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Project Title: Interfacial Radiolysis Effects in Tank Waste Speciation

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Number of post-doctoral fellows and visiting scientists actively involved in the project: 2 PDF's and 3 Visiting Scientists

Specific DOE problems that are being addressed by your project, and potential practical relevance to improved knowledge, techniques, processes, or technology.

The project meets several major DOE/EMSP needs for the mixed radioactive/chemical waste tanks: *i) improved understanding and prediction of toxic, flammable, and potentially explosive gas production (i.e., H₂, N₂O and volatile organics); ii) investigation of fundamental chemistry of radiation/chemical organics degradation; iii) basic studies of the surface chemistry of insoluble colloids in tank sludge, influencing sedimentation and the gas/solid interactions that may lead to gas entrapment phenomena.*

Research objective.

The intent of this program was to establish an understanding of the role of solid-state radiolysis, secondary electron interactions, charge transfer dynamics and the general effect of heterogeneous solids (interfaces and particulate surface chemistry) on tank waste radiation processes. Specifically, there was a need to understand the role of interfaces and solids in the generation of noxious gases and the mechanisms of organic compound degradation.

Research progress and Implications.

This report summarizes work after 3 years of a 3-year project.

- The interaction of ionizing radiation with nitrate and nitrite solids can contribute to the production of noxious gases in mixed-waste tanks. Low energy (5-100 eV) electron-beam induced gas generation from NaNO₃ surface is examined using laser resonance enhanced multiphoton ionization detection of the neutral desorption products, post irradiation temperature programmed desorption, secondary electron emission microscopy and Auger electron spectroscopy. The damage initially involves destruction of the nitrate group, decay of {NO₃}^{*} and production of non-thermal O and NO fragments. At higher electron fluences, thermalized NO and O₂ are also produced supposedly due to unimolecular dissociation of NO₃^{*}. NO₂ is also detected as a minor product. O₂ gas is found escaping from the irradiated NaNO₃ in thermal cycling, and is associated with thermal decomposition of several radiation defects. *These oxidants contribute to the degradation of organic waste constituents but also help initiate the generation of flammable gas.*
- Charge transfer across the silica nanoparticle/water interface was studied by picosecond pulse

radiolysis utilizing 20 MeV electrons. For the 7 - 22 nm silica particles studied, essentially all electrons generated in the silica cross the interface and appear as hydrated electrons. Organic molecules (methyl viologen) adsorbed on the silica nanoparticle surface capture these "interfacial" electrons very effectively. For high-level radionuclides stored in suspensions, the presence of particles could 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 safety concerns.

- Radiolytically produced NO_2 is shown as the dominant oxidant, promoting aging of the organic component of the mixed waste. Reactions of model organic complexants with NO_2 in water were studied in detail. The results show that nitrilotriacetate (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 $NTA > \text{iminodiacetate (IDA)} > \text{glycine} > \text{formate}$. The rates of production of carbonate and nitrate ions were measured at different hydroxide ion and NO_2 concentrations. The data from this program have improved a predictive computational model of radiation/thermal organic degradation in mixed tanks.

Planned Activities.

This EMSP program will formally conclude at the end of FY2000 and it has branched into several new funded programs: "Effects of Water Radiolysis in Water Cooled Nuclear Reactors" (NERI); "Mechanisms and Kinetics of Organic Aging in High-Level Wastes" (EMSP). Finally, a collaborative effort is underway with theorists at PNNL and NDRL to develop kinetic models by calculating thermochemical properties that are difficult to measure experimentally.

Information Access.

1. 1996-1997 Progress Report: <http://apollo.osti.gov/em52/1997projsum/54646.pdf>
2. 1997-1998 Progress Report: <http://apollo.osti.gov/em52/1998projsum/54646.pdf>
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5. R. Fessenden, D. Meisel, and D. M. Camaioni, "Addition of Oxide Radical Ions (O^-) to Nitrite and of Oxide Ions (O^{2-}) to Nitrogen Dioxide", *J. Amer. Chem. Soc. in press*.
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7. T. Schatz, A. R. Cook and D. Meisel, "Capture of Charge Carriers at the Silica Nanoparticle - Water Interface", *J. Phys. Chem. B*, 103, 10209 - 13, (1999).
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12. D. Meisel "Charge Transfer in Nanoparticles", In *Studies in Surface Science and Catalysis*, Vol. 103, "Semiconductor Nanoclusters - Physical, Chemical and Catalytic Aspects", P. V. Kamat and D. Meisel, Ed.; Elsevier: Amsterdam, pp. 79-97, 1997.
13. E. Papparazzo, R. Ponniah, N. Zema, M. Piacentini, and T. M. Orlando, "Electronic Structure of $NaNO_3$ Single Crystals", *in prep. Phys. Rev. B*.
14. D. Camaioni, N. Zevos, A. Sharma, J. Linehan and D. Miesel, "Mechanisms and Kinetics of the NO_2 with Complexants in Alkaline Solutions: I - Formate and Glycine, *in prep. J. Phys. Chem.*