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TANK WASTE CHEMISTRY - A NEW UNDERSTANDING OF WASTE AGING

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ABSTRACT

There is concern about the risk of uncontrolled exothermic reaction(s) in Hanford Site waste tanks containing NO_3^-/NO_2^- based salts and/or metal hydroxide sludges in combination with organics or ferrocyanides. However, gradual oxidation of the waste in the tanks to less reactive species appears to have reduced the risk. In addition, wastes sampled to date contain sufficiently large quantities of water so that propagation reactions are highly unlikely.

INTRODUCTION

Over the past 2 to 3 years a variety of independent information sources were studied to evaluate the risk of an uncontrolled exothermic reaction in Hanford Site high-activity waste tanks. The intensive, mostly theoretical study was based on limited data, but led to the tentative conclusion that the risk is greater than previously expected. The wastes contained in these tanks are NO_3^-/NO_2^- based salts and/or metal hydroxide sludges. In combination with these salts/hydroxides are water soluble and/or insoluble organics or ferrocyanides. It is these combinations that are of greatest concern.

Evidence to refute those preliminary conclusions about the high risk came first from an evaluation of waste transfer records and flowsheet-related documentation - an analysis that serves to bound the inventory of fuel in the high-NO_3^-/NO_2^- wastes. Second, tests with simulated wastes demonstrated that both the reactivity and energetics of potentially reactive species were lower than expected in systems containing ferrocyanide salts and in those containing the organic species. Third, the results from tests with actual waste materials, either cores or "grab" samples, generally demonstrated a lower reactivity for actual wastes than for freshly made simulants. These lower energy releases suggested degradation of the fuel value by radiolytic and chemical aging of the waste. This, the gradual (over tens of years) oxidation of the waste in the tanks to less reactive species, is the subject of this paper.

BACKGROUND

Production of nuclear weapons materials began at the Hanford Site in 1944. Production continued until 1990, when the last production reactor was shut down and processing of the irradiated metallic uranium fuel was suspended. During this entire period, radioactive wastes from the reprocessing operations have been stored as alkaline liquids and slurries in near-surface underground tanks. Between 1943 and 1964, 149 single-shell tanks (SST) ranging in capacity from 208 m^3 to 3,800 m^3 (55,000 to 1,000,000 gal) were constructed. Currently, the SSTs contain approximately 14,000 m^3 (36,000,000 gal) of waste as damp salt cake (predominantly sodium nitrate and sodium nitrite), and metallic oxides/hydroxides, and other insoluble metal salt sludges, plus about 2,300 m^3 (600,000 gal) of supernatant liquid. The waste represents an accumulation of material from 1944 to 1980, at which time active use of the SSTs ceased. Historically, 67 of these tanks are known to have leaked or are assumed to have leaked, necessitating additional treatment. Treatment consisted of the construction of new double-shell steel tanks (DST) and the concomitant pumping of the remaining liquids from the SSTs. As of 1992, the liquids in all but 44 of the SSTs have been reduced to the point that only a small non-drainable fraction remains. Of this fraction, only a small quantity can drain from the tank, and the remainder is held by capillary forces. These second generation tanks, the DSTs, offer better assurance that the environment will be protected from leakage of stored radioactive waste (1). Since 1971, 28 of the DSTs, ranging in size from 3,720 m^3 to 4,390 m^3 (984,000 to 1,160,000 gal), have been built at the Hanford Site.

Hanford Site wastes are unique in that they resulted from a wide variety of reprocessing flowsheets (e.g., the bismuth phosphate process, reduction oxidation, plutonium-uranium extraction, and the Thorex Process, as well as from uranium recovery activities). To reduce the volume of waste that was generated during the uranium recovery process, ^{137}Cs was removed from the supernatant solutions by the precipitation of ferrocyanide [$Na_2NiFe(CN)_6$ (ideal stoichiometry)] by which the cesium was scavenged to the sludge layer in the tank. The ferrocyanide- scavenging process was carried out using at least three flowsheets (2). Wastes were also added to the tanks as part of plutonium recovery and finishing operations, and as part of cesium and strontium removal and encapsulation efforts. As a result of the use of several plutonium recovery processes and a variety of methods to manage the volume of stored tank wastes, the chemical composition and radionuclide content of individual tanks varies widely.

DISCUSSION

A variety of organic solvents, complexing agents, surfactants, and other reagents were used in the various processes (refer to Table I). The wastes in the tanks contain some fraction of these organic species. In some wastes, the existence of significant quantities of either or both ferrocyanide and organic species with an excess of NO_3^-/NO_2^- oxidizers poses a potential safety problem, which has been the subject of much recent study. These studies are briefly discussed below.

Table I. Primary Energy Rich Chemicals Used In Waste Management and Chemical Processing Operations.

Compound Name	Use	Potential Degradation Products
Normal paraffin hydrocarbons	Carrier Solvent	Probably carboxylic acid fragments from carbon chain cleavage
Methyl isobutyl ketone (hexone)	Extraction solvent	Acetone and carboxylic acid fragments
EDTA and HEDTA	Complexants	Sodium formate and oxalate and other "intermediate degradation fragments from complexant cleavage
Tributyl phosphate	Extraction solvent	Butyl alcohol and possibly butyric acid
Citric acid	Complexant	Sodium formate and oxalate and other "intermediate" degradation fragments
Sugar	Denitrating agent	Reaction in acid leads to carbon dioxide and nitrous gases
Di-2-ethylhexyl phosphoric acid	Complexant	2-ethylhexyl alcohol and possibly carboxylic acid fragments
Assorted organic based surfactants	Decontamination operations	Probably carboxylic acid fragments from carbon chain cleavage
Sodium Nickle ferrocyanide	Decontamination operations	Soluble sodium ferrocyanide, sodium formate and ammonia

EDTA=Ethylenediaminetetraacetic.
HEDTA=N hydroxy-ethylenediaminetriacetic acid.

Degradation of Water Soluble Organics in Alkaline Wastes

Water soluble organics have been used extensively in the chemical processes used at the Hanford Site. In general, these water soluble organics consist of a class of organic complexants, such as ethylenediaminetetraacetic (EDTA), N hydroxy-ethylenediaminetriacetic acid (HEDTA), nitrilotriacetic acid (NTA), etc, and pH buffering agents, such as glycolic and citric acids. The generation of gases in the alkaline wastes in tank 241-SY-101 and the knowledge that these organics were used in the chemical processes, led to the studies of the mechanisms by which these organics decompose in alkaline solutions. This work is part of a cooperative effort that has been carried out at Georgia Institute of Technology, Argonne National Laboratory, Westinghouse Hanford Company, and Pacific Northwest Laboratory (PNL).

The earliest work on the decomposition of organics in alkaline waste solutions was performed by Delegard (3,4). Results from these studies indicate that the initial organic, in this case HEDTA or EDTA, were degraded by losing one and two carbon atoms from the moiety, yielding ethylene diaminetriacetate (ED3A). More recent studies confirm that these organics decompose by losing one- and two-carbon fragments from the molecule (5-8). These fragments ultimately yield, if the mechanism is correct, oxalate and formate plus H_2 and CO_2, which, in strongly alkaline environment, are converted immediately to CO_3^{-2}. Additionally, N_2O, NH_3, and N_2 gases are produced during the decomposition of these organics. As discussed below, this represents an overall decrease in the potential energy associated with the organic content of the waste.

Analytical results from the waste samples from tank 241-SY-101 suggest that the amount of parent organic (i.e., HEDTA or EDTA) is relatively small and represents less than 10% of the total organic present in the samples (8). At that time, the data suggested that there was a substantial amount of the organic in these samples that was not amenable to analysis using the derivitization methods. Oxalate and formate would not be detected using these techniques, but would be expected from the proposed mechanisms. These initial analytical results suggested that a substantial amount of the total organic carbon is present as moieties smaller than the presumed parent compounds, but as yet unidentified and/or quantified. This general degradation of the organics seems obvious, but without the studies performed over the past three years and analytical results obtained over the past two years, there would only be an ambiguous understanding.

Recent work by Bryan and Pederson and reported in reference (8) suggests that the mechanisms that occur at tank temperatures may also be effective in the destruction of these organics at elevated temperatures. Bryan and Pederson have investigated the autogenous destruction of EDTA at temperatures between 150 and 350 °C, below the critical temperature of water. In these experiments, the NO_2^- in the simulated wastes was used to destroy the organics yielding one mole of NH_3 per mole of organic nitrogen. Some NH_3 was also generated from organics that contained no nitrogens and from simulated waste without organics added. The quantity of the NH_3 so generated was, however, small. From the results of these experiments, some insight to the stoichiometry was obtained, assuming that the stoichiometry is approximately the same at tank temperatures as at the temperatures of Bryan and Pederson's experiments. These results suggest that OH^- is required for the destruction

of these organic species when the oxidation is carried to CO_3^{-2}; no OH^- is required for the destruction of EDTA to $C_2O_4^{-2}$. If this is the case, it would suggest that a substantial amount of the organic in tank 241-SY-101 has not been completely oxidized because the OH- concentration has not changed significantly over the past 6 years (9,10). Because the OH^- has not changed significantly, it can be assumed that the reactions have not taken the organic carbon completely to CO_3^{-2} or the net reaction suggested by Bryan and Pederson in reference (8) is not fully operable at tank temperatures. The reactions proposed by Ashby et al. in references (6,7) suggest that 4 to 10 moles of OH^- should be consumed for each mole of parent organic reacted to form oxalate and formate.

Hydrogen, N_2O, NH_3, and N_2 are generated in the experiments of Bryan and Pederson, reported in references (6,7), and in the mechanism proposed by Ashby et al. (5,8,11). These same gases are generated in the waste contained in tank 241-SY-101. While the data from the tank are confounding in that the information on the gas composition has only been obtained for the past three years, some information can be extracted. If one uses the information from the simulated waste studies as an indicator of the processes that are taking and have taken place in the tank, one can estimate the total amount of organic carbon that has been affected by the reactions. Using a generation rate of 50 mol H_2/d (10) obtained from the waste level data and one mole of H_2 per one or two moles of carbon (depending on the source of the H_2 - glyoxalate or formaldehyde - obtained from the simulated waste studies), the maximum amount of organic that could have been affected is 0.1 g/L or about 6% of the total organic carbon in the waste of tank 241-SY-101. Assuming for the moment that very little of the organic was oxidized to CO_3^{-2} and 6% is EDTA, very little of the original fuel value remains in the waste. This suggests that the safety margins used in the safety analyses for the waste in tank 241-SY-101 were quite conservative, since parent organic species were used to calculate the energy release during a hypothetical accident scenario.

The most energetic reaction of EDTA or HEDTA is the conversion of the organic species and NO_2^- to CO_3^{-2}, H_2O, and N_2. The enthalpy of this reaction is on the order of 5 MJ/mol. If the organic had been degraded to $C_2O_4^{-2}$ then the energy content of would have been degraded from the original 5 MJ (mol of EDTA) to the equivalent of about 1 MJ (5 mol oxalate). This represents a substantial reduction in the total energy that could be released during an accident involving the rapid decomposition of the organic content in the waste.

In short, the fuel value represented by the total organic carbon, a value to which EDTA, $C_2O_4^{-2}$, and $CHOO^-$ contribute, in tank 241-SY-101 waste and, in fact all wastes containing water soluble organics, is degrading with time due to the slow destruction of larger organic moieties (i.e., as the waste ages). While the analytical data are not yet complete, if the data collected to date are accurate, the assumed fuel value in tank 241-SY-101 has degraded substantially over the years relative to the assumptions made during the safety analyses. The analytical data suggest that the fuel value may have decreased by up to a factor of 4 due to aging of the organics in this and other alkaline waste currently stored in Hanford Site tanks. This general decrease in energy is further substantiated by the low exothermic values obtained from the differential scanning calorimeter analyses performed on actual waste samples.

Aging of Ferrocyanide Salts in Alkali-Containing Waste

Aging of ferrocyanide waste is the process by which insoluble sodium nickel ferrocyanide, when exposed to aqueous alkali above pH 13, either dissolves and is diluted or decomposes to a less fuel-rich form. As part of waste management operations, aluminum decladding waste or double-shell slurry from the concentration of reprocessing wastes was added to tanks containing bedded ferrocyanide (2). The ultimate goal of demonstrating aging is to verify a mechanism that could have taken place in the tanks over extended periods of time when the precipitated ferrocyanide was exposed to these highly alkaline wastes.

To validate the aging concept for ferrocyanides, two different "proofs" are needed. First, it must be demonstrated on both synthetic flow sheet material and on real wastes that the initially insoluble ferrocyanide salts dissolve and perhaps decompose. Second, a means of "delivering" the alkali to the bedded ferrocyanide wastes must be demonstrated.

The slow diffusion of materials in aqueous heterogeneous waste systems is well known, but the time scale on which such diffusion occurs is long. Dissolution of ferrocyanide salts within one meter of a highly alkaline waste over a 30-year period appears almost certain, but questions remain whether such diffusion-controlled process could dissolve wastes lower in the tank. Modeling and perhaps some experimental studies will be needed to determine whether the time scale required for diffusion of alkali through the deepest bed of settled waste is compatible with a diffusion-controlled dissolution mechanism.

Equations that describe the proposed chemistry of aging and are based on laboratory results of the dissolution of ferrocyanide simulants are presented below:

(Eq 1) $Na_2NiFe(CN)_6 + 2NaOH \longrightarrow Na_4Fe(CN)_6 + Ni(OH)_2$
Sodium Nickel Ferrocyanide — Sodium Ferrocyanide

(Eq 2) $Na_4Fe(CN)_6 + 2NaOH + 12H_2O \longrightarrow 6NaHCO_2 + Fe(OH)_3 + 6NH_3$
Sodium Formate

(Eq 3) $Na_3Fe(CN)_6 + 3NaOH \longrightarrow 6NaCN + Fe(OH)_3$
Sodium Ferricyanide

Too little is understood about destruction of insoluble complex ferrocyanide salts by radiation. Although preliminary data suggest that soluble ferrocyanide salts produce cyanide ion by radiolysis, it is not yet known what role radiolysis plays in the aging of Hanford Site ferrocyanide wastes.

PNL Aging Study Test Results

Results of aging studies now under way at PNL demonstrate that a vendor-prepared ferrocyanide simulant, $Na_2NiFe(CN)_6 \cdot Na_2SO_4 \cdot 4.5\ H_2O$, dissolves rapidly in aqueous base. This process may have occurred in the tanks over the last 35 years to dissolve, dilute, and more slowly destroy the

ferrocyanide compounds. Lilga et al. (12) investigated the effects of pH variation, [Na^+], anions present in SSTs, and gamma radiation on solubilization.

In the initial dissolution screening experiments, 1 g of the vendor-prepared material was refluxed for 96 h in 0.1 *M* (Experiment 1) or 1.0 *M* NaOH (Experiment 2). These experiments were performed in standard laboratory glassware. Table II summarizes the conditions and results of the two experiments.

The data indicate that vendor-prepared $Na_2NiFe(CN)_6$ dissolves in aqueous base according to Eq. (1) to give primarily insoluble $Ni(OH)_2$ and soluble $Na_4Fe(CN)_6$. Precipitation of $Ni(OH)_2$ apparently drives the ferrocyanide dissolution.

Atomic absorption analysis of the reaction supernates showed that essentially all of the iron is in solution after 96 hours at reflux conditions. Very little of the nickel is found in the supernate solutions. Environmental scanning electron microscopy (ESEM), energy dispersive spectroscopy (EDS), infrared (IR) spectroscopy, and X-ray diffraction (XRD) indicate that $Na_4Fe(CN)_6$ is the primary ferrocyanide compound in the soluble solids. IR, ESEM, EDS, XRD, and Mössbauer analyses showed that nickel was present in the reaction precipitate as $Ni(OH)_2$. Very little iron remained in the insoluble solids.

The presence of NH_3 was detected in both experiments. This is indicative of cyanide hydrolysis reactions. A greater degree of hydrolysis occurs in the more basic solution. The extent of hydrolysis, however, is very low after 96 hours with the largest yield on the order of 0.02% (0.02% of the cyanide groups were converted to NH_3).

A more detailed study was undertaken to determine the influence of pH, [Na^+], and the presence of single-shell tank (SST) simulant salts on the rate and extent of dissolution of the vendor-prepared $Na_2NiFe(CN)_6$ material. These reactions were performed at room temperature in Teflon® labware. Solutions were periodically sampled during the reaction and analyzed for iron using atomic absorption spectroscopy. At the conclusion of the experiment, the final pH was measured and the soluble and insoluble solids were analyzed using IR, ESEM, EDS, XRD, and occasionally using Mössbauer spectroscopy. In some cases, the supernate was analyzed for free cyanide, ferrocyanide, and ferricyanide using ion chromatography (IC). Table III summarizes the starting and final pH for some of these experiments.

Experiments to study the effect of initial pH on ferrocyanide dissolution were performed with starting pH values of 12, 13, and 14 (0.01 *M*, 0.1 *M*, and 1.0 *M* NaOH, respectively). The dissolution is 95% complete after 0.5 h stirring in 1 *M* NaOH (pH 14) at room temperature. The reaction at pH 12 is base-limited, but the base is rapidly consumed within 0.1 h. At pH 13, a slight excess of base is present; the dissolution proceeds rapidly at first, then slows to reach about 85% completion in 144 hours. Presumably, the dissolution would continue to completion at longer reaction times at pH 13.

Table II. Conditions and Results for Preliminary Experiments.

	Experiment 1	Experiment 2
[NaOH]	0.1 *M*	1.0 *M*
Initial pH	12.9	13.8
Final pH	10.5	13.0
$Na_2NiFe(CN)_6 \bullet Na_2SO_4 \bullet 4.5\ H_2O$ (g)	1.0005	1.0041
Moles $Fe(CN)_6^{-4}$ or Ni^{+2}	1.85×10^{-3}	1.86×1^{-3}
Weight of recovered solids (g)	0.3316	0.5113
Solution [Fe] (mg/L)	2030	1600
Moles Fe in solution	1.82×10^{-3}	1.43×10^{-3}
Fraction total Fe in solution	98%	77%
Solution [Ni] (mg/L)	39	3.3
Moles Ni in solution	3.32×10^{-5}	2.81×10^{-6}
Fraction total Ni in solution	1.8%	0.15%
$[NH_3]$ in gas (ppm)	30	375
Approx. moles NH_3 produced	8.04×10^{-8}	2.34×10^{-6}
Approx. %-yield NH_3	0.0007	0.02

Table III. Starting and Final Solution pH in Dissolution Experiments.

Experiment	Starting pH	Final pH
Variation		
0.01 *M* NaOH	12.0	11.6
0.1 *M* NaOH	12.9	12.4
1.0 *M* NaOH	14.0	13.4
1 *M*[NA^+] (as Na_2SO_4)		
0.1 *M* NaOH	12.9	12.4
SST Simulant Salts		
stirred	13.0	13.0
static	13.0	12.9
Gamma Pit		
irradiated	13.0	12.9
control	13.0	12.9

SST= Single-shell tank.

Very little dissociation of free cyanide occurred in the pH 14 experiment; the maximum [CN^-] is about 6 ppm (2.31×10^{-4} *M*) compared with about 2000 ppm (3.58×10^{-2} *M*) Fe. The increase in [CN^-] roughly parallels the [Fe] increase.

Experiments were performed in which the sodium ion concentration was maintained at 1.0 *M* by addition of Na_2SO_4 or $NaNO_3$ to determine if the sodium ion concentration influences the dissolution of ferrocyanide. Trends in solubility as pH is varied at 1.0 *M* [Na^+] are similar to those observed for solutions of different sodium ion concentrations. For experiments conducted at the same initial pH, the extent of dissolution tends to be lower at higher [Na^+]. Dissolution is greatly suppressed at pH 13 when 6 *M* Na^+ (as the nitrate salt) is present. This may be due to the influence of a common ion effect.

Experiments were also done to probe the influence of anions that would be present in the SSTs. Vendor-prepared material was dissolved in an aqueous solution of SST simulant salts (sodium salts of nitrate, nitrite, hydroxide, phosphate, carbonate, and sulfate) to give 1.0 *M* Na^+. The starting solution had an initial pH of 12.8 and was adjusted to pH 13. Results from these experiments showed that ferrocyanide dissolved faster in the pH 13 SST simulant salt solution than in either of the other pH 13 solutions. Whereas Na_2SO_4 and $NaNO_3$ suppressed dissolution, addition of SST salts enhanced dissolution. The enhanced rate of dissolution with SST simulant salts is thought to be due to buffering of the solution by phosphate. Data in Table III, which shows starting and final pH values, support the role of buffering.

Because the tank contents are not being actively mixed, an experiment investigating the dissolution of the vendor-prepared $Na_2NiFe(CN)_6$ in the presence of SST simulant salts was conducted under static conditions. The experiment was conducted in Teflon® labware at pH 13 with simulant salts added to give 1 *M* [Na^+]. To minimize disturbance, the solution was sampled less frequently (24-hour intervals) than the stirred solutions. Prior to each sampling, a 5-second stirring was required to ensure a homogeneous solution phase. As expected, the rate of dissolution is slower in the static solution. Nevertheless, appreciable dissolution occurs. About 40% is dissolved after 24 hours with no stirring and 90% dissolution is observed after 6 days.

In an initial screening experiment, it was found that gamma radiation does not appear to greatly affect the dissolution reaction. Similar rates were observed in unstirred irradiated and control solutions. A more complex mixture of iron cyanides in the insoluble fraction of the gamma radiation experiments is obtained, suggesting the possibility that an iron cyanide species re-precipitates from solution. Further work is needed to determine the identity of this species.

Solubilization experiments will be completed in fiscal year 1993. Dissolution of $Cs_2NiFe(CN)_6$ and the temperature dependence of the dissolution of flow sheet $Na_2NiFe(CN)_6$ in aqueous base will be investigated. More extensive gamma pit experiments are planned. Studies of ferrocyanide hydrolysis and the effects of high ionic strength and gamma radiation will also be conducted.

Degradation of Water-Insoluble Organics

Finally, drawing upon limited experimental data and a diverse array of literature, a case can be made that organic chemicals of the types utilized in waste management and chemical processing are, in general, not stable in the alkali radioactive environment of the tanks with respect to degradation products or other adducts. In most cases these reactions appear to take place slowly, but certain reactions appear to be quite rapid.

Radiolysis of water and nitrates generates reactive radicals that attack organic and inorganic species, making organic radicals, inorganic radicals, and higher valent metal ions (except for solvated electrons and hydrogen radical, which reduce many transition metals to lower valent states) (13-15). Some conditions reduce the role of e^- and hydrogen radical. Oxygen and gaseous nitrogen oxides scavenge e^- and hydrogen radical at near diffusion limits, so if tanks are air saturated or have dissolved gases of nitrogen oxide, then such reactions should be significant. Products so produced are of intermediate oxidation states and may be further oxidized or reduced depending on the constituents in the tanks. For example, species such as O_2^-, and HO_2^- reduce transition metals such as Fe(III) while oxidizing many classes of organic compounds.

Numerous competing reaction pathways are possible. Which pathway will dominate depends on the conditions in the tanks. These pathways are illustrated in Figure 1. Initiation of redox chain oxidations and radical-induced crosslinking by direct radiolysis of organic phases will receive serious evaluation as part of the program to resolve the organic waste safety issue at the Hanford Site (16).

The very low solubility of normal paraffin hydrocarbon (NPH) in high ionic strength aqueous solutions suggests that direct attack by aqueous-derived oxidizing radicals should not be favorable except for ionization events that occur at interfaces between aqueous and organic phases or organic and solid phases. In presence of oxygen, autoxidation chain reactions are possible in which hydroperoxides are initially produced and continue to react yielding alcohols, ketones, acids. Fragmentation of alkyl chains will occur via alkoxy radical intermediates. Organic-soluble transition metal complexes catalyze autoxidation. The generation of acetone from hexone is illustrated in Figure 2. Acetone is a ubiquitous material found in the condensate from waste volume reduction processes (by evaporation).

Certain transition metal ions [e.g., Cu(II), Fe(III), Cr(III), Cr(IV), Mn(III), Co(III), U(?), etc.] can oxidize radicals such that, even if oxygen concentrations are low, NPH could be oxidized via a redox chain reaction, instead of crosslinked. Oxygen, hydroperoxides, and peroxides are needed to recycle lower valent metals to upper valent states. Alternatively, if lower valent metals are transported to aqueous phase, then they would be oxidized by aqueous phase radiolysis intermediates (e.g., $O^{\cdot-}$, $NO_3\cdot$, H_2O_2). Transport back to the organic phase would propagate the redox chain reaction.

Work on waste simulants will be initiated later this fiscal year. Extensive efforts to speciate the waste degradation products found in the wastes are also under way.

Figure 1. Proposed Routes for the Degradation of Hydrocarbons. R and R' represent groups ranging from H to C_{35} n-alkyl.

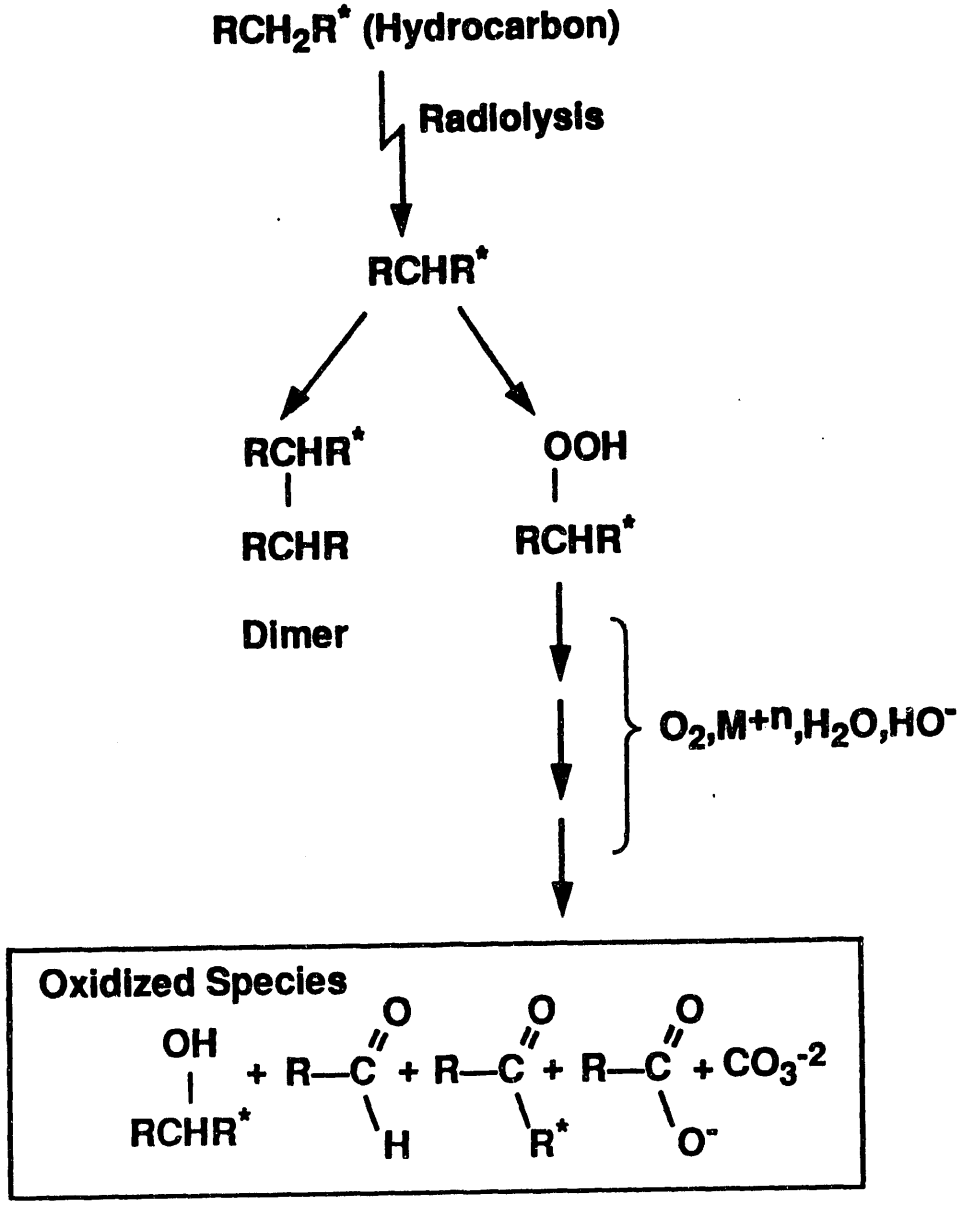

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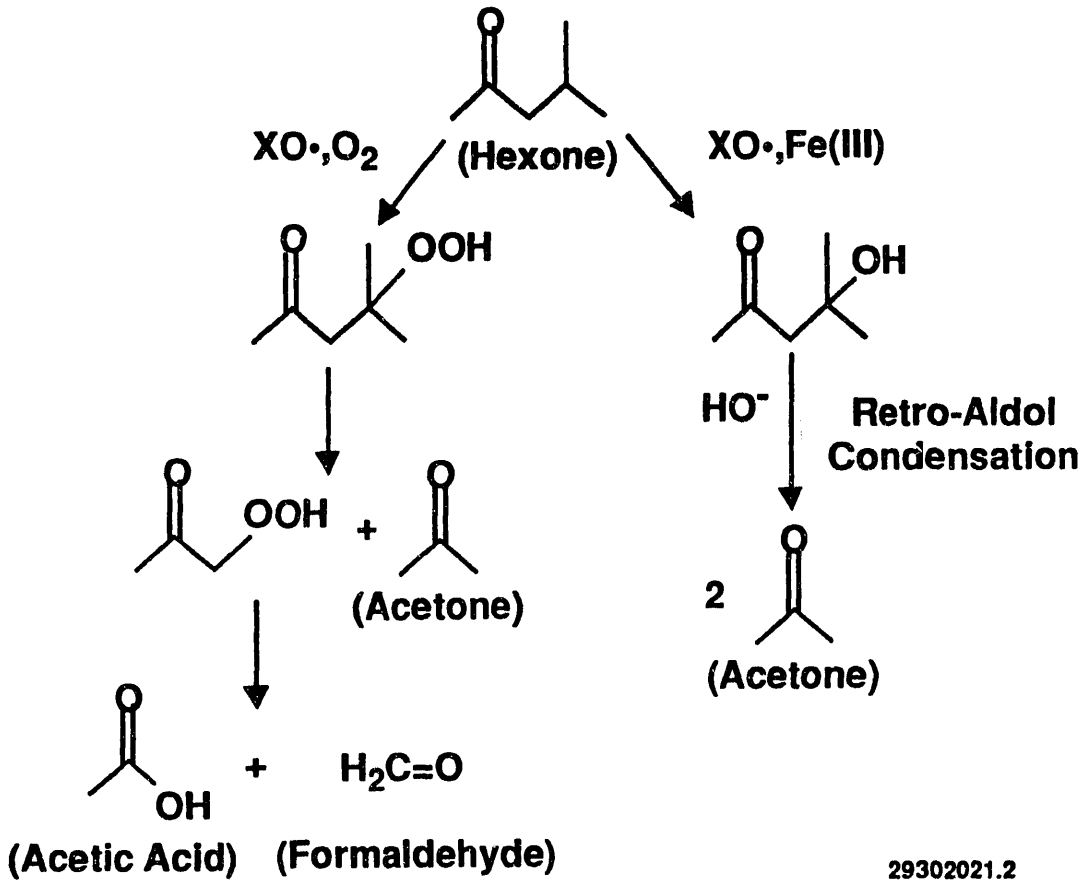
Figure 2. Proposed Routes for the Degradation of Hexone. XO• represents oxygen-centered radicals generated by radiolysis, i.e., O^{-}•, HO•, NO_3•, etc.



CONCLUSION

Evidence presented in this report suggests that the risk of an exothermic reaction of NO_3^- or NO_3^- with ferrocyanides or certain organics in Hanford Site high-activity waste tanks is lower then previously projected. Risk is decreased because of degradation (aging) in the tanks over the extended storage period.

Evidence to support these preliminary conclusions comes from tests with analogs of the materials in the tanks (i.e., simulated wastes) and in tests with actual tank waste. Such studies have demonstrated that the reactivity and energetics of potentially reactive species are lower then expected both in systems containing ferrocyanide salts and in those containing "complexant concentrates." The results of tests on actual wastes, either cores or "grab" samples, have demonstrated a generally lower reactivity for actual complexant or ferrocyanide wastes (17,18) than for freshly made simulants.

Finally, all tanks sampled to date contain a sufficiently large quantity of water that propagation reactions are highly unlikely, even if one assumes a 100% probability of initiation of an exothermic reaction. Although much work remains to be done, these results are encouraging.

Note: Teflon® is a trademark of E. I. du Pont de Nemours & Company.

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