Interfacial Radiolysis Effects
in Tank Waste Speciation

Progress Report

Principal Investigator

T.M. Orlando
(509) 375-6404 (Phone)
(509) 375-6442 (Fax)
tm_orlando@pnl.gov
Pacific Northwest National Laboratory
PO Box 999, MSIN K2-14
Richland, WA 99352

Contributors and Collaborators

D.M. Camaioni (PNNL)
K. Knutsen (AWU - Post Doctoral Fellow)
D. Meisel (ANL)

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 mixed chemical and radioactive waste cleanup. In particular, an understanding of radiolysis in mixed-phase systems typical of U.S. Department of Energy (DOE) heterogeneous, radioactive/chemical wastes will be established. This is an important scientific concern with respect to understanding tank waste chemistry issues; it has received relatively little attention. The importance of understanding solid-state radiolysis, secondary electron interactions, charge-transfer dynamics, and the general effect of heterogeneous solids (interface and particulate surface chemistry) on tank waste radiation processes will be demonstrated. In particular, we will investigate i) the role of solid-state and interfacial radiolysis in the generation of gases, ii) the mechanisms of organic compound degradation, iii) scientific issues underlying safe interim storage, and iv) the effects of colloid surface-chemical properties on waste chemistry.

Research Statement

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 energetic particles produced via the decay of radioactive ^{137}Cs and ^{90}Sr. Currently, there is a vital need to understand radiolysis of organic and inorganic species present in mixed waste tanks because these processes:

- produce mixtures of toxic, flammable, and potentially explosive gases (i.e., H_2, N_2O and volatile organics)

- degrade organics, possibly to gas-generating organic fragments, even as the degradation reduces the hazards associated with nitrate-organic mixtures

- alter the surface chemistry of insoluble colloids in tank sludge, influencing sedimentation and the gas/solid interactions that may lead to gas entrapment phenomena.

Unfortunately, the mixed chemical and radiolytic nature of the problem greatly complicates the interactions and the information available on radiolytic processes in multiphase heterogeneous systems is insufficient to develop either accurate safety margins or radiolysis models that adequately describe DOE tank waste chemistry to support technically sound decision making.

Research Progress

Controlled radiolysis studies of $NaNO_3$ solids and SiO_2 particles were carried out using pulsed, low- (5-150 eV) and high- (3 MeV) energy electron-beams at Pacific Northwest National Laboratory (PNNL) and at Argonne National Laboratory (ANL), respectively. The pulsed, low-energy electron beams probe the inelastic scattering and secondary cascading effects produced by high-energy beta and gamma particles. Pulsed radiolysis allows time-resolved measurements of the high-energy processes induced by these particles.

Using low-energy (1 0-75 eV) electron-beam irradiation of "nominally" dry $NaNO_3$ solution-grown and melt-grown single crystals, we observed H^+, Na^+, O^+NO^+, NO, NO_2, O_2, and $O(^3P)$ desorption signals. Our threshold measurements and yields indicate that the degradation proceeds mainly via destruction of the nitrate moiety. The H^+ and Na^+ yields are primarily related to the presence of water and Na metal, Na hydrides and oxides, or other defect sites on the salt surface. The water is due to diffusion from the bulk of solution-grown crystals and controlled water adsorption on melt-grown crystals. The metallization and/or metal hydride/oxide build-up is a result of the very large electron-beam degradation cross-section ($>10^{-16}$ cm^2) of $NaNO_3$.[1] The build-up of alkali-metal colloids during the irradiation of alkali-halide materials is well known[2] and is expected for other alkalai salts such as $NaNO_3$. Figure 1 shows the Na^+ desorption yield as a function of incident electron energy. The signal below the 33 eV is all due to Na buildup and the break seems to be associated with charge build-up, band-bending, and then charge release. Charge trapping and metallization is reduced at temperatures above 420 K,[1,3] a temperature higher than typically found in high-level liquid waste (HLLW) tanks.
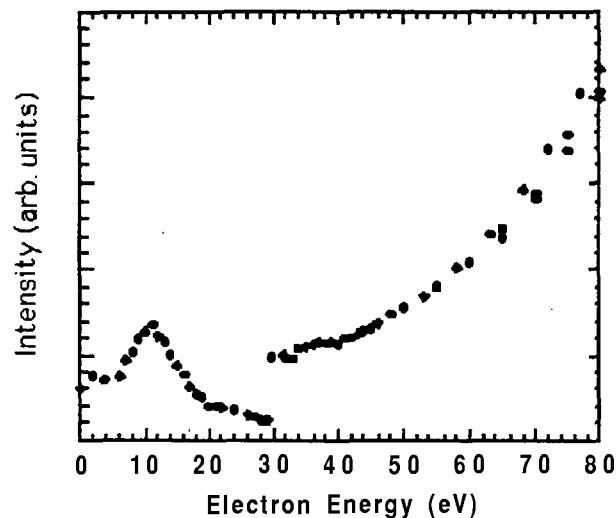

Figure 1. The Na^+ desorption yield as a function of incident electron energy. The data were obtained from an electron-beam damaged $NaNO_3$ crystal at room temperature.

The HLLW tanks contain a large fraction of solid components (colloids and salt cakes with enormous interfacial surface areas) and radiation-induced metallization may occur in the bulk. It is well known that the reaction of metallic sodium with water produces hydrogen gas and heat. We do not yet know whether mechanisms leading to sodium metallization at crystal-vacuum interfaces occur at crystal-water interfaces, but alternative processes involving charge transfer or energy transfer from crystal to interfacial water molecules still may provide pathways for hydrogen gas production. Thus, further work is underway to investigate the amount of molecular hydrogen produced during direct radiolysis of nitrate salts containing adsorbed and interstitial water.

Previous work[3] at PNNL has also demonstrated that excitation of $NaNO_3$ interfaces with 193 run photons (6.4 eV) results in the stimulated desorption (PSD) of predominantly $NO(^2\Pi)$ and $O(^3P_J)$. The 193 nm (6.4 eV) valence band excitation in $NaNO_3$ solids/interfaces has been correlated with the $NO_3^- \pi^* \leftarrow \pi$ and, and is below the nominal bandgap 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 $O(^3P)$. We favor a mechanism in which surface excitons decay to produce $NO(g) + O(g) + O^-(sf)$, either in one step, or via an NO_2^*- intermediate. This intermediate is consistent with the observation of NO_2^- as a primary bulk radiolysis product.[4,5] We have extended these studies under the EMSP program using low-energy electron-beam irradiation, and again observe $NO(^2\Pi)$ and $O(^3P_J)$ as the primary direct neutral desorption products. Figure 2 shows that the electron energy thresholds for O and NO production are between ~6-8 eV, which corresponds to the $\pi^* \leftarrow \pi$ band, but also overlaps the charge-transfer/ conduction band-transition in $NaNO_3$. In addition to the above-mentioned exciton dissociation channels, removal of an electron from the NO_3^- valence band results in the production of NO_3^*,
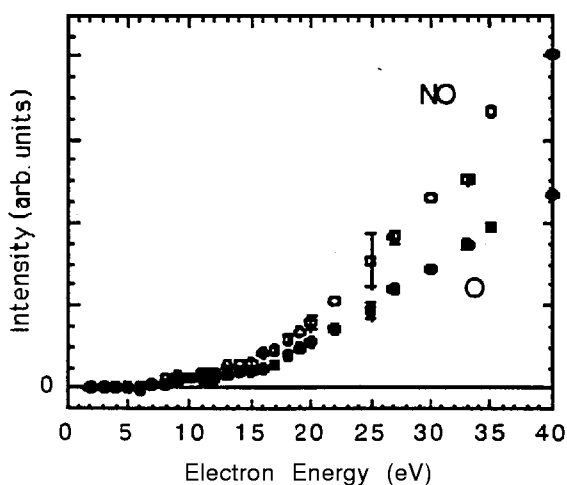

Figure 2. The threshold incident electron energies for the stimulated production and desorption of NO and O from $NaNO_3$ interfaces.

which can then dissociate to the neutral products detected. At incident energies above the conduction band, localization of secondary electrons at nitrate defect sites could result in the production of an excited species NO_3^{*2-} which, though stable in the bulk, can decay at the surface via a process known as dissociative electron-attachment to form $NO_2^* + O+$ e and $NO + O_2^*$ + e. The NO_2^* and O_2^* can further dissociate to form O^-, which can trap at the surface or in the bulk.

In addition to NO and O, some $O_2(g)$ and $NO_2(g)$ are produced from both electron stimulated desorption (ESD) and 193 nm PSD of $NaNO_3$. The relative time-dependent yields for NO, O_2, and NO_2 are displayed in Figure 3. Unlike NO and O, we believe these latter species are produced indirectly and do not represent direct products of $NaNO_3$ decomposition. In fact, the NO_2 data are well fit by a Maxwell-Boltmann distribution at the $NaNO_3$ surface temperature of 423 K, indicating interaction with the surface prior to desorption. Neither NO_2 nor O_2 shows the "hot" temperature component we observe in both NO and $O(^3P)$, but both show a 1-electron dependence upon electron fluence. Thus, they may result from ESD processes at defect sites (such as $NO_2^- + e \rightarrow NO_2 + 2e$), or from secondary reactions of the primary products (such as $O + NO_3^- \rightarrow O_2 + NO_2^-$). They are most likely not formed from recombination of the direct NO and O desorption products.
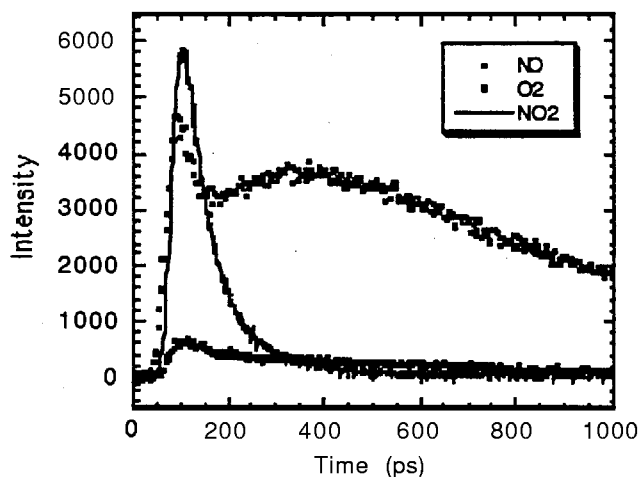

Figure 3. The NO, O_2, and NO_2 desorption yields from 100 eV ESD of $NaNO_3$. All signals have been adjusted for cracking in the quadrupole.

Comparison of 100 eV ESD and 193 nm PSD data shows that the velocity and state distributions of the neutral desorption products are very similar. The NO is clearly the predominant desorption product from both of these processes, with O_2 yields typically a factor of 10 smaller. The NO_2/NO yield ratio, however, is a factor of ~2 higher from ESD (~1/6) as opposed to PSD (~1/12). Our results clearly show that inter-facial radiolysis leads to the production of several reactants and oxidants, particularly Na, NO, and oxygen, which are difficult

to rationalize by homogeneous radiolytic models and may provide ready explanations to some observations in the tank.

Earlier studies at ANL on Hanford grout samples raise the possibility of gas generation from water in the pores by radiation that is absorbed by the solid concrete! Recent studies at PNNL on tank waste simulants addressed this issue, but the results were not conclusive.[7] Therefore, pulse radiolysis studies were initiated at ANL to address this question: can energy absorbed by solid particles dispersed in the aqueous phase escape the solid and lead to gas generation from the aqueous solution? Pulse radiolysis studies at the silica/water interface indicate that absorption of the radiation in the solid may lead to the appearance of charge at the liquid phase. This is demonstrated in Figure 4, which shows the absorbance by hydrated electrons (thus, by definition, are in the aqueous phase) following pulse irradiation of a sample containing 0% or 50% by weight SiO_2 particles. The decrease in the amplitude of the solvated electrons absorption is minimal despite the fact that the solids fraction increases considerably. These preliminary results seem to indicate that the yield of electrons in the liquid phase depends on both the solid and liquid fraction and does not necessarily decrease with decreasing water content. To date up to 60% weight of silica (in contact with glycerin to obtain refractive-index matching) was found to induce only a small reduction in the yield of solvated electrons. (These are thermal electrons that are stabilized by their hydration shell. In practical terms, they may generate hydrogen atoms or initiate other fuel-generating reduction processes.) Furthermore, our preliminary results indicate that this phenomenon may depend on particle size. It may be recognized that grout (or saltstone) may contain as much as 30% by weight water and our simulant comes close to this environment.
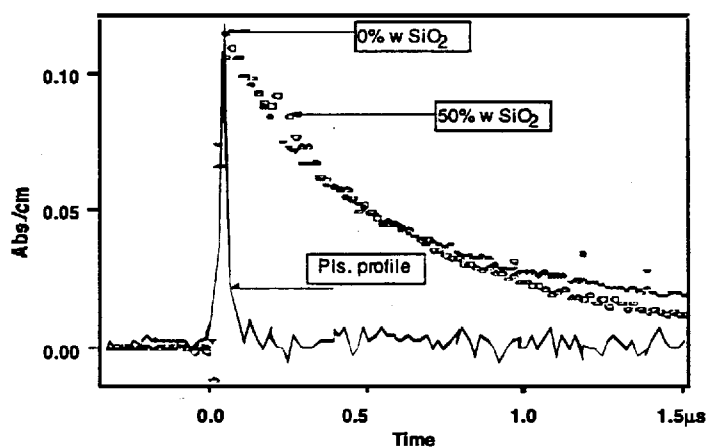

Figure 4. Histograms (absorbance vs time) of the decay of the solvated electrons in suspensions of SiO_2. Solid points - No silica. Open points - 50 wt. % silica.

In summary, the primary direct radiolysis products of $NaNO_3$ solid surfaces are NO, O, O[-], and Na. Secondary (indirect) radiolysis products such as O_2, NO_2, NO_2^-, NO_3^{2-}, NaO, NaH, and NaOH can also form in the bulk. The O_2 and NO_2 can then diffuse and react with inter-facial

species. High energy, pulse radiolysis studies at the silica/water interface produce solvated electrons and the yield seems independent of the water fraction. The solvated electrons and ionic and neutral desorption products are very reactive in the aqueous environment and are important in solution phase and interfacial reactions. As pointed out in an earlier study at ANL,[8] it is likely that NO reactions with organic radicals lead to the production of $N_2O(g)$ and $NH_3(g)$ in Hanford tank wastes. Thus, the electron-stimulated reactions of the desorption products, such as NO, NO_2, O,O_2, and Na-metal with water and organic radicals at salt interfaces are currently under further investigation.

References

1. Knutsen, K., and T.M. Orlando, *1996, Surf. Sci.,* 348: 146.

2. Weerkamp, J.R.W, J.C. Grootee, J. Seinen, and H.W. den Hartog, 1994, *Phys. Rev. B.* 50:9781.

3. Knutsen, K., and T.M. Orlando, 1997, In press, *Phys. Rev. B.,* May 15, 1997 issue.

4. Cunningham, J., in: "Radical Ions," eds. E. T. Kaiser and L. Kevan *(Inter-science, New* York, 1968) pp. 475-523.

5. Cunningham, J., and L.R. Steele, 1962, *Phys. Rev. Lett.* 9:47.

6. Jonah, C.D., S. Kapoor, M.S. Matheson, W.A. Mulac, and D. Meisel, 1994, Gas *Generation from Hanford Grout Samples,* ANL-9417, Argonne National Laboratory, Argonne, Illinois.

7. Bryan S.A., and L.R. Pederson., 1995, *Thermal and Combined Thermal and Radiolytic Reactions Involving Nitrous Oxide, Hydrogen, and Nitrogen in the Gas Phase; Comparison of Gas Generation Rates in Supernate and Solid Fractions of Tank 241-SY-101 Simulated Waste,* PNL- 10490, Pacific Northwest Laboratory, Richland, Washington.

8. Miesel, D., C.D. Jonah, S. Kapoor, S. Matheson, and M.C. J. Sauer, 1993, *Radiolytic and Radiolytically Induced Generation Gases from Synthetic Wastes,* ANL-93/43, Argonne National Laboratory, Argonne, Illinois.