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Oxidative Dissolution of Chromium from Hanford Tank Sludges Under Alkaline Conditions

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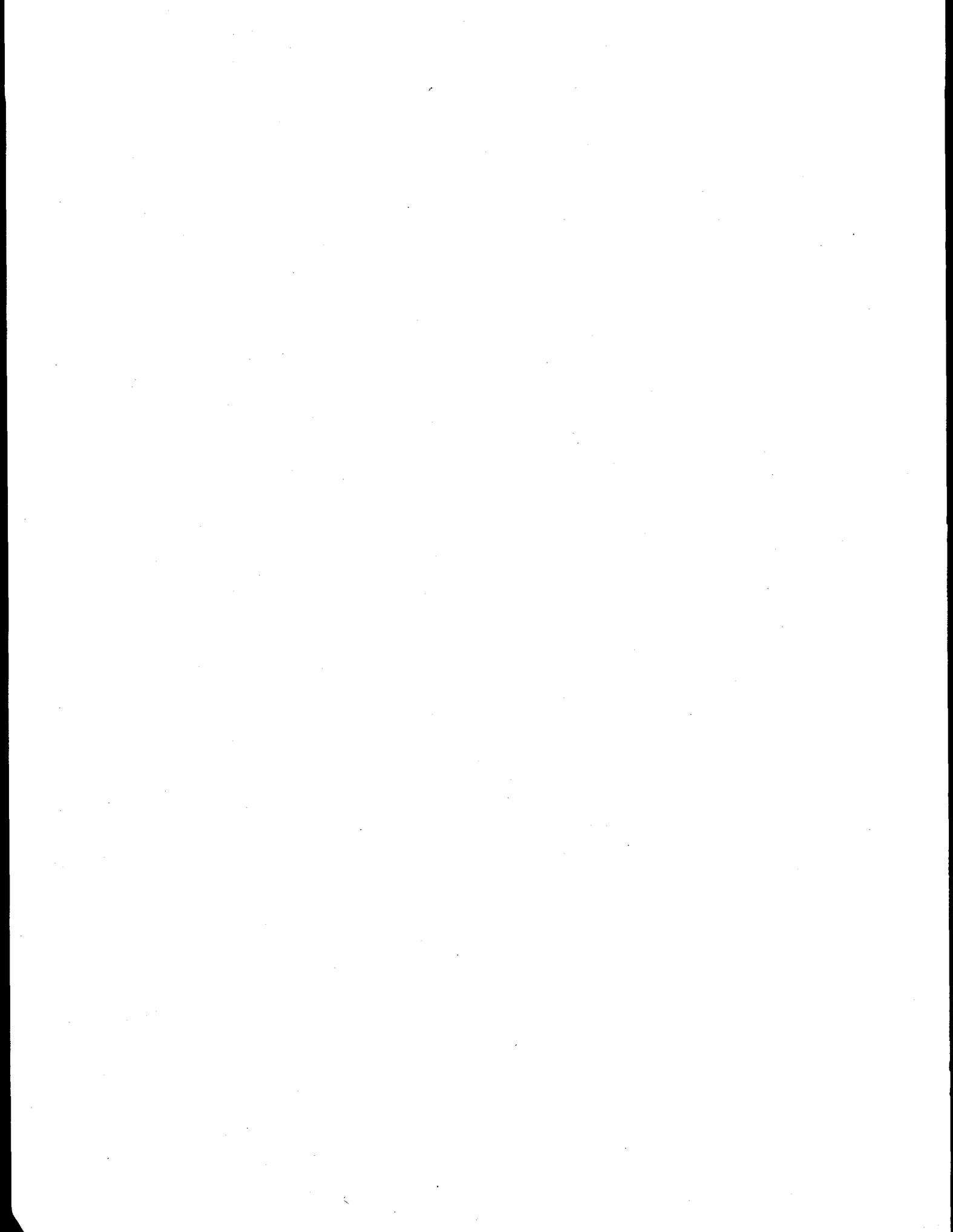
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Summary

Alkaline oxidative leaching has been performed on caustic leached sludges from the three following Hanford waste tanks: BY-110, S-107, and SX-108. These samples were chosen because they represent types of waste where significant amounts of Cr are located and show relatively poor dissolution of Cr during standard caustic leaching. The experiments involved tests with three chemical oxidants, permanganate, ozone and oxygen, and a blank, argon. The effects of varying the hydroxide concentration of the leachate (from 0.1 M to 3 M) and of time and temperature (from room temperature to 80°C) were also examined. Key findings from this study include the following:

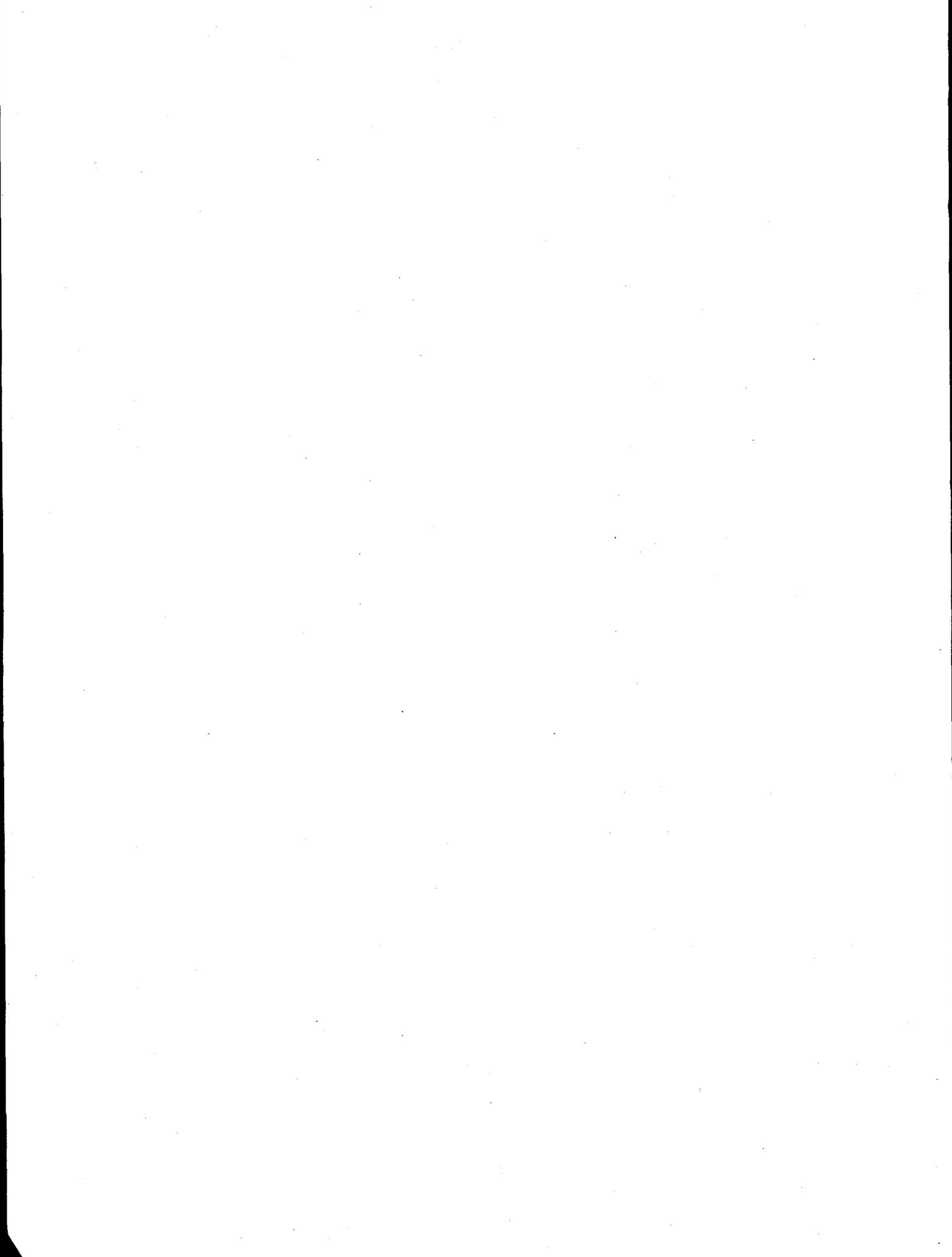
- Permanganate and ozone were the most effective chemical agents tested for additional Cr dissolution of previously caustic leached sludges under alkaline conditions, with 83 to 94% dissolution found with BY-110 and with 58 to 87% dissolution found with S-107, but with only 22 to 45% dissolution with SX-108.
 - Leaching at 3 M free hydroxide was as effective or more effective at dissolving Cr than leaching at 0.1 M free hydroxide, although the increase in effectiveness was small.
 - Heating to 80°C was required in several instances to achieve maximum Cr dissolution.
- Oxygen and argon were much less effective than ozone and permanganate at additional Cr dissolution of previously caustic leached sludges under alkaline conditions.
 - Leaching at 3 M free hydroxide was much more effective than leaching at 0.1 M free hydroxide for Cr dissolution. At 0.1 M free hydroxide, <10% Cr dissolution was found in all cases.
- Work performed to date appears to indicate a correlation between the presence of pure Cr phases in the sludges and the effectiveness of alkaline oxidative dissolution of Cr. This correlation explains the relatively poor Cr dissolution found for SX-108, where a mixed Al/Cr phase has been identified, compared to BY-110 and S-107, where, to the extent any Cr phases have been found, only pure Cr phases have been identified. If this explanation is valid, then more effective Al removal from SX-108 by extended caustic leaching should allow for a more effective alkaline oxidative dissolution of Cr.
- In all instances, visible spectroscopy indicated that the Cr dissolved by alkaline oxidative leaching was present in the +6 oxidation state, i.e., as chromate (CrO_4^{2-}), and not in the +3 oxidation state, i.e., as tetrahydroxochromium(III) $\{\text{Cr}(\text{OH})_4\}$.
- Little total α or Pu was dissolved by alkaline oxidative leaching of Pu at 0.1 M free hydroxide.
- Leaching at 3 M free hydroxide resulted in enhanced Pu dissolution, with up to 14% of the total Pu dissolving during leaching of BY-110 sludge with permanganate. The final Pu concentrations appear consistent with that expected for Pu(IV) in hydroxide solution. However, even with the greater Pu dissolution at 3 M free hydroxide, all of the alkaline oxidative leachate solutions would be classified as a Class A low-level waste even after concentration to 20 wt% Na.
- An alternative explanation for the observed Pu dissolution suggests that additional Pu dissolved in the leachate solutions that contained effective oxidants such as permanganate and ozone. However, Pu may have undergone reduction back to the +4 oxidation state between the time the test ended and time the final samples were prepared for analysis. Reprecipitation of Pu^{4+} would then return the leachate Pu activity to close to that expected based solely on Pu^{4+} solubility in alkaline media. The data to date do not distinguish between these two explanations.
- Scouting experiments using Cr(III) oxide as a model for the insoluble Cr present in the tank waste indicated that hydrogen peroxide was ineffective at dissolving Cr under alkaline conditions.



Acknowledgments

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1.0 Introduction

During the past few years, the primary mission at the U.S. Department of Energy's Hanford Site has changed from producing plutonium to restoring the environment. Large volumes of high-level radioactive wastes (HLW), generated during past Pu production and other operations, are stored in underground tanks on site. The current plan for remediating the Hanford tank farms consists of waste retrieval, pretreatment, treatment (immobilization), and disposal. The HLW will be immobilized in a borosilicate glass matrix; the resulting glass canisters will then be disposed of in a geologic repository. Because of the expected high cost of HLW vitrification and geologic disposal, pretreatment processes will be implemented to reduce the volume of immobilized high-level waste (IHLW).

The baseline sludge pretreatment flowsheet requires retrieving the sludge by sluicing and pumping with inhibited water (0.01 M NaOH/0.01 M NaNO₂), leaching the sludge with caustic (3 M NaOH), then washing the sludge with inhibited water to remove the added NaOH and the components dissolved during the caustic leaching step. The retrieval, leachate, and wash solutions will be combined and processed to remove ¹³⁷Cs (and possibly other radionuclides). The decontaminated solution will then be routed to the low-level waste (LLW) stream, where it will be immobilized in a glass matrix. The leached solids, which will contain the transuranic (TRU) elements and ⁹⁰Sr, will be handled as HLW (Orme et al. 1996).

The key step in the baseline sludge pretreatment flowsheet is caustic leaching of the sludge. Caustic leaching is expected to solubilize a large fraction of the Al, which is present in large quantities in Hanford tank sludges. Aluminum oxides/hydroxides are converted to the more soluble sodium aluminate to remove the Al. A significant portion of the P and S is also expected to be removed from the sludge by metathesis of water-insoluble metal phosphate and sulfate salts to insoluble hydroxide salts and soluble Na₃PO₄ and Na₂SO₄, respectively.

The solubility of Cr(III) is known to increase with increasing hydroxide concentration at room temperature (Rai, Sass, and Moore 1987), and it was expected that caustic leaching could remove substantial quantities of Cr from the Hanford sludges. This increased solubility of Cr(III) at high hydroxide concentration is due to the formation of the tetrahydroxochromium(III) anion.



Studies of the baseline Hanford sludge washing and caustic leaching process at Pacific Northwest National Laboratory and Los Alamos National Laboratory have been reported (Lumetta and Rapko 1994; Rapko, Lumetta, and Wagner 1995; Temer and Villareal 1995; Lumetta et al. 1996a; Lumetta et al. 1996b; Temer and Villareal 1996). Although for most of the key elements, the test results generally agree with the Tank Waste Remediation System (TWRS) flowsheet assumptions, Cr removal is much less than expected. Because of potential melter problems caused by the presence of Cr, the allowable limits for Cr in the melter feed might be low. For example, the Hanford Waste Vitrification Plant (as the plant was originally designed) feed specification for Cr is 0.34 wt% (Swanson 1993). Thus, methods to improve Cr removal from these sludges are of interest because they could lead to reduced disposal costs.

Certain Hanford tank sludges (e.g., double-shell tanks SY-102 and SY-103) contain significant quantities of Cr. Dilute hydroxide washing is expected to remove only ~30% of the Cr from SY-102 (Lumetta, Swanson, and Barker 1995) and only ~5% from SY-103 (Rapko, Lumetta, and Wagner 1995). Although caustic leaching tests have not been performed on SY-102 sludge, tests with SY-103 sludge indicated only another 7% removal of Cr by caustic leaching.

Significant quantities of Cr coupled with poor removals are not limited to double-shell tanks such as SY-102 and SY-103. Dilute hydroxide washing is expected to remove only ~25% of the Cr from the single-shell Tank S-107, and ~50% of the Cr from the single-shell Tank BY-110. Tests on these sludges indicate essentially no additional Cr removal by caustic leaching from BY-110 and only ~25% additional Cr removal from S-107 (Lumetta et al. 1996a).

Several studies with Hanford tank sludge simulants and with actual Hanford tank sludges indicate that treating water-washed and caustic-leached solids with oxidants can significantly increase the effectiveness of Cr removal. For example, treatment with KMnO_4 was found to be effective at removing Cr from washed SY-102 sludge. Indeed, a combination of dilute hydroxide leaching and KMnO_4 removed 96% of the Cr from SY-102 sludge (Lumetta, Swanson, and Barker 1995).

Similar results have been observed with several other sludges. Treating the caustic-leached sludge from SY-103 with a stoichiometric amount of KMnO_4 removed ~90% of the residual Cr, although treating the caustic-leached sludge from B-111 removed only an additional ~30% of its residual Cr (Rapko, Lumetta, and Wagner 1996). Treating a water-washed 101-SY sludge simulant with permanganate removed more than 90% of the water-insoluble Cr, and treating the actual, water-washed 101-SY sludge increased the soluble Cr concentration between 5 and 50 fold (Orth et al. 1995).

Chromium dissolves in the presence of permanganate when poorly soluble Cr(III) oxidizes to Cr(VI), which is highly soluble in alkaline media. This oxidation proceeds according to the following reaction:



For every mole of Cr leached from the sludge, one mole of Mn is added in the form of MnO_2 . Adding Mn to the sludge should not cause a major problem because the Mn limit in the HLW glass feed is expected to be much higher than that for Cr, although the Mn limit in the HLW glass feed has not been defined.

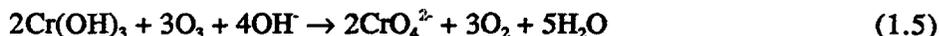
Alternatively, other oxidants could be examined that would add no additional mass to the HLW. Under alkaline conditions, the oxidation potential for the Cr(III) to Cr(VI) half reaction is given as



$$E^\circ = -0.12 \text{ V vs NHE (at } 1 \text{ M } [\text{OH}^-]) \quad (1.4)$$

To successfully oxidize Cr(III) to Cr(VI) under alkaline conditions, the potential for candidate oxidants should therefore be significantly greater (more positive) than -0.12 V. Three candidates that meet the above criterion are hydrogen peroxide (H_2O_2), $E^\circ = 0.87 \text{ V}$, oxygen (O_2), $E^\circ = 0.40 \text{ V}$, and ozone (O_3), $E^\circ = 1.24 \text{ V}$. For reference, permanganate's potential is 0.53 V.

Chromium(III) oxidation by ozone to alkaline-soluble chromate proceeds according to the following reaction:

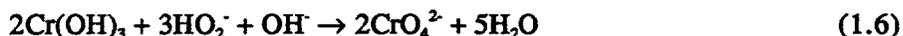


Unlike permanganate, whose reduced form (MnO_2) leaves an insoluble residue, the reduced form of ozone is gaseous oxygen, which obviously will add no additional mass to the residual sludge.

Previous studies have examined the consequences of contacting tank sludges with ozone under alkaline conditions. Ozone was contacted with sludge from SY-101 at 0.6 to 0.3 M hydroxide. Quantitative dissolution of Cr was observed; however, ~80% of the total Pu dissolved also (Delegard, Stubbs, and Bolling 1993). Leached sludges from tanks B-111 and SY-103 at $\leq 0.01 \text{ M NaOH}$ were

also examined: comparable Cr dissolution to that of permanganate treatment was observed. However, unlike the results from SY-101, less than 5% of the Pu was solubilized by treatment with ozone (Rapko, Lumetta, and Wagner 1996). Given the efficacy of ozone at Cr dissolution, and since the factors underlying Pu dissolution appear uncertain, ozone may still be considered a viable candidate oxidant.

Chromium (III) oxidation by hydrogen peroxide to chromate proceeds under alkaline conditions according to the following reaction:



Here, the reduced form of hydrogen peroxide leaves only water and so adds no additional mass to the residual sludge.

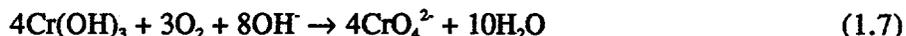
In addition, an aqueous alkaline peroxide treatment is used to oxidatively dissolve Cr(III) to form chromate for spectrophotometric analyses (Oelschläger 1955; Sandell 1959; Kirk-Othmer 1993). For these reasons, peroxide is an attractive candidate oxidant for sludge processing.

The application of alkaline peroxide solution to dissolve $\text{Cr}(\text{OH})_3$ (am) from sludge residues remaining after dilute alkali washing of simulated SY-101 waste and genuine tank wastes from SY-101 and SY-102 has been tested and reported (Delegard 1995). Oxidative dissolution of $\text{Cr}(\text{OH})_3$ (am) from the SY-101 simulant waste residues ranged from 30 to 65% at room temperature using 3 M NaOH and two contacts each with 1-fold and 10-fold stoichiometric peroxide, respectively.

Actual tank sludges behaved very differently than the simulant. Treating water-washed SY-102 sludge with a 10-fold excess of hydrogen peroxide in 0.1 M NaOH delivered in successive 5% aliquots at room temperature led to foaming in the reaction container and resulted in a less than 2% increase in the amount of dissolved Cr (Lumetta and Swanson 1993). In a more recent study, water-washed sludges from SY-101 and SY-102 were contacted with excess hydrogen peroxide in 3 M NaOH at room temperature. Effectively no additional Cr dissolution occurred over that observed through a standard caustic leach (Delegard 1995). These findings were discussed with Professor Nikolai N. Krot of the Institute of Physical Chemistry of the Russian Academy of Sciences. He proposed that additional tests be conducted to identify the effects of temperature and catalysts.

Accordingly, parametric tests were devised to determine the effects of temperature (room and 80°C), NaOH concentration (1 and 3 M), hydrogen peroxide and its addition method (at-once or stepwise), and catalyst {with or without 0.2 mM Co(II)} on the dissolution of Cr_2O_3 . Chromium(III) oxide was used to model the behavior of Cr in tank sludges because it represents the expected pure Cr(III) phase resulting from hydrothermal aging of $\text{Cr}(\text{OH})_3$ (am). If satisfactory results were obtained, testing Cr leaching with hydrogen peroxide could then be conducted at the optimum conditions on actual tank sludges.

Oxygen oxidation of Cr(III) proceeds according to the following reaction:



Here, the reduced form of the oxidant is water, which again adds no additional mass to the residual sludge.

In summary, work described in this report examines the effectiveness of solubilizing Cr from Hanford tank sludges previously leached with caustic by oxidation under alkaline conditions. The sludges examined were from tanks BY-110, S-107, and SX-108, all of which have previously undergone sludge washing and caustic leaching testing. The oxidants examined in this study included permanganate (MnO_4^-), ozone (O_3), and elemental oxygen (O_2). In addition, the ability of hydrogen

peroxide (H_2O_2) to dissolve Cr under alkaline conditions was investigated using Cr oxide as a model for the Cr in the sludges.

2.0 Experimental Materials and Methods

2.1 Oxidative Leaching of Cr from Hanford Tank Sludges

For a given sample of Hanford tank sludge, the Cr leaching tests were performed on sludge previously subjected to the steps in the baseline pretreatment process. Specifically, the sludge was washed with 0.01 M NaOH, twice leached with a (3 M) sodium hydroxide solution, and thrice washed with 0.01 M NaOH before leaching Cr. The general approach for pretreating the sludge before testing, which involves the following steps, is illustrated schematically in Figure 2.1:

- washing the sludge with 0.01 M NaOH to remove soluble salts such as NaNO_3 , NaNO_2 , NaOH, Na_2CO_3 , Na_3PO_4 , etc.
- leaching the sludge with 3 M NaOH at 100°C to remove additional elements such as Al^{3+} and such anions as PO_4^{3-} .
- washing the leached sludge with 0.01 M NaOH to remove added NaOH and materials dissolved in the caustic leaching step
- dividing the residual solids into several portions. A small fraction of a suspension of the caustic-leached sludge was removed, weighed, and evaporated to a constant weight at 105°C. With this measurement, the weight fraction of sludge in the suspension can be measured. Together with the previously measured concentration of Cr in the caustic-leached sludge (Lumetta et al. 1996a), the amount of sludge required to allow detection of 5% of the available Cr as chromate by visible spectroscopy was targeted. An additional constraint on the targeted amount of caustic-leached sludge was the presence of at least 0.25 grams of solid so as to provide for sufficient material for residue analysis after completing the Cr leaching tests. The leachate solutions were sampled at various times during the test to determine the free-hydroxide concentration by titration with standard 0.1 M HCl, the Cr(VI) concentration by visible spectroscopy, and the total alpha concentrations by liquid scintillation counting.
- separating the leachate solutions from the undissolved solids following contact with the solids. The residual solids were dissolved and analyzed along with the final leachate solutions. Inductively-coupled plasma/atomic emission spectroscopy (ICP/AES) was used to determine the major nonradioactive sludge components (especially Cr) and a radiochemical method, alpha energy analysis (both before and after a Pu separation step was performed) was used to determine if TRU elements dissolved significantly.

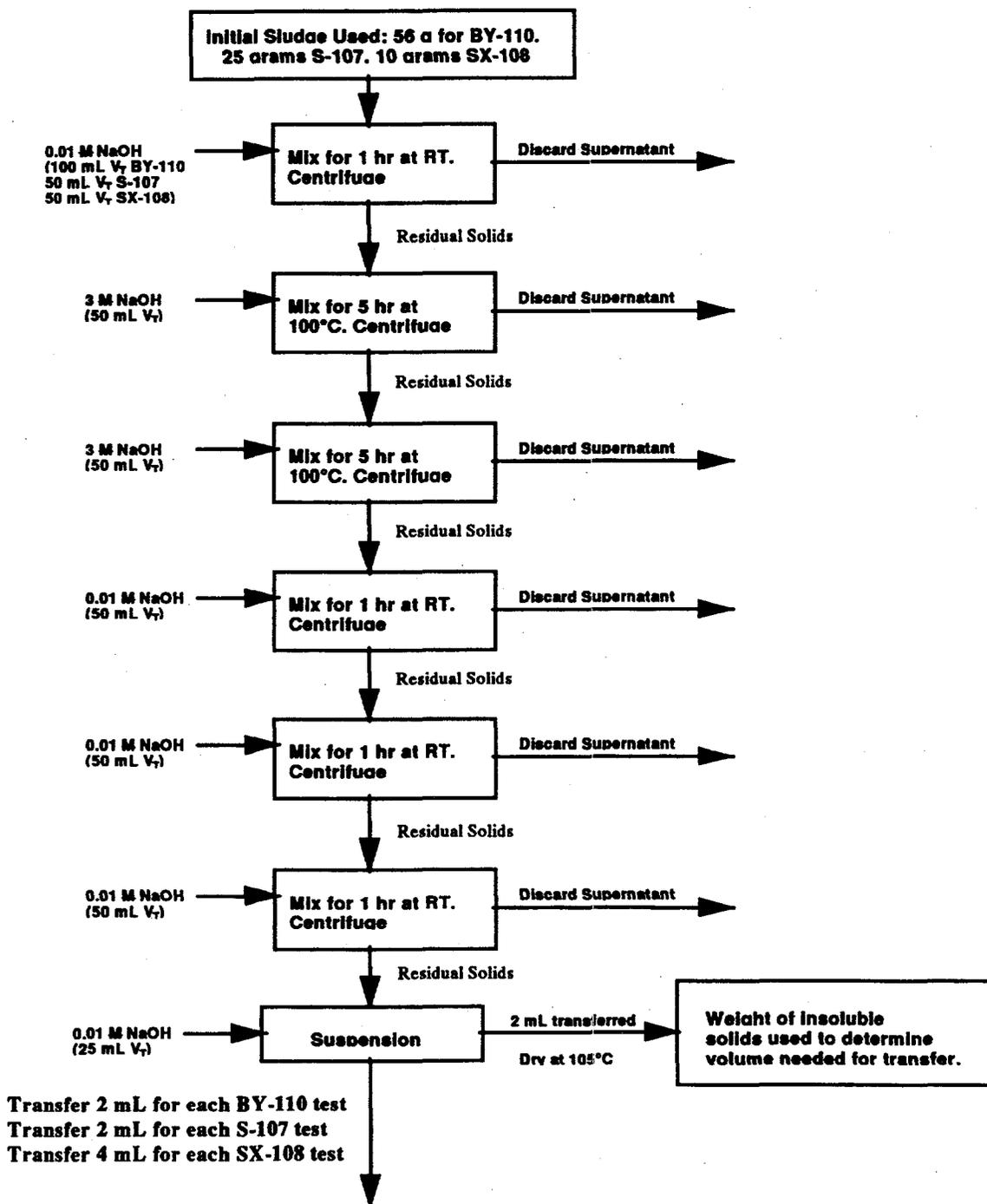


Figure 2.1. Schematic Representation of the Preparation of Sludges for the Cr Leach Tests

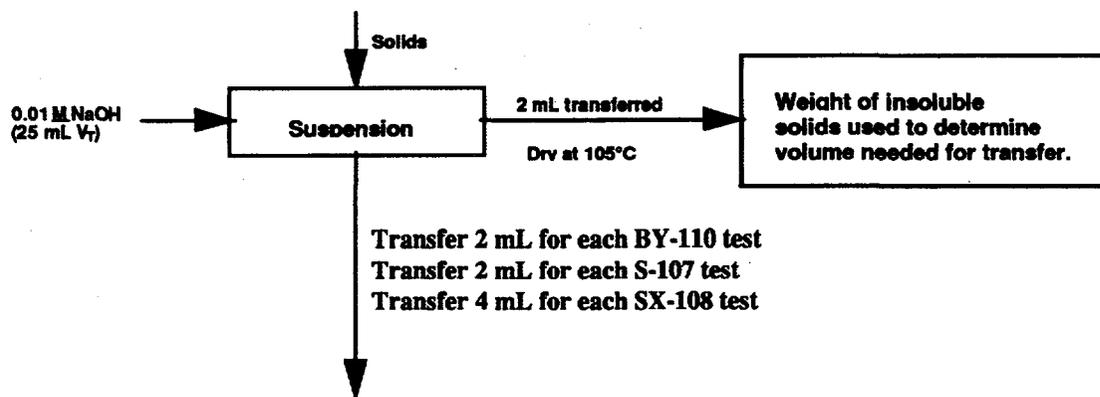


Figure 2.1. Continued

Three sludges were tested in this study: a sludge composite from BY-110, a sludge composite from S-107, and a sludge composite from SX-108. These samples were chosen because they were found to have significant concentrations of residual Cr following the sludge washing and caustic leaching testing conducted during FY 96 (Lumetta et al. 1996a) (Table 2.1). In addition, these sludges all represent major tank groups that are expected to have the largest contributions of residual Cr following the baseline pretreatment process (Colton 1996, Agnew 1997).

A suspension of the caustic-leached materials was transferred in the 325 Building hot cells to tared, 60-mL plastic bottles and reweighed. These weights, coupled with the Cr concentration reported for the leached sludges (Lumetta et al. 1996a), were used to calculate the amount of permanganate needed to achieve the desired ratio of permanganate:Cr. The bottles were transferred from the hot cells into the laboratory and centrifuged, and the supernatant was decanted off. The solids were suspended in either 0.1 M NaOH or 3 M NaOH as appropriate, and the oxidant was introduced. The total volume of these suspensions was 50 mL.

The flowrate of the gases introduced was monitored with a flowmeter and set at 19 cc/min. Ozone was generated from oxygen by an Ozone Research & Equipment Corporation Model O3V5-0 ozonator and was bubbled directly into the second and third solutions. Based on the calibration information contained in the owner's manual under the power and oxygen flow rate used in these tests, the gas that bubbled through the test suspensions (ca. 6 wt% ozone in oxygen) introduced an estimated 1.8 g of ozone/h. This kept these test solutions constantly in contact with fresh oxidant and introduced a large excess of oxidant over the course of the experiment. Oxygen was introduced similarly through the ozonator apparatus, but the absence of any radio frequency power prevented the formation of ozone. Argon was introduced directly through the flowmeter and into the test suspensions.

The reaction bottles were placed in an Al heating block in which five holes, sized to securely hold the 60-mL bottles, were cut. This Al block was placed on top of the five-place heater/stirrers. The depth of the holes kept the test solution entirely surrounded by the Al heating block. Four test samples were examined at one time; the fifth position contained a blank solution of hydroxide and contained a thermocouple. The presence of the thermocouple allowed for both temperature monitoring and temperature control to within 1°C.

Table 2.1. Summary of Sludges Used in Cr Leach Tests

| Tank | SOWRT Group | Primary Waste Type ^(a) | Secondary Waste Type ^(a) | [Cr] in Leached Sludge (µg/g solids) ^(b) |
|--------|-------------|-----------------------------------|-------------------------------------|---|
| BY-110 | III | TBP-F | EB-ITS | 19250 |
| S-107 | I | R | EB | 13100 |
| SX-108 | IV | R | None | 5760 |

(a) The waste types are defined as follows (Hill, Anderson, and Simpson 1995).
 EB Evaporator bottoms
 F Ferrocyanide-scavanged waste
 ITS In-tank solidification
 R High-level Reduction Oxidation (REDOX) process waste
 TBP Waste from tributylphosphate extraction

(b) As reported in Lumetta et al. 1996a.

As summarized in Table 2.2, eight tests were performed with BY-110 and S-107 sludge; only the first four tests were performed with SX-108 sludge. In the first test, a 0.1 M potassium permanganate/0.1 M NaOH solution was added to the sludge suspended in 0.1 M NaOH until a 100% stoichiometric excess (2:1) permanganate:Cr ratio was obtained. In the second test, a 0.1 M potassium permanganate/0.1 M NaOH solution was added to the sludge suspended in 3 M NaOH until a 2:1 ratio of permanganate to Cr was obtained. In the third test, the sludge, suspended in 0.1 M NaOH, was contacted solely with ozone. In the fourth test solution, ozone was added to sludge suspended in 3 M NaOH. In the fifth test, oxygen was added to sludge suspended in 0.1 M NaOH, and in the sixth test, oxygen was added to sludge suspended in 3 M NaOH. The seventh and eighth tests were designed as controls; argon gas was bubbled through sludge suspended in 0.1 and 3 M NaOH, respectively.

Table 2.2. Summary of Conditions in the Cr Leach Experiments

| Experiment # | Conditions | Targeted Oxidant:Cr Stoichiometry |
|--------------|----------------------------|-----------------------------------|
| 1 | Permanganate in 0.1 M NaOH | 2 |
| 2 | Permanganate in 3 M NaOH | 2 |
| 3 | Ozone in 0.1 M NaOH | Large Excess |
| 4 | Ozone in 3 M NaOH | Large Excess |
| 5 | Oxygen in 0.1 M NaOH | Large Excess |
| 6 | Oxygen in 3 M NaOH | Large Excess |
| 7 | Argon in 0.1 M NaOH | Not Applicable |
| 8 | Argon in 3 M NaOH | Not Applicable |

In a similar fashion to last year's Cr leach tests, the samples were stirred at room temperature for the first 24 hours, and the solutions were then heated at 80°C for the remainder of the experiment. After the samples were mixed with the oxidant, test samples were taken as soon as possible (0 hours), and then after 3 hours, 7 hours, 24 hours, and 31 hours of total reaction time. The aliquots were passed through a 0.2 micron filter before analysis by liquid scintillation counting and by ultraviolet visible (UV-vis) spectroscopy.

Portions of each of the sample aliquots were diluted as necessary with 0.01 M NaOH, and the spectra from 350 to 800 nm were recorded on a Spectral Instrument's 400 series CCD array UV-vis spectrophotometer. The chromate concentrations were determined by measuring the test solution's absorbance at 372 nm, which is the wavelength of maximum absorbance for chromate in the visible spectrum. The instrument was calibrated using standards-grade potassium dichromate in 0.05 M KOH according to standard procedures (Gordon and Ford 1972). The instrument showed good linearity from 1.75 to 0.01 absorbance units with a slope of 4967 L/mol-cm and a correlation coefficient of better than 0.9999, as compared to the expected slope of 4845 L/mol-cm and correlation coefficient of 1. The calibration curve was then used to calculate a sample's Cr concentration from its measured 372-nm absorbance.

The samples were centrifuged, and the supernatants were decanted after the tests were completed. The free [OH⁻] of the supernatant after testing was measured through titration with a standard HCl solution using a Mettler DL21 automatic titrator equipped with a Ross combination pH electrode (Orion Research Inc., Boston, Massachusetts). The residual solids were twice washed with the

appropriate concentration of NaOH to remove any components present in the interstitial liquid. After each wash, the samples were centrifuged, and the supernatant was added to the final leachate. The washed residual solids were suspended in distilled water, transferred to a small glass vial, and dried to a constant weight at 105°C. These residual solids were taken to the hot cells and dissolved either through a sodium peroxide fusion method (BY-110 and S-107) or by KOH fusion in a Ni crucible (SX-108). The content of the major metallic elements in both the supernatants and dissolved residues was determined by ICP-AES, and the activity due to TRU elements in both the supernatants and dissolved residues was determined by alpha energy analysis. A Pu separation step was employed to improve the detection limits and to determine the extent of Pu dissolution more precisely. Established procedures were used for these latter analyses.^(a)

2.2 Cr Leaching with Hydrogen Peroxide

A set of 20 experiments was designed to evaluate the optimum conditions for oxidative dissolution of reagent Cr₂O₃ by peroxide in alkaline solution. All chemicals were of reagent grade and not further purified. Distilled and deionized water was used throughout. The reaction vessels were capped 50-mL polypropylene centrifuge cones. Each experiment was performed using 10.0 mL of 1.0 or 3.0 M NaOH solution to which was added 0.100 ± 0.004 g Cr₂O₃ (0.132 M in total Cr) and a Teflon-clad magnetic stirbar. In selected tests, sufficient cobalt(II) nitrate was added to yield a solution 2 × 10⁻⁴ M in cobalt. For experiments conducted at elevated temperature (80°C), the centrifuge cones were placed in water baths on thermostatted stirrer hotplates. Tests conducted at room temperature used only stirring. Heat from the stirrer motor increased these room-temperature test solutions to 26°C. When the test solutions came to thermal equilibrium, 30% hydrogen peroxide was added to selected tests. The H₂O₂ was introduced in two manners (at once, or stepwise in four equal daily additions) to give 0.39 M total H₂O₂ (two-times the stoichiometric requirement for complete oxidative dissolution of Cr₂O₃). The test matrix is shown in Table 2.3.

The total reaction time was 4 days. At the end of 4 days, the test vessels were centrifuged, and the clarified supernatant was decanted to separate the solution from the undissolved Cr₂O₃.

(a) Analytical Chemistry Laboratory Department. *Analytical Chemistry Laboratory (ACL) Procedure Compendium*. PNL-MA-599. Pacific Northwest Laboratory, Richland, Washington.

Table 2.3. Test Matrix for Cr Dissolution by H₂O₂

| Expt. # | H ₂ O ₂ Addition Steps | Temperature, °C | [Co(II)], mM | [NaOH], M |
|---------|---|-----------------|--------------|-----------|
| 1 | 4 | 26 | 0.2 | 1 |
| 2 | 4 | 26 | 0.2 | 3 |
| 3 | 4 | 26 | 0 | 1 |
| 4 | 4 | 26 | 0 | 3 |
| 5 | 4 | 80 | 0.2 | 1 |
| 6 | 4 | 80 | 0.2 | 3 |
| 7 | 4 | 80 | 0 | 1 |
| 8 | 4 | 80 | 0 | 3 |
| 9 | 1 | 26 | 0.2 | 1 |
| 10 | 1 | 26 | 0.2 | 3 |
| 11 | 1 | 26 | 0 | 1 |
| 12 | 1 | 26 | 0 | 3 |
| 13 | 1 | 80 | 0.2 | 1 |
| 14 | 1 | 80 | 0.2 | 3 |
| 15 | 1 | 80 | 0 | 1 |
| 16 | 1 | 80 | 0 | 3 |
| 17 | none | 26 | 0 | 1 |
| 18 | none | 26 | 0 | 3 |
| 19 | none | 80 | 0 | 1 |
| 20 | none | 80 | 0 | 3 |

The supernatant solutions were analyzed spectrophotometrically for dissolved Cr present as chromate ($\lambda_{\text{max}} = 372 \text{ nm}$) as described above. Since a different sample chamber is used for radioactive vs. non-radioactive samples, the spectrophotometer was recalibrated. Absorbance standards were prepared by diluting a 0.0140 M K₂Cr₂O₇ stock solution in 1 M NaOH (dichromate [Cr₂O₇²⁻] rapidly hydrolyzes in alkali to form chromate). The standards showed excellent adherence to the Beer-Lambert Law ($R^2 = 0.9998$) with a molar extinction coefficient, ϵ , of $4836 \pm 20 \text{ L/mol-cm}$. The absorbance of direct or diluted portions of test solutions was measured at 372 nm. From this absorbance, the Cr (as chromate) concentrations were determined, and the fraction of Cr dissolved was calculated.

3.0 Results and Discussion

3.1 Alkaline Dissolution of Cr₂O₃ by Hydrogen Peroxide

The balanced design of the parametric tests and the fact that none of the parameters interacted allows for ready calculation of the average effects of varying the test parameters (e.g., temperature, NaOH concentration) on Cr₂O₃ dissolution. The results are summarized in Table 3.1.

Table 3.1. Effect of Test Variables on Alkaline Dissolution of Cr₂O₃ by Hydrogen Peroxide

| Parameter | Range | Effect (%) |
|---|-------------------|------------|
| [NaOH] | 1 → 3 <u>M</u> | +21 |
| Temperature | 26 → 80°C | +300 |
| H ₂ O ₂ | 0 → 0.39 <u>M</u> | +42 |
| H ₂ O ₂ additions | 1 → 4 | +6 |
| Co(II) catalyst | 0 → 0.2 <u>mM</u> | -1 |

The data show the relative improvements achieved by changing parameters over the selected ranges. Thus, increasing temperature from 26 to 80°C increased dissolution three-fold. Peroxide addition (to 0.39 M) increased dissolution 42%. The remaining parameters, NaOH concentration, stepwise H₂O₂ addition, and the presence or absence of a Co(II) catalyst had lesser influence.

Figure 3.1 illustrates the total Cr dissolution for these different variables. The plot clearly shows that dissolution was increased by increasing temperature and NaOH concentration. However, total Cr₂O₃ dissolution never exceeded 1%, and the enhancement provided by any H₂O₂ treatment, despite the use of a two-fold stoichiometric excess of oxidant, was marginal under the studied conditions.

3.2 Alkaline Dissolution of Cr from Actual Hanford Tank Wastes

3.2.1 Background

In last year's work on oxidative dissolution of Cr (Rapko, Lumetta, and Wagner 1996), the leach solutions had an initial free hydroxide concentration of 0.01 M. However, the consumption of hydroxide that occurred concomitant with Cr oxidation was sufficiently large that major changes in the free-hydroxide concentration occurred during the experiment. These changes increased the difficulty in interpreting the results concerning component dissolution. To prevent such complications in this year's study, higher concentrations of free hydroxide in the leach solutions were used: 0.1 and 3 M NaOH, respectively. Table 3.2 shows that little deviation in the targeted free-hydroxide concentrations occurred during the course of these experiments.

Another potential artifact that might complicate interpretation of the experimental results concerns the representative nature of each of the subsections of sludge used as conditions were altered. If the samples themselves significantly vary in composition from test to test, any comparisons drawn about the effects of varying the conditions would be questionable. Table 3.3 attempts to address this possibility. The table contains the ratios of some key, major, nonradioactive components in each sample used in the testing. These ratios were determined by summing up the mass of each component in the oxidatively leached sludges and in the leach solutions, calculating the total mass of each component and ratioing the moles present for the indicated elements. The ratios from last

year's caustic leaching study were obtained by taking the elemental concentrations of the elements, calculating the molar concentrations and then ratioing these molar concentrations. Two ratios are presented. The first presents the Al/Fe molar ratio. Since the major mass changes that occur during caustic leaching are primarily due to Al dissolution, the Al/Fe ratio should indicate whether the degree of Al removal was comparable to the results found during prior caustic leach testing. The second presents the Cr/Fe molar ratio and helps ensure that the Cr also behaved as previously reported. Having a caustic-leached sludge with similar properties to that described in the earlier caustic leaching study is important since some experimental parameters (such as the amount of added permanganate) were derived based on the Cr concentrations in the caustic leached sludge as measured in the earlier test.

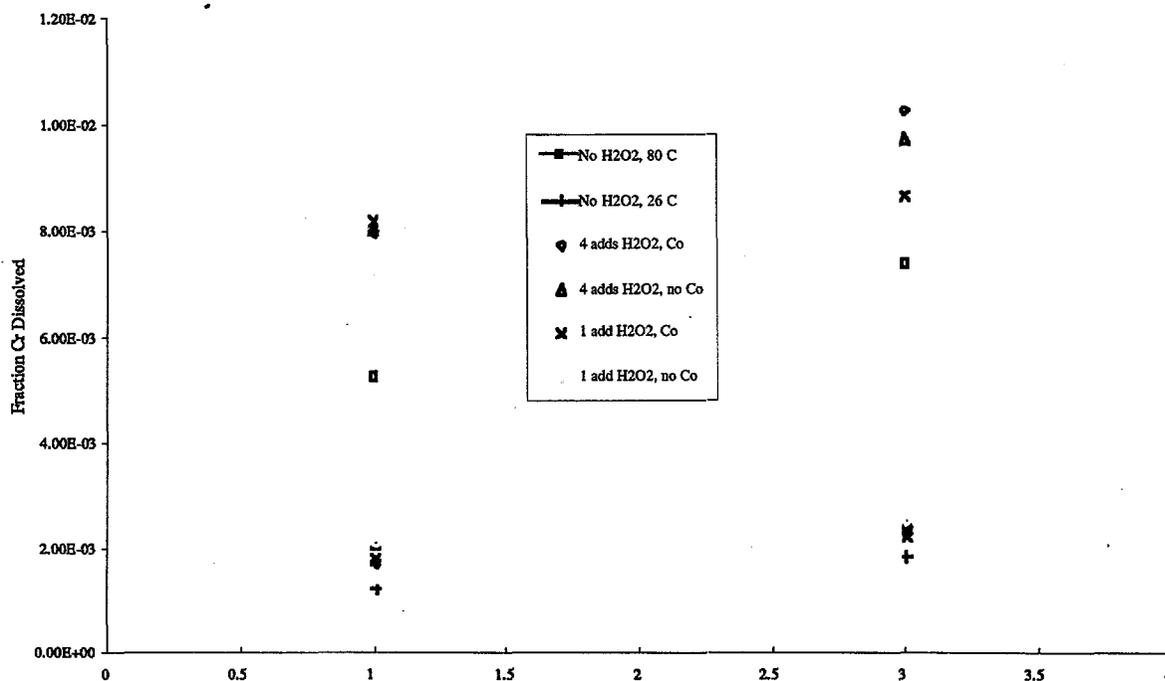


Figure 3.1. Cr Dissolution from Cr_2O_3 by Alkaline Hydrogen Peroxide

Table 3.3 shows two key features. The first is that, in general, the Cr/Fe and Al/Fe molar ratios are comparable to those reported in previous caustic leaching studies (Lumetta et. al. 1996). This is despite the larger leachate to solids ratios used here to prepare the sludges as well as the use of two 5-hour 3 M NaOH leach steps rather than the one 5-hour 2 M NaOH and the one 5-hour 3 M NaOH leaches previously studied. Somewhat more effective removal of Al and Cr was found for the BY-110 and S-107 samples compared to the previous caustic leaching studies, and somewhat less effective removal of Al and Cr was found with SX-108.

The second significant finding is that all of the subsamples of a particular sludge type have closely comparable ratios of Al, Cr, and Fe: this is remarkable given $\pm 15\%$ uncertainty in the concentration of each component in the ratio. This indicates that the method for distributing the sludges to each individual test vessel gave sludge with essentially the same composition. This lends confidence that meaningful comparisons can be drawn in the Cr leach behavior based solely on how the oxidative leach conditions are varied.

Table 3.2. Final Free-Hydroxide Concentration in Cr Leach Solutions

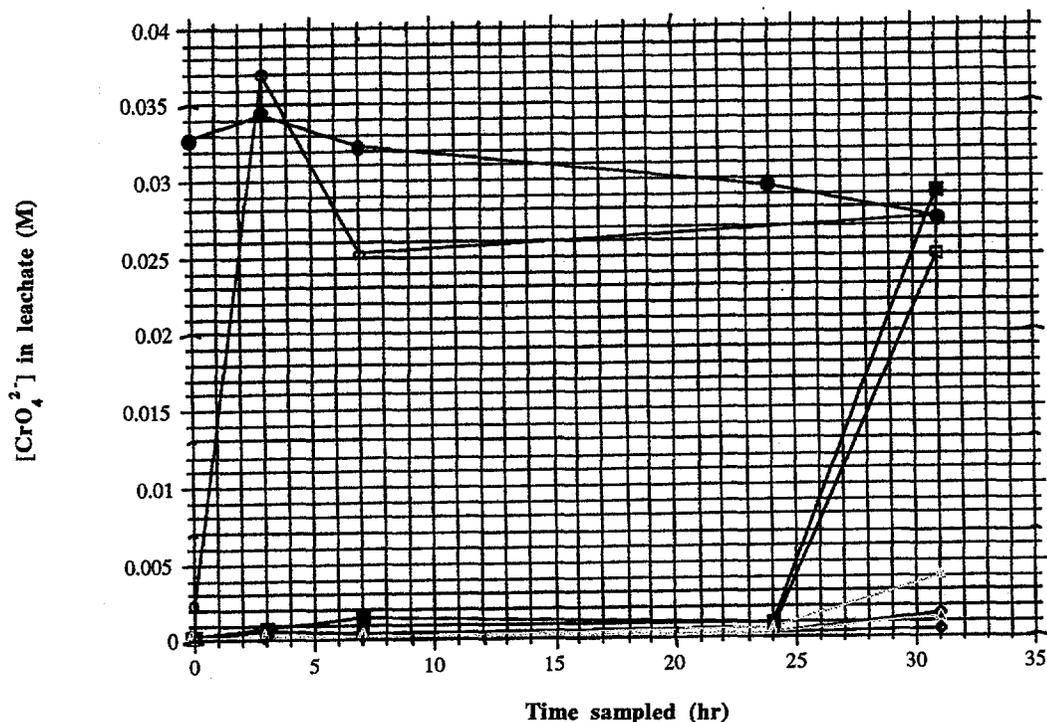
| Experiment | [OH] Found |
|--|-----------------------------|
| BY-110 (KMnO ₄ in 0.1 <u>M</u> NaOH) | 0.12 |
| BY-110 (KMnO ₄ in 3 <u>M</u> NaOH) | 2.59 |
| BY-110 (Ozone in 0.1 <u>M</u> NaOH) | 0.09 |
| BY-110 (Ozone in 3 <u>M</u> NaOH) | 2.77 |
| BY-110 (Oxygen in 0.1 <u>M</u> NaOH) | 0.10 |
| BY-110 (Oxygen in 3 <u>M</u> NaOH) | 2.90 |
| BY-110 (Argon in 0.1 <u>M</u> NaOH) | 0.16 |
| BY-110 (Argon in 3 <u>M</u> NaOH) | 2.81 |
| | |
| S-107 (KMnO ₄ in 0.1 <u>M</u> NaOH) | 0.11 |
| S-107 (KMnO ₄ in 3 <u>M</u> NaOH) | 2.76 |
| S-107 (Ozone in 0.1 <u>M</u> NaOH) | 0.45 (0.11 ^(a)) |
| S-107 (Ozone in 3 <u>M</u> NaOH) | 2.88 |
| S-107 (Oxygen in 0.1 <u>M</u> NaOH) | 0.12 |
| S-107 (Oxygen in 3 <u>M</u> NaOH) | 2.82 |
| S-107 (Argon in 0.1 <u>M</u> NaOH) | 0.10 |
| S-107 (Argon in 3 <u>M</u> NaOH) | 2.92 |
| | |
| SX-108 (KMnO ₄ in 0.1 <u>M</u> NaOH) | 0.10 |
| SX-108 (KMnO ₄ in 3 <u>M</u> NaOH) | 2.62 |
| SX-108 (Ozone in 0.1 <u>M</u> NaOH) | 0.09 |
| SX-108 (Ozone in 3 <u>M</u> NaOH) | 2.70 |
| (a) Contaminated with 3 <u>M</u> NaOH at the conclusion of the experiment. | |

3.2.2 Chromate Formation in Alkaline Leachate Solutions

Changes in the amount of Cr in the leachate solution were monitored by visible spectroscopy and are illustrated in Figures 3.2 through 3.4. Visible spectroscopy provides two pieces of information: the Cr concentration in solution and the oxidation state of Cr. If Cr is present in the +6 oxidation state, i.e., as CrO₄²⁻, maximum absorbance occurs at ~372 nm. If Cr is present in the +3 oxidation state, i.e., as Cr(OH)₃, a maximum absorbance at ~600 nm is observed. In all cases, absorbance at 372 nm only was observed, indicating that the dissolved Cr described below was present as chromate.

Table 3.3. Molar Ratios of Aluminum, Chromium, and Iron in Caustic-Leached Sludge Samples Before Alkaline Oxidation Testing

| Experiment | [Al]/[Fe] in Caustic Leached Sludge | [Cr]/[Fe] in Caustic Leached Sludge |
|---|-------------------------------------|-------------------------------------|
| BY-110 (Residue after Caustic Leaching) ^(a) | 0.234 | 0.169 |
| BY-110 (KMnO ₄ in 0.1 M NaOH) | 0.438 | 0.202 |
| BY-110 (KMnO ₄ in 3 M NaOH) | 0.443 | 0.195 |
| BY-110 (Ozone in 0.1 M NaOH) | 0.444 | 0.213 |
| BY-110 (Ozone in 3 M NaOH) | 0.520 | 0.225 |
| BY-110 (Oxygen in 0.1 M NaOH) | 0.447 | 0.204 |
| BY-110 (Oxygen in 3 M NaOH) | 0.495 | 0.203 |
| BY-110 (Argon in 0.1 M NaOH) | 0.482 | 0.208 |
| BY-110 (Argon in 3 M NaOH) | 0.507 | 0.214 |
| Mean | 0.472 ± 0.033 | 0.208 ± 0.009 |
| S-107 (Residue after Caustic Leaching) ^(a) | 25.8 | 0.644 |
| S-107 (KMnO ₄ in 0.1 M NaOH) | 40.5 | 0.622 |
| S-107 (KMnO ₄ in 3 M NaOH) | 43.8 | 0.711 |
| S-107 (Ozone in 0.1 M NaOH) | 39.9 | 0.589 |
| S-107 (Ozone in 3 M NaOH) | 38.4 | 0.771 |
| S-107 (Oxygen in 0.1 M NaOH) | 40.3 | 0.631 |
| S-107 (Oxygen in 3 M NaOH) | 34.9 | 0.652 |
| S-107 (Argon in 0.1 M NaOH) | 40.5 | 0.642 |
| S-107 (Argon in 3 M NaOH) | NA | NA |
| Mean | 39.8 ± 2.7 | 0.660 ± 0.061 |
| SX-108 (Residue after Caustic Leaching) ^(a) | 7.80 | 0.0863 |
| SX-108 (KMnO ₄ in 0.1 M NaOH) | 6.51 | 0.0669 |
| SX-108 (KMnO ₄ in 3 M NaOH) | 7.65 | 0.0783 |
| SX-108 (Ozone in 0.1 M NaOH) | 6.18 | 0.0639 |
| SX-108 (Ozone in 3 M NaOH) | 6.91 | 0.0725 |
| Mean | 6.81 ± 0.63 | 0.07 ± 0.006 |
| (a) Taken from FY 1996 caustic leaching study (Lumetta et al. 1996a). NA = Data not available. | | |



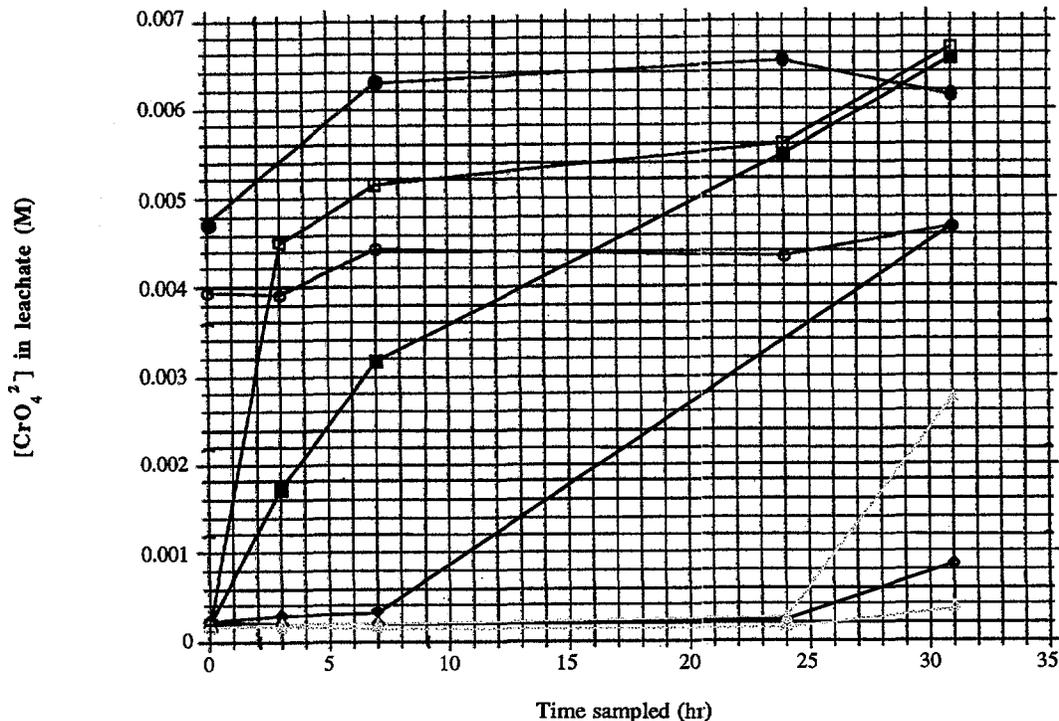
Red open circles: KMnO_4 in 0.1 M NaOH
 Red solid circles: KMnO_4 in 3 M NaOH
 Blue open squares: ozone in 0.1 M NaOH
 Blue solid squares: ozone in 3 M NaOH
 Black open diamonds: oxygen in 0.1 M NaOH
 Black solid diamonds: oxygen in 3 M NaOH
 Yellow open triangles: argon in 0.1 M NaOH
 Yellow solid triangles: argon in 3 M NaOH

Figure 3.2. Chromate Formation in Leachates Contacted with Caustic-Leached BY-110 Sludge

However, the sensitivity of the visible spectrum to the amount of dissolved Cr in the +6 oxidation state is >200 times the +3 oxidation state ($\epsilon(\text{CrO}_4^{2-}) = 4855 \text{ M}^{-1}\text{cm}^{-1}$; $\epsilon(\text{Cr}[\text{OH}]_4) = 22 \text{ M}^{-1}\text{cm}^{-1}$). So even if the absorbance due to chromate were 100 times the absorbance due to Cr(III), the concentration of Cr present as chromate would be only about half that of Cr present as Cr(III). Therefore, determination of the amount of Cr present in each oxidation state by visible spectroscopy alone should be viewed with caution. Comparison of the chromate concentration as determined by visible spectroscopy with a more sensitive method for total Cr present in solution, such as ICP-AES, allows a more sensitive measurement of the fraction of Cr in each oxidation state and is discussed below.

Each of the three sludges examined showed differing responses in the rate and magnitude of chromate formation as a function of the experimental conditions. The behavior of BY-110 (Figure 3.2) is fairly straightforward; contact with permanganate resulted in rapid formation of chromate, and extended times at room temperature or heating of the reaction vessel resulted in a decrease in the leachate's chromate concentration. The source of this decrease following extended reaction times is unknown. Ozone was ineffective at oxidizing Cr(III) to chromate at room temperature, but heating for several hours gave comparable leachate concentrations to those found by

permanganate treatment. Treatment with oxygen or in the absence of any introduced oxidant, i.e., the argon blank, gave little chromate formation with or without heating. Finally, the concentration of free hydroxide had little impact on the rate or the magnitude of chromate formation.

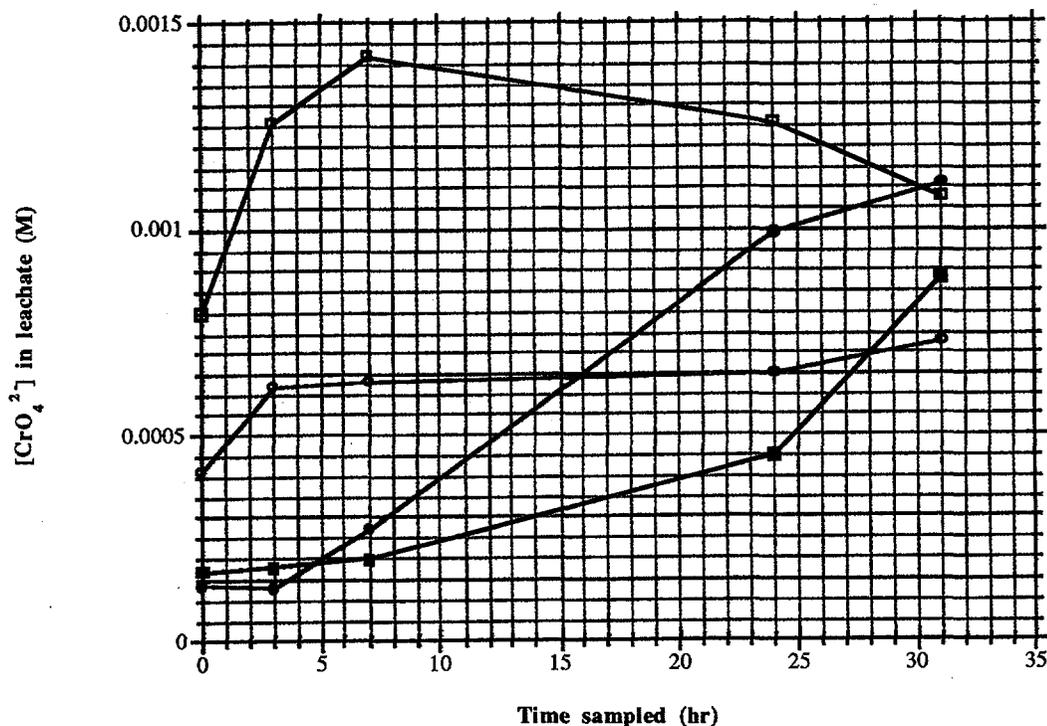


Red open circles: KMnO_4 in 0.1 M NaOH
 Red solid circles: KMnO_4 in 3 M NaOH
 Blue open squares: ozone in 0.1 M NaOH
 Blue solid squares: ozone in 3 M NaOH
 Black open diamonds: oxygen in 0.1 M NaOH
 Black solid diamonds: oxygen in 3 M NaOH
 Yellow open triangles: argon in 0.1 M NaOH
 Yellow solid triangles: argon in 3 M NaOH

Figure 3.3. Chromate Formation in Leachates Contacted with Caustic-Leached S-107 Sludge

The behavior with S-107 (Figure 3.3) is slightly more complex. Like BY-110, the formation of soluble chromate is rapid with permanganate, and additional heating or the concentration of free hydroxide had little influence on the final concentration of chromate. The formation of soluble chromate with ozone appears to be more effective at room temperature with S-107 than with BY-110, with a substantial portion of the total chromate dissolution occurring at room temperature, although in the 0.1 M NaOH case, heating does appear to promote some additional dissolution. Here the concentration of free hydroxide appears to have some influence on the rate of chromate formation, with chromate forming more rapidly at 0.1 M hydroxide than at 3 M NaOH, although the final chromate concentrations in the leachate are similar. Unlike the results found with BY-110, significant chromate formation was found when the leachate solutions were contacted with both oxygen and argon. The effect is much greater at high hydroxide than at low hydroxide, but the concentrations of

chromate at high hydroxide in the presence of oxygen are comparable to those observed with permanganate and ozone. The concentrations of chromate formed even in the presence of argon approached within a factor of 2 to 3 those found with the oxidants. Formation of chromate using oxygen as the oxidant is chemically reasonable, but chromate formation from Cr(III) hydroxide by contact with 3 M NaOH in the presence of argon is not reasonable. The chemical basis for chromate formation in this experiment remains unknown. At low hydroxide concentrations, little chromate formation is observed upon contact with either oxygen or argon.



Red open circles: KMnO_4 in 0.1 M NaOH
 Red solid circles: KMnO_4 in 3 M NaOH
 Blue open squares: ozone in 0.1 M NaOH
 Blue solid squares: ozone in 3 M NaOH

Figure 3.4. Chromate Formation in Leachates Contacted with Caustic-Leached SX-108 Sludge

The behavior of SX-108 is different from either BY-110 or S-107, although contacts with only two chemical agents, permanganate and ozone, were investigated. Here the major determining factor in chromate formation was hydroxide concentration. With either ozone or permanganate, contact with a low free-hydroxide solution gave rapid chromate formation at room temperature, and, at higher free hydroxide, Cr dissolution was slower, and heating was required to maximize chromate formation. A decrease in the leachate's chromate concentration was found for extended reaction times with ozone at low free hydroxide; the reason for this decrease remains unknown.

3.2.3 Rate of Dissolution of Alpha-Emitting Radionuclides In Alkaline Leachate Solutions

The rate and magnitude of dissolution of alpha-emitting elements was monitored by liquid scintillation counting, and the results are illustrated in Figures 3.5 through 3.7. Here the behavior is fairly straightforward and independent of sludge type. Most of the dissolution occurs during the first few hours at room temperature, although additional leaching time at room temperature and contact of the leachate with the sludge at elevated temperature gave small enhancements in the alpha activity in the supernatant. The most significant observation is that the amount of alpha activity in the supernatant appears to be independent of the presence or type of oxidant and is influenced almost entirely by the free-hydroxide concentration of the leachate, as the 3 M free-hydroxide concentrations always possess more alpha activity that the 0.1 M solutions.

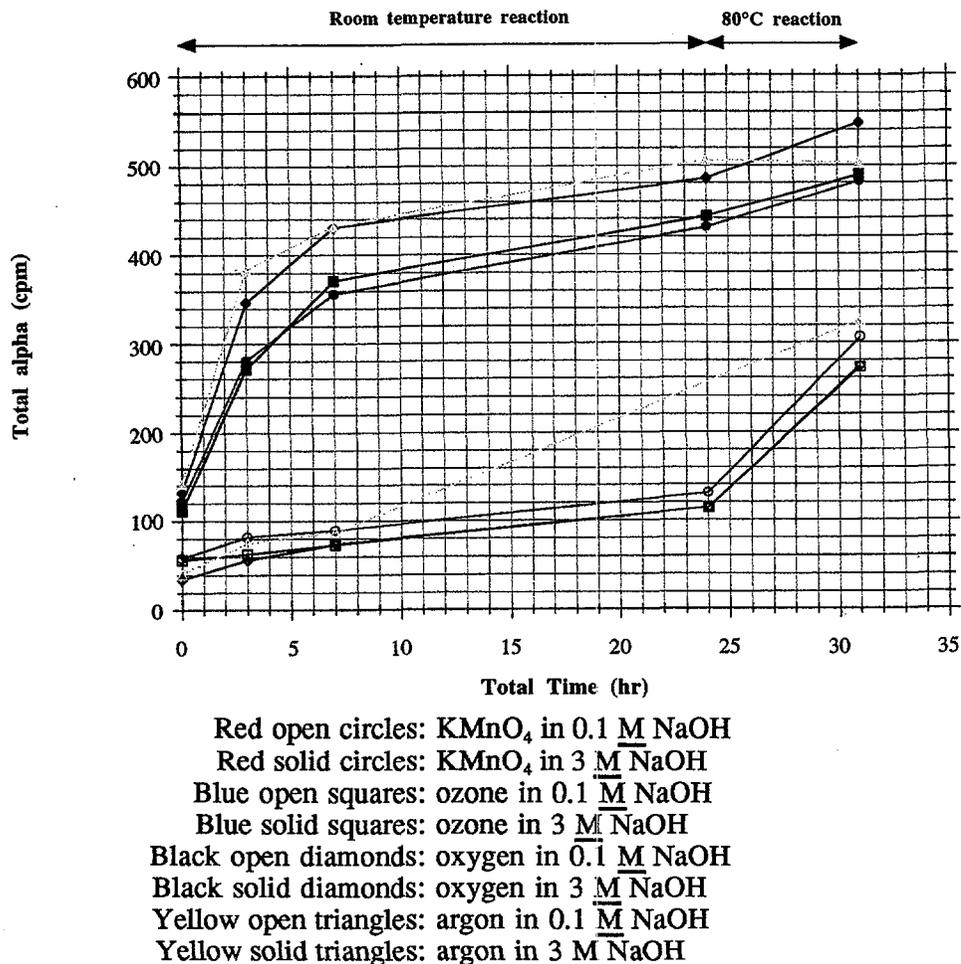


Figure 3.5. Alpha Activity in Leachates Contacted with Caustic-Leached BY-110 Sludge

3.2.4 Removal of Non-Radionuclides by Alkaline Oxidation

The amount of the major non-radionuclides removed by further alkaline leaching of these already sludge washed and caustic leached tank sludges in the presence and absence of added oxidants is summarized in Tables 3.4 through 3.11. These amounts were calculated by summing the mass of the component present in the leachate solution and in the residual solids and comparing the total amount with the amount of the component present in the leachate solution. Table 3.12 reveals

the [Al]/[Fe] and [Cr]/[Fe] molar ratios after further alkaline treatments with and in the absence of added oxidant. The molar ratio is reported since the final washings with 3 M NaOH leaves appreciable amounts of NaOH upon drying, which results in markedly lower final Al, Cr, and Fe concentrations compared to the 0.1 M NaOH leachings. Only three major nonradionuclides showed significant removal during oxidative alkaline leaching with all three sludges: Al, Cr, and Si. Although Cr dissolution is the focus of this study, a brief description of the behavior of these other non-radionuclides seems warranted.

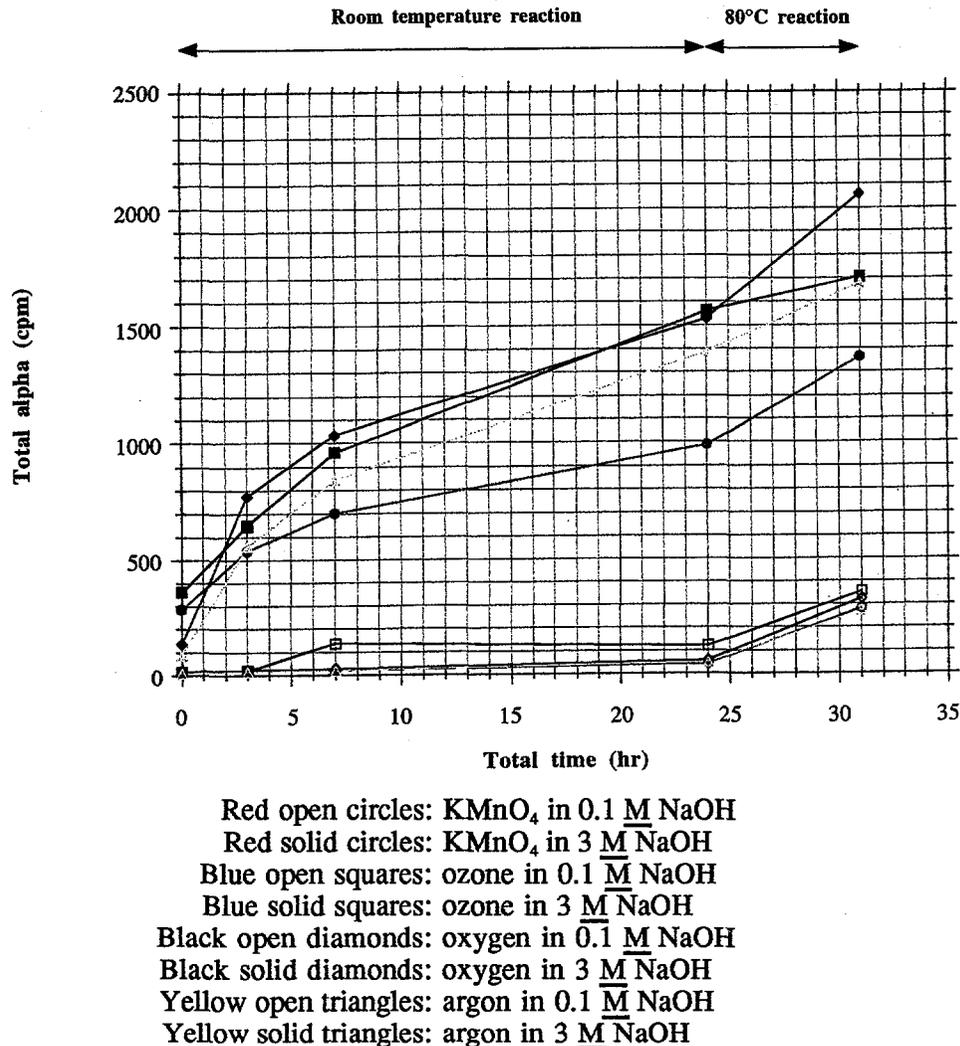


Figure 3.6. Alpha Activity in Leachates Contacted with Caustic-Leached S-107 Sludge

Aluminum dissolution with BY-110 was essentially independent of the free-hydroxide concentration and of whether or not a chemical oxidant was added, suggesting that a fixed amount of readily dissolvable Al remained after the preparative caustic leaching and that the remainder is in a phase poorly soluble or not readily dissolvable. Aluminum dissolution with S-107 and SX-108 is consistent with that expected upon contact with pure Al phases and consistent with the behavior generally seen during the standard caustic leaching tests, i.e., enhanced removal at higher free-hydroxide concentrations. Only small but variable changes occur in the behavior of Si dissolution as free hydroxide and added chemical oxidant are varied. The underlying chemical basis for these changes is unknown. Finally, the following is worth noting regarding S-107: although significant fractions of P appear to be dissolving as a result of these alkaline oxidative leaching steps, the amount of P present

before these contacts was small and close to the detection limit. Consequently, while it may seem like these treatments can remove large amounts of P, only small amounts of additional soluble P are present.

Further Cr dissolution from caustic-leached BY-110 sludge was enhanced by the presence of permanganate or ozone, with between 83 and 94% of the Cr being removed. Hydroxide concentration appears to have some influence on the fraction of Cr being removed, with from 7 to 11% additional Cr being dissolved by increasing the free-hydroxide concentration from 0.1 to 3 M. In short, at similar free-hydroxide concentrations, the use of either permanganate or ozone gave similar results. The use of either oxygen or no added oxidant (Ar) gave minimal (<10%) dissolution of Cr at 0.1 M free hydroxide, but significantly greater dissolution (11 to 28%) at 3 M free hydroxide. The surprising feature is that the fraction of dissolved Cr was greater when Ar (8 and 28% at 0.1 and 3 M [OH], respectively), rather than oxygen (2 and 11% at 0.1 and 3 M [OH], respectively) was introduced to the leachate solutions. The source of oxidant for the leachate in the presence of Ar remains unknown.

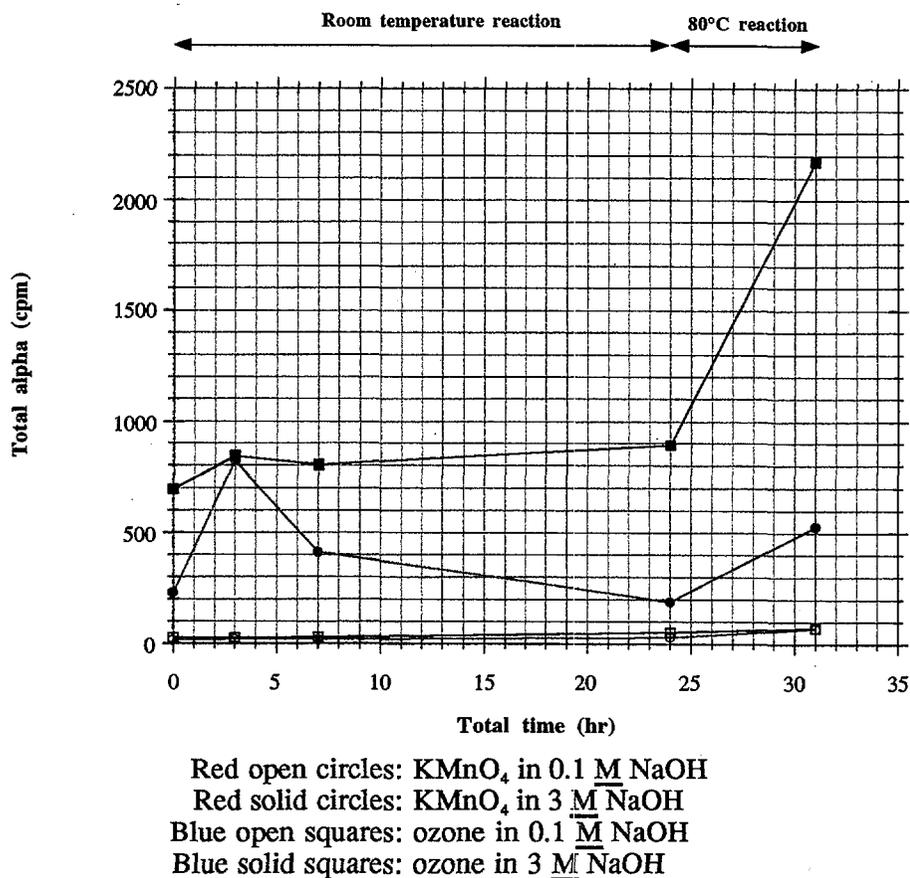


Figure 3.7. Alpha Activity in Leachates Contacted with Caustic-Leached SX-108 Sludge

Table 3.4. Percent Removal of Major Components Following Alkaline Oxidative Leaching of Caustic-Leached Sludge with KMnO_4 in 0.1 M NaOH

| Element | % Dissolved (BY-110) | % Dissolved (S-107) | % Dissolved (SX-108) |
|----------------|----------------------|---------------------|----------------------|
| Al | 41 | 11 | 8 |
| Bi | <1 | <4 | <5 |
| Ca | 1 | 8 | 6 |
| Cr | 83 | 58 | 22 |
| Fe | 1 | <1 | <1 |
| Mn | MG | MG | MG |
| Ni | <1 | 6 | NA |
| P | 3 | 49 | <4 |
| Si | 51 | 35 | 25 |
| Sr | <1 | <1 | <1 |
| U | 3 | <1 | <1 |
| Pu | 0.01 | 0.11 | 0.09 |
| total α | 0.16 | 0.04 | <0.01 |

MG = Mass gained due to added permanganate.
 NA = Data not available due to fusion methods (KOH in a Ni crucible).

Table 3.5. Percent Removal of Major Components Following Alkaline Oxidative Leaching of Caustic-Leached Sludge with KMnO_4 in 3 M NaOH

| Element | % Dissolved (BY-110) | % Dissolved (S-107) | % Dissolved (SX-108) |
|----------------|----------------------|---------------------|----------------------|
| Al | 52 | 36 | 18 |
| Bi | <1 | ND (<16) | ND (<5) |
| Ca | 1 | 27 | 8 |
| Cr | 94 | 80 | 45 |
| Fe | 1 | <1 | <1 |
| Mn | MG | MG | MG |
| Ni | <1 | 8 | NA |
| P | 7 | 59 | <3 |
| Si | 33 | 45 | 31 |
| Sr | <1 | <1 | <1 |
| U | 6 | <5 | <1 |
| Pu | 13.4 | 4.97 | 2.09 |
| total α | 3.39 | 3.37 | 0.9 |

MG = Mass gained due to added permanganate.
 NA = Data not available due to fusion methods (KOH in a Ni crucible).
 ND = Element not detected in either the solution or the residual solids.

Table 3.6. Percent Removal of Major Components Following Alkaline Oxidative Leaching of Caustic-Leached Sludge with Ozone in 0.1 M NaOH

| Element | % Dissolved (BY-110) | % Dissolved (S-107) | % Dissolved (SX-108) |
|----------------|----------------------|---------------------|----------------------|
| Al | 42 | 26 | 6 |
| Bi | <1 | <5 | <5 |
| Ca | 1 | 8 | 8 |
| Cr | 83 | 84 | 42 |
| Fe | 1 | <1 | <1 |
| Mn | <1 | <1 | <1 |
| Ni | <1 | 6 | NA |
| P | 1 | 41 | 0 |
| Si | 55 | 28 | 16 |
| Sr | <1 | <1 | <1 |
| U | <1 | <1 | <1 |
| Pu | 0 | 0.01 | 0.01 |
| total α | 0.2 | <0.01 | <0.01 |

NA = Data not available due to fusion methods (KOH in a Ni crucible).

Table 3.7. Percent Removal of Major Components Following Alkaline Oxidative Leaching of Caustic-Leached Sludge with Ozone in 3 M NaOH

| Element | % Dissolved (BY-110) | % Dissolved (S-107) | % Dissolved (SX-108) |
|----------------|----------------------|---------------------|----------------------|
| Al | 48 | 44 | 16 |
| Bi | <1 | ND (<17) | <18 |
| Ca | 1 | 8 | 8 |
| Cr | 90 | 87 | 33 |
| Fe | 1 | 5 | <1 |
| Mn | <3 | <2 | <1 |
| Ni | <1 | 7 | NA |
| P | 5 | 59 | <11 |
| Si | 27 | 24 | 33 |
| Sr | <1 | <1 | <1 |
| U | <2 | <5 | <7 |
| Pu | 3.91 | 0.13 | 0.09 |
| total α | 1.61 | 0.05 | <0.03 |

NA = Data not available due to fusion methods (KOH in a Ni crucible).
 ND = Element not detected in either the solution or the residual solids.

Table 3.8. Percent Removal of Major Components Following Alkaline Oxidative Leaching of Caustic-Leached Sludge with Oxygen in 0.1 M NaOH

| Element | % Dissolved (BY-110) | % Dissolved (S-107) |
|----------------|-------------------------|------------------------|
| Al | 44 | 10 |
| Bi | <1 | <5 |
| Ca | 1 | 6 |
| Cr | 2 | 8 |
| Fe | 2 | <1 |
| Mn | <1 | <1 |
| Ni | <1 | 5 |
| P | 57 | 41 |
| Si | 68 | 19 |
| Sr | <1 | <1 |
| U | <1 | <1 |
| Pu | <0.01 | <0.01 |
| total α | 0.13 | <0.01 |

Table 3.9. Percent Removal of Major Components Following Alkaline Oxidative Leaching of Caustic-Leached Sludge with Oxygen in 3 M NaOH

| Element | % Dissolved (BY-110) | % Dissolved (S-107) |
|----------------|-------------------------|------------------------|
| Al | 48 | 46 |
| Bi | <1 | <15 |
| Ca | <1 | <1 |
| Cr | 11 | 65 |
| Fe | 1 | 3 |
| Mn | <3 | <2 |
| Ni | <1 | 8 |
| P | 18 | 51 |
| Si | 33 | 10 |
| Sr | <1 | <1 |
| U | <2 | <3 |
| Pu | 0.19 | <0.01 |
| total α | <0.2 | <0.01 |

Table 3.10. Percent Removal of Major Components Following Alkaline Oxidative Leaching of Caustic-Leached Sludge with Argon in 0.1 M NaOH

| Element | % Dissolved (BY-110) | % Dissolved (S-107) |
|----------------|----------------------|---------------------|
| Al | 46 | 11 |
| Bi | <1 | <5 |
| Ca | 1 | 9 |
| Cr | 8 | 5 |
| Fe | 2 | <1 |
| Mn | <1 | <1 |
| Ni | <1 | 7 |
| P | 7 | 35 |
| Si | 66 | 39 |
| Sr | <1 | <1 |
| U | <1 | <1 |
| Pu | <0.01 | <0.01 |
| total α | 0.09 | <0.01 |

Table 3.11. Percent Removal of Major Components Following Alkaline Oxidative Leaching of Caustic-Leached Sludge with Argon in 3 M NaOH

| Element | % Dissolved (BY-110) | % Dissolved (S-107) |
|----------------|----------------------|---------------------|
| Al | 47 | NA |
| Bi | <1 | NA |
| Ca | <1 | NA |
| Cr | 28 | NA |
| Fe | 1 | NA |
| Mn | <3 | NA |
| Ni | <1 | NA |
| P | 33 | NA |
| Si | 25 | NA |
| Sr | <1 | NA |
| U | <1 | NA |
| Pu | 0.17 | NA |
| total α | <0.1 | NA |

NA = Data not available (see text)

Table 3.12. [Al]/[Fe] and [Cr]/[Fe] Molar Ratios in the Residual Solids Following Additional Alkaline Oxidative Leaching of Caustic-Leached Hanford Tank Sludge

| Conditions | BY-110 | | S-107 | | SX-108 | |
|----------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| | [Al]/[Fe] | [Cr]/[Fe] | [Al]/[Fe] | [Cr]/[Fe] | [Al]/[Fe] | [Cr]/[Fe] |
| No Leaching(a) | 5.67E+00 | 3.23E-01 | 8.68E+01 | 1.32E+00 | 1.14E+01 | 5.20E-01 |
| Sludge Washing (SW) Only(a) | 3.92E-01 | 1.90E-01 | 6.74E+01 | 1.01E+00 | 1.13E+01 | 1.30E-01 |
| Caustic Leaching (CL) Only(a) | 2.34E-01 | 1.69E-01 | 2.58E+01 | 6.44E-01 | 7.80E+00 | 8.63E-02 |
| CL + permanganate; 0.1 M NaOH(b) | 2.62E-01 | 3.52E-02 | 3.59E+01 | 2.60E-01 | 6.02E+00 | 5.22E-02 |
| CL + permanganate; 3 M NaOH(b) | 2.15E-01 | 1.25E-02 | 2.81E+01 | 1.44E-01 | 6.30E+00 | 4.30E-02 |
| CL + ozone; 0.1 M NaOH(b) | 2.62E-01 | 3.77E-02 | 2.97E+01 | 9.57E-02 | 5.80E+00 | 3.71E-02 |
| CL + ozone; 3 M NaOH(b) | 2.74E-01 | 2.35E-02 | 2.25E+01 | 1.07E-01 | 5.83E+00 | 4.86E-02 |
| CL + oxygen; 0.1 M NaOH(b) | 2.57E-01 | 2.03E-01 | 3.64E+01 | 5.81E-01 | NP | NP |
| CL + oxygen; 3 M NaOH(b) | 2.60E-01 | 1.84E-01 | 1.95E+01 | 2.36E-01 | NP | NP |
| CL + argon; 0.1 M NaOH(b) | 2.65E-01 | 1.95E-01 | 3.61E+01 | 6.12E-01 | NP | NP |
| CL + argon; 3 M NaOH(b) | 2.70E-01 | 1.56E-01 | NA | NA | NP | NP |

(a) Data taken from Lumetta et. al. 1996a
(b) Data taken from this work
NA = Data not available
NP = Test not performed

Like with BY-110, further Cr dissolution from caustic-leached S-107 sludge was enhanced by the presence of permanganate or ozone. With ozone as the oxidant, changes in free-hydroxide concentration appear to have little effect, with 84% of Cr being dissolved at 0.1 M [OH] and 87% at 3 M [OH]. However, with permanganate, the free-hydroxide concentration appears to have a significant effect, with 58% of the Cr being dissolved at 0.1 M [OH] and 80% at 3 M [OH]. The similarities in the % Cr removal at 3 M [OH] between ozone and permanganate together with the similarities observed in the percent Cr removal in other sludges following contact with these two oxidants suggest that the % removal value for S-107 upon contact with permanganate at 0.1 M free hydroxide may be unusually low. Contact of caustic-leached S-107 with oxygen and argon showed a similar response to free-hydroxide concentration changes as did BY-110. At 0.1 M free hydroxide, the % Cr dissolved was low, with 8 and 5% dissolution upon contact with oxygen and argon, respectively. Like with BY-110, the % Cr dissolved by oxygen at higher free-hydroxide concentrations increases. However, the magnitude of the increase is much higher than was observed with BY-110; with S-107, 65% of the Cr dissolved at 3 M free hydroxide, even more than the (suspiciously low) value found after contact with permanganate at 0.1 M free hydroxide. The amount dissolved by Ar at 3 M NaOH is unknown: due to analytical difficulties, the elemental concentration in the oxidatively leached sludge residue could not be measured, and so the fraction dissolved can not be calculated. However, the

chromate concentrations in the final leachate solution as shown in Figure 3.3 suggest that the amount of Cr dissolved was significantly less than that observed with permanganate, ozone, and oxygen at 3 M free hydroxide.

The low % Cr removal from S-107 sludge upon contact with permanganate at 0.1 M NaOH was unexpected. Having Cr dissolution with permanganate being so much lower than that observed with ozone (58 vs. 84% Cr dissolution, respectively) is unprecedented. One possible explanation that can be evaluated involves the amount of added permanganate; if a substoichiometric amount was present, a poorer than expected removal of Cr should result. Table 3.13 compares the ratio of the total amount of moles of Cr present in each test as determined by ICP-AES with the known amount of permanganate added.

As shown in Table 3.13, the ratio of permanganate to Cr in the sample is fairly consistent throughout the tests. Furthermore, at least a 100% excess of the 1:1 molar permanganate to Cr ratio required for the Cr(III) to chromate oxidation always existed. Consequently, the source of the low Cr removal remains unknown.

Table 3.13. Ratio of Added Permanganate to Cr in Alkaline Oxidative Cr Leach Test

| Sludge | [OH] | [Mn]/[Cr] |
|--------|------|-----------|
| BY-110 | 0.1 | 2.51 |
| BY-110 | 3 | 2.82 |
| | | |
| S-107 | 0.1 | 2.61 |
| S-107 | 3 | 2.73 |
| | | |
| SX-108 | 0.1 | 2.35 |
| SX-108 | 3 | 3.14 |

Further Cr dissolution from caustic-leached SX-108 sludge is lower than that observed with either S-107 or BY-110, ranging only from 22 to 45%. In addition, changes in the free-hydroxide concentration do not appear to produce any consistent response. With added permanganate, the % Cr dissolved increased with increasing free hydroxide, as was observed with BY-110 and to a lesser extent S-107. However, with added ozone, the % Cr removed decreased with increasing free hydroxide, dropping from 42% at 0.1 M [OH] to 33% at 3 M [OH].

This removal of Cr from SX-108 was unusually poor. This is the second sludge in which poor (< 80%) dissolution of Cr has been observed by alkaline oxidative leaching. Table 3.14 summarizes the results to date on Cr dissolution after contact with ozone and permanganate. It is interesting to note that the poor removal (except for the above noted case of S-107 with permanganate at 0.1 M free hydroxide) of Cr is associated with Cr being present in phases with other elements inert to oxidation (such as Bi(V) in the BiCrO₄ found in B-111 and Al(III) in the Al/Cr oxide found in SX-108). When Cr is present in a pure Cr phase, as with SY-103 and BY-110, high removals of Cr by alkaline oxidative leaching are observed. Therefore, one possible explanation for the poor leaching in B-111 and SX-108 is that the Cr is bound up with the unoxidizable and therefore unleachable elements in these phases and so is physically inaccessible to the oxidant. If this hypothesis is valid, then little additional Cr would ever be accessible by alkaline oxidative leaching with these types of sludges as long as the oxidation-inert elements remain. However, since extended leach times with caustic have been shown to greatly enhance Al removal in REDOX sludges such as SX-108, extended

caustic leaching followed by alkaline oxidative leaching should markedly improve the amount of Cr removed from the sludge. Testing of this hypothesis should be a goal for any additional studies.

Table 3.14. Summary of Cr Dissolution by Alkaline Oxidative Leaching with Ozone and Permanganate

| Sludge | Oxidant | [OH], <u>M</u> | % Cr Dissolved | Cr-Containing Phase {by TEM ^(a) } |
|--------|-------------------|----------------|----------------|--|
| B-111 | KMnO ₄ | <0.01 | 18 | BiCrO ₄ |
| B-111 | ozone | <0.01 | 12 | BiCrO ₄ |
| BY-110 | KMnO ₄ | 0.1 | 83 | Cr(O)(OH) - Grimaldite |
| BY-110 | ozone | 0.1 | 83 | Cr(O)(OH) - Grimaldite |
| BY-110 | KMnO ₄ | 3 | 94 | Cr(O)(OH) - Grimaldite |
| BY-110 | ozone | 3 | 90 | Cr(O)(OH) - Grimaldite |
| S-107 | KMnO ₄ | 0.1 | 58 | None identified |
| S-107 | ozone | 0.1 | 84 | None identified |
| S-107 | KMnO ₄ | 3 | 80 | None identified |
| S-107 | ozone | 3 | 87 | None identified |
| SX-108 | KMnO ₄ | 0.1 | 22 | Al/Cr |
| SX-108 | ozone | 0.1 | 42 | Al/Cr |
| SX-108 | KMnO ₄ | 3 | 45 | Al/Cr |
| SX-108 | ozone | 3 | 33 | Al/Cr |
| SY-103 | KMnO ₄ | <0.01 | 90 | Amorphous Cr(OH) ₃ |
| SY-103 | ozone | <0.01 | 89 | Amorphous Cr(OH) ₃ |

(a) transmission electron microscopy

To summarize, ozone and permanganate were the most effective at solubilizing Cr from the caustic-leached sludges. Cr dissolution in the presence of oxygen and argon was more variable and generally less effective. Using higher hydroxide concentrations often increased Cr dissolution in the presence of any particular chemical agent tested, although the effects were much more dramatic with the poorer solubilizing agents oxygen and argon. Finally, Cr dissolution from caustic-leached SX-108 was much poorer than with either S-107 or BY-110.

3.2.5 Cr Oxidation State in Alkaline Leachate Solutions

As noted above (Section 3.2.2), visible spectroscopy is much more sensitive for detecting Cr in the +6 oxidation state than in the +3 oxidation state. This raises the question of whether some fraction of the Cr may be present but undetected as Cr(III). The chromate concentration in the leachate solutions as determined by visible spectroscopy can be compared with the total Cr concentration in the leachate solutions as determined by ICP-AES to provide a more sensitive probe as to the fraction of Cr present in the +6 oxidation state.

The results are summarized in Table 3.15. The agreement between the measured chromate concentrations in the leachate and the total Cr concentrations is excellent, especially given the $\pm 15\%$ uncertainty associated with the total Cr measurements. In the few cases where a discrepancy exists beyond the 15% total Cr measurement uncertainty, the measured chromate concentration is higher than the total Cr measurement, not the other way around as expected if Cr(III) were present in the leachate solution. In short, all experimental evidence is consistent with the hypothesis that effectively all soluble Cr in these alkaline leachate solutions is present as chromate.

3.2.6 Dissolution of Transuranic Elements by Alkaline Oxidation

Tables 3.4 through 3.11 also describe the percent removal of alpha-emitting radionuclides (TRUs). Several trends are apparent. First, the fraction of alpha-emitting radionuclides found in the leachate solution appears to depend greatly on the free-hydroxide concentration. Little, if any, of the alpha activity in the sample is removed at 0.1 M [OH]. However, at 3 M free hydroxide, the fraction of alpha activity in the leachate can increase by over two orders of magnitude. Second, a marked difference exists in the fraction of alpha activity reporting to the leachate as a function of the oxidant added. The observed order for the fraction of alpha activity dissolved by oxidative alkaline leaching of BY-110, S-107, and SX-108 is permanganate > ozone > oxygen, rather than the ozone > permanganate > air observed previously for SY-103. Significant amounts of total alpha activity can be observed at high free hydroxide, with up to 4% dissolving with permanganate. Third, inspection of the concentrations of total alpha activity in the leachate as compared to the total Pu activity in the leachate indicates that the total alpha activity in the leachate is predominantly, if not exclusively, due to Pu dissolution. This is also supported by examining the percent-removed tables and noting that the Pu dissolution is greater than the total alpha dissolution, which is a combination of Pu and Am dissolution behavior. The only exception appears to be in 0.1 M free-hydroxide solutions contacted with caustic-leached BY-110 sludge. Here the majority of the total alpha activity is not due to Pu dissolution and is ascribed rather to Am dissolution. Fourth, the effectiveness of total alpha (Pu) dissolution is inversely related to the total alpha (Pu) activity present in the sample. For example, the percent Pu removal by permanganate at 3 M free hydroxide is BY-110 (13.4%) > S-107 (5%) > SX-108 (2.1%). The $^{239,240}\text{Pu}$ activity in caustic leached sludge, in $\mu\text{Ci/g}$, is SX-108 (45.4) > S-107 (4.04) > BY-110 (0.682) (Lumetta et al. 1996a). So, the $^{239,240}\text{Pu}$ activity in the leachate solutions does not correspond to the fraction of radionuclides dissolved for any particular sludge. In fact, the $^{239,240}\text{Pu}$ activity for the SX-108 leachate following contact with permanganate at 3 M free hydroxide (approximately $5 \times 10^{-4} \mu\text{Ci/mL}$ or $3 \times 10^{-8} \text{ M Pu}$, assuming ^{239}Pu) is comparable to both the S-107 and BY-110 leachate under similar conditions. This concentration of Pu is close to that previously reported ($2.6 \times 10^{-9} \text{ M}$ at 0.1 M [OH], 1 M [NO₃], and 1 M [NO₂]^(a); $4.5 \times 10^{-8} \text{ M}$ at 2 M [OH]; and 7.4×10^{-8} at 3 M [OH]) for aged Pu(IV) in NaOH at room temperature (Delegard 1987).

(a) C. H. Delegard, unpublished data

Table 3.15. Ratio of Chromate vs Total Cr in Leachate Solutions

| Experiment | [CrO ₄]/[Cr] Total |
|--|--------------------------------|
| BY-110 (KMnO ₄ in 0.1 M NaOH) | 0.99 |
| BY-110 (KMnO ₄ in 3 M NaOH) | 1.09 |
| BY-110 (Ozone in 0.1 M NaOH) | 0.92 |
| BY-110 (Ozone in 3 M NaOH) | 1.00 |
| BY-110 (Oxygen in 0.1 M NaOH) | 1.80 |
| BY-110 (Oxygen in 3 M NaOH) | 1.02 |
| BY-110 (Argon in 0.1 M NaOH) | 1.15 |
| BY-110 (Argon in 3 M NaOH) | 0.98 |
| | |
| S-107 (KMnO ₄ in 0.1 M NaOH) | 1.05 |
| S-107 (KMnO ₄ in 3 M NaOH) | 1.09 |
| S-107 (Ozone in 0.1 M NaOH) | 1.13 |
| S-107 (Ozone in 3 M NaOH) | 1.06 |
| S-107 (Oxygen in 0.1 M NaOH) | 1.11 |
| S-107 (Oxygen in 3 M NaOH) | 1.03 |
| S-107 (Argon in 0.1 M NaOH) | 1.01 |
| S-107 (Argon in 3 M NaOH) | 0.99 |
| | |
| SX-108 (KMnO ₄ in 0.1 M NaOH) | 1.13 |
| SX-108 (KMnO ₄ in 3 M NaOH) | 1.17 |
| SX-108 (Ozone in 0.1 M NaOH) | 0.96 |
| SX-108 (Ozone in 3 M NaOH) | 1.04 |

The enhanced dissolution of Pu with permanganate compared to ozone under the test conditions was unexpected given the significantly greater oxidation potential of ozone vs. permanganate in alkaline solution (1.24V vs. 0.58V, respectively). In addition, the order of MnO₄⁻ > ozone is opposite to that previously reported (Rapko, Lumetta, and Wagner 1996). Clearly, additional factors beyond simple thermodynamic considerations are involved.

One alternative explanation for the observed results is that Pu dissolves more extensively during the leach tests than the Pu analysis of the final leachate solution and residual solids indicates. This additional dissolved Pu (presumably in a higher oxidation state than +4, such as +6) then reduces down to the +4 oxidation state as the oxidant stops being replenished (ozone) or is exposed to light (permanganate is known to be light sensitive). The Pu⁺⁴ then reprecipitates between the time the test ended and the time the leachate aliquots are removed and prepared for analysis (the aliquots are removed after the suspension is cooled and centrifuged, and the leachate is isolated). This would explain the greater Pu concentration in leachates contacted with effective chemical oxidants such as permanganate and ozone (as indicated by effective Cr oxidation) and leachates contacted with less effective chemical oxidants (oxygen) or argon.

Although significant fractions of total α and Pu were observed in several of the leachate solutions, this amount of TRU material measured in the leachate solutions is unlikely to pose a problem for LLW disposal. Table 3.16 presents the expected TRU concentration in a LLW waste form containing

20 wt% Na. As shown below, the greatest concentration of TRU was found to be 3.1 nCi/g and was derived from the S-107 sludge leachate after contact with permanganate at 3 M NaOH. This indicates that the leachate solutions following alkaline oxidation, which will be vitrified, will not only be LLW (< 100 nCi/g), but likely a Class A LLW (< 10 nCi/g).

Table 3.16. Total α Concentration of Leachate Solutions at 20 wt% Na

| Sludge | [OH], M | Oxidant | Total α in Leachate (μ Ci/mL) | Total α at 20 wt% Na (nCi/g) |
|--------|------------|-------------------|--|--|
| BY-110 | 0.1 | KMnO ₄ | 2.74E-05 | 2.38E+00 |
| BY-110 | 3 | KMnO ₄ | 4.10E-04 | 1.19E+00 |
| BY-110 | 0.1 | O ₃ | 2.14E-05 | 1.86E+00 |
| BY-110 | 3 | O ₃ | 1.64E-04 | 4.75E-01 |
| BY-110 | 0.1 | O ₂ | 1.57E-05 | 1.37E+00 |
| BY-110 | 3 | O ₂ | <3.00E-05 | <8.70E-02 |
| BY-110 | 0.1 | Ar | 2.31E-05 | 2.01E+00 |
| BY-110 | 3 | Ar | <3.00E-05 | <8.70E-02 |
| | | | | |
| S-107 | 0.1 | KMnO ₄ | 2.11E-05 | 1.83E+00 |
| S-107 | 3 | KMnO ₄ | 1.07E-03 | 3.10E+00 |
| S-107 | 0.1 | O ₃ | <3.00E-06 | <2.61E-01 |
| S-107 | 3 | O ₃ | 7.57E-05 | 2.19E-01 |
| S-107 | 0.1 | O ₂ | <3.00E-06 | <2.61E-01 |
| S-107 | 3 | O ₂ | <3.00E-05 | <8.70E-02 |
| S-107 | 0.1 | Ar | <4.00E-06 | <3.49E-01 |
| S-107 | 3 | Ar | <2.00E-05 | <5.80E-02 |
| | | | | |
| SX-108 | 0.1 | KMnO ₄ | <5.00E-06 | <4.35E-01 |
| SX-108 | 3 | KMnO ₄ | 4.80E-04 | 1.39E+00 |
| SX-108 | 0.1 | O ₃ | <4.00E-06 | <3.48E-01 |
| SX-108 | 3 | O ₃ | <2.00E-05 | <5.80E-02 |

4.0 Summary and Recommendations

Sludge samples from the following three Hanford waste tanks have been leached with an alkaline oxidative solution: BY-110, S-107, and SX-107. These sludge samples were previously subjected to caustic leaching before these oxidative leaches. These sludge samples were previously subjected to caustic leaching. These sludges were chosen because they represent types of waste where significant amounts of Cr are located and show relatively poor dissolution of Cr during standard caustic leaching. The experiments involved tests with three chemical oxidants, permanganate, ozone and oxygen, and a blank, argon. The effect of varying the hydroxide concentration of the leachate (from 0.1 M to 3 M) and of time and temperature (from room temperature [RT] to 80°C) was also examined. Key findings from this study include

- Permanganate and ozone are the most effective chemical agents tested for Cr dissolution under alkaline conditions, with 83 to 94% dissolution found with BY-110, with 58 to 87% dissolution found with S-107, but with only 22 to 45% dissolution with SX-108.
 - Leaching at 3 M free hydroxide is as effective or more effective at Cr dissolution than leaching at 0.1 M free hydroxide, although the increase in effectiveness tends to be small.
 - Heating to 80°C was required in several instances to achieve maximum Cr dissolution.
- Oxygen and argon are much less effective than ozone and permanganate at Cr dissolution under alkaline conditions.
 - Leaching at 3 M free hydroxide is much more effective than leaching at 0.1 M free hydroxide for Cr dissolution. At 0.1 M free hydroxide, <10% Cr dissolution was found in all cases.
- Work performed to date indicates a correlation between the presence of pure Cr phases in the sludges and the effectiveness of alkaline oxidative dissolution of Cr. This correlation explains the relatively poor Cr dissolution found for SX-108, where a mixed Al/Cr phase has been identified, compared to BY-110 and S-107, where, to the extent any Cr phases have been found, only pure Cr phases have been identified. If this explanation is valid, then more effective Al removal from SX-108 by extended caustic leaching should allow for a more effective alkaline oxidative dissolution of Cr.
- In all instances, the Cr dissolved by alkaline oxidative leaching was found to be present in the +6 oxidation state, i.e., as chromate (CrO_4^{2-}), and not in the +3 oxidation state, i.e., as tetrahydroxochromium(III) $\text{Cr}(\text{OH})_4^-$.
- Little total α or Pu was dissolved by alkaline oxidative leaching of Pu at 0.1 M free hydroxide.
- Leaching at 3 M free hydroxide resulted in enhanced Pu dissolution, with up to 14% of the total Pu dissolving during leaching of BY-110 sludge with permanganate. The final Pu concentrations appear consistent with that expected for Pu(IV) in hydroxide solution. However, even with the greater Pu dissolution at 3 M free hydroxide, all of the alkaline oxidative leachate solutions would be classified as a Class A LLW even after concentration to 20 wt% Na.
- An alternative explanation for the observed Pu dissolution suggests that additional Pu dissolved in the leachate solutions containing effective oxidants such as permanganate and ozone. However, Pu may have undergone reduction back to the +4 oxidation state between the time the test ended and the final sample preparation. At the same time, the leachate Pu activity was reduced so it was close to that expected, based on Pu^{4+} solubility in alkaline media. The data to date do not distinguish between these two explanations.
- Scouting experiments using Cr(III) oxide as a model for the insoluble Cr in the tank waste indicate that hydrogen peroxide is ineffective at dissolving Cr under alkaline conditions.

Further laboratory-scale studies on alkaline oxidative leaching of Cr should initially focus on resolving two unresolved questions noted above; first, whether the amount of Pu dissolved in the leachate at the end of these tests decreases upon standing and second, whether a more extensive removal of aluminum from SX-108 can enhance Cr dissolution by alkaline oxidative leaching. Further work should also focus on identifying Cr-containing chemical species in the sludge both before and after enhanced leachings. Such Cr speciation information is needed to provide a sound chemical basis for understanding variable Cr dissolution behavior in these alkaline solutions and so perhaps, as has been suggested with SX-108, allow proposals for further remedial actions.

5.0 References

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