

# Environmental Management Science Program

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## **The NO<sub>x</sub> System in Nuclear Waste**

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## The NO<sub>x</sub> System in Nuclear Waste

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### Research Objective

The objective of this project is to assist EM sites in the resolution of outstanding safety issues involved in the temporary storage of high-level waste (HLW) in large tanks. To achieve this objective, mechanisms of the radiolytic and radiolytically induced processes that occur in the waste are quantitatively studied. The information is incorporated into a computer modeling of the tanks chemistry under various scenarios and the predicted results are rapidly conveyed to the site operators.

### Research Progress and Implications

This report summarizes the technical achievements of a 3-year project that is now in its 2nd year of operation. The project is a collaborative effort between the ANL and PNNL and is strongly coupled to another EMSP project ("Interfacial Radiolysis Effects in Tank Waste Speciation" PI: T. Orlando, PNNL) and to the safety programs at the Hanford site ("Organic Tanks Safety Program: Waste Aging Studies", PI D. Camaioni, PNNL). Information from the project is also shared directly with Westinghouse Savannah River personnel. In general, the basic studies are performed at ANL and PNNL and the information is continuously shared with Tanks Safety Programs. To further facilitate the exchange of information and the immediate incorporation of results into operations, we conducted at least twice a year "coordination meetings" at the various laboratories where the site operators (e.g. from DE&SH, Numatec, WSRC, etc.) participate, both to present their needs and to obtain updated information.

We have shown that, even at concentrations relevant to HLW, the yields of the primary reducing radicals of the NO<sub>x</sub> family are not altered significantly. Most primary radicals that results from the irradiation of water in highly concentrated waste simulants are rapidly converted to NO<sub>2</sub> radicals, and to a lesser degree to NO radicals. We determined quantitatively the rates of the major reactions involved in these conversions. An important intermediate in that conversion is the short-lived NO<sub>32</sub><sup>-</sup> radical, obtained from the reaction of e-aq and its precursors with nitrate. We determined the redox potential of this species (i.e., of the couple NO<sub>3</sub><sup>-</sup>/NO<sub>32</sub><sup>-</sup>) across the whole pH range. We also determined the analogous redox potential for the nitrite species (i.e. of the couple NO<sub>2</sub><sup>-</sup>/NO<sub>22</sub><sup>-</sup>). The results show that electron transfer from the nitrate di-anion to nitrite is thermodynamically favorable, but kinetically the reaction is sluggish. We believe, and kinetic modeling of the tanks chemistry seems to require it as well, that this reaction, NO<sub>32</sub><sup>-</sup> + NO<sub>2</sub><sup>-</sup> -> NO<sub>3</sub><sup>-</sup> + NO<sub>22</sub><sup>-</sup>, occurs in the tanks with an efficiency that is determined by the nitrite concentration. The implication of this important conclusion is that the chemistry in the tanks may be diverted from NO<sub>2</sub> to NO radicals at a [nitrite] dependent efficiency. Whereas NO<sub>2</sub> provides facile pathways to organic degradation, NO provides pathways for N<sub>2</sub>O generation. The NO<sub>2</sub> radical is important to the resolution of the organic tanks issue and NO, and subsequently N<sub>2</sub>O, is an important component of the flammable gas issue.

The primary radical, which oxidatively degrades the organic molecules in the waste tanks, is suspected to be NO<sub>2</sub>. To independently verify the identity of the major oxidizing radical, we compared radiolytic degradation results with results from degradation caused by genuine NO<sub>2</sub> gas. We contacted aqueous alkaline solutions of organic species with gaseous NO<sub>2</sub> IDA>Gly>formate were determined by competition experiments in which each of the aminocarboxylates was oxidized in the presence of formate-<sup>13</sup>C to obtain initial production rates of formate-<sup>12</sup>C and carbonate-<sup>13</sup>C. Similar reactivity patterns were obtained in both the radiolytic and NO<sub>2</sub> contact approaches.

Using methodologies based on conductivity changes that we developed in the 1st year of our project, we recently measured rate constants of reactions of organic radicals of model HLW compounds with  $\text{NO}_2^-$  (nitrite) and with  $\text{NO}_2$ . For the  $\text{NO}_2$  radicals, two possible pathways were identified: a) Electron transfer to form nitrite, and b) Radical combination to form nitro-organic moieties. The latter pathway (b) occurs either via the O or the N atoms at nearly equal probabilities. The O - ester hydrolyzes to produce nitrite.

Reaction rates of the same organic radicals with nitrite ( $\text{NO}_2^-$ ) were also measured. We find that electron transfer is a leading pathway and it becomes faster as the pH drops. This reaction is important in the tanks chemistry because it generates a carbonyl product on the organic side (e.g., aldehyde that may proceed to thermally generate  $\text{H}_2$ ) and NO from nitrite. As discussed above, the latter provides another route for production of  $\text{N}_2\text{O}$ .

We also attempted to determine the effect of particulate material in the waste composition on radiolytic yields. Yields of reducing radical at increasing concentrations of silica particles were measured. We find that if the particles are small enough (largest sizes measured were 22 nm in diameter) the concentration of reducing radicals actually increases. This is an observation of exceptional importance and direct relevance to the tanks chemistry, as well as to long term storage in waste forms other than glass (e.g., grout, saltstone etc.). Long term storage in a matrix composed of small particles may defeat the purpose of the matrix. It may “channel” the radiation energy into the small quantities of water that are present in the matrix pores. This effect may lead to very efficient radiolysis of water, along with its adverse effects. In tanks, it may lead to preferential generation of gaseous products in the vicinity of solid particles. This, in turn, favors attachment of gas bubbles to the solid particles, thus contributing to the gas retention problem. It may also alter the chemistry that prevails in tanks with floating organic layers following tank draining operations. As the aqueous phase is depleted, and the organic layer comes into contact with the solid-rich sludge phase, the enhanced deposition of energy in the vicinity of the particles may trigger enhanced organic radiolysis.

## Planned Activities

We will continue our studies of  $\text{NO}_2$ -radical chemistry and the effects of particles on radiolytic yields. We will study in detail the reaction mechanisms of amine-containing multi-functional molecules with  $\text{NO}_2$ , and will extend these studies to glycolate and acetate, which are known to be present in the HLW. These are model compounds for the chelators that are prevalent in the tanks' HLW. Since the chelators, their model compounds, and their degradation products, all contain at least three potential points of attack by the radical, -N-H, -C-H and  $-\text{CO}_2^-$ , the point of attack will determine the fate of the organic compound. We will also establish an absolute rate scale for these oxidation reactions that are presently determined only on a relative scale. In the study of the effect of particles on radiolytic reactions we will turn our attention to the fate of holes. Do they migrate to the aqueous phase, similar to the electrons, or do they remain in the solid and/or its surface?

We expect to provide absolute rate constants for  $\text{NO}_2$  reactions with the relevant organic molecules by the end of next year (i.e. end of the present grant award). This will allow incorporation of much of the data into a computer model of the tanks chemistry. On the same time scale, we will also determine if radiolytically generated holes, in silica particles of various sizes, migrate out of the solids into the aqueous phase. This may have major consequences to oxidative degradation of organics in the tanks and may impact other EMSP projects as well (e.g. “Ionizing Radiation Induced Catalysis on Metal Oxide Particles,” PI: T. Fryberger). We will organize at least two more “coordination meetings” during the lifetime of the project to enhance dissemination of the knowledge generated and its incorporation into operations.

## Other Access To Information

We disseminate our results directly to the Hanford and Savannah River sites in periodic reports and during internally organized “coordination meetings” with selectively invited site operator entities. Below is a list of formal publications and presentations:

## Publications

1. "Charge Carrier Transfer Across The Silica Nanoparticle / Water Interface," T. Schatz, A.R. Cook and D. Meisel, J. Phys. Chem., Submitted for publication
2. "Reducing Radicals In Nitrate Solutions. The  $\text{NO}_3^-$  System Revisited," A.R. Cook, N. Dimitrijevic, B.W. Dreyfus, D. Meisel, L.A. Curtiss and D.M. Camaioni, J. Phys. Chem., Submitted for publication
3. "Chemistry, Radiation, And Interfaces In Suspensions Of Nuclear Waste Simulants," D. Meisel, A. Cook, D. Camaioni, and T. 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)

## Presentations

1. "Radiation and Chemistry in the Management of Nuclear Waste. Radicals, Particles, and Interfaces" D. Meisel, Invited Lecture, "Research Needs and Opportunities in Radiation Chemistry", DOE-ER/BES Workshop, Chesterton, IN, April 19-22, 1998
2. "Radiation and Chemistry in the Nuclear Arena: Radicals, Particles and Interfaces," D. Meisel, Seminar, University of Notre Dame, Notre Dame, IN, April 2, 1998
3. Science and Technology in the Management of Nuclear Waste, D. Meisel, Water Program, University of Wisconsin, Madison, WI, November 6, 1997
4. "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, Annual Meeting, Am. Chem. Soc., Las Vegas, NV September 7-11, 1997.
5. "The Radiation Chemistry of the  $\text{NO}_x$  System Revisited" A.R. Cook, L.A. Curtiss, B. Dryefus, D. Camaioni and D. Meisel, Symposium on Future Directions in Radioactive and Mixed Waste Management, Annual Meeting, Am. Chem. Soc., Las Vegas, NV September 7-11, 1997.
6. "Interfacial Charge Transfer in Irradiated Suspensions. Implications to Nuclear Waste." T. Schatz, A.R. Cook and D. Meisel, Symposium on "Actinide Solution Chemistry", Annual Meeting, Am. Chem. Soc., Boston, MA, August 23-27, 1998