

**Interim Report**  
**US Department of Energy**

**THE NO<sub>x</sub> SYSTEM in NUCLEAR WASTE**

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Two no-cost extensions were requested and granted to last until February 28, 2001. The project was renewed from January 1, 2001.

## Table of Contents

1....Executive Summary.....	3
2....Objectives.....	5
3....Methods.....	5
4....Results .....	6
5....Relevance and Impact .....	12
6....Project Productivity.....	15
7....Personnel Supported.....	16
8....Publications .....	17
9....Interactions .....	18
10..Transitions.....	21
11..Future Work.....	21
12..References .....	22

## 1. Executive Summary

This interim report summarizes the activities and accomplishments of the EMSP project entitled “The NO<sub>x</sub> System in Nuclear Waste”. It also includes an element from the EMSP proposal entitled “Interfacial Radiolysis Effects In Tanks Waste Speciation” (PI – T. Orlando of PNNL). These two EMSP projects, and, later, another project entitled “Mechanisms and Kinetics of Organic Aging in High Level Wastes” (PI D. Camaioni of PNNL), were closely coordinated as they had similar objectives:

*To develop quantitative understanding and modeling capabilities of the chemistry in highly concentrated homogeneous and heterogeneous simulants of high level waste.*

Our early efforts outlined the mechanisms for hydrogen generation in waste simulants. Much effort that followed eventually led to the development of predictive, rather accurate (within a factor of 2-3), models for H<sub>2</sub> generation in the tanks. The present research focused on two directions:

- i) The consequences of radiolytically initiated oxidation reactions of organic chelators by reactive radicals, primarily of the NO<sub>x</sub> family, at realistic salt concentrations similar to those present in waste tanks, and
- ii) The effect of solid particles, present in the tanks at high levels, on the radiolysis of the aqueous phase and especially on gas generation rates.

At the technical level, the following were determined during the course of the project:

- a. NO<sub>2</sub> is a major oxidant in the tanks. Independent measurements with genuine NO<sub>2</sub> gas confirm that a major oxidant in tank simulants is NO<sub>2</sub> as was proposed from kinetic modeling of the radiation induced chemistry.
- b. Relative rates of the reactions of NO<sub>2</sub> (and other relevant oxidizing radicals such as OH and O) with various organic molecular components of the tanks waste have been measured. These values were useful to rationalize the rate of aging of the

organic content in the tank and were instrumental in resolving the “Organic Tanks” safety issue.

- c. The rates of reactions of model organic radicals, common in the tanks' chemistry, with  $\text{NO}_2$  and  $\text{NO}_2^-$  were determined.
- d. The redox potentials of two of the major reducing intermediates  $\text{NO}_3^- / \text{NO}_3^{2-}$  ( $E^0 = -0.89\text{V}$ ) and  $\text{NO}_2^- / \text{NO}_2^{2-}$  ( $E^0 = -0.47\text{V}$ ) were determined and the impact of these values on the course of reactions in the tanks was analyzed.
- e. We discovered that the original oxidizing radical from water ( $\text{OH}$ ,  $\text{pK}_a = 11.8$ ) in its basic form ( $\text{O}^-$ ) adds to nitrite to give the same strong reductant,  $\text{NO}_3^{2-}$ , as hydrated electrons give upon reaction with nitrate. Thus, the persistence of this reductant in waste simulants is enhanced. It is capable of reacting with various inorganic waste components (e.g., Tc(VII)) at relatively long times after the absorption of radiation.
- f. Theoretical computational methods to determine such redox potential were developed; they agree quantitatively with the experimental determinations. This capability is useful in the computational modeling effort planned for future studies.

Our efforts on heterogeneous systems led to the following conclusions:

- g. Electrons generated in solid silica by high-energy radiation ( $\beta$  and  $\gamma$  were tested) will escape into the water, and with the same efficiency, to generate the same products as if water was directly irradiated. The longest escape distances measured were 20 nm.
- h. Holes in the same particles ( $\text{SiO}_2$ ) remain trapped in the solid and thus store oxidation equivalents for long periods of time. Among the hole reactions observed are back reduction of  $\text{H}_2$  and oxidation of inorganic waste components (e.g., nitrite).

The overall conclusion from these studies (and recent other studies supported by DOE) is that the presence of solid particles suspended in water nearly *universally enhances* the chemistry that is induced by the radiolysis of water. Counter-intuitive as it is,

replacement of water by solids, non-hydrogen-containing oxides (e.g., SiO<sub>2</sub>) channels more of the radiation into the water than in their absence. The implications of these observations are very severe and far-reaching. They encompass many situations encountered in EM operations, from long-term storage of radioisotopes in grout, to transportation of fissile materials, to corroding metallic pipelines.

## **2. Objectives**

The objective of the project was to develop comprehensive quantitative understanding of the radiation-induced chemistry of the NO<sub>x</sub> system in waste simulants. Similarly, since the tanks' wastes are highly heterogeneous systems, the effects of particulate matter on the radiolytic yields were to be determined. When translated to site-specific concerns, quantitative modeling of these processes can be developed once the fundamental phenomena are understood. The results were to be transferred to site operators as soon as the experimental observations are confirmed to be reliable. Interpretation of the results and conclusions to specific issues, especially safety concerns, at the sites was a major goal.

## **3. Methods**

The project was a tight collaboration between the teams at the Notre Dame Radiation Laboratory (NDRL) and PNNL. The collaboration combined the expertise at the NDRL in radiation chemistry with that of the PNNL team in physical organic chemistry, specifically of the systems of interest to the EM issues. It utilized the radiation facilities at the NDRL on one hand and the expertise in organic chemistry and the computational facilities at PNNL. In addition, the collaboration ensured ready access to the Hanford and Savannah River sites for rapid exchange of information with the site operators and thus speedy implementation of the results to the field operations. Both teams have extensive interaction with the sites dating back to the Tanks Safety Program at Westinghouse Hanford and Savannah River (late 80's early 90's), focusing on gas-

generating tanks and the chemistry of the "organic tanks". The systems of interest remained those with composition typical of waste simulants as defined by Westinghouse Hanford.(1) These include high concentrations (few mole/l) of hydroxide, nitrate, and nitrite, and also medium concentrations (tenth mole/l level) of organic complexants and their known degradation products.(2)

#### **4. Results**

We briefly compile in the following our accomplishments during the original period of the proposal. We divide the summary into the two topics relevant to the extension request:

- i) The  $\text{NO}_x$  system in homogeneous solutions, its interaction with organic molecules and radicals and its implications to the EM needs and concerns, and
- ii) The effects of high loading of solid particles in aqueous suspensions. The loading is at levels of up to 50% weight of solid, therefore, the radiation is absorbed to a significant extent by both the solid and the aqueous sub-phases.

For each of these topics we outline first the scientific achievements and then their impact on systems of concern to the EM complex. In a separate section (Section 9) we list our efforts to disseminate the information collected in the course of performing the research and to learn about the emerging needs. These include, in addition to the traditional modes of publications and conference presentations, coordination meetings and meetings with representatives from various DOE-EM sites.

***i. The  $\text{NO}_x$  System:*** Most of our accomplishments on this effort were recently summarized in the ACS-EMSP Symposium proceedings.(3)

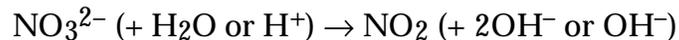
*4a. Role of  $\text{NO}_2$ :* We have verified the underlining premise of the original proposal that the dominant radical in the irradiated HLW is the  $\text{NO}_2$  radical. The verification came from experiments that showed that the reactivity of the active species in aging of a large number of organic HLW components is the same regardless of the

source of oxidation: irradiation or contact of the HLW simulants with genuine NO<sub>2</sub> gas. Thus a kinetic model that describes the chemistry in HLW should use reactivities of the latter along with those of the oxidizing species from water fragmentation (such as OH and O<sup>-</sup>) at the appropriate yields of each.

4b. *Formation and reactions of NO<sub>3</sub><sup>2-</sup> radicals(4)*: The only reductive reaction that generates this short-lived radical is:

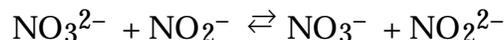


We determined the redox potential ( $E^\circ(\text{NO}_3^- / \text{NO}_3^{2-}) = -0.89 \text{ V}$ ) and we showed that it can generate H<sub>2</sub>. It can reduce many of the inorganic ions in the waste and was recently shown to reduce Tc(VII) to Tc(IV).(5) We also showed that protonation of this radical dianion leads instantaneously to decomposition to NO<sub>2</sub>:



thus catalyzing the conversion of a strongly reducing radical (fuel producing) to a strongly oxidizing one (aging promoter). Its generation from oxidizing radicals is discussed below (Section 4e).

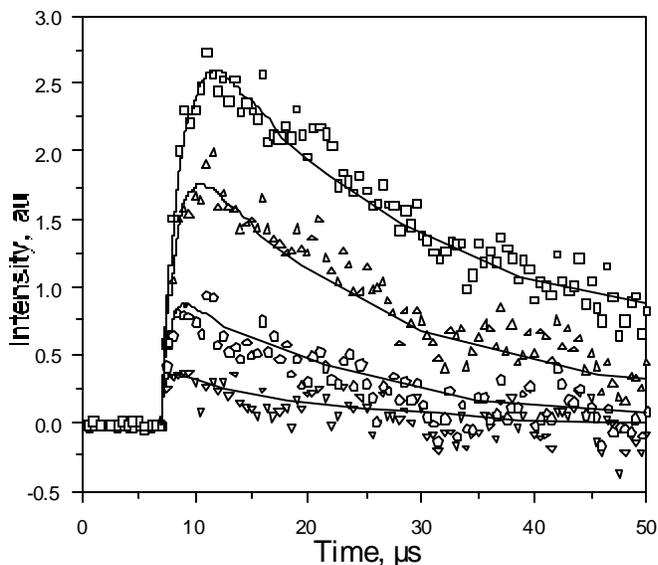
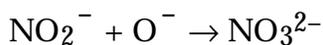
4c. *Possible conversion of NO<sub>3</sub><sup>2-</sup> to NO<sub>2</sub><sup>2-</sup>*. We also determined the redox potential of the NO<sub>2</sub><sup>-</sup> / NO<sub>2</sub><sup>2-</sup> couple ( $E_m = -0.47 \pm 0.02 \text{ V}$ ). Therefore, the reaction:



is feasible. If so, the product, NO<sub>2</sub><sup>2-</sup>, leads to NO radicals and the reactions of the latter need to be considered. We could not measure the rate constant for that transformation but we showed that it is  $< 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . Once this was realized we included in our coordination meetings representatives of another EMSP project (“Reactivity of Peroxynitrite: Implications for Hanford Waste Management”, PI: S. Lyman of BNL), whose research focuses on the NO radical and its derivatives (e.g., NO-O<sub>2</sub><sup>-</sup>).

4d. *Reactions of Precursors:* We have shown that the precursor to the hydrated electron,  $e^-_{\text{dry}}$ , generates the same reducing radical as the hydrated electron,  $e^-_{\text{aq}}$ , itself. At the high nitrate concentrations in HLW the radiolytically generated electrons react with the nitrate before they hydrate. Our observations imply that the same products are produced, but at different rates, as those from  $e^-_{\text{aq}}$ . Recent results show that this precursor is the ultimate source of all radiolytically produced  $\text{H}_2$  in water(6).

4e. *Generation of  $\text{NO}_3^{2-}$  from oxidizing radicals:* (7) We discovered that the strongly reducing radical,  $\text{NO}_3^{2-}$ , is produced by the strongly oxidizing radical  $\text{O}^-$  that is a major water fragmentation product at high pH's typical for HLW (Figure F1):



**Figure 1:** ESR signal of  $\text{NO}_3^{2-}$  produced from solutions that contained only nitrite,  $\text{N}_2\text{O}$ , and increasing  $[\text{OH}^-]=0.1, 0.3, 1, 2 \text{ M}$  from bottom up. An unequivocal proof that  $\text{NO}_3^{2-}$  is produced from the oxidizing radical  $\text{O}^-$ .

Prior to our discovery  $\text{O}^-$  was believed to react only via electron transfer leading to  $\text{NO}_2$  directly. Again this observation highlights the delicate balance between the reducing and oxidizing reactions in HLW. This transformation extends the lifetime of the reducing stage in the radiolysis and allows efficient scavenging of  $\text{NO}_3^{2-}$  (e.g., by  $\text{Tc(VII)}$ ).

4f. *Reactions of NO<sub>2</sub> with model organic substrates:* The relative rates (and an estimate for the absolute rate) of this major radical with a large number of model organic molecules were determined in HLW simulants. These include formate, glycolate, glycine, iminodiacetate (IDA), and nitrilotriacetate (NTA), EDTA and others both in radiolytic and NO<sub>2</sub> contact experiments (Table 1).<sup>(8)</sup> The information from these studies was seamlessly incorporated into the final topical report that signaled the closure of the Organic Tanks issue at Hanford.<sup>(9)</sup> It is also now utilized in the efforts to resolve the Flammable-Gas Generation issue at the site. Our earlier projects with the Tanks Safety Program at Hanford<sup>(1)</sup> were followed by efforts PNNL, Duke and Lockheed Martin Hanford that eventually led to accurate (within a factor of 2) estimates of the rate of gas generation in the tanks.<sup>(10)</sup>

**Table 1. Relative Rates of Disappearance of Organic Chemicals in Waste Simulants<sup>(a)</sup> by  $\gamma$  Radiolysis**

<b>Substrate<sup>(a)</sup></b>	<b>k<sub>rel</sub></b>	<b>Substrate</b>	<b>k<sub>rel</sub></b>
u-EDDA	<b>13</b>	Glycine	7
s-EDDA	<b>13</b>	Glycolate	5
IDA	<b>12</b>	EDTA	6
NTA	<b>10</b>	Formate	1 <sup>(c)</sup>
HEDTA	<b>14</b>	Citrate	0.7
		Acetate	0.7

- a. In 3.75 M NaNO<sub>3</sub>, 1.25 M NaNO<sub>2</sub>, 2 M NaOH and at 20°C.
- b. u-EDDA = unsymmetrical ethylenediaminediacetic acid, s-EDDA = symmetrical ethylenediaminediacetic acid.
- c. Defined value.

4g. *Reactions of NO<sub>2</sub> with organic radicals:* The rate of reaction of this strong oxidizing radical with several representative model organic radicals was measured. The rate constant is usually high but the reaction may be either an electron transfer :



generating nitrite, or a combination reaction:



leading to nitro and/or nitrite-ester products.

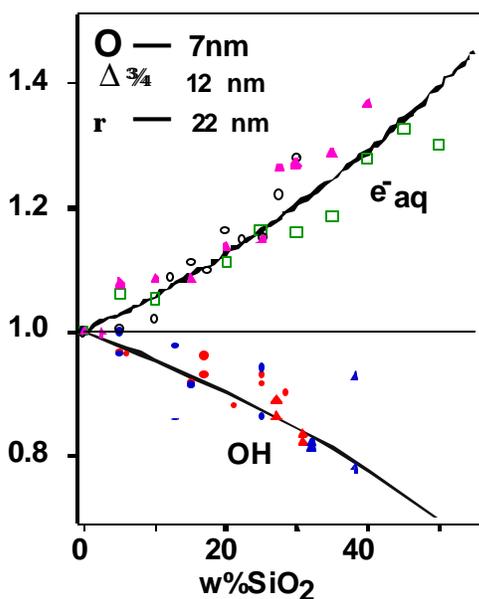
4h. *Reactions of nitrite, NO<sub>2</sub><sup>-</sup>, with organic radicals:* Because of the high concentrations of nitrite in the waste, this reaction is important. It is believed to lead to reduction of nitrite, eventually to NO. It's importance lies in the fact that it might prevent other reduction reactions that would otherwise be important in the absence of nitrite, e.g., reactions of the radicals with other inorganic solutes in the tanks or the reactions shown in Section 4g above.

**ii. Radiolytic Effects of Solid Particles:** Many of our accomplishments in this effort were recently summarized in another article in the ACS-EMSP Symposium proceedings.(11) These studies involved only silica particles and were aimed at determining if and to what extent energy that is absorbed by the solid particles finds its way out into the water phase. Clearly, if it does then it will induce aqueous chemical reactions just as absorption of radiation directly in aqueous solutions, for example those described in the Sections above.

4i. *Escape of electrons from SiO<sub>2</sub> particles (Upper Curve in Figure 2):* We discovered that all of the energy that is absorbed by nano-size particles (up to 22 nm diameter) generates electrons in water just as if the energy was absorbed in water itself. Thus these solids do not arrest the radiation effects. We emphasize that these observations have far reaching implication beyond the suspensions and the tanks chemistry. One

may view these particles as the “skin” along various other formations (porous grout, micron-size powders, etc.)

4j. *Trapping of holes in the particles (Lower Curve in Figure 2):* In sharp contrast to the electrons, we discovered that the holes are trapped in the particles before they can oxidize water. Again this is an observation of far reaching implications. In the context of organic degradation it implies that the fraction of energy that is absorbed in such particles cannot contribute to aging via OH radicals. Direct oxidation of organic substrates by trapped holes is perhaps possible, but then the relevant rates are not those that originate from water fragmentation.



**Figure 2:** Relative Concentration of  $e^-_{aq}$  (upper half) and OH radicals (lower half) upon increasing  $SiO_2$  Concentration. Upper Curve Is Sample Density indicating the increase in absorbed dose by the sample because of increasing  $SiO_2$ . Lower Curve Is Volume Fraction of Water indicating the decrease in absorbed dose in the aqueous phase.

4k. *Control of charge escape by surface modifications:* We found that implanting electron acceptors at the surface of the solid particles leads to capture of all of the electrons that would otherwise cross the interface into the water. However, merely changing the surface charge will affect the escape probability. Thus, on the one hand one can control the chemical consequences of the suspended particles. On the other hand, the identity of species adsorbed at the surface will determine the chemical consequences. In HLW compositions, where much of the surface is covered with

organic deposits, it is unlikely to change the fundamental observation of electron escape from the solid to the water.

*4l. Yields of H<sub>2</sub> from aqueous suspensions:* In addition to electrons and holes, other species may affect the all-important yields of H<sub>2</sub>. We find no new source of H<sub>2</sub> in heavily loaded silica suspensions. On the contrary we showed that the trapped holes (Section 4j above) back react with H<sub>2</sub> to reduce the yield. However, to avoid misinterpretations we hasten to emphasize that the increased yield of electrons (Section 4i) can, and will, contribute to increased yields of hydrogen unless they are eliminated (e.g., by the presence of nitrate in HLW).

All the information “bulleted” above was expediently transmitted, and implications were outlined, to the interested technical personnel at the various sites. Neither the closure of the Organic Tanks issue, nor the astonishing predictability that is now available to the Gas Generation program would be possible without the collaborative efforts of this team, starting with the Safety program of Westinghouse Hanford and continuing via the EMSP.

## **5. Relevance and Impact**

*a. Gas Generation and Organic/Nitrate Tanks at EM sites :* Safety issues relating to the Hanford and Savannah River tank wastes include the ignition of flammable gas mixtures in tank head-space, ignition of organic solvents present in floating layers atop the aqueous wastes, ignition of combustible solid wastes containing organic complexants mixed with nitrate/nitrite salts, and spontaneous bulk runaway chemical reactions. The Hanford Organic/Nitrate issue was brought to a closure, and we indicated in the Results Section above where our efforts contributed to that resolution.(9) The eruptive gas release events in the tanks raised concern that H<sub>2</sub> (and NH<sub>3</sub>) may ignite because they often were well within the flammability boundaries of H<sub>2</sub> in N<sub>2</sub>O. A recent report aimed at closure of the gas generation issue(12) emphasizes

the tight correlation between the rate of gas generation and organic oxidations and degradation in HLW. As is always the case in fuel gas generation, a reduction process, it must be coupled to an oxidation process. Predictive capabilities for one process assist in the predictability of the other. Our early efforts correlated the gas generation rate with the hydrogen content of the organics in the waste. Much effort that followed correlated the radiolytic gas generation rates with the TOC and eventually led to a model that realistically predicts these rates to within a factor of two for many of the tanks. The prospects for closure of the Flammable-Gas issue at Hanford this fiscal year now seem rather promising. This feat would have been impossible without the scientific basis laid by the effort of this program and its predecessors.

*b. Organic Floating Layers in the Tanks at the Idaho National Engineering Laboratory (INEL)* : This issue was of significant concern at the time of the original proposal.(13) A separate organic layer develops in the tanks of the new Waste Calcining Facility at the INEL. Similar concerns existed at Hanford as well. The concern is similar to the one discussed above except that the radiation is primarily absorbed by the floating organic layer material rather than by water. We have enough information within our records to provide realistic estimates of H<sub>2</sub> yields in such situations, provided we know the dose in these layers. To the best of our knowledge the issue at Hanford was resolved.(14) However, single shell tanks that contain floating organic layers will require removal of the layer in order to stabilize the tank, an operation that may bring the issue back to the front.

*c. Characterization Efforts (or lack of them):* One motivation for the original proposal was our attempt to assist in the waste characterization effort, which in turn was driven by the need to address storage safety issues. Closure of the Organic Tanks safety issue required a significant characterization effort. Samples from many of the tanks with high TOC were analyzed to identify and quantify the majority of organic compounds present. The characterization effort was aided by our project. We have shown that

degradation of waste simulants under storage conditions leads to oxidization of the organic chelators. Consequently their fuel value decreases with time, and with exception of oxalate ion, the organic end products are water-soluble. Knowledge of the oxidation mechanism was helpful in development of appropriate organic analytical methods. Furthermore, the analytical results, that found a wide variety of compounds not originally used in nuclear materials production processes, could be rationalized using the information obtained from our laboratory studies of waste simulants.

At present the characterization effort is focused on supporting waste retrieval and treatment activities. Analyzes are being performed to identify trace hazardous chemicals present in the wastes.(15) A rationale for the presence, and often the absence, of various chemicals is needed to satisfy federal and state regulators. Therefore, the predictive options that our effort offer become rather significant. Conversely, the inability to provide reliable composition information on the HLW is alarming to the Defense Nuclear Facilities Safety Board (DNFSB).(16) As our efforts, along with the efforts of the Organic Aging Program at Hanford demonstrated, the speciation of the final degradation products of the aging process can be determined, either by radiolytic or by NO<sub>2</sub> contact experiments.(8) Proposed degradation mechanisms(1) and aging experiments actually identified intermediate nitro, nitroso, and oxime functionalities,(17,18) but the related rates and in particular, computational predictive capabilities are still to be demonstrated.

*d. Generalized Mechanisms:* Absent clear speciation of many of the waste components generalized mechanisms and dependence of the yields on broad, non chemical-specific parameters (e.g., TOC or H-content rather than specific organic compounds) is necessary. This is where our program had, and promises in the future to have, its most evident impact. Correlation of H<sub>2</sub> rate of formation with TOC is a powerful predictor. Similar correlation of yields with hydrogen-density in the waste,

which is under development at present, will provide predictive capabilities to scenarios where the energy of radiation is deposited in the organic matter directly.

*e. Interfacial Processes:* The need to understand the processes in heterogeneous systems, and prior to that simply establishing the facts, hardly needs justification. Solid interfaces in contact with water are commonplace throughout the Complex. They are obviously present in the tanks, and they affect gas generation (via absorption of the radiation and catalysis at the interface). They appear at porous waste-storage formations (e.g., grout) and at cracks in glasses. Transportation of wet powders of spent fuel, temporarily stored in canisters at Rocky Flats, was delayed because of concerns of H<sub>2</sub> ignition when opened upon arrival at the Savannah River site. A similar situation pertains with the 94-1 issue at Los Alamos. Many of the concerns related to gas generation at wet interfaces were discussed at a recent Gas Generation Meeting in Savannah River (August 13, 1999) and again at the symposium on Gas Generation at the ANS meeting in Long Beach, CA (November 14-18, 1999). It is clear that information on the basic facts of the yields and rates of gas generation at the interface, especially at low levels of wetting is lacking. Our program provided this information (albeit still at merely an empirical level) along with some insight into the mechanistic origin. Efforts at Los Alamos and NDRL are now underway to elaborate on the basic observations provided by our program.

To summarize: The underlying chemistry of high-level liquid waste is the radiation chemistry of the NO<sub>x</sub> radicals in highly concentrated and often heterogeneous systems. Quantitative understanding of these processes continues to prove crucial in resolving safety issues associated with storing the waste in the tanks. Some of the concerns that this chemistry raises were addressed and resolved in the original proposal. Many issues remain to be further explored. We recently received a renewal

extension of our program with the aim to transform as much as possible of the effort from the laboratory experimental level to the computational regime.

## **6. Project Productivity:**

The project achieved many of its objectives as discussed in the previous Section. In particular, its impact on the Safety issues at Hanford is clear. Several changes were made during the project lifetime in response to changing circumstances. The tetraphenylborate (TPB) issue was not addressed during the project, even though it was outlined in the original proposal as possible direction. This issue became less important as the major source for the benzene was determined to be chemical catalysis and not radiolysis and as the use of TPB at the In Tank Precipitation process was put on hold. Another major deviation from our original proposed work is the consolidation of the heterogeneous part with the NO<sub>x</sub> direction. This was caused by relocation of PI's from Argonne to Notre Dame and from PNNL to Georgia Institute of Technology. The renewal request details these changes.

On the technical level, the exact chemistry that will occur in each tank will depend on specific parameters relevant to that particular tank. The most important parameters include the water content, nitrate/nitrite concentrations, pH, organic content and fraction of solid. Therefore, our efforts cannot provide a response to each scenario that may happen in various tanks. Rather, we offer the underlying principles and demonstrate their dependence on composition. In our renewal request we propose to develop a computational effort that will design computational-theoretical algorithms that could respond to these various scenarios.

## 7. Personnel Supported:

The following personnel were supported by this EMSP project:

At Argonne: Dr. N. Dimitrijevic (postdoc, remained at ANL), Dr. L. A. Curtiss, Dr. A. Cook (postdoc at ANL now at Brookhaven National Laboratory), Prof. A. Henglein, (sabbatical from the Hahn-Meitner Institute, Berlin, now retired), Mr. B. Dreyfus (a full year research student now at Harvard).

At PNNL: Dr. D. Camaioni, Dr. T. Orlando (Now at Georgia Tech), Dr. John C. Linehan, Dr. W. J. Shaw, Amit K. Sharma (Now at Rhodia, Inc., Cranbury, NJ).

At Notre Dame: Prof. D. Meisel (started at ANL moved to NDRL), Prof. A. Henglein, (sabbatical from the Hahn-Meitner Institute, Berlin, now retired), Dr. T. Schatz, Dr. H. Miyoshi (now at Tokoshima U., Japan), Mr. J. Collins (two-summer student, now graduating from Harvard).

Others: Prof. N. Zevos (sabbatical at ANL and PNNL, from SUNY-Potsdam, NY, now back at SUNY).

## 8. Publications:

### Per-Reviewed journals and books:

REDUCING RADICALS IN NITRATE SOLUTIONS. THE  $\text{NO}_3^{2-}$  SYSTEM REVISITED  
A. R. Cook, N. Dimitrijevic, B. W. Dreyfus, D. Meisel, L. A. Curtiss and D. M. Camaioni, J. Phys. Chem. B, 105, (2001); Web Edition ASAP of March 16, 2001.

RADIATION-INDUCED PROCESSES IN AQUEOUS SUSPENSIONS OF NANOPARTICLES AND NANOSCALE WATER FILMS.  
Thom Orlando and Dan Meisel, ACS Symposium Series 778, "Nuclear Site Remediation," Ed. G. Eller and W. R. Heineman, pp. 284-296, 2001.

RADIATION AND CHEMISTRY IN NUCLEAR WASTE: THE NOX SYSTEM AND ORGANIC AGING  
Dan Meisel, Donald Camaioni, and Thom Orlando, ACS Symposium Series 778, "Nuclear Site Remediation," Ed. G. Eller and W. R. Heineman, pp. 342-361, 2001.

ADDITION OF OXIDE RADICAL IONS ( $\text{O}^-$ ) TO NITRITE AND OXIDE IONS ( $\text{O}_2^-$ ) TO NITROGEN DIOXIDE.

Fessenden, R. W., Meisel, D., Camaioni, D. M., J. Am. Chem. Soc., 122, 3773-4 (2000).

CAPTURE OF CHARGE CARRIERS AT THE SILICA NANOPARTICLE - WATER INTERFACE  
Timothy Schatz, Andrew Cook and Dan Meisel, J. Phys. Chem. B, 103, 10209-13 (1999).

CHARGE SEPARATION ACROSS THE SILICA NANOPARTICLE/WATER INTERFACE.  
Nada M. Dimitrijevic, Arnim Henglein and Dan Meisel, J. Phys. Chem. B, 103, 7073-6 (1999)

CHARGE CARRIER TRANSFER ACROSS THE SILICA NANOPARTICLE / WATER INTERFACE.  
Timothy Schatz, Andrew R. Cook and Dan Meisel, J. Phys. Chem. B, 102, 7225-30, (1998)

### Not reviewed:

RADIATION INDUCED CHARGE CARRIERS IN AQUEOUS SUSPENSIONS OF NANOPARTICLES  
Dan Meisel, Proceedings of the Trombay Symposium on Radiation and Photochemistry, Volume II, 271-9, 2000.

THE AGING OF ORGANIC CHEMICALS IN HANFORD HIGH-LEVEL WASTES  
H. Babad and D. M. Camaioni, Proceedings of the Waste Management 2000 Conference, Feb.27-Mar 2, 2000, Tucson, Arizona.

CHEMISTRY, RADIATION, AND INTERFACES IN SUSPENSIONS OF NUCLEAR WASTE  
SIMULANTS  
Dan Meisel, Andrew Cook, Don Camaioni, and Thom Orlando, "Photoelectrochemistry", Ed. K. Rajeshwar, L. M. Peter, A. Fujishima, D. Meissner, M. Tomkiewicz, The Electrochemical Society Pub., Vol. 97-20, 350-7 (1997)

CHARGE TRANSFER IN NANOPARTICLES,  
Meisel, D., 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.

## **9. Interactions:**

Kick-off coordination meeting of project renewal at PNNL, Feb. 12, 2001. Present all PI's from Notre Dame and PNNL, representatives from TFA, CH2M Group, DOE-RL and others.

Coordination meeting at the Environmental Molecular Science Laboratory, PNNL Richland, WA April 29-30,1999. Present all PI's, Co-PI's and associated PNNL staff of the three projects, representatives of Tank Waste Focus Area, DOE-RL consultants; additional personnel from NDRL from PNNL.

Presentation by D. Meisel on "Fundamentals of Radiation Effects in Heterogeneous Systems" in Aiken, SC at the Rocky Flats - Savannah River meeting on Gas Generation, Aug. 13, 1999. Present representatives from Savannah River, Rocky Flats, LANL, ORNL, Co-PI's from NDRL, consultants.

Coordination Meeting in conjunction with the Symposium on "The Environmental Management Science Program", ACS Meeting, New Orleans, LA, August 22-26, 1999. Present All PI and Co-PI's of the three EMSP projects and a few other PI's from NDRL, BNL and PNNL.

Coordination meeting at the Notre Dame Radiation Lab, October 29-30, 1998. Present: All PI's and associated NDRL staff, theoretical component from EMSL.

Presentation by D. Camaioni on "Organic Aging in Hanford Waste Tanks," Hanford Tank Waste Safety Technical Exchange, June 2, 1998.

Coordination meeting at ANL, April 23-24, 1998. All PI's, associated ANL staff, representative from Duke Eng. Hanford, Westinghouse Savannah River, EMSP-PI's from Brookhaven National Lab.

Coordination Meeting in conjunction with PNNL's review of their EMSP Projects at the EMSL, PNNL, Richland, WA, Feb. 19-21, 1998. Present all PI's of the three projects, other PNNL - EMSP PI's, representatives from Duke Engineering, Numatec, RL consultants and others.

Coordination meeting at ANL, May 11-12, 1997. Present: All PI's and associated ANL staff, collaborators from State University of New York (Prof. N. Zevos).

Pacific Northwest National Lab (PNNL), April 22-23, 1997. Present: All PI's, associated PNNL staff, other PNNL - EMSP PI's, Hanford Waste Tank Safety Program staff, Hanford Site contractors (Duke Engineering, Numatec), and DOE-RL representatives, consultants and others.

Start of project coordination meeting at ANL, October 25, 1996. Present: All PI's from PNNL & ANL and related staff.

Presentation by D. Camaioni on "Radiolytic Aging." Workshop on the Safety Issue Resolution and Characterization Implementation Project, Nov. 16, 1996, Richland, WA.

Start of project coordination meeting, ANL, October 25, 1996. Present: All PI's and related staff.

### **Presentations in Conferences, Seminars etc.:**

#### THE NO<sub>x</sub> SYSTEM IN NUCLEAR WASTE: IMPACT AND PERSPECTIVES

Dan Meisel, Don Camaioni, Ian Carmichael, Invited Talk, DOE's Tank Focus Area Mid-Year Review, March 12-14, 2001, Salt Lake City, UT.

#### IONIZING RADIATION EFFECTS IN SUSPENSIONS OF NANOPARTICLES

Dan Meisel, Invited Talk, Symposium on "Radiolytic Effects in the Environment", Pacific Chem. Meeting, Honolulu, Hawaii, Dec. 14-19, 2000.

#### RADIOLYTIC EFFECTS IN SUSPENSIONS OF NANOPARTICLES

Mona Treuger and Dan Meisel, Radiation Chemistry Gordon Conference, June 25-30, 2000, Plymouth, NH.

#### RADIATION INDUCED CHARGE CARRIERS IN NANOPARTICLES

Dan Meisel, Invited Talk, Fry Award Symposium of the 2000 Annual Radiation Research Society Meeting, Albuquerque, NM, Apr. 29-May 3, 2000.

#### RADIOLYTIC AND THERMAL PROCESSES IN HOMOGENEOUS AND HETEROGENEOUS HIGH LEVEL WASTE

Dan Meisel, Don Camaioni, Thom Orlando, Invited Talk, Annual Meeting of the Environmental Management Science Program, Atlanta, GA, April 25-28, 2000.

#### THE NO<sub>x</sub> SYSTEM IN HETEROGENEOUS AND HOMOGENEOUS HIGH LEVEL WASTE

Dan Meisel, Annual Meeting of the Environmental Management Science Program, Atlanta, GA, April 25-28, 2000.

## RADIOLYTIC HYDROGEN GENERATION IN HETEROGENEOUS SYSTEMS

H. Miyoshi, T. Schatz and D. Meisel, Invited Talk, Symposium on "Long Term Disposition", Nuclear Division, ACS annual meeting, San Francisco, CA, March 26-30, 2000.

## THE AGING OF ORGANIC CHEMICALS IN HANFORD HIGH-LEVEL WASTES

H. Babad and D. M. Camaioni, Waste Management 2000 Conference, Feb.27-Mar 2, 2000, Tucson, Arizona.

## RADIATION INDUCED CHARGE CARRIERS IN AQUEOUS SUSPENSIONS OF NANOPARTICLE

Dan Meisel, Invited Talk, Trombay Symposium on Radiation & Photochemistry (TRSP 2000), Trombay, India, Jan. 12-17, 2000.

## RADIATION AND PHOTOCHEMISTRY IN SILICA NANOPARTICLES AND NANOBUBBLES

Dan Meisel, Seminar, Regional Research Laboratory, Trivandrum, India, Jan. 10, 2000.

## NANOBALLS AND NANOBUBBLES UNDER LIGHT AND RADIATION

Dan Meisel, Seminar, Indian Institute of Science, University of Bangalore, India, Jan. 7, 2000.

UNUSUAL SPECIES AND UNUSUAL REACTIONS OF THE NO<sub>x</sub> FAMILY

Dan Meisel, Inorganic Section Seminar, Department of Chemistry and Biochemistry, University of Notre Dame, IN, Dec. 3, 1999.

## GAS GENERATION FROM SOLIDS IN AQUEOUS SUSPENSIONS

Dan Meisel and Tim Schatz, Invited Talk, Annual Meeting, Am. Nuclear Soc., Long beach, CA, November 14-18, 1999.

## RADIOLYTIC EFFECTS IN HOMOGENEOUS AND HETEROGENEOUS HIGH LEVEL SIMULANTS

Dan Meisel, Don Camaioni and Thom Orlando, Invited Talk, Symposium on "The Environmental Management Science Program", Annual Meeting, Am. Chem. Soc., New Orleans, LA, August 22-26, 1999.

## RADIOLYTIC EFFECTS ON ORGANIC CHEMICALS IN HIGH LEVEL WASTES

D. M. Camaioni, A. K. Sharma, J. C. Linehan, and T. Orlando, N. Zevos, and D. Meisel, Symposium on "The Environmental Management Science Program", Annual Meeting, Am. Chem. Soc., New Orleans, LA, August 22-26, 1999.

## FUNDAMENTALS OF RADIATION EFFECTS IN HETEROGENEOUS SYSTEMS

D. Meisel, Rocky Flats - Savannah River Sites meeting on policy for the Defense Nuclear Facilities Safety Board, Aiken, SC, Aug. 13, 1999.

## RADIATION INDUCED CHARGE CARRIERS IN NANOPARTICLE SUSPENSIONS

Dan Meisel, Radiation Research Congress, Dublin, Ireland, July 16-24, 1999.

## IONIZING RADIATION INDUCED CHARGE CARRIERS IN COLLOIDAL NANOPARTICLE

Dan Meisel, Invited Talk, Symposium on "Nanomaterials", at the 195th Meeting of the Electrochemistry Society, Seattle, WA, May 2-7, 1999.

## RADICALS FROM IONIZING RADIATION IN SUSPENSIONS OF NANO-PARTICLES

Tim Schatz, Dan Meisel and Andrew Cook, Invited talk, Symposium on "Free radicals in the Condensed Phase", Annual Meeting, Am. Chem. Soc., Anaheim, CA, March 21-25, 1999.

REACTIONS OF NO<sub>2</sub> WITH ORGANIC COMPLEXANTS IN ALKALINE SOLUTIONS

D. M. Camaioni, A. K. Sharma, J. C. Linehan, N. Zevos, D. Meisel, Invited Talk, Symposium on "Free radicals in the Condensed Phase", Annual Meeting, Am. Chem. Soc., Anaheim, CA, March 21-25, 1999.

RADIOCATALYSIS: FUNDAMENTALS AND APPLICATIONS:

Dan Meisel, Seminar, Northwestern University, Evanston, IL, February 10, 1999.

CHARGE CARRIER ACROSS INTERFACES.

Dan Meisel, School of Engineering, Notre Dame, September 15, 1998

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, Aug. 23-27, 1998

INTERFACIAL CHARGE TRANSFER ACROSS THE NANOPARTICLE INTERFACE

Dan Meisel, Seminar, Chemistry Department, University of Notre Dame, Notre Dame, IN, May 25, 1998

RADIATION AND CHEMISTRY IN THE MANAGEMENT OF NUCLEAR WASTE. COLLOIDS, INTERFACES, AND RADICALS

Dan Meisel, Invited Talk, "Research Needs and Opportunities in Radiation Chemistry", DOE Workshop, Chesterton, IN, April 19-22, 1998

RADIATION AND CHEMISTRY IN THE NUCLEAR ARENA: RADICALS, PARTICLES AND INTERFACES

Dan Meisel, Seminar, Radiation Laboratory, University of Notre Dame, Notre Dame, IN, April 2, 1998

SCIENCE, TECHNOLOGY AND THE PUBLIC IN THE MANAGEMENT OF NUCLEAR WASTE

D. Meisel, Environmental Sciences Seminar, University of Wisconsin, Madison, WI, Nov. 6, 1997

THE RADIATION CHEMISTRY OF THE NO<sub>x</sub> SYSTEM REVISITED

A. R. Cook, L. A. Curtiss, B. Dryefus, D. Camaioni and D. Meisel, Annual Meeting, Am. Chem. Soc., Las Vegas, NV, Sept. 7-11, 1997

SOME FUNDAMENTAL STUDIES ON THE EFFECTS OF RADIATION AND INTERFACES IN HIGH LEVEL WASTES

D. M. Camaioni, K. Knutsen, J. C. Linehan, T. M. Orlando, A. Cook, and D. Meisel, Annual Meeting, Am. Chem. Soc., Las Vegas, NV, Sept. 7-11, 1997

CHEMISTRY, RADIATION, AND INTERFACES IN SUSPENSIONS OF NUCLEAR WASTE SIMULANTS

Dan Meisel, Joint Meeting of the Electrochemical Societies, Paris, France, Aug. 31 - Sep. 5, 1997

THE SILICA NANOBUBBLE: EXPECTATIONS AND OBSERVATIONS

Dan Meisel, Condensed Matter Seminar, James Frank Institute and Physics Department, University of Chicago, Chicago, IL, August 4, 1997

THE SILICA NANOBUBBLE

Dan Meisel, Seminar, Chemistry Department., University of Chicago, Chicago, IL May 5, 1997

THE SILICA NANOBUBBLE

Jim Norris and Dan Meisel, UOC/ANL Retreat, Oak Brook, IL, May 2, 1997

**10. Transitions:**

We offered to provide baseline information that will assist in the decision making process and in defending various operations before regulatory bodies (mostly the DNFSB). We believe we delivered. Sections 5 and 6 above give a detailed account of our efforts to transfer the information as expeditiously as possible to the end users.

**11. Future Work:**

A recently awarded grant details our proposed future work. Briefly, we will focus on the development of reliable theoretical and efficient computational descriptions of the chemistry of high level waste in highly concentrated solutions.

We will develop a theoretical model, and the corresponding computer codes, to afford an accurate account of the effect of high salt concentrations on the solvation and reactivity of radicals and radical ions radiolytically generated in the waste. A satisfactory treatment of these effects is not currently available.

We will determine the electronic structure of the reactive  $\text{NO}_x$  and  $\text{NO}_x^-$  species and provide a detailed computational analysis of the influence of microsolvation, dielectric and ionic strength effects on their properties. In particular the mechanism of their interaction with organic complexants, and with the radicals derived from these complexants, will be elucidated, allowing the prediction of product distributions and rates of formation. The relevant chemistry will be broadly surveyed employing an efficient computational scheme based on Density Functional Theory (DFT). The accuracy of this approach will be calibrated against high-level electronic structure calculations of related model systems.

The predictions from the theoretical model will be further validated by experimentally measuring the rate constants for key reactions between  $\text{NO}_x$  radicals and model complexants and between organic radicals and  $\text{NO}_x^-$  anions in tank simulants. Steady-state electron spin resonance (ESR) and time-resolved ESR detection will be used both

to identify the transients produced by *in situ* radiolysis and to determine their absolute rates of reaction. Product distributions, yields, and relative rates will be quantified by contact experiments with dilute NO<sub>2</sub> gas mixtures.

The resulting validated theoretical model will allow unambiguous determination of the pathways for oxidation of the organics, determination the rate constants of degradation under various conditions and the reliable prediction of the radiolysis products. Combined with our earlier studies and ongoing related projects at PNNL, we will provide a comprehensive, quantitative description having useful predictive capabilities for waste chemistry.

## 12. References:

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