Modeling of Boehmite Leaching from Actual Hanford High-Level Waste Samples

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ABSTRACT

The U.S. Department of Energy plans to vitrify approximately 60,000 metric tons of high-level waste (HLW) sludge from underground storage tanks at the Hanford Site in Southwest Washington State. To reduce the volume of HLW requiring treatment, a goal has been set to remove a significant quantity of the aluminum, which comprises nearly 70 percent of the sludge. Aluminum is found in the form of gibbsite and sodium aluminate, which can be easily dissolved by washing the waste stream with caustic, and boehmite, which comprises nearly half of the total aluminum, but is more resistant to caustic dissolution and requires higher treatment temperatures and hydroxide concentrations. Chromium, which makes up a much smaller amount (~3%) of the sludge, must also be removed because there is a low tolerance for chromium in the HLW immobilization process. In this work, the coupled dissolution kinetics of aluminum and chromium species during caustic leaching of actual Hanford HLW samples is examined. The experimental results are used to develop a model that provides a basis for predicting dissolution dynamics from known process temperature and hydroxide concentration.

INTRODUCTION

Approximately 60,000 metric tons of high level waste (HLW) sludge is currently contained in 177 underground storage tanks at the Hanford Nuclear Reservation in Richland, Washington. The U.S. Department of Energy plans to vitrify the sludge, which is composed of solids in the waste that have settled to the bottom, into a glass waste form for disposal in a geologic repository. As much as 70% of the sludge is composed of aluminum. Chromium is a minor component (~3%) of the sludge. The Hanford Waste Treatment Plant (WTP) has a processing target to remove significant aluminum such that it is no longer the waste-limiting component in the final HLW glass waste form. The chromium must also be removed before producing the glass waste forms because there is a low tolerance for chromium in the HLW immobilization process. The undesirable HLW sludge components such as aluminum and chromium will be removed by leaching with NaOH before glass formation. Successfully completing these objectives will allow a factor of nearly two reduction in the quantity of HLW glass that will be produced in the WTP. A similar reduction would be realized in treating Savannah River H-modified plutonium uranium extraction (PUREX) waste [1].

All of the solids remaining after leaching will be processed as HLW, so identifying the effect of process variables such as temperature and hydroxide concentration will allow better understanding of and control over the volume of solids requiring vitrification as well as the quantity of HLW glass formed. Nearly half of the aluminum in the tanks is found as boehmite (AlOOH), with the remainder being gibbsite ($Al(OH)_3$), sodium aluminate ($NaAlO_2$), and a small amount of alumino-silicate materials. Gibbsite and sodium aluminate are easily dissolved by heating under caustic conditions (e.g., 8 hours at 50°C with 3 M NaOH). Boehmite requires more aggressive conditions of higher temperatures and longer times to dissolve. Much of the chromium is insoluble and appears to be held up in the aluminum solids. Boehmite dissolves according to Equation 1.

$$AlOOH + OH^{-} + H_2O \leftrightarrow Al(OH)_4^{-} \qquad \text{(Eq. 1)}$$

Table I shows the distribution of aluminum and chromium in sludge waste across the tank farms. Nearly half of the aluminum and chromium in the tanks is found in the S and SX tanks.

Table I. Aluminum and Chromium Sources in Hanford Sludge Waste [2]

Tank (series)	Al, Kg	% Al	Cr, Kg	% Cr
U	3.97E+05	9.8	5.23E+03	4.7
T/TX/TY	3.73E+05	9.2	2.08E+04	18.7
SX	1.16E+06	28.4	3.25E+04	29.1
S	8.96E+05	22.0	1.65E+04	14.8
C	5.65E+05	13.9	5.16E+03	4.6
B/BX/BY	4.58E+05	11.2	2.30E+04	20.6
AN/AP/AW/AX/AY/AZ	1.97E+05	4.8	5.51E+03	4.9
A	2.83E+04	0.69	2.83E+03	2.5
Total	4.07E+06	100	1.12E+05	100

Table II shows the composition of typical S and SX tank sludges of interest. The AlOOH averages 88% of the solids fraction, with a standard deviation of 10.6% over the 16 tanks. The $Cr(OH)_3$ averages 3.6% of the solids fraction, with a standard deviation of 3.0%.

Table II. Percent Composition of Undissolved Solids in Typical S/SX Sludge [2]

	Analyte, Percent						
Tank	AlOOH	$Cr(OH)_3$	U_3O_8	FeOOH	$Bi(OH)_3$	ZrO_2	ThO_2
S-101	90.5	6.02	2.52	0.93	0.03	0.01	4.4E-05
S-104	96.1	1.77	1.46	0.67	0.002	0.02	7.9E-06
S-105	74.4	9.38	1.38	14.63	0.14	0.05	1.7E-03
S-107	89.9	1.99	2.21	1.02	0.01	4.87	9.0E-06
S-1110	86.5	7.96	2.34	3.03	0.11	0.02	1.8E-04
SX-103	89.2	8.32	0.54	1.88	0.02	0.02	1.8E-04
SX-104	92.4	4.74	1.22	1.57	0.04	0.02	8.1E-05
SX-107	95.9	1.35	1.30	1.38	0.05	0.02	6.3E-11
SX-108	85.6	4.86	1.64	7.72	0.02	0.16	9.6E-11
SX-109	92.8	5.19	0.89	1.04	0.03	0.01	1.4E-05
SX-110	95.6	1.70	1.26	1.34	0.05	0.02	1.3E-06
SX-112	95.9	1.35	1.30	1.38	0.05	0.02	8.0E-11
SX-114	95.6	1.79	1.25	1.33	0.05	0.02	1.9E-06
SX-115	83.4	1.18	1.13	14.24	0.04	0.02	1.1E-10
U-110	89.2	0.26	3.47	3.53	3.39	0.03	1.2E-01

There is also a significant inventory of chromium in the tank saltcakes from evaporated supernate that contains predominately sodium salts such as sodium nitrate and sodium nitrite. Table III shows the tanks with the greatest inventories of chromium in the saltcake across the Hanford tank farms.

Table III. Chromium Sources in Hanford Saltcake Waste [2]

Tank (series)	Cr, Kg	% Cr
A	4.35E+04	10.5
B	4.05E+03	1.0
BY	8.41E+04	20.2
R-Saltcake*	2.35E+04	5.6
S	2.04E+05	49.0
T	5.18E+04	12.5
Balance of Tanks	5.17E+03	1.2
Total	4.16E+05	100

*R-Saltcake is saltcake from self-concentration in S- and SX-Farms (1952-1966)

The BY112 and the S and SX tanks hold the greatest percentage of chromium, and Table IV shows the individual compositions of these saltcakes. As with the sludge, the saltcake consists mainly of aluminum. The aluminum averages 81% of the solids fraction, with a standard deviation of 11.5% over the 10 tanks. However, the amount of $Cr(OH)_3$ is higher than seen in the sludge, averaging 14.4% of the solids fraction, with a standard deviation of 9.7%. The chromium concentration is highest in the saltcakes containing the lowest amounts of aluminum.

Table IV. Percent Composition of Solids in High-Chromium-Bearing Saltcakes [2]

	Analyte, Percent						
Tank	AlOOH	$Bi(OH)_3$	$Cr(OH)_3$	FeOOH	U_3O_8	ZrO_2	ThO_2
BY-112	52.2	1.6E-02	39.4	5.0	3.3	2.7E-02	5.7E-03
S-106	74.5	2.5E-01	20.8	4.0	0.50	1.7E-02	4.7E-04
S-108	76.1	4.0E-02	19.4	3.1	1.3	5.2E-02	4.9E-04
S-110	86.5	1.1E-01	8.0	3.0	2.3	1.7E-02	1.8E-04
S-111	92.3	1.9E-02	7.4	0.14	0.20	6.4E-03	1.6E-04
SX-101	84.8	2.3E-02	12.4	1.6	1.1	2.5E-02	7.0E-05
SX-102	81.6	3.9E-02	15.4	2.0	0.88	7.2E-02	2.9E-04
SX-103	89.2	2.5E-02	8.3	1.9	0.54	2.2E-02	1.8E-04
SY-101	84.5	3.7E-02	14.5	0.75	0.18	2.2E-02	1.4E-03
SY-103	88.5	7.1E-02	8.7	2.2	0.51	4.7E-02	3.3E-02

Aluminum and chromium leaching studies have been performed on Hanford tank waste samples, and results used to develop a model for the dissolution of chromium in sludge. The dissolution of chromium from saltcake wastes is also discussed. Several dissolution studies on actual waste samples have been performed with waste samples containing a large fraction of boehmite [3-7]. The purpose of the work of this paper was to develop a model that appropriately describes the kinetic behavior of chromium leaching from these waste-dissolution tests and to determine the feasible hydroxide concentration and processing-temperature conditions for boehmite and chromium leaching in the Hanford WTP.

THEORY

A model for the dissolution of aluminum and chromium from S/SX tank sludges was developed, based on the following assumptions:

1. Boehmite is present to a greater degree than gibbsite.

2. Gibbsite dissolution is very fast in comparison to boehmite dissolution.
3. Chromium dissolution is simultaneous with aluminum and is controlled by two reaction rates. The first is a slow dissolution rate for Cr particles imbedded in boehmite agglomerates, and the second is a faster dissolution rate for Cr particles liberated from boehmite agglomerates.

It will be shown that experimentally determined concentrations of dissolved aluminum from actual tank solids over time and at various temperatures can be fit reasonably well to a first-order exponential equation. A rate constant, k_A, was obtained from this fit for the dissolution of aluminum. The rate of dissolution of aluminum can be written as:

$$\frac{dA}{dt} = -k_A A \, . \qquad \text{(Eq. 2)}$$

If it is assumed that the aluminum is present as 90% boehmite and 10% gibbsite [3], this equation can be solved for A:

$$A = 0.9 \exp(-k_A t) \, . \qquad \text{(Eq. 3)}$$

There are two rates for the dissolution of chromium. The first is a slow rate for chromium particles that are imbedded or occluded in boehmite aggregates. These chromium particles dissolve slowly until the boehmite aggregates break up and begin to dissolve. The rate of the occluded chromium dissolution is given by:

$$\frac{dC_O}{dt} = -k_{c_O} C_O - k_A A \cdot Fraction \, . \qquad \text{(Eq. 4)}$$

The second rate for the dissolution of chromium represents the dissolution of chromium particles that are either imbedded in the faster dissolving gibbsite aggregates, or dissolution of chromium particles that are liberated from the boehmite aggregates. These are the un-occluded chromium particles. The rate of un-occluded chromium dissolution is:

$$\frac{dC_{UO}}{dt} = -k_{C_{UO}} C_{UO} + k_A A \cdot Fraction \, . \qquad \text{(Eq. 5)}$$

where t = time
A = concentration of aluminum
k_A = rate constant for dissolution of aluminum
Fraction = fraction of chromium still occluded
$C_{O\,=}$ = concentration of occluded chromium
k_{CO} = rate constant for dissolution of occluded chromium
C_{UO} = concentration of un-occluded chromium
k_{CUO} = rate constant for dissolution of un-occluded chromium

Lumetta [4] found that the dissolution of chromium in high caustic solution at room temperature is significant, but heating the solution can cause chromium to re-precipitate as guyanaite (CrOOH). An oxidizing agent may be needed to oxidize the Cr(III), which is poorly soluble in alkaline media, to Cr(VI), which is highly soluble in alkaline media. Rapko et al. [8, 9] found permanganate to be an effective method for the additional dissolution of chromium from sludges that had previously been leached under alkaline conditions. The oxidation reaction is:

$$Cr\left(OH\right)_3 + MnO_4^{\;-} + OH^- \rightarrow CrO_4^{\;2-} + MnO_2 + 2H_2O \tag{Eq. 6}$$

The manganese limit in the HLW glass feed is not currently defined, but it is expected to be much higher than that for chromium. Consequently, slight excess additions of manganese to the sludge for complete reaction of chromium should result in minimum impact to HLW feed processing

EXPERIMENTAL APPROACH AND RESULTS

Lumetta et al. [3] studied the effect of caustic leaching at three concentrations of sodium hydroxide and three temperatures on Tank S-110 sludge samples. For the study, 211 g of the sludge was mixed with 0.01 M NaOH to give a total volume of 400 mL. This was then washed three times with 0.01 M NaOH. The sample was centrifuged, and the washed solids were transferred to a bottle and diluted with deionized water to a final volume of 1 liter. Nine aliquots, each weighing ~15 g, were then transferred to 125-mL bottles. To leach these samples, the appropriate amount of 10 M NaOH was added to each to reach the desired NaOH concentration. The leaching mixtures were then diluted to 100 mL with deionized water. A ratio of ~80 mL solution per gram of washed S-110 solids was chosen to avoid aluminum solubility limits in any of the test samples. Table V shows the final concentration of NaOH and the temperature at which each sample was run.

Table V. Leaching Conditions for Tank S-110 Sludge Samples [3]

Bottle ID	M NaOH	Temp °C
S-110-60-1	1.0	60
S-110-60-3	2.8	60
S-110-60-5	4.8	60
S-110-80-1	0.9	80
S-110-80-3	2.7	80
S-110-80-5	4.6	80
S-110-100-1	0.8	100
S-110-100-3	2.7	100
S-110-100-5	4.6	100

The samples were stirred with magnetic stir bars. The liquid level was held constant by occasionally adding deionized water to return the samples to their original volumes. Leachate samples were taken at 4, 8, 24, 72, and 168 hours after the start of the test. When the leachates were sampled, the stirring was stopped, and the solids were allowed to settle. The aliquot of sample removed was filtered, and 0.5 mL of the filtered leachate sample was acidified with 15 mL of 0.3 M HNO_3. Table VI shows the percentage of aluminum, chromium, calcium, iron, and silicon removed under these conditions.

Table VI. Conditions and the Percentage of Analytes Removed from Tank S-110 Sludge [3]

Leaching Conditions	Analyte				
	Al	Ca	Cr	Fe	Si
1 M NaOH, 60°C	39	56	49	1	57
3 M NaOH, 60°C	47	32	70	4	84
5 M NaOH, 60°C	50	63	81	10	88
1 M NaOH, 80°C	69	40	78	1	51
3 M NaOH, 80°C	91	0	89	7	87
5 M NaOH, 80°C	96	52	90	10	90
1 M NaOH, 100°C	91	48	87	1	52
3 M NaOH, 100°C	100	0	91	5	84
5 M NaOH, 100°C	100	56	93	11	90

Rapko [8] studied the effect of oxidizing conditions on the removal of chromium in U-108 and U-109 saltcake tank waste. For the study, the residual solids from dilute hydroxide washing of the saltcake were used. The solids were additionally washed with 0.1 M NaOH, until the supernatant, which was yellow due to the presence of Cr(VI), was colorless. The samples were divided into two aliquots, one that was to be used for contacts with 0.1 M sodium hydroxide, and one that was to be used for contacts with 3 M sodium hydroxide. The sample to be leached with 0.1 M sodium hydroxide was pretreated by washing with 0.1 M NaOH, leached with 3 M NaOH for 1 week, and then washed three times with 0.1 M NaOH. This was done to remove the bulk of the aluminum before the chrome leaching experiments.

Because the aluminum was expected to dissolve during the course of the leaching with 3 M NaOH, the 3 M NaOH contact sample was pretreated by washing with dilute hydroxide to remove any chromate that might be present in the sample.

Enough of the solid tank waste material was used for each test to have enough undissolved material at the end of the test for analysis purposes. The chromium concentration in the saltcake was obtained from the values reported by Lumetta et al. [5]. The desired amounts of material were weighed into plastic bottles, and the amount of permanganate needed to give a minimum of a 1:1 ratio of permanganate to chromium was added. Either 0.1 M or 3 M NaOH was added to each bottle of solids, to a final volume of 50 mL. High-purity oxygen and argon were introduced to the appropriate sample bottles at a flow rate of approximately 5 cc/min.

Six testing conditions for each tank were performed: permanganate in 0.1 and 3 M NaOH, direct oxygen purge of the 0.1 and 3 M NaOH contacts, and direct argon purge of the 0.1 and 3 M NaOH contacts. The samples were stirred at room temperature for the first 24 hours and then were heated at 80°C for the remainder of the experiment. Deionized water was added periodically to maintain the volume of the samples. The solids were allowed to settle before samples were removed for testing. Samples were taken at the beginning of the test (at 0 hours) and then intermittently throughout the test. The sample aliquots were filtered before being analyzed with ultraviolet visible spectroscopy. Tables VII and VIII show the compositions of the initial samples from the U-108 and U-109 tests as well as the composition after the various treatment conditions.

Table VII. Percent Composition of Initial and Final Leached U-108 Samples [8]

Analyte	Treatment Conditions						
	Initial Sample	0.1 M NaOH, $NaMnO_4$	3 M NaOH, $NaMnO_4$	0.1 M NaOH, O_2	3 M NaOH, O_2	0.1 M NaOH, Ar	3 M NaOH, Ar
$Cr(OH)_3$	36.4	1.0	0.1	49.1	4.0	43.1	54.6
$NaMnO_4$	0.9	48.7	60.6	1.2	2.7	0.4	1.2
AlOOH	19.9	14.2	0.7	11.8	1.8	16.0	4.5
U_3O_8	34.5	28.8	30.2	30.1	79.0	32.8	31.8
$NaNO_3$	3.9	3.9	4.9	3.0	2.9	3.3	3.1
$Ca(OH)_2$	0.5	0.4	0.4	0.6	1.6	0.6	0.7
FeOOH	1.4	1.2	1.2	1.5	4.3	1.3	1.9
SiO_2	1.0	0.8	0.8	1.1	1.7	1.1	0.5
$Bi(OH)_3$	1.5	1.0	1.0	1.6	1.9	1.6	1.8

Table VIII. Percent Composition of Initial and Final, Leached U-109 Samples [8]

Analyte	Treatment Conditions						
	Initial Sample	0.1 M NaOH, $NaMnO_4$	3 M NaOH, $NaMnO_4$	0.1 M NaOH, O_2	3 M NaOH, O_2	0.1 M NaOH, Ar	3 M NaOH, Ar
$Cr(OH)_3$	49.9	1.4	0.3	49.9	3.0	53.0	55.1
$NaMnO_4$	1.0	58.6	64.1	1.2	2.7	1.0	1.1
AlOOH	5.1	3.6	0.8	4.7	2.5	4.2	2.7
U_3O_8	34.2	28.8	25.6	34.7	76.9	32.2	31.1
$NaNO_3$	4.0	3.7	5.2	3.1	3.6	3.5	3.8
$Ca(OH)_2$	1.0	0.5	0.6	0.7	1.8	0.7	0.7
FeOOH	1.3	1.1	1.0	1.6	3.6	1.4	1.6
SiO_2	1.4	1.0	0.9	1.3	2.4	1.3	1.3
$Bi(OH)_3$	2.2	1.4	1.5	2.6	3.3	2.7	2.5

MODELING RESULTS

The data for the dissolution of aluminum from Tank S-110 sludge [3] in 3 M NaOH at 60, 80, and 100°C were fit to a first-order single exponential to obtain the rate constant for the dissolution of aluminum, k_A, as shown in Figure 1. The rate equations are shown for each temperature.

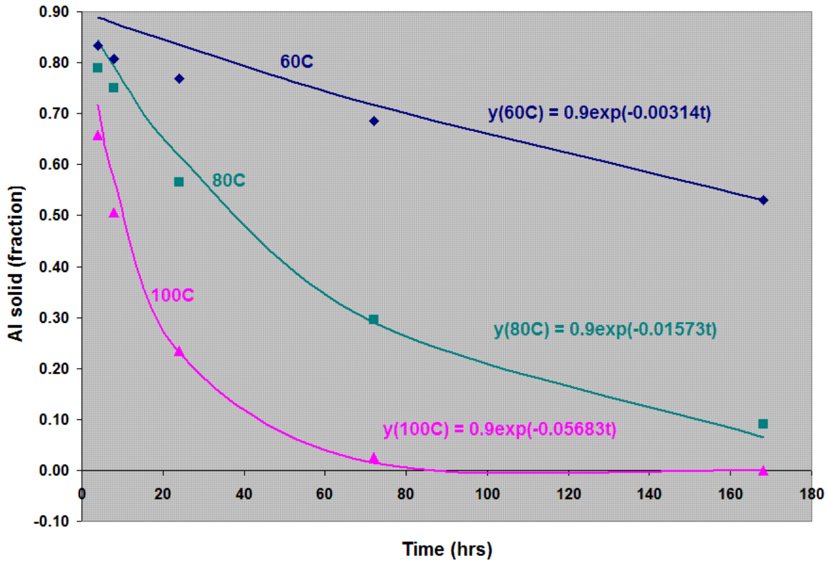

Fig. 1. Mass Fraction of Aluminum Solids in 3 M NaOH in Tank S-110

The rate constants for the occluded (k_{CO}) and un-occluded (k_{CUO}) dissolution of chromium were estimated to provide a minimum error fit to the dissolution-rate data based on the equations for dissolution (Equations 2, 4, and 5). Then the values for concentration of chromium were calculated. The estimates for the concentration of chromium were plotted with the actual data in Figure 2. As seen in Figure 2, at early times, the best-fit lines predict the chromium dissolution behavior, while at longer dissolution times, the best fit lines tend toward greater chromium dissolution than experimentally observed. This implies that in addition to aluminum dissolution, at least one other mechanism is important for chromium dissolution from the tank sludges.

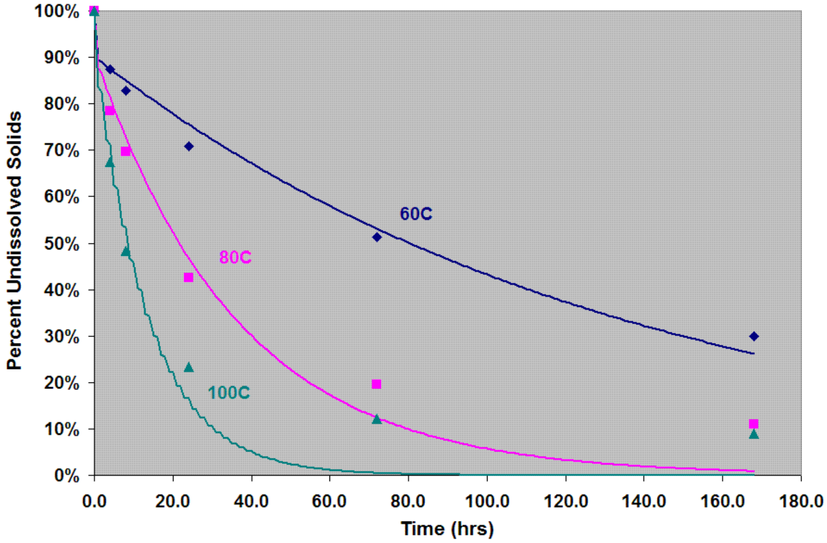

Fig. 2. Dissolution of Chromium: actual data and experimental fit as a function of percent undissolved solids

This effect can be seen from chromium dissolution studies as measured by Rapko [8] for tank saltcakes from Hanford Tanks U-108 and U-109. Chromium dissolution is shown as a function of time and treatment conditions for Tank U-109 in Figure 3. Similar results were observed for chromium dissolution in Tanks U-108 and U-109. Oxygen added to the tank with 0.1 M NaOH resulted in slow dissolution of chromium. Increased dissolution rates were observed with the use of permanganate for both tank samples. The treatment with 0.1 M NaOH and permanganate removed 96.6% of the chromium from U-108; this value increased to 99.6% with the 3 M NaOH contact. In the presence of either 0.1 or 3 M NaOH and no oxidant added, less than 5% of the chromium was removed. Treatment with 0.1 M NaOH and oxygen did about the same as with no oxidant, removing only 5% of the chromium from U-108 and 14% from U-109. The use of 3 M NaOH with oxygen, however, was effectively as successful as 3 M NaOH with permanganate, removing 94.4% of the chromium in U-108.

The insoluble chromium in the saltcakes discussed by Rapko may be important to the tank sludges as well. The existence of insoluble chromium species may have been initiated through evaporation campaigns, indigenous tank heats, or radiation fields. Its persistence makes chromium dissolution by direct leaching problematic and requires that oxidation studies be done that will define the dissolution parameters: temperature, and hydroxide and oxidant concentrations.

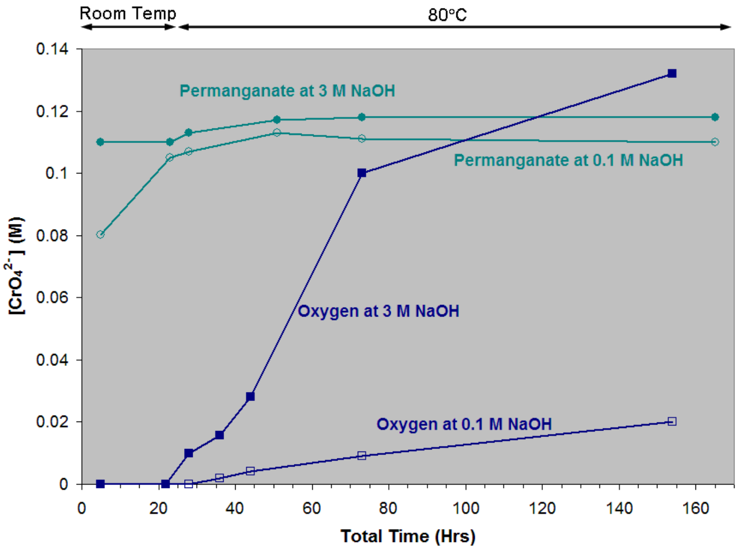

Fig. 3. Slow apparent oxygen dissolution rate in tank U-109

CONCLUSION

The coupled dissolution kinetics of aluminum and chromium species during caustic leaching of actual Hanford HLW samples was examined. Experimental sludge leaching results were used to develop a model that provides a basis for predicting dissolution dynamics from known process temperature and hydroxide concentration. The model assumes that chromium dissolution is simultaneous with aluminum dissolution and is thus controlled by two reaction rates. The first is a slow dissolution rate for chromium particles occluded in boehmite agglomerates, and the second is a faster dissolution rate for chromium particles liberated from boehmite agglomerates. Additionally, the model uses known information concerning the aluminum speciation and its general features, i.e., boehmite is present to a greater degree than gibbsite, and gibbsite dissolution is very fast in comparison to boehmite dissolution.

The data for the dissolution of aluminum from Tank S-110 sludge [3] in 3 M NaOH at 60, 80, and 100°C was used to validate the model approach, and it was shown that the model could predict dissolution behavior at early times, especially at temperatures between 80 and 100°C. However, at later times, the fit over-predicted chromium dissolution. Because these temperatures approach conditions that precipitate both aluminum and chromium, it is thought that the slower dissolution might be related to the precipitation of chromium or the chromium oxidation state.

For Hanford sludge samples, it appears that air oxidation alone is adequate for the treatment and removal of chromium. More aggressive oxidation techniques may be required to deal with the chromium present in saltcake. Additional testing is planned to further investigate the use of permanganate to achieve the oxidation of chromium in saltcake samples.

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