaTPB	36,300	100	6.0	
9	Shut down transfer			1.0	.3
10	Set up NaTitanate transfer			1.0	
11	Transfer NaTitanate	2,040	100	.3	
12	Shut down transfer			1.0	.1
13	Set up water flush			1.0	
14	Flush lines	1,000	100	.2	
15	Shut down flush			1.0	.1
16	Agitate			72.0	3.0
17	Downtime			229.9	9.6
18	Start up production (filtration)			24.0	
19	Filter to 10 wt %	793,900		117.4	
20	Shut down production			20.0	6.7
21	Set up chemical cleaning			18.0	
22	Soak			24.0	
23	Shut down cleaning			6.0	2.0
	End first batch				29.0
	Batch #2				
1	Set up supernate transfers			1.0	
2	Transfer salt solution	630,000	75	140.0	
3	Shut down transfer			1.0	5.9
4	Set up dilution water transfer			1.0	
5	Transfer dilution water	179,000	100	29.8	
6	Shut down transfer			1.0	1.3
7	Set up NaTPB transfer			1.0	
8	Transfer NaTPB	25,000	100	4.2	
9	Shut down transfer			1.0	.3
10	Set up water flush			1.0	
11	Flush lines	1,000	100	.2	
12	Shut down flush			1.0	.1
13	Agitate			72.0	3.0
14	Downtime			229.9	9.6
15	Start up production (filtration)			24.0	
16	Filter to 10 wt %	799,000		121.4	
17	Shut down production			20.0	6.9
18	Set up chemical cleaning			18.0	
19	Soak			24.0	
20	Shut down cleaning			6.0	2.0
	End of second batch				29.1

TABLE VIII. Hydroxide Flowsheet Process Timing (continued)

	Batch #3				
1	Set up supernate transfers			1.0	
2	Transfer salt solution	630,000	75	140.0	
3	Shut down transfer			1.0	5.9
4	Set up dilution water transfer			1.0	
5	Transfer dilution water	179,000	100	29.8	
6	Shut down transfer			1.0	1.3
7	Set up NaTPB transfer			1.0	
8	Transfer NaTPB	25,000	100	4.2	
9	Shut down transfer			1.0	.3
10	Set up water flush			1.0	
11	Flush lines	1,000	100	.2	
12	Shut down flush			1.0	.1
13	Agitate			72.0	3.0
14	Downtime			229.9	9.6
15	Start up production (filtration)			24.0	
16	Filter to 10 wt %	800,000		123.7	
17	Shut down production			20.0	7.0
18	Set up chemical cleaning			18.0	
19	Soak			24.0	
20	Shut down cleaning			6.0	2.0
	End of third batch				29.2
	Wash Cycle				
1	Set up wash			24.0	
2	Wash	50,000	14	59.5	
3	Add NaOH inhibitor	12,000	100	12.0	
4	Wash	55,000	14	65.5	
5	Add NaOH inhibitor	12,000	100	12.0	
6	Wash	75,000	14	89.3	
7	Add NaNO2 inhibitor	12,000	100	12.0	
8	Wash	55,000	14	65.5	
9	Shut down wash			42.0	15.9
10	Sample Tk 48			42.0	
11	Set up slurry transfer to Tk 49			1.0	
12	Transfer	133,000	100	22.2	
13	Shut down transfer			1.0	2.8
14	Set up chemical cleaning			20.0	
15	Soak			24.0	
16	Shut down cleaning			6.0	2.1
	End of wash cycle				20.8
	End of cycle				108.1

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