

FINAL REPORT
U. S. Department of Energy

Enhanced Sludge Processing of HLW: Hydrothermal Oxidation
of Chromium, Technetium, and Complexants by Nitrate

Principal Investigator: Steven J. Buelow
Institution: Los Alamos National Laboratory
Collaborators: Jeanne M. Robinson, Bernie, R. Foy, D. Kirk Veirs
Institutions: Los Alamos National Laboratory

Project Number: 54765
Grant Number: TTP A106SP21, Subtask 4
Grant Project Officers:N/A
Project Duration: Sept. 1, 1996 – Dec. 31, 1999

Table Of Contents

<u>Title</u>	<u>Page</u>
1. Executive Summary	1
2. Research Objectives	2
2a. Objective	2
2b. Background	2
3. Methods and Results	4
3a. Oxidation of chromium hydroxide using oxygen	5
3a.1 Effect of hydroxide on O ₂ reactions	5
3a.2 Effect of temperature on O ₂ reactions	6
3a.3 Effect of nitrate on O ₂ reactions	6
3a.4 Effect of oxygen on O ₂ reactions	7
3a.5 Global rate expression	7
3a.6 Reduction of chromate by EDTA	8
3a.7 Effect of aluminate on O ₂ reactions	10
3a.8 Summary of oxygen reactions	10
3b. Oxidation of chromium hydroxide using nitrate	11
3c. Transport and speciation experiments	13
3c.1 Diffusion experiments	13
3c.2 Conductance experiments	14
3d. Hydrothermal reactions of plutonium and americium	15
4. Relevance, Impact, and Technology Transfer	15
4a. New scientific knowledge focused on critical DOE environmental management problems	15
4b. Improvement of technologies and cleanup approaches to significantly reduce future costs, schedules and risks	16
4c. Bridging the gap between broad fundamental research and needs-driven applied technology	16
4d. Impact of project on individuals, laboratory, departments, and institutions	16
4e. Larger scale tests	16
4f. Benefits to scientific collaborators	17
4g. Advances in scientific understanding	17
4h. Additional scientific hurdles	17
4i. Interest by others	17
5. Project Productivity	18
6. Personnel Supported	19
7. Publications	19
7a. Published in peer- reviewed journals and books	19
7b. Published in unreviewed publications	19
7c. Accepted/to be submitted for publication	19

Table Of Contents (continued)

<u>Title</u>	<u>Page</u>
8. Interactions	20
8a. Participation/presentations at meetings, etc.	20
8b. Consultation and advisory functions	20
8c. Collaborations	20
9. Transitions	21
10. Patents	21
11. Future Work	21
12. Literature Cited	21
13. Feedback	23
14. Appendices	23

1. Executive Summary

The Office of Economic Management has identified treatment of High Level Waste (HLW) as the second most costly environmental problem facing the DOE. In order to minimize costs of disposal, the volume of High Level Waste (HLW) requiring vitrification and long term storage must be reduced. Methods for efficient separation of chromium from waste sludges, such as the Hanford Tank Wastes (HTW), are key to achieving this goal since the allowed levels of chromium in the high level glass control waste loading. At concentrations above 0.5 to 1.0 wt.% chromium prevents proper vitrification of the waste. Chromium in sludges most likely exists as the extremely insoluble oxides and minerals, with chromium in the +3 oxidation state. In order to solubilize and separate it from other sludge components, Cr(III) must be oxidized to the more soluble Cr(VI) state. Efficient separation of chromium from HLW could produce significant savings.

This project sought to lay the foundation for the application of hydrothermal processing for enhanced chromium separation from HLW sludges. Experiments were conducted which examined four areas:

- a. Oxidation of insoluble Cr(III) solids to soluble Cr(VI) using oxygen,
- b. Oxidation of insoluble Cr(III) solids to soluble Cr(VI) using nitrates,
- c. Transport properties and speciation of reducing and oxidizing agents under hydrothermal conditions,
- d. Reactions of plutonium and americium under oxidizing hydrothermal conditions.

From the results of our experiments in these areas, we have developed a fundamental understanding of chromium speciation, oxidation/reduction and dissolution kinetics, reaction mechanisms, and transport properties under hydrothermal conditions in both simple and complex salt solutions.

Experimental results show that at moderate temperatures (125-200°C), insoluble Cr(III) hydroxide can rapidly be oxidized to soluble Cr(VI). The rate of reaction increases with increasing oxygen and hydroxide concentration and increasing temperature. Experiments also show that sludge components such as aluminate can slow the oxidation/dissolution rate, and that at higher temperatures, organic components in the waste can consume the oxygen before it reacts with the chromium. Reactions of chromium with nitrate only become important at temperatures above 350°C. At lower temperatures the rates of dissolution are not controlled by transport properties. At higher temperatures, particularly near phase transition points, reagent transport could begin to slow and effect dissolution rates. A global rate expression was developed for the reactions involving oxygen and nitrates. The expression agrees well with the experimental results.

Future experiments should examine the reactions of HLW sludges with oxygen at temperatures between 100°C and 200°C at hydroxide concentrations between 1M and 6M. This work should be performed at the Hanford site. Work at Los Alamos will continue, supported by the Nuclear Weapons Program. It will focus on high temperature hydrothermal processes including the oxidation of organic material and TRU salts for purposes of waste minimization and TRU separation.

This project supported nine graduate and undergraduate students from four different universities, one post doctoral fellow, and one visiting faculty member. Collaborations with four faculty members from three university were developed. Seven presentations of this work have already been given at national scientific meetings, one paper has been published, and three other manuscripts are being prepared.

2. Research Objectives

2a. *Objective:* The objective of this project was to lay the foundation for the application of hydrothermal processing for enhanced chromium separation from HLW sludges. We sought to develop a fundamental understanding of chromium speciation, oxidation/reduction and dissolution kinetics, reaction mechanisms, and transport properties under hydrothermal conditions in both simple and complex salt solutions.

2b. *Background:* There are approximately 55 million gallons of high level, radioactive, caustic waste in 177 underground tanks at the Hanford site in Washington state. These legacy wastes were generated between 1946 and 1989, when uranium and plutonium were processed for nuclear weapons [1]. The chemical and radionuclide inventories in tanks are complex and vary with individual tanks [2]. Leaking of waste from tanks leading to the contamination of underground water has been identified as an ongoing problem [3,4]. The cleanup of Hanford tank waste, along with HLW stored at other sites, is currently the Department of Energy's largest and most complex project.

The current technology chosen to dispose of HLW is vitrification of HLW sludge in borosilicate glass. To minimize costs of disposal, the volume of HLW requiring vitrification and long term storage must be reduced. The key to successful volume reduction is the efficient separation and partitioning of non-radioactive elements such as Na, Cr, Al, and P from the HLW fraction. At concentrations above 0.5 to 1.0 wt.%, chromium forms spinel compounds and separates from the glass melt preventing proper vitrification of the waste. High concentrations of chromium also greatly increase the required melting process temperature. Methods for efficient separation of chromium from waste sludge, such as the Hanford Tank Waste, are key to achieving the volume reduction. Efficient separation of chromium from HLW could produce significant savings [5]. In order to solubilize and separate it from other sludge components, Cr(III) must be oxidized to the more soluble Cr(VI) state. The caustic leaching of Al, P, and Cr, and oxidative dissolution of chromium by MnO_4^- , O_3 , H_2O_2 , and O_2 from room temperature up to 100°C have been studied [6-8].

Chromium in HLW sludge exists most likely as extremely insoluble oxides and minerals, with chromium in the +3 oxidation state [9]. Different forms of chromium oxide such as CrOOH , amorphous $\text{Cr}(\text{OH})_3$, mixed oxides of Al/Cr, and BiCrO_4 , have been found in tank wastes [7]. As mentioned above, the chemistry of tank wastes is complex due to the mixture of unknown chemicals and non-uniformity. Because of radioactive handling concerns, it is also cost and time-consuming to identify all possible chromium species in individual tanks. However, the chemistry of chromium-containing inorganic species under hydrothermal environments has been well documented.

Thermodynamically, the forms of chromium oxide depend on the temperature and the solution environment. Phase transformations of chromium hydroxide in aqueous conditions were reported by Kruss and Tammana [10]. They claimed that hydrated $\text{Cr}(\text{OH})_3$ undergoes a transition to $\text{CrO}(\text{OH})$ at temperatures as low as 70°C . $\text{CrO}(\text{OH})$, hereafter written as CrOOH , is very stable until the system temperature reaches 540°C ,

where Cr_2O_3 is formed. The crystalline phase of CrOOH chromium oxide-water system was verified by Laubengaver and McCune [11]. Hydrothermal treatment also affects the physical characteristics of this hydroxide such as surface area, pore volume, pore size, and water content [12]. Carruthers et al. [13] reported that the calcination of chromium oxide gels in oxygen also forms CrOOH at 250 °C. However, they also found that as much as 45 % of chromium is in the Cr(VI) form, depending on the calcined temperature. Kubota [14] found that the decomposition of CrO_3 under an oxygen environment from 200 to 600 °C follows the chain from CrO_3 (<210 °C), Cr_3O_8 (210-280 °C), Cr_2O_5 (280-370 °C), CrO_2 (370-450 °C), and Cr_2O_3 (>450 °C). The reverse reaction of CrOOH to CrO_2 is possible at high pressures of nitrogen [15]. Based on the history of tank temperature profiles [16] and the analysis of potential hot spots in some radioactive waste tanks [17], an estimated temperature for chromium containing inorganic species precipitated and aged in waste tanks under caustic hydrothermal environments does not exceed 200 °C. This temperature leads to the conclusion that the forms of chromium oxide in HLW, except for those associated with other inorganic species, are predominantly $\text{Cr}(\text{OH})_3 \bullet 3\text{H}_2\text{O}$ and CrOOH .

Caustic leaching/washing methods have been established as the baseline separation technology for sludge treatment. It is not known whether caustic leaching/washing methods can achieve the required separation efficiency. Although thermodynamics favors certain phase transitions, reaction rates at ambient temperatures are uncertain and are complicated by the fact that through aging processes, sludge solids may have formed complex minerals which are not dissolved by either caustic or acid media. Entrainment and surface complexation reactions can also complicate these extraction reactions. Precipitated mineral species can entrain other inorganic constituents, such as TRUs, in their solid form. Also, the point-of-zero-charge of minerals in the sludge can lead to surface complexation reactions, which will only allow releases of certain constituents in both alkaline and acid pH ranges; that is, negatively charged ions (e.g. TcO_4^- and I^-) may be bound to particle surfaces at pH ranges different than those that bind positively charged ions (e.g., UO_2^{2+} and Sr^{2+}).

Early experiments on caustic leaching of Hanford tank sludge from several different tanks produced highly variable results [18-21]. The removal efficiency, for example, varied over a wide range for aluminum (16-85 percent), chromium (48-88 percent), and phosphorus (13-98 percent). This is undoubtedly due, in part, to the widely varying composition and speciation of these elements in the various tanks and even within the sludge of a single tank, since results from different cores of a single tank also varied widely. In addition, many species likely to be highly intractable to simple caustic wash have been identified in Hanford tank sludge, including aluminosilicates and aluminum oxyhydroxides. Many of the alkali cations (particularly sodium) may be tied up as counterions in these intractable matrices.

More recent results by Rapko et. al. [7, 22] show that oxygen, permanganate, and ozone can effectively dissolve Cr from some HLW sludge. [7, 22] Experiments were conducted at low temperatures, generally less than 80°C. The reactions involving

permanganate were essentially complete within several hours, while those using oxygen required several days. These studies demonstrated oxidative dissolution of Cr using high level tank wastes, but could not, because of the limited amount of HLW sludge samples and the added costs associated with handling radioactive material, explore a wide range of reaction conditions. The work of our project complements these studies. We have obtained kinetic information over a wide range of operating conditions and developed global rate expression for the oxidation of chromium by oxygen under caustic hydrothermal conditions.

3. Methods and Results

Previous experiments at Los Alamos have shown that hydrothermal processing could dissolve chromium, reformulate solids, oxidize metals, and destroy organic complexants [23-26] in HLW simulants. Unlike traditional sludge treatments that require the use of organic reagents, strong acids, or strong bases, hydrothermal processing uses oxidizers present in the wastes, such as nitrates or air, and does not require additional reagents [24, 26]. A schematic of a hydrothermal unit for the treatment of HLW is shown in Figure 1. Waste is slurried, pressurized, heated, and held at reaction temperature for a time sufficient to complete the desired chemical processes (oxidation, reduction, dissolution). It is then cooled and depressurized, and the solid, liquid, and gaseous products are separated for disposal or further treatment. Reaction temperatures can range from 125 to 550 °C and pressures from 1 to 1000 bar.

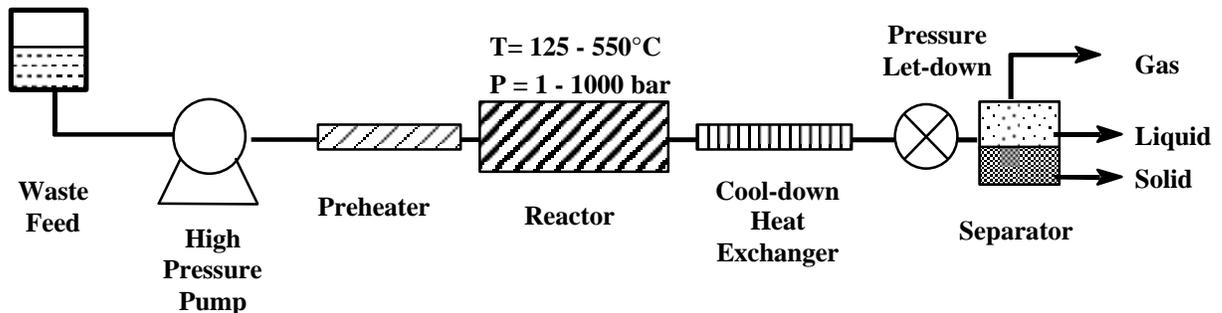


Figure. 1. Schematic of Hydrothermal Treatment Process

To accomplish the goals of this project, experiments were conducted in for main areas:

- e. Oxidation of insoluble Cr(III) solids to soluble Cr(VI) using oxygen,
- f. Oxidation of insoluble Cr(III) solids to soluble Cr(VI) using nitrates,
- g. Transport properties and speciation of reducing and oxidizing agents under hydrothermal conditions,
- h. Reactions of plutonium and americium under oxidizing hydrothermal conditions.

Summaries of the results in these four areas are given below.

3a. *Oxidation of Chromium Hydroxide using Oxygen:* The conversion of chromium(III) to chromium (VI) by oxygen via the reaction $4\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O} + 3\text{O}_2 + 8\text{NaOH} \rightarrow 4\text{Na}_2\text{CrO}_4 + 22\text{H}_2\text{O}$ was studied using a Teflon lined batch reactor (Figure 2) from 75-200 °C at pressures from 10-35 bar. Reaction times ranged from 0.5 to 100 hours. The initial $\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ concentration was held constant at 0.005 M while the effects of hydroxide, EDTA, nitrate and Fe^{+3} were each examined. The mole ratio of O_2/Cr was varied between 1.0 and 8.4. The conversion of Cr(III) to Cr(VI) was monitored as the CrO_4^{-2} product using ion chromatography and UV/VIS spectroscopy.

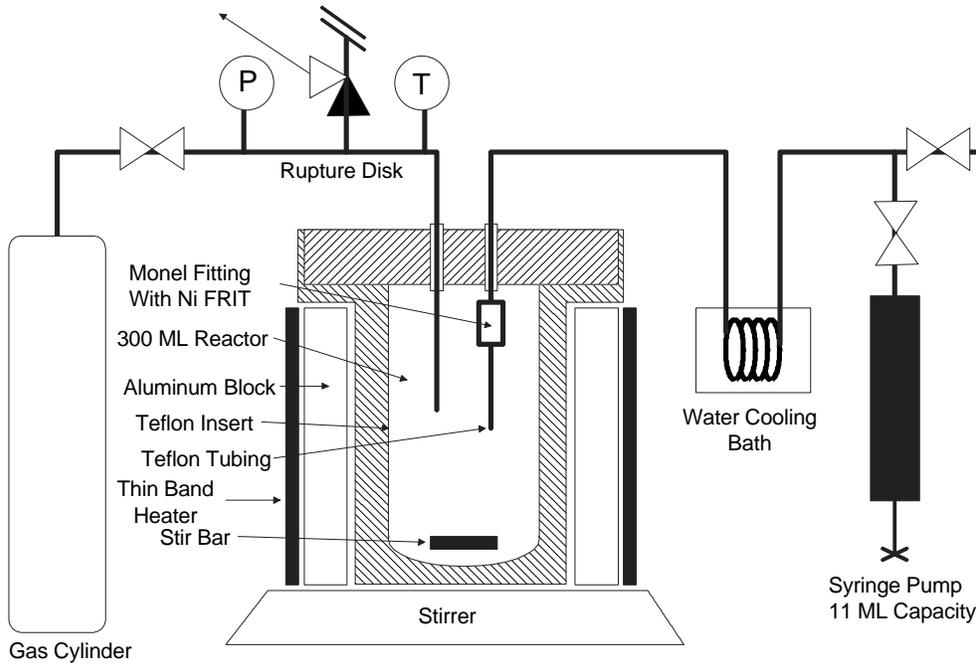


Figure. 2. Schematic Diagram of Teflon Lined, Stirred Batch Reactor.

3a.1. *Effect of Hydroxide on O_2 Reactions:* When the HLW sludges are treated, they will be washed with sodium hydroxide to remove soluble components. The concentration of the sodium hydroxide will effect the rate of chromium oxidation. Figure 3 shows the rate of Cr(III) conversion for various hydroxide concentrations. The rate of reaction of Cr(III) with oxygen varies nearly linearly with hydroxide concentration. Oxygen solubility decreases with increasing hydroxide concentration.

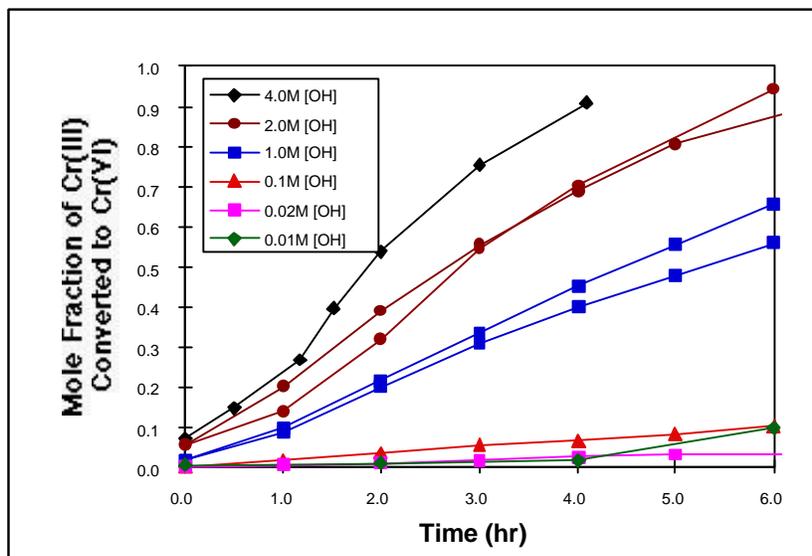


Figure 3. Effect of hydroxide on Cr(III) reaction with oxygen at 125 °C. $[O_2] = 1$ to 2 mM. Total Cr concentration is 5 mM.

3a.2. *Effect of Temperature on O_2 Reactions:* The rate of dissolution of Cr(III) increases with temperature. Figure 4 shows the variation from 75°C to 200 °C. The increase in rate is due not only to an Arrhenius effect but also to an increase in oxygen solubility.

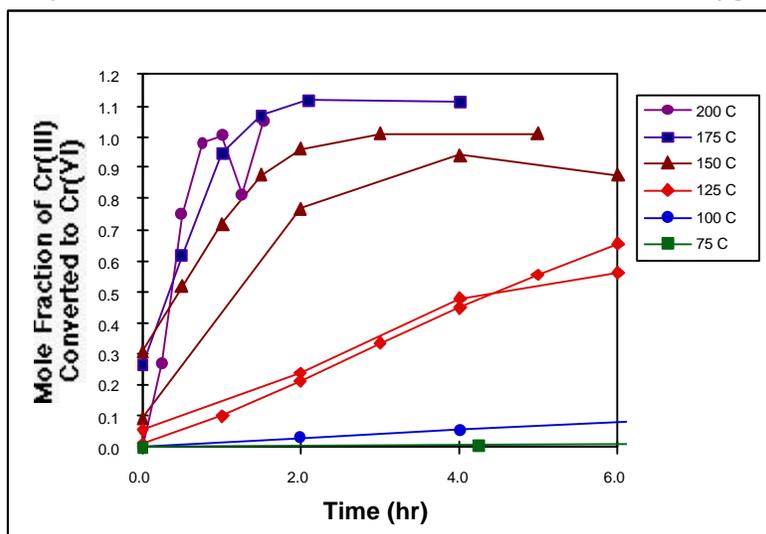


Figure 4. Effect of temperature on Cr(III) reaction with oxygen. $[O_2] = 1$ to 4 mM. $[OH^-] = 1M$. Total Cr concentration is 5 mM.

3a.3. *Effect of Nitrate on O_2 Reactions:* The concentration of nitrate in the tanks is high. Washing of the sludge should remove most of the residual nitrate. Figure 5 shows the mole fraction of Cr(III) converted to Cr(VI) as a function of time at 125°C for several different concentrations of nitrate. The figure shows that nitrate does not interfere with the conversion reaction. At temperatures below 300°C, the rate of reaction of nitrate with

Cr(III) is slow. At temperatures below 200°C nitrate does not significantly effect the rate of Cr(III) reaction with oxygen.

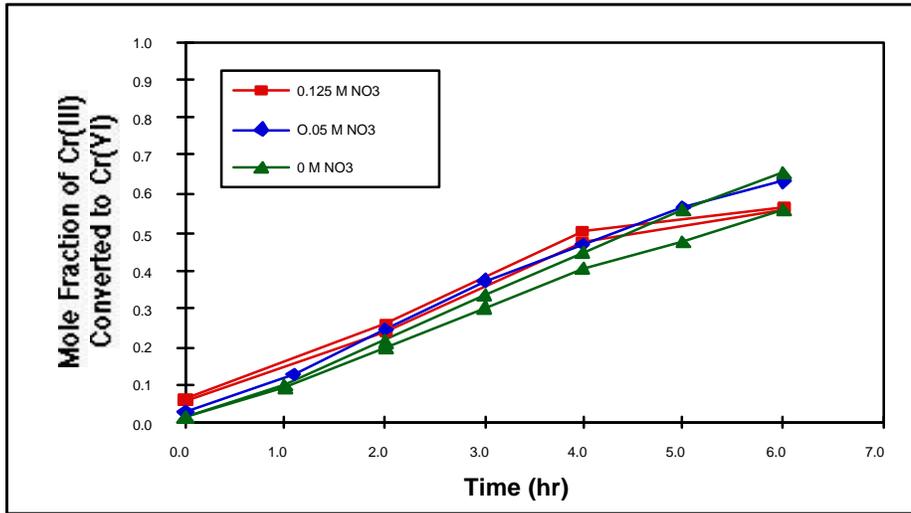


Figure. 5. Effect of nitrate on Cr(III) reaction with oxygen at 125°C. [O₂] = 1.4 mM. [OH⁻] = 1M. Total Cr concentration is 5 mM.

3a.4. *Effect of Oxygen on O₂ Reactions:* The rate of Cr(III) dissolution increases with oxygen concentration. The dependence is nearly half order (Figure 6). The concentration of dissolved oxygen is determined by the Henry's Law constant and depends on temperature, partial pressure of oxygen, and the salt concentration.

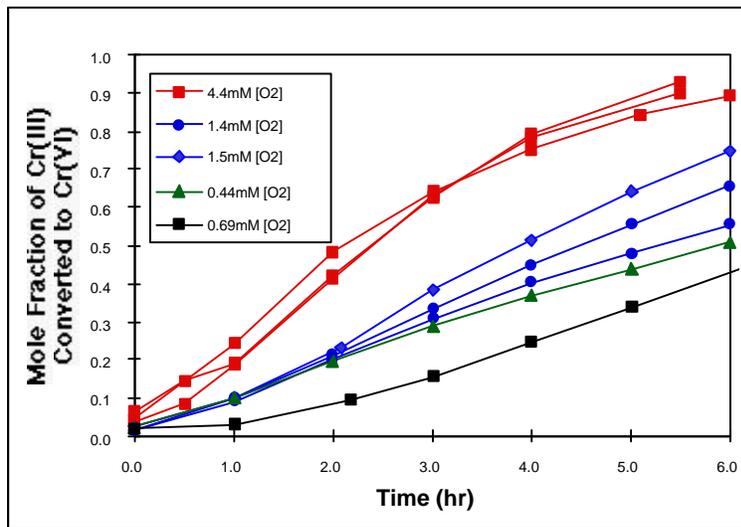


Fig. 6. Effect of oxygen on Cr(III) reaction with oxygen at 125°C. [OH⁻] = 1M. Total Cr concentration is 5 mM.

3a.5. *Global Rate Expression:* From the data in Figures 3 to 6, the dissolution of Cr(OH)₃ · 3H₂O by oxygen obeys the global rate expression:

$$r(\text{Mhr}^{-1}\text{g}^{-1}) = 12882 \exp((-52.5\text{kJ/mol})/RT) [\text{O}_2]^{0.52} [\text{OH}]^{0.81}.$$

This expression yields the $d[\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}]/dt$ per gram of $\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$. Figure 7 shows the agreement between the calculated and measured reaction rates.

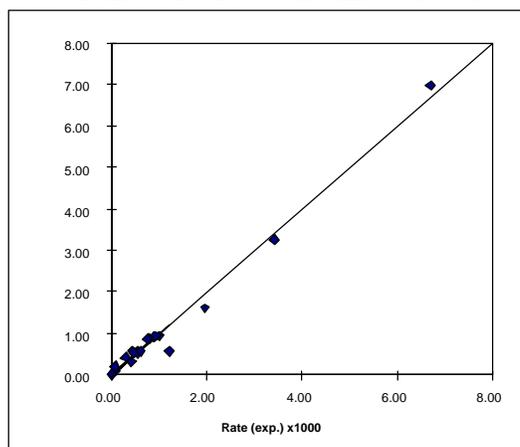


Figure 7. Parity plot for the dissolution of Cr(III) by oxygen, based on the experimentally determined global rate expression.

3a.6. Reduction of Chromate by EDTA: EDTA is present in the tank wastes and could reduce Cr(VI) back to Cr(III). Therefore we studied the reduction of chromate by EDTA. We found that the reaction rate is more than ten times slower than the oxidation of Cr(III) to chromate under similar conditions in the absence of oxygen (Figure 8).

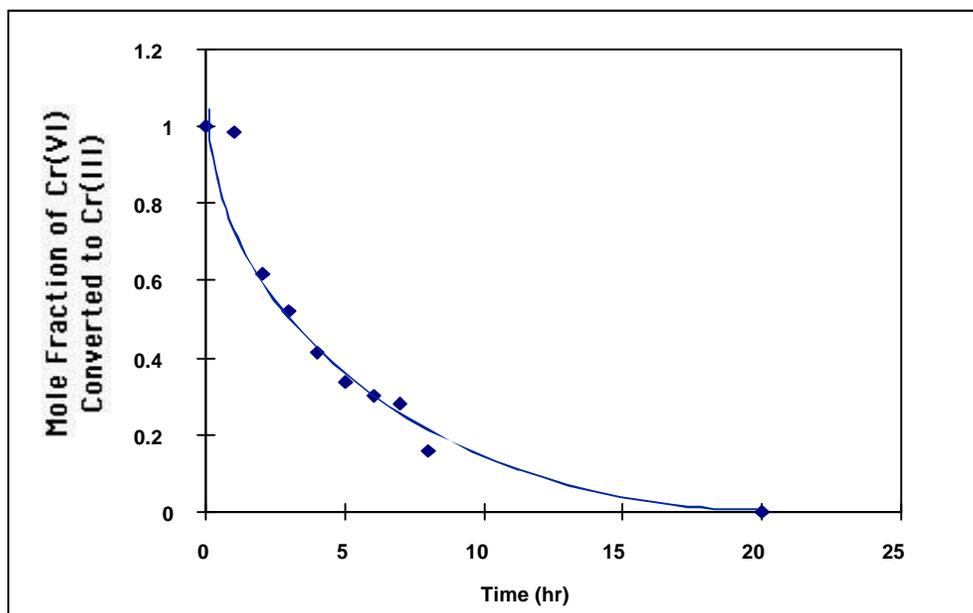


Fig. 8. Reduction of chromate back to Cr(III) by EDTA at 200°C in the absence of O_2 . $[\text{OH}^-] = 1\text{M}$. $[\text{EDTA}] = 11.6\text{ mM}$. $[\text{CrO}_4^{2-}] = 5.8\text{mM}$.

However, EDTA reacts rapidly with oxygen and can, thus, cause incomplete oxidation of Cr(III). Figure 9 shows that the mole fraction of Cr(III) converted to chromate is

decreased when EDTA is present. For the experiments shown, Cr(III) oxidation requires 1.9 mmoles of O_2 , whereas 4mM EDTA would consume 3.7 mmoles of O_2 if fully oxidized. The competition between these two processes varies with temperature. Figure 10 shows, that as the temperature is increased, the rate of EDTA oxidation exceeds the rate of Cr(III) oxidation. For example, at 200°C, only 20% of the Cr(III) has reacted before all the O_2 is consumed. Therefore, excess oxygen is required at higher temperatures.

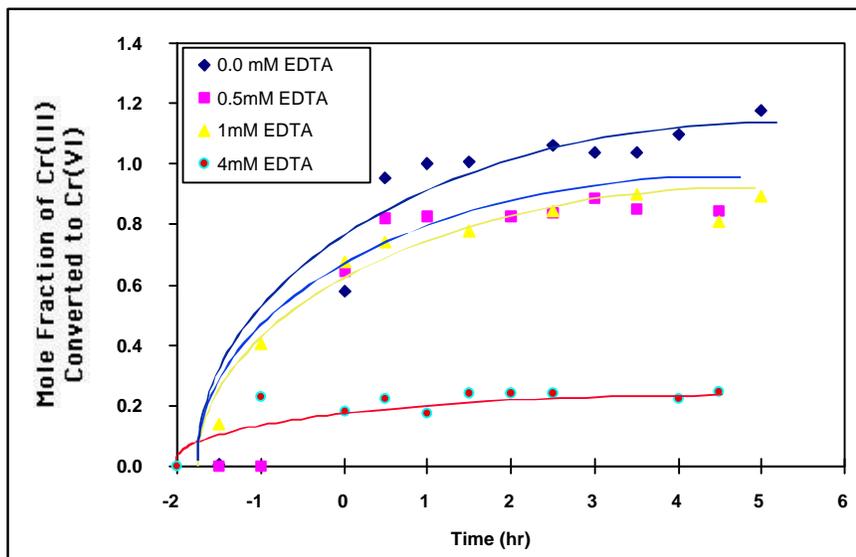


Figure 9. The effect of the consumption of O_2 by reaction with EDTA on the conversion of Cr(III) to Cr(VI) at 200°C. $[OH^-] = 1M$. $O_2 = 2.5$ mmoles.

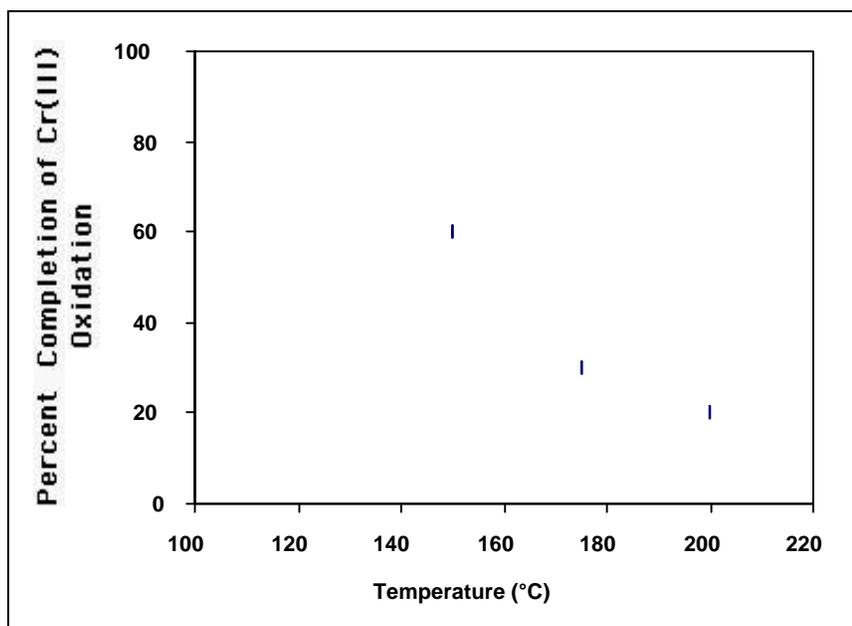


Figure 10. Percent completion of Cr(III) oxidation as a function of temperature in the presence of EDTA (4mM) and O_2 (2.5 mmoles) . $[OH^-] = 1M$.

3a.7. *Effect of Aluminate on Oxygen Reactions.* Aluminate is a major component of the sludge. Figure 11 shows the dependence of the rate of Cr(III) oxidation on aluminate concentration at 1M and 2M NaOH. We found that aluminate at high concentrations decreases the rate of Cr(III) oxidation.

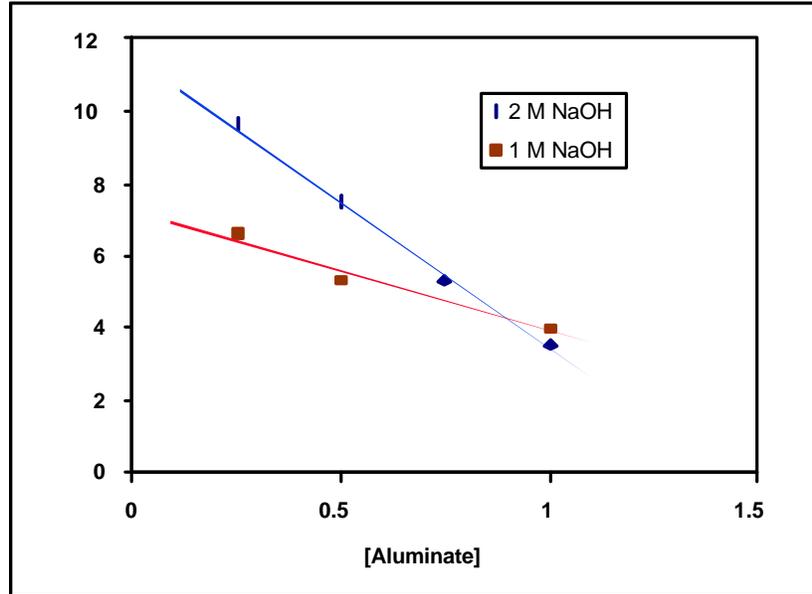


Figure 11. Effect of the concentration of aluminate on the conversion of Cr(III) to chromate at 125°C. $[O_2] = 1$ to 2 mM. Total Cr concentration is 5 mM.

3a.8. *Summary of Oxygen Reactions:* Our understanding of the conversion of Cr(III) to soluble chromate by reaction with oxygen is shown schematically in Figure 12.

Reaction Summary

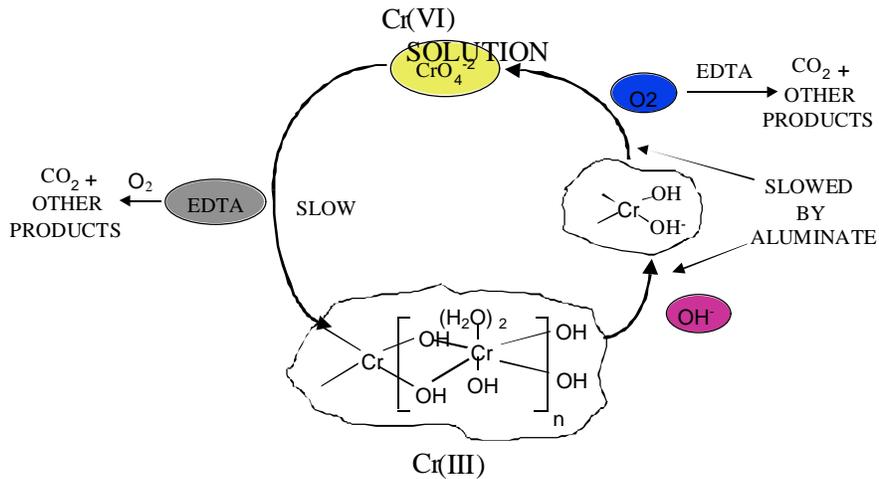


Figure 12. Schematic representation of the oxidation of Cr(III) by oxygen.

We found that:

$\text{Cr}(\text{OH})_3$ is rapidly oxidized by O_2 .

Increasing hydroxide and O_2 concentrations increases rate of Cr(III) oxidation.

Increasing temperature increases the rate of Cr(III) oxidation.

EDTA slowly reduces Cr(VI) to Cr(III).

EDTA reacts rapidly with O_2 at higher temperatures reducing O_2 concentrations.

At high concentrations, aluminate slows Cr oxidation.

Nitrate and Fe^{+3} have little effect on Cr oxidation at temperatures below 200°C .

At temperatures above 400°C , nitrate rapidly oxidizes chromium.

3.b Oxidation of Chromium Hydroxide using Nitrate

We have also studied the oxidation of Cr(III) to chromate in a flow reactor (Figure 13) at higher temperatures than obtainable in the batch reactor (Fig. 2). The conversion of chromium (III) to chromium (VI) by nitrate via the reaction $2\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O} + 3\text{O}_2 + 3\text{NaNO}_3 + 4\text{NaOH} \rightarrow 2\text{Na}_2\text{CrO}_4 + 2\text{Na}_2\text{CrO}_4 + 8\text{H}_2\text{O}$ was studied from $300\text{-}400^\circ\text{C}$ at 276 bar. The initial $\text{Cr}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ sample was 0.14 g and the hydroxide concentration was 1M. The NaNO_3 concentration was varied from 0.025 to 0.125 M. The conversion of Cr(III) to Cr(VI) and the final NO_3 and NO_2 concentrations were monitored using ion chromatography.

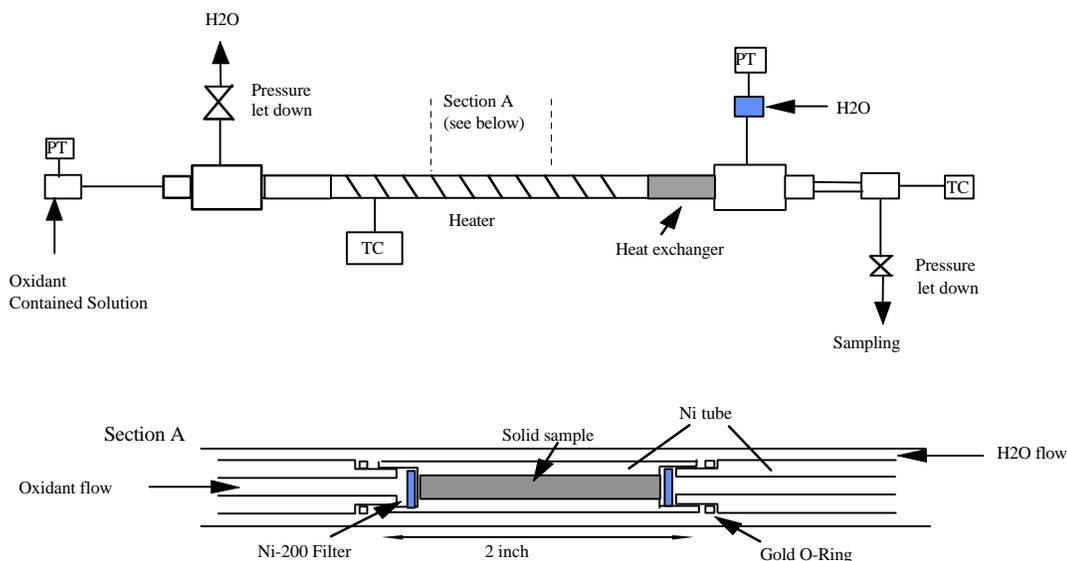


Figure 13. Schematic of Flow Reactor for Oxidation of Cr(III).

We found that the oxidation of Cr(III) to Cr(VI) shows a first order dependence on the concentration of nitrate (Figure 14) but is independent of hydroxide concentration above 0.5 M (Figure 15).

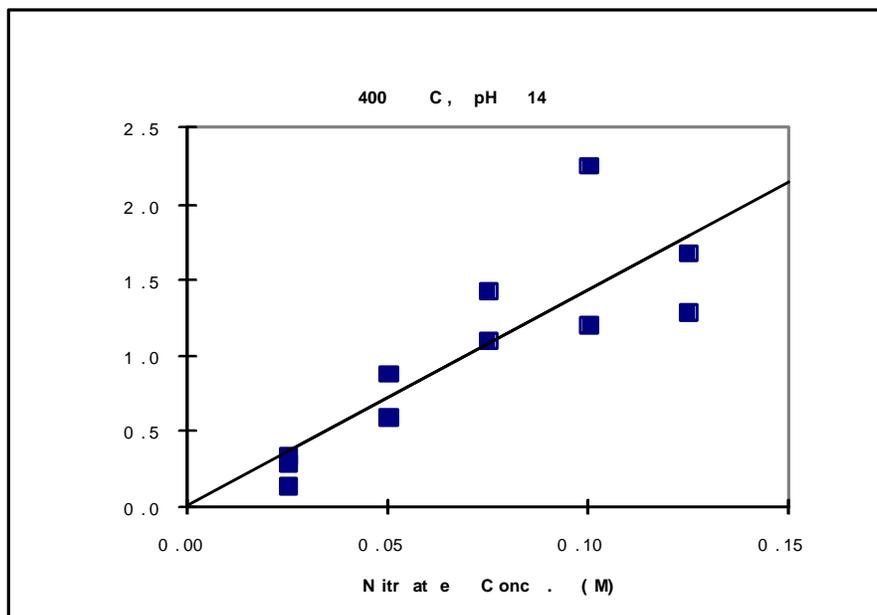


Figure 14. Effect of Nitrate concentration on the oxidation of Cr(III) at 400°C.

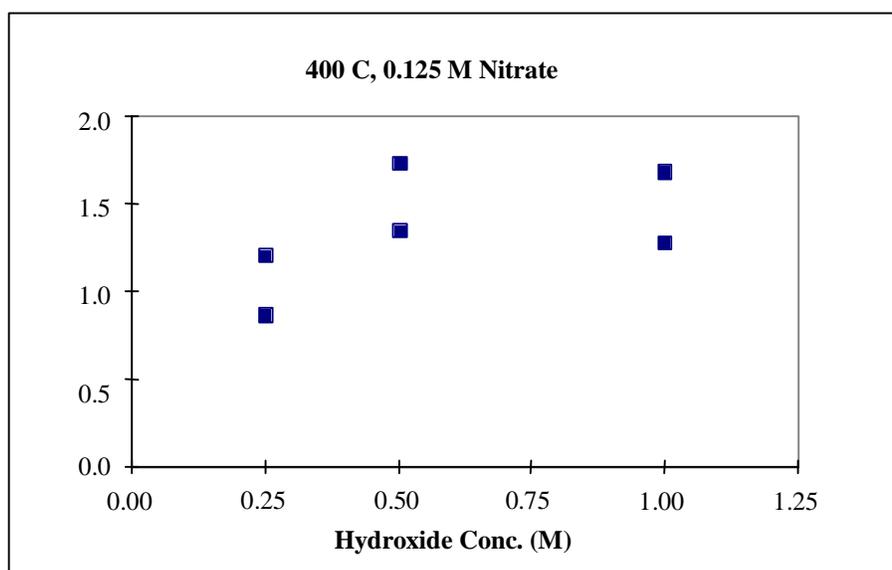


Figure 15. Effect of hydroxide Concentration on Cr(III) oxidation at 400°C.

The oxidation of Cr(III) by nitrate is temperature dependent Figure 16; the reaction is very rapid above about 375°C. A fit to the Arrhenius equation yields $k = 7.0 \times 10^{27} \exp(-78.9 \text{ (Kcal/mol)/RT})$, as shown in Figure 17.

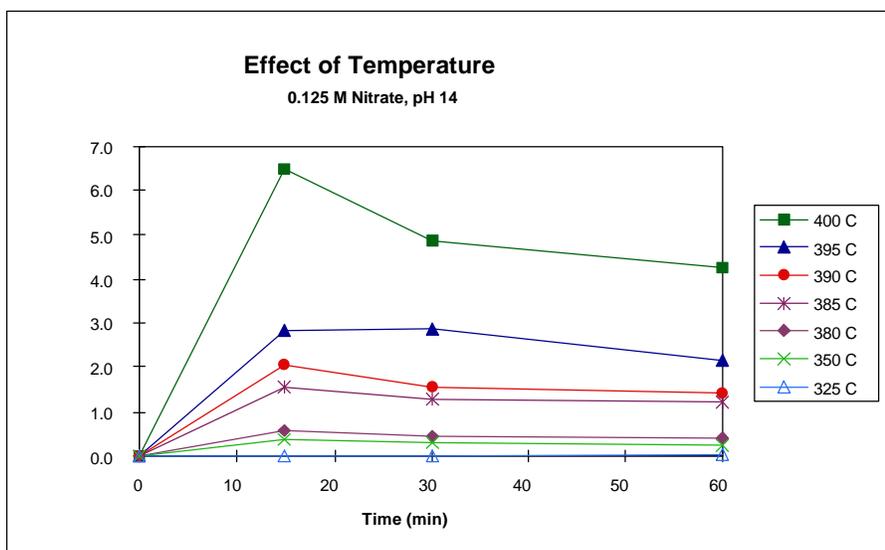


Figure 16. Temperature dependence of the oxidation of Cr(III) by nitrate.

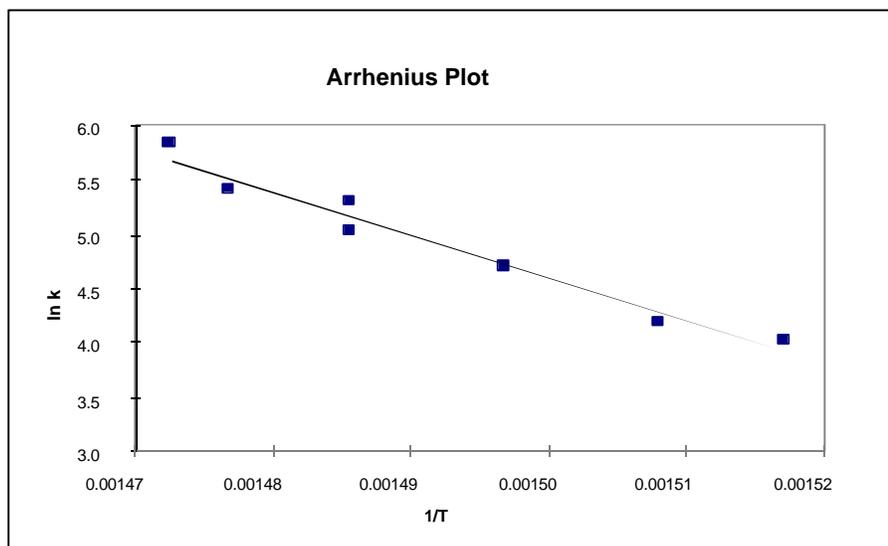


Figure 17. Arrhenius behavior of the oxidation of Cr(III) by nitrate.

3.c *Transport and Speciation Experiments:*

3.c.1 *Diffusion Experiments:* Molecular interdiffusion coefficients were determined for both organic and inorganic molecules in subcritical and supercritical water. Inorganic molecules studied were nitrate salts of lithium, sodium, potassium, cesium, calcium, and strontium; and sodium nitrite. Organic molecules studied were acetone and benzophenone. Diffusion coefficients were determined by analysis of Taylor dispersion profiles. The Taylor dispersion profiles were detected by UV absorbance at the peak

absorbance of the absorbing species. Fluid temperatures ranged from 25°C to 400°C at pressures ranging from 300 bar to 500 bar. Experimental values were compared with predictions from molecular interdiffusion models based on hydrodynamic and kinetic theory.

Experimental diffusion coefficients for alkali nitrates, alkali earth nitrates, and stable organic molecules were measured using the Taylor dispersion technique. A detailed description of the technique and results are given elsewhere [27]. Briefly, an organic or salt solution is injected into a laminar flow tube. The near delta function concentration profile of the injected material broadens as it flows down the tube. The concentration profile is measured at the exit from the tube. A diffusion coefficient is calculated from the final concentration profile.

Diffusion coefficients increase about 20 fold between 25°C and 300°C with little or no pressure dependency at pressures above the critical pressure of water. The diffusion coefficient doubled between 300°C and 350°C. The critical slowing down of the diffusion process was important as far as 300 bar from the phase separation pressure at near-critical subcritical and supercritical temperatures. Conditions, where critical effects were observed, corresponded to reduced temperatures between 0.9 and 1.2, reduced pressures between 1 and 1.6, and reduced solution densities between 1 and 1.4. The diffusion coefficient reached a plateau value at reduced densities greater than 1.4.

Diffusion coefficients in hydrothermal solutions could be estimated within 20% by the Stokes-Einstein equation [27] at conditions where critical effects were negligible. The uncertainty in the estimates depended on the uncertainty in the effective radius of the ion/molecule. The effect of the critical slowing down on the effective radius could be estimated by a semi-empirical model [27]. When ionic conductance data were available, the Nernst-Einstein equation [27] yielded estimates for the molecular diffusion coefficients within 20%.

The effective radius of the diffusing species could be estimated from hydration numbers, association constants, and geometric considerations. The procedure to calculate the effective radius can be optimized once hydration and association equilibrium constants and expressions for the packing order become available. The fraction of each species in solution could then be calculated from hydration equilibrium equations and association equilibrium equations (and reaction equilibria). The effective radius for each species in solution could be calculated from geometric relationships for a given coordination number (number of water molecules and other ions surrounding the central ion) and the chemical/thermodynamic characteristics of the clustering species. The average diffusion coefficient is the weighted harmonic average of the diffusion coefficients of the various species.

A manuscript summarizing the results of this work has been prepared and will be submitted to the *Journal of Physical Chemistry*. A paper discussing the work was presented at the Thirteenth Symposium on Thermalphysical Properties.

3c.2. Conductance Experiments: Electrical conductance measurements for lithium, sodium, cesium, and calcium nitrate as a function of concentration, temperature, and

pressure were obtained. Concentrations, temperatures, and pressures ranged from 0.001 m to 0.040 m, 25°C to 505°C, and 100 bar to 500 bar, respectively. These results were obtained using a simple Pt-electrode with hydrothermal sodium chloride solutions as the calibration standards.

The alkali nitrates show series behavior similar to the alkali chloride series: the electrical conductance decreases with decreasing cation radius. This seemingly paradoxical result is due to the stronger electric field and, hence, the greater tendency for ion pairing and larger solvation spheres associated with the smaller cations. Nearly complete ion association is observed at low-density supercritical conditions. A detailed description of the experiments and results are given elsewhere [27, 28].

3d. Hydrothermal Reactions of Plutonium and Americium: In collaboration with the Nuclear Weapons program, a continuous flow hydrothermal reactor was built and installed in the Plutonium Facility at Los Alamos National Laboratory. The reactor typically operates at 540°C and 400 bar. Mixtures containing organic reducing agents, oxygen, nitrate, plutonium, and americium were studied. In general, the organics rapidly react with the oxidizer, while the plutonium and americium are converted to insoluble solids that can easily be filtered from the liquid effluent. Separation factors of TRU from the combustible material can be as high as 10^7 . The TRU levels in the liquid effluent are near or below industrial discharge limits. A detailed description of the experiments and results are given elsewhere [29].

4. Relevance, Impact and Technology Transfer

4a. New scientific knowledge focused on critical DOE environmental management problems: The treatment of high level wastes stored in underground tanks is one of the most important challenges facing the DOE. Improvements in the separation of non-radioactive elements, in particular chromium, can greatly reduce the cost of treatment and final disposal. The new scientific knowledge from this project is directly focused on the separation of chromium from inorganic sludges. It provides kinetic data needed to design chromium separation units based on hydrothermal reactions of chromium with oxygen and nitrates. It also provides preliminary information on the effects of other waste constituents, such as organics, hydroxide, and aluminates. The results from this project can also be applied to other DOE management problems. The use of hydrothermal oxidation of TRU metals is being tested at Los Alamos National Laboratory. Collaborative experiments at Los Alamos have already demonstrated that hydrothermal oxidation of TRU contaminated combustible materials produces insoluble TRU metal oxides that can easily be filtered from product effluents. Separation factors of TRU from the combustible material can be as high as 10^7 . Most of the combustible material is contaminated with nitrates and many have chromium. The scientific knowledge gained from this project adds to the information needed to elucidate the behavior of metals under oxidizing hydrothermal conditions for the treatment of combustible wastes.

4b. Improvement of technologies and cleanup approaches to significantly reduce future costs, schedules, and risks, and to meet DOE compliance requirements: This project demonstrated that insoluble chromium (III) species can rapidly be oxidized to soluble chromium (VI) species by air under moderate hydrothermal conditions. The reaction times (several hours) and reaction conditions (moderate temperature and pressure) are such that the process could possibly be conducted as the waste is being pumped from the underground storage tanks to the treatment facilities. The improved removal of chromium would result in cost savings by reducing the volume of high level waste glass that needs to be produced and could also improve glass quality. Reducing the quantity of glass produced should also shorten schedules and reduce the risks due to exposure and operations.

4c. Bridging the gap between broad fundamental research and needs-driven applied technology development: Although the focus of this project was to elucidate the hydrothermal oxidation chemistry of chromium(III) species, it produced much of the data needed to evaluate the feasibility of hydrothermal treatment of HLW sludge. It also provides the data needed to generate conceptual designs for treatment units. Kinetic information and the global reaction rate models generated from this project can be used to estimate the size of reactors and pumps needed for separation. The effects of oxygen and hydroxide concentrations on reaction rates can be used to select and optimize reaction conditions. This project provided much of the engineering data needed for design of a pilot scale unit.

4d. Impact of the project on individuals, laboratories, departments, and institutions: The treatment of the wastes stored in the underground tanks at the Hanford site is an enormous task. It will be years, and possibly even decades, before treatment will begin. The information provided by this project can be used in the short term by the Hanford site to evaluate treatment strategies. In the longer term, it can be used to design pilot scale tests using samples of HLW sludge. Results from such tests would provide the data needed for the final design of the separation process. The results from this project are also being used by Los Alamos National Laboratory to evaluate hydrothermal process of TRU contaminated wastes. Application of hydrothermal technology at Los Alamos by the Nuclear Weapons Pit Rebuild Program will occur in the near future. A full-scale hydrothermal unit for the treatment of TRU contaminated organic liquids is currently being designed and should be operating next year.

4e. Larger scale trials: The next step in the testing and evaluation of this technology should be laboratory scale tests using sludge samples from the high level storage tanks. The results from these tests should validate the kinetic data and global rate model developed by this project. At that point, a comparison with the baseline technology should be made to determine if larger scale testing is justified.

This project has demonstrated that chromium(III) complexes can be rapidly dissolved by reaction with air under mild hydrothermal conditions. This hydrothermal

process could be a significant improvement over the current baseline technology.

This project has created the experimental capacity and expertise to study oxidation and reduction reactions of insoluble metal compounds over a wide range of hydrothermal conditions. For this project, new reactors were developed which operate at temperatures ranging from 100°C to 500°C and pressures from ambient to 400 bar. These reactors allow chemical reaction rates ranging from seconds to hours to be quantitatively measured.

4f. Benefits to scientific collaborators: Over the course of this project, we have hosted many visiting students and faculty from Furman University in Greenville, South Carolina; Xavier University in Louisiana; The University of Texas at Austin; and the University of New Mexico. The first and most important capability shared with these visitors is the design and safe operation of high temperature, high pressure hydrothermal reactors. Additionally, our collaborators have learned to use *in situ* absorption and Raman spectroscopy to study hydrothermal reactions and to use a variety of analytical techniques (ion chromatography, UV/visible spectroscopy, x-ray fluoresces, x-ray photoelectron spectroscopy) to analyze hydrothermal reaction products.

4g. Advances in scientific understanding: The chemistry of chromium under hydrothermal conditions is very complex. This project helped to elucidate the oxidation and reduction chemistry of chromium at elevated temperatures under hydrothermal conditions important to sludge processing. It provided kinetic information on the oxidation of chromium by oxygen and nitrates, and the reduction of chromium by organic complexing agents.

4h. Additional scientific hurdles: This project was not able to use high level waste sludge for testing. Additional testing using sludge from the underground storage tanks needs to be performed, in order to validate the kinetic models developed thus far. The HLW sludges are complex mixtures. Thus far, we have tested simulants but have not been able to test Hanford sludge and cannot be certain that chromium morphology and composition or general matrix effects may significantly alter the rate of the chromium reactions. This work would best be performed by researchers at the Hanford site.

4i. Interest by others: The Nuclear Weapons Programs Pit Rebuild project has been interested in our project. They are evaluating hydrothermal processing for the treatment of TRU contaminated combustible materials. The chemistry of metals under hydrothermal conditions is of general interest to them. The technology developed by this project for examining the oxidation/reduction behavior of metals under hydrothermal conditions has been used by them to examine the hydrothermal reactions of plutonium and americium. A contact for this work is Laura Worl, NMT-9, Los Alamos National Laboratory. General Atomics Corporation has also been interested in our project. They are developing hydrothermal processing for the treatment of hazardous wastes such as explosives, propellants, and chemical warfare agents. In general, they are interested in

new applications of hydrothermal technology. In particular, they are interested in the chemistry of chromium which can be important in the hydrothermal processing of hazardous wastes. Chromium is a common corrosion product and is present in many hazardous wastes. The levels of chromium in the liquid effluent from hydrothermal reactors must be controlled in order for the effluent to meet discharge standards. By understanding the chemistry of chromium under hydrothermal conditions, it may be possible to control its form and partitioning in the solid and liquid effluent streams from a waste treatment unit.. Mike Spritzer at General Atomics Corporation is a contact for this work.

5. Project Productivity

The principle goal of this project was to lay the foundation for the application of hydrothermal processing for enhanced chromium separation from HLW sludge. We sought to develop a fundamental understanding of chromium speciation, oxidation/reduction and dissolution kinetics, reaction mechanisms, and transport properties under hydrothermal conditions in both simple and complex salt solutions. Overall we have accomplished this goal. As summarized in Section 3 of this report, we have made major accomplishments in each of the technical areas listed in the project goal. We found that:

Cr(OH)₃ is rapidly oxidized by O₂.

Increasing hydroxide and O₂ concentrations increases the rate of Cr(III) oxidation.

Increasing temperature increases the rate of Cr(III) oxidation.

EDTA slowly reduces Cr(VI) to Cr(III).

EDTA reacts rapidly with O₂ at higher temperatures, thereby reducing O₂ concentrations.

At high concentrations, aluminate slows Cr oxidation.

Nitrate and Fe⁺³ have little effect on Cr oxidation at temperatures below 200°C.

At temperatures above 400°C, nitrate rapidly oxidizes chromium.

Diffusion rates of nitrates and organic molecules increase significantly with temperature but slow near phase transitions points.

At high temperatures, plutonium and americium rapidly react with oxygen to form insoluble solids that can easily be filtered.

We have also developed a simple global rate expression for the reaction of Cr(OH)₃ with both oxygen and nitrate under hydrothermal conditions.

In the project proposal, most of the research effort focused on high temperature reactions using nitrates. Experiments during the first year of the project demonstrated that oxygen was a better oxidant at lower temperatures. This was an unexpected result with important practical applications. Because of this discovery, more effort was directed toward the study of reactions involving oxygen than had initially been planned. Additionally, the project proposal had included experiments examining the oxidation of technetium. Because the project funding was less than requested in the proposal, this work was dropped before the project started.

6. Personnel Supported

Staff and technicians partially supported by this project at Los Alamos National Laboratory are:

Steven J. Buelow Bernard R. Foy
Jeanne M. Robinson Ron Martinez
Adam Martinez Mike Sedillo
Rhonda McInroy Loan Le

Graduate students (GRA) and undergraduate students (UGS) supported by this project are:

Marcel Goemans (GRA) and Tyler Mosher (GRA) from The University of Texas at Austin,
Byron Buckley (UGS/GRA) and James Nevens (UGS) from Furman University, Cedric Montgomery (UGS) and Tiyonnoh Baker (UGS) from Xavier University of Louisiana,
Karen Steenhoudt (GRA) and Julie Valdez (UGS) from The University of New Mexico, and
Sonia Martinez (GRA) from The University of Toledo, Ohio.

The postdoctoral fellow supported by the project was:

Zhong Yi Ding.

Visiting faculty member partially supported by this project was:

Prof. Rosemary Effiong from Xavier University .

7. Publications

7a. Published in peer-reviewed journals and books:

Goemans M.G.E; Funk T.J.; Sedillo M.A.; Buelow, S.J.; Anderson, G.K.;
“Electrical Conductances of Aqueous-Solutions of Inorganic Nitrates at 25-505°C and 100-490 Bar,” *Journal of Supercritical Fluids*, v 11(#1-2) pp.61-72, 1997.

7b. Published in unreviewed publications: None

7c. Accepted/ to be submitted for publication:

Goemans, M.G.E.; Butenhoff, T.J.; Gloyna, E.F.; Anderson, G.K.; Buelow S.J.
“Molecular Diffusion of Inorganic Nitrate Species and Ketones in Subcritical and Supercritical Water,” to be submitted to the *Journal of Physical Chemistry*.

Ding, Z.Y.; Mosher, T.; Foy, B.R.; Robinson, J.M.; Buelow, S.J. “Oxidative Dissolution of Chromium Trihydroxide by Oxygen under Hydrothermal Conditions,” to be submitted to *Environmental Science & Technology*.

Buckley, B.; Ding, Z.Y.; Foy, B.R.; Robinson, J.M.; Buelow, S.J. “Oxidative Dissolution of Chromium Trihydroxide by Nitrate under Supercritical Water

Conditions,” to be submitted to *Journal of Supercritical Fluid*.

8. Interactions:

8a. Participation/presentations at meetings, etc.:

S.J. Buelow “Hydrothermal Processing of TRU Contaminated Wastes,” at The Third International Conference on Oxidation Technologies, Cincinnati, OH, October, 1996.

M.G.E. Goemans, T.J. Butenhoff, E. F. Gloyna, G. K. Anderson, and S. J. Buelow “Molecular Diffusion of Inorganic Nitrate Species and Ketones in Subcritical and Supercritical Water,” Paper presented at the Thirteenth Symposium on Thermophysical Properties, Boulder, Colorado, June 22-27, 1997.

T. Mosher, Z.Y. Ding, S.J. Buelow, B.R. Foy, J.M. Robinson “Dissolution of Chromium Oxide in Hydrothermal Conditions by Nitrate,” Paper presented at AIChE 1997 Annual Meeting, Los Angeles, CA, November 16-21, 1997.

S.J. Buelow “Hydrothermal Processing of High Risk Wastes,” Paper presented at SCWO Short Course, SUPERCRITICAL WATER OXIDATION--Engineering Solutions--Effective Wastewater Treatment and Sludge Management, The University of Texas, Austin, Texas, February 26-27, 1998.

B. Buckley, T. Mosher, Z.Y. Ding, S.J. Buelow, B.R. Foy, J.M. Robinson “Dissolution of Chromium Oxide under Hydrothermal Conditions,” Paper presented at AIChE 1998 Spring Meeting, New Orleans, LA, March 9-12, 1998.

Z.Y. Ding, B. Buckley, T. Mosher, K. Steenhoudt, B.R. Foy, J.M. Robinson, S.J. Buelow, “Enhanced Sludge Processing of HLW: Hydrothermal Oxidation of Chromium,” Presented at the Environmental Management Science Program Workshop in Rosemont, IL, July 27-30, 1998.

S.J. Buelow, J.M. Robinson, Z.Y. Ding, R. Effiong, B.R. Foy, T. Mosher, R.E. McInroy J. Neves, “Oxidative Dissolution of Chromium Hydroxide by Oxygen under Hydrothermal Conditions,” Presented at the ACS 1999 Fall Meeting in New Orleans August 22-26, 1999.

8b. Consultative and Advisory Functions: None

8c. Collaborations: The collaborators who spent time working at Los Alamos in our laboratory included Professor Tony Arrington from Furman University and four of his students Dana Olsen, Joshua Golden, David Pond, and Ginger Denison; and Professor Rosemary Effiong from Xavier University and two of her students Cedric Montgomery and Tiyonnoh Baker.

At Los Alamos National Laboratory, we have collaborated with Laura Worl, examining the chemistry of plutonium and americium under hydrothermal conditions.

We have also collaborated with Professors Earnest Gloyna and Keith Johnston from the University of Texas at Austin.

9. Transitions

The results from this project can also be applied to other DOE management problems. The Nuclear Weapons Programs pit rebuild project has been interested in this project. They are evaluating hydrothermal processing for the treatment of TRU contaminated combustible materials. The chemistry of metals under hydrothermal conditions is of general interest to them. The technology developed by this project for examining the oxidation/reduction behavior of metals under hydrothermal conditions has been used by them to examine the hydrothermal reactions of plutonium and americium. Most of the combustible materials are contaminated with nitrates and many have chromium. The scientific knowledge gained from this project adds to the information needed to elucidate the behavior of metals under oxidizing hydrothermal conditions for the treatment of combustible wastes. A contact of this work is Laura Worl, NMT-9, Los Alamos National Laboratory.

10. Patents None.

11. Future Work

Future experiments should examine the reactions of HLW sludges with oxygen at temperatures between 100°C and 200°C at hydroxide concentrations between 1M and 6M. This work should be performed at the Hanford site. Work at Los Alamos will continue, supported by the Nuclear Weapons Program. It will focus on high temperature hydrothermal processes including the oxidation of organic material and TRU salts for purposes of waste minimization and TRU separation.

12. Literature Cited

- 1) Gephart, R. E.; Lundgren, R. E. "Hanford Tank Clean Up - A Guide to Understanding the Technical Issues," Battelle Pacific Northwest Labs., Richland, WA.; Department of Energy, Washington, DC., 1996.
- 2) Agnew, S. F. "Hanford Tank Chemical and Radionuclide Inventories: HDW Model 1)Gephart, R. E.; Lundgren, R. E. "Hanford Tank Clean Up - A Guide to Understanding the Technical Issues," Battelle Pacific Northwest Labs., Richland, WA.; Department of Energy, Washington, DC., 1996.
- 2) Agnew, S. F. "Hanford Tank Chemical and Radionuclide Inventories: HDW Model Rev. 4," Los Alamos National Laboratory, 1996.

- 3) Wodrich, D. D.; Honeyman, J. O.; Wojtasek, R. D. "Treatment and Disposal of High Level Radioactive Waste at the Hanford Site: The Technical Challenge," Westinghouse Hanford Company, 1994.
- 4) Rudzinski, S.; Agnew, S.; Gibbs, R.; Goeckner, J.; Holzmer, M.; Melvin, J.; Noonan, V.; Cheney, C.; Fettus, G. "Review of the Federal Management of the Tank Waste Remediation System (TWRS) Project at the Department of Energy's Hanford, WA Site," 1998.
- 5) Watrous, R. A. *Feed Specification for HLW Vitrification, Technical Presentation to Waste Processing Architecture Group*; Watrous, R. A., Ed., 1994.
- 6) Lumetta, G. J.; Rapko, B. M.; Wagner, M. J.; Liu, J.; Chen, Y. L. "Washing and Caustic Leaching of Hanford Tank Sludges: Results of FY 1996 Studies. Revision," Pacific Northwest National Lab., Richland, WA, 1996.
- 7) Rapko, B. M.; Lumetta, G. J.; Wagner, M. J. "Oxidative Dissolution of Chromium from Hanford Tank Sludges under Alkaline Conditions," Pacific Northwest Lab., Richland, WA, 1997.
- 8) Rapko, B. M.; Lumetta, G. J.; Wagner, M. J. "Oxidative Dissolution of Chromium from Hanford Tank Sludges under Alkaline Conditions," Pacific Northwest Lab., Richland, WA, 1996.
- 9) Vojtech, O.; Susmilch, J.; Urbanec, Z. "Effect of Chromium Oxide on the Properties of Simulated Nuclear Waste Glasses.," Battelle Pacific Northwest Labs., Richland, WA.; Department of Energy, Washington, DC., 1996.
- 10) Kruss, G. G.; Tammana, E. G. *Zeitschrift für anorganische Chemie*. 1954, 276, 275.
- 11) Laubengaver, A. W.; McCune, H. W. *J. Amer. Chem. Soc.* 1952, 74, 2362-2364.
- 12) Okopnaya, N. T.; Chertov, V. M. *Katal. Katal.* 1978, 1079.
- 13) Carruthers, J. D.; Fenerty, J.; Sing, K. S. W. *Bulk and Surface Properties of Chromium Oxide Gels*; Carruthers, Wiley-Inter. Science: New York, 1969, pp 127-135.
- 14) Kubota, B. *J. Amer. Ceram. Soc.* 1961, 44, 239-248.
- 15) Shibasaki, Y.; Kanamaru, F.; Koizumi, M.; Kume, S. *J. Amer. Ceram. Soc.* 1973, 56, 248.
- 16) Agnew, S. F. "Analysis of the History of 241-C Farm," Los Alamos National Laboratory, 1993.
- 17) Barker, J. J. *J. Environ. Sci. Health* 1996, A31, 1487-1503.
- 18) Memorandum from Teresa B. Fryberger, EM-532 (Fryberger:3-7688) to Distribution dated May 23, 1994. Subject: April 11-12, 1994, Sludge Treatment Workshop.
- 19) Delegard, C.H.; Stubbs, A.M.; Boiling, S.D. "Laboratory Testing of Ozone Oxidation of Hanford Site Wastes from Tank 241-SY-101," Westinghouse Hanford Company, Richland, WA, 1993.

- 20) Lumetta, G.J.; Swanson, J.L.; Barker, S.A. "Process Chemistry for the Pretreatment of Hanford Tank Wastes," *Chemical Pretreatment of Nuclear Waste Disposal*. Schulz, W.W.; Horwitz, E.P., eds. Plenum Press, New York, 1995.
- 21) Orth, R.J.; Zacher, A.H.; Schimdt, A.J.; Elmore, M.R.; Elliott, K.R.; Neuenschwander, G.G.; Gano, S.R. "Removal of Strontium and Transuranics from Hanford Tank Wastes via Addition of Metal Cations and Chemical Oxidants –FY 1195 Test Results," Pacific Northwest National Laboratory, Richmond, WA, 1995.
- 22) Rapko, B. M. "Oxidative Alkaline Dissolution of Chromium from Hanford Tank Sludges: Results of FY 98 Studies," Pacific Northwest National Laboratory, 1998.
- 23) Oldenborg R.; Robinson J.M.; Buelow S.J.; Dyer R.B.; Anderson G.; Dell'Orco P.C.; Funk K.; Wilmanns E.; Knutsen K.; "Hydrothermal Processing of Inorganic Components of Hanford Tank Wastes," Los Alamos National Laboratory, 1994.
- 24) Dell'Orco P. C.; Foy B.R.; Wilmanns E.G.; Le L.A.; Ely J.; Patterson, K.; Buelow S.J. "Hydrothermal Oxidation of Organic Compounds by Nitrate and Nitrite," *ACS Symposium Series* Vol. 179, 608, 1995.
- 25) Oldenborg, R.; Buelow, S.J.; Anderson, G.; Baca, G.; Brewer, R.; Dell'Orco, P.C.; Foy, B.R.; Knutsen, K.; Le, L.A.; McInroy, R.; McFarland, R.; Moore, S.; Robinson, J.M.; Rodgers, P.; Shaw, R.; Wilmanns, E. "Evaluation of IPM Selection Criteria for Hydrothermal Processing," Los Alamos National Laboratory, 1994.
- 26) Foy, B.R.; Dell'Orco, P.C.; Wilmanns, E.; McInroy, R.; Ely, J.; Robinson, J.M.; Buelow, S.J. "Reduction of Nitrate and Nitrite Under Hydrothermal Conditions," *Physical Chemistry of Aqueous Systems*, ed. H. J. White Jr., J. V. Sengers, D. B. Neumann, and J. C. Bellows, pp. 602-609, Begell House, New York, 1995.
- 27) Goemans, M.G.E. *Molecular Diffusion and Mass Transfer in Subcritical and Supercritical Water*, Ph.D Dissertation, The University of Texas at Austin, 1996.
- 28) Goemans M.G.E; Funk T.J.; Sedillo M.A.; Buelow, S.J.; Anderson, G.K.; "Electrical Conductances of Aqueous-Solutions of Inorganic Nitrates at 25-505°C and 100-490 Bar," *Journal of Supercritical Fluids*, v 11(#1-2) pp.61-72, 1997.
- 29) Worl, L.A.; Buelow, S.J.; Le, L.E.; Padilla, D.D.; Roberts, J.H.; Veirs, D.K. "Hydrothermal Processing of Actinide Contaminated Organic Wastes," To be published.

13. Feedback: Overall the EMSP program is well run. The current proposal submittal and reporting processes are efficient and not overly burdensome.

14. Appendices: None