ANL/CHM/RP--94829

THE NO_x SYSTEM IN NUCLEAR WASTE

ANNUAL REPORT TO THE EMSP, SEPTEMBER 30, 1997

Principal Investigator: DAN MEISEL, Chemistry Division, Argonne National Laboratory,
Argonne IL 60439. Tel. (630) 252-3472, fax (630) 252-7068,
email: dani@anl.gov

Co-PIs: Don Camaioni, Energy and Environmental Sciences Division,
Pacific Northwest National Laboratory, Richland, WA 99352
Thom Orlando, Environmental Molecular Sciences Laboratory,
Pacific Northwest National Laboratory, Richland, WA 99352

Team Members: Prof. Nada Dimitirievic, Visiting Scientist, ANL
Dr. Andy Cook, Assistant Scientist, ANL
Prof. Nick Zevos, Visiting Scientist, ANL and PNNL

Technical support personnel, ANL: Dr. O. Makarova, C. Kharas, B. Dreyfus, J. Collins

Synopsis

We highlight below our results from the title project. The project is a coordinated effort of the three Co-PIs to assist the Safety Programs at the Hanford and other DOE Environmental Management Sites. We present in the report our observations and interactively discuss their implications for safety concerns. We focus on three issues:

a. Reducing radicals in the NO_x system

We show that the only reducing radical that lasts longer than a few ns in typical waste solutions, and is capable of generating hydrogen, is NO₃[•]. We measured the lifetime of this species across the whole pH range (3 ≤ pH ≤ 14) and found it to be shorter than ~15 μs, before it dissociates to give the strongly oxidizing NO₂ radicals. We found that it reacts with many proton donors (H⁺, phosphate, borate, NH₄⁺, amines) in a reaction that is not merely an acid-base equilibrium reaction but is probably a dissociative proton transfer. We estimate the redox potential from theoretical considerations and obtain an experimental verification. We conclude that it is highly unlikely, although thermodynamically possible, that this radical will generate hydrogen in waste solutions.

b. Aging of organic chelators and their degradation products by NO₂

Methodologies to study the degradation of organic substrates (including the important waste components, formate and oxalate) to CO₂, or carbonate, by NO₂ were developed. This radical dimerizes and disproportionates to nitrate and nitrite. Therefore, mineraliza-

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

tion of the organic substrates competes with the disproportionation of NO_2 . Among the organic substrates, formate and oxalate are also mineralized but because they are of low fuel value their mineralization is not very helpful, yet it consumes NO_2 .

c. *Interfacial processes in aqueous suspensions*

Yields of charge transfer from solid silica particles to water and other liquids were measured. If the particles are small enough, essentially all of the charge that is originally deposited in the solid escapes into the liquid. This implies that the solid/liquid interface does not provide a significant barrier to the transfer of charges into the solution when the particles are very small (≤ 20 nm). Electrons may reach the liquid and generate hydrogen, for example. On the other hand, the same mechanism may also provide a pathway for oxidative aging of organics by holes even when the organic is dissolved in the liquid or adsorbed on the solid surface.

We have started to study reactions of NO_2 . Methodology and instrumentation to measure reactions of relevant organic radicals with NO_2 and with its parent NO_2^- were developed. Because of low extinction coefficients, conductivity will be the method of choice.

Background

The goal of this project is to establish the chemistry and physics that dominate the radiolytically initiated processes that occur in waste tanks across the EM complex. To achieve this goal we are coordinating our efforts with another EMSP project at PNNL ("Interfacial Radiolysis Effects in Tank Waste Speciation", PI: T. Orlando) and with the Safety Programs at the Hanford site (most closely with the Organic Aging program at Hanford; PI: D. Camaioni of the PNNL and with the Flammable Gas Generation program at Richland). The "Interfacial" project provides us with insight into the effects of interfaces in high level liquid waste (HLLW), a problem of much concern in understanding the physics and chemistry of the waste. Coordination with the Safety Programs provides us a conduit to the needs at the sites on one hand and allows dissemination of information in an expedited fashion on the other. In addition, we utilize some of our current resources from the Office of Basic Energy Sciences to assist in solution of relevant problems that are more basic in nature than is possible to address in the EMSP. An example of such a problem is the theoretical calculation of the redox potential of the NO_3^{2-} radical (see below).

We believe that this intensive interaction is essential if the program is to have an impact on operations in the field. A recent report from the Organic Tanks Safety Program at PNNL

exemplifies our approach and the benefits that it entails¹. To enhance the interaction we arranged last year three coordination meetings, two at ANL and one at PNNL. A workshop was also organized at the PNNL that included most groups that are active in tanks chemistry issues from essentially all organizations at the Hanford site. Preliminary results of our project were recently published². Further results are at various stages of publication³. We will distribute this report across the complex.

Scientific Issues: Because of the high concentrations of nitrate and nitrite in essentially all large waste tanks, and because of the high efficiency of scavenging of the primary radicals from water radiolysis by $\text{NO}_3^-/\text{NO}_2^-$, the majority of the radicals are of the NO_x family generated radiolytically shortly after the deposition of energy in the waste (ns range or shorter). Specifically, one can show that most of the radicals, OH or $\text{O}^\cdot$ radicals and e^-_{aq} , reactions 1, 2 and 3, are efficiently converted to NO_2 via:

or in basic solutions:

In ideal solutions $G(\text{NO}_2) \sim 6$ molecule per 100 eV of deposited energy. H atoms are converted to NO via reaction 4, with an ideal yield of 0.6 molecule per 100 eV.

Once the radicals are converted into NO_2 ($E^0(\text{NO}_2/\text{NO}_2^-) = 1.04 \text{ V}$) and NO, the radiation will induce only oxidation processes. It should, however, be recognized that, even though NO_2 is a strong oxidant, an organic oxidation product from its reaction on the "aging" route to mineralization (i.e., to CO_2 or carbonate) could still be an efficient source for H_2 . Formaldehyde is but one example.

Reaction 2 in the "bordered" section above is a bottleneck in the transformation from a reducing environment to an oxidizing one. To our knowledge, the solvated electron is the only radical that reduces nitrate. A recent publication shows that H atoms do react with NO_3^- , but it con-

cludes that the product is directly NO_2 .⁴ We reach below a similar conclusion for the protonated form of the dianion radical, $\text{HNO}_3^{\cdot-}$. The initial product of reaction 2, the $\text{NO}_3^{\cdot-}$ radical, is a strong reductant; its redox potential is unknown but from its reactivity we deduce that it has to be more negative than -0.5 V (see below). Thus, as long as it exists in solution, the potential for the generation of H_2 from water cannot be excluded. The probability that it does occur is, however, rather small. On one hand, we know that it is inefficient in homogeneous nitrate/nitrite solutions (because $G(\text{H}_2)$ decreases upon increasing NO_x^- concentrations). On the other hand, we know that in the presence of noble metal catalysts, for example Pt or Pd, which may be present as daughter products from radionuclides decay, the radical dianion can generate H_2 . Therefore, we decided to study the relevant chemistry of $\text{NO}_3^{\cdot-}$. In this context, the shorter it lives the smaller is the concern, provided it is transformed to NO_2 .

We have essentially completed our studies of the $\text{NO}_3^{\cdot-}$. Two other issues are the focus of our current studies: Reactions of NO_2 radicals and reactions at heterogeneous colloidal interfaces. Both were discussed in detail in our proposal. We describe below the methodology that we developed in order to follow directly the reactions of NO_2 . This direction will continue next year, when the bulk of the data collection will occur. This effort is, and will be, strongly coupled to the "Aging" studies that take place at the PNNL.

The second issue is far more difficult and has only been started; nonetheless, it already raises serious doubts regarding conventional thinking about the fate of the energy deposited in solid particles. We will show that much of that energy can become available at the interface and generate typical radiolytically initiated reactions in aqueous solution.

Results and Discussion

1. Protonation of $\text{NO}_3^{\cdot-}$ Radicals

The radical dianion was generated by pulse radiolysis according to reaction 2, in solutions containing 0.02 M NO_3^- ($t_{1/2} = 3.5$ ns), and its lifetime was determined across a broad pH range by following its characteristic absorption at 270 nm. The half-lives are shown in Figure 1 along with simulation results obtained using the Chemical Kinetics Simulator (CKS) from IBM (The CKS is a trademark of IBM. It is freely distributed via the IBM web site on the Internet). The CKS allows a Monte Carlo computation of an unlimited number of chemical rate laws; in our case, it includes over 40 reactions, and their presently known corresponding rate constants, that describe the radiolysis of the nitrate solution.

Figure 1. The dependence of the half-life of the NO_3^{2-} radical on pH. Circles - experimental determination; triangles - simulation using the Chemical Kinetics Simulator from IBM.

The simulation describes the observations reasonably well. It is in acceptable agreement with published data, where available. It extends the observations to the pH range relevant to waste tanks and we also verified that the lifetime of NO_3^{2-} is not dependent on ionic strength. Traditionally, the explanation for the lifetime dependence stems from the acid-base equilibria of reactions 5 and 6.

However, we noticed that the half-life of the radical across the whole pH range is inversely proportional to the buffer concentration when one is used. Figure 2 shows that this is not expected if the presently accepted scheme of acid-base equilibria and the lifetimes of the various $\text{NO}_3^{\cdot-}$ species involved (reactions 5 and 6) are correct. At the published pK_a for $\text{NO}_3^{\cdot-}$ of 7.5, and of 9.2 for borate, the largest effect on the rate of decay could have been an acceleration of only a few percent. Therefore, only a few percent of $\text{NO}_3^{\cdot-}$ could protonate in this pH range and only a negligible effect of [borate] on its decay rate can be expected.

Figure 2. Decay of the $\text{NO}_3^{\cdot-}$ radical monitored at 270 nm. Circles are experimental points; broken line is simulation assuming fast acid-base equilibrium of the radical; solid curve is simulation assuming only the forward reaction of phosphate to directly give NO_2 . Solution contained $[\text{NaNO}_3] = 2.5 \times 10^{-2}$ M and 5×10^{-3} M phosphate buffer at pH 7.5.

We conclude that the reaction with borate (in its acidic form, $\text{B}(\text{OH})_3$) is not simply a proton-transfer equilibrium. This turns out to be a general observation and was observed at pHs as high as 11. It holds for other acid forms of various buffers including NH_4^+ and amines (specifically cyclohexyl-amino-propyl sulfonate, $\text{C}_6\text{H}_5\text{NHC}_3\text{H}_6\text{SO}_3^-$, labeled CAPS for the basic,

and CAPSH⁻ for its acid, forms respectively; pK_a = 10.4). Table 1 shows the rate of the reaction that we depict in equation 7 as a dissociative proton transfer. The optical spectrum obtained at the end of reaction 7 does resemble the published one for the protonated radicals of reactions 5 and 6.

Table 1. Rate constants^a for proton transfer from various "acids" to NO₃²⁻.

HA	k, M ⁻¹ s ⁻¹	pK _a
H ⁺	4.50 × 10 ¹⁰	
H ₂ PO ₄ ⁻	5.27 × 10 ⁸	7.21
NH ₄ ⁺	3.60 × 10 ⁸	9.25
B(OH) ₃	8.40 × 10 ⁷	9.24
CAPSH ⁺ ^b	1.10 × 10 ⁷	10.4
NH ₃	3.40 × 10 ⁶	
MeOH	(1.2±0.2) × 10 ⁴	15.0
t-BuOH	≤ 2 × 10 ⁴	16.9
H ₂ O	1.24 × 10 ³	15.7
	(6.80 × 10 ⁴ s ⁻¹)	

^aAll were determined in this study. Some of the same rate constants were previously determined under various conditions. ^bCAPS = cyclopropyl-aminopropane-sulfonic acid.

Boric acid is not strikingly outstanding in the correlation of rate constant vs pK_a that may be constructed from the data in Table 1 (Figure 3). On the other hand, when the reaction of other acids is a proton transfer reaction, boric acid is outstandingly slower, even relative to acids of higher pK_a. It is commonly accepted that boric acid acts as a general Lewis acid, an hydroxide ion acceptor as in equation 8.⁵

In the case of the NO₃²⁻ radical, reaction 7 translates to:

Figure 3. Free energy correlation between the rate constant of protonation and the pK_a of the corresponding general acid. Open circles indicate the correction of the rate constant for electrostatic interactions between the reactants.

Why this proton transfer is so unusual is beyond the scope of the present study. We address this question from the theoretical point of view in our studies under the auspices of the Chemical Sciences Division of DOE Basic Energy Sciences. But regardless of the theoretical basis, the correlation of Figure 3 is expected to hold regardless of the identity of the specific buffer or amine. This type of free energy correlation (kinetics vs thermodynamics) is most useful in providing predictive capabilities and we seek it on every opportunity.

In conclusion of this section: The NO_3^{2-} is clearly the initial product, but it seems that its protonated form does not exist. Thus, it is converted to NO_2 even faster in the presence of Lewis acids, reducing the probability of fuel-generating reduction processes.

2. Redox Potential

The one electron redox potential of the $\text{NO}_3^-/\text{NO}_3^{2-}$ couple was computed to be -1.05 V (all potentials are vs NHE)³. Attempts to use pulse radiolysis to measure the equilibrium constant of the radical dianion with various reference couples (reaction 9) failed for various reasons.

Methyl viologen (MV^{2+} , $E^0 = -0.45$ V) is quantitatively reduced by NO_3^{2-} , and the MV^+ radical remains completely stable indicating that the equilibrium is strongly to the right. On the other hand, p-nitrobenzonitrile ($E^0 = -0.60$ V) is reduced at a slower rate and the radical, which is otherwise stable, decays relatively fast; perhaps via the back equilibrium. However, we cannot exclude contribution from a reaction of the radical with NO_2 (see below). Therefore, at present we suspect that the theoretical value is too negative. Our current estimate from the experimental results is $E^0 \sim -0.75$ V. Regardless of the exact value, the radical dianion is clearly a strong reductant. It can generate hydrogen from water, but most probably will not, as discussed in the conclusions section.

3. Reactions of Precursors and Ionic Strength Effects

The high concentration of salts, and nitrate in particular, in HLLW raises two questions that were addressed:

- are the same products that were studied at relatively low concentrations, for example NO_3^{2-} , relevant in the highly concentrated solutions of the HLLW, and
- can the rate constants that were determined at low ionic strength be converted to the relevant conditions.

The answer to both questions is in the affirmative. We have shown that the same species are generated at very high (up to 5 M) nitrate concentrations and we have tested existing theories to show that rate constants of reactions with highly charged species, where the largest changes are expected, can be calculated from their values in ideal solutions.

The nitrate ion is one of the most efficient scavengers for the precursor of the hydrated electron. The concentration at which only 37% of the initially produced thermally relaxed electrons escape scavenging prior to solvation is very low: $C_{37} = 0.45 \text{ M}^6$. Because of the low C_{37} and because the concentration of nitrate in HLLW is extremely high, the identity of the product, P in reaction 2a, needs to be verified. Is $\text{P} = \text{NO}_3^{2-}$ or not?

Figure 4. Dependence of the yield of MV^+ radicals, normalized to the yield at low ionic strength, on $[NO_3^-]$. Absorbance was measured at the MV^+ bands at $\lambda = 600$ and 394 nm. All solutions contained 1 mM MV^{2+} .

Note that e_{th}^- in reaction 2a signifies a thermal electron before it became solvated. This reaction is different from the electron absorbed in the "direct effect", where the electron has not yet thermalized. To test that question we measured the yield of MV^+ from reaction 10 at increasing

$NaNO_3$ concentrations. The normalized Absorbance from MV^+ , as determined at 600 and 394 nm, at several doses in the range of 0.25 - 0.50 krad per pulse, are given in Figure 4. We chose to use low doses because the rate of formation of MV^+ becomes slow at high ionic strength (see below) and therefore recombination of radicals becomes significant under such conditions. The results shown in Figure 4 were corrected for the increase in density of the solutions upon the increase in electrolyte concentrations assuming that the absorbed dose is proportional to the density. This correction amounts to 26% at the highest nitrate concentration used in the figure.

As can be seen in Figure 4, up to 30% decrease in the yield of $MV^{\cdot-}$ can be observed at 5 M of $NaNO_3$. Several factors, real or artifacts, may lead to the observed decrease. The high ionic strength may cause spectral changes. However, recording the spectrum of MV^+ at low and high nitrate concentrations revealed no spectral differences (except at $\lambda < 300$ nm where NO_2 and other NO_x products from direct effects, absorb light). Ion pairing of the parent molecules, or the radicals, as a cause for the reduction was also rejected because the zwitterionic viologen, 4,4'-bis(propyl-sulfonato) bipyridinium (ZV), gave the same results as MV^{2+} . On the other hand, some of the radiation is absorbed directly by the nitrate. Assuming that this "direct effect" is proportional to the electron density of each component, 37% of the radiation is directly absorbed by nitrate at 5 M concentration. That fraction, similar to the reduction in the yield of viologen radicals, produces directly NO_2 , and perhaps NO , but not the reducing NO_3^{2-} . Thus, we conclude that the reaction of the precursor to the hydrated electron with nitrate produces a reducing radical, presumably the same NO_3^{2-} radical dianion. Most importantly, this reducing radical can still generate H_2 just like the NO_3^{2-} .

As can be expected from the charge of the reactants of reaction 10, the rate should be sensitive to the ionic strength of the solution. Figure 5 shows the rate constant as a function of μ , the ionic strength, which was controlled by varying the concentration of $NaNO_3$. The rate was measured at $\lambda = 600$ and 394 nm, the strong bands of the MV^+ product. The least squares fit to the Brönsted-Bjerrum modified Debye-Huckel equation (equation 11) yields: the rate constant at zero ionic strength, $k_0 = (1.3 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, the product of the charges, $Z_a Z_b = -4.2 \pm 0.2$,

$$\log \frac{k}{k_0} = \frac{1.018 Z_a Z_b \sqrt{\mu}}{1 + 0.329 d \sqrt{\mu}} \quad (11)$$

and an effective reaction distance $d = 2.48 \pm 0.2 \text{ \AA}$. The very satisfactory fit to the experimental results in Figure 5 indicates that we can predict with acceptable accuracy the rate constants at high concentrations even for highly charged species. The parameters obtained from the fit verify that we are dealing with the same species in all these experiments: The doubly charged, indeed NO_3^{2-} (from Reaction 10 one expects $Z_a Z_b = -4$), whose product is eventually NO_2 .

Figure 5. The dependence of the rate constant for the reaction of NO_3^{2-} with methylviologen (MV^{2+}) on ionic strength. The rate was measured at the MV^{2+} bands at $\lambda = 600$ and 394 nm. Ionic strength was varied by changing $[\text{NaNO}_3]$. Solid curve is the least squares fit to equation 11 using $k_0 = 1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $Z_a Z_b = -4.2$, and $d = 2.48 \text{ \AA}$.

4. Reactions of NO_2

This radical is believed to be the major radical that is generated by the radiolysis, as already emphasized above. The Organics Aging program at PNNL and the Hanford site already measures relative rates of this species with the organics of relevance to the tanks. Our goal in this EMSP project is to provide an absolute scale to the relative rate measurements, and together with the Aging program, determine the oxidation products and develop a workable mechanism. To achieve this goal, we have recently added a Visiting Scientist at PNNL who is performing the product analysis from genuine NO_2 (rather than from irradiated waste simulants) oxidation reactions with the organic chelates. Details of this effort will be reported later. Here we describe our efforts to determine absolute rate constants for the NO_2 reactions.

Because of the low extinction coefficient of NO_2 , optical detection of this radical is difficult. To overcome this difficulty we resort to the conductivity technique. The disadvantage of this technique is its lack of specificity. It follows the changes in the conductivity of the ions in the solu-

tion and, thus, any ionic change is reflected in the measurement. Nonetheless, it is very helpful when some preliminary information is available. In our case, we know that reactions 1-3 generate NO_2 and, accordingly, OH^- replaces NO_2^- (reaction 1) or 2OH^- replaces NO_3^- in reactions 2 and 3.

Figures 6 and 7 show the changes in conductivity following a pulse of irradiation of several solutions. The former shows the conductivity changes at early times and the latter at longer times. No changes are observed beyond those shown in Figure 7, up to 1 sec, and, therefore, we assume that these are representative of the "stable" products. The early times are necessary in order to understand the changes in the system. The longer times are directly relevant to the tank chemistry.

The solid curves in both figures are the conductivity changes in nitrite solutions, saturated with N_2O at pH 10, due to:

at fast times (thus an increase in conductivity), and to:

Thus the decrease in conductivity. This last reaction is the one that is always competing with the reactions of NO_2 with any substrate and is the baseline competition in the Aging studies at PNNL. Clearly we can (and will) measure the details of this reaction.

The dashed curves in Figs. 6 and 7 show the changes in conductivity upon the addition of i-propanol to a solution containing nitrate. Here NO_2 is generated from NO_3^- , via NO_3^{2-} (reactions 2 and 3) but the OH radicals react with the alcohol, RH , according to:

At fast times the changes in conductivity are, therefore, due to reactions 2 and 3 only. At longer times the conductivity decreases (Figure 7) because of

Thus, in this system, NO_2 oxidizes i-propanol radicals to acetone.

Figure 6. Conductivity changes following pulse irradiation of several NO_2 -generating solutions. Solid curve: N_2O -saturated 0.5 mM NaNO_2 . Dashed curve: Ar-saturated 0.5 mM NaNO_3 solution containing 0.1 M i-propanol. Dotted curve: Ar-saturated 0.5 mM NaNO_3 solution containing 0.1 M t-butanol. All solutions at pH 10; all normalized to 0.96 krad per pulse.

The dotted curves in the two figures are from experiments similar to the previous one except that t-butanol replaced i-propanol. The radical of t-butanol is well known to be much less prone to oxidation than that of i-propanol. We see at long times (Figure 7) no change in conductivity. This is attributed to the cross-recombination reaction:

(otherwise, $\text{R}+\text{R}$ and NO_2+NO_2 will show the conductivity changes that we see in the absence of the nitrate or alcohol, respectively). The generic reaction 15 is of much concern in the tank chemistry; it is a source of nitration products. At Savannah River nitrobenzene has been detected among the products of the radiolytic degradation of tetraphenylborate following the "In Tank Precipitation" (ITP) process. Whether this is a product of a radical reaction with NO_2 or NO_2 reaction with an organic molecule in the ITP is yet unclear.

Figure 7. Conductivity changes following pulse irradiation of several NO_2 -generating solutions. Solid curve: N_2O -saturated 0.5 mM NaNO_2 . Dashed curve: Ar-saturated 0.5 mM NaNO_3 solution containing 0.1 M i-propanol. Dotted curve: Ar-saturated 0.5 mM NaNO_3 solution containing 0.1 M t-butanol. All solutions at pH 10; all normalized to 0.96 krad per pulse.

The results of these two figures indicate our course in the immediate future. We will expand these studies to include the organic chelates and their degradation products. We think that these experiments will provide rate measurements for the reactions of organic radicals with NO_2 (reactions 14 and 15). A similar approach will be utilized to measure the rate of reaction of R with the parent ions, primarily with NO_2^- .

5. Interfacial Charge Transfer

This section is closely coordinated with another EMSP project ("Interfacial Radiolytic Effects", same Co-PIs). We discuss here only the studies at ANL, which focus on the solid/liquid interface. The studies at PNNL focus on the basics of the solid/gas interface. Because the HLLW is heavily loaded with solid particles, we are concerned about the fate of the radiation that is initially deposited in the particles. The question that is addressed at present is very fundamental:

Does the energy that is absorbed by the particles, in particular inert particles such as silica, contribute to any products in the aqueous phase? The answer to that question may have broad implications for the HLLW management, in the tanks and beyond - for the long-term storage medium. We have raised this concern in conjunction with the grout storage option at the Hanford site.^{7,8} Inasmuch as a similar option, the saltstone option, is still being considered at Savannah River, the question remains relevant. In addition, the question directly impacts on the contribution of particles in HLLW to the chemistry in the tanks.

To address this question, we pulse-irradiated aqueous solutions that contain increasing concentrations of SiO₂ small colloidal particles (Ludox from DuPont; monodispersed particles of diameter ≥ 2 nm). These suspensions remain transparent up to 50%w SiO₂ in water and, therefore, allow optical detection of the processes that occur in the suspension. We followed the generation of solvated electrons at 600 nm. The radiation energy is deposited in the suspension, partially in the liquid phase and partially in the solid particles. As the weight % of the particles increases, an increasing fraction of the energy is deposited in the solid. The exact fraction is easily calculated because it is proportional to the density of the material. However, here we emphasize the qualitative observations. If the energy (or charges) that is deposited originally in the particles remains in the solid, then the yield of solvated electrons must decrease upon increasing the %w of SiO₂. This, of course, is the desired effect of the solid particles (or solid matrix in long-term storage). Energy and charges that remain in SiO₂ cannot produce H₂, for example. If, however, they do migrate to the interface then the efficacy of the solid matrix is questionable.

Figure 8 shows the optical absorption signal at 600 nm from a suspension of silica in glycerin. The height of the signal immediately after the pulse is proportional to the yield of solvated electrons, one of the strongest reductants known ($E^0 = -2.9$ V). We have changed the medium from water to glycerin because the aqueous suspensions could not sustain more than 50%w of SiO₂. Beyond that level of loading, the particles precipitate and the suspension becomes opaque, preventing optical detection. On the other hand, the refractive index of glycerin is similar to that of silica so that even when the particles precipitate, the suspension remains translucent. The purpose and conclusions of the experiments are, however, the same (solvated electrons in glycerin are very similar to their counterpart in water). Furthermore, we conducted the same experiments in water up to 50%w of silica with the same results.

Figure 8. Yield of solvated electrons, e_{sol}^- , in neat glycerin and in heavily loaded SiO_2 suspensions (60%w SiO_2 in glycerin). Solid points are for the neat solvent. Open triangles and open squares are for two independent experiments with the suspensions. Note that the height of the signal is the same in the neat solvent and the suspension, indicating the same yield of e_{sol}^- .

The results in Figure 8 are rather surprising. The yield of electrons that are generated in the solvent is independent of the loading with silica. In other words, even though a significant fraction of the energy is initially going into the solid, charges from ionization of the particle migrate to the interface and induce reactions in the liquid. We view the processes that follow the generation of charge carriers in the solid by the radiation as a competition between three pathways (see Scheme I):

Scheme I. Radiolytically initiated processes in solid particles suspended in solution. CB and VB are the conduction and valence bands of the material, respectively. e^- and h^+ are electrons and hole, respectively. The subscript t indicates trapping and subscript sol indicates solvated electrons. The curved arrow indicates deposition of radiation energy in the particle. Processes a,b,c represent recombination, trapping and interfacial crossing, respectively.

Process a. As the charges migrate they may recombine. Electrons and holes in the solid particle may recombine with one another and regenerate the parent molecule in the lattice (and release heat).

Process b. The charge carriers may be trapped in the bulk of the solid. Many traps exist in the particle and more may be "dug" by the charge carriers. Once the charges are trapped, or are annihilated in the previous process, the effect of radiation is relatively **innocuous**. However, accumulation of a large number of trapped charges, even at deep traps (i.e. at low free energy), may result in adverse effects, such as disintegration of the particle.

Process c. The charge carriers may encounter the interface during their migration and cross into the liquid. This of course is the least desirable process from the safety concern perspective. Traps at the surface are a special case in this regard since the electron may or may not cross the interface from such traps depending on the depth of the trap. Phenomenologically, a surface trapped charge that causes reactions in the liquid is not distinguished here from direct transfer of free carriers.

One may predict that the probability of processes a and b increases as the size of the particle increases. For a given excess energy that the charge may carry, its mean free path before it

encounters an opposite charge (process a) or a trap (process b) is independent of its size. But, the probability that it will encounter the interface increases as the size of the particle decreases. Thus, the yield of solvated electrons should increase as the size decreases. Preliminary results indicate that this is indeed the case. The yield of e_{sol}^- decreases for larger particles at a given loading. Detailed analysis of the size dependence of the yield will be conducted in the near future, but we may provide some encouraging observations at this early stage. Because the yield seems to depend on the size when the particles are at the tens of Å range, it will probably be very small when a large fraction of the energy is absorbed by large particles. Thus, if the particle sizes in the HLLW are in the micron range, most of the energy (i.e., charges) will remain trapped in the solid.

We address in our studies only the fate of electrons. One is curious about the consequences of this analysis to hole reactions. This question is intimately related to another EMSP project at PNNL, ("Ionizing Radiation Induced Catalysis on Metal Oxide Particles", PI: T. Fryberger). We can only speculate that because the mobility of the holes in the oxides is usually, but not always, lower than that of electrons, the probability that they will find a trap (or even create a trap) is higher. Therefore, the fraction of holes that reaches the surface is probably smaller than the fraction of electrons. Those that reach the surface generate OH radicals from the water or directly oxidize adsorbed species. The obvious candidate for such an oxidation is NO_2^- , but organic substrates may adsorb preferentially, and thus degrade faster than nitrite via this mechanism. We may address this question in the future under a separate project.

Conclusions and Implications

The implications of our results to the specific questions that are the focus of the present report will now be summarized. The half-life of NO_3^{2-} in solutions similar to those in the waste tanks is shorter than $\sim 15 \mu\text{s}$. Any fuel-generating reduction reaction has to be faster than that. The presence of ammonia and complexing amines in some of the waste solutions only enhances this conclusion; it accelerates the transformation to the oxidizing radicals. Other proton sources may further reduce the risk. Generation of H_2 will require an unusually efficient catalyst (high concentrations of small particles of noble metals) that to our knowledge is unavailable in the tanks. A possible source of protons in the tanks are metal-hydroxides, $\text{M}(\text{OH})_n^{n+}$; we have no information on their reactivity with this radical. However, any reaction of hydroxide is expected to follow the same pattern and therefore can only shorten the time window for H_2 generation.

Computer simulation of complex sequences of reactions is simple with presently existing codes for desktop computers. The particular CKS simulator that was used here is limited only by the 32 bit addressing of the computer. It already provided useful guidelines in the execution of the experimental program and there is no reason why it cannot evolve into the much larger modeling effort needed to describe the chemistry of waste tanks. However, incorporation of the inhomogeneous stages of the "spur" kinetics into this modeling tool will require some programming effort. Nonetheless, our experience with predictive modeling of this early stage of the radiation chemistry indicates that at high concentrations of solutes this stage is not very significant.

We have in place techniques and methodologies to determine rates of NO_2 radicals with organic substrates. The disproportionation reaction of this radical depends on dose rate but so does any other reaction of NO_2 with any radical in the HLLW. Whether NO_2 will disproportionate, react with another radical or with a molecular component in the waste will depend on relative rate constants. The absolute values of some of these constants will be determined in the near future. Relative rates will be determined at the PNNL. In HLLW, degradation of organics to CO_2 is the preferred route, but even formate or oxalate will reduce the fuel value of the organic. How efficient this route is will be determined by these relative rate constants and the concentration of the organic.

The deposition of radiation in solid particles, even in highly inert broad band-gap solid insulators, such as silica, may lead to fragmentation of the water. Fragmentation water products that are generated via this route may contribute to the generation of fuels in the waste. However, we suspect that the particles in the waste are very large so the fraction of energy that escapes into the liquid is probably small. Similar arguments may be raised as regards the oxidizing holes. However, holes that may reach the interface will contribute to the degradation of organic substrates just as the direct radiolysis of water. Again, the fraction of holes that will reach the interface is probably small in realistic systems.

References

- 1) D.M. Camaioni; W.D. Samuels; J.C. Linehan; A.K. Sharma; M.O. Hogan; M.A. Lilga; S.A. Clauss; K.L. Wahl; J.A. Campbell, "Organic Tank Safety Program FY97 Waste Aging Studies" Pacific Northwest National Laboratory Report: PNNL-11670, September 1997
- 2) D. Meisel; A. Cook; D. Camaioni; T. Orlando, "Chemistry, Radiation, and Interfaces in Suspensions of Nuclear Waste Simulants", in "Photoelectrochemistry", edited by L.M.P. K.

- Rajeshwar, A. Fujishima, D. Meissner, M. Tomkiewicz, The Electrochemical Society Pub., 350-357 (1997)
- 3) a. A.R. Cook; B.W. Dreyfus; N. Dimitrijevic; D. Meisel; L.A. Curtiss; D.M. Camaioni, J. Phys. Chem., *to be published* (1997). "Reducing Radicals In Nitrate Solutions. The NO_3^{2-} System Revisited"
- b. A. R. Cook, L. A. Curtiss, B. Dryefus, D. Camaioni and D. Meisel, "The Radiation Chemistry Of The No_x System Revisited"
- c. D. M. Camaioni, K. Knutsen, J. C. Linehan, T. M. Orlando, A. Cook, and D. Meisel, "Some Fundamental Studies On The Effects Of Radiation And Interfaces In High Level Wastes", Book of Abstracts - Annual Meeting, Am. Chem. Soc., Las Vegas, NV, Sept. 7-11, 1997
- 4) S.P. Mezyk; D.M. Bartels, J. Phys. Chem. 101, 6233-6237 (1997). "Temperature dependence of hydrogen atom reaction with nitrate and nitrite species in aqueous solution"
- 5) N.N. Greenwood, "Comprehensive Inorg. Chem.; N.N. Greenwood, ed., 1973; Vol. 1, p. 886
- 6) R.K. Wolff; M.J. Bronskill; J.W. Hunt, J. Chem. Phys. 53, 4211-4215 (1970). "Picosecond pulse radiolysis studies. II. Reactions of electrons with concentrated scavengers"
- 7) D. Meisel; C.D. Jonah; S. Kapoor; M.S. Matheson; W.A. Mulac, "Radiolytic and Thermal Generation of Gases from Hanford Grout Samples", 1993, ANL Report 93/42, October 1993.
- 8) C.D. Jonah; S. Kapoor; M.S. Matheson; W.A. Mulac; D. Meisel, "Gas Generation from Hanford Grout Samples", 1994, ANL Report 94/7, March 1994.

Distribution

ANL

Cook, A.
Dimitiriev, N.
Helt, J. (3)
Kharas, C.
Makarova, O.
Strachan, D.
Thurnauer, T.

DOE

Gress, M.
Laufer, A.
Massey, R.,
Milman, W.
Roesler, G.
Rosenwald, G.W. (RL)

PNNL

Brothers, J.
Bryan, S.
Camaioni, D.
Campbell, J.
Fryberger, T.
Orlando, T.
Pederson, L.
Zevos, N.

DE & S Hanford

Cash, R.
Johnson, G.D.
Meacham, J.

Savannah River

Bibler, N.
Walker, D.

Others

Babad, H.
Stock, L.