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**Oxidative Dissolution of Chromium
from Hanford Tank Sludges Under
Alkaline Conditions**

**B. M. Rapko
G. J. Lumetta
M. J. Wagner**

July 1996

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest National Laboratory
Operated for the U.S. Department of Energy
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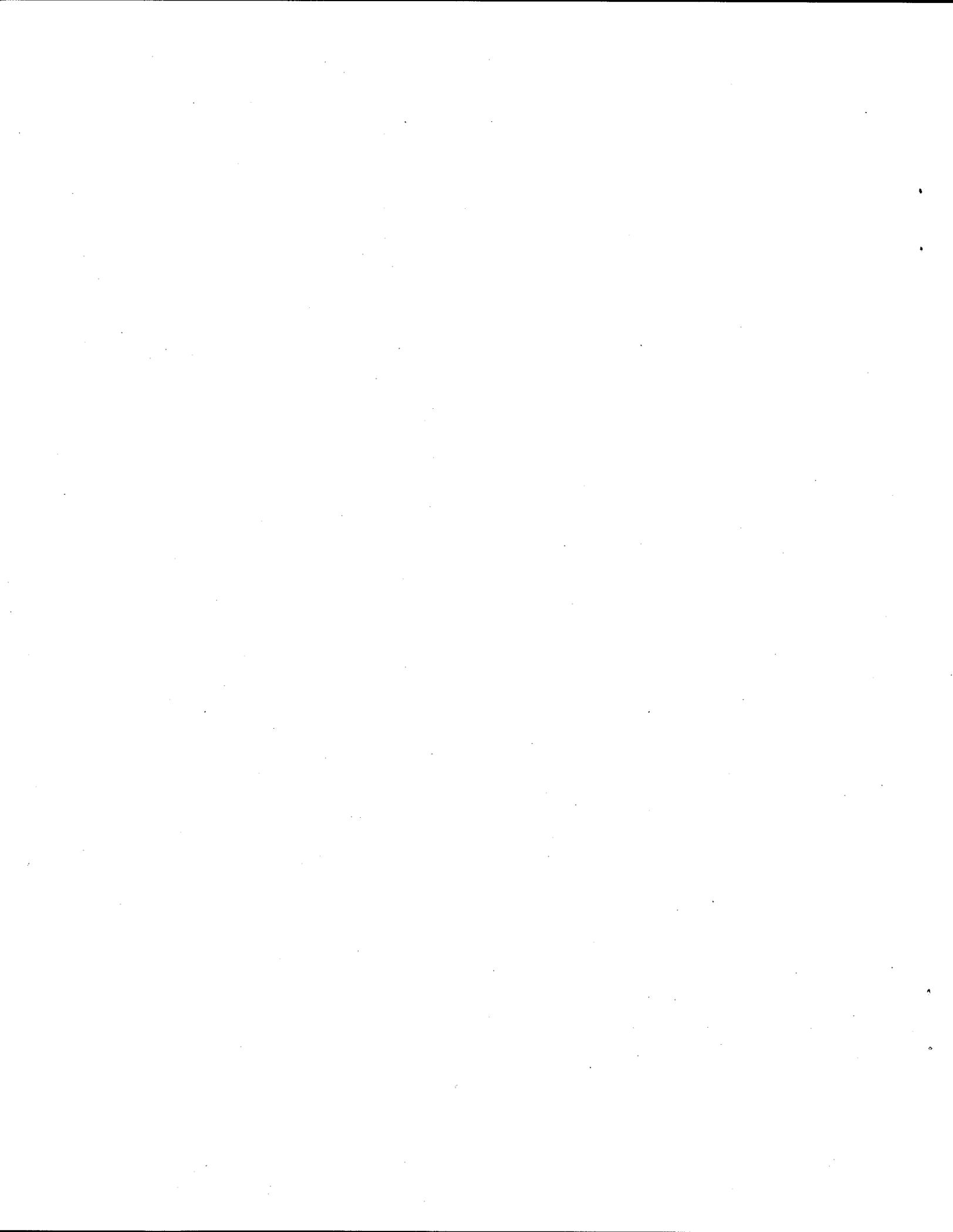
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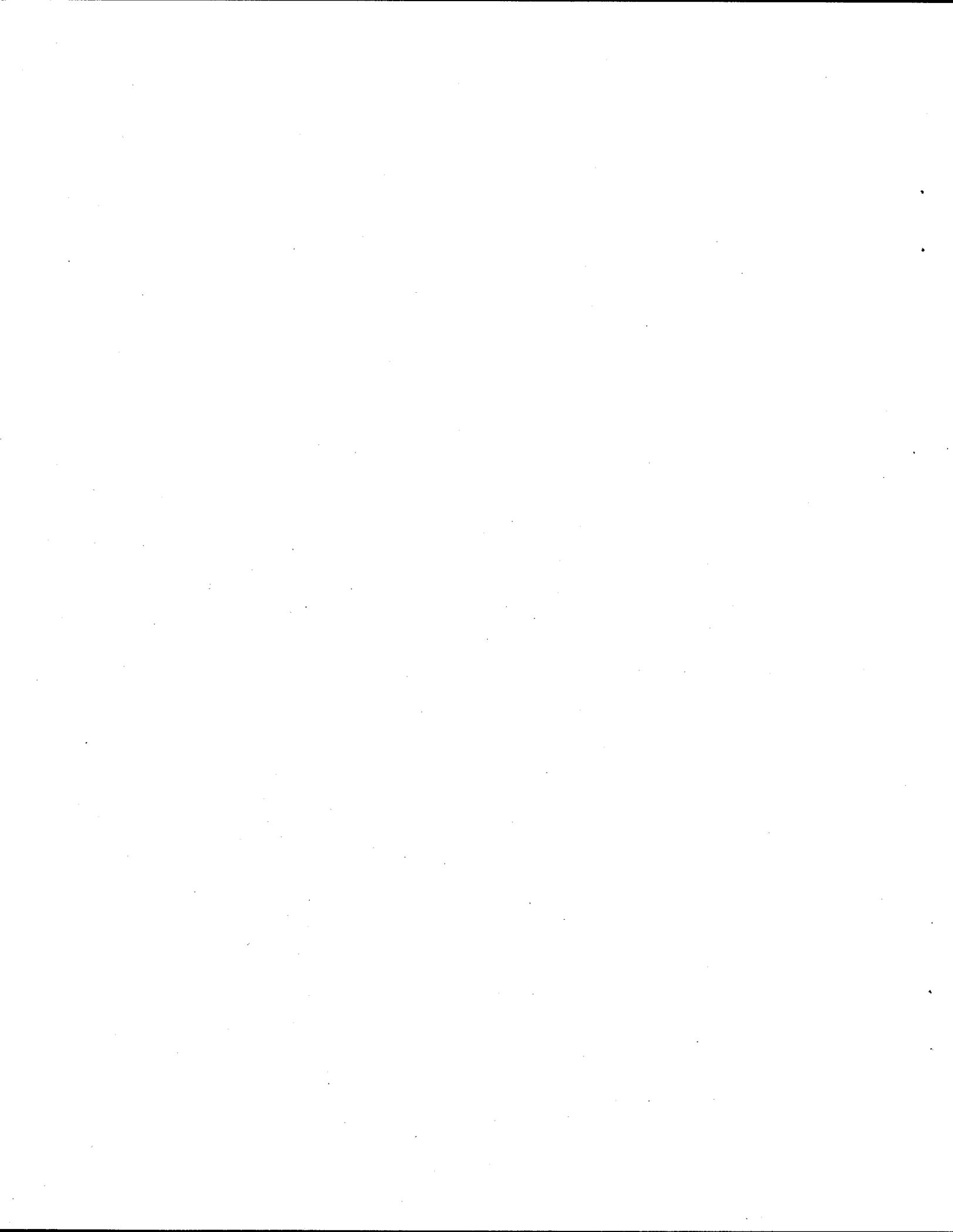
Summary

Because of the expected high cost of vitrifying and disposing of high-level waste at the U.S. Department of Energy's Hanford Site, pretreatment processes are being developed to reduce the anticipated volume of borosilicate glass. Sludge washing and caustic leaching, the baseline sludge pretreatment process, is expected to leach out a substantial portion of the ^{137}Cs , possibly other radionuclides, and a significant portion of such major nonradionuclides as Al or P. The decontaminated solution will be routed to the low-level waste stream, where it will be immobilized in a glass matrix. The leached solids, which will contain the transuranic elements and ^{90}Sr , will be handled as high-level waste. Previous studies indicate that poor removal of chromium in the +3 oxidation state [Cr(III)] occurs during baseline pretreatment. Because the concentration of Cr allowed in high level waste glass is low, a relatively small amount of Cr in the sludge can have a relatively large impact on the volume of high level waste glass produced. For this reason, additional leach steps to remove Cr would be desirable, and oxidative alkaline leaching has been proposed as a simple addition to the baseline sludge pretreatment. This report describes small-scale screening tests on the oxidative alkaline leaching of Cr performed with actual Hanford tank sludges.

In this study, oxidative alkaline leaching of washed and caustic-leached Hanford Tank sludges from Tanks B-111 and SY-103 was evaluated. Two types of oxidants, KMnO_4 and O_3 , were investigated as a function of time, temperature, and (for permanganate) Mn to Cr ratio. Reaction times were rapid with both oxidants, and very little additional Cr dissolved upon further heating of the solution to 80°C . Analysis of the reaction of sludge with either 1:1 or excess permanganate to Cr indicates that insoluble MnO_2 will be produced under any practical processing conditions.

The oxidation of Cr(III) to soluble CrO_4^{2-} allows for good dissolution of Cr during oxidative alkaline leaching with high Cr(III) sludges. Calcium is the only other element that dissolves significantly, probably due to changes in the supernatant pH rather than any direct oxidant-Ca reaction. Under the test conditions, less than a third of the available Cr dissolved with B-111 sludge, but 90% dissolved with SY-103 sludge. Heating the dried sludges in air at 80°C for several hours oxidized some Cr(III) to Cr(VI) and may have oxidized a small portion of Pu. Some enhanced dissolution of Pu was observed when ozone was contacted with SY-103 sludge, although the concentrations should not prohibit the formation of low-level-waste glass if the oxidative leaching supernatant is combined with the caustic leach supernatant. For B-111, oxidative alkaline leaching did not reduce the amount of high-level glass required because no further dissolution of the glass-limiting component, P, was observed. For SY-103, however, it reduced the amount of high-level glass required by 90%. Either permanganate or ozone appears to be about equally effective. However, the nature of the glass-limiting component can change. If ozone is used Cr remains the glass limiting component; if permanganate is used, the glass limiting component changes to Mn.

Further studies in at least three areas are suggested: 1) examine why Cr dissolves so differently in B-111 sludge than in SY-103 sludge, 2) examine why Pu dissolves so differently in SY-103 sludge than in SY-101 sludge, which was described in an earlier report, and 3) examine the rate that Pu dissolves in SY-103 sludge (if Pu dissolves more slowly than Cr, then controlling the contact time could minimize Pu dissolution).



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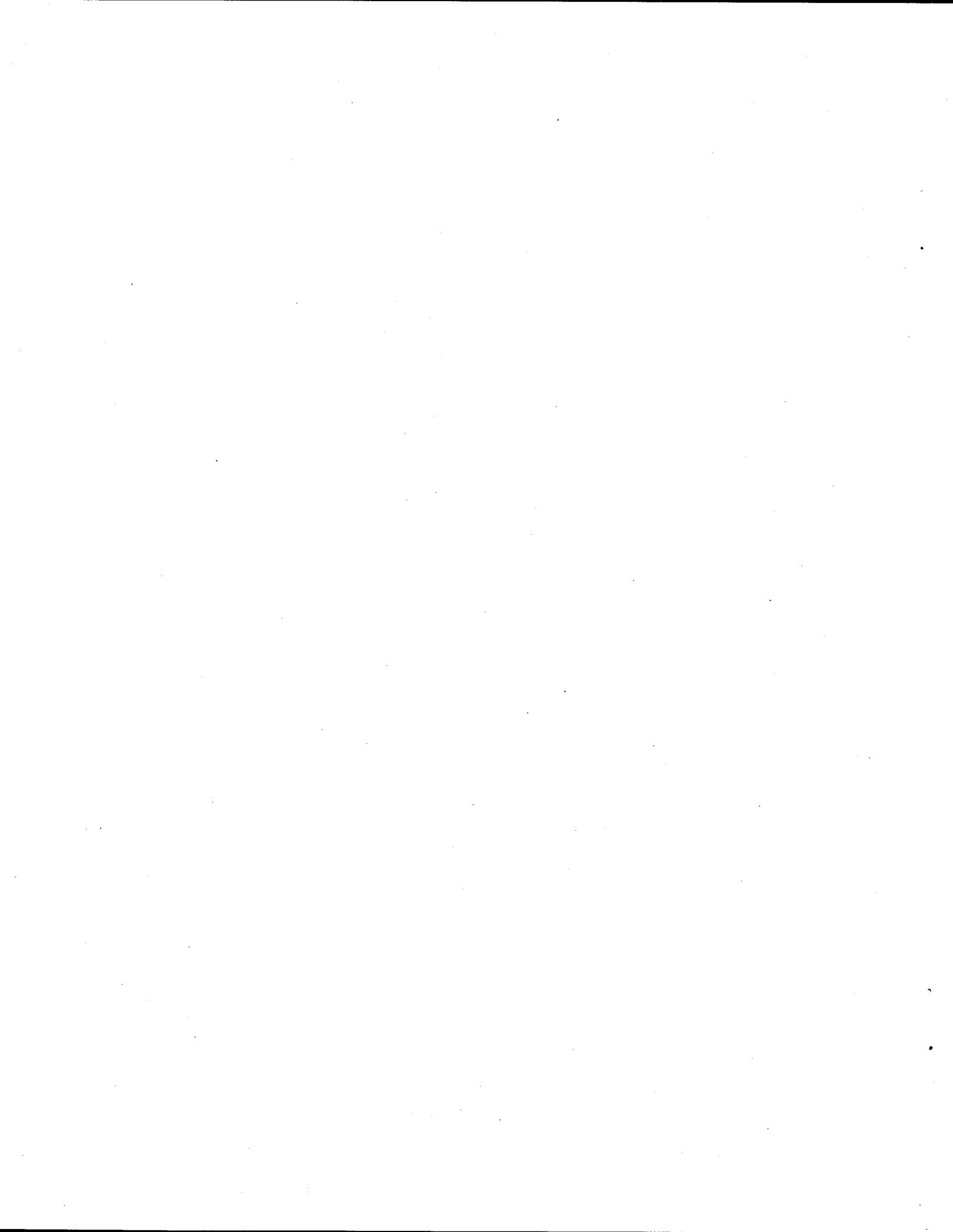
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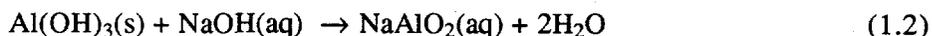
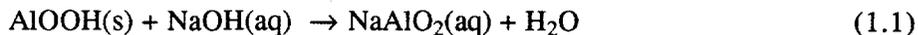


1.0 Introduction

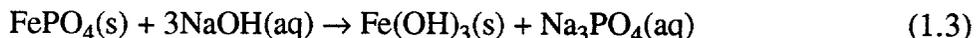
During the past few years, the primary mission at the U.S. Department of Energy's Hanford Site has changed from producing plutonium to restoring the environment. Large volumes of high-level radioactive wastes (HLW), generated during past Pu production and other operations, are stored in underground tanks 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 borosilicate glass produced in disposing of the tank wastes.

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 1995).

Leaching the sludge with caustic, a key step in the baseline sludge pretreatment flowsheet, is expected to remove a large fraction of the Al, which is present in large quantities in Hanford tank sludges. The removal of Al is based on the conversion of aluminum oxides/hydroxides to sodium aluminate. For example, boehmite and gibbsite are dissolved according to the following equations (Weber 1982).



A significant portion of the P is also expected to be removed from the sludge by metathesizing water-insoluble metal phosphate salts to insoluble hydroxide salts and soluble Na₃PO₄. An example of this is shown for iron(III) phosphate in the following equation.



Similar metathesis reactions can occur for insoluble sulfate salts to remove sulfate from the high-level waste stream.

Enhanced Cr dissolution has been observed at highly caustic versus mildly basic solutions and may be due to the increased solubility of Cr(III) at high hydroxide concentrations (Rai et al. 1987). The increased solubility of Cr(III) at high hydroxide concentration is due to the formation of the tetrahydroxochromium(III) anion.

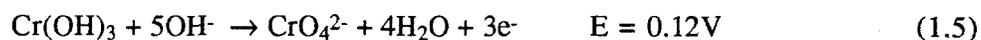


Studies of the baseline Hanford sludge washing and caustic leaching process have been reported (Lumetta and Rapko 1994; Rapko et al. 1995; Temer and Villareal 1995). Although tests to date indicate that, in general, the baseline process performs within the baseline assumptions, in some cases, lesser amounts of certain components are removed than assumed in the baseline pretreatment flowsheet. Thus, methods to enhance or supplement the performance of the caustic leaching process are of interest because they could lead to reduced disposal costs.

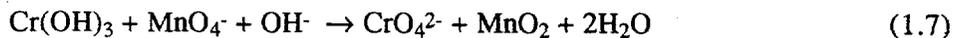
This report describes small-scale screening tests performed with actual Hanford tank sludges under the Alternative Alkaline Washes of Hanford Sludges Project (project number 24712) at the Pacific Northwest National Laboratory and is funded by the Tank Focus Area of the U.S. Department of Energy's Office of Science and Technology.^(a) The work was designed to investigate approaches to enhance removal of Cr following sludge washing and caustic leaching.

Certain Hanford tank sludges (e.g., from tanks SY-102 and -103) contain significant quantities of Cr. Dilute hydroxide washing is expected to remove only ~30% of the Cr from SY-102 (Lumetta and Swanson 1993; Lumetta et al. 1995) and only ~5% from SY-103 (Rapko et al. 1995). Although caustic leaching tests have not been performed on SY-102 sludge, tests with SY-103 sludge indicated that caustic leaching only removes 8% more Cr. 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, improved methods are needed to remove Cr from these sludges.

Treatment with oxidants such as potassium permanganate, KMnO_4 , was found to be effective at removing Cr from washed SY-102 sludge. Indeed, combining dilute hydroxide leaching and KMnO_4 removed 96% of the Cr from SY-102 sludge (Lumetta and Swanson 1993, Lumetta et al. 1995). Chromium removal by this method is based upon the oxidation of insoluble Cr(III) to Cr(VI), which is soluble in alkaline media. Under alkaline conditions, permanganate is a sufficiently potent oxidant to readily oxidize Cr(III) as the following electrochemical half reactions indicate.



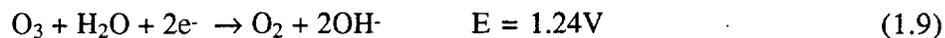
As these half reactions indicate, this oxidation proceeds according to the following equation.



In this instance, 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 problem because the Mn limit in the HLW glass feed is expected to be much higher than that for Cr. However, the Mn limit in the HLW glass feed has not been definitively defined. Thus, the possibility exists that Mn could become a glass-limiting component if the permanganate leaching method is used. The above reaction has been shown to proceed through an intermediate step in which the soluble manganate ion (MnO_4^{2-}) is formed (Lumetta and Swanson 1993). This offers the possibility that the reaction can be controlled in such a manner that the liquid is separated from the HLW solids before MnO_2 is formed (and precipitated).

Because of the possibility that the introduction of additional Mn might prove to be glass limiting, this study also sought to explore the potential of a viable alternative oxidant for Cr leaching, one that would not add any more mass to the leached sludges. Two likely alternative oxidants are hydrogen peroxide, H_2O_2 , and ozone, O_3 . As the following electrochemical half reactions indicate, either of these materials is potent enough to effectively oxidize Cr(III) under alkaline conditions.

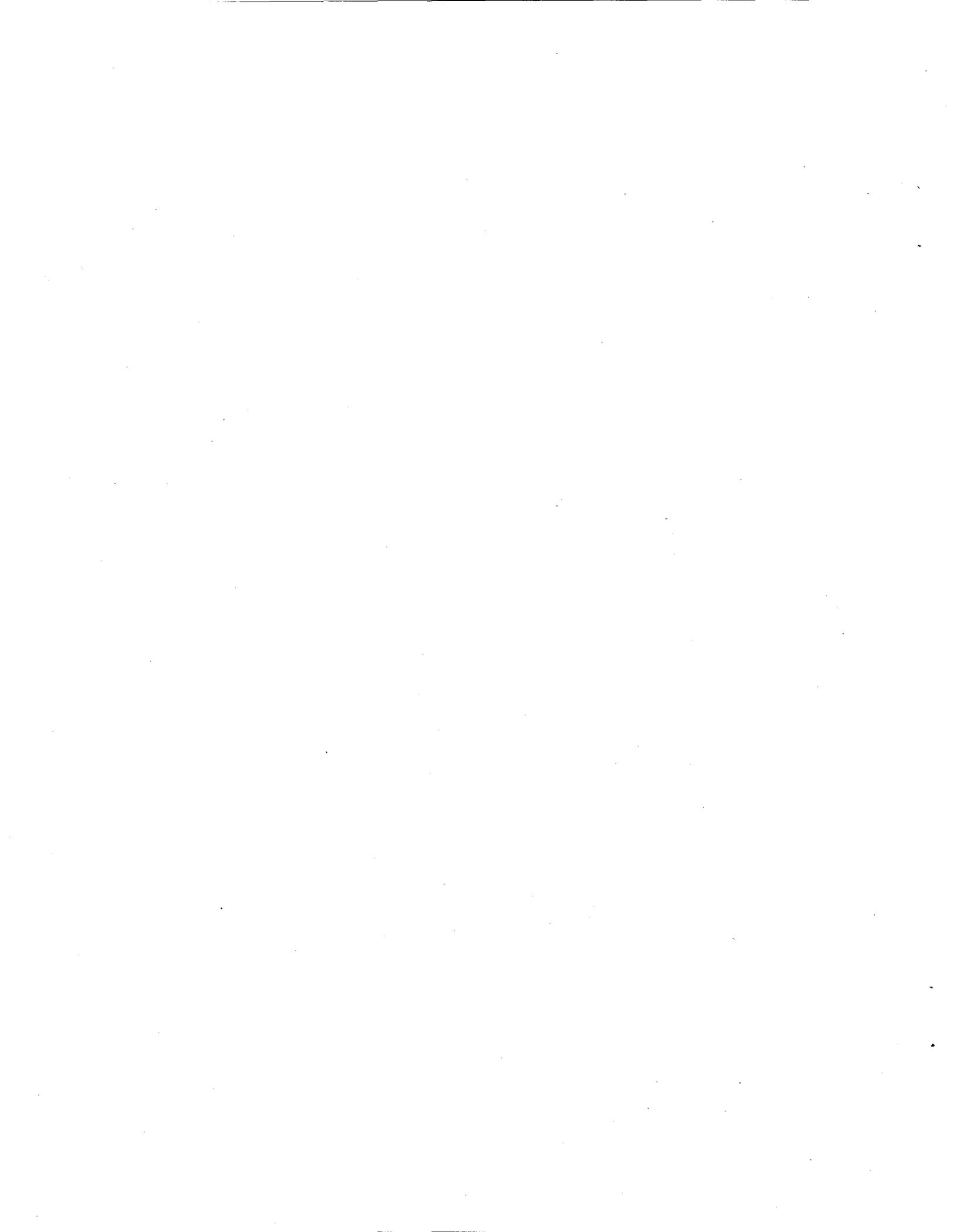
^aPacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.



Furthermore, with these oxidants, the reduction products are innocuous, forming either hydroxide (from hydrogen peroxide) or oxygen (from ozone).

A previous study has already investigated the effects of contacting hydrogen peroxide with a Hanford tank sludge (Lumetta and Swanson 1993). In that study, contacting SY-102 sludge previously washed with 0.1 M NaOH with a large excess of hydrogen peroxide (relative to the available Cr) caused the solution to foam and little, if any, Cr dissolved. For this reason, only ozone was considered in this study as an alternative oxidant to permanganate.

The objectives of this work were to 1) demonstrate the removal of Cr from Hanford tank sludges by oxidation to Cr(VI) and 2) survey the impact of time, temperature, and choice of oxidant on the Cr(VI) dissolution.



2.0 Experimental

For a given sample of Hanford tank sludge, the Cr leaching tests were performed on sludge previously subjected to the baseline pretreatment process; that is, the sludge was washed with 0.01 M NaOH/0.01 M NaNO₂ and leached with a (3 M) sodium hydroxide solution before performing the Cr leaching test. The general test approach involves the following steps.

- washing the sludge with 0.01 M NaOH/0.01 M NaNO₂ to remove soluble salts such as NaNO₃, NaNO₂, NaOH, Na₂CO₃, Na₃PO₄, etc.
- leaching the sludge with 3 M NaOH at 100°C to remove additional elements such as Al³⁺ and such anions as PO₄³⁻
- washing the leached sludge with 0.01 M NaOH/0.01 M NaNO₂ to remove added NaOH and materials dissolved in the caustic leaching step
- dividing the residual solids into several portions {One portion is analyzed without contact with additional reagents; each of the other portions is contacted with solutions containing the oxidant. Parameters such as temperature, time, and oxidant concentration (for permanganate) are varied to determine how these affect the leaching process. The leachate solutions are sampled at various times to determine the Cr(VI) concentration.}
- separating the leachate solutions from the undissolved solids following contact with the solids {The residual solids are dissolved and analyzed along with the leachate solutions. Inductively-coupled plasma atomic emission spectroscopy (ICP/AES) is used to determine the major nonradioactive sludge components (especially Cr) and a radiochemical method, alpha energy analysis, is used to determine if TRU elements dissolved significantly.}

Two sludges were tested in this study, a sludge composite from the double-shell tank SY-103 and a sludge composite from the single-shell tank B-111. These samples were chosen because they were found to have the largest concentrations of residual Cr following sludge washing and caustic leaching of the double-shell and single-shell tank sludges, respectively, examined in FY 1995 (Rapko et al. 1995). These sludge samples came from material that had been examined previously by X-ray absorption spectroscopy (Rapko et al. 1996; Rapko et al. 1995). Each of these dry sludge samples was slurried with water and divided into five tared plastic vials. The suspensions were then dried to constant weight at 80°C to determine the amount of sludge in each test sample. These weights, coupled with the Cr concentration reported for the leached sludges (Rapko et al. 1995), were used to calculate the amount of permanganate needed to achieve the desired Cr:permanganate stoichiometry. 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 bubbled through the test solutions was ca. 3 wt% in ozone, which kept these test solutions constantly in contact with fresh oxidant.

Five sets of tests were performed with each sludge. Four of the tests were similar in design with each sludge first being suspended in 0.01 M in NaOH. In the first test, a 0.1 M potassium permanganate/0.01 M NaOH solution was added until a stoichiometric (1:1) permanganate:Cr ratio was obtained. In the second test, a 0.1 M potassium permanganate/0.01 M NaOH solution was added until a 0.1 ratio of permanganate to Cr was initially present. No permanganate was added to the third test solution; this solution was contacted solely with ozone. The fourth test solution was a 0.01 M NaOH blank; neither permanganate nor ozone was added. In each case, the amount of 0.01 M NaOH was adjusted so the total volume of added permanganate and hydroxide solutions was constant, 15 mL for the B-111 test and 50 mL for the SY-103 test.

The samples were stirred at room temperature for the first 16 hours, and the solutions were then heated at 80°C for the duration of the experiment. Periodic sampling occurred after 1 hour, 5 or 7 hours, 16 hours, 23 hours, 30 hours, and 37 hours of reaction time. Before each sampling, the solutions were weighed, and mass losses due to evaporation were replenished by adding water.

Each of the sample aliquots was diluted with 0.01 M NaOH, and the spectrum from 350 to 800 nm was recorded on a Spectral Instrument's 400 series CCD array ultraviolet (UV)-vis spectrophotometer. The chromate concentration was 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 to 0.05 absorbance units with a slope of 4853 and a correlation coefficient of better than 0.99999, as compared to the theoretical slope of 4845 and correlation coefficient of 1. This measured calibration curve was then used to calculate a sample's Cr concentration from its measured 372-nm absorbance.

Upon completion of the test, the samples were centrifuged and the supernatant removed by decanting. No attempt to wash the residual solids and so remove interstitial liquid was made because the large solutions to solids ratios used in these experiments (typically 250-500 mL/g for SY-103 and 75-150 mL/g for B-111) should result in a negligible contribution of the interstitial liquid to the ratio of any supernatant component vs the residual solid. The pH of the supernatant both before and after testing was measured with a Mettler DL21 automatic titrator equipped with a Ross combination pH electrode (Orion Research Inc., Boston, Massachusetts). The residual solids were dissolved for analysis in nitric acid or nitric acid/HF, as required. 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. Established procedures were used for both of these latter analyses.^(a)

The fifth test was designed to test whether or not, in the presence of excess (3:1 KMnO₄ to Cr) oxidant, the partial reduction of soluble permanganate to soluble manganate alone would occur and so oxidize Cr. This different objective led to an alternative procedure. Here, a three fold excess of permanganate to Cr was added and the suspension contacted for 15 minutes. An aliquot was removed and its visible spectrum recorded. The supernatant was then separated from the solids by centrifugation and decantation and analyses of each phase performed as described previously.

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

3.0 Results and Discussion

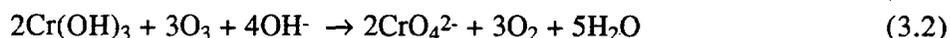
The pH of the solutions both before and after testing is shown in Table 3.1. In general, the test solutions are characterized by significant drops in pH during the course of these tests. The decrease in the pH of the blank samples was usually less than that observed in the leach solutions, which indicates that these pH reductions are due to other chemical phenomena besides environmental effects like sorption of carbonate from the atmosphere. These observed pH decreases are larger for the tests with SY-103 sludge than with the B-111 sludge.

Table 3.1. Changes in the pH of Cr Leach Test Solutions

<u>Sludge Tested</u>	<u>Leach Test</u>	<u>Initial pH</u>	<u>Final pH</u>
B-111	A	11.3	10.3
B-111	B	11.6	12.3
B-111	C	11.3	9.4
B-111	D	11.4	9.1
B-111	E	11.4	10.4
SY-103	A	11.7	7.7
SY-103	B	Not performed	Not performed
SY-103	C	12.0	7
SY-103	D	12.0	6.5
SY-103	E	12.0	11.4

A = Stoichiometric KMnO_4 Reaction; B = 3 fold Excess KMnO_4 Reaction; C = Sub-stoichiometric KMnO_4 + Ozone Reaction; D = Ozone Reaction; E = 0.01 M NaOH Blank

These results appear to be consistent with the expected stoichiometry, as indicated below, for Cr oxidation in the leach solutions. For both Cr oxidations, base is consumed. This should lead, as observed, to a decrease in the solution's pH as Cr oxidation proceeds. In addition, since more hydroxide is consumed during an ozone oxidation of Cr compared to a permanganate oxidation, the magnitude of the decrease should be much greater for the ozone tests as compared to permanganate. Conditions C and D in Table 3.1 refer to the ozone leach tests while A and B refer to permanganate leach tests. Consistent with this explanation, the ozone leach tests show a lower final pH, even though, as described later, the final amounts of oxidized Cr are comparable. Finally, since the concentration of dissolved Cr in the SY-103 tests was much greater than with B-111, (see below), this increased oxidation of Cr should consume additional hydroxide and lead, as observed, to a greater lowering of the pH of the supernatant. In short, the observed changes in solution pH are qualitatively consistent with Cr dissolution through oxidation of insoluble $\text{Cr}(\text{OH})_3$ to soluble CrO_4^{2-} .



The dissolution of Cr as a function of time was followed by monitoring changes in chromate concentration through visible spectroscopy. These changes are shown in Figures 3.1 and 3.2. Maximum absorbance of chromate in the visible region occurs around 372 nm (Gordon and Ford

1972). During these leach tests, the visible spectrum from 350 to 800 nm was tracked as a function of time. No evidence for any other species with absorbances in the visible region besides chromate or permanganate was seen. Absorbance by permanganate in the visible spectrum occurs from 500 to 600 nm, and so does not interfere with chromate. Therefore, the absorbance at 372 nm can be directly related to the solution's chromate concentration.

The leaching behavior of both B-111 and SY-103 sludges shows similar trends. Surprisingly, chromate was present in the blank leach solutions. This chromate appears not to be a result of a specific reaction with the blank solution (0.01 M NaOH), as the characteristic yellow color of chromate was observed immediately upon contact of the solids, and little change in the blank's chromate concentration occurred during the testing. Previous studies indicate that chromate is not present at the conclusion of the sludge washing and caustic leaching test (Rapko et al. 1996). The most plausible explanation for its presence at the beginning of these leach tests is that some oxidation of Cr occurred during the drying of the sludge before the testing began (80°C in air for several days). This air oxidation appears significant: often as much as 25% of the total leached Cr was

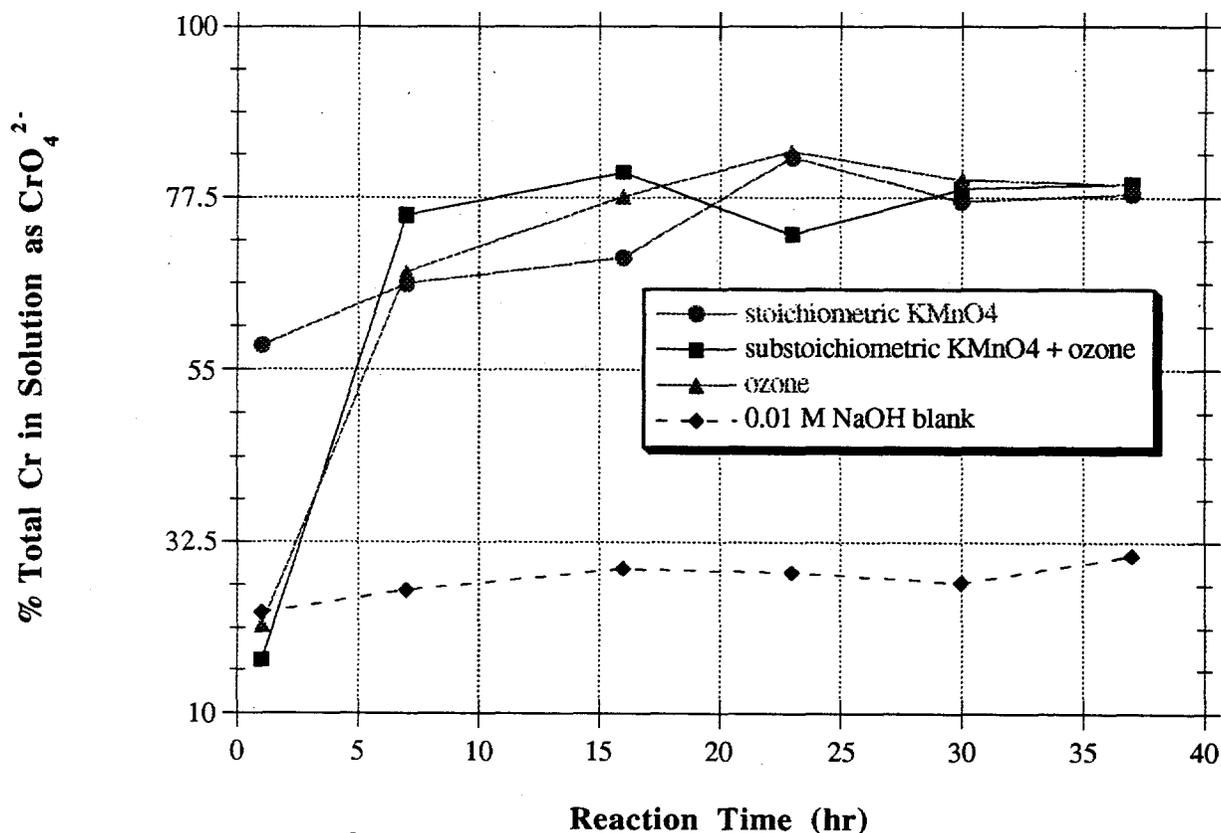


Figure 3.1 Kinetics of Cr Leach Tests with SY-103 Sludge

dissolved in the blank. Although the details of this oxidation are unknown, the presence of dry solids may be significant since little additional Cr dissolution occurred in the sludge suspensions while heating during the blank leach test.

Oxidation of chromate by permanganate appears to be quicker than oxidation by ozone. The permanganate oxidations are mostly complete within 1 hour at room temperature; the ozone oxidations are somewhat slower and continue for the first 16 hours at room temperature, although most of the Cr dissolution occurred within the first 7 hours. Higher temperatures (80°C) and longer reaction times gave little additional oxidative dissolution of Cr.

The final supernatant and the residual solids were analyzed by ICP-AES and alpha energy analysis to verify the Cr dissolution results based on visible spectroscopy and to examine the selectivity of Cr leaching under these oxidizing conditions. Tables 3.2 and 3.3 summarize the amounts of major elements and radionuclides that were removed by these oxidative Cr leaching tests. In general, the selectivity for Cr dissolution by the permanganate and/or ozone treatments is excellent. Among the non-radionuclides, only Cr, Ca in the SY-103 tests, and Mn (where excess Mn was added)

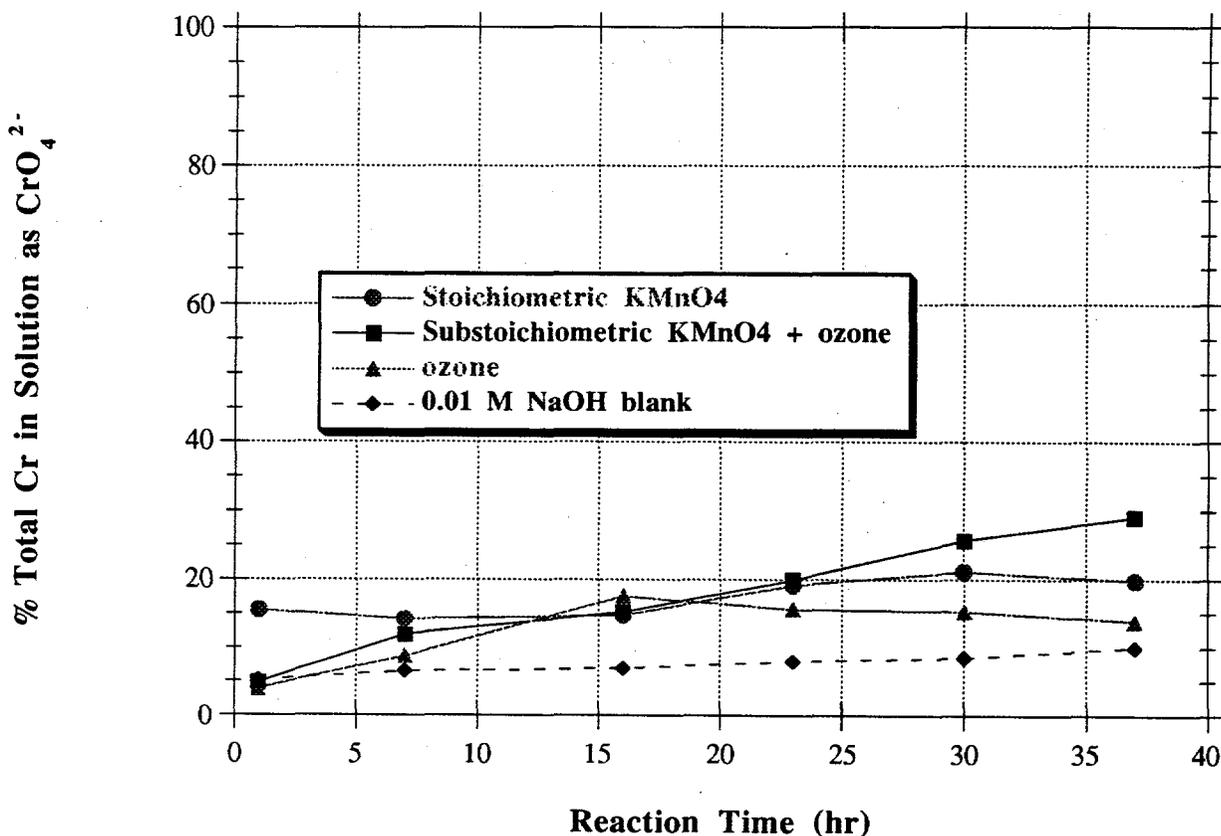


Figure 3.2. Kinetics of Cr Leach Tests with B-111 Sludge

Table 3.2. Percent Removal of Major Sludge Component During Cr Leach Testing of SY-103 as Measured by ICP-AES and Alpha Energy Analysis

<u>Component</u>	<u>Test A</u>	<u>Test B</u>	<u>Test C</u>	<u>Test D</u>	<u>Test E</u>
Al	0.2	2.4	0.4	0.3	10.9
Bi	1.2	2.0	< 2.0	< 1.6	< 2.2
Ca	7.1	12.7	29.3	38.8	9.1
Cr	89.8	60.1	91.8	88.7	34.0
Fe	0.1	< 0.1	0.2	0.2	0.4
Mn*	0.2	23.3	0	0.1	0
Na*	79.3	79.7	84.1	81.9	80.7
Si	< 2.7	< 4.2	< 3.1	3.4	< 2.4
Total Alpha	< 0.01	< 0.02	0.13	0.74	0.11
²³⁹ Pu	Not available	Not available	1.3	5.3	0.02
²³⁸ Pu and ²⁴¹ Am	Not available	Not available	0.02	0.12	0.1

* = Includes component contributions due to added permanganate and 0.01 M NaOH

Test A = Stoichiometric KMnO₄ Reaction

Test B = 3 fold Excess KMnO₄ Reaction

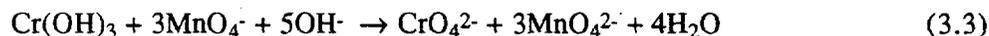
Test C = Sub-stoichiometric KMnO₄ + Ozone Reaction

Test D = Ozone Reaction

Test E = 0.01 M NaOH Blank

show significant enhanced dissolution as compared to the blank. The dissolution of non-radionuclides in the 0.01 M NaOH blank tests show the behavior expected from prior sludge washing and caustic leaching tests (Rapko et al. 1995). The enhanced dissolution of Ca in the SY-103 tests closely parallels the final pH of the supernatants, and the increasing solubility of Ca in these more acidic supernatants likely explains this behavior.

Analysis of the ICP-AES data provides some information as to the behavior of permanganate during these leaching tests. Detectable manganese in solution is found only where excess permanganate was introduced or for the stoichiometric permanganate reaction with SY-103. In the latter case, a small amount of permanganate remained in solution at the end of the test. However, the presence of soluble manganese alone does not distinguish between two possible Cr oxidation reactions with excess permanganate. One mechanism involves a 1:1 Mn:Cr reaction as described earlier. The second involves a 3:1 Mn to Cr stoichiometry as shown below.



If oxidation of Cr occurs through the former mechanism, the residual solids should have a higher concentration of manganese due to the precipitation of MnO₂ than if the latter mechanism is involved. Indeed, if the excess permanganate proceeds by a single, three-electron oxidation, the

Table 3.3. Percent Removal of Major Sludge Component During Cr Leach Testing of B-111 as Measured by ICP-AES and Alpha Energy Analysis

<u>Component</u>	<u>Test A</u>	<u>Test B</u>	<u>Test C</u>	<u>Test D</u>	<u>Test E</u>
Al	2.0	1.6	0.5	0.7	2.6
Ca	2.7	3.7	2.3	2.8	2.1
Cr	18.1	18.0	26.9	12.3	5.0
Fe	0.01	0.01	0.01	0.01	0.02
Mn*	< 0.04	39.7	< 0.16	< 0.33	< 0.33
Na*	74.7	72.0	72.3	76.9	68.6
P	< 0.3	< 0.6	< 0.3	< 0.3	< 0.3
Si	0.2	6.9	3.2	4.7	3.8
Total Alpha	< 0.02	< 0.04	< 0.02	< 0.07	< 0.07
²³⁹ Pu	Not available				
²³⁸ Pu and ²⁴¹ Am	Not available				

* = Includes component contributions due to added permanganate and 0.01 M NaOH

Test A = Stoichiometric KMnO₄ Reaction

Test B = 3 fold Excess KMnO₄ Reaction

Test C = Sub-stoichiometric KMnO₄ + Ozone Reaction

Test D = Ozone Reaction

Test E = 0.01 M NaOH Blank

amount of manganese added should be equivalent to the 1:1 oxidation. However, if the mechanism proceeds by three one-electron oxidations, no MnO₂ should occur, and the amount of permanganate present in the residual solids should be roughly equivalent to the blank. Tables 3.4 and 3.5 provide the information needed to distinguish between these alternatives. Table 3.4 uses the ICP-AES data to verify that the assumption of Cr present based on analysis of a previous sludge washing and caustic leaching test together with the known weight of sample used in the test gave the desired Mn:Cr ratio. As shown in Table 3.4, the agreement between the calculated and measured Mn:Cr ratios is good. Table 3.5 reveals how much Mn precipitated during the Cr leaching tests with permanganate. The observed Mn present in the residual solids was ratioed to that of a known, plentiful, inert component, Fe. As shown in Table 3.5, the reaction with excess permanganate with both SY-103 and B-111 sludges gave a Mn:Fe ratio very close to the ratios observed for the stoichiometric permanganate reaction and very much different than the ratios present in the sludges in the absence of added permanganate. This information strongly suggests that Cr oxidation in the presence of excess permanganate cannot be stopped with the formation of manganate ion, but will proceed to form insoluble MnO₂ even under the mild conditions (15 minutes at room temperature) of these tests.

Table 3.2 reveals significant increased total alpha activity in the ozone leaching with SY-103. However, the SY-103 blank supernatant also showed detectable total alpha activity; the reason for this is not understood, although the same oxidation that produced chromate in the blank test is a likely explanation. The presence of ²³⁹Pu was directly detected in the ozone treated supernatants. However,

Table 3.4. Cr to added KMnO_4 ratio in B-111 and SY-103 Leach Tests

Sample	Total Moles Cr in Test ($\times 10^5$)	Total Moles KMnO_4 Added ($\times 10^5$)	Mn/Cr Calculated	Mn/Cr Found
Stoichiometric B-111	1.79	2.22	1	1.24
Excess B-111	2.16	6.06	3	2.81
Substoichiometric B-111	2.02	0.2	0.1	0.099
Stoichiometric SY-103	74.5	74	1	0.99
Excess SY-103	56.3	147	3	2.61
Substoichiometric SY-103	43.2	4.23	0.1	0.098

Table 3.5. Manganese and Iron Concentration in Selected Residual SY-103 and B-111 Solids

Sample	Residual Fe (μg)	Residual Mn (μg)	Fe/Mn
B-111 with Stoichiometric KMnO_4	47000	1700	27.6
B-111 with Excess KMnO_4	54100	1720	31.5
B-111 0.01 M NaOH Blank	35480	184	193
SY-103 with Stoichiometric KMnO_4	15430	46480	0.332
SY-103 with Excess KMnO_4	9370	18090	0.518
SY-103 0.01 M NaOH Blank	5440	1550	3.51

alpha energy analysis also indicated the presence of ^{238}Pu and/or ^{241}Am . It is not clear from the experimental data whether any Am is dissolved during the test. Based on previous sludge washing and caustic leaching test results with SY-103 (Rapko et al. 1995) the amount of ^{238}Pu activity in the leached sludge is ca. 0.1 the ^{241}Am activity. Since the total amount of ^{238}Pu and ^{241}Am present in the test sample is known the ^{238}Pu present in the test sample can be estimated. Assuming comparable dissolution behavior for each Pu isotope, the expected activity due only to dissolution of ^{238}Pu can be calculated. Significantly greater ^{238}Pu and ^{241}Am activity in the supernatant could only occur with Am dissolution. However, the measured values are only 14% and 22% of the expected activity due to ^{238}Pu alone in the ozone and permanganate and the ozone-only tests, respectively. Therefore, the available data do not distinguish between Pu dissolution only and combined Pu and Am dissolution.

4.0 Discussion

Two Hanford tank sludges have been examined to determine whether selective oxidative dissolution of Cr can occur. Overall, the results are encouraging: little enhanced dissolution of any other non-radionuclide was observed. The exception was Ca, and the increased dissolution is consistent with the changes in the supernatant pH that occur as hydroxide is consumed during the oxidation of Cr. The rate at which Cr dissolved was followed by monitoring the appearance of chromate with visible spectroscopy. The presence of chromate indicated that oxidative dissolution of Cr was occurring since previous examination of the leached sludges by X-ray absorption spectroscopy has shown that Cr is present only as Cr(III) in these leached sludges (Rapko et al. 1996). The presence of chromate then in the blank solution immediately upon mixing was a surprise and is rationalized by assuming the oxidation of Cr when the sludge was dried in air at 80°C before testing. The amount of Cr removed was determined by ICP analysis of the supernatant and residual solids at the end of the test. As a check on the methods, the chromate concentration in the supernatant at the end of each test can be compared with the Cr concentration in each supernatant as determined by ICP-AES. If the enhanced dissolution of Cr is due solely to Cr oxidation, the amount of Cr in the supernatant as determined by ICP-AES should be equivalent to the amount of chromate in the supernatant as determined by visible spectroscopy. Table 4.1 compares the Cr molarity of the supernatant as determined by each method. Except for the B-111 blank, agreement between the two methods appears to be fair, within ca. +/- 15%. Within a series of sludge tests, the ratio appears to be fairly consistent. It is likely that the observed discrepancies refer to the precision of the measurement itself rather reflecting significant contributions of Cr(III) dissolution to the overall amount of Cr(III) observed. Evidence supporting this claim comes from the observation that within a series of sludge tests, the measured Cr concentrations are fairly consistent. Since the pH values in the SY-103 test range over almost 5 pH units and noting the marked dependence of Cr(III) solubility on pH (Rai et al. 1987), if Cr(III) dissolution provided a significant contribution, more variability within the SY-103 series should be observed. Further support for the hypothesis that only Cr(VI) makes a significant contribution to the overall Cr concentration comes from comparing the ICP vs visible spectroscopy Cr concentrations between B-111 and SY-103. If Cr(III) dissolution were contributing, then all sludge tests should show, contrary to the results with the B-111 test samples, a ratio of Cr concentration (ICP)/ Cr concentration (Vis) greater than 1.

Although the oxidative dissolution of Cr by permanganate or ozone appears reasonably selective, how effective will this treatment be in reducing the amount of high level waste that needs to be vitrified? Table 4.2 compares the limiting components, using the methods described in Rapko, et al. (1995), in preparing glass before and after an oxidative leach for the removal of Cr. For B-111, oxidative leaching of Cr has little impact on the number of glass logs required to vitrify this sludge since Cr is only the third limiting component. Oxidative leaching had no detectable impact on the limiting component, P. The additional manganese that results from the precipitation of MnO₂ has no impact because of the relatively large amount of Mn compared to Cr initially present in this sludge.

The situation for SY-103 is quite different. In this high Cr sludge, the use of either oxidative leaching agent results in large decreases in the amount of glass required to vitrify the sludge. Because of the large amounts of Cr, precipitation of Mn adds a sufficiently large amount of this element that the residual Mn and Cr are now effectively equivalent as the primary glass limiting agent. In other words, treatment with either ozone or permanganate would require about the same amount of glass to vitrify the waste; the difference is in the glass-limiting component.

Although decreasing the amount of glass required to vitrify the remaining solids as HLW is key to evaluating the effectiveness of an oxidative alkaline leaching treatment, it is also important to ensure that such treatments do not introduce any problematic materials into the aqueous, waste LLW fraction. The only significant, problematic component found in the aqueous fractions of these tests came from the detection of some TRU elements in the aqueous phase while testing SY-103 sludge with ozone and in the SY-103 blank. For all testing with the B-111 sludge and with the

Table 4.1. Molarity of Cr in Test Supernatant at the Conclusion of Testing

Test Sample	<u>M</u> Cr(ICP)	<u>M</u> CrO ₄ ²⁻ (Vis)	Cr(ICP)/ CrO ₄ ²⁻ (Vis)
B-111 with Stoichiometric KMnO ₄	2.17E-04	2.37E-04	0.91
B-111 with Excess KMnO ₄	2.59E-04	Not available	Not available
B-111 with Substoichiometric KMnO ₄ / Ozone	3.63E-04	3.92E-04	0.93
B-111 with Ozone	1.28E-04	1.44E-04	0.89
B-111 0.01 <u>M</u> NaOH Blank	4.74E-05	9.43E-05	0.50
SY-103 with Stoichiometric KMnO ₄	1.34E-02	1.21E-02	1.11
SY-103 with Excess KMnO ₄	6.87E-03	Not available	Not available
SY-103 with Substoichiometric KMnO ₄ / Ozone	7.93E-03	6.85E-03	1.16
SY-103 with Ozone	9.44E-03	8.42E-03	1.12
SY-103 0.01 <u>M</u> NaOH Blank	2.21E-03	2.00E-03	1.10

permanganate-only oxidative leaching of SY-103 sludge, no evidence exists for any dissolution of TRU elements during leaching. Prior sludge washing and caustic leaching of SY-103 showed comparable alpha activity in the final, 0.01 M hydroxide washes, and prior sludge washing and caustic leaching of B-111 showed no activity in the final, 0.01 M hydroxide washes (Rapko et al. 1995). In this respect, the blank behavior is consistent with that previously reported; although the lesser activity in the permanganate contacts with SY-103 is problematic. In any event, enhanced Pu dissolution is observed for SY-103 upon contact with ozone. Why enhanced Pu dissolution with ozone was not then observed in B-111 is unknown. Although the total alpha activity present in the samples is an order of magnitude greater for SY-103 than for B-111, the concentrations of ²³⁹Pu, the most readily oxidized TRU element, are roughly equivalent.

Finally, it is of interest to compare these results to other recent reports describing the contact of Hanford Tank sludges with oxidants under alkaline conditions. The first report has already been mentioned (Lumetta and Swanson 1993). Here, a composite sludge from Hanford Tank SY-102 was washed with dilute hydroxide, and the washed sludge was treated with an excess of KMnO₄. Results comparable to the SY-103 permanganate tests were found as 86% of the Cr dissolved, and no total alpha activity was found in the leach supernatants. The second report (Orth et al. 1995) looked at contacting a whole composite (sludge and supernatant) of waste from Tank SY-101 with permanganate. Here the presence of tank supernatant and the organic complexants contained within gave an appreciable Pu activity before the permanganate was introduced. The desired function for permanganate was to destroy the organic complexants. With the destruction of the organic ligands complexed to Pu, the solubility of Pu should decrease. In this test, a five-fold increase in soluble Cr

Table 4.2. Impact of Oxidative Dissolution of Chromium in Alkaline Media on Glass Required for Sludge Vitrification

<u>Leaching Treatment</u>	<u>Largest Number of Glass Canisters (Limiting Component)</u>	<u>2nd Largest Number of Glass Canisters (Limiting Component)</u>	<u>3rd Largest Number of Glass Canisters (Limiting Component)</u>
B-111 with no oxidative leaching	197 (P)	142 (Na)	111 (Cr)
B-111 with stoichiometric KMnO ₄	197-196 (P)	Na (?)**	91 (Cr)
B-111 with ozone	197-196 (P)	Na (?)**	98 (Cr)
B-111 with 0.01 M NaOH (Blank)	197-196 (P)	Na (?)**	106 (Cr)
SY-103 with no oxidative leaching	5030 (Cr)	190 (Al)	84 (Na)
SY-103 with stoichiometric KMnO ₄	589 (Mn)	503 (Cr)	190-189 (Al)
SY-103 with ozone	553 (Cr)	190-189 (Al)	Na (?)**
SY-103 with 0.01 M NaOH (Blank)	3320 (Cr)	169 (Al)	Na (?)**

*Aqueous concentrations below detection limits; calculated changes range from no dissolution to the impact of dissolution at detection-limit concentrations.

**The amount of residual sodium cannot be evaluated from the available experimental data

was noted, and the Pu concentration decreased by over 90%. These trends are qualitatively consistent with the results reported in this study.

The final report looked at treatment of a whole tank composite from tank SY-101 with ozone (Delegard et al. 1993). Here, treatment with ozone with the sludge at room temperature for several hours led to essentially quantitative dissolution of Cr and up to 80% dissolution of Pu. The Cr results compare well with the SY-103 test in this report: the discrepancy in the amount of Pu dissolved deserves comment. Two differences in the design of these experiments might lead to this differing Pu dissolution behavior. The first difference lies in the nature of the sample. In this report, washed and leached solids were examined: in the SY-101 study, a mixture of tank solids and supernatant was used. The supernatant contains a large amount of organic material not present in the leached sludges. The reaction with ozone was shown to convert these organics to carbonate. The presence of large amounts of carbonate should lead to enhanced solubility of Pu under alkaline conditions and may contribute to the observed differences in Pu dissolution behavior. The second difference lies in the hydroxide concentrations of the two test supernatants. In the SY-103 sludge described in this report, the initial pH was 12, i.e., the solution was initially 0.01 M in NaOH. At the conclusion of the ozone leaching, the solution's pH was almost neutral for SY-103 and was around 9.5 for the B-111 test. For the SY-101 test, the solution was initially about 0.6 M in hydroxide and decreased to about 0.3 M in hydroxide by the end of the ozonolysis. Pu in its higher oxidation states should be soluble at these higher hydroxide concentrations. The explanation for the differing Pu dissolution behavior in these two reports may well lie in some combination of these different experimental conditions.

In conclusion, the oxidative leaching of Hanford Tank sludges generally agrees with previous work on similar systems. The major exception is in the Pu dissolution behavior upon treatment of the sludges with ozone, and two possible differences in experimental conditions have been identified as potentially explaining the results.

5.0 Summary and Conclusions

Highlights of this study are summarized as follows.

- Oxidative alkaline leaching of washed and caustic leached Hanford Tank sludges B-111 and SY-103 was evaluated. Two types of oxidants, KMnO_4 and O_3 , were investigated as a function of time, temperature, and (for permanganate) Mn to Cr ratio.
- With both oxidants, reaction rates were rapid. At room temperature, the reaction with permanganate was mostly completed within 1 hour; the reaction with ozone appeared complete within several hours. Subsequent heating to 80°C resulted in little additional Cr dissolution.
- From a processing standpoint, the reaction with either a 1:1 or excess permanganate to Cr ratio proceeds through a single, three-electron reaction with concomitant formation of insoluble MnO_2 rather than three one-electron reactions with concomitant formation of soluble MnO_4^{2-} .
- Selectivity for Cr dissolution by oxidative alkaline leaching is good. The only other element significantly dissolved is Ca, and this most likely correlates to changes in the pH of the supernatant during Cr leaching rather than any direct oxidant-Ca reaction.
- The dissolution of Cr by oxidative alkaline leaching appears to be entirely due to oxidation of Cr to form CrO_4^{2-} . Agreement between the observed chromate concentration and the total Cr concentration as determined by ICP-AES is generally within $\pm 15\%$.
- The two sludges differed significantly in the extent of Cr dissolution under the test conditions. Less than a third of the available Cr dissolved with B-111. The dissolution was much more effective with SY-103: 90% of the Cr typically dissolved.
- Heating of the dried sludges in air at 80°C for several hours appears to be sufficient to oxidize some Cr(III) to Cr(VI). Heating may also oxidize a small portion of the Pu.
- Enhanced TRU dissolution was observed during oxidative leaching of SY-103 with ozone. However, the concentration of dissolved TRUs was comparable to that observed during sludge washing and caustic leaching of SY-103 and so should have little adverse impact on LLW glass formation.
- The impact of oxidative alkaline leaching on the amount of high-level glass required to vitrify the sludge was estimated.
 - For B-111, oxidative alkaline leaching yields no reduction in the amount of high-level glass required since no dissolution of the glass limiting component, P, was observed.
 - For SY-103, oxidative alkaline leaching reduces the amount of high-level glass required by 90%. Either permanganate or ozone appears to be about equal in effectiveness. However, the nature of the glass-limiting component changes from Cr, if ozone is used, to Mn, if permanganate is used.

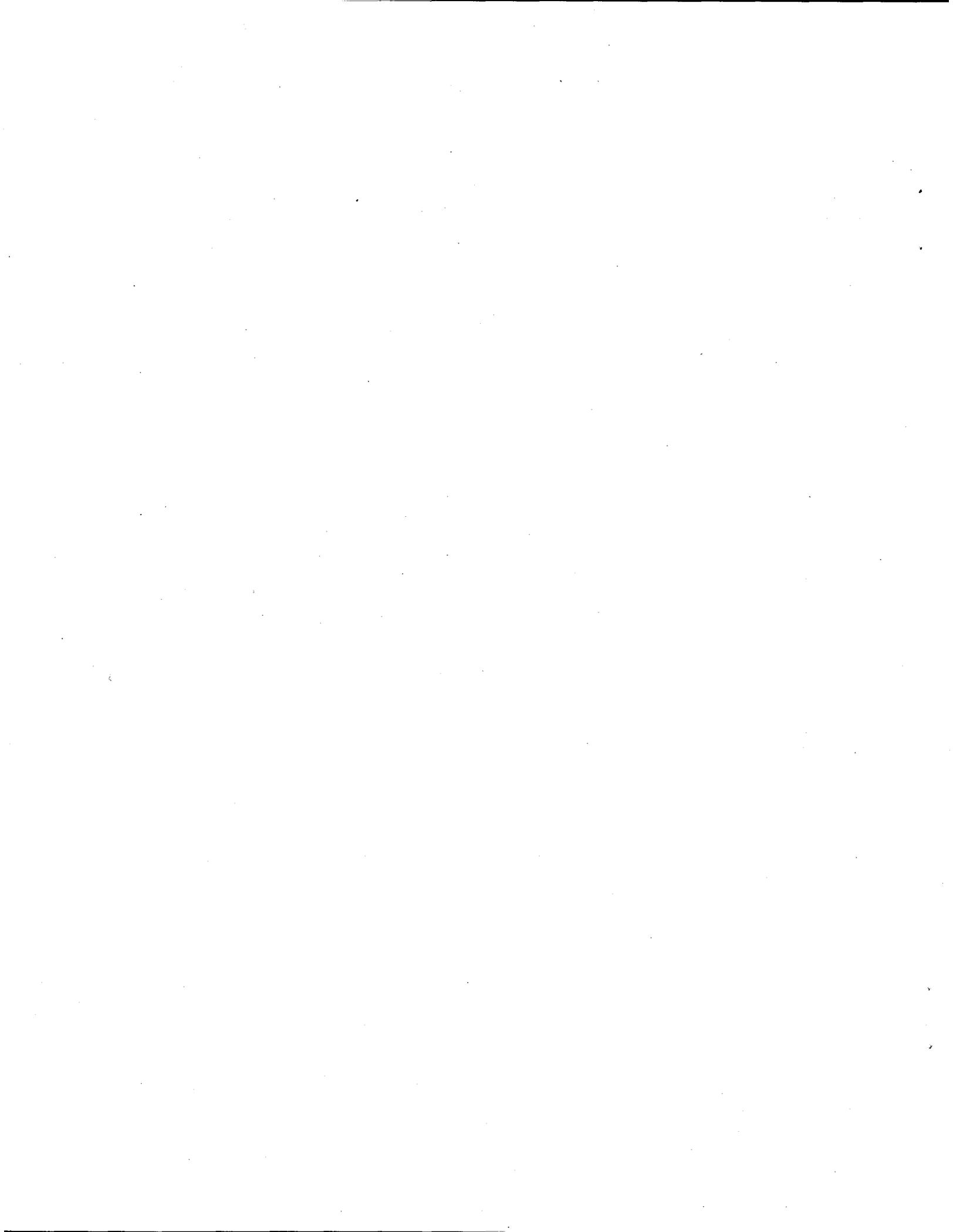
This study also leaves several important questions unanswered. One question concerns the variability in Cr dissolution between B-111 sludge and SY-103. Is this a question of the Cr being in two significantly different chemical environments: one easily leachable, which predominates in SY-103 but is minor in B-111 and one resistant to even the great oxidizing potential of ozone, which

predominates in the B-111, but is minor in SY-103? Alternatively, is this a question of having varying amounts of Cr(III) in different physical environments: one easily leachable, such as a pure Cr(OH)₃ phase, and one inaccessible, such as Cr buried within an Al(OH)₃ or a Fe(OH)₃ phase? A final possible explanation, insufficient reaction time, is unlikely given the data in Figures 3.1 and 3.2, except for perhaps the test with B-111 in contact with both ozone and permanganate. In short, identification of the chemical environment of Cr both before and after oxidative alkaline leaching in greater detail should allow for a better understanding as to the ultimate effectiveness of this type of selective leaching.

Another question deserving more detailed study concerns the variability in Pu dissolution observed between SY-103 sludge examined in this report and the SY-101 sludge and supernatant noted in an earlier report. As mentioned above, differences in pH and/or carbonate concentrations might be responsible. Further work on the impact of alkaline oxidative leach as a function of hydroxide concentration and carbonate concentration would be useful to map out the boundary conditions for selective Cr leaching. Finally, the rate of Pu dissolution in these SY-103 samples during alkaline oxidative leaching should be explored in more detail. If the rate of Pu dissolution lags sufficiently behind that of Cr, then control of contact time might prove an easy method to minimize Pu dissolution. Pu dissolution as a function of time and temperature was not addressed in these studies; future work should include this aspect of alkaline oxidative leaching.

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