

ORGANIC ANALYSES OF AN ACTUAL AND SIMULATED MIXED WASTE: HANFORD'S ORGANIC COMPLEXANT WASTE REVISITED

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Reanalysis of the organics in a mixed waste, an organic complexant waste from the U. S. Department of Energy's Hanford Site, has yielded an 80.4% accounting of the waste's total organic content. In addition to several complexing and chelating agents (citrate, EDTA, HEDTA and NTA), 38 chelator/complexor fragments have been identified, compared to only 11 in the original analysis, all presumably formed via organic degradation. Moreover, a misidentification, methanetricarboxylic acid, has been re-identified as the chelator fragment N-(methylamine)imino-diacetic acid (MAIDA). A nonradioactive simulant of the actual waste, containing the parent organics (citrate, EDTA, HEDTA and NTA), was formulated and stored in the dark at ambient temperature for 90 days. Twenty chelator and complexor fragments were identified in the simulant, along with several carboxylic acids, confirming that myriad chelator and complexor fragments are formed via degradation of the parent organics. Moreover, their abundance in the simulant (60.9 % of the organics identified) argues that the harsh chemistries of mixed wastes like Hanford's organic complexant waste are more than enough to cause organic degradation, even in the absence of radiation.

Huge inventories of toxic wastes, encompassing many different categories, are being reported and cataloged around the world. The motivations are many and varied, including increased environmental awareness and ecological disasters like Chernobyl.¹ Governments and private institutions scramble to deal with waste in its many forms, ranging from household wastes to complex industrial and military wastes, including radioactive wastes. Certainly among the most complex of the various waste types are the mixed wastes, which contain both radionuclides and toxic chemicals. These wastes pose a major challenge to scientists and engineers charged with the daunting task of stabilizing and disposing of them.^{2, 3} The origins of mixed wastes can be quite varied. Some have been generated during defense-related reprocessing of spent nuclear fuel, while others are generated in commercial nuclear operations.⁴⁻¹⁰

The increasing frequency of reports in the literature suggests that considerable research is currently underway to characterize the chemistry of mixed wastes and to develop and/or implement technologies for managing them, e. g., vitrification, cementitious grouting, incineration, etc. Historically, the analysis of organics in mixed wastes has received much less attention than their inorganic and radiochemical contents. However, recent studies indicate that mixed wastes often contain complex mixtures of organics.⁴⁻¹⁰ Our laboratory has analyzed a number of mixed wastes, ranging from commercial wastes^{6,10} to defense wastes from the Department of Energy's Hanford Site in Washington state.^{9, 10} Prompted by the needs of engineers charged with managing the wastes, our analytical goal has been nothing less than their total chemical characterization, particularly the organic content.

The first mixed waste analyzed in our laboratory was an organic complexant waste derived from reprocessing spent fuel for defense purposes at the Hanford site 20-plus years ago. Using analytical methods specifically tailored for nuclear-related organics, we reported the presence of the chelating agents EDTA, NTA, and HEDTA and the complexing agent citric acid.¹ Other mixed wastes analyzed in our lab since have also contained chelating and complexing agents.^{6,9}

These compounds have been used extensively in the nuclear industry as decontamination agents, etc.¹¹⁻¹⁴

The identification of the chelating and complexing agents in mixed wastes is not particularly surprising. However, our analyses also reveal the presence of structurally related chelator and complexor fragments, occasionally at relatively high concentrations.^{6, 9, 10} For example, we reported the presence of eleven different fragments in the original analysis of the organic complexant waste, presumably derived from the radiolytic, thermal, and/or chemical degradation of the parent chelating and complexing agents.¹⁰ In the literature, a few chelator fragments had been reported in studies on heated and irradiated aqueous solutions of chelating and complexing agents^{15, 16}, but their structures are much simpler than the chelator fragments identified in the mixed wastes.^{6, 9, 10} One study did examine HEDTA degradation under conditions simulating mixed wastes.¹⁷

In the original analysis of the organic complexant waste, we also reported the presence of several other chemical classes, including mono- and dicarboxylic acids, alkanes and phthalate esters.¹⁰ All of the organics reported, including the chelating and complexing agents and the chelator/complexor fragments, accounted for 75.1% of the waste's total organic content (TOC). We speculated on the missing 24.9%, suggesting that it might be due to other classes of organics, e. g., polymers, not analyzable by our analytical strategy. Alternatively, we suggested that the missing organics might be other classes of degradation products of the chelating and complexing agents, e. g., amines and nitroso compounds, also not analyzable by our analytical methods.

In this study, we report the results of a reevaluation of the analytical data of the original analysis of Hanford's organic complexant waste. Using experience gained since that initial analysis, we have identified 38 chelator/complexor fragments, increasing the TOC accounting for the waste up to 80.4%. We also report the results of an analysis of a simulant of the actual organic complexant waste, prepared by undergraduate students. The simulant was prepared and stored in the dark at ambient temperature, without any radiation, to test whether the harsh chemical environment of the organic complexant waste alone is enough to cause the degradation of parent chelating and complexing agents.

Experimental

Actual Organic Complexant Waste

The organic complexant waste was generated during various reprocessing campaigns, in which organic species such as chelating agents were used to improve the waste's properties, e.g., by extraction of heat-producing radionuclides. The result is an organic-rich (44 g TOC/L), radioactive (1 Ci/L) mixed waste, based on analyses by Westinghouse Hanford Corporation's Hanford Engineering Development Laboratory.

Because of its high radioactivity, the waste was diluted 500-fold with distilled water before organic analyses were undertaken.¹⁰ Consequently, the sample analyzed was a clear solution, with no solids or colloidal material. All of the sample preparation for the actual waste was performed in radiation labs at Hanford's Pacific Northwest Laboratory.

Simulated Organic Complexant Waste

A simulant of the organic complexant waste was prepared by students at Southwest Missouri State University, based on past analyses of the actual waste. The simulated waste consists of an inorganic matrix plus specific organic complexing and chelating agents, which were added to simulate the actual waste.

Inorganic 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 [1]: HNO₃, 2.60 M; Al(NO₃)₃•9H₂O, 210 mM; Fe(NO₃)₃•9H₂O, 38 mM; Ca(NO₃)₂•4H₂O, 25 mM; Cr(NO₃)₃•9H₂O, 4.5 mM; KNO₃, 46 mM; La(NO₃)₃•6H₂O, 0.28 mM; Nd(NO₃)₃•5H₂O, 0.98 mM; Mg(NO₃)₂•6H₂O, 11 mM; Mn(NO₃)₂, 7.2 mM; Ni(NO₃)₂•6H₂O, 8 mM; Zn(NO₃)₂•6H₂O, 7.4 mM; Na₂HPO₄, 22 mM; NaCl, 41 mM;

$\text{Na}_2\text{B}_4\text{O}_7$, 21 mM; $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 0.42 mM; $\text{Pb}(\text{NO}_3)_2$, 1.8 mM; $(\text{NH}_4)_6\text{M}_2\text{O}_{24} \cdot 4\text{H}_2\text{O}$, 0.45 mM; $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 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 they decompose in an acidic environment, releasing volatile species. The completed waste matrix was very alkaline (pH 13.5), biphasic (~31% solids), and amber in color.

Simulated Waste Preparation. Four parent organics (64 mM citrate, 38 mM HEDTA, 31 mM EDTA and 7.3 mM NTA) were added to a 15 mL aliquot of the inorganic waste matrix in a glass scintillation vial and thoroughly mixed. These concentrations were selected to match those determined in the earlier analysis of the actual organic complexant waste.¹⁰ The simulated waste was then stored in the dark at ambient temperature for 90 days.

Preparation of Analytical Samples

Triplicate 0.5 mL aliquots of the diluted actual waste and undiluted simulant were carefully transferred to 5 mL reaction vials and dried on a heating block under N_2 at 50 °C. 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 dried 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 (aqueous on top, organic on bottom). Part of the chloroform layer (0.6 mL), which contained the methylated organics, was transferred to a reaction vial and frozen prior to gas chromatography (GC) and combined GC/mass spectrometry (GC/MS) analysis.

GC Analysis

Capillary GC analyses were performed on a Hewlett-Packard (HP) 5890 Gas Chromatograph equipped with a flame ionization detector (FID). The instrument was also equipped with a splitless injection system attached to a 30 m x 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 minutes.

GC/MS Analysis

GC/MS analyses were performed on a Hewlett Packard 5989A GC/MS instrument in the electron-impact (EI, 70eV) mode. The gas chromatograph was equipped with a 30 m x 0.25 mm I. D. fused silica capillary column coated with 0.25 μm of SE-54. The column was programmed from 40 °C to 300 °C at 5 °C per minute, where it was maintained isothermally for 10 minutes. A splitless injection system was used to introduce the sample onto the GC/MS instrument. A mass range of 50 to 400 amu was scanned by the GC/MS instrument's HP UNIX data system.

Quantitation

Hydrophilic organics identified in the waste's methylated hydrophilic extracts were quantitated using external standards as described in earlier studies.^{9, 18} A response factor, expressed as nanograms of analyte per total ion chromatogram (TIC) area counts, was computed for methylated standards of citrate, NTA, EDTA, HEDTA, IDA and HEIDA (see Table 1 for full nomenclature) under analytical conditions identical to those of the sample analyses. One of these standard response factors was assigned in the quantitation of each chelator/complexor fragment identified in the actual and simulated wastes based on structural similarities with the standards.

Materials

Simulated Waste Components and Analytical Standards. The parent chelating and complexing agents used in the simulant and as GC standards in the analyses, including the two commercially available chelator fragments IDA and HEIDA, were purchased from Aldrich Chemical Company (Milwaukee, Wisconsin). 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, Pennsylvania).

Reagents, Solvents, and Glassware. The BF₃/methanol (14% w/v) used in the methylation reaction was purchased from PIERCE (Rockford, Illinois). All of the solvents used in the analytical procedure, described previously, were redistilled-in-glass solvents purchased from Fisher Scientific (Fair Lawn, New Jersey). Deionized water, pre-purified 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

Actual Organic Complexant Waste

Original Analysis.

In the original analysis of the actual organic complexant waste¹⁰, four chelating and complexing agents were reported: citric acid, HEDTA, EDTA and NTA. These compounds are commercially available and have been used extensively in nuclear waste reprocessing and decontamination because they form very strong chelates with a variety of metal ions, notably heavy metals and actinides.^{19, 20}

A number of structurally related compounds were also identified. Methanetricarboxylic acid was reported in the original analysis, presumably a complexor fragment, or degradation product, of citrate. Seven chelator fragments were reported: IDA, ED3A, HEDDA, E₂DTA, HEIDA, MeHEDD'A and MeEDD'A. Three more chelator fragments were detected on the basis of similar mass spectral behavior, but their structures were not completely identified. Molecular weights (MW's) of 122, 173 and 247 were assigned on the basis of chemical ionization (CI) GC/MS. These compounds were presumed to be derived from the radiolytic and/or chemical degradation of the parent chelating and complexing agents identified in the waste, i. e., citrate, HEDTA, EDTA and NTA.

Three other classes of organics were also reported. Mono- and dicarboxylic acids were identified, ranging in concentration from 0.1 to 2.5 mM. Such compounds also complex metal ions but the association is much weaker than that of the metal chelates and complexes of citrate and the chelating agents.^{19, 20} A number of alkanes ranging from nC₂₃ to nC₃₅ were also identified, accounting for 5.7% of the waste's TOC content. These compounds are undoubtedly derived from oils and solvents used in waste reprocessing. Finally, two phthalate esters were identified, which are commonly used as plasticizers. All of these organics accounted for 75.1% of the actual waste's TOC content, leaving 24.9% unaccounted.

Reanalysis

In general, reevaluation of the original analytical data from the actual waste confirmed the identifications and quantitations of most of the organics previously reported,¹⁰ but also yielded a surprise or two, and many new compound identifications.

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Earlier Results Confirmed. Nearly all of the original organic identifications stood up to the reanalysis. The presence of the four chelating and complexing agents (citrate, HEDTA, EDTA and NTA) is reaffirmed, at the same concentrations previously reported. Reanalysis of the data on the carboxylic acids did not yield any changes. Five monocarboxylic acids, in concentrations ranging from 2.50 mM to a trace, were reidentified (Table 1). Eight dicarboxylic acids, ranging from 2.04 mM to a trace, were also reidentified. The presence of a number of normal alkane hydrocarbons, totalling 7.77 mM, was also reaffirmed. Finally, the two phthalate esters, dibutyl- and dioctylphthalate, were reconfirmed. All of these compounds account for 75.1% of the actual waste's TOC content as previously reported.¹⁰

Reidentifications and New Chelator/Complexor Fragments. Careful reanalysis of the analytical data, using experience and insights on chelator/complexor fragment analysis acquired since the original analysis of the organic complexant waste, did yield a surprise and many new compound identifications. Perhaps the biggest single change in the reanalysis is the disappearance of the complexor fragment, methanetricarboxylic acid. It is reidentified as the complexor fragment MAIDA (see Table 1 for full nomenclature), based on low resolution GC/MS analysis, along with CI-GC/MS and GC-NPD (nitrogen phosphorous detection) results reported in a parallel study.¹⁸ This chelator fragment clearly contains nitrogen, which escaped our notice in the original analysis.

The largest collective advance of the reanalysis is the identification of myriad new chelator fragments. The original analysis reported ten chelator fragments: seven completely identified and three partially identified with respect to molecular weight. Reanalysis of the data has increased the total to 38 chelator fragments, all of which are totally identified (Table 1). Some of the chelator fragments were identified as intramolecular lactones and lactams using insights from analytical strategies reported in parallel studies of other wastes.^{9, 10, 18} The presence of IDA (most abundant at 188 mM) and ED3A (third in abundance at 17.9 mM) is reaffirmed. The major new entry is MAIDA at 28 mM, which had been previously reported as methanetricarboxylic acid, as outlined previously. Of the many new chelator fragments identified, some are small in size, e.g., EtIA, but many are large molecules, e.g., HEIAEDDA, in some cases much larger than the presumed parent chelating agents, e.g., EDTA. The former are presumably simple degradation products, whereas the latter are presumably recombination products of smaller fragments.

The many chelator fragments identified in the reanalysis of the actual waste account for 54.5% of the organics identified to date, and 43.8% of the waste's TOC content. This class of compounds is, therefore, a major contributor to the actual waste's organic content, along with the chelating and complexing agents. Our lab has identified chelator fragments in a variety of mixed wastes, including other defense wastes,^{9, 10} commercial wastes^{6, 10} and environmental leachates of buried nuclear wastes.^{21, 22} Much is known about the chemistry of chelating and complexing agents in mixed wastes, but very little, if anything, is known about the properties of the chelator and complexor fragments.

Latest TOC Accounting and Missing Organics. Reanalysis of the actual waste has boosted the actual waste's TOC accounting to 80.4%, up 5.3% from the original analysis. The increase is due to the many new chelator fragments identified. What about the 19.6% TOC that is still missing? Results of methods validations in parallel studies on other mixed wastes indicate that the analytical procedure described in this study is quite efficient, at least as far as it goes.⁹ However, it is likely that other classes of organics are present in the organic complexant waste; classes for which the analytical procedures used to date do not work. Likely candidates for the missing organics include: very low-MW organic acids, low-MW polar organics and high-MW, or polymeric, species. Low MW organic acids, including oxalate, acetate and glycolate, are used extensively in the nuclear industry and may be present in the waste. Such acids could also be formed from the degradation of complexing and chelating agents. The analytical procedure described in this report would render such low-MW organic acids chromatographable by GC. However, their methyl esters are very volatile and were likely lost in the solvent reduction steps of the sample preparation. Also, there may be low-MW, polar organics, e.g., amines and nitroso compounds, that cannot be esterified by methylation and could, therefore, remain unanalyzable by GC. For example, EDTA is known to degrade to methylamines at higher temperatures (>200°C).¹⁶ Other derivatization reactions, e.g., acetylation and/or silylation, or high-performance liquid chromatography (HPLC) procedures may work for such organics.

Table 1
Organics in Complex Concentrate Mixed Waste

Compound ^(c)	Concentration (mM) ^(a,b)	
	Actual	Simulant
Chelating/Complexing Agents		
Citric Acid	64.4	61.
N-(2-Hydroxyethyl)ethylenediaminetriacetic Acid, (HEDTA) (d)	37.5	10.
Ethylenediaminetetraacetic Acid, (EDTA)	31.4	8.6
Nitrilotriacetic Acid, (NTA)	7.33	6.90
Chelator/Complexor Fragments		
Iminodiacetic Acid, (IDA)	188	101
N-(Methylamine)iminodiacetic Acid, (MAIDA)	28.0	9.2
Ethylenediaminetriacetic Acid (ED3A) (e)	17.9	2.0
N-(Carboxy)ethylenediamine-N', N'-diacetic Acid, (CEDDA) (e)	5.32	
N-(Carboxy)ethylenediamine-N',N'-diacetic Acid, (CEDD'A)	2.73	0.0
N-(Methyl, ethyl)iminocarboxy Acid, (MeEtIC)	2.52	
N-(Ethylene)ethylenediaminetriacetic Acid, (EeED3A)	2.28	
N-(2-Hydroxyethyl)iminodiacetic Acid, (HEIDA) (d)	2.14	0.51
N-(2-Hydroxyethyl)-N'-(methyl)ethylenediamine-N, N'-diacetic Acid, (MeHEDD'A) d)	1.83	0.17
N-(di-ethyl)iminocarboxy Acid, (Et ₂ IC)	1.54	
N-(3-Carboxypropyl)iminocarboxyacetic Acid,(CPICA)	1.12	
N-(Methyliminocarboxy)ethylenediamine-N-acetic Acid, (MICEDA) (e)	1.09	
N-(Ethyl)propylenediaminetriacetic Acid (EtPD3A)	1.09	
Ethylenediaminecarboxytriacetic Acid, (CED3A)	1.08	
N-(3-carboxypropyl)-N-iminoacetic Acid, (CPIA)	1.07	0.21
N-(Ethyl)ethylenediamine-N-acetic-N'-carboxy Acid, (EtEDC'A) (e)	1.02	
Propylenediaminecarboxytriacetic Acid, (CPD3A)	0.91	2.98
N-(Methylamine)-N'-(methyl)ethylenediamine-N',N'-diacetic Acid, (MeMAEDD'A)	0.90	0.8
N-(2-Hydroxyethyliminoacetic)ethylenediamine-N', N'-diacetic Acid, (HEIAEDDA) (d)	0.89	
N-(Hydroxymethyl)ethylenediamine-N', N'-diacetic Acid, (HMEDDA) (e)	0.83	
N-(Ethyl)-N'-(2-hydroxyethyl)ethylenediamine-N-carboxy-N'-acetic Acid, (Et'HEDC'A) (d)	0.77	
N-(Methyl, 2-hydroxyethyl)iminocarboxy Acid, (MeHEIC)	0.67	
N-(Ethyl)ethylenediamine-N', N'-carboxyacetic Acid, (EtEDCA) (e)	0.58	1.8
N-(Ethylene)iminocarboxyacetic Acid, (EtICA)	0.23	
N-(Methylamine)ethylenediaminetriacetic Acid, (MAED3A)	trace	3.43
N-(Methyl)iminocarboxyacetic Acid, (MeICA)	trace	trace
N-(Ethyl)iminoacetic Acid, (EtIA)	trace	
N-[2-(Methylidene)ethyl]iminocarboxyacetic Acid,(MEICA)	trace	
N-(2-Hydroxyethyl)ethylenediamine-N',N'-diacetic Acid, (HEEDD'A)	trace	
N-(Ethyl)iminocarboxyacetic Acid, (EtCA)	trace	

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 (BF₃/Methanol), acids identified as methyl esters. d) Identified as lactone by GC/MS and past GC/FTIR analyses [6-10]. e) Identified as lactam by GC/MS and past GC/FTIR analyses [6-10]. f) Percent total organic carbon (TOC) computed as the ratio: concentration (g C/L) of organics identified vs. nominal concentrations of parent organics added to the simulant.

Table 1 (continued)
Organics in Complex Concentrate Mixed Waste

Compound ^(c)	Concentration (mM) ^(a,b)	
	Actual	Simulant
Chelator/Complexor Fragments (continued)		
N-(methyl)-N,N'-(di-methylamine)ethylenediamine-N'-acetic Acid, (MeD'MAED'A)		4.55
N-(Hydroxy)-N-(carboxy)ethylenediamine-N',N'-diacetic Acid, (HCEDDA)		3.90
N-(Methyl)iminodiacetic Acid, (MeIDA)		2.78
1,1,2-Tricarboxyethane, (3CE)		2.65
N-(Ethyl) iminodiacetic Acid, (EtIDA)		trac
N-(Ethyl)-N,N'-(di-methylamine)propylenediamine-N'-acetic Acid, (EtD'MAPD'A)		trac
N-(2-Carboxyethyl)iminodiacetic Acid, (CEIDA)		trac
N-(2-aminoethyl)ethylenediamine-N'-(Ethylene)-N'-carboxy Acid, (AE'EDEeC)		trace
Monocarboxylic Acids		
Docos-13en-oic Acid	2.50	0.77
Hexadecanoic Acid	2.04	1.2
Tetradecanoic Acid	0.68	0.43
Octadecanoic Acid	0.54	0.8
Hexanoic Acid	trace	
Dicarboxylic Acids		
Hexanedioic Acid	2.04	1.3
Nonanedioic Acid	0.83	
Pentanedioic Acid	0.60	
Tetradecanedioic Acid	0.43	
Hydroxybutanedioic Acid	0.33	
Butanedioic Acid	0.10	
Propanedioic Acid	0.02	
Octanedioic Acid	trace	
Miscellaneous		
nC ₂₃ -nC ₃₅	7.77	
Dibutylphthalate	1.24	0.0
Diethylphthalate	0.05	trac
Unknowns		
MW 188		2.3
MW 230		trac
MW 252		trac
TOC Recovery (%) ^(f)	80.4%	85.5%

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 (BF₃/Methanol), acids identified as methyl esters. d) Identified as lactone by GC/MS and past GC/FTIR analyses [6-10]. e) Identified as lactam by GC/MS and past GC/FTIR analyses [6-10]. f) Percent total organic carbon (TOC) computed as the ratio: concentration (g C/L) of organics identified vs. nominal concentrations of parent organics added to the simulant.

Polymers may also account for the missing TOC. They are occasionally used in nuclear operations, e. g., flocculating agents such as polyacrylamides and chelating agents such as Dow Chemical's NS-1. Organopolymers could also be formed from the degradation of the waste's organics. Polymeric, nonvolatile organics are not amenable to GC analysis, which requires volatilization into the gas phase. HPLC, utilizing steric exclusion chromatography, would probably be the method of choice. Recent advances in HPLC-MS and supercritical fluid chromatography-MS (SFC-MS) instrumentation may facilitate the identification of the nonvolatile organics, just as GC/MS analysis has made rigorous identification of gas chromatographable organics like the chelator fragments possible.

Simulated Organic Complexant Waste

Parent Organics

All four of the parent organics were identified in the simulated waste after 90 days of storage in the dark at ambient temperature, but not at the original concentrations. The recovery of citrate was highest at 96.6%, reflecting a loss of 3.4%. In comparison, 5.9 % of the NTA disappeared. The biggest losses occurred with EDTA (72.1% loss) and HEDTA (71.6% loss). The experimental error ranged from 5-10%. The relative stabilities of the parent compounds are clearly different, with EDTA and HEDTA being much more labile. The significant losses of EDTA and HEDTA in the simulant strongly suggest that extensive organic degradation is capable of occurring in the actual waste, even under extremely mild conditions used. Apparently, radiolysis is not necessary to degrade EDTA and HEDTA extensively, suggesting that waste chemistry alone, without radiolysis, is a major force in organic degradation in mixed wastes. The results of a parallel time study on chemical degradation of chelating and complexing agents in a simulated waste confirm this observation.²³

Chelator and Complexor Fragment Formation

Twenty different chelator fragments were identified in the simulant, ranging from 101 mM to a trace (Table 1). The actual waste contained more chelator fragments (38), not surprising given the age of the waste (20+ years) and the contribution of radiolysis to its organic degradation. In general, the chelator fragment composition of the simulant is remarkably similar to that of the actual waste. For example, the two most abundant chelator fragments in the simulant, IDA and MAIDA, were also the most abundant fragments in the actual waste. The chelator fragments represent 47.9% of the organics identified in the simulant. Clearly, chemical degradation can be extensive, and the formation of chelator fragments very important.

Five carboxylic acids, four mono- and one dicarboxylic, were also identified in the simulant, accounting for 28.8% of the organics identified in the simulant. These compounds are presumably derived from the degradation of citrate and the carbon moieties in the nitrogen-containing chelating agents. Interestingly, virtually every monocarboxylic acid identified in the simulant was also present in the actual waste. In contrast, most of the dicarboxylic acids identified in the actual waste are missing in the simulant, suggesting that increased storage time and/or radiolysis is necessary for their formation. Detailed simulation studies will have to be conducted to explore these possibilities.

TOC Accounting in the Simulated Waste

The various organics identified in the simulant account for 85.5% of the TOC originally added as the parent organics. This recovery is significant and encouraging for several reasons. First, the high recovery argues that our experimental strategy is capable of accounting for much of the chelating and complexing agent degradation. Results of parallel studies support this conclusion.⁹ Second, the simulant's TOC recovery is similar to that of the actual waste (80.4%). This similarity argues that most of the missing TOC content is likely due to unanalyzable degradation products than to other parent organics, e. g., polymers, none of which were added to the simulant. More methods development and exploratory analyses on actual and simulated wastes will have to be performed to test this speculation. Nevertheless, a prudent next step in the exploratory analysis of mixed wastes would be to look for other classes of degradation products of chelating agents, e. g., amines and nitroso compounds.

Concluding Remarks

Comparison of the actual and simulated waste analyses confirms that the chelator and complexor fragments identified in the actual organic complexant waste are clearly remnants of parent organics, originally added to the actual waste in reprocessing campaigns. Considerable research indicates that chelating and complexing agents may complicate the management of nuclear wastes because they chelate metal strongly,^{19, 20} thereby destabilizing waste forms, e.g., cementitious grouts, or by interacting with and enhancing the environmental mobility of certain radionuclides leached from buried wastes by groundwater.^{13, 21, 22, 24, 25, 26} The chelator and complexor fragments, like their parent compounds, may, in some cases, destabilize waste forms or enhance the environmental mobility of radionuclides, perhaps even more so than the parent organics themselves.¹⁶ Moreover, the formation of gases like CO₂, CO, and H₂ during organic degradation may result in volume expansion, release of toxic gases, or development of potentially explosive systems.³

The chelator and complexor fragments identified in both the actual and simulated wastes account for the majority of the wastes' TOC contents. Moreover, their abundance and diversity in the simulant argues that the actual's waste's harsh chemistry, e. g., extremely high pH and ionic strength, is enough to generate them. However, a parallel radiolysis study on another simulant indicates that radiolysis causes even more extensive and varied organic degradation.¹⁸ Clearly, the organic content of nuclear wastes is dynamic, not static. This situation may complicate waste management efforts.

More studies, both on actual and simulated wastes, are needed to characterize organic degradation and to assess its real impact on the management of mixed wastes. The use of simulated mixed wastes like the one described in this study means that such studies can be carried out in a controlled laboratory setting. This approach also means that undergraduates may begin training in mixed waste management at the university, earlier than otherwise possible, without the hazards of radiation exposure early in their training.

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