

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

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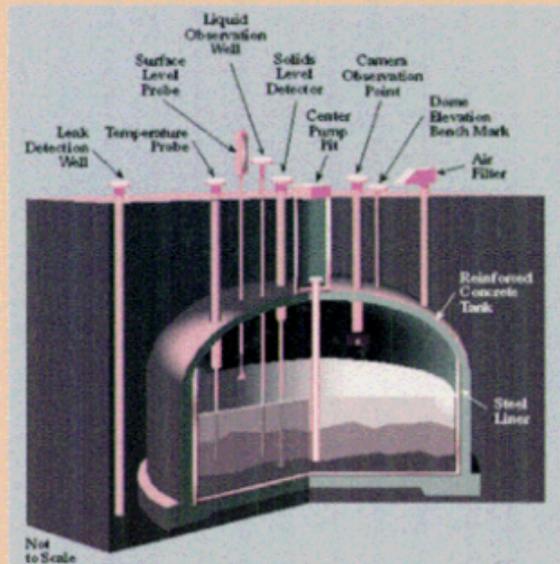
**BNL**

**emsp**

**Environmental Management Science Program**

# Background

## Radiation Chemistry of Nuclear Waste



### Composition:

- ▶ Highly alkaline nitrate and nitrite
- ▶ Organic solvents and complexants

### Radiolytic Transformation:

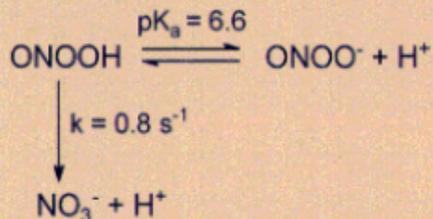
- ▶ Flammable gas evolution
- ▶ Generation of peroxyxynitrite - powerful oxidizing and nitrating agent

# Peroxynitrite

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## ► Properties

Peroxynitrite,  $\text{O}=\text{N}-\text{O}-\text{O}^-$ , is a strong oxidant of emerging environmental and biological significance. As an anion, peroxynitrite is fairly stable, but its conjugate peroxynitrous acid decomposes rapidly producing primarily nitrate:



## ► Reactivity

Peroxynitrite is a powerful oxidizing and nitrating agent for organic compounds. Three pathways for these reactions have been identified:

- proton-catalyzed
- carbon dioxide-catalyzed
- metal-catalyzed

# Research Objectives

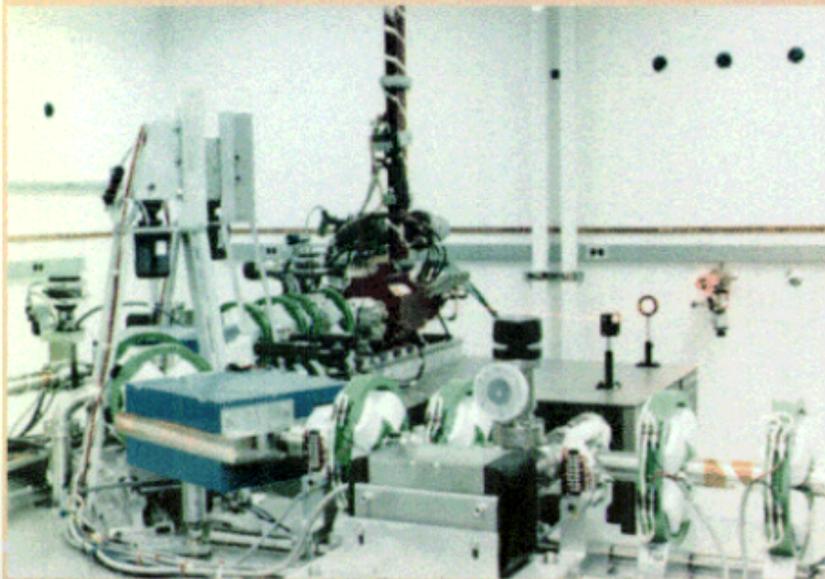
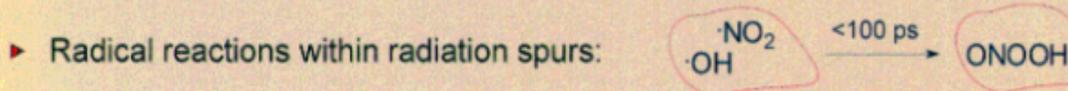
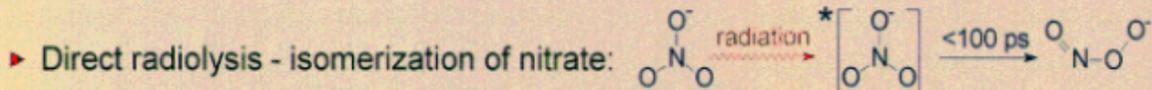
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The broad objective of this project is to provide quantitative mechanistic information relevant to: (i) the extent and nature of radiation-induced chemical modification of the nuclear defense waste that occurs during storage and (ii) the extent of 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 chemical mixtures simulating the various phases (salt cake, slurry, supernatant) of radioactive waste;
- Through mechanistic studies of proton-, metal-, and  $\text{CO}_2$ -catalyzed oxidations by peroxyxynitrite, to estimate the extent of peroxyxynitrite-mediated oxidative degradation of organic waste components and determine the feasibility of using peroxyxynitrite in remediation technologies, e.g., for the destruction of organic complexants and the removal of chromium for more efficient vitrification

# Radiolytic Generation of Peroxynitrite



New Laser Electron Accelerator Facilities at BNL (LEAF) provide picosecond time resolution for studying fast radiation-induced reactions

# I. Oxidation of Peroxynitrite by Inorganic Radicals

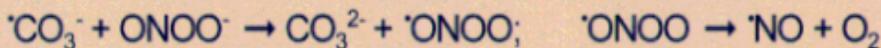
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- ▶ Radicals ( $\cdot\text{OH}$ ,  $\cdot\text{NO}_2$ ,  $\cdot\text{CO}_3^-$ ) created by  $\text{H}^+$ - and  $\text{CO}_2$ -catalyzed peroxynitrite decompositions and by ionizing radiation are potent oxidants; we found that these radicals can oxidize peroxynitrite anion.

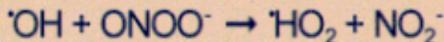
These reactions may control the level of radiation-induced peroxynitrite accumulation in nuclear waste and contribute to  $\cdot\text{NO}$ ,  $\cdot\text{O}_2^-$ , and  $\text{O}_2$  generation

- ▶ Reaction pathways

- electron transfer:

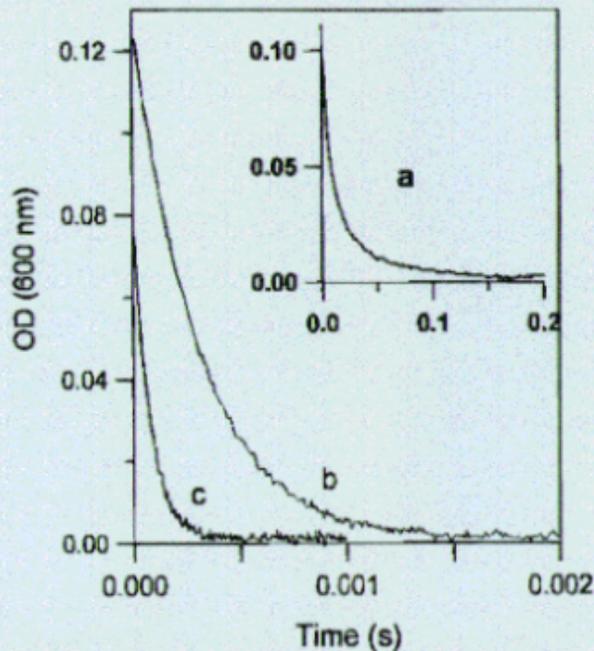


- atom abstraction:



# Reaction Between $\cdot\text{CO}_3^-$ and $\text{ONOO}^-$

## Carbonate Radical Decay Kinetics



Curve a: no  $\text{ONOO}^-$  added

Curve b: with 0.3 mM  $\text{ONOO}^-$

Curve c: with 1.3 mM  $\text{ONOO}^-$

## Pulse Radiolysis Data

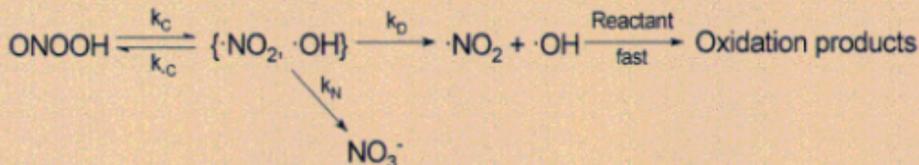
Rate Constants for Oxidation of ONOO <sup>-</sup> and HOO <sup>-</sup> by Radicals				
R/R <sup>-</sup> couple	E <sup>0</sup> (R/R <sup>-</sup> ) (V)	k <sub>11</sub> (R/R <sup>-</sup> ) (M <sup>-1</sup> s <sup>-1</sup> )	k(R + ONOO <sup>-</sup> ) (M <sup>-1</sup> s <sup>-1</sup> )	k(R + HOO <sup>-</sup> ) (M <sup>-1</sup> s <sup>-1</sup> )
·OH/OH <sup>-</sup>	1.9	300	4.8x10 <sup>9</sup>	7.0x10 <sup>9</sup>
CO <sub>3</sub> <sup>-</sup> /CO <sub>3</sub> <sup>2-</sup>	1.59	0.4	3.7x10 <sup>5</sup>	3.5x10 <sup>7</sup>
·N <sub>3</sub> /N <sub>3</sub> <sup>-</sup>	1.33	3.7x10 <sup>8</sup>	7.2x10 <sup>8</sup>	3.2x10 <sup>9</sup>
·NO <sub>2</sub> /NO <sub>2</sub> <sup>-</sup>	1.04	9.6	< 2x10 <sup>4</sup>	n.d.
ClO <sub>2</sub> <sup>-</sup> /ClO <sub>2</sub> <sup>-</sup>	0.93	3.3x10 <sup>4</sup>	3.2x10 <sup>4</sup>	8.0x10 <sup>4</sup>
·HO <sub>2</sub> /HO <sub>2</sub> <sup>-</sup>	0.75	17		

By comparing the rate constants for ONOO<sup>-</sup> and HOO<sup>-</sup> oxidation and using Marcus equation  $k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$  the oxidation potential of ONOO<sup>-</sup> can be estimated as:

$$E^0(\cdot\text{ONOO}/\text{ONOO}^-) = 0.8 \text{ V}$$

## II. Pathways of Peroxynitrite Reactivity

- ▶ Peroxynitrite decomposition in the pH range 5-10 has been studied in order to resolve a long standing controversy concerning involvement of hydroxyl radical in the peroxynitrite reactivity
- ▶ The results of this study strongly support formation of free hydroxyl radical via peroxo bond homolysis in ONOOH:



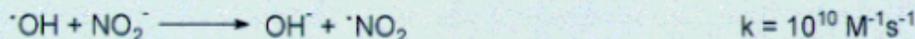
- Product yield = cage escape yield:  $Y_o = \frac{k_D}{k_D + k_N} = 0.29$

- Rate-limiting is the free radicals formation

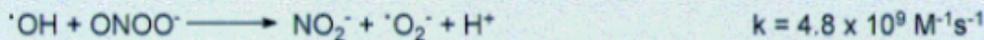
- Observed ONOOH decomposition constant:  $k_o = (k_D + k_N) \frac{k_c}{k_c + k_D + k_N} = 0.8 \text{ s}^{-1}$

# Mechanism of Peroxynitrite Decomposition

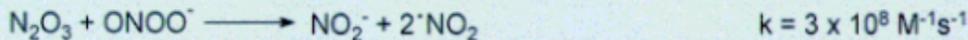
## Radical initiation



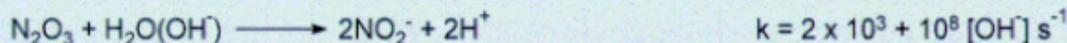
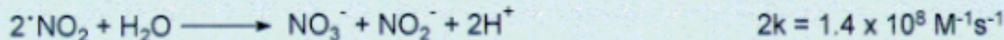
## Oxygen production



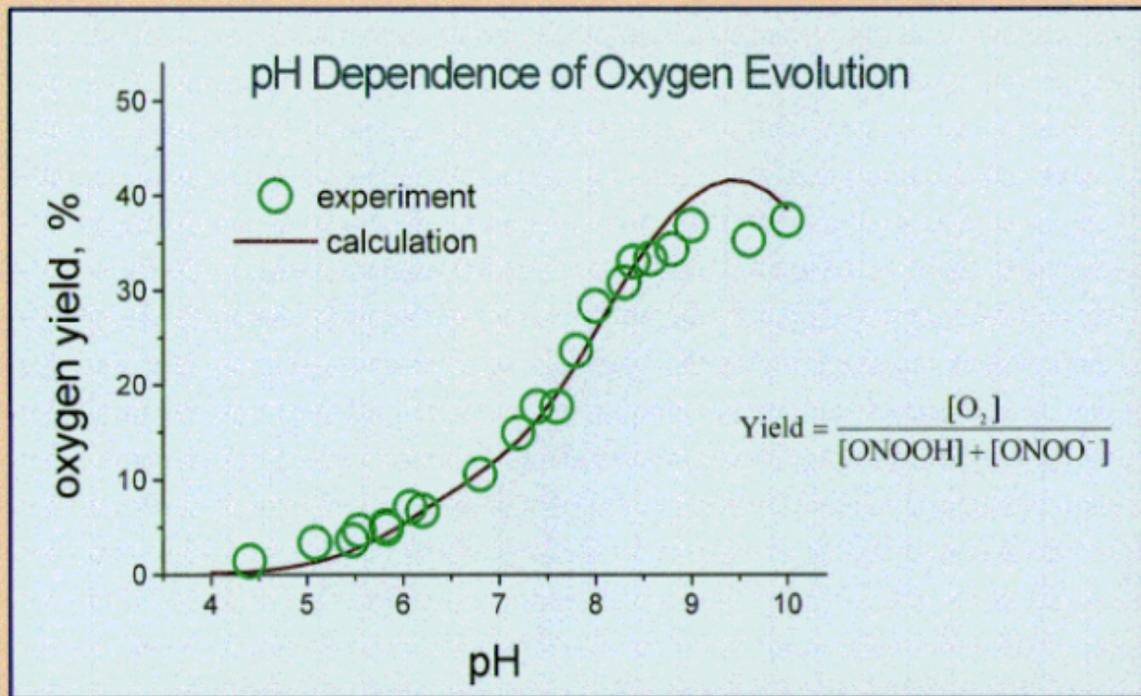
## Radical chain propagation



## Termination



# Kinetic Modeling of Oxygen Yields



Mechanistic understanding has been developed that, despite apparent reaction complexity, allows its accurate dynamic modeling

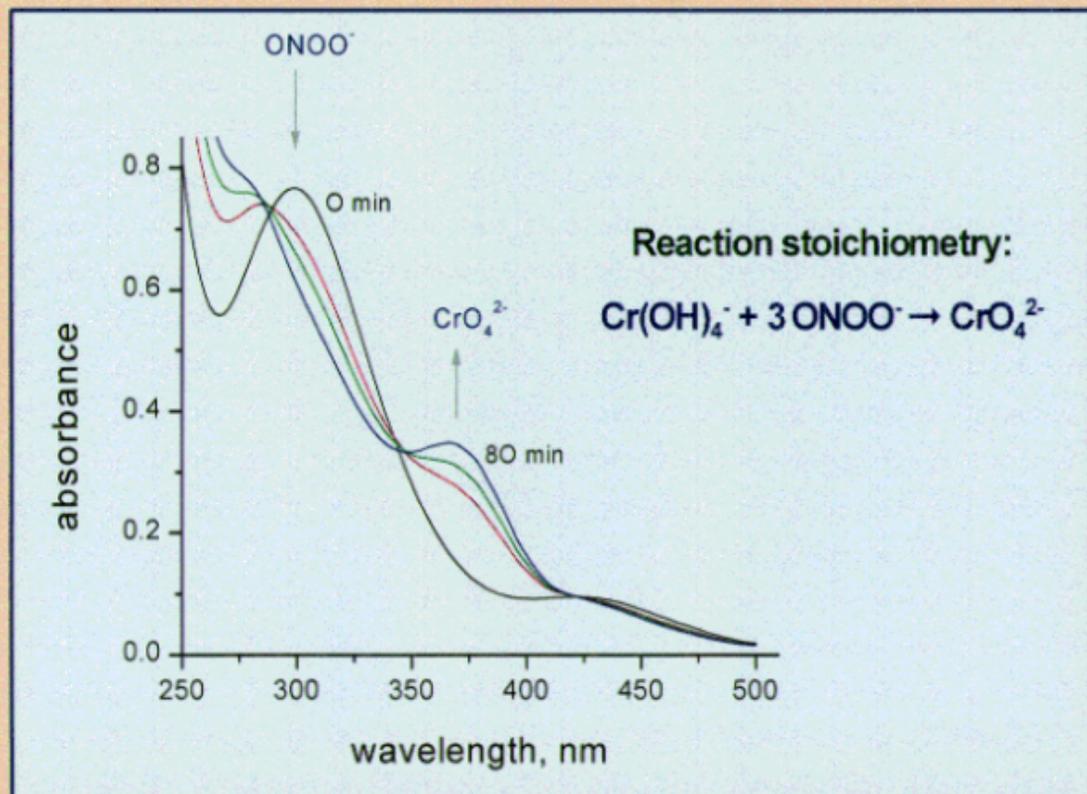
### III. Oxidative Dissolution of Chromium Hydroxide by Peroxynitrite

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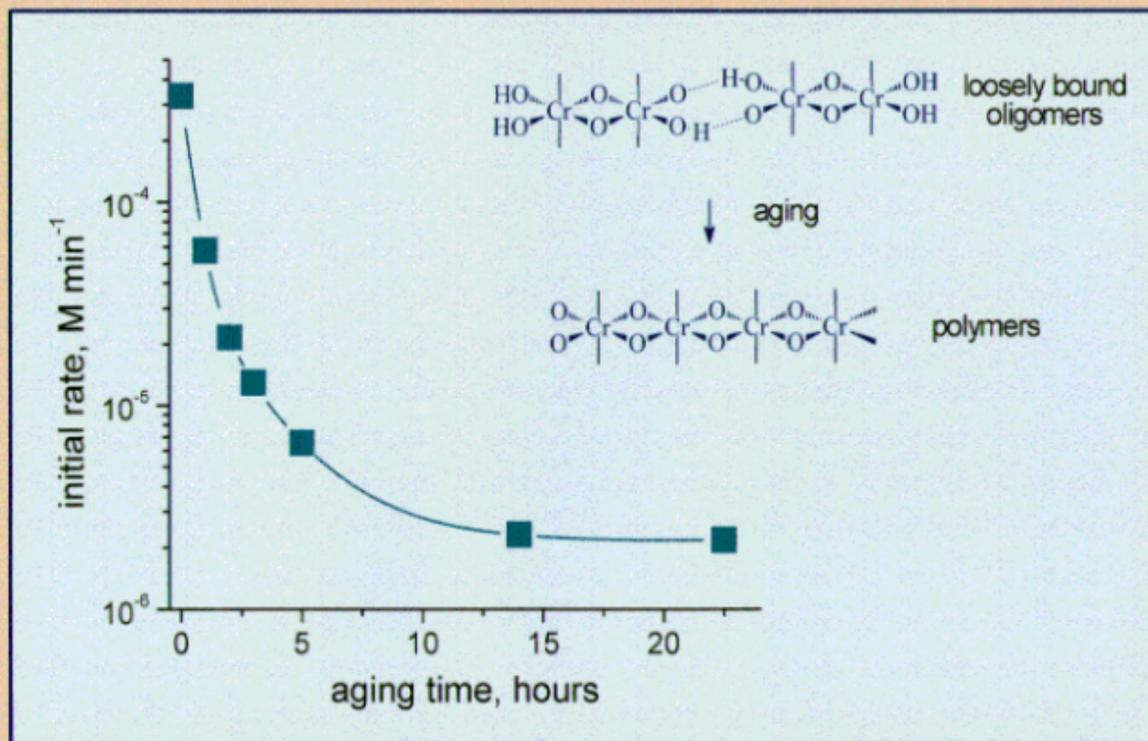
#### Summary of the Experimental Observations

- ▶ In strongly alkaline solutions, peroxynitrite rapidly oxidizes freshly precipitated chromium(III) hydroxide into soluble chromate,  $\text{CrO}_4^{2-}$
  - ▶ The oxidation of aged precipitate is slower and does not proceed to completion
  - ▶ In mixed Cr/Mn hydroxides, Cr(III) is oxidized by peroxynitrite more rapidly and completely
  - ▶ The presence of Fe(III) does not significantly affect the rate of reaction
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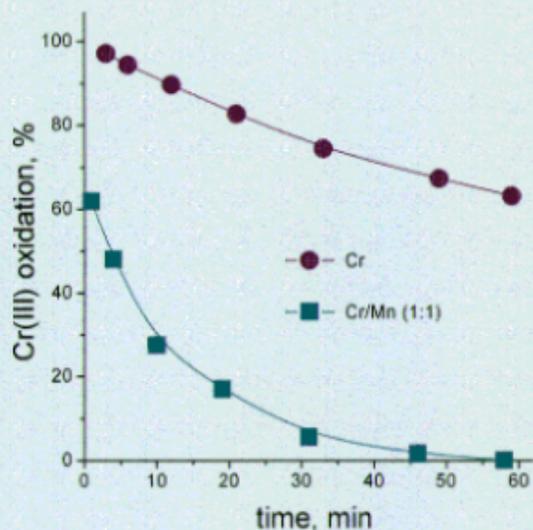
# Oxidation of Cr(III) by Peroxynitrite in 0.1 M NaOH



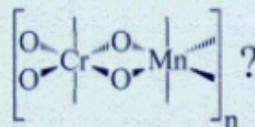
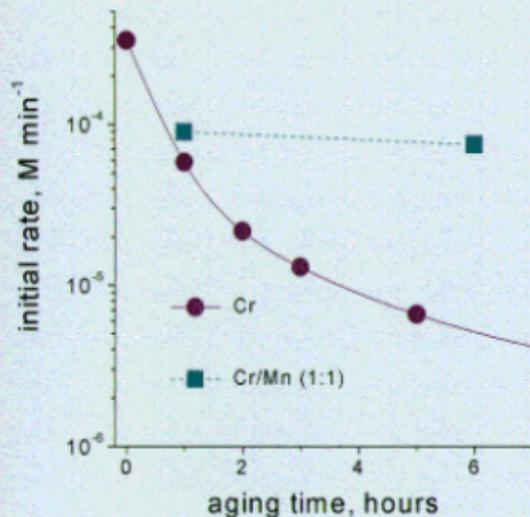
# Effect of Aging on Cr(III) Oxidation



# Effect of Mn on Aging and Oxidation of Cr(III) Hydroxide



- Mn accelerates oxidation of Cr(III)
- Oxidation proceeds to completion



- Aging is slower in mixed Cr/Mn hydroxide

# Conclusions and Implications

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- ▶ Radiolytically-generated free radicals oxidize peroxyxynitrite in alkaline solutions
  - These reactions may, at least in part, control the levels of radiation-induced peroxyxynitrite accumulation in nuclear waste and contribute to the generation of  $\text{NO}_x$  species emitted by the waste tanks
  - Nitrogen dioxide, the dominant free radical in the waste, does not efficiently scavenge peroxyxynitrite
- ▶ Peroxyxynitrite decomposes to nitrate, nitrite, and oxygen
  - The reaction mechanism includes intermediary formation of nitric oxide, superoxide, and hydroxyl radicals
  - Decomposition of peroxyxynitrite can be an important source of oxygen within the waste
- ▶ Peroxyxynitrite oxidizes insoluble chromium hydroxide to soluble chromate
  - This reaction is promoted by manganese
  - This reaction has a potential for oxidative removal of chromium from the waste sludges

# Planned Activities

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▶ Second year

- Studies of the yields and mechanisms of radiation-induced peroxyxynitrite generation in solid nitrate and nitrite and their concentrated solutions
- Finishing studies of oxidative dissolution of chromium

▶ Third year

- Mechanistic studies of metal- and  $\text{CO}_2$ -catalyzed oxidation of organic complexants by peroxyxynitrite
  - Developing generalized dynamical model for the peroxyxynitrite reactivity pathways in the radioactive waste
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# Acknowledgments and References

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- ▶ The PIs are indebted to the following researchers for their contributions to this project

Oleg V. Gerasimov, Brookhaven National Laboratory

Sara Goldstein and Gidon Czapski, The Hebrew University of Jerusalem

John W. Coddington, Washington State University

- ▶ Publications

- Described in this poster

1. Goldstein, S.; Saha, A.; Lymar, S. V.; Czapski, G., "Oxidation of Peroxynitrite by Inorganic Radicals: A Pulse Radiolysis Study", *J. Am. Chem. Soc.* (1998), 120, 5549-5554
2. Lymar, S. V.; Hurst, J. K., "Radical Nature of Peroxynitrite Reactivity", *Chem. Res. Toxicol.* (1998), in press
3. Coddington, J. W.; Hurst, J. K.; Lymar, S. V., "Hydroxyl Radical Formation During Peroxynitrous Acid Decomposition", *Proc. Natl. Acad. Sci. USA*, submitted

- Recent, relevant to this project

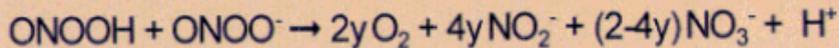
1. Lymar, S. V.; Hurst, J. K., "CO<sub>2</sub>-Catalyzed One-Electron Oxidation by Peroxynitrite: Properties of the Reactive Intermediate", *Inorg. Chem.* (1998), 37, 294-301
2. Merenyi, G.; Lind, J., "Free Radical Formation in the Peroxynitrous Acid/Peroxynitrite System", *Chem. Res. Toxicol.* (1998), 11, 243-246

# Oxygen Generation by Peroxynitrite

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## Summary of the Experimental Observations

- ▶ Nitrate, nitrite, and oxygen are the final products of peroxynitrite decomposition, whose stoichiometry is:



where  $0 \leq y \leq 0.5$  is the pH-dependent oxygen yield

- ▶ Free radical scavengers (alcohols, acetate, benzoate, etc.) inhibit  $\text{O}_2$  formation in a manner that is quantitatively consistent with their reactivity toward the  $\cdot\text{OH}$  radical
  - ▶ Excess of nitrite reverses inhibition by the  $\cdot\text{OH}$  scavengers at pH above 8, but is itself inhibitory under more acidic conditions
  - ▶  $\text{CO}_2$  - completely suppresses oxygen evolution
- 