THE NO_x SYSTEM IN HOMOGENEOUS AND HETEROGENEOUS NUCLEAR WASTE**DE-FG07-99ER14938**

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A. INTRODUCTION

This is the final technical report of the above-mentioned EMSP project. It summarizes the activities under that project throughout its lifetime. The project formally covers the period of September 15, 1998 to September 14, 2004, which includes the original project (from 1998), a three-year extension (starting September 15, 2000) and a no-cost extension of one year. In fact, even this six-year period follows at the heels of earlier EMSP and other projects by the same PI's from PNNL and Notre Dame (and from Argonne prior to that), which resulted in a broad outline of the chemistry in the Hanford waste tanks. Of particular emphasize in these projects was the generation and retention of flammable gas mixtures in the tanks and the interaction of organics compounds in the tanks with the ionizing radiation of the mixed-waste. Annual technical reports were regularly and on time submitted, and therefore, this report should be consulted with the previous reports, as well as the many publications that resulted from the activities associated with this project. The list of PI's given above includes various participants that contributed substantively at various degrees to understanding of the relevant chemistry of the system over the years.

This project addressed generic safety concerns that arise at essentially all high-level waste (HLW) storage sites. It focused on the effects of organic chemicals in stored nuclear waste and their impact on pretreatment and tank closure issues. Managing the tank wastes and site cleanup activities requires understanding of the chemistry of organics in aqueous basic solutions that contain high nitrate and nitrite concentrations under the field of γ and β irradiation. We quantitatively characterize the important chemical processes that are induced by radiolysis of the organic complexants, and their degradation products, during the storage in tanks. Furthermore, concerns that arise from pretreatment and tank

closure issues, e.g., Tc speciation, can be rationalized with the mechanistic knowledge developed here. None of the Hanford tanks is currently on a watch list, partially due to the predictive understanding of the tanks' chemistry that was developed by these projects and their predecessor activities. Because concerns that arise from gas generation in waste tanks are significant, and because the effect of particulate material on gas generation and retention is so evidently pronounced, we also studied the influence of solid particles on the production of H_2 . However, in agreement with the EMSP project managers only a few systems, specifically, the effect of silica particles, were studied. Furthermore, because of the current lack of understanding of the interfacial processes, computation and theory were not attempted in the heterogeneous-systems effort. The project was closely coupled to another EMSP project (81883) and exchange of information between the two related studies is frequent.

During the report period we developed a computational approach that can describe the fate of organic complexants in HLW. This includes selection of an appropriate computational model, improvement of existing solvation treatments for anions, and development of a theoretical procedure to account for high ionic strength. The model provides an accurate evaluation of the extent of hazardous material, including flammable gases, generation. Experiments to outline pathways and verify computational predictions were also described. Degradation of aminocarboxylate-chelates shows a rich radical-chemistry that results from oxidation by NO_2 , OH and O^- radicals. Preliminary results indicate, contrary to prior assumptions, that many radicals react with nitrite, NO_2^- , by addition (preferentially to the nitrogen) rather than via electron-transfer redox processes.

B. OBJECTIVES

The objective of this project is to quantitatively characterize the important chemical processes that are induced by radiolysis of nuclear waste. The relevance and significance of the proposed studies are primarily to assist in formulating defensible decision-making processes. The study provides generic information that could be applied to the various scenarios that may arise in the processing and handling of HLW. The project focused on the effects of organic chemicals in stored nuclear waste and their impact on pretreatment and tank closure issues. Recognizing that experiments cannot reproduce every conceivable realistic scenario, the project emphasized computational methodologies. Starting from first principles, we were able to compute the reaction pathways of the important radicals with relevant organic substrates. The adequacy of the calculated results was calibrated against experiments performed

in homogeneous concentrated aqueous solution. The effects of media of realistic composition on the rates of the various processes were calculated, and the consequences to safety issues at the tank farms were evaluated. Similarly, but only at the experimental level, knowledge of the effects of particulate material (silica as model for sludge) on the yield of gases was studied. When translated into site-specific concerns, quantitative modeling of these processes can allow estimation and evaluation of safety issues associated with the storage of HLW in tanks, in sludge residues temporarily remaining at the bottom of the tanks, or at pretreatment facilities.

C. RESULTS AND DISCUSSION

The passage of ionizing radiation through waste solutions generates highly reactive radicals (OH, O^- , and H) from water that may attack the dissolved organic species directly or induce production of other radicals that subsequently react. High concentrations of hydroxide, nitrate and nitrite ions in waste solutions rapidly convert the primary radicals of water radiolysis (e^-_{aq} , OH, and H) to NO_2 (from e^-_{aq} and OH), O^- , and NO (from H atoms). NO_2 and O^- are primarily responsible for radiolytically-induced degradation of organic complexants.^{1,2} The kinetics of NO_2 radicals reacting with multifunctional organic compounds, such as the complexants ubiquitous in the waste tanks, are sparsely documented. While some rate data are available for O^- reactions, information on its reaction mechanisms and ultimate products is limited. Results from EM-, EMSP-, and BES-supported projects at PNNL and NDRL have begun to remedy this situation. Details of the relevant reactions follow below.

Reactions of NO_2 radicals and the effect of NO_2^- : A γ -radiolysis study of simulated waste solutions showed that all the complexants are degraded.² Furthermore, the selectivity observed in these systems is very different than that expected for OH and O^- , consistent with the premise that NO_2 is generated in the waste simulant.³ Confirmation of the NO_2 selectivities has been obtained by this EMSP project from NO_2 gas contact experiments. It shows high selectivity for aminocarboxylate and glycolate anions over formate ion, in contrast to the reverse selectivity of OH and O^- .⁴ From these observations we also conclude that reactions of NO_2 with complexants are sluggish, occurring with rate constant on the order of 1-100; whereas OH and O^- react with rates that range from 10^7 - $10^{10} \text{ M}^{-1} \text{ s}^{-1}$. How NO_2 attacks the

multifunctional complexants is not known. Other modes (e.g., H-abstraction, electron transfer) and different sites of attack (e.g., amino, alkyl, and carboxyl groups) are possible and will depend on the specific substrate molecule.

We have shown that NO_2 radical is the dominant oxidizing species in typical waste compositions. The interactions of this radical with multifunctional complexants, such as glycolate, and amino-carboxylates were investigated. Initial work focused on simple reactions of NO_2 . Relative rate constants were measured and reaction products were identified. Electron transfer and H-atom abstraction pathways were identified and the relative importance of a substitution/elimination route was assessed. In highly basic aqueous solution calculations predicted and experiments verified that the oxidizing NO_2 is readily converted into NO_3^{2-} , a strong reductant. A survey of the expected radicals from the simplest multifunctional complexants was used to calibrate the efficiency and accuracy of the chosen computational procedure using a density functional theory approach. A detailed computational study of the radiolytic oxidation of selected aminocarboxylates in basic aqueous solutions predicted the formation of a number of radical species not reported in earlier experimental work. The calculations also revealed the mechanism for generation of carbon dioxide and the carboxyl radical, CO_2^- and offered a route to the unusual rearrangement products experimentally observed during long-time radiolysis of waste simulants.

Following earlier observations from NO_2 “contact” and radiolysis experiments with waste simulants that contained glycine, we found that glycine degrades to 2-amino-3-hydroxysuccinate (hydroxyaspartate), oxalate, formate and carbonate ions. We also observed that high concentrations of nitrite ion suppress the production of hydroxyaspartate during radiolysis or contact of glycine with NO_2 . These observations are of concern because they indicate that fuel-rich organics do not necessarily degrade to less energetic and innocuous products. Therefore, we became interested in understanding how hydroxyaspartate forms and why is it suppressed by nitrite ion. Recent work shows that the hydroxyaspartate forms by aldol condensation of glycine with glyoxylate ion. Glyoxylate is an intermediate in the oxidation of glycine and other complexants (HEDTA, EDTA, NTA, glycolate) that were commonly used at Hanford and stored in the tanks. We, and others at Georgia Tech, have shown that glyoxylate converts to H_2 and oxalate in highly basic solutions.

Our observation of efficient condensation of glyoxylate with glycine under these very same conditions was not known. We have proven it by showing that hydroxyaspartate is generated in good yields when glycine is added to alkaline (1 M NaOH) solutions of glyoxylate in the absence of radiation or NO_2 . The following aldol condensation mechanism is proposed:

The mechanism for suppression of the condensation reaction by nitrite ions is not clear yet. Possible reactions include addition of NO_2^- to glyoxylate that slows the rate of the aldol condensation:

Alternatively, nitrite ion may oxidize glycine radicals directly to oxalate without forming glyoxylate, as in the following:

Both pathways require addition to nitrite, a theme that increasingly becomes evident in the reactions of NO_2^- .

Our studies on radiolytic and photolytic oxidation reactions of aminocarboxylate ions have provided a significant advance in understanding the mechanism of OH attack.⁵⁻⁸ Complementary electronic structure calculations have yielded insight into the mechanism of the radiolytic oxidation in the model complexants glycine and its methylated derivatives.^{5,6} Attack by the hydroxyl radical in basic solution had previously been shown to produce a carbon-centered radical, presumably via hydrogen abstraction.⁹ Theoretical predictions of prompt decarboxylation following electron transfer to give the

aminomethyl radical,⁶ and suggestions that competitive H-abstraction would produce the aminyl radicals previously inferred from pulse radiolysis studies,⁵ have been verified by observations of both radical products by time-resolved EPR spectroscopy (TRESR) and spin trapping experiments.^{7,8} β -Scission of the aminyl radical has been theoretically described,⁶ and the mechanism of formation of the previously-detected carboxyl radicals¹⁰ has thus been discovered.⁶ The reaction of NO_2 with aminocarboxylate anions results in a similar distribution of products that appear to derive from decarboxylation and H-abstraction pathways. A common intermediate, involving the glycine zwitterion radical, that allows partition between these two reaction paths has recently been proposed⁶ in OH oxidation. Sophisticated solvent models are needed to determine whether a similar intermediate is indeed a participant in such electron transfer reactions involving NO_2 . A similar approach is also needed to clarify the mechanism of interaction of NO_2 and other NO_x radical species with the other multifunctional chelators present in the waste, such as glycolate and citrate.

Further chemistry implicating the interaction of NO_x^- ions with organic radicals is expected, based on product analysis of wastes from 101-SY core samples, the PUREX process, and the “Red Oil” extractants. For example, the reaction is reminiscent of a key step in the free-radical chain mechanism of alkylation in organic nitro-compounds, proposed by Kornblum and coworkers.¹¹⁻¹⁵ Nitrite addition to aryl radicals is well documented^{16,17} and the use of nitromethane as a spin trap leads to products of the type shown in the generic Reaction 6.

From our computational approach the reaction pathway can be mapped, and the nature of transition states and magnitude of the barriers to reaction can be determined, which allows the estimation of reaction rates. In recent years, methods have emerged that permit the prediction of gas phase thermochemical and spectroscopic properties accurately enough to support and sometimes challenge experimental data. Density functional theory (DFT) methods allow a reasonably accurate survey of the various species at a modest computational cost. Our initial findings indicate that reliability should be assessed in particular cases by recourse to high-level composite methods such as G3¹⁸ or CBSRAD.¹⁹

To describe the presence of a solvent, most extant reaction field approaches are based on the underlying assumption of an isolated solute dissolved in pure water. Chemical interactions in the waste tanks of concern are complicated by the presence of high ionic strength. While the effect on free energies of solvation is probably not large, high ionic strength will influence chemical properties, particularly pK_a values.²⁰ Indeed, uncertainty in the pK_a governing the OH/O^- equilibrium, which is unknown in concentrated ionic solution, is a major obstacle²¹ to quantifying the reactions of these primary radiolytic species with NO_2^- and NO_3^- in waste tanks. This issue is discussed below.

The strength of the electronic structure modeling can be demonstrated by a simple example, the reaction of NO_2 with formate. The calculations suggest three modes of attack for this reaction:

- (i) H-atom abstraction via transition state TS-1:

- (ii) Attack on carboxyl group via a transition state, TS-II, with structure similar to the formylnitrate radical anion, $\text{HC}(=\text{O})\text{ONO}_2^{\bullet-}$:

- (iii) Attack on carboxyl group via a transition state, TS-III, with structure similar to the formylperoxynitrite radical anion, $\text{HC}(=\text{O})\text{OONO}^{\bullet-}$:

These transition states are depicted below with bond-lengths given in Å:

Structures were first optimized in the gas phase then using a dielectric continuum model to simulate the stabilizing effects of aqueous solution. The barrier ($\Delta G^\ddagger$) to H abstraction was calculated to be ~ 17 kcal/mol, and although endergonic by 6 kcal/mol, the mechanism seems plausible because rapid reactions of the initial products, deprotonation of HNO_2 by OH^- and oxidation of CO_2^- , would drive the reaction to nitrite and CO_2 . Product formation from the other transition states would require deprotonation to the HCO_2 moiety in TS-II or TS-III to be concerted with or subsequent to electron transfer to NO_2 . Our results suggest that the barriers are too high for sequential electron transfer-proton transfer steps. To assess the barriers for proton transfer concerted with electron transfer requires that the role of water be explicitly considered. This has not yet been done.

The formylperoxynitrite radical anion-like transition state shows a tendency to cleave NO, concerted with O-O bond formation. Although the energetics for producing peroxyformate ion and NO are prohibitive, the driving force to products CO_2 , NO , and OH^- is exergonic by 60 kcal/mol. Therefore, it

is conceivable that water might catalyze hydrogen transfer from C to O concerted with NO scission so that formation of peroxyformate is avoided.

Significant yields of decarboxylation products arise in reactions of glycolate, glycine, IDA, and NTA. Analogous pathways are relevant to these reactions, as it is not plausible for decarboxylation to occur as a result of H abstraction from C-H bonds in these compounds. In addition, analogous mechanisms of attack on amino or hydroxyl groups are plausible and also may lead to effective decarboxylation by β -scission of carboxyl radicals.

Modeling solvation and ionic strength effects: The high concentration of ionic species in the waste solutions requires specialized treatment to account for the effect of ionic strength on reaction dynamics

and equilibria. Important segments of a new computer program have been composed for numerical solution of the Poisson-Boltzmann equation (PBE) that describes both bulk dielectric and salt ionic strength effects on solvation. This program is based on a new and highly efficient mathematical formulation already produced in this project.²² We have recently developed improved numerical approaches for solute cavity construction and integration, accelerating convergence by utilizing linear interpolation of boundary elements and also providing a new method for surface characterization that allows treatment of complicated cavity shapes such as often occur when including explicit first-shell water molecules in the quantum calculation.²³ These elements are coupled together to produce a program that is efficient and accurate enough for routine use in conjunction with modern electronic structure calculations of solute properties. A key practical problem involves the evaluation over standard Gaussian basis functions of exponentially-screened potentials, where the Debye screening parameter increases with ionic strength. This has been solved by making a multi-Gaussian fit of the exponential, thereby reducing the integral evaluation to standard well-known formulas. Up to 25 Gaussians have been provided in the fit, which should give more than adequate precision in even the most demanding circumstances.

Nonlinear contributions arising from the excess osmotic pressure of the ionic atmosphere make evaluation of the full solvation energy from the electrostatic potential more difficult to handle than was originally anticipated. We are therefore concentrating first on developing a computer program for the simpler linearized PBE, which is adequate for solutions of low ionic strength. All the main features and advantages of our new approach to the full nonlinear PBE also apply to this case, with the simplification that the linearized solution can be reached without need for iteration. An efficient program for the linearized case is being developed, tested, and validated as a module in the HONDO electronic structure package.

In conjunction with the issues relevant to tanks waste, the OH/O^- radical system is of particular interest. At the high pH of nuclear-waste solutions, radiolysis of water leads to the formation of O^- radicals, rather than OH ($\text{p}K_{\text{a}} = 11.8$ in dilute solution). The O^- radical-ion, in turn, reacts with the organic complexants and their radiolysis fragmentation products. Analogous reactions of OH with the anionic forms of these aminocarboxylic acids were studied and were found to be close to diffusion controlled. The rates and pathways of these reactions with O^- have not been well characterized, but

indications are that they are also rapid. Both OH and $\text{O}^\bullet$ are strong oxidizing radicals, but are generally acknowledged to react differently because of the charge on the basic form. The latter also responds differently to high ionic strength. The present modeling code allows estimation of the contribution of each of these two species at the various ionic strengths.

We have completed a thorough search of the potential surfaces of clusters $\text{O}^\bullet(\text{H}_2\text{O})_n$ and the corresponding $(\bullet\text{OH})(\text{OH}^-)(\text{H}_2\text{O})_{n-1}$, $n=1$ to 5, using standard electronic structure procedures. For each value of n , a number of isomers have been identified, which are (local) minima in the potential energy surfaces. (For $n=4$, over 20 isomers have been identified with energies within 8 kcal/mol of the lowest-energy isomer.) We find that, for $n=1$ or 2, the $\text{O}^\bullet(\text{H}_2\text{O})_n$ structures are lowest in energy, but for higher n the forms $\text{O}^\bullet(\text{H}_2\text{O})_n$ and $(\bullet\text{OH})(\text{OH}^-)(\text{H}_2\text{O})_{n-1}$ are comparable in energy. In the $\text{O}^\bullet(\text{H}_2\text{O})_n$ form, $\text{O}^\bullet$ sits at the surface of a cluster and the unpaired electron is in an oxygen 2p orbital perpendicular to the surface. The exact structure of the cluster is significant because it reflects the delocalization of the charge among the cluster components, which will significantly affect solvation energies in small molecules and radicals.

For many of the ions present in the waste we use solvation models based on a continuum dielectric representation of the solvent with the solute molecule inside a molecule-shaped cavity embedded in the continuum. In these models, the interaction of the solute with the solvent is simulated by means of effective charges induced by the solute electron density at the cavity boundary. Important results of benchmark comparisons of experiment and theory have been the finding that anions are not treated well by most standard dielectric continuum models. A powerful *semi-empirical* protocol that allows computational results to be directly equated with experimental measurements and correlation of cavity shape with quantum mechanical descriptors was developed. Several approaches were tested to determine the shape of the embedded molecule. We finally focused on the interlocking spheres approach. Table 1 lists hydration energies for common species in the waste solutions: O_3^- , NO_2^- , HCO_2^- , NO_3^- and ClO_2^- along with the radii, which reproduce well the experimental values. The radii for the central atom are well predicted by two parameters, the atomic charge Q_x and the X-O bond distance, $D_{\text{X-O}}$. We anticipate that our approach can be extended to anions outside the training set, eventually to systems for which solvation data are lacking.

Table 1: Gibbs Free Energies of Hydration, Cavity Radii, Bond distance and Atomic charges.

Species	$-\Delta G_s^*$ kcal/mol	R_o Å	D_{x-o} Å	R_x Å	Q_x CHELPG charges
O^-	100	1.46			
O_2^-	82	1.56			
O_3^-	70	1.59	1.352	2.12	0.076
NO_2^-	69	1.6	1.264	2.04	-0.087
HCO_2^-	75	1.47	1.252	2.19	0.860
NO_3^-	65	1.53	1.260	2.42	1.180
ClO_2^-	64	1.53	1.634	2.71	0.432

Fate of the organic radicals and the effect of nitrite: Details of the decay channels for complexant-derived radicals are were elucidated by a combination of theoretical computations and time-resolved electron spin resonance experiments.²³ We use time-resolved electron spin resonance (TRESR) detection to identify and to follow the evolution of radicals formed in these radiolytic reactions. We determined that the organic radical, $(CH_3)_2C^\bullet-OH$ adds to nitrite:

We have measured the yield of this reaction to be about 30% of the yield of the organic radicals. Theoretical studies indicate that several other reaction channels, such as the formation of oxygen-bonded species, which rapidly cleave NO, are competitive. Further experimental work measured relative yields of $(CH_3)_2C(OH)NO_2^{\bullet-}$ as a function of the amounts of the parent molecules, 2-propanol and acetone.

A prototype of this class of reactions is the reaction of hydrogen atoms with nitrite ions. Hydrogen atoms themselves are present in the tanks from the radiolysis of water, and we confirmed that they react primarily with nitrite ions to form $HNO_2^{\bullet-}$ radicals:

The hydrogen atom bonds to the nitrogen, as opposed to the oxygen sites, of the nitrite ion. The $\text{HNO}_2^{\bullet-}$ radical was identified unequivocally by time-resolved electron spin resonance.²⁴ This bonding via the nitrogen atom is in stark contrast to protonation of the NO_2^{2-} radicals, which occurs via the reaction of nitrite with hydrated electrons. Thus, reduction of nitrite by the acidic form of hydrated electrons (H atom) leads to a very different product than the reduction by e_{aq}^- .

Monitoring radicals from the radiolysis of the model chelator, 2-aminobutyrate anions, $\text{H}_2\text{N}-\text{CH}(\text{C}_2\text{H}_5)\text{CO}_2^-$, we detected identical TRESR spectra at pH 10 (from OH) and pH 13.5 (from O^-). Thus, both radicals produce the same set of transients from aminobutyrate in spite of their characteristically different modes of oxidative attack. Ethyl radicals, CH_2CH_3 , which were directly observed, and $\text{CO}_2^{\bullet-}$ radicals, which were identified by spin-trapping, are formed by β -scission of the initially produced N-centered aminyl radical:

Formally, the initial reaction of O^- (and OH) is an H-atom abstraction reaction from the amino center of the substrate, $\text{H}_2\text{N}-\text{CH}(\text{C}_2\text{H}_5)-\text{CO}_2^-$. An analogous mechanism may lead to the scission of an (amino) acid residue from chelators, EDTA for example.

Formal electron transfer also occurs and was observed in the oxidation of $\text{H}_2\text{N}-\text{C}(\text{CH}_3)_2-\text{CO}_2^-$ to give the transient zwitterionic radical $\text{H}_2\text{N}^+-\text{C}(\text{CH}_3)_2-\text{CO}_2^{\bullet-}$. The latter decarboxylates to give $\text{H}_2\text{N}-\text{C}(\text{CH}_3)_2$ radicals. A possible pathway for further evolution of complexant fragmentation is through reactions of organic radicals with high nitrite concentrations in nuclear-waste tanks, e.g.:

The rate constant for Reaction 7, $k_7 = 7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, was measured using the TRESR technique. Although the value is smaller than diffusion controlled, this reaction can be a significant evolutionary pathway for organic radicals because of the high nitrite concentrations in the tanks. We presently hypothesize that the product is addition to the nitrite. Several other reactions of reactive radicals with NO_2^- , such as α -hydroxy radicals from alcohol moieties, show ESR spectra of the addition products.

Radiolytic effects in heterogeneous systems: In this effort we determined the effect of solid particulates on radiolytic yields from aqueous suspensions. This task was not activated during most of the lifetime of the project because of reduced levels of funding. Nonetheless, the prevalence of interfaces across the DOE Complex compelled us to initiate a few preliminary experiments to determine if our initial expectations of pronounced effects of the solid-liquid interfaces on the tanks chemistry could be determined. Our early results show that radiation energy that is deposited in solid particles may escape the solid and lead to water degradation products.²⁵ Specifically, reducing charge carriers (electrons) can escape silica particles and generate the most powerful reductants, e^-_{aq} . Reports that appeared later in the literature confirm and strengthen this conclusion.²⁶⁻²⁸ Experimental tools to determine yields and rates of gas generation at the solid-oxide interface have been developed. Two types of experiments were performed: In the first, yields of H_2 from wet suspensions at decreasing levels of water wetting were directly measured. In the second, yields of early reducing radicals in similar suspensions were also determined at early times following the radiolysis. In the first sequence of experiments no increase in the total yield of H_2 obtained either from silica or from Fe_2O_3 particles could be observed upon increasing the solid weight percentage. As the percentage of the solid suspended in the water increases the yield of H_2 formation also increases, indicating energy transfer between the two phases. Time domain results show that the yield of electrons escaping from silica into the water, e^-_{aq} , is identical to the yield that could have been obtained from the same volume of silica if it would have been occupied by water. Thus at least up to 50% wt, silica does not reduce e^-_{aq} yield.²⁵ In sharp contrast, the holes are trapped in the particles before they can oxidize water. In the context of organic degradation discussed above, it implies that the fraction of energy that is absorbed in the silica particles cannot contribute to aging via OH radicals.²⁹

The time domain experiments were recently extended to determine the largest distance that the thermal electrons can migrate in the solid particles before recombination or annihilation occurs. These experiments show the longest distance that allows transfer of electrons from the solid (silica) to the aqueous phase is 15 nm. Furthermore, our experiments reveal that the ejected electrons can be scavenged at the interface, before they solvate in the aqueous phase. Recent experiments suggest that the adsorption of scavengers at the particles surface may intervene in the charge recombination process within the solid. The yield of reducing species at the interface from energy absorbed by the particles

exceeds $G=6$ molecules/100 eV. For comparison, the equivalent yield in water is only 2.8. For silica, with a bandgap of 9 eV, the theoretical maximum yield is $G=11$. Apparently, the adsorbed acceptor intervenes in the recombination of holes and electrons. In order to rationalize such high yields, capture of excitons had to be invoked. Thus, the possibility that the high adsorbate concentrations in the highly heterogeneous waste may increase significantly the yield of reduction equivalents must therefore, be considered.^{30,31}

D. FUTURE DIRECTIONS

We have submitted a request for extension of this project (“*The NO_x System in Homogeneous and Heterogeneous Nuclear Waste*”, PI D. Meisel of NDRL, Co-PI’s I. Carmichael, D. M. Chipman, G. L. Hug of NDRL, and D. Camaioni of PNNL). Detailed description of the proposed studies was described in that request. It is evident that as waste tanks move towards complete decontamination and decommissioning the importance of the effect of the heterogeneity of the waste, the interaction between the solid and the liquid phases and contribution of the radiation-induced reactions in the solid should increase. This is also the area where basic knowledge is most lacking.

In the context of baseline knowledge required for safe treatment and handling of HLW, we propose the following three broad directions:

(a) Theoretical computations of energies and rates of NO_x/NO_x⁻ reactions with HLW components under realistic conditions. An important component of this effort should screen proposed mechanisms and identify reaction schemes that might be important in the tanks chemistry. Code to perform the computations has been developed and refinements and improvements are currently being added. The level of computational power is now at the brinks of replacing the need for experimental testing. Specific waste systems should be fed into the developed code and tested and compared with experimental results, including actual waste data.

(b) Experimental determination of mechanistic pathways, their energies and rate coefficients, and comparison with the theoretical predictions. Experimental rate information has been collected, leading to characterization of previously unappreciated important classes of radical-addition reactions with NO_x and NO_x⁻. Extension to include systems of similar and new structures should be attempted, and mechanisms for N₂O (the major oxidant in the flammable gas mixtures generated in the waste) and ammonia (a major nitrogen-containing component) generation should be developed. With the increased

activities towards pretreatment and permanent storage of HLW, specific systems that emerge as the tanks chemistry changes need to be addressed.

(c) Experimental measurements of radiolytic yields of gases generated in heterogeneous systems that include particles at various levels of wetting. Heterogeneous systems are becoming the focus of interest in the pretreatment of HLW. Similar interfaces are also of utmost importance in other energy related issues, such as environmental remediation, energy production in IV-generation nuclear reactors, and hydrogen utilization in hybrid systems. These areas will all require better understanding of interfacial processes of short-lived intermediates.

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EFFECTS OF RADIATION ON NANOPARTICLES

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D. Meisel, University of Bologna, Bologna, Italy, March 22, 2004.

MODELING THE CHEMISTRY IN HIGH-LEVEL WASTE TANKS: EFFECTS OF RADIATION AND HEAT ON WASTE SIMULANTS.

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NEW METHODS FOR DIELECTRIC CAVITY CONSTRUCTION AND INTEGRATION

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THEORY AND EXPERIMENT IN AMINO ACID RADIOLYSIS

I. Carmichael & G.L. Hug, Argonne National Laboratory, April 14, 2003.

THE EFFECTS OF ORGANICS AND THEIR AGING PRODUCTS ON GAS GENERATION,
D. M. Camaioni Meeting on Gas Generation Information Needs for the Waste Treatment Plant,
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Dan Meisel, Seminar, Chemistry Department, Indiana State University, Terra Haut, IN, October
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CONSTRUCTION AND DESTRUCTION OF NANOPARTICLES AND THEIR RADIOLYTIC
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Dan Meisel, Seminar, Chemistry Department, Brookhaven National Laboratory, Upton, NY,
October 4, 2001.

THE RADIATION CHEMISTRY OF DEFENSE NUCLEAR WASTE

Don Camaioni, Thom Orlando and Dan Meisel, Am. Chem. Soc. Meeting, Chicago, IL, Aug. 26-
30, 2001.

NO_x IONS AND RADICALS IN HOMOGENEOUS AND HETEROGENEOUS NUCLEAR WASTE

Ian Carmichael, Gordon L. Hug, Dan Meisel, and Donald M. Camaioni, Am. Chem. Soc.
Meeting, Chicago, IL, Aug. 26-30, 2001.

THE ROLE OF LOW ENERGY ELECTRONS IN THE RADIATION CHEMISTRY OF
HOMOGENEOUS AND HETEROGENEOUS SYSTEMS

Simon Pimblott, Jay LaVerne and Dan Meisel, Miller Conference on Radiation Chemistry, April
7-12, 2001, Windermere, UK.

THE NO_x 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, 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_x SYSTEM IN HETEROGENEOUS AND HOMOGENEOUS HIGH LEVEL WASTE

Dan Meisel, Don Camaioni, Thom Orlando, 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.

RADIATION INDUCED CHARGE CARRIERS IN AQUEOUS SUSPENSIONS OF NANOPARTICLE

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

UNUSUAL SPECIES AND UNUSUAL REACTIONS OF THE NO_x 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, Symposium on "Nanomaterials for Energy Conversion", at the 195th Meeting of the Electrochemistry Society, Seattle, WA, May 2-7, 1999.

CONTRIBUTIONS FROM SOLID PARTICLES TO GAS GENERATION IN LIQUIDS

Dan Meisel, Tanks Focus Area Review at the Environmental Molecular Science Laboratory, Richland, WA April 30, 1999.

OXIDE ION (O_2^-) VS. OXIDE RADIOL (O^-) TRANSFER TO NO_x IONS AND RADICALS

Dan Meisel, Tanks Focus Area Review at the Environmental Molecular Science Laboratory, Richland, WA April 29, 1999.

RADICALS FROM IONIZING RADIATION IN SUSPENSIONS OF NANO-PARTICLES

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

REACTIONS OF NO_2 WITH ORGANIC COMPLEXANTS IN ALKALINE SOLUTIONS

D. M. Camaioni, A. K. Sharma, J. C. Linehan, N. Zevos, D. Meisel, 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.

H. OTHER ACTIVITIES

This project was tightly integrated with Project No. 81883. Integration activities included coordination meetings at PNNL and at NDRL, exchange of seminars between the two partners to the project, meetings with site operators at Hanford and meetings within other projects of the EMSP program, such as EMSP meetings at ACS symposia. In addition, results from these two projects with active participation of PI's, assisted the Bechtel Hanford Waste Treatment Research and Technology Department in addressing issues concerning H_2 generation by waste streams in the Hanford Waste Treatment and Immobilization Plant. Details of these activities were summarized in annual reports.