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Hydrothermal Treatment of Hanford Waste Constituents

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ABSTRACT

The destruction of nitrates, organics, and ferrocyanides contained in underground storage tanks at the Department of Energy Hanford site in Washington state would significantly reduce the volume, hazard, and toxicity of the waste, while meeting pretreatment requirements for vitrification and grouting. The purpose of this study was to investigate the applicability of supercritical water oxidation for the destruction of nitrates, organics, and ferrocyanides. Laboratory studies were performed studying oxidation/reduction reactions of nitrate with a simple organic compound, methanol, and with ammonia. Additional studies examined the reaction of nitrate with ferrocyanide. When reacted with methanol above 500°C, greater than 99% of the nitrate was destroyed at the shortest residence times (< 6 seconds). At the same conditions, greater than 80% of the methanol was converted to bicarbonate and carbon dioxide. Studies involving the reaction of nitrate and nitrite with ammonia indicated that the reaction proceeds to completion in short residence times at temperatures above the critical point of water (374.2°C). Ferrocyanide also reacted rapidly with nitrate above the critical point, to produce carbon dioxide and ammonia.

INTRODUCTION

Department of Energy weapons production facilities have generated a wide variety of hazardous and mixed wastes resulting from the enrichment and recovery of nuclear materials. Perhaps the most dramatic waste problem is evident at the former production facility in Hanford, Washington, where over 150 million gallons of mixed waste are stored in corroded underground storage tanks. This waste is highly hazardous, containing a radioactive component (uranium, technetium), a toxic component (ferrocyanides, heavy metals), and an organic component (EDTA, HEDTA). Sodium nitrate is the main component in the tanks, constituting up to 50% by weight of the waste. The current plan for the ultimate safe disposal of these tank wastes consists of a reduction in volume, removal of certain radionuclides with the TRUEX process, followed by vitrification and grouting, to reduce the leachability of hazardous components[1]. These solid waste forms will eventually be stored in a Department of Energy repository.

Due to the complex nature of these tank wastes, most conventional treatment technologies cannot meet pretreatment requirements prior to vitrification and grouting.

An important pretreatment requirement is the removal of nitrates and ferrocyanides, which tend to weaken the integrity of the solid waste form. Also, organic matter should be completely removed, and certain heavy metals, such as chromium, need to be separated. Currently, no treatment technology has been shown viable for achieving all of these pretreatment goals.

Supercritical water oxidation (SCWO) is an innovative treatment technology for the destruction and separation of hazardous components in wastewater streams [2,3]. The technology has been demonstrated on bench and pilot scales for a variety of complex waste streams. The process involves the oxidation of organic matter in water above its critical point (374.2°C, 22.1 MPa). Because many electrolytes exhibit only slight solubilities at these conditions [4], inorganic separations can also occur in supercritical water media .

Supercritical water exhibits properties which drastically differentiate it from water at ambient conditions. The dielectric constant of water changes from a value of 80 at 20°C and 0.1 MPa to values below 10 at supercritical conditions[5]. As a result, water behaves decidedly non-polar at supercritical conditions, solvating organic components nearly completely while poorly solvating inorganic electrolytes. The viscosity of supercritical water is gas-like, more than 20 times below that of room temperature water. One result of this reduced viscosity is a corresponding increase in diffusion coefficients of species. This increase results in reactions not being mass-transfer limited, but kinetically limited. At temperatures above 500°C, residence times less than 20 seconds are required to achieve greater than 99.99% destruction of many organic compounds. The density, on the other hand, remains liquid-like, with values from 0.05 to 0.35 g/cm^3. The relatively high density of water allows high throughputs of process streams for the short residence times required for reaction.

The reduced solubility of inorganic constituents in supercritical water allows for a fluid-solid separation at these conditions. Certain inorganic electrolytes, such as salts of radioactive isotopes, may be selectively separated in a properly designed reactor [6,7]. This separation might be especially applicable for the treatment of mixed wastes, such as Hanford tank wastes, which require the efficient removal and concentration of the radioactive component and the destruction of the organic constituent. The solubility of inorganic constituents can be adjusted through proper manipulation of pressure and temperature conditions. High pressures (> 50 MPa) tend to favor increased solvation, while low pressures (< 30 MPa) favor electrolyte dissociation [8].

As a result of these its properties, supercritical water oxidation is capable of effectively treating both the inorganic and organic components of a waste stream. This feature makes the technology attractive for mixed waste streams such as Hanford tank wastes. In fact, supercritical water oxidation stands as the single technology with the potential for achieving all pretreatment goals for tank wastes within a single process unit.

The objective of this research was to examine the use of supercritical water for the treatment of Hanford tank wastes. Specifically, methods were investigated for the destruction of a simple organic compound, methanol, with nitrate. The destruction of nitrate and nitrite was also examined using ammonia as a reducing agent. This study was limited to homogeneous systems, where the sodium salt of nitrate remained soluble. The motivation of this study was twofold. First, since nitrate is already present in tank wastes, it was desired to see if nitrate was a strong enough oxidizer to destroy ferrocyanides and organic constituents present in the waste at reasonable residence times. Second, the feasibility of destroying nitrates with simple organic compounds and ammonia was assessed.

EXPERIMENTAL METHODS

All experiments were performed in the reactor schematically shown in Figure 1. The primary feature of this apparatus is a fluidized sandbath, which served to preheat feed streams and provide an isothermal reaction zone. Reactant feeds were separately preheated to reaction temperature in the sandbath and with the use of auxilliary clamshell heaters. The preheated streams were mixed at a tee. A coiled piece of tubing (alloy C276, 6.35 mm OD X 2.11 mm ID) leading from the mixing tee served as an isothermal reactor. The total volume of the reactor, prior to quenching, was 13.1 ± 0.25 mL. The uncertainty arises from the knowledge of the exact point of reaction quench. Reaction quench was achieved with a heat exchanger placed at the reactor exit from the sandbath.

Following the quench, the reacted stream was filtered and let down to atmospheric pressure with the use of a backpressure regulator (Tescom). Nine thermocouples (Type K) were used to monitor surface and fluid temperatures in the preheaters and the reactor. An Inconel sheathed thermocouple, in contact with the fluid at the mixing tee, provided the primary determination of reaction temperature. Surface thermocouples placed at various positions on the reactor tube were within 1 to 2°C of the fluid temperature at the mixing tee. Pressure was measured with transducers (Ashcroft, K1) placed near the pump outlet and immediately preceding the backpressure regulator.

Feed streams were pumped to the apparatus with low pulse, high performance liquid chromatography (HPLC) feed pumps (LDC Constametric 3000). These pumps accurately metered flow from 0 to 10 mL/min for both feed streams. Feed solutions were prepared daily using analytical grade sodium nitrate, sodium nitrite, ammonium chloride, and methanol. Methanol solutions were fed from polyethylene bags with zero headspace, to eliminate volatilization losses. Sodium nitrate, sodium nitrite, and ammonium chloride solutions were fed from pyrex beakers. Flow rates of the feed streams were determined by measuring the weight loss of sodium nitrate/nitrite solution over time. The total volumetric flow rate was measured with a graduated cylinder and a stopwatch. Methanol/ammonium chloride solution flow rates were calculated knowing the total flow rate and the sodium nitrate/nitrite solution flow rate.

The system was brought to temperature by flowing deionized water through both preheaters and the reactor while the sandbath reached the desired temperature. When steady conditions were reached, indicated by the stabilization of pressure and temperatures, the deionized water was switched to feed solutions. A stopwatch was started at this time. After approximately 30 minutes, sampling of the effluent was initiated. For each residence time, three sets of 40 mL quadruplicate samples were taken. Upon the completion of sampling at a residence time, flow rates were adjusted to provide a new residence time, and the system was equilibrated for 30 minutes, and samples were collected for this new condition. This generally continued until samples were collected at five residence times. For three of these five residence times, gas samples were collected. Each set of four samples was analyzed for pH, chloride (if applicable), nitrate, nitrite, ammonia, methanol, total organic carbon, total inorganic carbon, sodium, and the corrosion metals, iron, chromium, molybdenum, and nickel.

Gas sampling was accomplished by switching the three-way valve after the backpressure regulator to a gas liquid separator. This separator consisted of a 2.54 cm OD stainless steel vessel into which the effluent stream flowed. The vessel was connected to a vacuum pump equipped with a liquid nitrogen trap, for the efficient removal of water vapor. A gas sample was collected by pumping out the separator to below 0.1 torr of pressure. A fixed volume of effluent (~ 80 mL) was collected in the separator. After the proper effluent volume was collected, the three-way valve was switched to allow direct effluent collection. The gas in the separator was then expanded into an evacuated gas sample cylinder, which was saved for analysis by gas chromatography and fourier transform, infrared (FTIR) spectroscopy. Pressures at all stages were measured with a 1000 torr baratron (MKS). With the total pressure of gas collected per unit effluent, the volume of the separator, and the partial pressure of gases determined analytically, the reaction yield of gaseous products could be accurately determined.

Gas products were analyzed with a gas chromatograph, using a chrompack capillary column, helium as the carrier gas, and a thermal conductivity detector. This arrangement allowed the detection of nitrogen, oxygen, carbon monoxide, methane, and nitrous oxide. For some gas samples. infrared spectra was obtained using a Perkin-Elmer FTIR spectrometer. Anions (nitrate, nitrite, chloride) were analyzed with an ion chromatograph, using a weak bicarbonate/carbonate eluent, an AS4 separation column (Dionex), and an anion micromembrane suppressor. Ammonia was measured with an ion specific electrode. Methanol concentrations were determined by gas chromatography. All metals (sodium, chromium, molybdenum, iron, and nickel) were measured by inductively coupled plasma spectroscopy.

RESULTS AND DISCUSSION

Experiments investigated the reactions of nitrate with methanol, nitrate with ammonia, nitrate with ferrocyanide, and nitrite with ammonium. Pyrolysis experiments examined decomposition rates (in the absence of oxygen) for methanol and nitrate. Molar ratios of reactants were varied to aid in the determination of reaction orders. Mass balances were performed to verify analytical results.

Reactions of Nitrate with Methanol. Sodium nitrate was reacted with methanol at temperatures from 450°C to 525°C at 4400 psi. Molar ratios ($NaNO_3$: MeOH) ranged from 1:3 to 5:1. These experiments used sodium nitrate below its solubility limit in supercritical water [7]. This ensured that heterogeneous chemistry was limited to wall reactions. Flow rates were used such that conditions in the reactor met the criteria for turbulent flow, that is the calculated Reynold's number was greater than 2100. This condition was necessary to consider the reactor as a plug flow system for kinetic analyses.

Above 500°C, nitrate was destroyed to near its detection limit. At 525°C, 4400 psi, a nitrate feed concentration of 197 mg/L, and residence times ranging from 5 to 10 seconds, greater than 99.9% of all nitrate was converted to nitrogen by-products. The primary nitrogen by-product was ammonia (87.2%), with a small amount of nitrite (< 5% conversion). Methanol conversions were 70 and 71% at the same conditions. Carbon was recovered exclusively as bicarbonate and unreacted methanol. Gaseous products N_2O and N_2 were detected, but not quantitatively analyzed. Similar results at 500°C indicated that the reaction was to rapid to follow in the sandbath apparatus at these temperatures. As a result, further experiments investigated this reaction at lower temperatures.

At 475°C and 4400 psi, the reaction of nitrate with methanol was sufficiently slow to accurately observe trends in reaction by-products. To elucidate reaction orders and mechanisms, four experiments were conducted at 475°C, at four different nitrate to methanol stoichiometries. Experiments were conducted at nitrate: methanol molar ratios of 1:3, 1:1, 2:1, and 5:1. For feed ratios of 1:3 and 1:1, the feed nitrate concentration was 1.06E-02 M. For ratios of 2:1 and 5:1, nitrate feed concentrations were 2.12E-02 M and 5.30E-02 M, respectively. Figure 2 shows the effect of the different stoichiometries on nitrate removal, shown as C_e/C_f.

As seen in Figure 2, nitrate removal is dependent on the concentration of methanol. Lines shown are exponential fits, the slopes of which are proportional to reaction rates. For the three conditions with the same methanol concentration (1:1, 2:1, 5:1), nitrate removal was constant. When the methanol concentration was increased by a factor of three, nitrate removal also increased by a factor of three. This would imply that nitrate removal was first order in methanol concentration. Furthermore, the ratio of slopes of the two lines was 3.5:1, approximating the molar ratio of methanol to nitrate. This observation also indicated that nitrate destruction was first order in methanol concentration. Figure 3 shows an analagous plot for methanol removal. With increases in nitrate concentrations, methanol removal also increased. The ratios of the slope of different stoichiometries fits to the 1:1 stoichiometry slope were 0.38, 2.1, and 4.6, respectively for 1:3, 2:1, and 5:1 nitrate: methanol stoichiometries. From this data, it appeared that methanol destruction was first order in nitrate concentration.

For each experiment performed, total mass balances were conducted. Figure 4 shows a typical result for an experiment at 475°C, with a 1:1 molar ratio of nitrate:methanol. This figure shows the distribution of reaction by-products with residence time, as well as the nitrogen and carbon mass balances with residence time. For this experiment, 96% of the nitrogen and 108% of the carbon were recovered. Carbon was recovered exclusively as bicarbonate and total organic carbon, which consisted primarily of methanol. As shown in the figure, nitrate and methanol disappear at approximately the same rate. This equimolar disappearance would indicate that the reaction is first order in both reactants at this temperature and pressure. While these components disappear, increases in nitrite, nitrous oxide, ammonia, and bicarbonate ion (measured by total inorganic carbon) are observed. Mass balances tend to be less complete at the longest residence time for both carbon and nitrogen. For carbon, this decrease can be attributed to increased reaction and conversion to bicarbonate, and subsequent precipitation on reactor walls. Indeed, the carbon missing from effluent samples was found in reactor rinse samples. The missing nitrogen was not recovered in the rinse water, and is likely attributable to the production of nitrogen gas, for which the analytical sensitivity was reducted due to background concentrations in water samples. This trend of lower mass balances at the longest reaction times, coupled with the observation of increased nitrous oxide with increasing flow rates, which was evident in most experiments, also indicated the possibility of nitrogen gas formation. Although several products of nitrate destruction (ammonia, nitrite, nitrous oxide, and nitrogen gas) were observed, no products of incomplete methanol destruction were found. In their studies of methanol oxidation with oxygen, Webley et al. suggested a mechanism inolving an initial step oxidation step of methanol to carbon monoxide[9]. The carbon monoxide was then converted in fast steps to carbon dioxide. It is possible that a similar step occurs with nitrate, producing CO and nitrite in a slow step. The CO could then be converted to a fast step via further oxidation with nitrite and nitrate. Further work needs to be done to determine a mechanism for the reaction.

Due to the unexpected formation of nitrous oxide and the formation of nitrogen gas, it was evident that side reactions were occurring simultaneously with direct nitrate/methanol reactions. Possibilities included the reaction of nitrate and nitrite with ammonia, reactions of nitrite with methanol, and reactions of nitrate/nitrite with reactor walls, to form oxidized corrosion metals. As a result, reactions were conducted with nitrite/nitrate ammonia to determine the relative rate of these reactions.

Reactions of Nitrate/Nitrite with Ammonium For these studies, ammonium chloride and sodium nitrate /nitrite were reacted over the temperature range of 350°C to 450°C at 4400 psi. A fixed molar ratio of 1:1 was employed for most experiments, although a 1:2 nitrate: ammonia experiment was performed at 365°C. At these conditions, residence times ranged from 10 to 90 seconds, with water densities varying from 0.65 to 0.20.

Reactions of nitrate/nitrite with ammonium have previously been studied by Katkovskaya, et al. in near saturated steam systems [10]. These researchers suggested the following reactions as the main pathways for nitrite and nitrate reactions with ammonium ion in the liquid phase of saturated steam solutions:

$$NH_4^+ + NO_2^- \text{--------->} N_2 + 2H_2O \qquad (1)$$
$$4\,NH_4NO_3 \text{---------->} 2NO_2 + 3N_2 + 8H_2O \qquad (2).$$

These studies were conducted at pressures and temperatures (< 10 MPa, 280-310°C) considerably below values in the present work.

At the higher pressures used in the current work, near complete reaction of nitrite with ammonium was observed at 365°C. Using sodium nitrite and ammonium chloride at feed concentrations of 0.01 M and residence times of 26 to 58 seconds, ammonia removal efficiencies ranged from 97.2% to 98.3%. Corresponding nitrite removals varied from 98.7% to 99.3%. These removals resulted in nitrite and ammonia concentrations near their analytical detection limits in the effluent. The only apparent by-products of the reaction were nitrogen gas and trace quantities (< 10 mg/L) of nitrate ion. The nitrogen recovered in gas samples was 110% of that fed to the reactor, also indicating that the reaction proceeded to completion. The total nitrogen mass balance resulted in 112% recovery of nitrogen. At 350°C and 4400 psi the results were nearly identical. These studies indicated that reaction (1) is the apparent reaction occurring at these temperature and pressure conditions. Because the reaction occurs so rapidly, a kinetic analysis has not been possible using the current apparatus.

When sodium nitrate was reacted with ammonium chloride at 4400 psi and temperatures of 350°C to 380°C, complete reaction was not observed. Figures 5 and 6 show nitrate and ammonia removal data as a function of temperature and residence time. On these figures, removal efficiency is displayed as Ce/Cf on a logarithmic axis. Lines drawn are exponential fits, the slopes of which are proportional to reaction rates. Reaction rates increase with temperature from 350°C to 380°C. At 380°C, no ammonia was detected in effluent samples (<0.1 mg/L) at residence times greater than 40 seconds, indicating a complete reaction. Experiments conducted at 450°C showed no ammonia remaining at residence times as low as 6.5 seconds. No effect from subcritical to supercritical transition seems apparent, as removal efficiency data does not unexpectedly jump with the critical transition. These rates for ammonia oxidation are much faster than those observed for oxidation with oxygen gas, as measured by Webley and Tester [11]. In that study, ammonia conversion was less than 10% at temperatures below 600°C and a pressure of 24.8 MPa. Perhaps the ionic attraction between nitrate and ammonium makes nitrate a stronger oxidizer for this system.

For experiments conducted at 350°C, 365°C, and 380°C, respectively, nitrogen mass balances were 82%, 116%, and 102%, indicating near or complete recovery of all reaction by-products. Figure 6 shows the conversion of total nitrogen to nitrous oxide and nitrogen as a function of residence time at 350°C and 380°C. At 350°C and 365°C, conversion to nitrous oxide and nitrogen increases with increasing residence time. At 350°C, only 6.8% to 11.4% of all nitrogen is converted to gaseous by-products. Gaseous conversions of 78% to 87% resulted from reaction at 380°C. The remainder of total nitrogen was present in the effluent as unreacted nitrate and ammonium. Nitrogen/nitrous oxides selectivities varied from 4.8 to 7.0 at 350°C, 8.1 to 9.1 at 365°C, and 5.0 to 7.4 at 380°C. No trend in selectivity occured with residence time at 350°C or 365°C, but selectivity increased with increasing residence time at 380°C. Also at 380°C, nitrous oxide conversion decreased with increasing residence times, contrary to patterns observed at lower temperatures.

Unlike nitrite/ammonium reactions, molar nitrate removal rates differed from molar ammonia removal rates. For all reactions conducted, nitrate was present in molar excess in effluent streams. Also, nitrite and nitrous oxide were present as by-products. These indicated that the reaction was not 1:1, and that possible side reactions were occurring. For these reactions, nitrate was present in 125% molar excess, after being reacted at equimolar ratios.

Observation of the ammonium/nitrate reaction indicate that the global rate equation proposed by equation 2 did not describe the current experimental results. While this reaction suggests a 1:1 nitrate: ammonium stoichiometry, our results suggest a 0.75:1 ratio. Furthermore, the production of nitrous oxide is not predicted by equation 2. This gas was a significant by-product of reactions above 350°C. Trends in product distribution and selectivity suggest that more the overall reaction consists of at least two primary steps, one which results in nitrogen production and one that results in nitrous oxide production. Because nitrous oxide is also an oxidant, it may participate in further side reactions. Further experimental work is being conducted to elucidate the reaction mechanism.

Reactions of Nitrate/Hydrogen Peroxide with Ferrocyanide. Potassium ferrocyanide ($K_4Fe(CN)_6$) was reacted at 500°C and 4400 psi with hydrogen peroxide and sodium nitrate. A feed concentration of 46.1 mg/L of $Fe(CN)_6^{4-}$ was utilized. For hydrogen peroxide, a molar ratio of 1:19 $K_4Fe(CN)_6$) : O_2 was used (2 H_2O_2 ----> 1 O_2). With nitrate, a molar ratio of 1 $K_4Fe(CN)_6$: 12 $NaNO_3$ was employed. These ratios were computed based on the complete conversion of cabon to carbon dioxide, nitrogen to nitrous oxide, and iron to iron (III) oxide. A constant total flow rate of 10.0 mL/min provided a residence time of 9.1 seconds at experimental conditions.

In all experiments, ferrocyanide was completely reacted. Ferrocyanide, ferricyanide, and cyanide were all below the analytical detection limit (< 0.1 mg/L) in reactor effluents. The primary nitrogen conversion products when reacted with peroxide was ammonia. When reacted with nitrate, reaction products consisted of excess nitrate with its decomposition product, nitrite, and ammonia. Potassium was recovered in the effluent as K^+, while iron, although not quantitavely recovered, was found primarily as a red particulate, Fe_2O_3, on the filter preceding the back pressure regulator. Bicarbonate was the sole by-product of carbon conversion. Some bicarbonate was recovered in water rinses of the reactor, indicating precipitation as a sodium or potassium salt at experimental conditions. For this set of experiments, 98% of the potassium fed was recovered, while 93% and 124% recoveries were determined for nitrogen and carbon, respectively. It is uncertain why such a high carbon recovery was found for carbon.

Corrosion was not severe for these experiments. For reactions with nitrate, chromium concentrations were less than 0.5 mg/L in the effluent. Molybdenum, iron, and nickel concentrations were all below 0.07 mg/L. Approximately 2 mg of chromium was recovered in the rinse water, indicating that some chromium precipitated as a sodium or potassium salt.

APPLICATION TO HANFORD TANK WASTES

These experiments have demonstrated the capabilities for organic carbon, ferrocyanide, and nitrate destruction in homogeneous, high temperature water solutions. These conditions were used purposely to obtain an idea of rates at which reactions occurred in uncomplicated systems. In reality, the tank wastes at the Hanford Reservation are concentrated slurries, with up to 50% solids. Sodium nitrate concentrations are much higher than those used in these experiments, being up to 50% by weight of the total waste. Finally, other contaminants, such as heavy metals, aluminum, and radionuclides further complicate this waste stream.

The increased concentrations of sodium nitrate should drastically increase rates of organic and ferrocyanide destruction. The extremely high concentration of oxidant may allow the reaction to occur at subcritical temperatures. Because sodium nitrate is in a molten state above 310°C, its processing through a hydrothermal reactor should cause no plugging problems. Solutions up to 5 wt% in $NaNO_3$ have been successfully processed through different supercritical water oxidation reactors without plugging [12]. Other inorganic constituents, such as the heavy metals and aluminum, will likely form insoluble salts with the high concentrations of anions present in the waste. These materials cause some potential for plugging, but it is possible that these inorganic constituents may be soluble in the sodium nitrate molten phase, and preferentially partition there. It has been shown previously that salts become increasingly more soluble in concentrated aqueous salt solutions at high temperatures [13]. Such solubilization of these inorganic species would result in a two phase water-ionic melt solution through a reactor. The ionic melt, because it is fluid, should cause no plugging problems in the preheater or reactor zones.

If ammonia is used to reduce nitrates, the resulting waste stream will be a concentrated sodium hydroxide stream with radionuclides and heavy metals in solution. Sodium hydroxide, like sodium nitrate, is also molten at temperatures above 310°C; thus, other electrolytes should partition into the sodium hydroxide melt phase. The increased pH resulting from reaction will also help in keeping inorganic constituents in solution through the cooldown heat exchanger. Radionuclides and other undesirable inorganic constituents may then be removed from the one-phase sodium hydroxide solution with extraction and ion-exchange technologies. Gases from the reactions (N_2 and N_2O) can be released to the atmosphere after catalytic conversion of the N_2O to N_2.

With the present information, it is unclear what temperatures and pressures will be optimal for the treatment of Hanford wastes with hydrothermal processing. More studies need to be performed on a larger scale to address solubility, corrosion, and rate issues.

CONCLUSIONS

The use of supercritical water oxidation and hydrothermal processing to destroy ferrocyanides, organics, and nitrates has been demonstrated on a laboratory scale. When reacted above 500°C with a simple organic compound, methanol, nitrate destruction efficiencies were greater than 99%, with corresponding methanol DRE's greater than 70%. Similarly, nitrate could also be destroyed with high efficiencies by reaction with ammonium ion. This reaction occurred to completion (> 99% destruction of ammonia) at temperatures above the critical point of pure water (374.2°C). Nitrogen was converted completely to nitrogen gas and nitrous oxide. The reaction occurred very quickly at temperatures of 350 to 365°C as well. Nitrite/ammonia reactions also occurred very rapidly, completely reacting at 365°C, 4400 psi, and residence times less than one minute. Unlike the nitrate/ammonia reaction, this reaction appeared to be 1:1 in stoichiometry, and produced only nitrogen gas. Finally, nitrate also successfully converted ferrocyanides to bicarbonate and ammonia at 500°C and a residence time of 9.1 seconds.

These preliminary results suggest that supercritical water oxidation may be capable of achieving pretreatment requirements for Hanford tank wastes. While high excess concentrations of nitrates can be used to destroy the organic matter and ferrocyanides in the waste, ammonia can be added to convert nitrate to gaseous products. Furthermore, there is some indication that these reaction steps may occur quickly enough below the critical point of water to use subcritical reaction conditions. The destruction of the organics, ferrocyanides, and nitrates in the Hanford wastes would result in a new waste form which has less volume, less potential for explosion, less toxicity, and more suitable for vitrification, grouting, and perpetual disposal.

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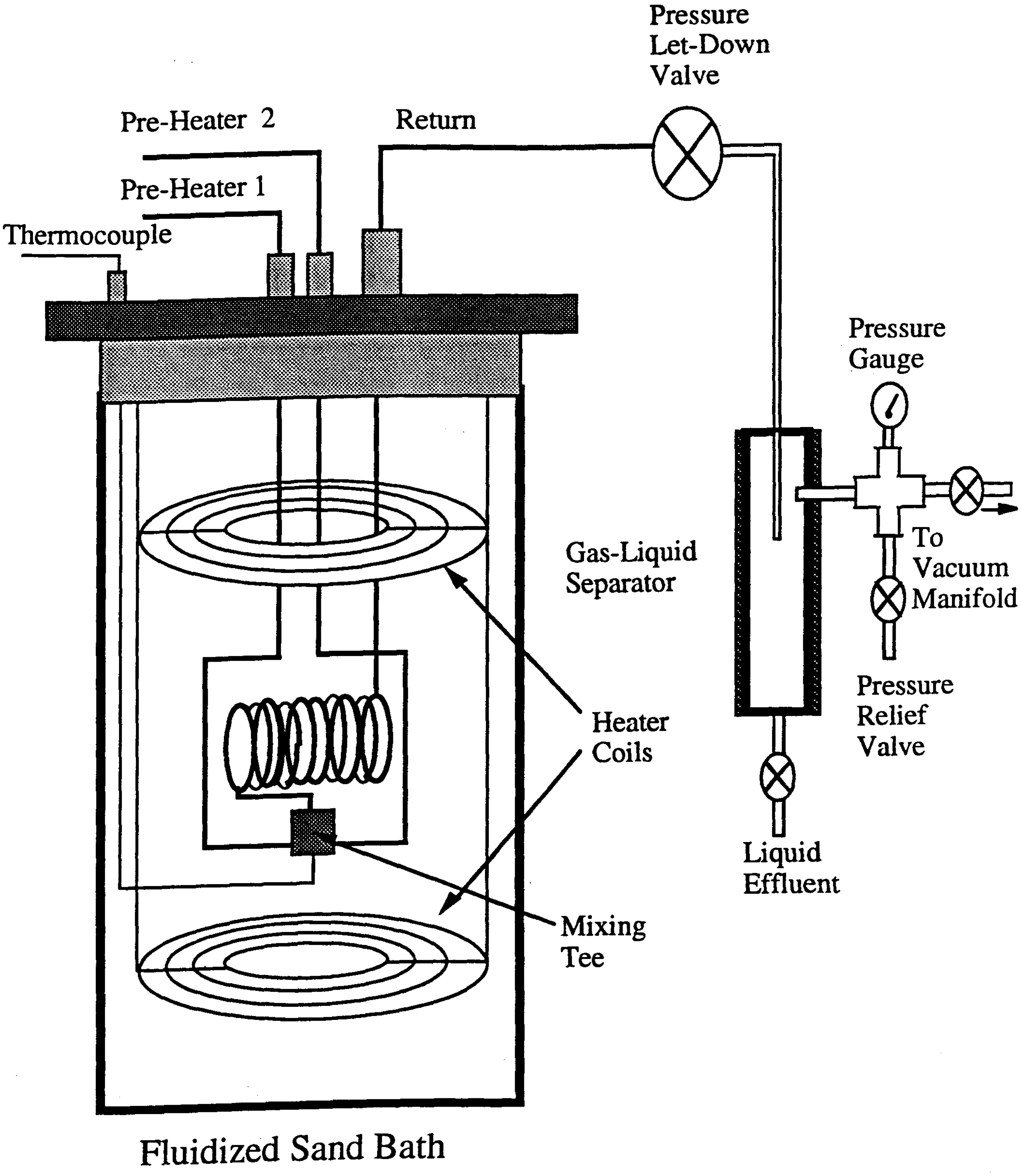

Figure 1. Schematic of Sandbath Reactor

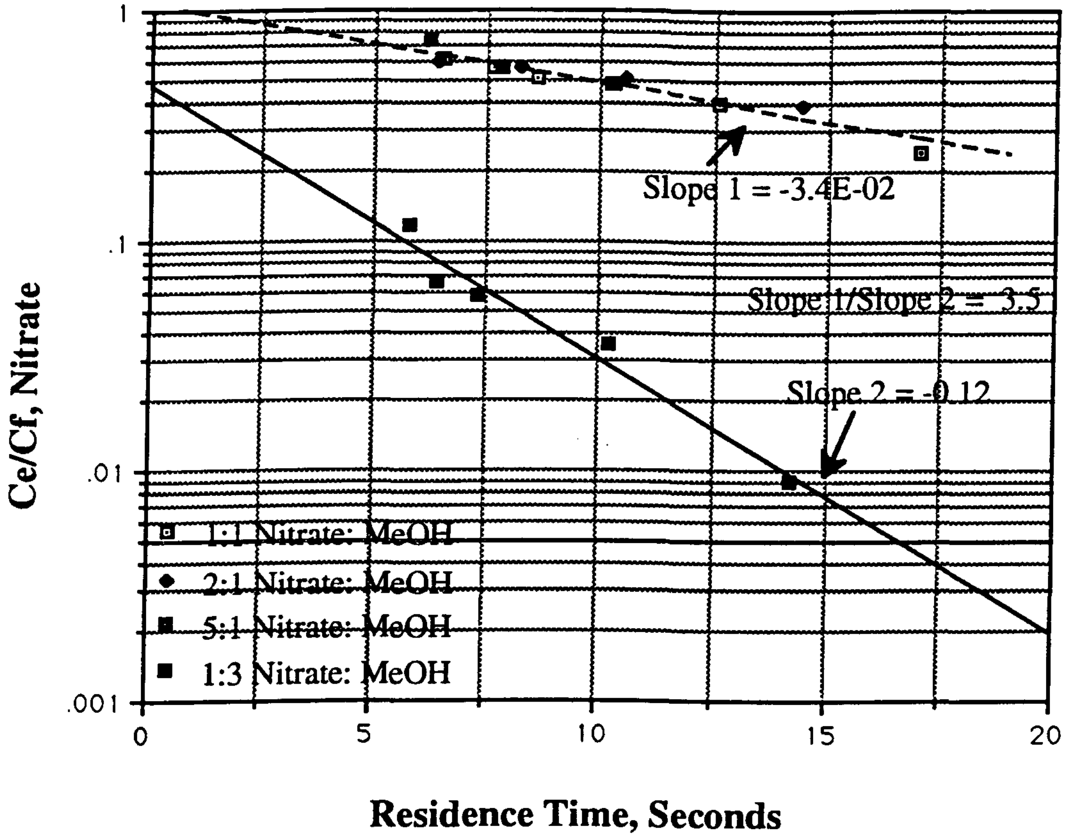

Figure 2. Nitrate/Methanol Reaction: Nitrate Removal as a Function of Methanol Concentration and Residence Time

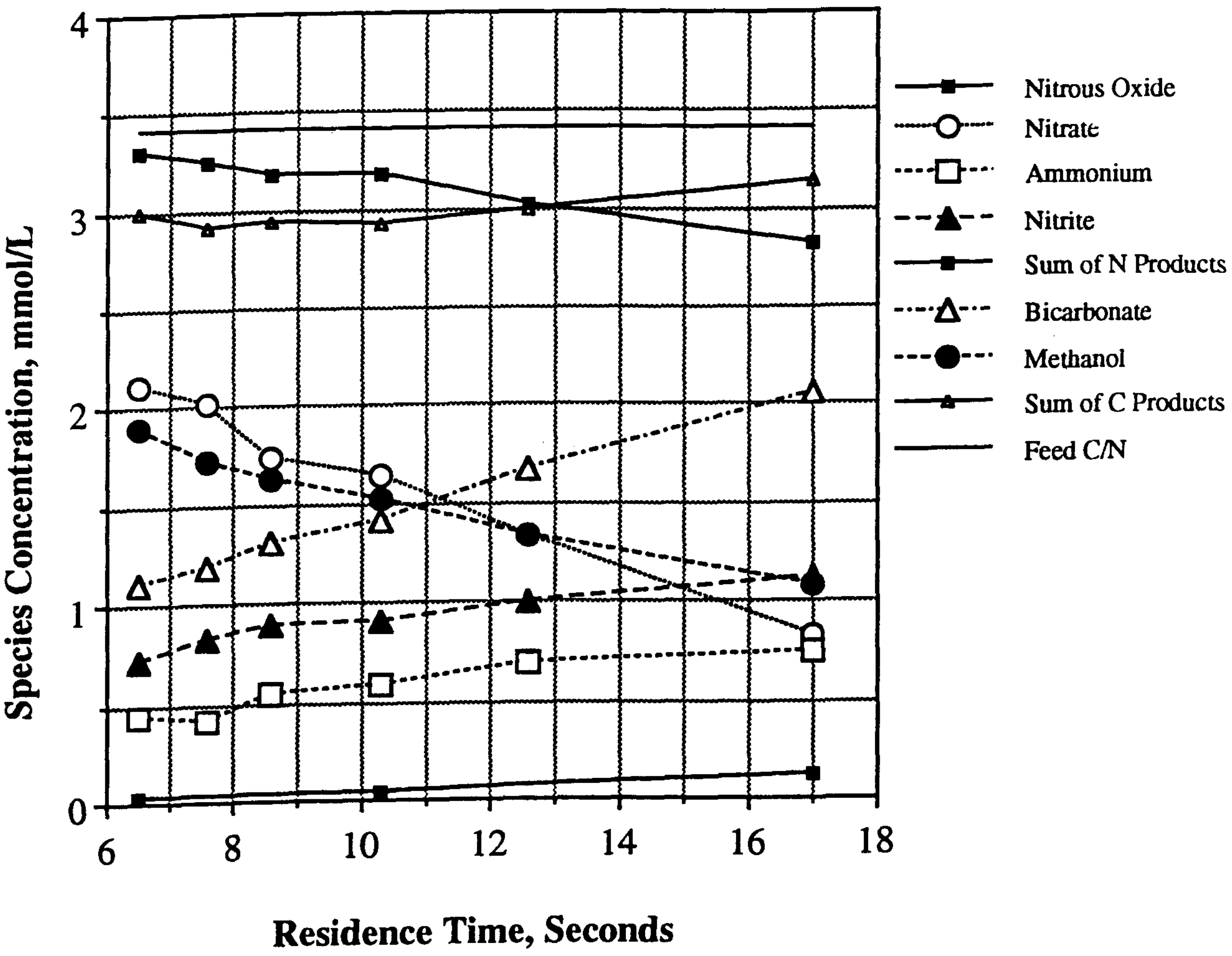

Figure 3. Nitrate/Methanol Reactions: Product Distributions and Mass Balance at 475°C

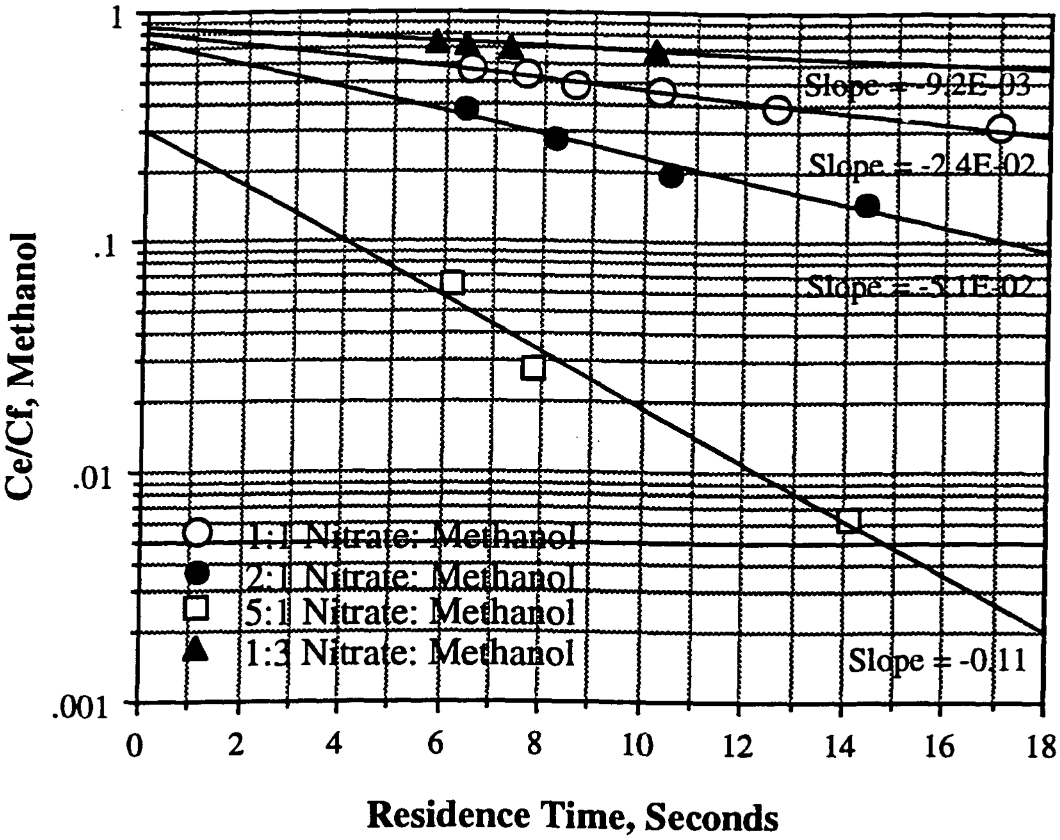

Figure 4. Nitrate/Methanol Reaction: Methanol Removal as a Function of Nitrate Concentration and Residence Time

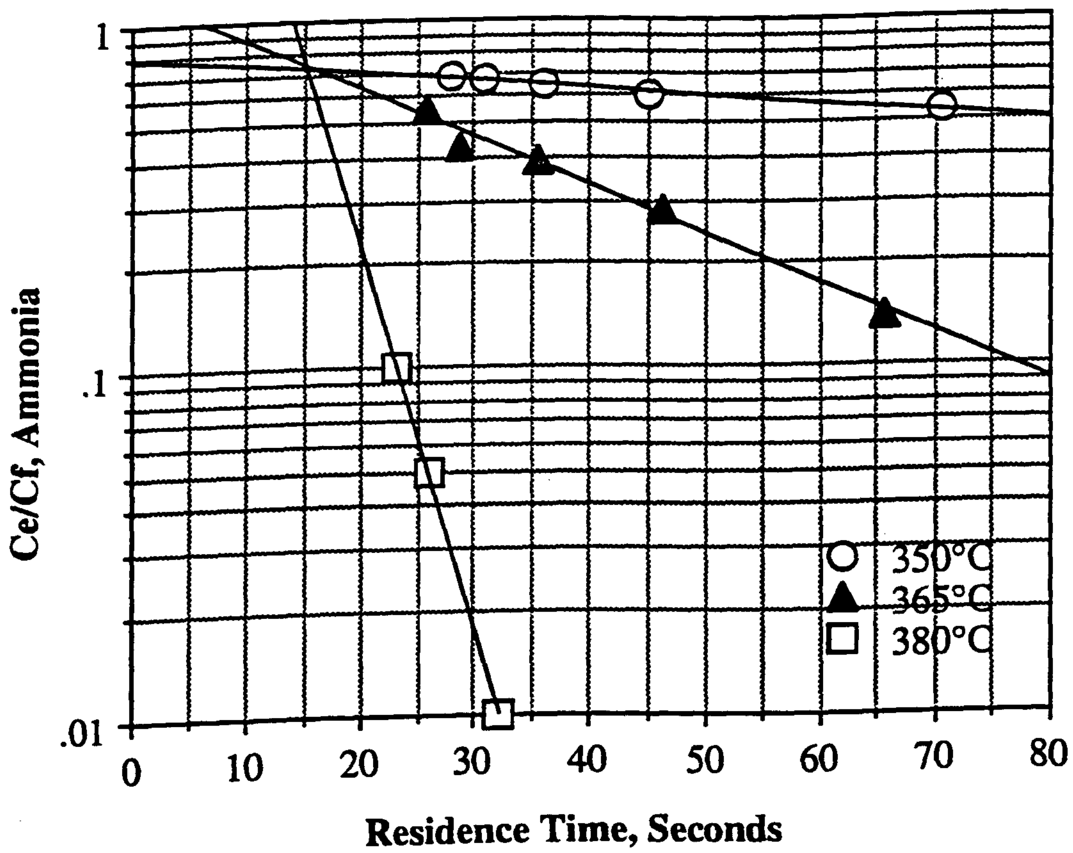

Figure 6 Nitrate/Ammonia Reactions: Ammonia Removal as a Function of Residence Time and Temperature (4400 psi, equimolar feed concentration)

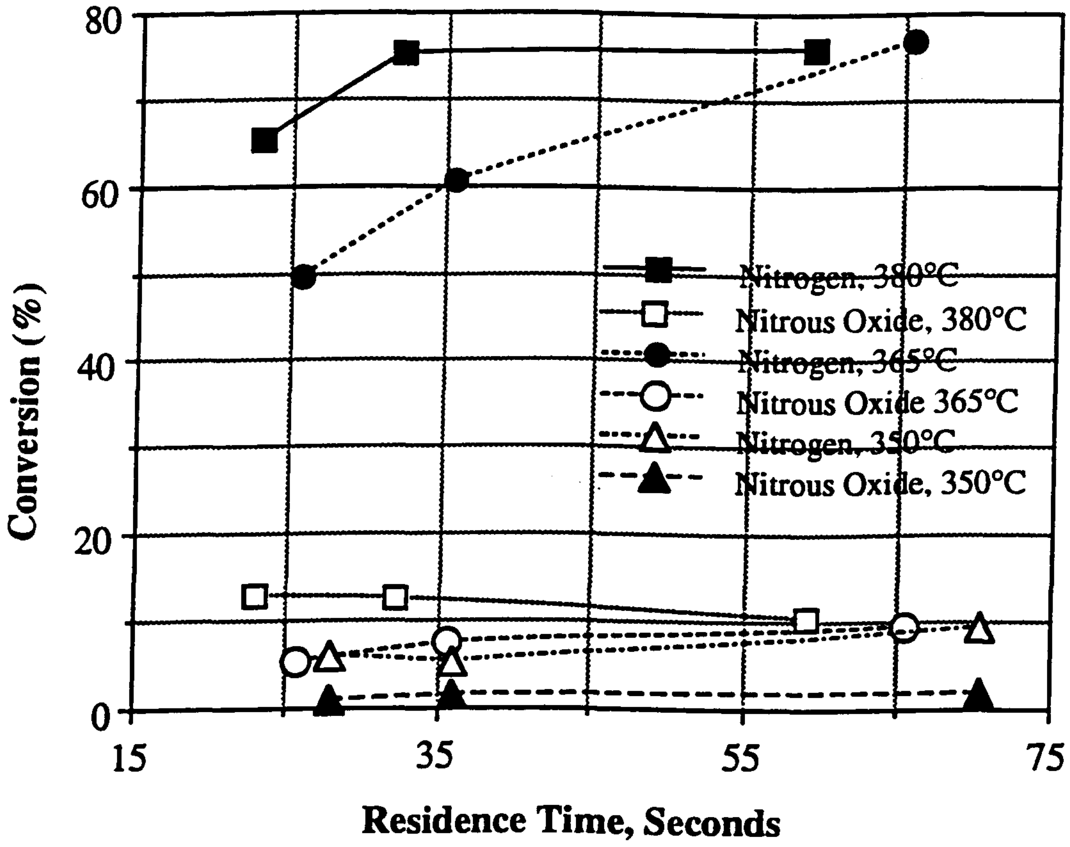

Figure 7. **Nitrate/Ammonia Reaction: Percent Conversion to N_2 and N_2O Gases**