

THE AGING OF ORGANIC CHEMICALS IN HANFORD HIGH-LEVEL WASTES

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ABSTRACT

Aging of chemicals in stored wastes at the Hanford Site in southeastern Washington State has a direct bearing on several safety issues, including gas generation and chemical-behavior hazards associated with fuel-nitrate combustion accidents. This paper summarizes research [i] directed at determining the fate of organic chemicals added to the tank wastes, in particular with respect to learning how the energy content changes [ii]. The results show that radiation and heat promote redox reactions between organic compounds (reducing agents) and nitrates/nitrites (precursors to oxidizing agents) in the wastes. We find that production of H_2 , N_2 , and N_2O by radiolysis is significant and that it occurs concurrently with the disappearance of organic species and appearance of oxidized fragments of the original species. The observations are consistent with progressive degradation to species with more C-O bonds and fewer C-H and C-C bonds, resulting in an overall lower energy content of the organic inventory. The results of studies using both simple and complex waste simulants show quantitatively that the energy content of the wastes should decrease due to aging. However, the lifetimes and aging rates of organic complexants strongly depend on radiolytic and thermal exposure, and therefore the degree of aging varies from tank to tank. Since much of the waste was concentrated by passing through high-temperature evaporators, little of the original chelators remain. This is seen in analyses of actual waste in which significant fractions of the total organic carbon is sodium oxalate. However, some organic waste did not go through high-temperature evaporators and still contains original organic complexants and their remnants. Most of this waste is too wet to sustain runaway reactions and not likely to dry out in the foreseeable future. Two high-heat tanks with the potential to dry out have significant total organic carbon content. However, the combined effects of heat and radiation are expected to degrade the energetic carbon before the waste evaporates to dryness.

INTRODUCTION

Uranium and plutonium production at the Hanford Site produced large quantities of radioactive byproducts and contaminated process chemicals (stored in underground tanks) that are awaiting treatment and disposal. Having been made strongly alkaline and then subjected to successive water-evaporation campaigns to increase storage capacity, the wastes now exist in the physical forms of saltcakes, metal oxide sludges, and aqueous brine solutions. In the 1990s, issues were raised over concern that tanks containing organic process chemicals mixed with nitrate/nitrite salt wastes might be at risk for fuel-nitrate combustion accidents. Resolution of the issues required a multifaceted approach because of the complexity of tank wastes and a lack of detailed information on waste composition[iii]. It included reviewing historical records, developing new methodologies, retrieving waste samples for laboratory analyses, testing waste simulants, and

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studying the underlying phenomena. Here we summarize efforts on one facet of the problem, understanding the chemistry of waste aging.

Organic-containing wastes have been stored in underground storage tanks at Hanford for nearly half a century, during which time they have been constantly exposed to radiation and heated to temperatures of up to 140°C (284°F). The wastes contain hydroxide, nitrate, nitrite, aluminate, oxides of transition metals, including noble metals, radioactive elements (e.g., uranium, plutonium, cesium, strontium), and many other substances, such as organic complexants, solvents, and extractants. Many of the single-shell tanks had been sampled and the total organic carbon (TOC) contents measured. However, knowledge of the TOC in a particular storage tank was insufficient to bound the safety risk.

The organic compounds that were added to the tanks are divided into two main classes: complexants and solvents. The major organic complexants believed to have been added to the tanks are glycolate, citrate, hydroxyethylethylenediaminetriacetate (HEDTA), and ethylenediaminetetraacetate (EDTA). Allen [iv] estimated the approximate quantities that were used at Hanford:

- glycolic acid, 8.8×10^5 kg
- citric acid, 8.5×10^5 kg
- hydroxyethylethylenediaminetriacetic acid, 8.3×10^5 kg
- ethylenediaminetetraacetic acid, 2.2×10^5 kg.

Process extractants and solvents of concern that were used in chemical processes and stored in the tanks are tributyl phosphate (TBP), normal paraffin hydrocarbons (NPHs), and methyl isobutyl ketone (hexone). Other processes also used organic solvents and organic phosphate extractants. Di(2-ethylhexyl)phosphoric acid diluted with hydrocarbon solvent was used in the waste fractionation and encapsulation process. The reflux solvent-extraction process used TBP/carbon tetrachloride [v] and dibutyl butyl phosphonate/carbon tetrachloride for extraction solvents [vi]. Considerable quantities of hexone were used in the Reduction-Oxidation Process, the initial solvent-based reprocessing flow sheet at Hanford.

Energetics and reactivity tests performed by Fauske & Associates, Inc. [vii,viii] showed that complexants and organic salts pose the greatest risk of propagating reactions. Despite the high potential energy content of test compounds (dodecane, mineral oil, tributyl phosphate, and sodium di-2-ethylhexyl phosphate, calcium dibutyl phosphate [DBP], and sodium stearate), the compounds did not ignite when heated with $\text{NaNO}_3/\text{NaNO}_2$ mixtures. Instead, the solvent components vaporize away from the ignition source and TBP and DBP decompose, liberating hydrocarbon gases, before ignition temperatures are attained. On the other hand, the complexants and low-molecular-weight carboxylic acid salts (e.g., acetate, butyrate, and succinate) have sufficiently high thermal stability to keep them in contact with an ignition source until melt temperatures (~ 200 to 250°C) are attained, and propagating reactions ensue. Therefore, the focus of concern was on aging of the organic complexants.

Mechanisms of Organic Aging

Complex mechanisms are involved in the degradation of organic chemicals in tank wastes. This section summarizes some pertinent literature on radiolytically and thermally induced reactions. For a primer on the wide range of chemistry organic reactions that may occur, the report by Stock and Pederson [ix] is recommended. Passage of ionizing radiation through the wastes generates highly reactive radicals that either oxidize the organic species directly or induce production of other radicals that subsequently oxidize the organic species. Little temperature dependence is observed because the oxidizing radicals react with relatively low energies of activation. Reaction rates are controlled by the rate of generation of radicals, which is controlled by the radiation dose rate and the selectivity of the radicals for various organic functionalities. Products depend on how the radicals attack the organic species and on how the resulting organic radicals convert to products, e.g., combination with NO, NO₂, O₂, or oxidation by NO₂⁻.

Oxidizing and Reducing Radicals Generated by Radiolysis of Wastes

Pathways for radiolytic aging are expected to involve the generation of O⁻ and NO_x radicals that, in turn, attack and oxidize the organic complexants [x]. Although primary intermediates of water radiolysis are e⁻, H, and OH, Equations 1–4 show that these species will convert to NO_x radicals in wastes that are high in nitrate and nitrite ions.

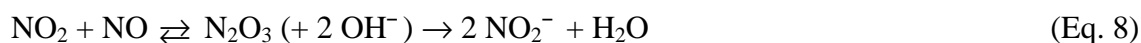
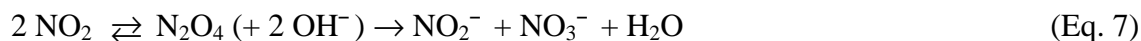


Essentially all of the electrons are scavenged by nitrate to make the reducing radical, NO₃²⁻. It is short-lived, dissociating to NO₂ in less than 15 μsec [xd]. The pK_a for HO is 11.8. In highly alkaline solutions, HO may convert to O⁻, which also reacts with nitrite to produce NO₂, but at a rate that is significantly below the diffusion limit.



Reactions of O⁻ with many organic species have rate constants that are equal to or greater than the rate constant for reaction with nitrite ion [xi,xii]. Thus, the radiation-induced degradation of organic complexants is expected to be dominated by reactions of O⁻ and NO₂ with organic species.

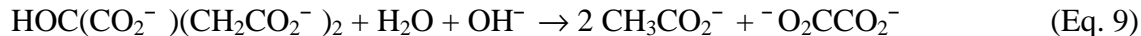
Quenching reactions exist for NO₂ and NO, namely recombination and hydrolysis to nitrate and nitrite ion, as shown in Equations 7 and 8. Overall rate constants for Equations 7 and 8 are about 10⁸ M⁻¹s⁻¹ [xiii,xiv].



The oxidation potential of NO ($E^\circ \sim -0.35 \text{ V}$) [xv] is not great enough for it to oxidize organic species. NO_2 is a much better oxidizing agent ($E=1.0 \text{ v}$) [xv]. However, since reactions 7 and 8 are bimolecular in NO_x radicals, rates of NO_2 attack on organic substrates need not be large. As we show later, rate constants on the order of $1 \text{ M}^{-1} \text{ s}^{-1}$ will be sufficient. Given the moderate-to-low dose rates common to single-shell tank wastes [xvi], steady-state concentrations of NO_2 are much lower, so oxidation of organic species should be more efficient.

Thermal Aging of Organic Complexants

Workers at the Georgia Institute of Technology [xvii,xviii] studied the thermal reactions of the major complexants in aqueous solutions. The studies show that citrate degrades to acetate and oxalate in the presence of hydroxide alone. glycolate and HEDTA degradations require nitrite and are catalyzed by aluminum and hydroxide ions, and EDTA is essentially inert. The reaction of citrate produced little gas and was not catalyzed by aluminate. Therefore, the reaction can be formulated “classically” as a “reverse Claisen” reaction. The overall reaction (Equation 9) shows that 2 C-C bonds are converted to 2 C-H bonds and a C=O bond. Consequently, the enthalpies of the organic species change little.



The thermal oxidation of glycolate and HEDTA is a complex reaction for which the fundamental mechanism is unknown. The oxidation kinetics is complex. Inhibition by O_2 and autocatalysis has been observed. Ashby et al. proposed the mechanism by which aluminum catalyzed the nitrosation of alcohol functional groups. However, Camaioni and Autrey [xix] have ruled out this mechanism, showing that aluminate ion does not catalyze nitrosation of primary alcohols such as ethanol and glycolate.

RESULTS

Accelerated waste aging studies were performed to explain waste-characterization data and determine the effect of organic aging on combustion hazards of high-level wastes (HLWs). These studies simulated waste aging by γ -irradiating non-radioactive waste simulants. The studies included work with simple homogeneous simulants containing 1 or 2 organic components in concentrated alkaline solutions of nitrate and nitrite as well as complex simulants that contained the majority of organic chelators and a mix of inorganic components that predominate in the wastes. Results from the former are described first.

Radiolytic Aging of Organic Species

Table I shows the relative rate constants for disappearance of the major complexants and remnant molecules in simulant solutions during radiolysis. These were obtained by γ -irradiating

a series of solutions that contained complexant and formate-¹³C. After irradiation, the solutions were analyzed by nuclear magnetic resonance (NMR) to obtain the change in concentration of complexant relative to the yield of carbonate-¹³C.

Table I. Relative Rates of Disappearance of Organic Chemicals in Waste Simulants^(a) by γ Radiolysis

<i>Substrate</i> ^(a)	<i>k_{rel}</i>	<i>Substrate</i>	<i>k_{rel}</i>
u-EDDA	13	Glycine	7
s-EDDA	13	Glycolate	5
IDA	12	EDTA	6
NTA	10	Formate	1 ^(c)
HEDTA	14	Citrate	0.7
		Acetate	0.7

(a) In 3.75 M NaNO₃, 1.25 M NaNO₂, 2 M NaOH and at 20°C. (b) u-EDDA = unsymmetrical ethylenediaminediacetic acid, s-EDDA = symmetrical ethylenediaminediacetic acid, iminodiacetic acid (IDA), nitrilotriacetic acid (NTA). (c) Defined value.

The results show that glycolate and nitrogen-containing complexants are more reactive than formate by factors of 5 to 20. Compounds such as citrate and acetate are slightly less reactive than formate. Preliminary work on DBP, butyrate, and succinate suggest these compounds have reactivities similar to acetate and citrate. The reactivities of ethylenediaminetriacetate (ED3A) and ethylenediaminemonoacetate (EDMA) have not been measured, but by analogy to related compounds, similarly high reactivity is expected.

Table II shows results of a study of the radiolytic yield of carbonate from formate in the simulants. The yield increases with the concentration of formate, reaching a maximum value of ~2 molecules/100 eV. Meisel et al. [xa] described a chemical kinetic model for radiolysis of alkaline solutions of nitrate and nitrite. This model was adapted by adding reactions necessary to describe the oxidation of formate [i]. Results for the model are compared with experimental observations in Table II.

Table II also lists estimates of the fraction of carbonate resulting from attack by OH, H, O⁻, and NO₂. The model shows that O⁻ is the dominant oxidant of formate in the high radiation fields used in the experiments. However, the dose rates in tank waste are much smaller; in range between 10² to 10⁴ Rad/h [xvi]. The last line in

Table II shows that reducing the dose rate increases the yield of carbonate and the fraction of oxidation by NO₂. This behavior is expected since NO₂ oxidation of formate competes with second-order radical recombination reactions.

Table II. Yields and Fractions of Carbonate Ion Produced from H, OH, O⁻, and NO₂ During γ -Radiolysis of HLW Simulants^a Containing Formate Ion

Concentration <i>M</i>		Dose Rate	$G(\text{CO}_3^{2-})$		% Distribution of CO_3^{2-}			
<i>OH⁻</i>	<i>HCO₂⁻</i>	<i>Rad/h</i>	<i>Model</i>	<i>Expt</i>	<i>OH</i>	<i>O⁻</i>	<i>NO₂</i>	<i>H</i>
2	0.1	1×10 ⁶	1.0	0.8	4	92	3	1
2	1.0	1×10 ⁶	2.1	2.0	15	71	9	4
0.1	0.1	1×10 ⁶	0.3		32	51	14	4
2	0.1	1×10 ⁴	1.4		3	74	22	1
2	0.1	1×10 ³	1.8		2	56	42	1

(a) Simulant: 1.25 M NaNO₂, 3.75 M NaNO₃, 2 M NaOH; experimental dose rate was 0.5×10^6 Mrad/h.

Products of Degradation

When possible, products from competition experiments were identified from the chemical shifts of NMR peaks that appeared after γ irradiation (Table III). Irradiated, oxidized samples were spiked with authentic materials to corroborate assignments (see Table III) based on chemical shift information. The chemical shifts of compounds of interest depended on ionic strength such that they had to be specifically determined for the highly caustic and high-ionic-strength solutions used in these studies.

Formate was almost always a significant product. More than two moles of formate are produced per mole of EDTA consumed, ~1 mole formate is formed per mole of glycolate consumed, and for citrate, acetate, and HEDTA, ~0.5 mole formate is formed per mole of species consumed. Oxalate is also produced and presumably carbonate.

The pathway for NTA degradation is better understood. Readily identifiable products are IDA, glycine, and formate. In one experiment, 45% of the starting NTA remained, 17% was IDA, and 29% was glycine. These products accounted for 91% of the nitrogen originally present in NTA. We presume the missing N is due to inorganic N, including NH₃. This progression of products is consistent with the reactivities measured for NTA, IDA, and glycine by competition with formate-¹³C (see Table I). The yield of formate-¹²C was 83%, which suggests that cleavage of R₂NCH₂CO₂⁻ by oxidative decarboxylation is a significant pathway for NTA and IDA.

The major products of EDTA radiolysis besides formate are ED3A, s-EDDA, and NTA. Peaks in the “after radiolysis” proton NMR spectrum consistent with products such as IDA, glycine, u-EDDA, and glycolate were identified. Resonances for hydroxyethyl groups such as HEDTA were not observed in the NMR spectra.

Table III. Products Identified by NMR from Radiolytic Oxidation of Complexants in Nitrate/Nitrite/Hydroxide Solutions^(a)

<i>Substrate</i>	<i>Rel. Amt.</i>	<i>Positively Identified^(b)</i>	<i>Possibly Present</i>	<i>Not Present^(d)</i>
EDTA	major	ED3A, s-EDDA, IDA, Formate		HEDTA
	minor	Acetate, Glycolate, Glycine	u-EDDA, NTA ^(c)	
HEDTA	major	s-EDDA, IDA, Formate	NTA ^(c)	EDTA, ED3A
	minor	Glycine	u-EDDA	
u-EDDA	major	IDA, Formate	^(c)	NTA
	minor	Glycine		
s-EDDA	major	IDA, Formate	EDMA	
	minor	Glycine	^(c)	
NTA	major	IDA, Formate		
	minor	Glycine		
IDA	major	Glycine, Formate		

(a) In all cases, carbonate (and oxalate) is assumed to be a product based on the results with ¹³C labeled glycine. In addition, almost all substrates yielded trace amounts of glycolate and acetate upon prolonged radiolysis. (b) Assigned based on proton and ¹³C NMR experiments. (c) Proton NMR resonances of unidentified products are present. (d) NMR resonances of these compounds were not detected.

The EDDA product mixtures contained IDA and formate as the major products. A major product tentatively identified as EDMA was found in the s-EDDA but not u-EDDA mixture. Glycine was a minor product, and only trace quantities of acetate and glycolate were formed. No products other than formate could be identified from the ¹H NMR spectra of irradiated solutions of citrate, succinate, butyrate, butanol, and DBP.

Radiolytic Aging of Waste Simulants

Aging tests were performed using a simulant that was developed for Fauske Associates, Incorporated (FAI) energetics and reactivity tests [xx]. The simulant, designated SIM-PAS-95-1c for FY 1996 studies and SIM-PAS-95-1d for FY 1997 studies, is a modified version of the SIM-PAS-94 simulant, which Scheele [xxi] developed from B-plant chemical inventories and process flow sheets.

The simulant (Table IV) is a heterogeneous mix of metal oxide/hydroxide precipitates and aqueous solutions containing a variety of inorganic anions, but mainly nitrate, nitrite, and hydroxide, and the organic complexants, HEDTA, EDTA, citrate, and glycolate. The density is ~1.27 g/mL, and the carbon content is 21 g/L or 4.5 wt% (dry basis). The SIM-PAS-95-1d simulant has the same components as SIM-PAS-95-1c, although the concentration of EDTA was lower, and the concentration of glycolate was higher.

Table IV. Composition of Simulant

<i>Species</i>	<i>mg/g</i>	<i>Species</i>	<i>mg/g</i>	<i>Species</i>	<i>mg/g</i>
HEDTA ³⁻	17	Al ³⁺	1.5	Ca ²⁺	0.08
EDTA ⁴⁻	3.1	F	1.3	Mn ²⁺	0.07
Citrate ³⁻	17	Pb ²⁺	1.1	Cr ³⁺	0.04
Glycolate	11	PO ₄ ³⁻	0.5	Cl ⁻	0.004
NO ₃ ⁻	109	SO ₄ ²⁻	0.5	Pd ²⁺	0.003
Na ⁺	107	Bi ²⁺	0.4	Rh ³⁺	0.003
OH ⁻	39	Ce ³⁺	0.4	Ru ⁴⁺	0.003
NO ₂ ⁻	38	Ni ²⁺	0.1	H ₂ O	640
Fe ³⁺	2.6				

Aging tests were performed over a variety of radiation doses, temperatures, and cover gas compositions of either pure Ar or 20/80 O₂/Ar. The simulant was also heated at 90°C for up to eight months under cover gases that started out as either pure Ar or 20/80 O₂/Ar. To foster reproducible results, the simulant was prepared before each irradiation by measuring exact quantities of 3 homogeneous stock solutions into the reactor vessel. The same vessel was used for each irradiation, and it was placed in the same location relative to the radiation source. The radiation flux was 3×10⁵ rad/h. After irradiation, the contents of the vessel were quantitatively transferred, and analyzed for organic compounds, carbonate, nitrate, and nitrite. In addition, another sample of the simulant was mixed and then analyzed without having been irradiated. We present analytical results showing how organic aging is affected by temperature, time, radiolytic dose, and O₂ in the cover gas. Gases analyzed in the headspace above the aged mixtures include Ar, O₂, N₂, N₂O, H₂, CO, CO₂, and CH₄.

Effect of Radiation Dose on Aging

Figure 1 shows the disappearance of starting organic species and appearance of oxalate, formate, and carbonate as a function of radiation dose and time at 70°C. The results show that all the complexants and their remnants are susceptible to radiolytic degradation. The kinetic lifetimes obtained from fitting species concentrations to exponential decay functions ($C=C_0e^{-t/\tau}$) suggest that the reactivities of the complexants decrease in the order: HEDTA>EDTA>glycolate >citrate. Similar results were obtained for runs at 40 and 90°C. The results also show that highly oxidized products grow in without delay. Nitrate decreases with increasing dose, while nitrite and ammonia increase. And, gaseous products, H₂, N₂O, and N₂ accumulate in the headspace above the aged simulant. These reaction products are all consistent with radiolysis-induced redox chemistry in which organic species are reductants and radiolytically generated species (O⁻ and NO₂) are oxidants.

The amounts of missing carbon goes through maximum values of ~25 and ~15% at ~100 Mrad at 70 and 90°C, respectively. The lower amounts of missing carbon in 90°C experiments are probably due to the more rapid consumption of intermediate compounds and the fact that less EDTA was used in the simulant. Carbonate production at 90°C is nearly twice as fast as at 70°C (see Figure 1). The disappearance of carbon in starting species appears biexponential at 70° and

exponential at 90°C. This behavior may be due to the higher fraction of glycolate in the 90°C, PAS-95-1d simulant.

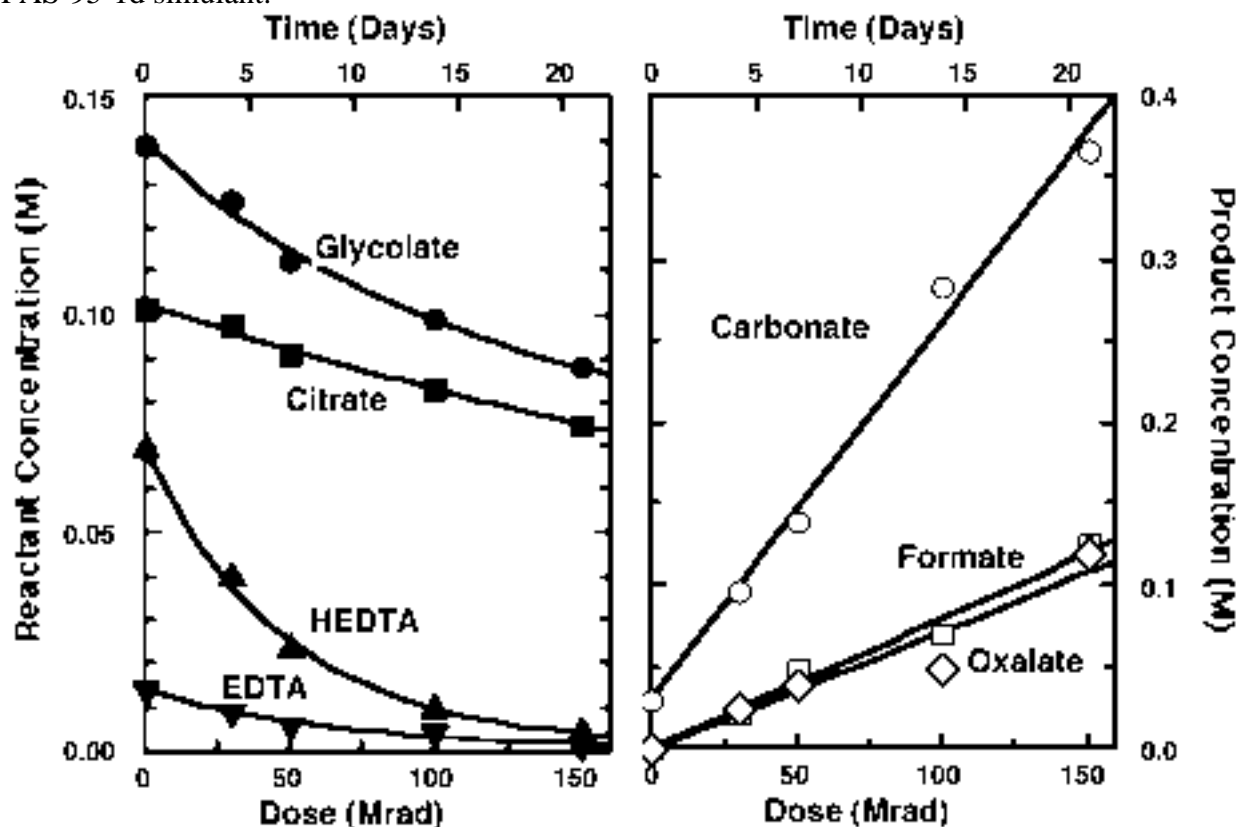


Figure 1. Disappearance of Complexants and Appearance of Products in a Radiation Field of $\sim 3 \times 10^5$ rad hr⁻¹ at 70°C; headspace gas is initially 20/80 O₂/Ar.

Effect of Temperature on Radiolytic Aging

Aging tests were run at 40, 70, and 90°C to evaluate the effect of temperature on radiolytic aging. Table V lists results for samples that received γ doses of 40 to 50 Mrad. The effects on disappearance of the chelators seem small and may be masked by experimental scatter. Amounts of glycolate, citrate, HEDTA, and EDTA found at 40 and 70°C are similar. At 90°C, less glycolate is present compared to 70°C, but the amounts of HEDTA and citrate present at 90°C are greater than at 70°C. The formate, oxalate, and carbonate products show a trend of increasing yield with increasing temperature. The results imply that rates of disappearance of chelators are controlled by the intensity of the radiation field (i.e., dose rate), whereas formation of products depends on thermally activated “ionic” processes (e.g., hydrolyses) that convert intermediates to end products. Consistent with this view, the fraction of unidentified carbon (subtract total carbon values in lines 2, 3, or 4 from line 1, Table V) decreases with increasing temperature. Gas analyses show an increase in the yield of H₂ on going from 70 to 90°C.

Table V. Effects of Temperature on Radiolytic Aging of SIM-PAS-95-1d Simulant

<i>T, Dose</i> °C, Mrad	<i>Reactants/Products, mg C/g</i>								
	<i>For- mate</i>	<i>Oxa- late</i>	<i>Gly- colate</i>	<i>Citrate</i>	<i>HEDTA</i>	<i>EDTA</i>	<i>CO₃²⁻</i>	<i>Org C</i>	<i>Total</i>
20°, 0	0.00	0.00	3.7	5.6	6.5	0.80	0.16	16.5	16.7
40°, 43	0.14	0.34	3.3	4.7	1.9	0.36	1.1	10.8	12.0
70°, 47	0.21	0.41	3.3	5.0	1.8	0.38	1.4	11.1	12.5
90°, 50	0.52	1.0	2.7	5.7	2.6	0.37	1.7	12.9	14.7

The yield of H₂ increases from G~0.03 at 40°C to G~0.1 at 90°C. A similar trend for H₂ production was noted in radiolytic aging of simulant SY1-SIM-94C [xxii]. This trend may indicate that reaction paths to H₂-producing aldehyde intermediates are favored by higher temperatures. Formaldehyde and glyoxal degrade in alkaline solutions with irradiation producing [xxiii,xxiv]. Finally, we mention that yields of H₂ are relatively unaffected by either the presence or absence of O₂ in the headspace gas or Fe in the simulant.

Thermal Aging of the Simulant

Figure 2 shows how the organic composition of the simulant changed with time at 90°C in the absence of γ radiation. Note that the time scale for thermal aging (Figure 2) is significantly longer than that for radiolytic aging (Figure 1): 120 days in the former; 20 days in the latter. Even after heating for three months at 90°C, negligible EDTA has reacted. Thus, the degradation of organic species observed is mainly caused by radiolysis.

Figure 2 also shows the effect of having O₂ in the headspace above the simulant. When O₂ is initially present glycolate decreases, rapidly consuming about 20% of the initial amount. Then the decrease is gradual. The O₂ in the cover gas was maximally 0.2 mmol. There was 2.5 mmol of glycolate in condensed phase. Cover gas analyses showed that 71% of the O₂ was consumed after 1236 hours at 90°C. This probably is why consumption of glycolate (0.19 M at t=0) slowed down after 20% was consumed. In the absence of O₂, glycolate degradation appears to be autocatalytic or initially inhibited. Effects of O₂ on citrate and HEDTA disappearance rates are negligible. The effect on carbonate production is more pronounced: carbonate forms nearly *twice* as fast in the presence of O₂. EDTA reactivity does not appear to be different, although heated samples in either case were routinely found to contain ~30% higher concentrations of EDTA than were measured in unaged samples of the simulant. Reasons for this anomalous behavior are unknown. One possibility is that degradation products of HEDTA interfered with EDTA analyses.

Headspace gas analyses were obtained from samples that had been heated for 1330 and 2330 hours respectively. The analyses show that N₂O and H₂ were generated at comparable rates when O₂ was initially present, but N₂O was generated faster than H₂ when O₂ was initially absent. Similar observations about the effects of O₂ on gas production have been reported for simulants [xviii] and real wastes [xxv]. However, our observations of the effects on organic aging contrasts with recent observations for HEDTA in a much simpler simulant (sodium nitrite, aluminum hydroxide, sodium hydroxide) in which consumption of HEDTA was inhibited by O₂ [xviii].

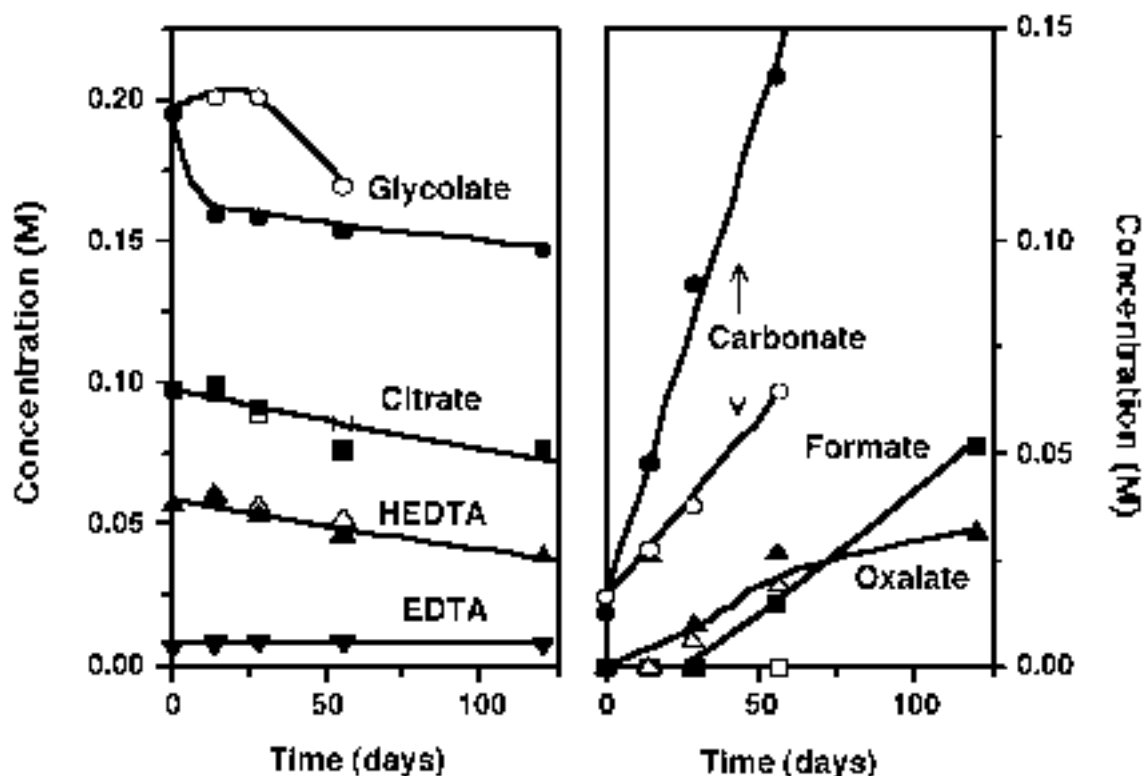
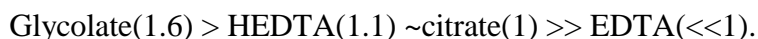
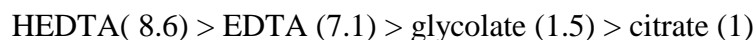


Figure 2. Disappearance of Starting Organic Compounds and Appearance of Products Versus Time at 90 °C in the Absence of γ Radiation; key: (filled symbols) headspace gas initially 20/80 O₂/Ar, (open symbols) headspace gas initially 100% Ar

The relative reactivities of organic species towards thermal degradation are significantly different than those observed for radiolytic aging. Thermal rate constants for disappearance show the following trend (relative reactivities in parentheses):



Whereas radiolytic reactivities (see Table I) decrease in the order:



Thermal reactivities of citrate and EDTA are the inverse of their radiolytic reactivities. Under actual tank waste storage conditions, radiolytic dose rates are ~1000 times smaller than those used to obtain the results shown in Figure 1. Therefore, the time to achieve similar doses in tank wastes will be about 1000 times longer; i.e., several decades. Tank waste storage times are about 100 times (17 years = 6200 days) longer than times shown in Figure 2. Thus, thermally activated processes may contribute to organic aging of tank wastes and cause complexants to age more uniformly than might be indicated by Figure 1. The results suggest that lifetimes and aging rates of organic complexants will strongly depend on the radiolytic and thermal history of individual tank wastes.

DISCUSSION

We focus our discussion on applying the above results and literature information to understand aging of tank wastes. We start by reviewing analytical data of actual wastes. Then we discuss the key factors that control rates of aging and we go on to estimate the contributions that radiolytic and thermal aging have made and are likely to make in the future toward reducing the organic carbon and energy content of organic tank wastes.

Organic Species Found in Tank Wastes

The preceding sections show that oxalate ion is a product of organic aging. Oxalate ion and TOC concentrations have been measured on samples from 52 single-shell waste storage tanks (SST). The data have been compiled in the *Organic Complexant Topical Report* [iii]. The results for 7 tanks are inconclusive; the TOC concentrations are below 0.1% in 13 tanks; the results for the other 32 are shown in Table VI. Seven SSTs had oxalate concentrations sufficient to account for more than 75% of the TOC (Tanks BY-109, BY-102, BY-105, BY-107, BY-110, BY-111, BY-112, and C-106); 18 tank wastes had oxalate concentrations sufficient to account for 25 to 75% of the measured TOC (Tanks A-101, AX-101, AX-103, BX-110, BY-101, BY-104, BY-108, BY-110, S-101, S-102, S-106, S-107, SX-101, SX-106, S-111, U-107, and U-108). Seven tanks had less than 25% of the TOC identified as oxalate (Tanks A-102, AX-102, C-104, C-105, U-102, U-105, and U-106).

Samples from a number of waste tanks have now been speciated for organic compounds. In general, the analyses clearly show the wastes have aged to the same compounds found in aging studies performed here and at Georgia Tech [xvii]. Some tanks have significant TOC that is not oxalate, e.g., AX-102, U-105 and U-106. Analyses of samples from these tanks show that the organic inventory is consistent with partial aging of these wastes. Table VII lists organic results for several tanks [iii]. The inventory of organic species includes the original complexants, a variety of intermediate degradation products, formate and oxalate.

The quantitative analyses shown in Table VI and **Table VIII** are consistent with laboratory aging studies showing degradation of complexants to chelator fragments and carboxylate salts such as oxalate and formate. Oxalate ion appears to persist in the wastes, attaining higher concentrations than formate and many other aging intermediates. Oxalate ion probably has low reactivity compared with the chelators and other fragments. Also, the solubility of oxalate ion in tank waste supernates is very low [xxvi]. Since oxidation of the organic species mainly occurs in the aqueous solution phase, these conditions favor the accumulation of oxalate ion in the solid components of the wastes.

Table VI. Fractions of TOC that are Oxalate in Tank Wastes [iii]

<i>Tank</i>	<i>TOC wt%, wet</i>	<i>%TOC as Oxalate</i>	<i>Tank</i>	<i>TOC wt%, wet</i>	<i>%TOC as Oxalate</i>
A-101	0.31	44	BY-112	0.71	96
A-102	1.11	22	C-104	1.00	11
AX-101	0.62	38	C-106	1.34	>99
AX-102	1.87	12	S-101	0.22	52
AX-103	0.52	43	S-102	0.33	57
BX-110	0.15	62	S-106	0.23	58
BY-101	0.48	74	S-107	0.20	67
BY-102	0.33	>99	S-111	0.17	71
BY-104	0.67	52	SX-101	0.53	56
BY-105	0.73	95	SX-106	0.39	36
BY-106	0.51	75	U-102	0.74	18
BY-107	0.52	79	U-103	0.64	9
BY-108	0.39	46	U-105	1.23	22
BY-109	0.33	85	U-106	2.16	12
BY-110	0.64	43	U-107	0.18	38
BY-111	0.55	86	U-108	0.42	27

TOC concentrations are mean values calculated from the best basis inventory and % carbon as oxalate ion evaluated from inventory or sampling data.

Radiolytic Contribution to Organic Aging in Tank Wastes

Rates of radiolytic aging are primarily governed by the dose rate. It determines the rate of production of oxidizing radicals. Complex computer models are needed to describe the details. However, the overall effects on energy content can be understood and quantified with simple models.

Predicting Radiolytic Aging in Wastes

From data in Figure 1, we found that the energy content and TOC of the PAS-95-1 simulant declined linearly with accumulated dose. The rates of change in energy are 1.0 J/g/Mrad at 40 and 70°C, and 1.3 J/g/Mrad at 90 °C, and in terms of TOC, 2.3×10^{-3} , 2.0×10^{-3} , and 3.2×10^{-3} wt% C/Mrad at 40, 70, and 90°C, respectively. The rates provide a means for estimating the change in energy/organic content of waste due to absorbed radiation dose. From fundamental principles, one can estimate comparable rates of aging.

Typical values for oxidation reactions of complexants are summarized in Table VII. In general, we find that the aging coefficients for reactions cluster between 0.3 and 1.6 J/g/Mrad with values of ~1 predominating.

Table VII. Changes in Nitrate Reaction Enthalpies Due to Aging Reactions

<i>Reaction Type</i>	<i>??H_r</i> <i>kJ/mol</i>	<i>Aging Coefficient.</i> <i>(J/g/Mrad)</i>	
		<i>G=2</i>	<i>G=3</i>
$R_2NCH_2-CH_2NR_2 \rightarrow 2 HCO_2^- + R_2NH$	-540±60	1.1	1.6
$R_2NCH_2-CH_2NR_2 \rightarrow R_2NCH_2CO_2^- + R_2NH$	-410±30	0.8	1.2
$R_2NCH_2CO_2^- \rightarrow R_2NH + HCO_2^- + CO_3^{2-}$	-330±20 ^(a)	0.7	1.0
$R_2NCH_2CO_2^- \rightarrow R_2NH + C_2O_4^{2-}$	-350±20 ^(a)	0.7	1.1
$HOCH_2CO_2^- \rightarrow C_2O_4^{2-}$ or $HCO_2^- + CO_3^{2-}$	-330	0.7	1.0
HCO_2^- or $C_2O_4^{2-} \rightarrow 1$ or $2 CO_3^{2-}$	-170±10	0.3	0.5

(a) Value for sodium salt of glycine is ~50% greater than average

Contributions to radiolytic aging up to the present and into the future can be estimated with knowledge of the waste dose rates. Stauffer [xvi] reports current γ dose rates, historical γ doses, and past and current temperatures for SST wastes. For many tanks, contributions from ^{90}Sr , a β emitter, are negligible. However, in tanks with high Sr sludge loading, contributions to the dose rate from ^{90}Sr are significant. Stauffer's data [xvi] is conservative for these tanks. For example, the total dose rate in tank AX-102 (TOC ~5.7 wt% C, wet), is ~2300 rad/h, 7-fold greater than the γ dose rate [xvi]. Best-basis inventories of ^{90}Sr and ^{137}Cs are listed in the Tank Waste Inventory Network System (TWINS) [xxvii]. This data can be used to obtain finer estimates of aging rates in tanks that contain high Sr sludge loadings.

Table VIII. Analyses of Organic Species (wt%) in Tank Waste Samples [iii]

<i>Tank Sample</i>	<i>Acetate</i>	<i>Citrate</i>	<i>Glycolate</i>	<i>Formate</i>	<i>Oxalate</i>	<i>EDTA</i> ⁴⁻	<i>HEDTA</i> ³⁻	<i>IDA</i> ²⁻	<i>NTA</i> ³⁻	<i>TOC</i>
A-101 C154 S10 UH	0.2			0.3	3.8	0.02				1.2
A-102 96-AUG-3	0.2	0.1		0.2	1.4					1.0
AW-101 C139 S21 UH	0.09	0.02	0.05	0.1	1.0				0.006	1.5
AX-102 95-AUG-007		0.5	0.8	0.5	1.8	0.3	0.1	1.2		3.5
B-106 C93 S1 UH	0.003			0.01						0.2
BY-102 C157 S4	0.01			0.004	6.8					1.9
BY-104 C116 SLG		3.0			5.4					1.8
BY-105 C108 S1 DL	0.1	0.2		0.09						0.2
BY-107 C161 S1	0.14			0.06	2.6					0.9
BY-110 C101 S7	0.09			0.04	9.5					2.1
BY-110 C103 S4 UH	0.04				3.7					0.8
BY-110 C113 S8	0.07			0.01	0.04					0.2
C-104 C162 S2 UH	0.3			0.2	0.2					0.9
C-105 C76 S1 DL	0.2	0.4		0.05	0.05				0.10	0.4
C-201 TNK COMP	0.1			0.02	3.7				0.11	
U-105 C136 S7UH	0.07	0.4	0.4	0.7	0.8	0.4	0.5			2.2
U-106 C148 S2UH	0.04	0.6	0.4	0.3	0.5	0.6	0.7			2.4
U-107 C134 SLG	0.04	0.09		0.1	0.2					0.2
U-108 C141 S4 UH	0.06		0.2	0.2	0.5	0.1	0.03			0.6

Thermally-Activated Organic Aging

Non-radiolytic (thermal) decomposition reactions contribute to aging. When tank temperatures are high, thermally-activated processes can rapidly age the organic constituents. The results for thermal aging of the PAS-95 simulant shows that TOC and energy content decreases with increasing time of exposure at 90°C. Analytical results show that HEDTA, glycolate, and citrate were degraded and that carbonate grew in approximately linearly with time. The initial rates of carbonate production were 0.6 wet wt% C/y in the presence of O₂ and 0.3 wet wt% C/y in the absence of O₂. Extrapolated over several years, this rate of production could yield significant reductions in TOC.

Tank wastes at higher temperatures show more aging than wastes at lower temperatures. For example, of Tanks A101, AX-102, U-105, and U-106, only A-101 has a significant fraction (44%) of its TOC as oxalate. The dose rate for U-105, U-106, and A-101 are relatively low. Stauffer [xvi] estimates the g dose rate for A-101 is 301 rad/h. The amount of ⁹⁰Sr in A-101 is ~8 times smaller than the amount of ¹³⁷Cs so that the b dose rate is inconsequential. Stauffer [xvi] lists the historical temperatures of A-101, AX-102, U-105, and U-106 as 79, 46, 35, and 36°C, respectively; current temperatures are 66, 27, 34, and 35°C [xvi]. Review of temperature measurements for U-106 shows that in or about 1976, U-106 was filled with waste that was only ~50°C; it then cooled rapidly to ~30°C. Under such conditions little thermal aging would have occurred. The fraction of TOC that is oxalate in U-106 is only 12% (see Table VI). What aging that has occurred may be attributed primarily to radiolytic effects. Tank A-101 waste was ~80°C when it was filled; current temperature is ~66°C. Accordingly, a significant fraction (44%) of the TOC in this waste is oxalate (see Table VI). We conclude that the degree of aging depends strongly on the temperature history of the waste.

Predicting rates of Aging in High Heat-Load Waste Tanks

Certain tanks such as AZ-101 and AZ-102 have significant enough radionuclide inventories that dose rates and temperatures are elevated more than other tanks. These tanks must be actively ventilated to maintain supernatant temperatures below bulk waste or supernate boiling points. If active ventilation were interrupted, the wastes could dry out within several years and perhaps heat these wastes causing bulk runaway reactions. However, if the complexants in these wastes are substantially aged already, or age rapidly during the time that water is boiled off, then the propagation hazard will be mitigated.

The results and discussion in previous sections provide information that may be used to estimate rates of thermal and radiolytic aging for these tanks. The PAS-95 aging experiments performed with and without irradiation provide baseline data for estimating complexant aging to acetate, succinate, formate, oxalate, and carbonate. Table IX lists the thermal rate of formation and the radiolytic yields measured at 90°C. Multiplying the radiolytic yield by the dose rate (Mrad/y) gives a rate of formation that can be combined with the thermal rate of aging to obtain an overall rate.

Table IX. Radiolytic Yield and Thermal Rates of Formation of Aging Products from PAS-95 Simulants at 90°C

<i>Aging Product</i>	<i>Radiolytic Yield (gC/kg/Mrad)</i>	<i>Thermal^(a) (gC/kg/y)</i>
Formate	0.007	
Acetate	0.0003	1
Succinate	0.008	5
Oxalate	0.001	3
Carbonate	0.036	2.3

(a) In the absence of O₂.

The AZ-101 and AZ-102 wastes may be similar to the PAS-95 simulants, but they certainly are not identical. Therefore, the rates in Table IX must be scaled to correct for differences. For thermal aging, studies [xvii,xxviii] suggest that rates of aging depend on TOC, aluminate, hydroxide and nitrite concentrations. Also, gas-production rates show large temperature dependencies with $E_a \sim 90$ kJ/mol [xvii,xxv,xxix].

As discussed previously, the radiolytic rate depends mainly on dose rate and radiolytic yield of oxidants. If concentrations of organic complexants are sufficiently high, then the yield of products may approach or even exceed one-half the yield of oxidants. If TOC concentrations are not sufficiently large to scavenge oxidants competitively with disproportionation reactions (Equations 5 and 6), then smaller yields may occur.

Table X lists characterization data taken from a quarterly report on the status of double-shell tank composition [xxx]. Data are provided for liquid and sludge fractions of the wastes, and a third entry for each tank shows data taken from the best Basis Inventory/Best Basis/TCR Tank Inventory database. These data are used to obtain average total dose rates and TOC concentrations for entire tank wastes.

Thermal aging is assumed to occur only in the liquid fraction because the complexants, except oxalate [xxvi], are very soluble. So the liquid thermal rates are combined with the entire waste radiolytic rates to obtain the total entire waste aging rate. Because ⁹⁰Sr is largely in the sludge fraction and ¹³⁷Cs mainly in the liquid fraction, the entire waste-rate estimates effectively combine the radiolytic effects of both ¹³⁷Cs and ⁹⁰Sr decay. For this reason, the rates are higher than the liquid aging rates. Since the supernates will concentrate over time, these aging rates may increase as the radionuclides and reactants concentrate.

Table X. AZ-101 and AZ-102 Characterization Data

Tank Waste ^(a)	Vol kL	H ₂ O %	SpG	TOC g/L	TOC wt%	NO ₂ ⁻ M	Al ^(b) M	OH ⁻ M	⁹⁰ Sr Ci/kg	¹³⁷ Cs Ci/kg
AZ-101-L	3230	70.7	1.21	1.13	0.093	1.35	0.03	0.75	0.0011	1.4
AZ-101-S	132	43.1	1.48	13.50	0.91	1.39	0.03	0.75	33	1.5
AZ-101 ^(c)	3280		1.22	1.85	1.5				1.6	1.9
AZ-102-L	3000	82.9	1.11	1.62	0.15	0.65	0.06	0.12	0.0017	1.0
AZ-102-S	357	53.8	1.41	6.35	0.45	0.59	0.06	0.13	7.0	0.81
AZ-102 ^(c)	3360		1.14	1.7	1.5				0.97	1.1

(a) L = liquid; S = sludge. (b) From sample analysis data in the Tank Waste Inventory database. (c) Values derived from Best Basis Inventory database, except that specific gravity (SpG) is weighted average of values for liquid and sludge fractions.

In conclusion, the results suggest that if the wastes were allowed to heat up to boiling, then much of the existing inventory of TOC would convert to carbonate and oxalate within 2 to 5 y. The results for AZ-101 sum to ~0.6 g C/kg/y (average of the sum for liquid and entire waste aging rates to carbonate and oxalate ions) so that the TOC would oxidize in 2 to 3 years. The estimated drying time for AZ-101 is 4 y [iii]. The AZ-102 rates sum to ~0.3 g C/kg/y so that the TOC in this tank would convert to oxalate and carbonate ions in ~5 y. The estimated time for AZ-102 to dry out [iii] is 10 y. The rates of conversion to carbonate ion are ~2 times the rates to oxalate ion. However, the PAS simulant measurements model the disappearance of the more reactive, more energetic carbon remaining in the waste, i.e., the higher energy carbon of the original complexants and their immediate remnants such as NTA and IDA. The AZ-101 and AZ-102 wastes are already aged [xxxi,xxxii]. Therefore, if one-third of the TOC is now oxalate, then the TOC in these tanks may age to equal amounts of carbonate and oxalate ions during the times it would take the wastes to dry out in the event that active cooling is interrupted. Significant production of formate, acetate, and succinate is also predicted by the PAS-95 [i]. These compounds are less reactive thermally [xvii] and radiolytically (see Table I) than the nitrogen-containing complexants and their remnants. However, as they build up and more reactive species disappear, radiolytically-generated oxidants may be expected to degrade these remnants to oxalate and carbonate ions as well.

CONCLUSIONS

The Waste Aging Studies task has shown that radiation and heat promote redox reactions between organic compounds (reducing agents) and nitrates/nitrites (precursors to oxidizing agents) in the wastes. Radiolysis and heating of waste simulants causes conversion of NO₃⁻ to NO₂⁻, N₂, and N₂O and probably NH₃ concurrent with the disappearance of organic species and the appearance of highly oxidized fragments of the original species. The observations are consistent with progressive degradation to species with more C-O bonds and fewer C-H and C-C bonds, resulting in an overall lower energy content of the organic inventory.

Effects of Aging on Organic Nitrate-Reaction Enthalpies

The simulated-waste aging studies using the PAS-95 simulants show quantitatively that the energy content of the wastes should decrease because of aging. The energy content of the

simulants declined steadily with increasing radiolytic dose; a radiation dose of 100 Mrad at 70°C decreased the energy content of the waste simulant by ~25% from a starting value of ~1300 J/g dry simulant. Much of the remaining enthalpy is due to undegraded glycolate, citrate, and chelator fragments. We also established that the decline in energy content is temperature dependent, declining more rapidly at 90°C than at 40 or 70°C. Aging occurs at a much slower rate in the absence of radiation, but for long storage times at elevated temperatures, certain species, namely HEDTA, citrate, and glycolate, are susceptible to thermal degradation [xxviii, xvii, xviii]. The results suggest that lifetimes and aging rates of organic complexants strongly depend on radiolytic and thermal histories. This partly explains the tank-to-tank variations in organic aging (based on organic analyses) observed in actual waste samples (see Tables Table VI and Table VIII).

TOC measurements have been obtained from a significant number of tank wastes. These results have been used to screen for tanks that could have sufficient fuel to undergo propagating reactions [viii,iii]. The assessment essentially converts TOC to enthalpy by assuming a proportionality factor, i.e.,

$$\Delta H_r (\text{kJ/g waste}) = \text{TOC (mg/g waste)} \times \Delta H (\text{kJ/g C}) \quad (\text{Eq. 10})$$

Presently, the conversion factor is taken to be the reaction enthalpy of sodium acetate. Our PAS-95 simulants aging tests suggest that the actual conversion factor decreases as a consequence of aging. Recent analytical data (see Table VIII) for actual waste samples enables the reaction enthalpy of the samples to be calculated. We estimated the enthalpies per gram of carbon in the samples and found that the energy was only ~70% of the energy for pure acetate. Thus, as currently used, TOC is a conservative and therefore a useful initial screen for problem tanks.

Mechanistic Understanding of Organic Aging

Mechanistic and kinetic results of Waste Aging Studies corroborate the hypothesis [x] that NO_2 is the dominant radical responsible for radiolytic oxidation of complexants. We note that the reactivities of citrate, glycolate, EDTA, and HEDTA measured in simple homogeneous simulants are comparable to those observed in the more complex heterogeneous simulants studied (see Table IV and Figure 1). This suggests that the same oxidizing species are acting in homogeneous and heterogeneous systems. The modeling results for formate and glycine suggest that the oxidizing species in alkaline systems are primarily NO_2 and O^- . However, under conditions likely to be encountered in actual wastes, i.e., low dose rates, the dominant oxidizing species is NO_2 (see Table II).

The modeling effort provides the first measurements of rate constants for reactions of NO_2 with carboxylates and complexants. The absolute rate constant for formate is $\sim 10 \text{ M}^{-1}\text{s}^{-1}$ and, for glycine, $70 \text{ M}^{-1}\text{s}^{-1}$. The ratio of these rate constants agrees well with the relative reactivities listed in Table I. Thus, rate constants for the other complexants may be estimated from newly determined relative rate constants.

The multiple roles that nitrite plays are noteworthy. Firstly, it reduces OH/O^- and forms NO_2 . Secondly, nitrite ion combines with organic radicals, thereby facilitating the conversion of

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complexants to simple innocuous products such as oxalate, formate, and carbonate. Absent this step, the products from complexants would be complicated, and perhaps more troublesome issues would be raised for storage, retrieval, and pretreatment activities. Lastly, nitrite also is required for thermal degradation of complexants.

Finally, although the safety issue surrounding safe storage of organic wastes is closed, studies [xxxiii] that elaborate the fundamental science continue under the Environmental Management Science Program because of the impact that increased understanding can have on other issues that involve high-level organic mixed wastes. These issues include the resolution of flammable gas safety issues and answers to questions about the impact of organic chemicals on retrieval and pretreatment activities.

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