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Interfacial Radiolysis Effects in Tank Waste Speciation

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Research Objective

The purpose of this program is to deliver pertinent, fundamental information that can be used to make technically defensible decisions on safety issues and processing strategies associated with storage and clean up of DOE mixed chemical and radioactive wastes. The radioactive and chemical wastes present in DOE underground storage tanks contain complex mixtures of sludges, salts, and supernatant liquids. These "mixtures," which contain a wide variety of oxide materials, aqueous solvents, and organic components, are constantly bombarded with gamma quanta, beta and alpha particles produced via the decay of radioactive isotopes. Currently, there is a vital need to understand radiolysis of organic and inorganic species present in mixed waste tanks because these processes: *a) produce mixtures of toxic, flammable, and potentially explosive gases (i.e., H_2, N_2O and volatile organics) b) degrade organics, possibly to gas-generating organic fragments, even as the degradation reduces the hazards associated with nitrate-organic mixtures, c) alter the surface chemistry of insoluble colloids in tank sludge, influencing sedimentation and the gas/solid interactions that may lead to gas entrapment phenomena.*

Research Progress and Implications

This report summarizes the technical achievements of a 3-year project that is now in its 2nd year. Progress in three areas is reported: 1) radiation effects at $NaNO_3$ crystal interfaces, 2) reactions of organic complexants with NO_2 in water, and 3) radiation effects in oxide particles. The research disclosed in this report is the result of collaborations between the listed investigators, who closely coordinate their efforts on this project, another EMSP project located at ANL ("The NO_x System in Nuclear Waste," PI: D. Meisel) and a project in the Tank Waste Safety Program at the Hanford Site ("Waste Aging Studies Project," PI: D. M. Camaioni).

Radiation Effects at Crystalline $NaNO_3$ Interfaces: The low energy (5-100 eV) electron-stimulated desorption (ESD) of neutrals from $NaNO_3$ single crystals is compared with our previous state-resolved 193 nm (6.4 eV) photon-stimulated desorption (PSD) study. The PSD study demonstrated that excitation of $NaNO_3$ interfaces with 193 nm photons (6.4 eV) results in the stimulated desorption of predominantly $NO(^2?)$ and $O(^3P_J)$. The 6.4 eV valence band excitation in $NaNO_3$ solids/interfaces has been correlated with the $NO_3^-\pi^*\leftarrow\pi$ band, and is below the nominal band gap energy of ~8 eV. Excitations of this band create localized excitons, which couple to phonons and trap at surface and/or defect sites. Decomposition of these excitons results in the direct desorption of both thermal and non-thermal $NO(^2\Pi)$ and $O(^3P)$.

The controlled low-energy electron-beam irradiation studies carried out in this EMSP program also demonstrate that $NO(^2\Pi)$ and $O(^3P_J)$ are the primary direct neutral desorption products. In addition to NO and O, some $O_2(g)$ and $NO_2(g)$ are produced from both 100 eV ESD and 193 nm PSD. Unlike NO and O, we believe that $O_2(g)$ and $NO_2(g)$are produced indirectly and do not represent direct products of $NaNO_3$ radiolysis. In fact, the NO_2 data are well fit by a Maxwell-Boltsmann distribution at the $NaNO_3$ surface temperature of 423 K, indicating interaction with the surface prior to desorption. In contrast, both the O and NO velocity distributions are *non-thermal*, with a significant portion of their populations "hotter" than the $NaNO_3$ surface temperature. The product yields and $NO(^2\Pi)$ and $O(^3P_J)$ velocity distributions obtained from ESD and PSD are essentially identical. Therefore, the final states involved in ESD and PSD must be similar. *This is an important result since it allows us to*

initiate "radiation" induced processes at $NaNO_3$ interfaces by selectively exciting the $NO_3^-\pi^*\leftarrow\pi$ band.

We conclude from these experiments that the primary direct radiolysis products of $NaNO_3$ solid surfaces are NO, O, and O^-(sf). Secondary (indirect) radiolysis products are O_2 and NO_2. The latter are formed below the surface in the bulk crystal, but may diffuse to the surface and react with interfacial species. The generation of strongly oxidizing radicals, O and O^-, and NO at $NaNO_3$ interfaces is important since organic radicals generated at the interface can react with NO to produce nitrogen-containing organic species. The decay of these species can lead to the production of HNO (NO^- in aqueous conditions) which can undergo recombination reactions and directly yield N_2O(g). The importance of this interfacial reaction pathway is currently being investigated by controlled electron-beam induced radiolysis of $NaNO_3$ surfaces containing multilayers of CH_3OH. Methanol radicals, $HOCH_2$• and CH_3O•, are generated from both direct interactions of CH_3OH with energetic electrons and reactions with oxidizing radicals, O and O^-(sf), That are generated by electron impact of the nitrate interface. The methanol radicals are expected to react with NO that is generated concurrently by electron impact of the nitrate interface. These reactions should produce N_2O, or its precursor, as well as other compounds that may degrade to nitrogenous and H_2 gases in tank wastes.

Reactions of Model Organic Complexants with NO_2 in Water: Radiolysis of homogeneous aqueous waste solutions generate primarily OH/O^- and NO_2. Since nitrite concentrations are high in aqueous wastes, a significant fraction of the O^- generated at the solution crystal interfaces will probably convert to NO_2. Therefore, reactions of NO_2 with organic species in solution are being studied. Though NO_2 is one of the dominant oxidizing radicals generated by radiation effects on nuclear waste, there is little knowledge of its reactions with organic compounds that were used in nuclear materials processing and stored in waste tanks. Waste aging studies have been performed at the Hanford Site to explain waste characterization data and predict effects of organic aging on the potential combustion hazards of organic containing nitrate-rich wastes. These studies simulated waste aging by gamma-irradiating non-radioactive waste simulants. We are performing complementary experiments in this EMSP project to verify the role of NO_2 and to elucidate reaction kinetics and products for development of mechanistic kinetic models. The experiments contact aqueous alkaline solutions of organic species with N_2 containing <100 ppm NO_2. The NO_2 dissolves in the solutions and hydrolyzes competitively with reduction by organic solutes. Preliminary experiments have surveyed the reactions of nitrilotriacetate (NTA), iminodiacetate (IDA), glycine, and formate. Products were analyzed using ^1H and ^{13}C nuclear magnetic resonance spectroscopies and ion chromatography. The results show that NTA degrades via stepwise dealkylation giving mainly formate, carbonate and oxalate. Formate degrades to carbonate when reacted with NO_2, but at a slower rate. Relative reactivities from competition experiments show NTA>IDA>glycine>formate. We note that very similar results have been obtained in Hanford Waste Aging Studies that irradiated simulated waste solutions that contained these compounds. Therefore, the NO_2 contact experiments appear to corroborate our view that NO_2 is a dominant species responsible for radiolytic oxidation of organic chemicals in DOE tank wastes at Hanford and Savannah River sites.

Radiation Effects in Oxide Particles: To begin studying radiation chemical effects in solutions containing colloidal oxide particles, pulsed radiolysis studies of silica-loaded aqueous solutions were carried out at ANL. These pulse radiolysis studies indicate that absorption of the radiation in the solid particles may lead to the transfer of charge across the particle-liquid interface and initiate chemistry at the interface and in the surrounding solution. Since the fraction of energy (ionizing radiation) absorbed by the particles increases with loading, this observation suggests that the absorption of radiation by the solid particles causes electrons to be ejected into the surrounding solution. If the radiation effects were localized within silica particles, the yield of solvated electrons should decrease. Instead, the yields follow the average sample densities that are calculated from particle concentrations and the density of silica. The results have many practical implications. For high level radionuclides stored in suspensions in large tanks, the presence of the particles will promote generation of water radiolysis products (of particular concern is H_2) in the vicinity of the particles. This may increase the probability of retention of products near the particles, e.g. by gas-bubble attachment to the particle, and may lead to serious safety concerns.

Concluding Statements: *The implication to tank waste chemistry of the above research on interfacial radiolysis effects is that radiation absorbed by solid waste components ($NaNO_3$ crystallites and metal oxide particles) will result in chemistry at waste interfaces and in solution phases.* Therefore, heavily solids-laden wastes may contribute, not deter, radiolytic aging. Radiolysis of both the solid and liquid-phase clearly contribute to the production of species which are involved in the generation of gases such as H_2, N_2O and NH_3.

Planned Activities

The project will continue activities in the above areas. At PNNL, radiolytic processes occurring at $NaNO_3$ crystal interfaces with organic overlayers will be studied using ESD techniques. Initial experiments will condense thin layers of methanol on a $NaNO_3$ crystal and irradiate with 100 eV electrons. Then, the crystal will be slowly warmed to desorb the organic layers into a mass spectrometer to detect and identify products. Experiments will also start studies of solutions using a novel apparatus that inject beams of liquids into a vacuum chamber where the beams are irradiated and radiolysis products are detected using mass spectrometers and sensitive laser diagnostics. Solutions to be studied will include aqueous $NaNO_3$ and metal oxide colloids. In collaboration with the ANL EMSP project, "The NO_x System in Nuclear Waste," we will continue studies to elucidate mechanisms of NO_2 oxidations of organic complexants and measure relative rate constants using a reactive dissolution apparatus that passes dilute (ppm) concentrations of NO_2 through aqueous solutions of substrates. Substrates targeted for study include aminocarboxylates, glycolate, acetate, and formate. At ANL, studies of the effects of particles on radiolytic yield will continue. Attention will focus on the fate of holes that are initially generated in the particle. The research will try to determine if they migrate to the aqueous phase, similar to the electrons, or remain on the solid and its surface.

Other Access To Information

This project and the ANL EMSP project, "The NO_x System in Nuclear Waste," are strongly coupled with the "Waste Aging Studies" project at the Hanford Site such that the basic studies are performed at ANL and PNNL and the information is continuously shared with the Tank Waste Safety Program. Information from the projects is also shared directly with Westinghouse Savannah River personnel. To further facilitate the exchange of information and the immediate incorporation of results into operations, we conduct at least semi-annual "coordination meetings" in which the site operators (e.g. from DE&SH, Numatec, WSRC, etc.) participate both as contributors and observers. In addition, we participate in national and international meetings of scientific societies, e.g. the American Chemical Society, the Electrochemical Society, and the American Physical Society.

Program Publications and Presentations

"Chemistry, Radiation, and Interfaces In Suspensions Of Nuclear Waste Simulants," D. Meisel, A. Cook, D. Camaioni, and T.M. Orlando, in "Photoelectrochemistry", Ed. K. Rajeshwar, L.M. Peter, A. Fujishima, D. Meissner, M. Tomkiewicz, The Electrochemical Society Pub., Vol. 97-20, 350-7 (1997).

"Low-energy (5-100 eV) Electron and Ultraviolet (6.4 eV) Photon-stimulated Desorption of Neutral Fragments from $NaNO_3$ Single Crystals," K. Knutsen, and T.M. Orlando, *Appl. Surf. Sci.* in press.

"Charge Carrier Transfer Across The Silica Nanoparticle/Water Interface," T. Schatz, A. R. Cook, and D. Meisel, *J. Phys. Chem.*, Submitted for publication

"Quantum-Resolved Studies of Electron-Stimulated Processes in Wide Band-Gap Materials", T.M. Orlando, M.T. Sieger , W.C. Simpson, and K. Knutsen, International Conference on Desorption Induced by Electronic Transitions (DIET) VII, Ambleside UK, April 8-11, 1997.

"UV Photon- and Low-Energy (5-100 eV) Electron-Stimulated Processes at Environmental Interfaces", T.M. Orlando, M.T. Sieger, W.C. Simpson, D.P. Taylor, and K. Knutsen, The 24th IEEE International Conference on Plasma Science, San Diego, CA, May 19-22, 1997.

"A Comparison between UV-Photon and Low-Energy Electron-Stimulated Desorption Processes from Wide Band-Gap Materials", T.M. Orlando, D.P. Taylor , W.C. Simpson, and K. Knutsen, The Fourth International Conference on Laser Ablation, COLA '97, Monterey, CA July 21-25, 1997.

"Some Fundamental Studies on the Effects of Radiation and Interfaces in High Level Wastes," D.M. Camaioni, D.M., K. Knutsen, J.C. Linehan, T.M. Orlando, A. Cook, and D. Meisel, Symposium on *Future Directions in Radioactive and Mixed Waste Management*, 214th ACS National Meeting, Las Vegas, NV September 8, 1997.