Mechanisms and Kinetics of Organic Aging in High-Level Nuclear Wastes

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Research Objective

Specific DOE problems addressed by this project concern issues arising from organic chemicals in highly radioactive wastes stored at Hanford and Savannah River DOE sites. The organic chemicals, including complexants, are relatively energy-rich such that their presence in nitrate-rich wastes is a potential safety issue. The organic chemicals degrade by radiolytic and thermal pathways to a wide range of species including flammable and toxic gases (H₂, N₂, NH₃, and organic vapors) that also pose safety hazards. Organic complexants interfere with removal of radionuclides during pretreatment to produce low-level waste feed to treatment facilities. The reducing characteristics of organic chemicals cause changes in oxidation states of metal ions, altering metal ion solubility and adversely affecting pretreatment goals. Also, knowledge of the organic degradation products likely to be present in wastes is needed to develop analytical methods to address DOE and regulatory agency requirements for water.

The objective is to develop basic understanding of organic degradation reactions that occur in HLW and assemble models that describe rates and products of degradations. Emphasis is placed on the reactions of complexants and their associated degradation product.

Research Progress and Implications

This report summarizes work after 1.5 years of a 3-year project. The work divides into (1) studies of reactions that initiate by, or originate from, radiation effects (2) studies of thermally-activated reactions that occur in the absence of radiation, and (3) use of computational methods to characterize reaction intermediates. Information obtained has been instrumental in closing tank safety issues at the Hanford site.

1. The study of radiation-induced organic degradation is closely coordinated with other EMSP projects that work to understand radiation effects in homogeneous solutions (“The NO₅ System in Nuclear Waste,” D. Meisel, P.I.) and at interfaces with oxides and solid sodium nitrate (“Interfacial Radiolysis Effects in Waste Tank Characterization,” T. Orlando, P.I.). These projects show that due to the high concentrations of sodium nitrate and nitrite in HLW, radiation from radionuclide decay ultimately generates NO₅ radicals. Since little is known of the reactions of NO₅ with organic chemicals in HLW, the work focuses on elucidating these reactions. Products and rates of reactions are measured by contacting NO₅ with aqueous solutions containing organic solutes. From the products and analogies to related systems, reaction mechanisms are inferred and quantitative kinetic models constructed.

2. Of the major complexants used in Hanford nuclear materials processing, only HEDTA and glycolate are readily oxidized by thermal reactions to give flammable gases. Nitrite ion supplies the oxidizing equivalents while aluminate ion or other aluminum species is a catalyst. Prior investigations (Ashby et al. ACS Symp. Ser. 1994. 554, 247-283) proposed that aluminate ion
catalyzes the nitrosation of alcohol functional groups in glycolate and HEDTA. The so-formed organic nitrite ester then degrades yielding precursors to $\text{H}_2$, $\text{N}_2\text{O}$, and $\text{NH}_3$. Recent tests conducted by this project contradict this mechanism. The rates of saponification of EtONO (a model for HEDTA) and nitritoacetate (nitrite ester of glycolate ion) were measured in the absence and presence of aluminate ion and no enhancement of rate was observed with aluminate. If aluminate catalyzes formation of RONO from nitrite ion and ROH, then it should catalyze the reverse reaction, i.e., saponification of RONO. Therefore, alternative mechanisms are required to explain and ultimately predict the thermal reaction kinetics. One such mechanism under consideration is that suggested by Stock (PNNL-11702 Rev. 1, 1997) in which aluminum ion binds both ROH and nitrite ion, thereby fostering intramolecular hydrogen transfer and electron transfer reactions.

3. Solution properties of organic intermediates are being characterized by theoretical methods in collaboration with computational chemists at PNNL’s Environmental Molecular Science Laboratory and at the Notre Dame Radiation Laboratory. Computational methods complement experimental measurements, guide future experiment, and provide thermochemical data that cannot be easily measured. The initial work is evaluating newly developed quantum-mechanical dielectric-continuum models for characterizing solvated radicals, ions and zwitterions relevant to organic tank chemistry.

**Planned Activities**

Work will continue on the above 3 efforts. Rates and products of NO$_2$ reacting with larger organic structures in alkaline solutions will be measured and the data incorporated into predictive kinetic models. The investigation of thermally-initiated aluminum-catalyzed oxidations will shift focus to testing new mechanisms for oxidation of glycolate, HEDTA and related structures. Computational work will survey the ability of solvation models to reproduce solution properties of 1- and 2-carbon systems. If satisfaction is obtained from available methods, calculations will extend to the relevant polyfunctional systems.

**Information Access**