

# **MICROBIALLY PROMOTED SOLUBILIZATION OF STEEL CORROSION PRODUCTS AND FATE OF ASSOCIATED ACTINIDES**

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## **Lead Principal Investigator**

Yuri A. Gorby  
Pacific Northwest National Laboratory  
P.O. Box 999 Battelle Blvd. MS P7-50  
Richland, WA 99352  
509-373-6177  
yuri.gorby@pnl.gov

## **Co-Investigators**

Gill G. Geesey  
Montana State University  
Center for Biofilm Engineering  
409 Cobleigh Hall  
Bozeman MT 59717  
406-994-4770  
gill\_g@erc.montana.edu

Frank Caccavo, Jr.  
Department of Biology  
Whitworth College  
Mail Stop 3902  
300 W. Hawthorne Road  
Spokane, WA 99251  
509-777-4576  
fcaccavo@whitworth.edu

James K. Fredrickson  
Pacific Northwest National Laboratory  
P.O. Box 999 Battelle Blvd. MS P7-50  
Richland, WA 99352  
509-373-6177  
jim.fredrickson@pnl.gov

## **Specific DOE Problems**

DOE needs statements call for “biological and physical chemical parameters for effective decontamination of metal surfaces using environmentally benign aqueous-based biopolymer solutions and microbial processes with potential for decontaminating corroding metal surfaces”. Improved understanding of the fundamental processes of microbial reductive dissolution of iron oxide scale on corroding carbon steel will support assessment and potential application of an environmentally-benign and cost effective strategy for in situ decontamination of structural metal surfaces and piping.

## **Research Objective**

The research is designed to develop a safe and effective biological approach for decontaminating mild and stainless steels that were used in the production, transport, and storage of radioactive materials.

## Research Progress and Implications

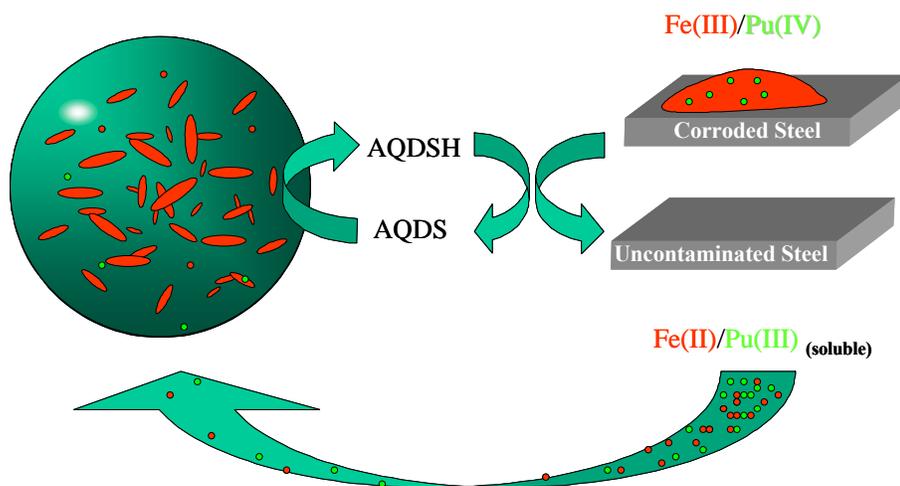
This report summarizes research progress made during the 3-year tenure for this project. An extension with minimal carryover funds was requested and granted to complete and submit manuscripts for publication. During this research, we have:

- Demonstrated that Fe(III)-reducing bacteria reduce Pu(IV) (insoluble) to Pu(III) (soluble)
- Confirmed that the bacteria sorb and accumulate trivalent cations, such as Pu(III).
- Demonstrated that bacteria attached to oxide surfaces are very difficult to remove. Concluded that recovery of bacteria with sorbed Pu(III) would be impractical.
- Demonstrated that Fe(II) and reduced quinone-like compounds, which are both products of anaerobic respiration, can reduce chemically reduce solid Pu(IV) to dissolved Pu(III).
- *Conceptualized a bead-based system that effectively removes Pu from iron oxides and accumulates Pu(III) in beads of sodium alginate that can be easily separated from the bulk aqueous phase.*

Dissimilatory iron-reducing bacteria enzymatically reduce and dissolve iron oxides, which are common components of corrosion films, and release soluble species of plutonium, Pu(III). Consistent with our previous hypothesis, cell surfaces sorb Pu(III) and remove it from the bulk aqueous phase. However, we incorrectly hypothesized that bacteria with sorbed actinides could be easily detached and recovered from the surfaces that they had colonized and enzymatically altered. In fact, we have demonstrated that although cells do naturally detach from oxide surfaces during their growth cycle, they leave behind negatively charged reactive portions of their outer surface that are strong sorbants for cations. Without a means for recovering both intact bacteria, their subcellular products and associated contaminants, the use of iron reducing bacteria for decontaminating corroded steel surfaces would not be feasible. Hence, we have targeted an approach that avoids direct contact and attachment of cells to the corrosion films but allows for reduction, dissolution, and sorption of corrosion products and associated actinides.

### ***Description of Bead-Based Treatment***

Iron reducing bacteria are encapsulated in small beads of sodium alginate. Encapsulation prevents direct contact between the bacteria and the contaminated oxide surface. Anthraquinone disulfonate (AQDS) is used as a dissolved electron shuttle to carry electrons from the bacteria to Fe(III) and Pu(IV) on the corrosion film. AQDS reduces Fe(III) to Fe(II) and Pu(IV) to Pu(III). The reduced forms of these metals are very soluble and partition to the aqueous phase. The bacterial surface and the sodium alginate sorb and accumulate Fe(II) and Pu(III). The beads, which now contain most of the Pu(III), can be easily separated from the bulk aqueous phase. The benign process requires no hazardous chemicals or extreme pH conditions.



**Figure 1.** This illustrates a conceptual model of a bead-based system for decontaminating corroded steels. Metal reducing bacteria are enrobed in porous alginate beads. Oxidized anthraquinone disulfonate, AQDS, which will serve as a dissolved electron shuttle between immobilized cells and elements in the corrosion film, diffuses into the beads and is enzymatically reduced by the bacteria. The reduced AQDSH diffuses out of the bead and chemically reduces and dissolves Fe(III) and Pu(IV) in the corrosion film. Soluble Fe(II) and Pu(III) sorb to cationic exchange sites within the alginate beads. The beads and accumulated actinides can then be easily separated from the bulk aqueous phase and the uncontaminated steel.

## Planned Activities

The remainder of the project will target the publication of manuscripts that are nearing completion. Additionally, we will examine further the concept and feasibility for using the bead-based approach to remove a range of heavy metals and radionuclides from contaminated iron corrosion films and from contaminated aqueous liquids.

## Information Access

- Rai, D, Y.A. Gorby, J. K. Fredrickson, D.A. Moore, and M. Yui. 2002. Reductive Dissolution of  $\text{PuO}_2(\text{am})$ : The Effect of Fe(II) and Hydroquinone. *J. Sol. Chem.* (accepted)
- Gorby, Y.A., J. Mclean, A. Dohnalkova, A. Korenevsky, Kevin Rosso, Evgen Vinogradov, and T.J. Beveridge. 2002. Membrane vesicles form the dissimilatory iron reducing bacterium *Shewanella putrefaciens* strain CN32. *FEMS microbial. Lett* (in review)
- Das, A. and F. Caccavo, Jr. 2001. Adhesion of the dissimilatory Fe(III)-Reducing bacterium *Shewanella alga* BrY to crystalline Fe(III) oxides. *Curr. Microbiol.* 42:151-154
- Caccavo, F. and A. Das. 2002. Adhesion of Dissimilatory Fe(III)-Reducing Bacteria to Fe(III) Minerals. *Geomicrobiol. J.* (accepted)
- Das, A. and F. Caccavo, Jr. 2000. Dissimilatory Fe(III) oxide reduction by *Shewanella alga* BrY requires adhesion. *Curr. Microbiol.* 40:344-347.