WASTE MANAGEMENT, Vol. 13, pp. 237–244, 1993
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0956-053X/93 $6.00 + .00
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ORIGINAL CONTRIBUTION

CHEMO-DEGRADATION OF CHELATING AND COMPLEXING AGENTS IN A SIMULATED, MIXED NUCLEAR WASTE

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ABSTRACT. The effect(s) of the chemical composition of stored mixed wastes on the stability of their organic content was investigated. A nonradioactive simulant of a mixed waste was formulated to mimic a complex concentrate waste stored at the U.S. Department of Energy's Hanford Site. The simulant consisted of an alkaline inorganic matrix plus the chelating agents ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), and the complexing agent citric acid. The simulant's total organic content remained fairly constant (82–102% recoveries) for 171 days at ambient temperature, suggesting that little organic degradation had occurred. However, detailed analyses of the organics by gas chromatography/mass spectrometry (GC/MS) revealed that, collectively, 61.7% of the parent organics had degraded. Moreover, the individual parent compounds degraded differentially, with the HEDTA being the most labile. Twenty-one degradation products were identified, consisting mainly of complexor and chelator fragments. Such extensive changes in the organic composition of the simulant will undoubtedly have to be factored into the management of mixed wastes.

INTRODUCTION

Analyzing mixed nuclear wastes, which contain both radionuclides and hazardous chemicals, often as complex mixtures, has long challenged radiochemists and inorganic analysts. More recently, several studies indicate that mixed wastes often contain complex mixtures of nuclear-related organics as well (1–6). In addition to priority pollutants, which are regulated by the Environmental Protection Agency, compounds identified include chelating agents like EDTA, NTA and HEDTA (see Table 1 for complete nomenclature) and complexing agents like citric acid, which are not regulated per se. Such compounds have been used extensively by the nuclear industry in decontamination and isotope extraction processes (7–9).

RECEIVED 9 DECEMBER 1992; ACCEPTED 1 MARCH 1993.
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Acknowledgements—Three students—Bradley Osborn, Timothy White, and Kevin Polach—assisted in preparing the inorganic matrix of the simulated waste. The author is particularly indebted to Mr. Robert Hackley of TSD Analytical for helping with some of the initial GC/MS analyses. The research was funded by an SMSU Faculty Research Grant. The Hewlett-Packard 5989A GC/MS (MS Engine) instrument was purchased with the generous support of the National Science Foundation's Instrumentation and Laboratory Improvement (ILI) Program (Grant USE-9051582) and Syntex Corporation.

Most important, the organic analyses of the mixed wastes have revealed the presence of a family of structurally related compounds, so-called chelator and complexor fragments, occasionally at relatively high concentrations (1–3). In these studies, gas chromatography/mass spectrometry (GC/MS) analysis, combined with solvent extraction and chemical derivatization, has proven invaluable for identifying unknown chelator fragments like ethylenediaminetriacetic acid (ED3A), for example. Solution studies in several laboratories suggest that such compounds in mixed wastes are presumably derived from the chemical, radiolytic, thermal, and/or biological degradation of the parent organics (10–13). In some wastes, the chelator and complexor fragments may dominate the organic content, indicating that the organic chemistry of nuclear waste is very dynamic (2). However, the nature of the organic degradation process itself has remained a mystery, at least until recently.

In a recent study, a strategy was proposed and tested for studying organic degradation in nuclear wastes in a controlled laboratory environment by using simulated wastes (14). A simulated complex concentrate waste was prepared by adding four parent organics (EDTA, NTA, HEDTA, and citric acid) to an inorganic matrix (without any radioac-

TABLE 1
Organics Identified in a Simulated Mixed Waste over Time

Compound[c]	Concentration (mM)[a,b] after *n* Days					
	0	19	45	66	90	171
Parent Organics						
Citric Acid	38.80	36.17	30.68	28.79	18.34	14.66
Nitrilotriacetic Acid (NTA)	8.50	9.14	7.06	6.93	4.98	3.84
N-(2hydroxyethyl)ethylenediaminetriacetic Acid (HEDTA)[d]	11.50	7.87	6.66	6.42	7.68	6.30
Ethylenediaminetetraacetic Acid (EDTA)	13.70	13.41	12.00	8.96	5.59	3.55
Chelator and Complexor Fragments						
Iminodicarboxy Acid (ICC)	0.10			2.32	0.47	0.46
Iminodiacetic Acid (IDA)		10.10	19.23	14.00	10.81	12.11
N-(2-Hydroxyethyl)iminodiacetic Acid (HEIDA)[d]			3.70			
N-(Methyl)iminodiacetic (MeIDA)				7.54	2.95	3.34
N-(Ethyl)ethylenediamine-N-acetic,N′-carboxy Acid (EtEDC′A)[e]			0.76	0.18	0.16	0.15
N-(Ethyl)ethylenediamine-N′,N′-carboxyacetic Acid (EtEDCA)[e]			0.30	trace	0.39	0.46
N-(Ethyl)iminodiacetic Acid (EtIDA)					12.72	14.13
N-(3-carboxypropyl)-N-iminoacetic Acid (CPIA)		0.10	0.22		0.06	0.07
N-(Methylamine)iminodiacetic Acid (MAIDA)	0.10	0.03	5.56	1.38	2.77	3.04
1,1,2-Tricarboxyethane (3CE)					0.06	0.07
N-(Carboxy)ethylenediamine-N′,N′-diacetic Acid (CEDD′A)[e]			0.27	trace	trace	
N-(Carboxy)ethylenediamine-N,N′-diacetic Acid (CEDDA)			0.08	trace	0.18	0.15
N,N′-(di-methyl)ethylenediamine-N,N′-diacetic Acid (Me2EDD′A)				trace	0.14	0.50
N-(Ethyl)-N,N′-(dimethylamine)propylenediamine-N′-acetic Acid (EtDMAPD′A)			0.33		0.82	0.91
Ethylenediaminetriacetic Acid (ED3A)[e]	0.2		2.18	0.52	1.66	1.82
N-(Methylamine)-N′(methyl)ethylenediamine-N,N′-diacetic Acid (MeMAEDD′A)			1.15	0.34	2.52	2.73
N-(2-Carboxyethyl)iminodiacetic Acid (CEIDA)			0.80	0.14	0.14	0.15
N-(Carboxymethylidine)ethylenediamine-N,N′-diacetic Acid (CMEDDA)			0.09			
N-(Hydroxy,carboxy)ethylenediamine-N′,N′-diacetic Acid (HCEDDA)	0.1				0.12	0.15
N-(Methylamine)ethylenediaminetriacetic Acid (MAED3A)			4.93	0.46	1.31	1.52
Ethylenediaminecarboxytriacetic Acid (EDC3A)		0.08	0.06	0.05	0.02	0.02
Unknown (MW 161)				16.26	6.54	7.3
Undecanoic Acid	0.4	0.08	0.47			
Hexadecanoic Acid	0.26	0.37	0.08	0.05	0.02	0.02
Octadecanoic Acid			0.06	0.07	0.01	
Propanedioic Acid	1.6	5.28	6.3	3.38	17.29	19.29
Undecanedioic Acid		0.1	0.40	0.19	0.1	0.15
TOC Recovery (%)[f]	90.1	85.5	102	89.6	88.0	81.9

[a]No entry indicates compound is below detection level. [b]Exact contributions of unknown organics to waste's total organic content cannot be determined unequivocally. [c]Methylated (BF_3/Methanol), acids identified as methyl esters. [d]Identified as lactone by GC/MS and past GC/FTIR analyses (1–3). [e]Identified as lactam by GC/MS and past GC/FTIR analyses (1–3). [f]Percent total organic carbon (TOC) computed as the ratio of the concentration (g C/L) of organics identified vs. nominal concentrations of source-term organics added to the simulated waste.

tivity), which was formulated based on past analyses of an actual complex concentrate waste (3). Aliquots of the simulant were then γ-irradiated in a ^{60}Co-source for 0–100 h, followed by sample preparation and GC/MS analysis. The parent organics degraded exponentially, before tapering off; 80% had disappeared by 100 h of irradiation. Numerous degradation products (27 in all), mainly complexor and chelator fragments, ranging from small to complex molecules, were identified by GC/MS analysis. Moreover, the simulated waste's organic content decreased with increasing radiation, indicating that radiolytic degradation is not only vigorous but dispersive as well. Compounds that lay outside the

range of the analytical procedure, such as gases, amines, or nitroso-organics, were presumably formed.

Radiation is, therefore, clearly responsible for extensive organic degradation in mixed wastes, but is it the only available energy source? Admittedly, many of these wastes have extremely high radioactivities, e.g., 1 Ci/L or more. However, the thermal and chemical environments of the wastes can also be quite harsh. For example, wastes exist at elevated temperatures because of heat-producing nuclear decay. Moreover, the complex concentrate waste, upon which the simulated waste was modeled, has a severe pH of 13.5 and molar concentrations of myriad inorganics (3). Is this mixed waste's chemistry severe enough to contribute much to the organic degradation?

In this paper we describe the results of our first study on the chemical degradation of chelating and complexing agents in a simulated mixed waste. We prepared the simulant of the complex concentrate waste as a mixture of an inorganic matrix and several chelating and complexing agents. We then stored aliquots of the simulant in the dark at room temperature for 0–171 days, to study the effects of the waste's chemical matrix on organic degradation. Each waste sample was subsequently analyzed for its hydrophilic organic content, particularly any emerging chelator and complexor fragments, as well as any remaining parent organics, i.e., the chelating and complexing agents originally added to the waste.

EXPERIMENTAL

Experimental Design

Simulated waste matrix preparation. The inorganic matrix of the simulated waste was prepared according to the following composition, based on past inorganic analyses of an actual complex concentrate waste (3): HNO_3, 2.60 M; $Al(NO_3)_3 \cdot 9H_2O$, 210 mM; $Fe(NO_3)_3 \cdot 9H_2O$, 38 mM; $Ca(NO_3)_2 \cdot 4H_20$, 25 mM: $Cr(NO_3)_3 \cdot 9H_20$, 4.5 mM; KNO_3, 46 mM; $La(NO_3)_3 \cdot 6H_2O$, 0.28 mM; $Nd(NO_3)_3 \cdot 5H_2O$, 0.98 mM; $Mg(NO_3)_2 \cdot 6H_2O$, 11 mM; $Mn(NO_3)_2$, 7.2 mM; $Ni(NO_3)_2 \cdot 6H_2O$, 8 mM; $Zn(NO_3)_2 \cdot 6H_2O$, 7.4 mM; Na_2HPO_4, 22 mM; NaCl, 41 mM; $Na_2B_4O_7$, 21 mM; $Cu(NO_3)_2 \cdot 3H_2O$, 0.42 mM; $Pb(NO_3)_2$, 1.8 mM; $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 0.45 mM; $Cd(NO_3)_2 \cdot 4H_2O$, 0.55 mM; NaOH, 6.75 M; $NaNO_3$, 2.04 M; Na_2CO_3, 1.22 M; $NaNO_2$, 800 mM; and Na_2SO_4, 7.2 mM.

Concentrated nitric acid was added to half the final volume of deionized water, followed by sequential addition of the above inorganics. Most of the salts were added, in the order specified above, to an acidic solution to maximize their initial solubility. The solution was then neutralized with sodium hydroxide. Sodium carbonate and sodium nitrite were added to a basic solution, because these species are volatile in an acidic environment. The completed waste matrix was very alkaline (pH 13.5), biphasic (~31% solids), and amber in color.

Simulated, mixed waste samples and the time study. Four organics were added to 15 mL aliquots of the inorganic waste matrix, in each of six glass scintillation vials, as follows: EDTA, 11.8 mM; NTA, 12.0 mM; HEDTA, 19.5 mM, and citric acid, 42.6 mM. These concentrations were selected to match those determined in an earlier analysis of the actual complex concentrate waste (3). Each scintillation vial was then wrapped in aluminum foil to exclude light, and stored at ambient temperature for 0, 19, 45, 66, 90, and 171 days to study the effect(s) of chemical energy on organic degradation. Each time point was immediately prepared for organic analysis at the allotted time.

Preparation of Analytical Samples

Replicate 0.5 mL aliquots of each time point were carefully transferred to a 5 mL reaction vial and concentrated to dryness on a heating block under N_2 at 50°C. The first two time points (0 and 19 days) were analyzed in quadruplicate because of greater uncertainty in their analyses. The remaining time points were analyzed in triplicate. Given the high solids content of the simulated waste, samples had to be vortexed (shaken rapidly) and quickly pipetted to insure uniform sampling. The resulting residue of each sample was methylated in the sealed vial with 1 mL BF_3/methanol (14% w/v) at 100°C for 20 min. After cooling, 1 mL of chloroform was added to the methylation mixture in the reaction vial. The mixture was vortexed and transferred to a test tube containing 3 mL of 1 M KH_2PO_4 buffer solution (pH 7), with a 0.2 mL chloroform rinse. The mixture was vortexed, and then centrifuged on a low-speed, tabletop centrifuge to separate the two phases. Part of the chloroform layer (0.6 mL), which contained methylated hydrophilic organics, was removed, placed in a reaction vial, and evaporated to dryness under nitrogen at room temperature. The residue was immediately redissolved in chloroform, yielding an extract of methylated hydrophilic organics. Each analytical sample was frozen prior to GC and combined GC/MS analysis.

GC Analysis

Capillary GC analyses were performed on Hewlett-Packard (HP) 5880 and 5890 Gas Chromatographs, each equipped with a flame ionization detector

(FID) and a nitrogen-phosphorus detector (NPD). Each instrument was also equipped with a splitless injection system attached to a 30 m × 0.25 mm inside diameter (I.D.) fused silica capillary column coated with a 0.25-μm film of SE-54. From an initial value of 40°C, the column temperature was programmed at 5°C per minute to 300°C, and finally maintained isothermally at 300°C for 10 min.

GC/MS Analysis

GC/MS analyses were performed on HP 5985 and 5989A GC/MS instruments and an HP GC/MSD instrument in the electron-impact (EI, 70eV) or the chemical ionization (CI) mode with CH_4 as the CI gas. The gas chromatographs were equipped with 30 m × 0.25 mm I.D. fused silica capillary columns coated with 0.25 μm of SE-54; each column was programmed from 40°C to 300°C per min, where it was maintained isothermally for 10 min. A splitless injection system was used to introduce the sample onto the GC/MS or GC/MSD instrument. A mass range of 50–400 amu was scanned by the GC/MS instruments' computers.

Quantitation

Hydrophilic organics identified in the waste's methylated hydrophilic extracts were quantitated using external standards as described previously (1,14). Response factors, expressed as nanograms of analyte per Total Ion Chromatogram (TIC) area counts, were computed for each standard under analytical conditions identical to those of the sample analyses. The response factor for citric acid was used to quantitate organic acids, including complexor fragments like the carboxylic acids, presumably derived from the degradation of citric acid. Response factors for the chelating agents EDTA, NTA, and HEDTA, as well as the commercially available chelator fragments IDA and HEIDA, were assigned to the chelator fragments unavailable commercially, based on GC behavior and structural similarities.

Materials

Simulated waste components and analytical standards. The parent organics and chromatographic standards (citric acid, EDTA, HEDTA, NTA, IDA and HEIDA) were purchased from Aldrich Chemical Company (Milwaukee, WI). The inorganics used to prepare the waste matrix were purchased from a variety of chemical suppliers.

Chromatographic columns. The SE-54 fused silica capillary columns used in the GC and GC/MS analyses were purchased from Supelco, Inc. (Bellefonte, PA).

Reagents, solvents, and glassware. The BF_3/methanol (14% w/v) used in the methylation reaction was purchased from PIERCE (Rockford, IL). All of the solvents used in the analytical procedure (described previously) were redistilled-in-glass solvents purchased from Fisher Scientific (Fair Lawn, NJ). Deionized water, prepurified for laboratory use, was further purified on a SYBRON/Barnstead NANOpure®* system (Barnstead) containing two ion-exchange resins and one charcoal filter. All glassware was cleaned in an RBS 35®† detergent/deionized water solution (20 mL RBS 35 concentrate/L water, v/v) followed by NANOpure® water rinses.

RESULTS AND DISCUSSION

Degradation of the Parent Organics

The total concentration of chelating and complexing agents decreased steadily with increasing time (Table 1). Initially, the parent compounds appear to degrade linearly, followed by a rate decrease after 90 days (Fig. 1). All of the chelating and complexing agents were essentially accounted for in the initial sample; the recovery of parent organics on day zero was 95.5%. After 171 days, only 39.3% of the parent compounds remained. The chemistry of the waste's inorganic matrix clearly degrades the compounds extensively.

The individual parent compounds degraded at different rates (Fig. 2). Extensive degradation was observed immediately, with the exception of EDTA. The EDTA analyses yielded 100+% recoveries in the early time points. This is undoubtedly an analytical artifact. Control samples, consisting of EDTA plus the inorganic waste matrix, were prepared and analyzed. Fluctuations in the EDTA recovery were observed in early time points (0 and 19 days). The reason for these fluctuations is not clear at this point, but they may be due to initial solubility problems or unique chelation behavior by EDTA. In the simulated waste, both citrate and NTA underwent appreciable degradation immediately (9.9% and 29.2%, respectively) followed by similar degradation rates. In contrast, HEDTA degraded much more rapidly at 41%. Its marked depletion in the zero-day sample suggests that HEDTA is particularly sensitive to chemical degradation. Exactly the same sort of behavior was observed in the zero-radiation sample of an earlier radiolysis study (14). This increased instability suggests that HEDTA might be a very good candidate for synthesizing chelator fragments in future studies.

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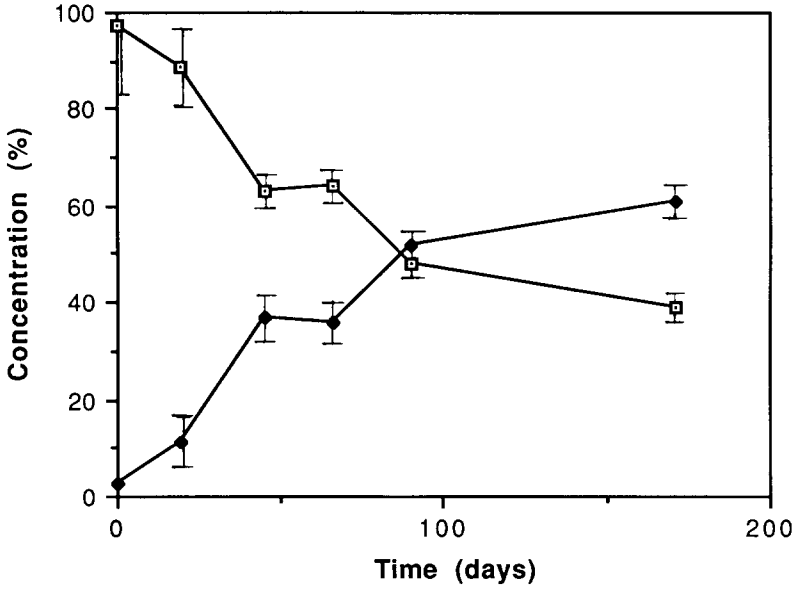

FIGURE 1. Collective plots of the net disappearance (▣) of a mixture of parent organics (EDTA, NTA, HEDTA and citric acid) and the collective appearance (♦) of degradation products, mainly chelator and complexor fragments, in a simulated mixed waste stored in the dark at ambient temperature for up to 171 days. Concentration (%) values for both plots were computed as the per cent ratio of total parent organics (mM) remaining or total degradation products (mM) formed vs. the total concentration of parent organics (mM) originally added to the simulated waste.

A number of factors are likely responsible for the differential degradation of the various parent organics, particularly the immediate disappearance of NTA and HEDTA, with the most likely among them being a combination of the high pH and ionic strength, as well as the high metal ion concentrations. In actual mixed wastes, the high radiation and harsh chemical environment are certainly the obvious energy sources. Temperature, a byproduct of nuclear decay, must also be considered. However, solution studies in the literature indicate that thermal degradation of such compounds is most pronounced above 200°C (8,12).

The literature contains substantial information on the degradation of chelating and complexing agents in aqueous solution. For example, there is ample evidence that cations bind differentially to chelating and complexing agents, altering their structural and chemical properties, including susceptibility to degradation (7,15). Studies have been carried out on the thermal or radiolytic decomposition of chelating and complexing agents in aqueous

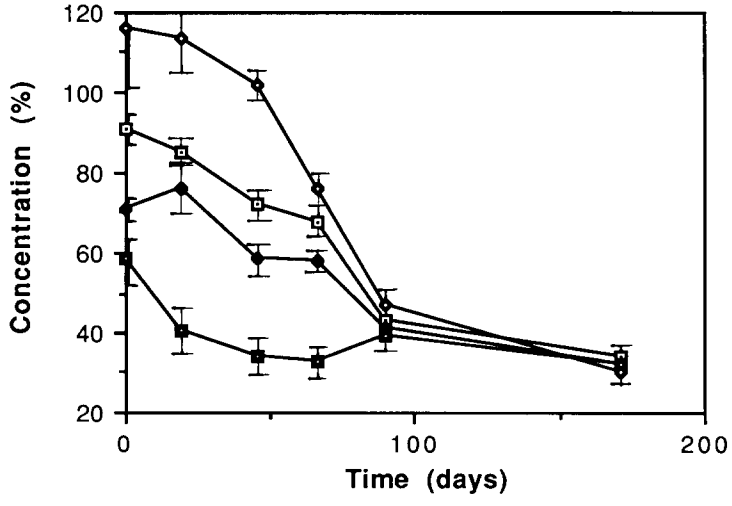

FIGURE 2. Individual plots of the disappearance of each parent organic from the organic mixture (◆ EDTA; ♦ NTA; ■ HEDTA and ▣ citric acid) in the simulated mixed waste stored in the dark at ambient temperature for up to 171 days. Concentration (%) values were computed as the per cent ratio of the individual parent organic (mM) remaining vs. the parent organic (mM) originally added to the simulated waste. See Figure 1 for the collective degradation plots of the mixture of parent organics.

solution (11,12,16,17). However, very little data existed in the literature until recently on the degradation of chelating and complexing agents over extended periods of time under conditions simulating the harsh environments and ages of actual wastes, decontamination operations, or waste management procedures such as volume reduction (9,10,14). Moreover, most of the information available on the thermal and radiolytic stability of chelating and complexing agents deals with synthetic, single-component solutions. The complex composition, e.g., 18 different cations, of the simulated waste used in this degradation study precludes any facile comparisons.

Formation of Degradation Products

The rate of emergence of chelator and complexor fragments mirrors the degradation of the parent compounds (Fig. 1). Numerous chelator and complexor fragments, 21 in all, were identified by GC/MS analysis (Table 1). They all bear structural similarities to one or more of the parent organics. The degradation products range from a small fragment like iminodicarboxy acid (MW 105) to larger species like EDC3A (MW 278; see Table 1 for complete nomenclature). An unknown compound with MW 161 and a number of carboxylic acids were also identified in several samples. Based on the GC/NPD analyses and mass spectral fragmentation patterns, the unknown is clearly a chelator fragment. It contains nitrogen and shares several mass spectral fragmentation ions with EDTA. Accurate mass high resolution mass spectrometry will probably have to be performed to identify the compound.

Comparison of the distribution of the chelator fragments formed in this chemical study with that of the earlier radiolysis study indicates that radiation produced a greater variety of chelator fragments, with a marked predominance of larger species (14). These larger chelator fragments are presumably derived from the recombination of reactive, smaller fragments formed during radiolysis. Such behavior is not surprising given the energetic nature of radiolysis reactions. In contrast, one would not expect this phenomenon in chemically mediated degradation, and it is not observed in this study.

Given the experimental design of this initial chemical degradation study (i.e., a mixture of four organics in the waste matrix) and the complexity of the pool of degradation products identified, it is not possible to trace the origin of each chelator or complexor fragment. Experiments with individual parent organics need to be performed, and are currently being planned. However, judging from the structural complexity of the products identified, it is clear that the chemical degradation of chelating and complexing agents is both varied and complex.

A number of carboxylic acids were also identified. They may be derived mainly from citric acid degradation, probably with some involvement from the acetate ligands of the chelating agents. The dicarboxylic acids, particularly propanedioic acid, are probably derived from citrate degradation. Alternatively, some of the acids, particularly the larger compounds, may be contaminants or analytical artifacts, at least in part, but extreme care was taken during the study to exclude contamination. Individual degradation studies will have to be performed to confirm the source(s) of the acids.

Comparison of the organic contents of the simulated waste with that of the actual complex concentrate waste from the Hanford Site is very revealing. Most of the chelator and complexor fragments identified in the simulated waste had also been detected and/or identified in the actual waste in an earlier study (3), providing fairly good agreement given the disparate and complex origins of the two "wastes." For example, chelator fragments like IDA and ED3A are major components in both the actual and simulated wastes. Carboxylic acids were also identified in both wastes.

The literature suggests even more parallels. In those solution studies where the degradation products were actually analyzed, various species were detected, ranging from gases, e.g., H_2, CO, CO_2, and NH_3, to alkylamines and a few chelator fragments (8,11). Also, EDTA degrades into IDA and HEIDA, even autocatalytically in the presence of Fe^{3+} (8). In contrast, NTA degraded more slowly in the same study; MeIDA was the major product (8). All of these chelator fragments, and many more, were identified in both the actual an simulated wastes, including this simulant (3,14).

Organic Recoveries and Chemical Degradation

The mass balance for the organic content of each time point was computed as the percent total organic carbon (TOC) recovery, relative to the concentration of the parent organics originally added to the simulated waste. The TOC content of each time point was, in turn, computed by quantitating each organic species as g C/L. The TOC recoveries remained fairly constant over the 171-day study, ranging from 81.9–102%, with an average of 89.5%. This suggests that chemically mediated degradation of chelating and complexing agents in mixed wastes like the simulant is a conservative process. In marked contrast, increasing the irradiation of the simulant in the earlier radiolysis study resulted in a progressive loss of the TOC, up to 73% (14). In this chemical degradation study, the loss is not only much lower (~0–19%) but also fairly constant.

A likely explanation for part of the TOC loss is the analytical efficiency, which typically ranged

from 2–10%, the only exceptions being the first two EDTA time points (0 and 19 days) at 11–16%. Another possible reason for the TOC loss is that degradation products are formed that lie outside the analytical "scope" of the procedure used in this study. Based on solution studies in the literature, compounds like alkylamines, gases like CO_2, and volatile organics are among the likely candidates for the missing organics (8,11). Expansion and refinement of the analytical scheme, to include additional analytical procedures like amine derivatization and purge-and-trap analysis for gases, are currently being planned.

Concluding Remarks

Recent analyses of mixed nuclear wastes have revealed the presence of chelator and complexor fragments, occasionally at very high concentrations, presumably derived from the radiolytic, thermal, and/or chemical degradation of chelating and complexing agents (1,2,3). The earlier radiolysis study on a simulant of a complex concentrate waste confirmed that radiation is clearly a major force in organic degradation (14). The high radiation field of the actual complex concentrate waste, ~1 Ci/L, is certainly more than enough to produce such organic degradation (3). However, the results of this study indicate that the harsh chemical environment of the mixed waste is also responsible for extensive degradation. Similar chelator fragments were produced in this chemical study and the earlier radiolysis study, but radiation promotes the formation of larger, more complex chelator fragments as well (14). The two forces, along with temperature, undoubtedly work in tandem to produce the organic degradation observed in actual wastes.

The experimental approach of using simulated wastes for studying organic degradation in nuclear wastes appears to be very promising. As discussed earlier, the organic contents of the actual and simulated complex concentrate wastes proved to be very similar. The correlations are very compelling, given the disparate origins of the wastes, and tend to validate the concept of using simulated wastes to study organic degradation under controlled laboratory conditions. Another, perhaps more compelling, argument can be offered for simulation studies. Students, particularly undergraduates, who are otherwise "genetically impressionable," may participate in nuclear-related research, without the hazards of radiation exposure. Otherwise, student participation in such research is effectively precluded. Given the acknowledged, and growing, need for developing future scientists and engineers in waste and environmental management, new approaches, like the one outlined in this study, need to be developed and implemented.

On a practical, perhaps more compelling note, the findings of laboratory studies on simulated wastes, like the one described in this report, should be of immediate and practical benefit to engineers charged with the daunting task of managing actual mixed wastes. For example, consider the differential degradation rates observed for the parent organics, particularly the rapid degradation of the HEDTA. This information could be used to facilitate the selection of specific chelating agents for future nuclear operations, e.g., decontamination campaigns. Given the potentially adverse impact of chelating agents on a waste's management, it might be advantageous to select a chelating agent that degrades most extensively. Again, however, care needs to be exercised before jumping to facile conclusions. It is clear that organic degradation is vigorous and very complex, but much remains to be learned about the specifics of the process itself.

In general, increasing evidence in the literature argues that the presence of organics, combined with the process of organic degradation, may have profound waste management and environmental implications. Considerable research in several laboratories indicates that the presence of chelating and complexing agents may complicate the management of nuclear wastes by destabilizing waste forms, e.g., cementitious grouts, or by enhancing the environmental mobility of certain radionuclides leached from wastes (17–22). For example, calcium sequestering by chelating agents may greatly destabilize cementitious grouts (21). Environmentally speaking, chelating agents may render otherwise immobile radionuclides mobile via subsurface groundwater transport. For example, migration of EDTA chelates of radioactive cobalt and plutonium were observed at a shallowland burial site of low-level nuclear waste (20,22). Even naturally occurring organics like humic and fulvic acids appear to mediate the subsurface transport of certain radionuclides (19,23). The deleterious effects of chelating and complexing agents on mixed nuclear wastes suggest, perhaps, that organic degradation is not only desirable but should even be enhanced. However, solution studies suggest that some chelator fragments may be even more potent chelating agents than their parent compounds (8).

Clearly, the chemistry of the chelator and complexor fragments, e.g., chelating capacity, needs to be studied before their impact on waste management and the environment can be properly assessed. However, with few exceptions, notably IDA and HEIDA, such compounds are not commercially available. They may have to be chromatographically isolated from simulated wastes like the one described in this study. Alternatively, they may have to be synthesized using procedures based on

degradation studies like the one described here (10,14).

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Open for discussion until 29 October 1993.