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Caustic Dissolution of Chromium Compounds Present in Hanford Tanks

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ABSTRACT

The primary function of the waste treatment plant (WTP) at Hanford site is to treat high-level and low-activity liquid waste and immobilize it by glass vitrification for final disposal. Currently, there are approximately 200,000 m³ of radioactive waste in 177 underground storage tanks. All of them will be immobilized, followed by closing the tank farms, disposing of the immobilized low-activity waste (ILAW), shipping immobilized high-activity waste (IHLW) to offsite disposal facilities, decontaminating and decommissioning (D&D), and removing the treatment facilities and infrastructure. Because of the expected high costs associated with HLW immobilization and disposal, pretreatment processes will be performed to reduce the volume of the immobilized HLW.

Certain Hanford wastes contain chromium at concentrations that strongly affect the volume of IHLW that can be vitrified. Chromium interferes with the HLW immobilization process; it causes, indirectly, shortness of the heating electrodes and clogging of the pour spout, thus jeopardizing the operation and life of the melter. For these reasons, minimization of the residual chromium concentration in the tank waste is an important pretreatment objective.

Chromium is present in significant quantities in several of the Hanford waste tanks. It has been proposed that the chromium will be dissolved through caustic leaching in the Hanford Waste Treatment Plant currently under construction. In caustic conditions, the concentration of dissolved chromium is influenced by the concentration of caustic and various anions. Therefore, it is important to fully understand the effect various anions that are present in the Hanford waste have on the boehmite and gibbsite dissolution so that the process can be optimized.

To determine the influence of various anions, a series of dissolution tests were performed with different caustic and anion concentrations. The tests were carried out using a special vessel with a blade spinning at 200 rpm and at a range of 97 -100 degrees in temperature. Samples were taken at 0, 1, 2, 4, 8, and 24 hour intervals. This work focused on determining the equilibrium concentration of chromium in solution under the varying caustic and anion combinations and concentrations.

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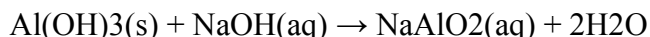
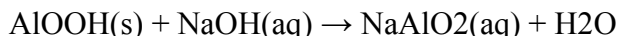
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INTRODUCTION

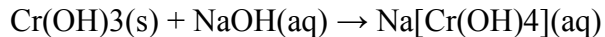
Currently, there are approximately 200,000 m³ of radioactive waste in the 177 underground storage tanks located at the U.S. Department of Energy's (DOE) Hanford Site. As part of the remediation efforts for these underground storage tanks, DOE plans to retrieve, immobilize, and dispose of this radioactive waste. The waste in the tanks is generally divided into three categories: supernatant, saltcake, and sludge. The liquid supernatant is alkaline, with high concentrations of salts such as sodium nitrate (NaNO₃), sodium nitrite (NaNO₂), sodium hydroxide (NaOH), sodium carbonate (Na₂CO₃), sodium phosphate (Na₃PO₄), and sodium sulfate (Na₂SO₄).

Dilute hydroxide washing is the minimum pretreatment that would be performed on Hanford tank sludge. In this method, the sludge is mixed with dilute (0.1 M or less) NaOH, and then some sort of solid/liquid separation is performed. This is meant to remove water-soluble sludge components (mainly sodium salts) from the HLW stream. Dilute hydroxide is used rather than water to maintain the ionic strength high enough that colloidal suspensions are avoided.

Caustic leaching (sometimes referred to as enhanced sludge washing or ESW) represents the baseline method for pre-treating Hanford tank sludge. Caustic leaching is expected to remove a large fraction of the Al, which is present in large quantities in Hanford tank sludge. The Al will be removed by converting aluminum oxides/hydroxides to sodium aluminate. For example, boehmite and gibbsite are dissolved according to the following equations (Weber 1982):



Based on its known chemical behavior, Cr(III) was expected to be removed by caustic leaching according to the following equation:



However, studies conducted at the Pacific Northwest National Laboratory (PNNL) have suggested that the behavior of chromium in the caustic leaching process is more complex than previously thought.

Chromium in tank sludge exists in both the +3 and +6 oxidation states. Chromium, when initially present in the +6 oxidation state, is effectively removed from the Hanford tank sludge solids by alkaline washing and caustic leaching. When present in the +3 oxidation state, however, chromium often dissolves poorly in simple alkaline-wash and caustic-leach solutions. Even when initially present in its +3 oxidation state, prior studies have shown that chromium exists only in caustic-leach solutions in its +6 oxidation state. Therefore, adding an oxidant to the sludge might be expected to facilitate conversion of

Chromium (III) to its more alkaline-soluble form (chromate [CrO₄²⁻]) and so enhance its leaching from the sludge.

EXPERIMENTATION

The composition of the waste in the Hanford tanks is a very complex mixture of chemicals. In order to find out which component of the waste is hindering the dissolution of chromium, the following compounds were studied and analyzed:

- Oxalate
- Sludge
- Supernate
- Gibbsite
- Boehmite

To obtain a good understanding of the dissolution of chromium, a full scale matrix was created by a PNNL scientist. A specific amount of chromium was added to each of the 15 samples in the reaction vessel. The reaction vessel had a mechanical stirrer, a thermocouple, and a port for sampling while being air-tight. A heating mantle was used to keep the vessel at a constant temperature throughout the test. Samples were taken at 0, 1, 2, 4, 8, and 24 hours. A final sample was also taken when the solution came to room temperature. The samples were then passed through a 0.2- μm Nylon® syringe filter to remove all solid matter that might be present in the sample. The next step was to analyze the samples to determine how much chromium had dissolved by measuring its concentration. Table 1 shows the amounts used for each of the 15 samples and Table 2 shows the matrix used in the chromium testing. Figure 1 provides a schematic drawing of the caustic leaching test set-up.

Table 1 Amounts (g) Used in Cr Testing

Test ID	19M NaOH	DI water	Sodium Oxalate	Fe-Rich Sludge	Supernate	Gibbsite	Boehmite	CrOOH
CR-1	400.54	397.8	0	0	0	0	0	3.86
CR-2	200.27	198.9	6.5	264	14	57.2	57.2	1.93
CR-3	400.54	397.8	13	0	0	0	0	3.86
CR-4	200.27	198.9	0	264	0	0	0	1.93
CR-5	400.54	397.8	0	0	28	0	0	3.86
CR-6	400.54	397.8	0	0	0	114.4	0	3.86
CR-7	400.54	397.8	0	0	0	0	114.4	3.86
CR-8	200.27	198.9	6.5	264	0	0	0	1.93
CR-9	400.54	397.8	13	0	28	0	0	3.86
CR-10	200.27	198.9	0	264	14	0	0	1.93
CR-11	400.54	397.8	0	0	0	114.4	114.4	3.86
CR-12	200.27	198.9	0	264	0	57.2	0	1.93
CR-13	400.54	397.8	13	0	0	114.4	0	3.86
CR-14	400.54	397.8	0	0	28	114.4	0	3.86
CR-15	200.27	198.9	6.5	264	14	0	0	1.93

Table 2. Matrix to Used in Cr Testing

Test ID	OH-	Oxalate	Sludge	Supernate	Gibbsite	Boehmite
CR-1	X					
CR-2	X	X	X	X	X	X
CR-3	X	X				
CR-4	X		X			
CR-5	X			X		
CR-6	X				X	
CR-7	X					X
CR-8	X	X	X			
CR-9	X	X		X		
CR-10	X		X	X		
CR-11	X				X	X
CR-12	X		X		X	
CR-13	X	X			X	
CR-14	X			X	X	
CR-15	X	X	X	X		

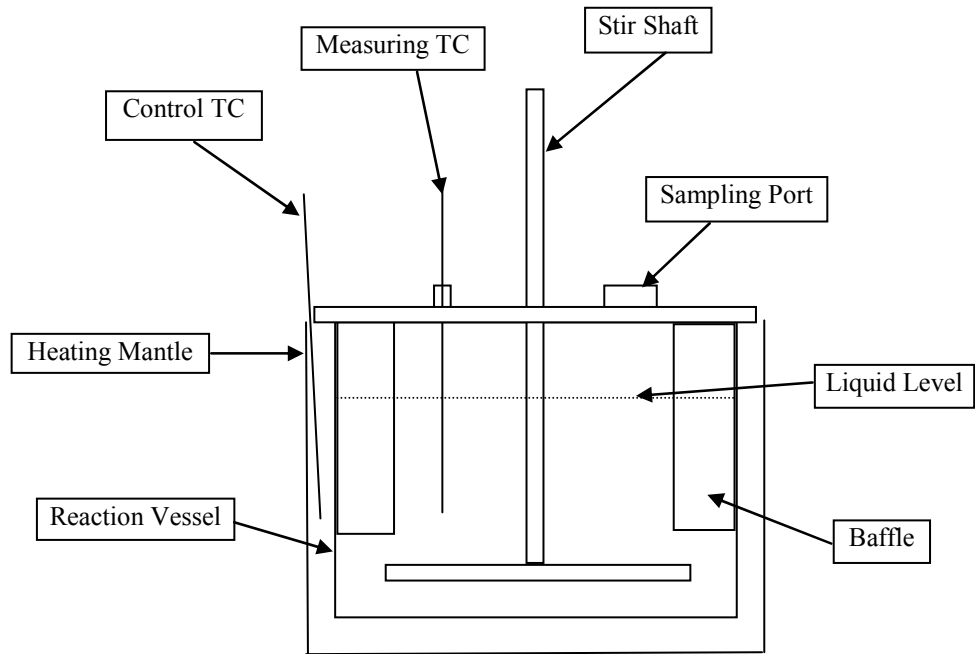


Figure 1. Schematic drawing of the caustic leaching test setup.

INDUCTIVELY COUPLED PLASMA (ICP)

Inductively coupled plasma (ICP) is an analytical technique used for the detection of trace metals in environmental samples. The primary goal of ICP is to get elements to emit characteristic wavelength specific light which can then be measured. The technology for the ICP method was first employed in the early 1960's with the intention of improving upon crystal growing techniques. Since then, ICP has been refined and used in conjunction with other procedures for quantitative analysis. Following is a cursory look at the driving forces behind this analytical tool, its use in series with other analytical tools, and environmental applications of ICP.

Often, ICP is used in conjunction with other analytical instruments, such as the atomic emission spectroscopy (AES) and the mass spectroscopy (MS). This is an advantageous practice, as both the AES and MS require that sample to be in an aerosol or gaseous form prior to injection into the instrument. Thus, using an ICP in conjunction with either of these instruments eliminates any sample preparation time which would be required in the absence of an ICP.

DATA & RESULTS

Once the samples were filtered and processed, they were sent to an analytical laboratory for analysis. Table 3 provides the concentration of chromium removed from the solutions.

Table 3. Sample Concentrations of Chromium

Sample Number	Concentration
CR1-0	5.84E-05
CR1-1	9.46E-04
CR1-2	7.42E-04
CR1-4	7.00E-04
CR1-8	9.36E-04
CR1-24	2.30E-03
CR1-F	2.40E-03

Sample Number	Concentration
CR2-0	2.05E-03
CR2-1	3.77E-03
CR2-2	4.73E-03
CR2-4	6.24E-03
CR2-8	8.82E-03
CR2-24	1.38E-02
CR2-F	1.41E-02

Sample Number	Concentration
CR3-0	8.85E-06
CR3-1	4.74E-04
CR3-2	4.23E-04
CR3-4	4.52E-04
CR3-8	7.90E-04
CR3-24	2.19E-03
CR3-F	2.24E-03

Sample Number	Concentration
CR4-0	2.61E-03
CR4-1	6.43E-03
CR4-2	7.88E-03
CR4-4	1.01E-02
CR4-8	1.35E-02
CR4-24	2.11E-02
CR4-F	2.35E-02

Sample Number	Concentration
CR5-0	6.46E-05
CR5-1	6.66E-04
CR5-2	6.56E-04
CR5-4	6.74E-04
CR5-8	1.02E-03
CR5-24	2.43E-03
CR5-F	2.56E-03

Sample Number	Concentration
Cr-6-0	5.58E-05
Cr-6-1	2.69E-04
Cr-6-2	3.17E-04
Cr-6-4	4.54E-04
Cr-6-8	7.14E-04
Cr-6-24	1.91E-03
Cr-6-F	2.02E-03

Sample Number	Concentration
Cr-7-0	3.38E-05
Cr-7-1	1.86E-03
Cr-7-1repeat	1.85E-03
Cr-7-2	1.19E-03
Cr-7-4	9.59E-04
Cr-7-8	1.18E-03
Cr-7-24	2.44E-03
Cr-7-F	2.75E-03

Sample Number	Concentration
Cr-8-0	2.19E-03
Cr-8-1	4.46E-03
Cr-8-2	6.66E-03
Cr-8-4	8.13E-03
Cr-8-8	1.11E-02
Cr-8-24	1.76E-02
Cr-8-F	1.77E-02

Sample Number	Concentration
Cr-9-0	5.05E-06
Cr-9-1	7.75E-04
Cr-9-2	6.72E-04
Cr-9-4	6.21E-04
Cr-9-8	8.78E-04
Cr-9-24	2.21E-03
Cr-9-F	2.35E-03

Sample Number	Concentration
Cr-10-0	2.21E-03
Cr-10-1	5.57E-03
Cr-10-2	7.28E-03
Cr-10-4	8.36E-03
Cr-10-8	1.04E-02
Cr-10-24	1.56E-02
Cr-10-F	1.59E-02

Sample Number	Concentration
CR-11-0	5.79E-05
CR-11-1	3.86E-04
CR-11-2	4.86E-04
CR-11-4	5.48E-04
CR-11-8	8.25E-04
CR-11-24	2.01E-03
CR-11-F	2.09E-03

Sample Number	Concentration
CR-12-0	2.34E-03
CR-12-1	4.66E-03
CR-12-2	6.39E-03
CR-12-4	8.02E-03
CR-12-8	1.04E-02
CR-12-24	1.65E-02
CR-12-F	1.66E-02

Sample Number	Concentration
CR-13-0	6.22E-05
CR-13-1	2.71E-04
CR-13-2	2.93E-04
CR-13-4	4.11E-04
CR-13-8	6.38E-04
CR-13-24	1.80E-03
CR-13-F	1.85E-03

Sample Number	Concentration
CR-14-0	1.08E-04
CR-14-1	2.58E-04
CR-14-2	3.07E-04
CR-14-4	4.28E-04
CR-14-8	6.58E-04
CR-12-24	1.86E-03
CR-14-F	1.87E-03

Sample Number	Concentration
CR-15-0	2.22E-03
CR-15-1	4.36E-03
CR-15-2	5.85E-03
CR-15-4	7.20E-03
CR-15-8	9.46E-03
CR-15-24	1.50E-02
CR-15-F	1.56E-02

After obtaining the data from the analytical laboratory, the concentration of chromium vs. time was plotted to observe which of the chemicals was hindering the reaction (Figure 2).

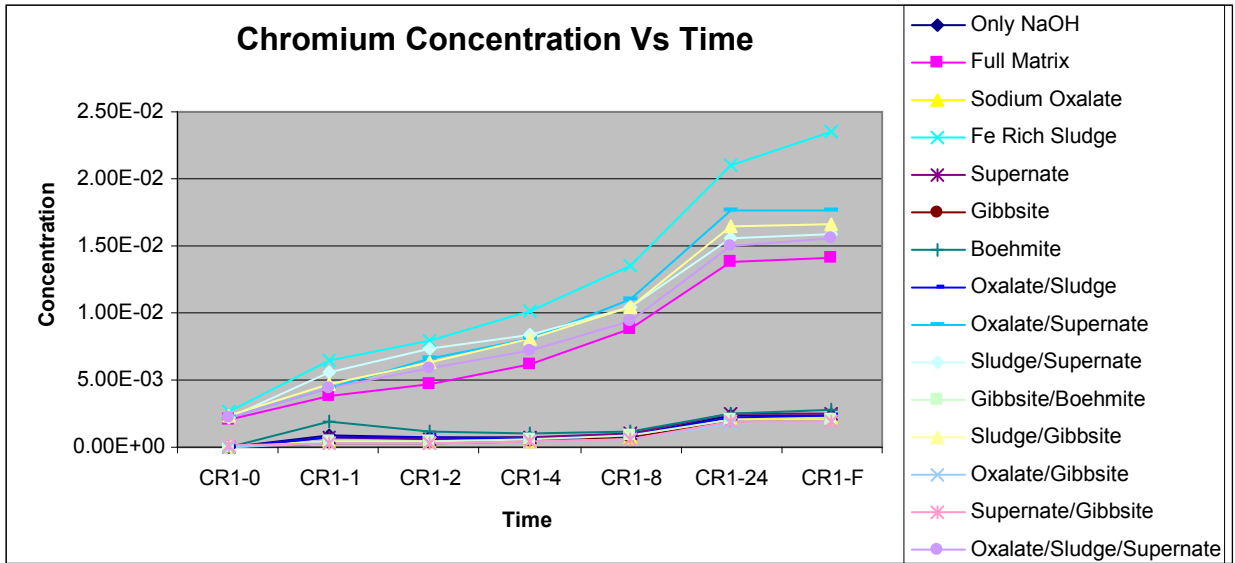


Figure 2. Chromium concentration over time.

CONCLUSIONS

The results obtained in the course of this investigation led to the following key conclusions concerning the caustic dissolution of Cr (III) solid phases under alkaline conditions by sodium hydroxide. Studies were most extensive for Cr(III) hydroxide phases because they seem to be the most likely form of Cr(III) in Hanford tank sludge, especially after caustic treatment.

1. Oxalate was previously believed to be the hindering compound that slowed down the reaction of chromium, but by observing the graph, it is concluded that oxalate has no effect on the reaction.
2. When chromium is interacting only with the iron rich sludge, as in sample # 4, we can see that the reaction did not reach equilibrium in a 24-hour period, as the other samples did.
3. It seems that the iron rich sludge is making a side reaction that is keeping the reaction going past the 24-hour equilibrium point.

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