

Project ID: **59982**

Project Title: **Reactivity of Peroxynitrite: Implications for Hanford Waste Management and Remediation**

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RESEARCH OBJECTIVE:

To provide quantitative mechanistic information relevant to: (i) the extent and nature of radiation-induced chemical modification of the nuclear waste that occurs during storage and (ii) the extent of accumulation of peroxyxynitrite in the waste and its potential use in remediation.

Within this context, the specific goals are:

To determine the radiochemical yields of peroxyxynitrite in mixtures simulating the various phases (salt cake, slurry, supernatant) of nuclear waste;

Through mechanistic studies of metal-, proton-, and CO_2 -catalyzed oxidations by peroxyxynitrite, estimate the extent of peroxyxynitrite-mediated oxidative degradation of organic waste components and determine the feasibility of using peroxyxynitrite for the destruction of organic complexants and the removal of chromium for more efficient vitrification.

RESEARCH PROGRESS AND IMPLICATIONS:

This report summarizes work after 2 years of a 3 year project.

Reactivity of Peroxyxynitrite in Aqueous Solution (publications 1-9)

Mechanistic studies of H^+ -catalyzed decomposition of peroxyxynitrite (ONOO^-) has demonstrated that peroxyxynitrous acid (ONOOH , pK_a 6.6) undergoes homolysis producing strongly oxidizing NO_2 and OH radicals with a 28% yield. An extensive (90%) oxidation of EDTA was observed in the presence of 200-fold excess of ONOOH at pH 6. Similarly, CO_2 -catalyzed oxidations by peroxyxynitrite proceeds via formation of NO_2 and carbonate (CO_3^-) radicals with a 35% yield. The CO_3^- radical was shown to remain deprotonated even at $\text{pH} < 0$, contrary to the previous reports of low radical acidity. The pulse radiolysis studies have shown that OH and CO_3^- oxidize ONOO^- with the rate constants of 7.7×10^6 and $4.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, respectively, generating an unstable ONOO radical, that decomposes into NO and O_2 .

Soluble CuEDTA and FeEDTA complexes and heterogeneous Fe , Cu , and Mn oxides on a SiO_2 support were tested as catalysts of EDTA oxidation in alkaline solutions. CuEDTA and Cu/SiO_2 were found to be the most active and selective, decomposing 80% and 70% of EDTA, respectively, within an hour. FeEDTA worked 2-3 times slower than Cu catalysts; Mn -based catalysts were inactive. The ONOO^- ion rapidly oxidized freshly precipitated Cr(III) hydroxide to a soluble chromate; aged precipitates dissolved much slower (tens of hours) because of a formation of massive hydroxide-oxide. Coprecipitation with Mn greatly enhanced Cr(III) oxidation; in mixed Cr-Mn hydroxide the reaction was less sensitive to aging and more rapid (tens of minutes).

Implications: Decomposition of peroxyxynitrite can be an important source of oxygen within the Hanford waste and may, at least in part, be responsible for the generation of nitric oxide emitted from the storage tanks. Strongly oxidizing hydroxyl and carbonate radicals produced in H^+ - and CO_2 -catalyzed peroxyxynitrite reactions can significantly contribute to the chemical modification of the waste during its storage. Application of peroxyxynitrite for the destruction of the waste organics and for the removal of chromium from the waste can be considered.

Radiation-Induced Formation of Peroxyxynitrite in Solid Nitrates (publication 10)

We found that uv- and g-irradiation of solid alkali nitrates resulted in the accumulation of peroxyxynitrite, nitrite, and O_2 . The peroxyxynitrite formation was supported by optical and Raman spectral changes in irradiated samples and chemical analyses upon dissolution. Similarities between light- and radiation-induced reactions imply that the ONOO^- -forming step is an

isomerization of the electronically excited NO_3^- . The initial radiation yields (G, molecules/100 eV) and the quantum yields at 248 nm (F, %) are summarized in the Table:

Product	Peroxynitrite		Nitrite	
	G	F	G	F
NaNO_3	0.60	1.1	0.37	0.16
KNO_3	0.73	4.8	1.3	0.64
CsNO_3	1.9	9.7	0.8	0.98

Large G-values indicate that a significant fraction of the radiation energy that is initially deposited by ionization is converted into electronic excitation via a charge recombination process. While NO_2^- was produced at a constant rate, the accumulation of ONOO^- decelerated with irradiation time because both formation and decay of ONOO^- were induced by γ -radiation. The decay rate was first-order in

both radiation intensity and $[\text{ONOO}^-]$; the data indicate that a long-range electron or energy transfer and a radical chain reaction are involved.

Implications: Peroxynitrite is a major product in irradiated solid nitrates. Its radiation yields are large enough to support peroxynitrite accumulation in the Hanford waste. The waste dissolution may result in significant release of the energy and the oxidizing equivalent stored in peroxynitrite.

PLANNED THIRD YEAR ACTIVITIES: Mechanistic time-resolved studies of radiation-induced peroxynitrite generation and decomposition in solid nitrates using the pulse radiolysis and flash-photolysis techniques. Continued studies of metal- and CO_2 -catalyzed oxidation of organic complexants and oxidative dissolution of chromium. Developing generalized dynamical model for the peroxynitrite reactivity pathways in the radioactive waste.

Publications

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4. Coddington J.W., Hurst J.K., Lymar S.V., AHydroxyl Radical Formation During Peroxynitrous Acid Decomposition@, *J. Am. Chem. Soc.*, **121**, 2438-2443 (1999)
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