

DESTRUCTION OF NITRATES, ORGANICS, AND FERROCYANIDES BY HYDROTHERMAL PROCESSING

J.M. Robinson, B.R. Foy, P.C. Dell'Orco, G. Anderson, F. Archuleta, J. Atencio, D. Breshears, R. Brewer, H. Eaton, R. McFarland, R. McInroy, T. Reynolds, M. Sedillo, E. Wilmanns and S.J. Buelow

Chemical and Laser Sciences Division
Los Alamos National Laboratory
Los Alamos, NM 87545

ABSTRACT

This work targets the remediation of the aqueous mixed wastes stored in the underground tanks at the Department of Energy site in Hanford, Washington via hydrothermal processing. The feasibility of destroying the nitrate, organic, and ferrocyanide components of the wastes under supercritical and near critical conditions (623°K to 873°K, 22.1 MPa to 103.4 MPa) is addressed. The reduction of nitrate to nitrogen gas and other non NO_x products by reaction with methanol and with ammonium was investigated from 723°K to 798°K at 30.3 MPa. Above 773°K, nitrate was destroyed to near its detection limit (0.1 ppm) in less than 10 seconds. The reaction followed first order kinetics in nitrate and methanol at 748°K, producing primarily ammonium and bicarbonate. The reaction of nitrate with ammonium chloride produces mainly N₂ and N₂O and is complete in less than 30 seconds at temperatures near the critical point (647.2 °K, 22.1 MPa) of pure water. The reaction of nitrate with ammonium hydroxide is less rapid. Destruction efficiencies ranged from 16 percent at 748°K and residence times below 15 seconds to 78 percent at 800°K and 12 second residence time. These results suggest that ammonia may be used to convert residual nitrate, in excess of that needed to oxidize the organics in the tanks, to releasable gases. Potassium ferrocyanide reacted completely with excess nitrate and with excess hydrogen peroxide at 773°K and 30.3 MPa. A simulated single shell tank (SST) slurry was processed. Hydrothermal treatment appeared to reformulate the waste, as well as destroy the nitrate component when a reducing agent was added.

A novel method was developed for determining the solubility of nitrate salts in supercritical water solutions at pressures ranging from 24.8 MPa to 30.3 MPa (3600 psi to 4400 psi) and temperatures from 723°K to 798°K. Sodium nitrate solubilities ranged from 293 mg/kg at 24.8 MPa and 798°K to 1963 mg/kg at 30.3 MPa and 723°K. Solubility was found to vary directly with pressure, and inversely with temperature. An empirical relationship was developed for the estimation of sodium nitrate solubility at water densities between 0.08 and 0.16 kg/L and temperatures between 723°K and 798°K. A small volume batch reactor equipped with optical diagnostics was used to monitor the phase behavior of a diluted variant of a tank 101-SY simulant. Preliminary results suggest that a single phase is formed at 83 MPa at 773°K.

INTRODUCTION

Our research concerns the hydrothermal (hot aqueous) chemistry and reaction kinetics of waste components that are relevant to the DOE site in Hanford, WA. Decades of plutonium processing and related activities have generated large amounts of complex wastes that are currently stored in underground carbon steel tanks. This waste is radioactive, precluding many conventional treatment technologies, and contains a large proportion of nitrate, as well as organics. Some tanks also contain precipitated ferrocyanides from cesium scavenging operations.

Hydrothermal processing refers to the redox reactions of chemical compounds in supercritical or near-critical aqueous solutions. The physical and chemical properties of water near or above its critical point (647.2°K, 22.1 MPa) are vastly different from those of ambient water. The density dependent properties can be varied greatly by relatively small changes in temperature and pressure. The dielectric constant of water changes from a value of 80 at 293°K and 0.1 MPa to values below 10 at supercritical conditions (1). As a result, supercritical water is quite non-polar and organic components are nearly completely solvated, while inorganic electrolytes are poorly solvated. Many electrolytes exhibit reduced solubility (2) so that inorganic separations can be performed in supercritical fluid media. This feature may be particularly useful in treating mixed wastes. The viscosity of supercritical water is gas-like, less than 20 times that of room temperature water. A

corresponding increase in diffusion coefficients causes reactions to be kinetically limited rather than mass-transfer limited. Thus, at temperatures above 773°K, residence times of less than 20 seconds are required to achieve greater than 99.99% destruction of many organic compounds with oxygen. The density of supercritical water, on the other hand, remains liquid-like, with values from 0.05 to 0.7 kg/L. Short residence times are required for reaction because the relatively high density permits high process throughput.

The work described here addresses some of the outstanding issues concerning the feasibility of destroying nitrates, organics, and/or ferrocyanides by hydrothermal processing and is divided into two sections. The first section will discuss the kinetics of the destruction of nitrate with several reducing agents such as methanol and ammonia and the destruction of ferrocyanides by reaction with nitrate or hydrogen peroxide. The second section concerns measurements of the solubility and phase behavior of salts found in the tanks, particularly sodium nitrate and a simulant for the watch-listed tank 101-SY, under hydrothermal processing conditions.

DESTRUCTION OF HANFORD TANK WASTE CONSTITUENTS

Experiments with sodium nitrate and various reducing agents were conducted in a tubular flow reactor in which the reactor tubing was coiled and immersed in a fluidized sand bath heater. The reactor is described in detail elsewhere (3).

Two separate pre-heater tubes were similarly coiled and immersed, so that at the point of mixing, the two feed streams had reached reaction temperature. The heated length and volume of the reactor tubing were measured carefully, yielding a reactor volume of 13.1 ± 0.25 mL. With carefully measured reactor volume, temperature, and flow rate, the reaction residence time could be accurately determined. This section describes the hydrothermal reactions of methanol, ammonium and ferrocyanide with nitrate. The destruction of nitrate by other reducing agents, such as acetate and formate, is currently under investigation.

Methanol/nitrate

Sodium nitrate was reduced with methanol at temperatures from 723°K to 798°K at 30.3 MPa. Molar ratios (NaNO_3 : MeOH) ranged from 1:3 to 5:1. Sodium nitrate was kept below its solubility limit in supercritical water (620 mg/kg at 28.8 MPa, 782°K (4)) to ensure that heterogeneous chemistry was limited to wall reactions. Flow rates were chosen such that conditions in the reactor met the criteria for turbulent flow; that is, the calculated Reynold's number exceeded 2100. This condition was necessary to consider the reactor as a plug flow system for kinetic analyses.

Above 773°K, nitrate was destroyed to near its detection limit (0.1 ppm). At 798°K and residence times ranging from 5 to 10 seconds, greater than 99.9% of all nitrate in the feed (0.197×10^{-3} kg/L) was converted to products. The primary nitrogen product was ammonium (87.2% conversion), with a small amount of nitrite (5% conversion). Gaseous products N_2O and N_2 were detected qualitatively. Methanol conversions were 70 and 71% under the same conditions. Carbon was recovered exclusively as bicarbonate and unreacted methanol. Using oxygen gas as an oxidant, Webley et al. reported methanol conversions less than 21% in SCW at 24.8 MPa, temperatures between 793°K and 803°K, and residence times near 9 seconds (5). Oxidation products included CO , CO_2 , and H_2 . CO was not observed in the present work (H_2 has not yet been analyzed). Thus, it appears that sodium nitrate is a more effective oxidant than oxygen gas under these conditions.

Figure 1 shows reactant and product profiles at 748°K, starting with equimolar nitrate and methanol. For this experiment, mass balances were 96% for nitrogen and 108% for carbon. Carbon was recovered exclusively as bicarbonate and total organic carbon, primarily methanol. As shown in the figure, nitrate and methanol disappear at approximately the same rate, suggesting that the reaction is first order in both reactants at this temperature and pressure. While these components disappear, increases in nitrite, nitrous oxide, ammonium, and bicarbonate ion (measured as total inorganic carbon) are observed. Mass balances tend to be poorer at the longest residence time for both carbon and nitrogen. For carbon, this discrepancy can be attributed to more complete reaction and conversion to bicarbonate, and subsequent precipitation on reactor walls. Indeed, the carbon missing from effluent samples was found in reactor rinse water after cool down to room temperature. The missing nitrogen was not recovered in the rinse water, and is likely attributable to the production of nitrogen gas. Due to interference from dissolved N_2 gas in the feed water, however, the N_2 produced by reaction at these low feed concentrations could not be accurately quantified.

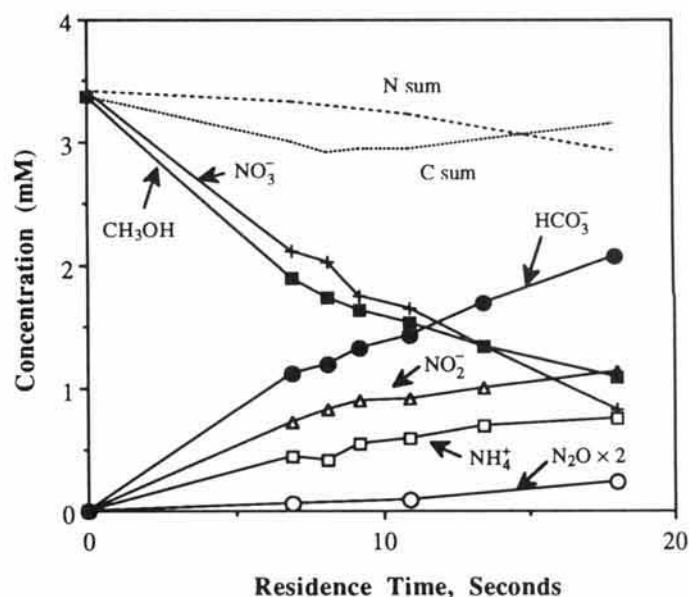


Fig. 1. Sodium Nitrate/Methanol Reactions: product distribution and mass balance at 748°K and 30.3 MPa.

Nitrate and Nitrite with Ammonium

The production of ammonium from the nitrate/methanol reaction prompted us to investigate the reaction of ammonium with residual nitrate. The reactions of nitrate and nitrite with ammonium have been studied in water solutions below 373°K (6,7) and in saturated steam solutions from 473°K to 623°K (8). In acidic aqueous solutions below 373°K, nitrate and nitrite react rapidly with ammonium. Strong acidities allow the formation of H_2NO_3^+ and H_2NO_2^+ complexes which are important intermediates in the conversion of nitrate and nitrite to nitrous oxide and nitrogen gas, respectively. In saturated steam solutions, ammonium nitrate and nitrite intermediates are thought to be formed, resulting in nitrogen gas and water production. Some nitrogen dioxide production is also proposed in the nitrate reaction, although this species is scrubbed to an ionic nitrogen species when the solution is returned to ambient conditions. At temperatures from 593°K to 673°K, solid ammonium nitrate is believed to decompose through free radical mechanisms, following an initial homolytic cleavage. The primary decomposition product is nitrous oxide (9).

Due to the non-ionic nature of hydrothermal water, it is expected that nitrate can exist only in an ion pair with sodium except at very high pressures. Calculations for ammonium hydroxide have shown that the predominant species present below 50.0 MPa and 773°K are ammonia and water (10). The presence of these reactant species indicates that previously discussed mechanisms for nitrate/ammonium reactions are inapplicable in hydrothermal water systems.

In these studies, sodium nitrate was reduced with ammonium chloride and with ammonium hydroxide near 30 MPa. Equimolar ratios were used for most experiments. Reactions with ammonium chloride have been discussed elsewhere (3), and will only be briefly summarized here. When ammonium chloride was reacted with sodium nitrate, complete reaction of ammonium was observed at 30.0 MPa, 653°K, and residence times less than 30 seconds. Nitrous oxide and nitrogen gas were the only observed products, with at most 12 % of the reacted nitrogen converted to nitrous oxide. Approximately

0.8 moles of nitrate were consumed for each mole of ammonia. Under the experimental conditions, water still retained ionic solvent characteristics, which might support previously discussed mechanisms. These reactions occurred too rapidly to be studied at higher temperatures in our apparatus. In contrast, ammonia produced from the oxidation of methanol did not appear to be rapidly oxidized. Consequently, a different form of ammonia was sought for reaction with sodium nitrate. Ammonium hydroxide, a water adduct of aqueous ammonia, was selected for further investigations.

Ammonium hydroxide and sodium nitrate were reacted at concentrations of 3.5 mM/L at 30.0 MPa and 743°K to 803°K. Mass balances between 90 and 110 % for nitrogen confirmed that all important reaction products were detected. Products included nitrogen gas, nitrous oxide, and nitrite ion. For all experiments, less than 2% of nitrogen reacted was converted to N_2O . Conversion to nitrite increased with residence time and temperature. This was caused by the decomposition of sodium nitrate to sodium nitrite and oxygen. Product distributions at 773°K are shown in Fig. 2. From the evaluation of all data, approximately 1.1 ammonium molecules were consumed for each NO_x^- molecule reacted. The relative absence of nitrous oxide from the product streams provided additional evidence that reactions previously considered in aqueous and gas phase studies were not representative of the reactions occurring in hydrothermal water between these species.

Nitrate/nitrite disappearance data, plotted as the fraction remaining versus residence time, are shown in Fig. 3 as a function of temperature. The y-axis in this figure shows the sum of the nitrate and nitrite effluent concentrations relative to the nitrate feed concentration. This reaction appeared to be much slower than the analogous ammonium chloride reactions. At 745°K, nitrogen conversions less than 16% were found at residence times below 15 seconds. Destruction efficiencies of NO_x^- as high as 78% were achieved at 800°K and a residence time of 12 seconds. Arrhenius behavior was observed for the first order removal of NO_x^- over the 55°K range of these measurements. From the data for 1:1 molar ratios of ammonium hydroxide to sodium nitrate, the measured activation energy is 224 kJ, and the pre-exponential factor is 6.40×10^{-13} per second. Results collected from ammonium hydroxide studies indicate that this species reacts at similar rates to the ammonia produced in nitrate/methanol reactions. This form of ammonia is also likely representative of the ammonia intermediate formed in the hydrolysis of organic amines.

Even with the higher temperatures required for ammonium hydroxide oxidation, sodium nitrate still appears to be a more powerful oxidant for ammonia than oxygen in hydrothermal systems. In a study of ammonia oxidation with oxygen by Webley and Tester (11), a residence time of 10.9 seconds at 953 K and 24.8 MPa resulted in only 10.9% ammonium conversion. In another study, Killilea and coworkers reported that ammonia (from urea) was oxidized ten to forty percent from 923 to 963°K (12). Apparently, the activation energy for oxidation of ammonium with nitrate is substantially lower than for oxidation with oxygen.

Ferrocyanide with Nitrate and Hydrogen Peroxide

Potassium ferrocyanide ($K_4Fe(CN)_6$) was reacted at 773°K and 30.3 MPa with hydrogen peroxide and with sodium nitrate in respective molar ratios of 38:1 and 12:1 relative to a feed concentration of 0.046×10^{-3} kg/L of $Fe(CN)_6^{4-}$. These

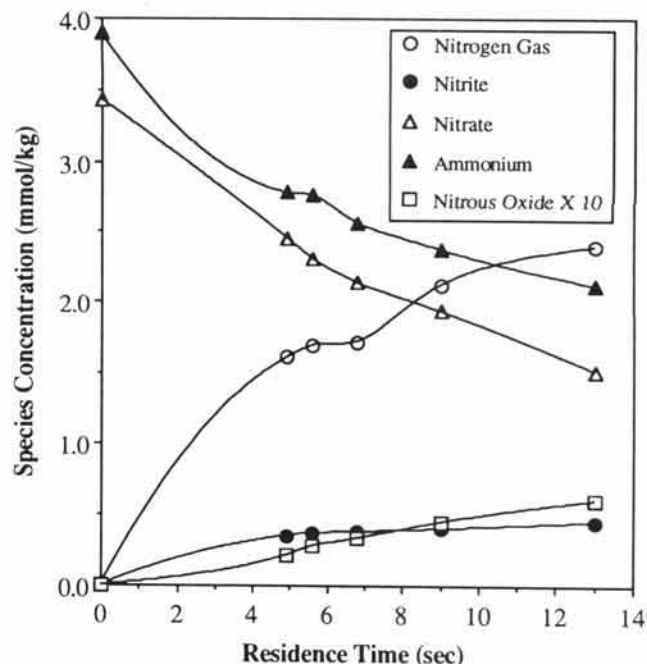


Fig. 2. Sodium Nitrate/Ammonium Hydroxide reactions: product distribution at 773°K and 30.3 MPa.

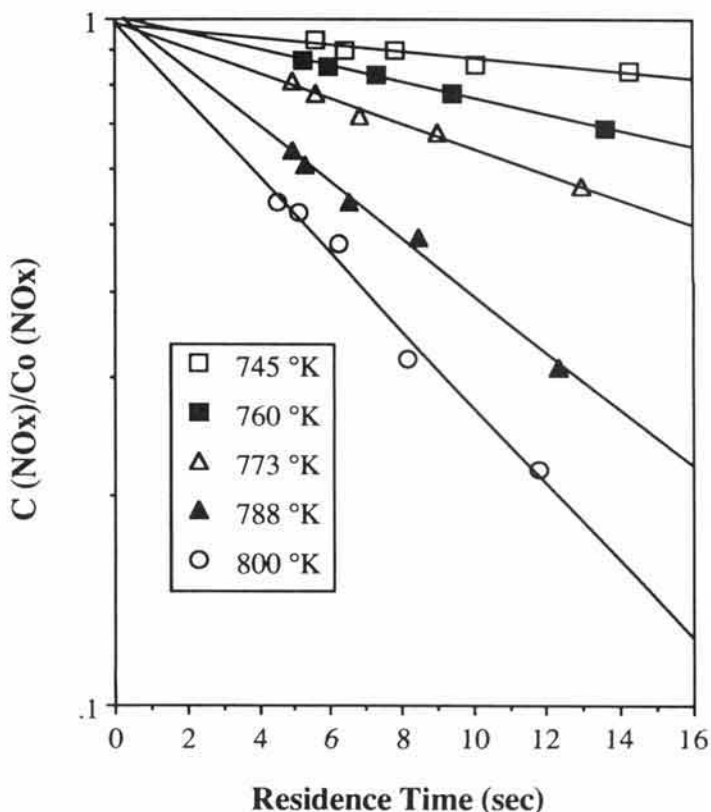


Fig. 3. Temperature dependence of NO_x^- Removal by Reaction with Ammonium Hydroxide at 30.0 MPa.

ratios were computed based on the complete conversion of carbon 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.

In all experiments, ferrocyanide was completely reacted. Ferrocyanide, ferricyanide, and cyanide concentrations were all below the analytical detection limit (< 0.1 mg/L) in reactor

effluents. The primary nitrogen conversion product for $\text{Fe}(\text{CN})_6\text{-4}$ reacted with peroxide was ammonium. When reacted with nitrate, nitrite and ammonium were produced. Potassium was recovered in the effluent as K^+ , while iron, although not quantitatively recovered, was found primarily as a red particulate, Fe_2O_3 , on the filter preceding the back pressure regulator. Bicarbonate was the sole product of carbon conversion. Some bicarbonate was recovered in water rinses of the cooled reactor, indicating precipitation as a sodium or potassium salt at reaction 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 the carbon balance is high.

SOLUBILITY AND PHASE BEHAVIOR OF HANFORD TANK WASTE CONSTITUENTS

In addition to organics and in some cases, ferrocyanides, the Hanford tanks contain a complex and varying matrix of metal salts. While NaNO_3 is the primary component in the tanks, K, Al, Fe, Ni, and other metals are also present as the nitrate, phosphate, or sulfate salts. The feasibility of using hydrothermal processing as a pretreatment for the destruction of organics, nitrates, and ferrocyanides depends, in part, on the ability to pump the waste through the reactor. Because we know the lead about the phase behavior and solubility of salts under hydrothermal conditions, we are investigating these issues to avoid reactor plugging. Sodium nitrate, sodium aluminate, and the phosphate salts cause the most concern. We have established an experimental and theoretical modeling program to address the solubility and phase behavior of metal salts at the pressures (22.1 MPa to 103.4 MPa) and temperatures (623°K to 873°K) of interest to hydrothermal processing. There is a paucity of such information reported for pure salt solutions, let alone for mixtures. Furthermore, the waste from any one tank is expected to vary widely in composition. Therefore, we are developing a roadmap of operating conditions (temperature, pressure) under which the waste stream is a single (fluid) phase in the reactor, for varying simulated waste compositions. This information is also critical to avoiding plugging the cooldown/heat exchanger and pressure letdown devices downstream of the reactor. In addition, mass transport limitations between phases and heterogeneous reactions (except at the walls) are eliminated.

Solubility of Sodium Nitrate

Our experiments measured the solubility of sodium nitrate in water at pressures from 24.8 MPa to 30.3 MPa and temperatures from 723°K to 798°K using a new method (13). To determine the role of cation size in the solubility of 1:1 nitrate salts, we also measured the solubility of lithium and potassium nitrate salts. These salts melt below the critical temperature of water. Sodium nitrate and nitrite melt at 579.8°K and 544°K, respectively, while nitrate salts of lithium and potassium melt at 537°K and 607°K. (14) As a result, a precipitated phase of these salts in equilibrium with the supercritical water vapor will be molten. The experimental approach used for determining the solubility of sodium nitrate in this study was somewhat different from conventional methods for measuring solubility. Several investigators have used systems where steam was flowed through salt beds, with the equilibrium electrolyte concentration in the exiting steam

representing the solubility (15,16) or other methods (17). These methods are not readily applicable to sodium nitrate because it decomposes at temperatures near the critical point for water, and because it is highly soluble in subcritical water.

The current method relies on the efficient separation of solids once they are formed. This approach was used because of its relative simplicity and because previous work suggested that separation of electrolytes near their solubility limits in supercritical water was possible (4). Figure 4 shows the apparatus used for measuring the solubility of sodium nitrate and the other 1:1 nitrate salts. A packed bed precipitation

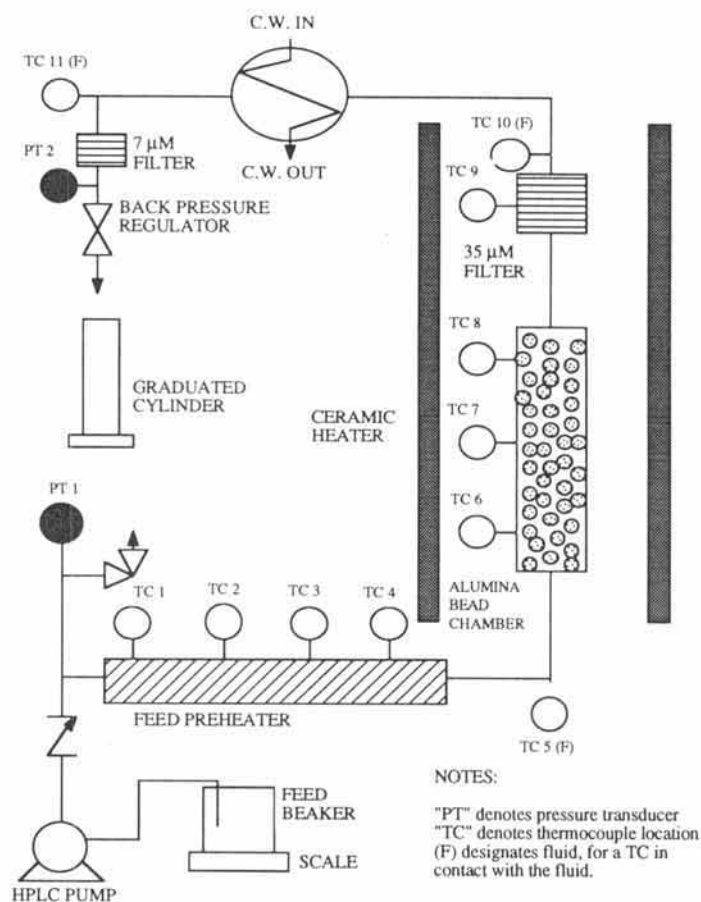


Fig. 4. Hydrothermal unit for measuring salt solubility.

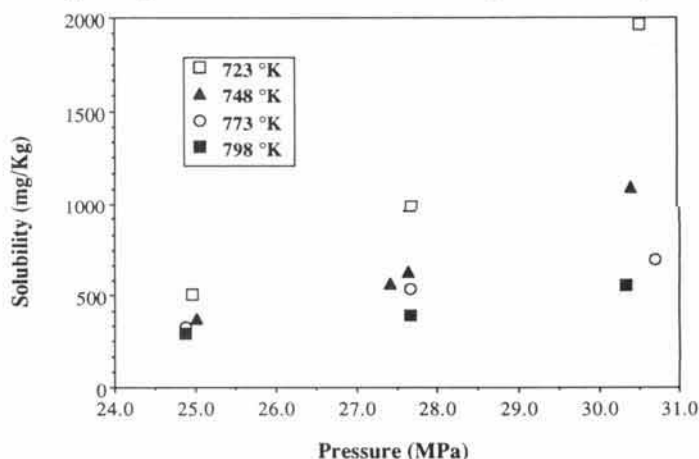


Fig. 5. Sodium Nitrate solubility as a function of temperature and pressure.

chamber is used to provide high surface areas for nucleation and crystal growth. A filter at the outlet serves to capture whatever nucleates did not accumulate in the precipitation chamber. The fluid thermocouple at the exit of the high temperature filter measured the operating temperature. Generally, 90 to 110% recovery of the nitrogen and sodium was measured using ion chromatography.

The solubility of sodium nitrate was determined from the measured concentration of nitrate in the effluent under steady state flow conditions. These values are plotted in Fig. 5 as a function of pressure at four temperatures from 723°K to 798°K (450°C to 525°C). The error bars are typically smaller than the size of the data points. The solubility of sodium nitrate increases with increasing pressure (and therefore water density), and decreases with increasing temperature. Solubilities range from 293 mg/kg at 798°K and 24.8 MPa to 1963 mg/kg at 723°K and 30.3 MPa.

A semiempirical relationship based on a simple hydration model for solvation was derived for predicting sodium nitrate solubility as a function of water density. This model has been successfully applied to many electrolytes over wide ranges of temperature and pressure (18). The relationship indicates that the logarithm of the solubility increases directly with the logarithm of the density. Figure 6 shows a plot of the data at all temperatures and pressures. Note that the x axis is linear. The slope of the fit is related to the hydration number; the fit suggests that three water molecules are required to solvate one sodium nitrate molecule (13). The intercept of the fit is proportional to the equilibrium constant for the dissociation of sodium nitrate. Typically, equilibrium constants are temperature dependent, and the hydration number may or may not vary with temperature. Over the small temperature interval in this work, little difference in hydration number or equilibrium constant was found for fits to the data at a fixed temperature, although more data points are needed to confirm trends at individual temperatures. Similar plots for association reactions of NaCl at high temperatures reveal little difference in intercepts over 100°K intervals (19). The same work showed no change in the slope for association reactions above the critical temperature for pure water.

Figure 6 demonstrates that even a small increase in density has a large effect on salt solubility. For a twofold increase in density from 0.079 kg/L to 0.15 kg/L, the solubility of sodium nitrate increases nearly eight fold. Figure 7 shows the density of pure water as a function of temperature at three pressures from an empirical equation of state (20). The calculation illustrates how small changes in pressure or temperature markedly alter the density of the supercritical fluid, and hence, the solubility of a metal salt in solution. For example, at 773°K, a threefold pressure increase from 34.5 MPa to 103.4 MPa increases the density nearly fourfold. If the empirical relationship between the logarithm of the solubility and the logarithm of the density holds outside the conditions of Fig. 6, a much larger increase in the solubility of sodium nitrate is anticipated upon tripling the pressure.

Solubilities of potassium and lithium nitrate at 748°K were determined and compared with sodium nitrate solubilities at the same temperature. Lithium, with the smallest ionic radius, exhibited the highest solubility of the three, while potassium, with the largest ionic radius, displayed the lowest solubility. Determination of hydration numbers for solvation revealed that lithium > sodium > potassium, which was qualitatively expected.

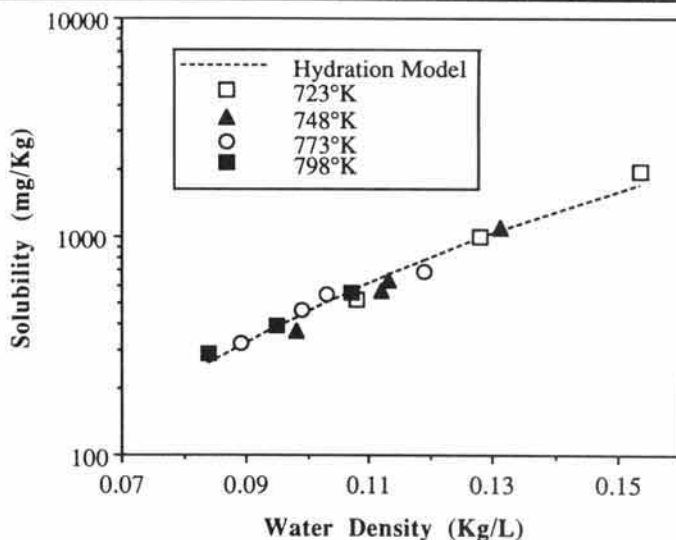


Fig. 6. Sodium Nitrate solubility as a function of density.

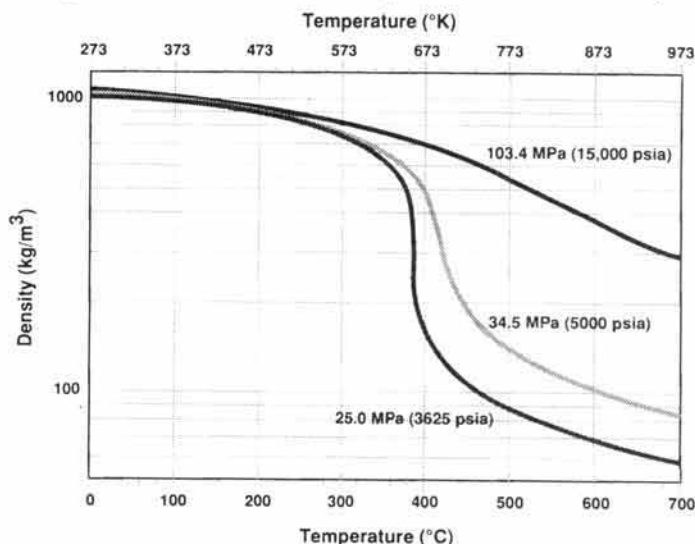


Fig. 7. Calculated pressure and temperature dependence of the density of pure water.

Phase Behavior of Hanford Waste Simulants

In survey experiments on the bench scale, we have processed several Hanford tank waste simulants. We have demonstrated continuous nonplugging operation of a 45 wt. percent NaNO_3 slurry through a 2.5 mm diameter reactor at 823°K and 31.0 MPa. A single shell tank (SST) sludge simulant prepared by Pacific Northwest Laboratory was processed undiluted at 782°K and 30.0 MPa. The simulant contained nearly 50 percent inorganic salts by weight, primarily as aluminum oxide/hydroxide and sodium nitrate. Numerous trace metal salts (including phosphates) and silicon dioxide were also present. Using sucrose as a reducing agent, the nitrate level was decreased 84% at 53 seconds residence time. A flocculent solid residue was produced which suggests that the waste is reformulated by hydrothermal processing and may be amenable to new postprocessing separation schemes. In this initial test, the small diameter (1.6 mm i.d.) cold/hot lines eventually plugged. Our designs for pilot scale hydrothermal processing units use larger diameter tubing (12.7 mm i.d. minimum), in keeping with our results for the test with 45 wt. percent NaNO_3 . In addition, we will likely operate at higher pressure than these tests, because the density, and hence salt solubility, is greater (Figs. 6 and 7).

The reformulation of the SST simulant is in concert with our earlier results for other Hanford tank waste simulants with high salt content prepared here (4). We demonstrated selective *in situ* separation of a metal salt from the other salts in the reactor effluent by careful control of temperature and pressure. For example, Sr was nearly completely separated from Na, Cs, Cr and Cl without reactor plugging at 713°K and 24.8 MPa in 60 seconds.

Since these preliminary experiments were completed, we have developed a small volume batch reactor to identify the temperature and pressure regimes in which plugging in a flow reactor can be avoided. Figure 8 shows the optical cell for studying high temperature phase equilibria of Hanford waste simulants. Faceted diamonds with a clear aperture of 0.6 mm are clamped into the wall of a Hastelloy tube (6.24 mm o.d., 2.1 mm i.d.), using gold washers to form a seal. The tube is surrounded by a brass sleeve that is heated by two temperature-controlled coaxial resistance heaters. The temperature in the cell is monitored by a type K thermocouple inserted into the Hastelloy tube in very close proximity to the region between the diamond windows. The cell is operable at temperatures up to 837°K and pressures up to 138 MPa.

Phase changes in the simulant under hydrothermal processing conditions are monitored by two coaxial optical systems. A white-light source enters the cell from the left (Fig. 8). On the right, a lens forms a magnified image of one of the diamond windows on a color CCD camera. Using a beamsplitter, a helium-neon laser counterpropagates through the cell, and a second beamsplitter is used to reflect the transmitted HeNe beam to a photodiode. The CCD camera is equipped with a blue filter to block scattered laser light, and the photodiode is equipped with a bandpass filter to discriminate against white light. The CCD camera system allows visual observation of phase changes, which can be seen in several ways. When solid precipitates from solution, crystals may be seen growing on the window or dropping out of the bulk of the solution. When a liquid phase forms (starting from a single phase vapor), density gradients, and sometimes droplets of liquid, are visible. The laser diagnostic provides a more sensitive indication of the onset of vapor-liquid equilibrium, since the density gradients give rise to large changes in the amount

TABLE I
Composition of Undiluted Variant of Hanford
Simulant SYI-SIM-92 A

Compound	Molarity
Sodium Nitrite	3.95
Sodium Nitrate	2.39
Sodium Hydroxide	2.45
Sodium Aluminate	2.05
Sodium Carbonate	2.41
Sodium Phosphate, Tribasic	0.18
Potassium Nitrate	0.15

of light reaching the detector, i.e., the signal becomes very noisy.

We have performed preliminary investigations of the solubility of a variant of the Hanford simulant SYI-SIM-92 A (21). The composition of the simulant, shown in Table I, differed from the composition of SYI-SIM-92A in three ways. First, the TOC was converted to carbonate ion so oxidation of the TOC would not occur during the measurement. Second, chloride and fluoride anions were omitted to avoid corrosion of the cell. Third, trace metals were omitted because Na, K, and Al, the main metals in the waste, are expected to be most important in plugging. When mixed at the concentrations shown in Table I, not all components dissolved and a white slurry was formed. When this slurry was diluted to four times its original volume, as expected for the Initial Pretreatment Module, all components went into solution.

The waste solution was heated in the optical cell at a pressure of 82 MPa. A small amount of solid precipitated as crystals on the windows, which did not entirely redissolve at 723°K. When the pressure was subsequently lowered to about 62 MPa, a phase change occurred, indicating the presence of both a vapor and a liquid phase (in addition to the small amount of solid phase as crystals on the windows). Upon raising the pressure to 100 MPa and the temperature to 773°K, all components appeared to go into solution in a single phase. When the pressure was lowered to about 83 MPa (12000 psi) at a constant temperature of 773°K, a vapor-liquid phase transition was first observed, followed almost immediately by the appearance of a solid phase (or perhaps several solid phases). These preliminary results suggest that a minimum temperature of about 773°K and a minimum pressure of about 83 MPa are required to keep all components of the (diluted) simulant in solution in a single phase. Subsequent examination of the phase behavior of another simulant variant containing sodium nitrate, sodium nitrite, sodium hydroxide and sodium carbonate at the same concentrations showed that, at the same temperature of 773°K, a single (fluid) phase exists above about 8000 psi (55 MPa).

SUMMARY

The destruction of nitrates, organics, and ferrocyanides wastes contained in underground storage tanks at the Department of Energy Hanford site in Washington state would significantly reduce the volume, the hazards, and the toxicity of the waste, while addressing pretreatment requirements for

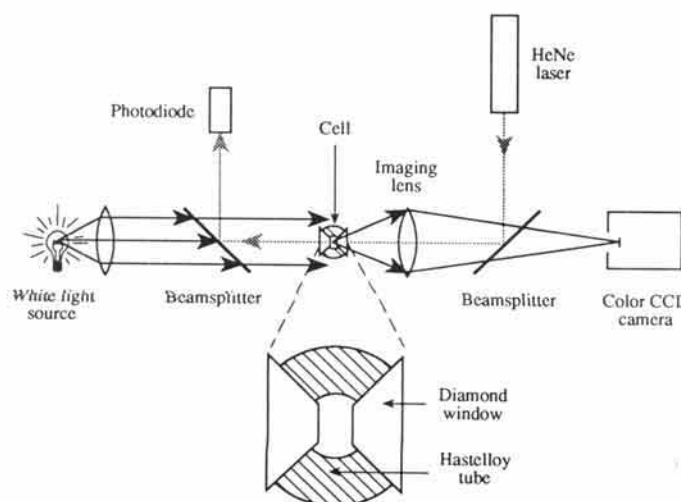


Fig. 8. Schematic diagram of hydrothermal cell for monitoring simulant phase behavior using optical diagnostics.

vitrification and grouting. Hydrothermal processing, the redox reaction of chemical compounds in supercritical or near-critical aqueous solutions, is a promising new technique for the destruction of hazardous wastes. We have carried out experiments in tubular flow reactors and batch reactors that are designed to explore the chemistry and kinetics of reactions in supercritical fluids at pressures up to 103 MPa (15000 psi) and temperatures up to 873°K, for reaction times in the range of seconds to minutes. Experiments at Los Alamos have demonstrated that organics, nitrates, and ferrocyanides can be rapidly and efficiently destroyed by chemical reactions in high temperature aqueous solutions (573-773°K, 21-31 MPa, 3000-4500 psi). Laboratory studies examined the redox reactions of nitrate with a highly refractory organic compound (methanol), with ammonium, and with ferrocyanide. Nitrate is reduced by methanol in the temperature range 723°K to 773°K (residence times 5-30 sec), and by ammonium at 623-653°K (20-80 sec). Above 773°K, greater than 99% of the nitrate was destroyed at the shortest residence times (<6 seconds) while greater than 80% of the methanol was converted to bicarbonate and carbon dioxide. The reaction of nitrate and nitrite with ammonium chloride is complete within 30 seconds at temperatures near the critical point of water (647.2°K). The reaction of nitrate with ammonium hydroxide proceeds less rapidly and exhibits Arrhenius behavior from 745°K to 800°K. These studies suggest that ammonium, an inexpensive reducing agent, can be used to convert excess nitrate to nitrogen or N₂O following the oxidation of organics by nitrate in the tank mixtures. Ferrocyanide also reacted rapidly with nitrate above the critical point, producing bicarbonate and ammonium. Laboratory scale experiments at Los Alamos have also demonstrated that single shell Hanford tank waste simulants can be treated by hydrothermal processing. The treatment appeared to reformulate the waste, in addition to destroying the nitrate and added TOC constituent.

Hydrothermal processing can be considered a supporting technology to the Hanford grouting and vitrification technologies for the tank wastes. A critical issue in evaluating the utility of hydrothermal processing for remediation of Hanford tank wastes is plugging of the reactor by the highly concentrated salts in the waste. Several experiments were performed to support development of a thermodynamic model of the phase behavior of salts at high temperature and pressure. The thermodynamic model will provide a roadmap of operating conditions for treating Hanford tank waste matrices, which are expected to widely vary in composition, even from a single tank. The solubility of sodium nitrate increases from 24.8 MPa to 30.3 MPa and varies inversely with temperature from 723°K to 798°K. A linear relationship between the log of the solubility and the log of the density was observed. In another reactor equipped with optical diagnostics, measurements of the phase behavior of a tank 101-SY simulant by light scattering found that a single phase is formed in the reactor above 83 MPa at 773°K for a particular variant of the simulant.

In conjunction with technologies for actinide treatment, hydrothermal processing forms the basis for an integrated process for treating a number of mixed wastes. The range of process conditions available in the post-reactor regions of a hydrothermal processing plant could provide advantageous conditions for redox or physical separations of the radioactive portions of mixed wastes. The fate of radionuclides in hydrothermal processing and the amenability of the effluent to

post-processing separations is currently under investigation at Los Alamos.

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