

# Contaminant-Organic Complexes: Their Structure and Energetics in Surface Decontamination Processes

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## Research Objective

The current debate over possible decontamination processes for U.S. Department of Energy (DOE) facilities is centered on disparate decontamination problems, but the key contaminants (uranium [U], plutonium [Pu], and neptunium [Np]) are universally important. There is no single decontamination technique or agent for all metal surfaces and contaminants with which DOE is faced. However, more innovative agents used alone or in conjunction with traditional processes can increase the potential to reclaim for future use some of these valuable resources or, at the least, decontaminate the metal surfaces to allow disposal as nonradioactive, nonhazardous material. This debate underscores several important issues: 1) regardless of the decontamination scenario, metal (Fe, U, Pu, Np) oxide film removal from the surface is central to decontamination; and 2) simultaneous oxide dissolution and sequestration of actinide contaminants against re-adsorption to a clean metal surface will influence the efficacy of a process or agent and its cost.

This renewal project is a logical extension of our previous work and will build strongly upon its findings to address the above issues. Current research will extend the scientific understanding of powerful, microbially produced chelates (siderophores) and newly developed information resulting from a fiscal year 1998 Environmental Management Science Program (EMSP) project by further investigating the use of siderophores and siderophore-like designed chelates as decontamination and sequestering agents. Investigations focus on critical actinide contaminants (i.e., U, Pu, Np), and catecholamide siderophores. Our scientific theme is evaluation of siderophores as complexants for tetravalent actinides sorbed to Fe oxide surfaces and dissolution of actinide solids.

The continued research integrates 1) studies of macroscopic dissolution/desorption of common actinide (IV) (Th, U, Pu, Np) solids and species sorbed to and incorporated into Fe oxides, 2) molecular spectroscopy (Fourier transform infrared [FTIR], Raman, x-ray absorption spectroscopy [XAS]) to probe the structure and bonding of contaminants, siderophores and their functional moieties, and how these change with the chemical environment, and 3) molecular mechanics and electronic structure calculations to design model siderophore compounds to test and extend the MM3 model. Our goals are 1) to develop the fundamental knowledge necessary to relate the energetics of contaminant and Fe oxide dissolution, contaminant desorption and the structure/reactivity of siderophores, and 2) to develop the information necessary to tailor catecholamide-type siderophore structure and properties to DOE's disparate metal surface decontamination needs.

Research progress from all three participating institutions is presented to give a complete overview of ongoing efforts. These are

- Pacific Northwest National Laboratory (PNNL) efforts in the areas of Fe oxide dissolution, desorption of surface sorbed contaminants on Fe oxide surfaces (primarily Th), and MM3 modeling of siderophore structures
- Ohio State University (OSU) work in the area of dissolution of substituted Fe oxides and Cr oxides, and the desorption of Eu from these surfaces
- Princeton University's efforts in spectroscopy of Fe oxide surface sorbed siderophore structure.

## Research Progress and Implications

### Pacific Northwest National Laboratory

Dissolution studies to date have concentrated on the hydroxamic acid-type ligands with one, two and three hydroxamate functional groups; acetohydroxamate, routhotrillic acid, and desferrioxamine B (DFB). Batch-type pH-stat investigations have shown dissolution rates of iron oxides (goethite, hematite, and magnetite) increase by more than an order of magnitude as the number of functional groups per molecule increase (i.e., acetohydroxamate, routhotrillic acid, and DFB) even though the total concentration of hydroxamic acid groups remains constant. Unlike oxide dissolution in the presence of ethylenediaminetetraacetic acid (EDTA), the Fe oxide dissolution rate appears to decrease linearly as pH is increased from 4.5 to 9.0. This suggests that, unlike EDTA, there is limited binuclear adsorption of the ligand, or readsorption of the dissolved Fe-siderophore at low pH when the surface is positively charged. In addition, these results imply that siderophores, in general, will easily and quickly dissolve Fe oxide mineral surfaces under less harsh conditions and with less waste.

Thorium is a tetravalent ion that is a good analog to the tetravalent actinides U(IV), Pu(IV), or Np(IV); its solubility in 0.1 M NaNO<sub>3</sub> is approximately  $5 \times 10^{-3}$  M to  $5.5 \times 10^{-5}$  M from pH 3 to 5, respectively. Upon precipitation, it forms an amorphous ThO<sub>2</sub>, and at higher temperatures or long aging times, formation of a crystalline ThO<sub>2</sub> is observed. Th(IV) studies were performed at 25°C, Th = [ $1 \times 10^{-5}$  M], pH 4.0, 1g/L hematite (a major corrosion product). Th(IV) adsorption to hematite, for the conditions utilized, increased rapidly from 0% sorbed to 100% sorbed over the pH range 3 to 4.5. After adsorption, two different hydroxamates (routhotrillic acid, and DFB) were utilized to desorb the Th and dissolve hematite. The rates of desorption and dissolution were studied as a function of time, hydroxamates type, and aging of the Th-hematite surface complex. Results to date from these studies show that sorbed Th is fully solubilized by both

siderophores. However, the rhototrillic acid exhibits a faster rate of solubilization than the trihydroxamate, DFB. In addition, it is clear from that the rate of Fe solubilization is slowed by the presence of Th. The Fe and Th release curves show two distinct regions that exhibit different solubilization rates. During the early period of solubilization (about 180 min), Th release is faster than the sorbed Fe but, as time progresses, these two rates become essentially equal. Once most of the Th is desorbed, Fe solubilization continues at a rate comparable to that observed without Th.

Although it is believed that, like other metals, Th sorbs to hematite forming a mononuclear surface complex, it should, at higher surface densities, begin to form polynuclear surface species and surface-bound mixed metal oxides. The above experiments were performed at a Th(IV) concentration that is approximately a factor of ten below its solubility at pH 4.0. Because of this, we are currently assuming its surface species is a mononuclear inner-sphere complex that is homogeneously distributed over the hematite surface (this assumption will be tested by XAS analysis later this year). However, the possibility exists that even at these low concentrations, Th surface speciation is a mix of mononuclear and polynuclear species, which will impact data interpretation. Regardless, the data presented here does show that Th is rapidly removed from the hematite surface and that its latter rate is equal to that of Fe solubilization. Interestingly, the sum of the Th and Fe release rates is about equal to the Fe release rate in the absence of Th. These results are different from that observed for hematite sorbed Eu release (OSU); these differences are currently being explored.

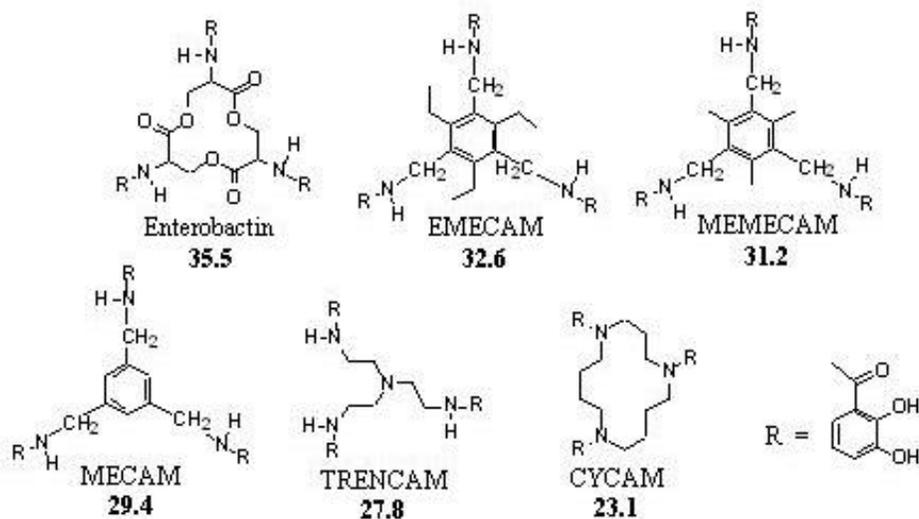
The Th(IV) studies began under the previous project and are currently being completed. Primarily, aging studies of Th on the surface of hematite prior to exposure to a siderophore are ongoing to test the potential for time-dependent polynuclear species formation and its impact on Th solubilization. More data is required before definitive conclusions can be drawn about Th solubilization or a comparison made between the behavior of Th and Eu. We expect to generate that data over the next 6 months, including surface spectroscopy of Th from which a more discriminating picture of Th surface speciation and its mechanism of solubilization will be elucidated.

In the first 3 years of the project, we used molecular modeling methods to investigate a series of tris-catecholate ligands. Structural criteria for the design of multidentate catecholates ligands were derived from 1) an examination of crystal structure data and 2) geometries and potential energy surfaces obtained from electronic structure calculations. These structural criteria were incorporated within a molecular mechanics model. Application of this model yielded the first quantitative structure-stability relationship for Fe(III) complexation by tris-catecholamide ligands. This result establishes a method that can be used to evaluate the metal ion affinity of other possible catecholate ligand architectures. Thus, our previous studies provided criteria to design catecholate-based hosts and methods to evaluate quantitatively the metal ion binding

potential of proposed host structures. Building upon this information, we have initiated the computer-aided design of bis-, tris-, and tetrakis-catecholate ligands that are structurally organized for complexation with tetravalent actinides U(IV), Np(IV), and Pu(IV).

An extended MM3 model has been developed for Fe(III) complexes with catecholamides. Assignment of Fe-O stretch, Fe-O-C bend, and Fe-O-C-C torsion parameters was based on geometries and potential energy surfaces from density functional theory calculations and crystal structure data, and were investigated at the MP2 level of theory. These included rotational potential surfaces for several C-C bond types and hydrogen bonds involving phenol. The resulting model describes empirical relationships between force constants and physical properties. In addition to these metal-dependent interactions, several unknown intra-ligand interactions reproduce crystal structures with the expected level of accuracy. By changing only the M-O stretching parameters, a good agreement between calculation and experiment is obtained for other metal ions. In addition, we have found that this model is applicable to tropolonate complexes. Published barriers to octahedral inversion are reproduced to within  $\pm 2$  kcal/mol for  $[\text{Al(III)}(\text{tropolonate})_3]$  and  $[\text{Ga(III)}(\text{cat-echolamide})_3]^{3-}$ .

Application of this model has led to the first quantitative structure-activity relationship for catecholamide ligands. Conformational searches yielded the lowest energy forms of the six protonated ligands shown in Figure 1. Conformational searches were also run to identify the lowest energy forms of their Fe(III) complexes. We obtained the difference in steric energy



**Figure 1.** The Six Tris-Catecholamide Siderophore Architectures That Have Been Studied. Relative affinities for Fe(III) are given as pFe values (10  $\mu\text{M}$  ligand, 1  $\mu\text{M}$  Fe(III), and pH 7.4).

between the Fe-L complex and the hexaprotonated ligand. A plot of pFe vs. this energy difference yields the linear correlation. This result suggests that this method can be used to screen other candidate architectures for ligands based on the catecholamide donor group.

PNNL is collaborating with the Department of Chemistry, University of California, Berkeley, providing computer-aided host design to assist with the discovery of improved metal ion sequestering agents. The potential for UC-Berkeley to supply several siderophore-like (Figure 1) compounds is under discussion; the compounds will be used for testing hypotheses regarding actinide (IV) solubilization and sequestration. Current laboratory experiments on solubilization of Th(IV)O<sub>2</sub> and desorption of Th(IV) sorbed to oxide surfaces are nearing completion. Results have been submitted or are being submitted to scientific journals.

## Ohio State University

Investigations to date have focused on studying the dissolution of oxides and desorption of metals by the siderophore DFB, with different metal ions adsorbed onto the solids. To further understand the effects of sorbed metals on oxide dissolution by DFB, XAS was used to probe the surface structural environment of sorbed metal ions. With the knowledge of the interactions between DFB, oxides, and metal ions, we can have a better understanding of how siderophore reacts with iron oxides in an environment where multiple metals including different lanthanides and actinides are present. Our results indicated that while DFB effectively dissolved iron oxides with different adsorbed metals, this process was affected also by the type of the metal adsorbed.

Two different solids, hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and 15% Cr-substituted hematite ( $\alpha$ -Fe<sub>1.69</sub>Cr<sub>0.31</sub>O<sub>3</sub>), were used as substrates, and different metals including Ga, Zn, Pb, and Eu were chosen as adsorbates representing different types of metals. Macroscopic sorption studies were conducted for metals on these solids with initial metal concentration of 10<sup>-4</sup>M, solid surface area of 40 m<sup>2</sup>/L, and 0.01M NaNO<sub>3</sub> as background electrolyte over the pH range between 4 to 9. It was found that the percentage adsorption isotherms of most of these metals was not affected by different substrates under the experimental conditions used in this study, with the exception of Zn, for which the adsorption edge shifted to a lower pH value with Cr-substituted hematite (data not shown).

For the kinetic dissolution experiments, the solid concentrations were adjusted to have 40 m<sup>2</sup>/L of initial solid surface areas in each sample. The samples were reacted with different metals at an initial concentration of 10<sup>-4</sup>M with 0.01M NaNO<sub>3</sub> as background electrolyte for 24 hours before adding 10<sup>-3</sup> M DFB. All dissolution experiments had been conducted at solution pH of pH = 7 ± 0.1 over a 60-hour period after adding DFB at 25°C purged with nitrogen gas. The extent of metal ion desorption by DFB was also measured for all samples as shown on Figure 2 (only Zn and Eu shown here). Metal ion desorption occurred rapidly, and the extent of metal

desorption reached a plateau for all metals under investigation within 2 hours of reaction time. Although DFB has a higher affinity to Fe than to other metals under investigation, metal ions were desorbed from the solid surfaces faster than Fe dissolution at the beginning of the reaction after DFB was added. The extent of metal ion desorption from solid surfaces by DFB varied among different metal ions, probably due to DFB-metal complexation reactions.

Figure 3 shows that Fe release increases with time for all samples, unlike the behavior of metal ion desorption. In general, Cr substitution enhanced Fe release by DFB as much as ten times more than that of pure hematite. No Cr release, however, was observed for all samples during the reaction time in this study. For pure hematite, samples with adsorbed metals had less dissolved Fe by DFB than the one without. Different types of metal ion seemed to have no

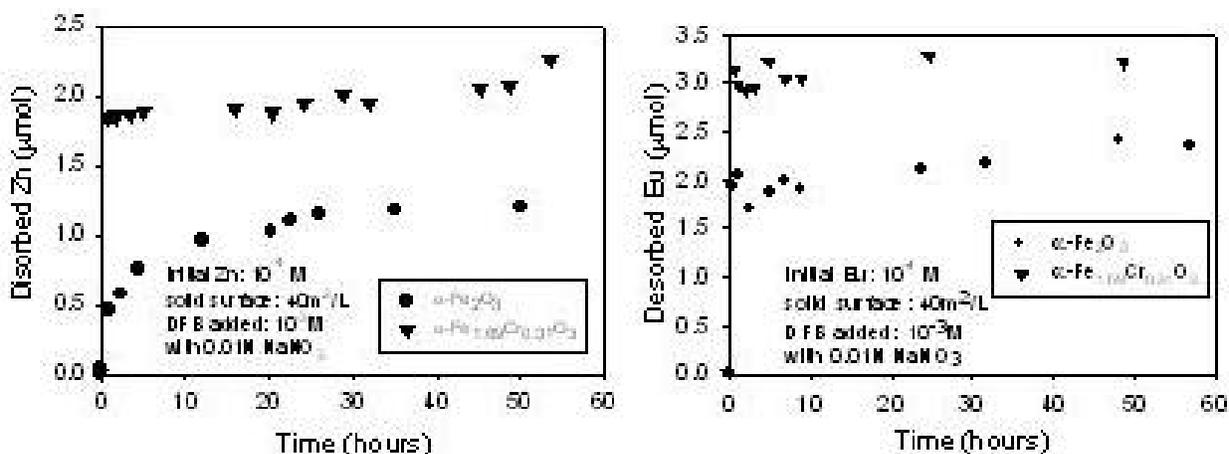


Figure 2. Metal Ion Desorption from Different Solids by DFB

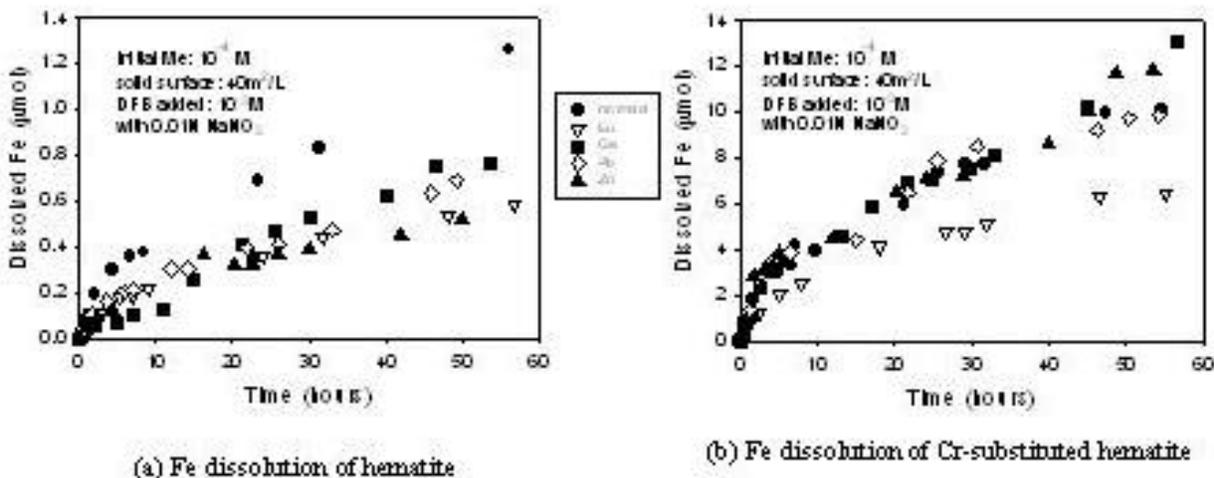


Figure 3. Fe Dissolution of Hematite and 15% Cr-Substituted Hematite by DFB with Different Adsorbed Metal Ions vs. Reaction Time

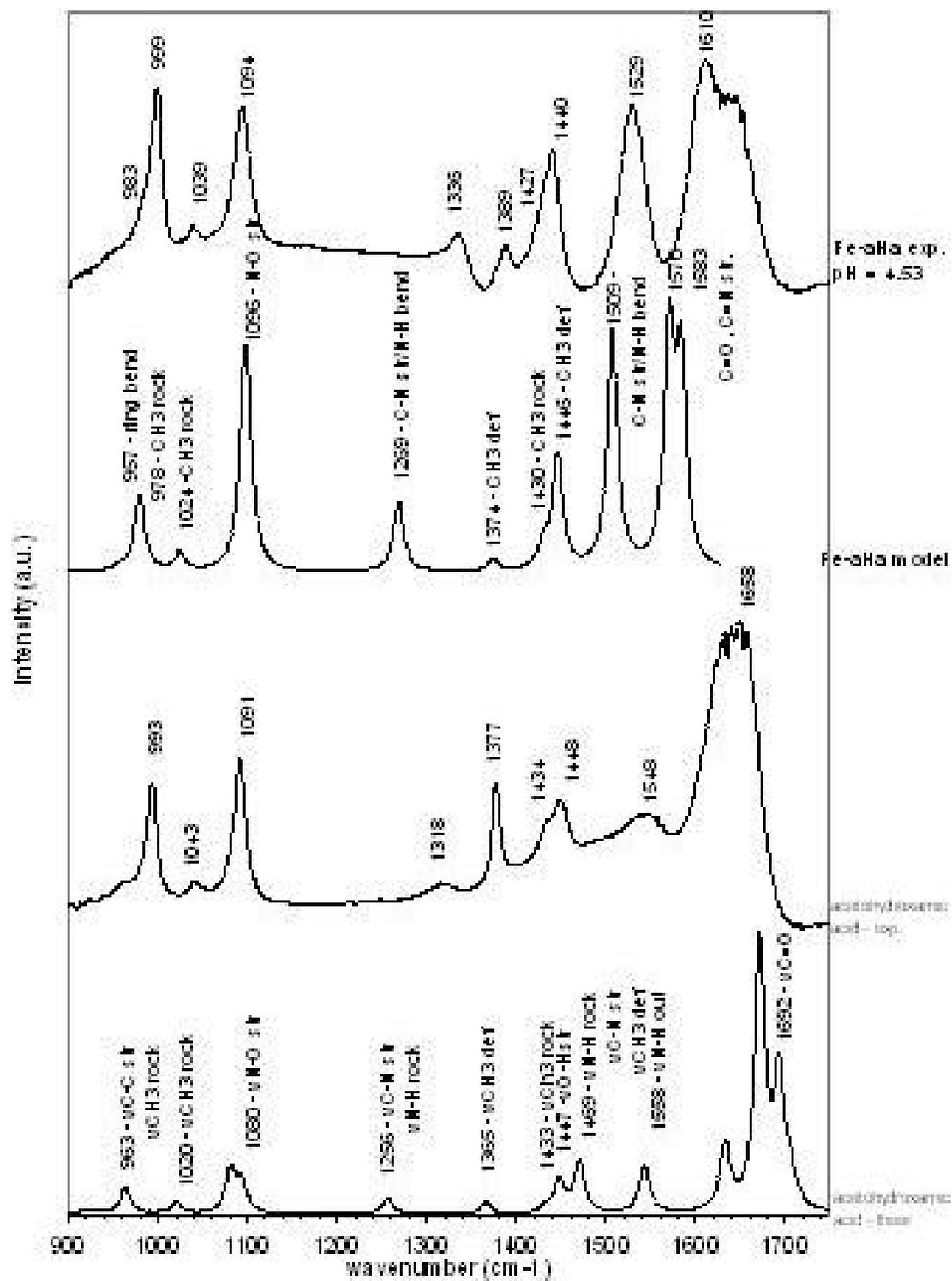
significant effects on Fe dissolution under these experimental conditions. This result suggested that while adsorbed metals blocked available surface sites on hematite surfaces for DFB, causing less Fe release, Fe dissolution by DFB from the well crystalline structure of hematite was not affected by the adsorbed metal ions.

For 15% Cr-substituted hematite, on the other hand, most of the metals had no effect on Fe dissolution by DFB except for Eu, from which less dissolved Fe was observed. Our previous studies also showed that adsorbed Eu retarded Fe release by DFB from iron oxides and Cr-substituted iron oxides with different extent of Cr substitution. It is not clear why the system with Eu behaved differently from systems with other metals by the results from these macroscopic experiments. One possible explanation is that since Eu can form spinel structure as that of hematite, Eu may be incorporated into the oxide structure or forms stronger bonded complexes on the oxide surfaces comparing to the other metals. While Cr substitution introduces disorder to the oxide structure enhancing the Fe dissolution by DFB, strongly adsorbed Eu still blocks the surface site in the disordered oxide structure and thus reduces Fe dissolution. Our results from XAS study indicated that Eu forms strong surface complexes on solid surfaces. To date, the spectroscopic results from other metals were not conclusive, requiring further investigation.

## **Princeton University**

We have been working on the functional group chemistry of model siderophore molecules, such as acetohydroxamic acid (aHa) and DFB, using vibrational (infrared [IR] and Raman) and XAS (C-, and N-groups in the ligand, and Fe-ligand complexes) in aqueous solutions and at the mineral-water interfaces. These experimental studies are complemented with theoretical calculations (Gaussian - B3LYP/6-31G(d) basis set) to gain insight on the structure and reactivity of model siderophores in aqueous solutions. We focused our preliminary studies on the protonation and deprotonation, and Fe<sup>3+</sup> complexation of aHa and desB. We conducted a series of studies to understand the variations in the chemical state of siderophore molecule as a function of pH and Fe<sup>3+</sup> ion concentration. Theoretical calculations were used to verify the vibrational spectra and the band assignments, and in the identification of energetically favored chemical species. To mimic the aqueous conditions in theoretical calculations of aHa, three water molecules were included adjacent to the hydroxamate groups.

The protonation and deprotonation reactions of aHa in aqueous solutions were examined by Holmen et al. (1997), and our experimental spectra agree with their reported values. However, our spectral analysis and interpretation differ from theirs. A series of ATR-FTIR (pH 4.5 to 10) and Raman spectroscopy (pH 6 to 12) studies on aHa solutions showed dramatic changes in the vibrational bands of hydroxamate functional group, and small changes in the alkyl group vibrations with aHa deprotonation and Fe<sup>3+</sup> complexation (Figure 4). The most noticeable



**Figure 4.** Experimental and Theoretical Vibrational Spectra of aHa in Protonated and its Fe-Complex Forms. The spectral analysis is done based on the theoretical calculations.

changes in the vibrational spectra of aHa (either because of protonation or  $\text{Fe}^{3+}$  complexation) are as follows: 1) changes in the vibrational bands of  $\text{C}=\text{O}$ , indicating the variations in the double bond character and the  $\text{C}-\text{O}$  bond length, 2) changes in the  $\text{C}-\text{N}$  stretch, which is related to the deprotonation/ protonation of the molecule, and 3) changes in the  $\text{N}-\text{O}$  stretch. Our theoretical and experimental studies give evidence that the proton connected to the oxygen atom leaves during deprotonation rather than the one connected to N.

In the neutral aHa molecule, the carbonyl peak is at  $1658\text{ cm}^{-1}$  and shifts to  $1610\text{ cm}^{-1}$  upon complexation with  $\text{Fe}^{3+}$ . This is due to the increasing bond length of  $\text{C}=\text{O}$  as it becomes complexed to iron and also due to the emergence of a  $\text{C}=\text{N}$  stretch character due to the resonance properties of aHa. In addition, the  $\text{N}-\text{O}$  stretch shifts from  $1091\text{ cm}^{-1}$  to  $1094\text{ cm}^{-1}$  upon complexation. In previous papers, the  $\text{N}-\text{O}$  stretch was assigned to low-energy bands around  $900\text{ cm}^{-1}$ , but calculations involving water and deuterated water seem to favor our new assignment. This reassignment of  $\text{N}-\text{O}$  stretch is important to the prediction of metal-hydroxamate complexes, since the  $\text{N}-\text{O}$  group is at the center of  $\text{Fe}-\text{aHa}$  complex. Another shift that directly probes the iron-binding site is the amide II and amide III bands, which are related to a coupling of  $\text{C}-\text{N}$  stretch and  $\text{N}-\text{H}$  bend. The amide II is attributed to mainly  $\text{N}-\text{H}$  bend as well as the  $\text{NOH}$  bend and amide III is mainly attributed to  $\text{C}-\text{N}$  stretching. From Figure 1, amide II shifts to lower frequencies and amide III goes to higher frequencies. This corresponds to a more constrained  $\text{N}-\text{H}$  bond and shorter  $\text{C}-\text{N}$  bond, which in agreement with both experimental and theoretical data.

## Planned Activities

At PNNL, future studies will focus on the catecholamide siderophores. Investigations will continue to focus on the Fe oxides (goethite, hematite, and magnetite). However, studies of  $\text{UO}_2$  and  $\text{PuO}_2$  dissolutions will begin during the last quarter of fiscal year 2002 and continue into the final year of this project. Modeling efforts will continue to expand to include the hydroxamate siderophores. In the final year of this project, investigations are anticipated with actual contaminated steel coupons from the Hanford Site.

Results of OSU studies indicated that types of metal ions affected Fe dissolution by DFB. This finding is significant because decontaminating processes in DOE facilities encounter different lanthanides and actinides. To have a better understanding of the iron dissolution and metal desorption processes by DFB, we will focus our work on

1. dissolution experiments with actinides, thorium, and uranium
2. further XAS studies on different metal ion sorption on the oxides
3. effects on iron dissolution with different siderophores.

Princeton's analysis and interpretation of the experimental and theoretical results of aHa will aid in the interpretation of the nature of desB, a bigger molecule but with the same functional moieties as aHa, in aqueous solutions and at the interfaces. X-ray spectroscopic studies on aHa and desB and their Fe<sup>3+</sup> complexes in aqueous solutions and mineral surfaces will further increase our knowledge on this system. In the coming months, our focus will be on the x-ray spectroscopy evaluation of aHa and desB in aqueous solutions, and the vibrational spectroscopy of these molecules on Fe- and Cr-doped Fe-oxide surfaces.

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## Information Access

### Publications (bold signifies output since renewal)

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Chen CC and SJ Traina. Macroscopic and Microscopic Investigation of Europium and Neodymium Partitioning at Iron Oxide-Water Interfaces. In preparation.

Chen CC and SJ Traina. Sorption of Strontium, Lead, Zinc, and Europium on Iron Oxides and Cr-Substituted Iron Oxides. In preparation.

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## **Presentations**

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