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Project Title: **Contaminant-Organic Complexes, Their Structure and Energetics in Surface Decontamination Processes**

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Project Objectives

There are a wide variety of compounds that are naturally occurring biodegradable organic chelates (siderophores) that appear to be more effective at oxide dissolution and actinide complexation than EDTA or other organic acids now used in decontamination processes. These chelates bind hard acids [Fe(III) and actinides(IV)] with extraordinarily high affinities. For example, the binding constant for the siderophore enterobactin with iron is about 10^{50}, and its binding constant for Pu(IV) is estimated to be as high. Hence, this project is investigating the efficacy of using siderophores (or siderophore-like chelates) as decontamination agents of metal surfaces. The specific goals of this project are as follows:

1. develop an understanding of the surface interaction between siderophores (and their functional moieties), iron, and actinide oxides; their surface chemical properties that foster their dissolution; and the conditions that maximize that dissolution

2. develop the computational tools necessary to predict the reactivity of different siderophore functional groups toward oxide dissolution and actinide(IV) solubilization

3. identify likely candidate chelates for use in decontamination processes.

To meet these objectives, the project combines molecular spectroscopy and computational chemistry to provide basic information on the structure and bonding of siderophore functional groups to metal (iron and uranium) oxide specimens common to corrosion products and scales on carbon steel and stainless steel encountered in U.S. Department of Energy (DOE) facilities. The project explores fundamental scientific aspects of oxide mineral surface chemistry and dissolution related to chelate-induced solubilization. The spectroscopic and computational aspects of this project are complemented by macroscopic dissolution and solubilization studies of oxides and associated contaminants. From this combination of molecular, macroscopic, and computational studies, structure-function and structure-reactivity relationships will be developed.

Problem Statement

DOE must decontaminate and decommission a large number of surplus facilities. At present there are about 7,000 contaminated facilities that require deactivation and decommissioning. A major need associated with this effort is improvement of metal surface decontamination. DOE is responsible for the disposal of approximately 180,000 metric tons of metal (mostly steel) associated with their nuclear facilities. Much of this metal is steel and iron, which develops a passivity layer where radionuclides and other contaminants are retained. Continued deposition of corrosion products on the steel surfaces allows radioactive materials to be continually sorbed to these secondary oxide layers, incorporated into their structure, or occluded by overgrowth.

Oxides of the type important to steel passivity layers and secondary scale layers are found in nature and have been shown to sorb foreign ions (such as actinides) to their surface, incorporate them into their structure, and occlude them from the bathing solution via overgrowth mechanisms. Contaminants associated with steel surface films, corrosion pits, and cracks are present as mixed solids or surface sorbed species. Regardless of where they reside, the critical step in decontamination is the dissolution of the oxide surface film. As dissolution of the oxide film occurs, solubilization of radioactive contaminants will follow. DOE-EM led surveys and workshops focused on understanding decontamination and

decommissioning (D&D) needs at its production and processing sites and concluded that new, more effective decontamination techniques for metal surfaces and equipment are a high priority. The candidate facilities include gaseous diffusion plants, reactors, isotope processing plants, fuel reprocessing plants, hot cells, gloveboxes, and waste/storage processing facilities. Equipment ranges from highly contaminated tanks, extraction columns, and piping to surfaces with trace amounts of radioactive contamination such as gloveboxes, piping, and other surfaces.

Research Progress

This research program, which began in late FY 1998, is separated into four activities on siderophore chemistry (Table 1). These tasks are centered on central investigative themes 1) macroscopic dissolution studies (C. Ainsworth, PNNL), 2) optical spectroscopy (D. Friedrich and C. Ainsworth, PNNL), 3) x-ray absorption spectroscopy (XAS) (S. Traina, OSU, and S. Myneni, LBNL), and 4) computational chemistry (B. Hay, PNNL). All studies use the same set of solids that were prepared in bulk and whose surface and chemical properties have been determined (i.e., surface area, electrophoretic mobility, etc.). Dr. Sam Traina (Ohio State University) produced, characterized, and distributed the solids. In addition, to focus the effort, a series of siderophores and siderophore analogs is being used throughout the planned research (Table 2). These chelates represent the three major classes of biologically produced chelates and will allow the spectroscopic and macroscopic researchers to build a data set relating reactivity to molecular scale information on ligand surface structure and orientation that will be broadened using computational tools. The chelates (or siderophores) are purchased, synthesized, or isolated from specific bacterial or fungal cultures.

Macroscopic Dissolution Studies

Initially, this task is directed at obtaining the specific compounds listed in Table 2. To date, two hydroxamates, Desferrioxamine B and ferrichrome, have been purchased from Sigma. Both of these siderophores are trihydroxamates but have different structures. A dihydroxamate, rhodotorulic acid, is being collected from culture growth of *Rhodotorula pilimanae* (ATCC 26423). Likewise, a catecholate (agrobactin) siderophore and an aminocarboxylate (rhizoferrin) siderophore are being collected from culture growth of *Agrobacterium tumefaciens* (ATCC 23308) and *Rhizopus microsporus* var. rhizopodiformis (ATCC 66276). These three organisms have been received from the American Type Culture Collection and are currently being cultured in iron-free media.

This task's primary objective centers on determining solubilization of iron and uranium from oxide sols under a range of environmental variables (i.e., pH, ionic strength, ionic composition, ligand and solid type and concentrations). The goal of this task is to develop kinetic dissolution data that can be used in calculating structure-reactivity relationships relating solution complexation data to dissolution rates and finally to ligand surface structure.

Preliminary oxide dissolution investigations have begun. These studies are centering on 1) determining the effectiveness of batch systems versus stirred-flow cell systems, 2) detection options for iron and the reactive ligand, and 3) time dependence. We are working with acetohydroxamate, Desferrioxamine, and a well-characterized goethite. Preliminary data suggest that, by varying the residence time, solid solution ratio, and pH in a stirred-flow cell system, dissolution rates can be readily obtained with minimal waste of siderophore.

Table 1. Objectives, Initial Hypotheses, and Experiments Governing Investigations in the Four Tasks

	Task 1	Task 2	Task 3	Task 4
Objectives	Determine the dissolution rate of oxides as a function of pH, ligand concentration, chromium content, and ionic composition	Identify dominant surface species responsible for oxide dissolution and its time-resolved spectra	Identify the structure and coordination chemistry of sorbed metals and their interaction with ligands	Using molecular mechanics, correlate aqueous structure function data to oxide dissolution rate data
Hypotheses	pH of maximal dissolution rate will be > the oxide zpc for catecholate ligands and < the oxides zpc for hydroxamate ligands; surface speciation is critical to rate	Mononuclear bidentate surface complex primarily responsible for dissolution but mechanism will have multiple species and parallel reaction paths	Metal surface speciation will vary with surface concentration, time, and oxide phase and will affect ligand's ability to desorb metals and dissolve oxide	Aqueous binding affinities for ligands with iron and f-block metals will correlate to the maximal oxide dissolution rate
Experiments/Results	Dissolution rate studies of oxide phases at variable pH, ligand concentration, and chromium content • identification of optimum dissolution rates and conditions • mechanisms and ligand binding structure suggested • presence/absence of incongruent dissolution • rates of reaction vary with extent	Static and time-resolved studies with different oxide phases in varying conditions • identify surface speciation of ligands • species vary with chemical conditions but a primary species responsible for dissolution • reactions are related to surface charge and site density	Determine ability of ligands to promote metal desorption and the metals effect on ligand promoted oxide dissolution • metal clusters form with increasing surface metal concentration and time • as metal concentration increases ligand promoted desorption rate decreases • ligand reacts with stable metal surface species	Extend the MM3 parameter set to treat ligands with catechol and hydroxamate and their iron and f-block metal complexes • extended MM3 model reproduces features of known compounds • model correctly locates observed configurations of ligands and metal complexes • correlates ligand structure/reactivity and dissolution rates

Table 2. Set of Siderophores and Siderophore Analogs To Be Used in the Planned Research

Class	Siderophore	Representative Model Ligand
Hydroxamates	Desferrioxamine B	Acetohydroxamate, benzohydroxamate
Catecholates	Enterobactin	Catechol, 3-hydroxysalicylate
Aminocarboxylates	Rhizoferrin	EDTA, glycine

Optical Spectroscopy

Task 2 (optical spectroscopy) will investigate the bonding and structure of ligands and the surface speciation under conditions similar to those in the macroscopic dissolution studies. The goal of this task is to develop the fundamental basis by which we can refine macroscopic reactivity interpretations and relate them to aqueous structure-function relationships.

Preliminary studies have centered on collecting infrared spectra of acetohydroxamic acid that were obtained from 400 to 4000 cm^{-1} using horizontal attenuated total reflectance (HATR) measurements. An ATR trough cell was obtained that is compatible with the low pHs of the solutions and suspensions of interest. The ATR cell was installed and aligned in a Bruker IFS66/VS. This spectrometer has conventional N_2 gas purge and the ability to evacuate the bench and sample chamber, thereby eliminating absorbances from CO_2 and water.

Spectra of lyophilized goethite agreed well with published analyses. Signal to noise of the spectra was greatly enhanced when the goethite powder was pressed against the ATR crystal using a powder press. Solutions and suspensions of acetohydroxamic acid at pH 3 and pH 6, with and without goethite, were obtained under vacuum. However, to obtain vacuum spectra, the samples were placed in the trough cell and a cover clamped to the cell. This clamping caused undetected movements of the ATR and its mount, thereby causing some spectral artifacts. Generally, spectra of these solutions and suspensions agreed with previous published work, but subtle spectral features were masked. Subsequent analyses will be performed either using conventional nitrogen gas purge or by use of a flow-cell cover plate. The cover plate allows atmospheric isolation thereby enabling evacuation of the bench and eliminates cell misalignment due to clamping and unclamping.

X-Ray Absorption Spectroscopy

Task 3 (XAS) will work closely with Task 2 as these two spectroscopies approach the structure and bonding issues from different aspects; they are complementary (hence confirmatory to one another) and noninvasive. Hence, a consistent model of oxide-chelate adsorption/dissolution may be obtained. However, before initiating these studies, a series of oxides were required for Tasks 1 through 3. These oxides have been prepared and sent to the principal investigators of the other tasks. Dr. Sam Traina, as a university collaborator, has a separate contract with the EMSP and has developed a report of this project under his DOE contract (DE-FG07-98ER14926). For more detailed information on this task, see Dr. Traina's annual report.

Chromium substitution for iron in maghemite and hematite can occur during the corrosion of chromium-containing steels. The goal of this study was to characterize the effects of chromium substitution on some fundamental properties of hematite and maghemite and the substitution's effect on ligand adsorption and oxide dissolution. Hematite (α-Fe_2O_3) was synthesized using Fe(III) perchlorate instead of Fe(III) nitrate. Eskolaite (α-Cr_2O_3) was synthesized from Cr(III) perchlorate in a manner analogous to that used for hematite. The resulting chromium-precipitate was heated at >600°C. Samples of α-$Fe_{2-x}Cr_xO_3$ were synthesized by mixing solutions of Cr(III) and Fe(III) nitrate in an $(NH_4)_2CO_3$ buffer. Calcination of these materials at 400°C produced the mixed-metal oxides. Maghemite (γ-Fe_2O_3) was synthesized by heating synthetic magnetite to 250°C. Mixed-metal maghemites (γ-$Fe_{2-x}Cr_xO_3$) were generated in a like fashion from synthetic Cr(III) magnetites.

To date, 11 solids have been synthesized, with hematite and maghemite synthesized in substantial quantities. The hematite-eskolaite series contains the following members: hematite, 95% iron, 90% iron,

75% iron, 50% iron, 25% iron, and eskolaite. Also a partial series of maghemite-eskolaite has been produced. Members of this series include maghemite, 90% iron, 75% iron, and eskolaite. In addition, magnetite has been synthesized.

X-ray diffraction (XRD) identification has been performed on each of the synthesized minerals. The hematite-eskolaite series shows that with increasing chromium content the characteristic peaks gradually shift from hematite to eskolaite. The XRD also shows changes in crystallinity within the series. The same XRD changes are seen in the maghemite-eskolaite series. In both series the degree of peak shift and changes in crystallinity will be determined by further XRD analysis using an appropriate internal standard. This will allow for peak positions and intensities to be known relative to the internal standard.

Infrared and thermal analysis has been performed on all samples. This data are still being analyzed. Color analysis was accomplished for each sample. This shows differences in the color of the mineral with changes in the ratio of iron:chromium. Color analysis also shows that more drastic color changes can be attributed to chromium substitution than with iron substitution.

Surface area measurements were performed on all the minerals. The hematite-eskolaite series exhibits the following trend with respect to surface area: 90% iron hematite> 95% iron hematite> 75% iron hematite> hematite> eskolaite> 50% iron hematite> 25% iron hematite. Similarly, the maghemite-eskolaite series data shows the following: 75% iron maghemite> 90% maghemite> maghemite> eskolaite. From these data, it appears that small substitutions of chromium increase surface area, but as the chromium substitution increases, the surface area is lowered to less than that of the end members.

Molecular Modeling

The goal of Task 4 is to correlate siderophore structure to metal oxide dissolution rates. As a first step toward this goal, we are attempting to correlate siderophore structure with metal ion binding affinity in aqueous solution. This will be accomplished through a molecular mechanics (MM3) approach that has proven successful with other types of ligands. The approach requires the development of an extended force field to handle the specific system under study. We have focused initially on a series of catecholamide ligands and their complexes with Fe(III). This system was chosen because (a) the catechol functional group is important in siderophore chemistry and (b) Fe(III) binding constant data are available for a series of seven structurally varied tris-catecholamide ligands, thus providing an experimental benchmark for the model.

Force-field development for catecholamides and their Fe(III) complexes is in progress. This task involves the development of new MM3 parameters for interactions that are exclusive to catecholamide structure as well as for interactions between the metal ion and the catecholamide. The parameterization is being accomplished using both experimental data (crystal structures) and electronic structure calculations. A survey of the Cambridge Structural Database has been carried out to gather statistical data on the geometric features of the basic catecholamide subunit in its two stable conformations, shown in Figure 1. This ligand subunit contains several interactions that are not included in the current version of MM3, such as the rotational potential surface for the C-C bond connecting the phenyl ring to the amide and the strength of the intramolecular hydrogen bonds. These interactions are being investigated with ab initio density functional theory and molecular orbital calculations. The potential surface for the C-C bond rotation has been obtained at the RHF/6-31G*, BLYP/DZVP2, and MP2/DZVP2 levels. These data will be used to fit the required torsional parameters. The hydrogen bond interaction is under investigation at the MP2/DZVP2 level. The Cambridge Structural Database has also been used to identify the geometric features of catechol when chelated with first row transition metals. A preliminary set of parameters for Fe(III) dependent interactions has been derived by fitting to the crystal structure data.

Figure 2. The Two Conformers of Catecholamide. The one on the left is stabilized by an intramolecular O--HO hydrogen bond; the one on the right is stabilized by an intramolecular O--HN hydrogen bond.

Planned Activities

Future efforts will focus on the primary objectives of each task. All tasks have received at least some of the oxides. In addition, each task has the same representative model ligands and the siderophores that could be purchased. Below is a brief description of the next year's efforts in each task.

Task 1 will continue to produce and disseminate siderophores as they are collected and purified from microbial culture. Dissolution studies will focus on developing rate data for the model ligands and siderophores using oxides distributed by Task 3.

Task 2 efforts in the coming year will focus on developing the bonding and structure of the representative model ligands at the water-oxide interface using those oxides developed for this project. In addition, specific attention will be centered on synthesizing and collecting spectra on a di-functional group model ligand. This compound will have two different reactive moieties that will allow spectral differentiation between the groups and hence a clearer picture on multi-moiety compound surface binding.

Future efforts in Task 3 will focus on determination of the surface charge properties of these solids followed by macroscopic sorption studies and x-ray absorption measurements of Eu(III) sorption by these solids.

Efforts in Task 4 will center on completing the MM3 parameterization for catecholamides and their iron complexes. Efforts will also benchmark the model by determining its ability to predict known solid-state structures. Once this is deemed reasonable, the model will be used to correlate siderophore structure with metal ion binding affinity in aqueous solution.