Mechanisms of Radionuclide-Hydroxycarboxylic Acid Interactions for Decontamination of Metallic Surfaces

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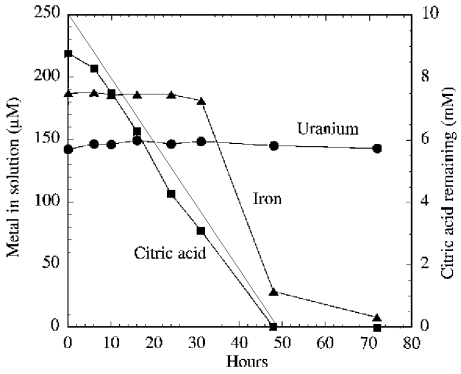
Introduction

This project addresses key fundamental issues involved in the use of simple and safe methods for the removal of radioactive contaminants from slightly contaminated steel and other surfaces at the DOE sites so that the metals can be reused. The goals of this research are to (i) determine the nature of the association of radionuclides with the metal surfaces commonly found at sites targeted for decontamination and decommissioning, such as stainless steel, plain carbon steel and copper; (ii) selectively remove the low levels of radionuclides such as U and Pu, from contaminated metallic surfaces using hydroxycarboxylic acids (citric acid and its analogs) by elucidating the coordination, complexation, dissolution and removal mechanisms; and (iii) recover radionuclides in a concentrated form by biodegradation followed by photodegradation of the extract containing radionuclide-organic complexes thereby resulting in significant reduction in secondary waste generation.

Approach

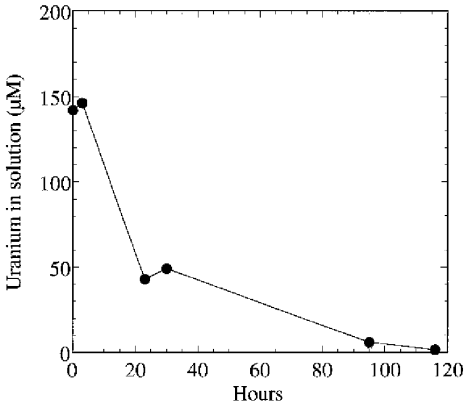
The overall process consists of three steps: (i) surface decontamination, (ii) biodegradation, and (iii) photodegradation. Citric acid, a naturally occurring organic complexing agent, is used to extract metals and radionuclides from contaminated steel surfaces by formation of different types of complexes such as bidentate, tridentate, binuclear, and polymeric species. The solution containing the metals and radionuclides is then subjected to biodegradation, resulting in bioprecipitation of metals such as Co, Cs, and Sr which are recovered in a concentrated form. Uranium however, forms a binuclear complex with citric acid that is not biodegraded and remains in solution. The supernatant containing the uranium is separated and upon exposure to light undergoes rapid photodegradation resulting in the precipitation of uranium as a stable oxide ($UO_3 \cdot 2H_2O$). Uranium is recovered in a concentrated form after photodegradation for recycle or disposal.



Fate of Citric Acid, Iron, and Uranium During Biodegradation of Citric Acid Solution

Key Experimental Results

Initial results indicate the predominant form of rust on low carbon steel surfaces consists of lepidocrocite, magnetite, and ferrihydrite phases. EXAFS analyses at the U absorption edge show the U present as uranyl hydroxide, -oxyhydroxide, -hydroxochloro, and $U(\mu_2\text{-}O)Fe$ species with the oxide. Surface analysis of U contaminated coupons showed that U is predominantly associated with the surface of the oxide and some occluded in the oxide matrix. The ability of citric acid to extract uranium from corroded steel is dependent upon the association of the uranium with the oxide matrix. Biodegradation of citric acid solution containing iron and uranium resulted in removal of iron (96%) from solution. Uranium however, was recalcitrant due to the nature of the complex formed. Photodegradation of citric acid solution following biodegradation resulted in complete precipitation of uranium.



Fate of Uranium During Photodegradation of Citric Acid Solution

Economics and Market Potential

The BNL Citric Acid Process is very versatile and can be applied to decontamination of various forms of materials including steel and concrete surfaces. In addition to its wide range of applicability, this technology minimizes generation of secondary waste streams, and recovers environmentally and economically important metals in a concentrated form.

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Decontamination of Metallic Surfaces by Citric Acid

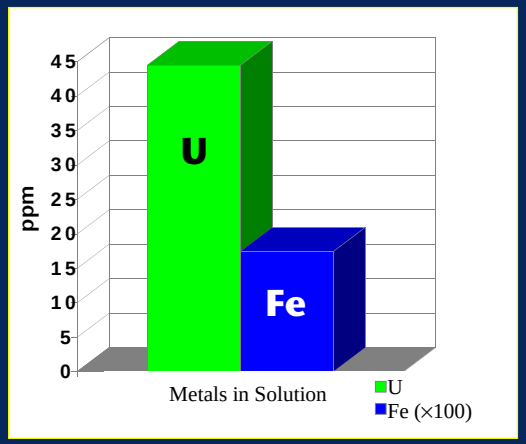
BROOKHAVEN NATIONAL LABORATORY
managed by Brookhaven Science Associates for the U.S. Department of Energy
STONY BROOK STATE UNIVERSITY OF NEW YORK

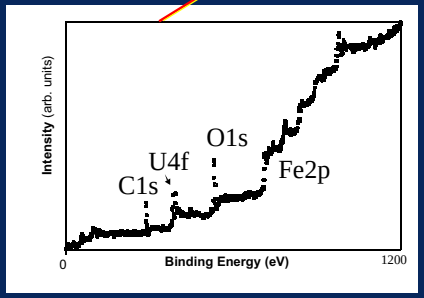
CORRODED MILD STEEL COUPON BEFORE AND AFTER CITRIC ACID TREATMENT

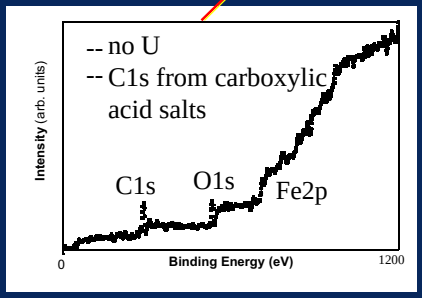
Area immersed in 0.1 M citric acid and rinsed

Corroded area primarily composed of ferrihydrite, lepidocrocite and magnetite

ICP-AES ANALYSIS OF CITRIC ACID SOLUTION

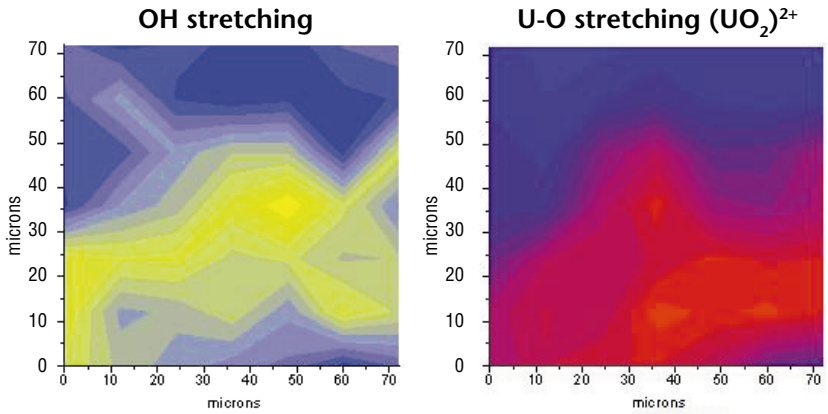






X-RAY PHOTOELECTRON SPECTROSCOPY (XPS) SURFACE ANALYSIS

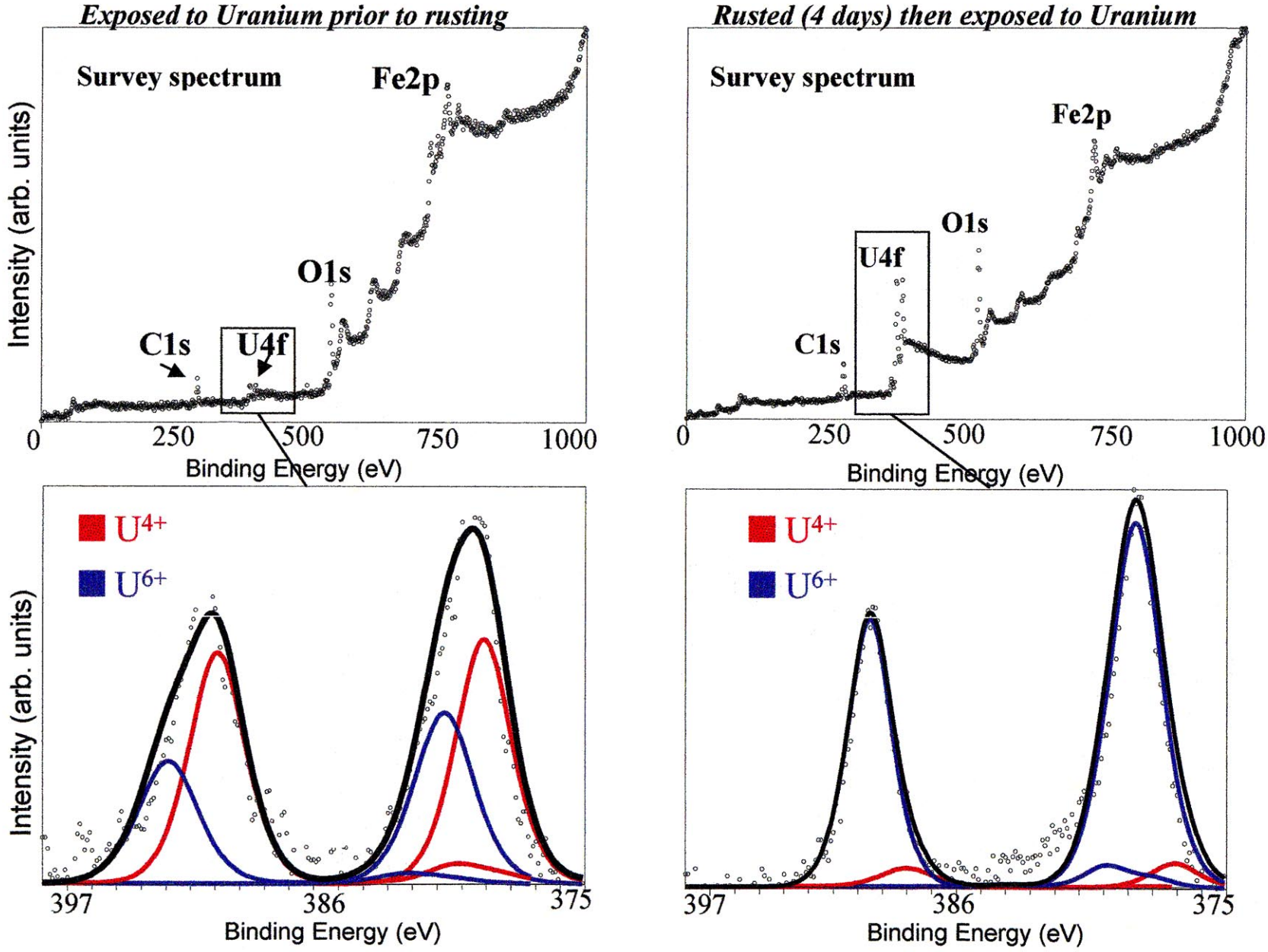
SYNCHROTRON INFRARED MICROSPECTROSCOPY OF CARBON STEEL EXPOSED TO URANYL NITRATE



Uranyl groups are spatially associated with steel corrosion product

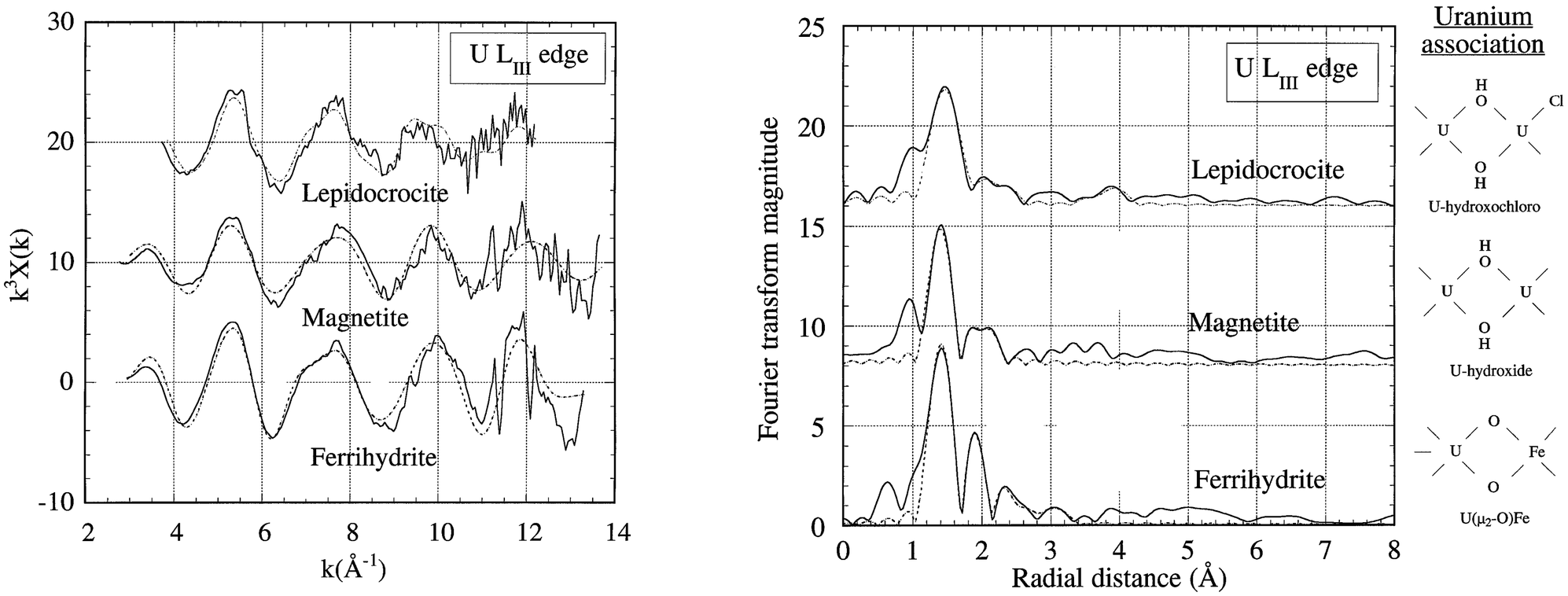
- Citric acid is a naturally occurring and environmentally friendly organic compound.
- Surface analysis indicates selective removal of uranium by citric acid.
- Citric acid inhibits further corrosion of steel surfaces through formation of carboxylic acid salts.
- Reduction of waste stream is achieved through biodegradation/photodegradation with uranium recovery.

XPS of Uranium Contaminated Low Carbon Steel Surfaces



Coupon exposed to U(6+) prior to rusting showed a mixture of U(4+) and U(6+)
Coupon rusted prior to exposure showed a higher level of U contamination, predominantly as U(6+)

EXAFS Analysis of Uranium Association with Iron Oxides



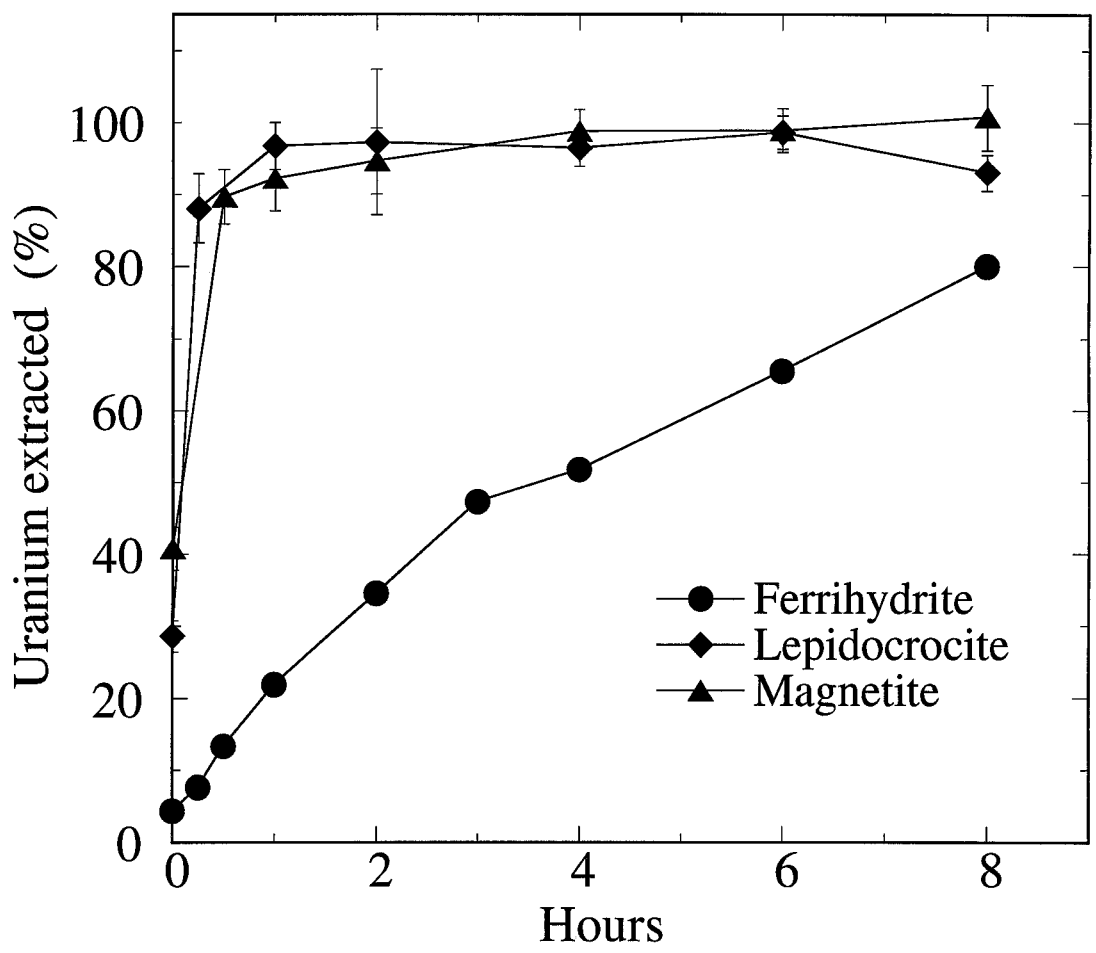
Uranium association with iron oxides: uranium hydroxochloro species with lepidocrocite; uranium hydroxide with magnetite; bidentate complex with Fe in ferrihydrite. Experimental data (-); theoretical fit (---).

EXAFS Structural Parameters for Uranium Association With Iron Oxides

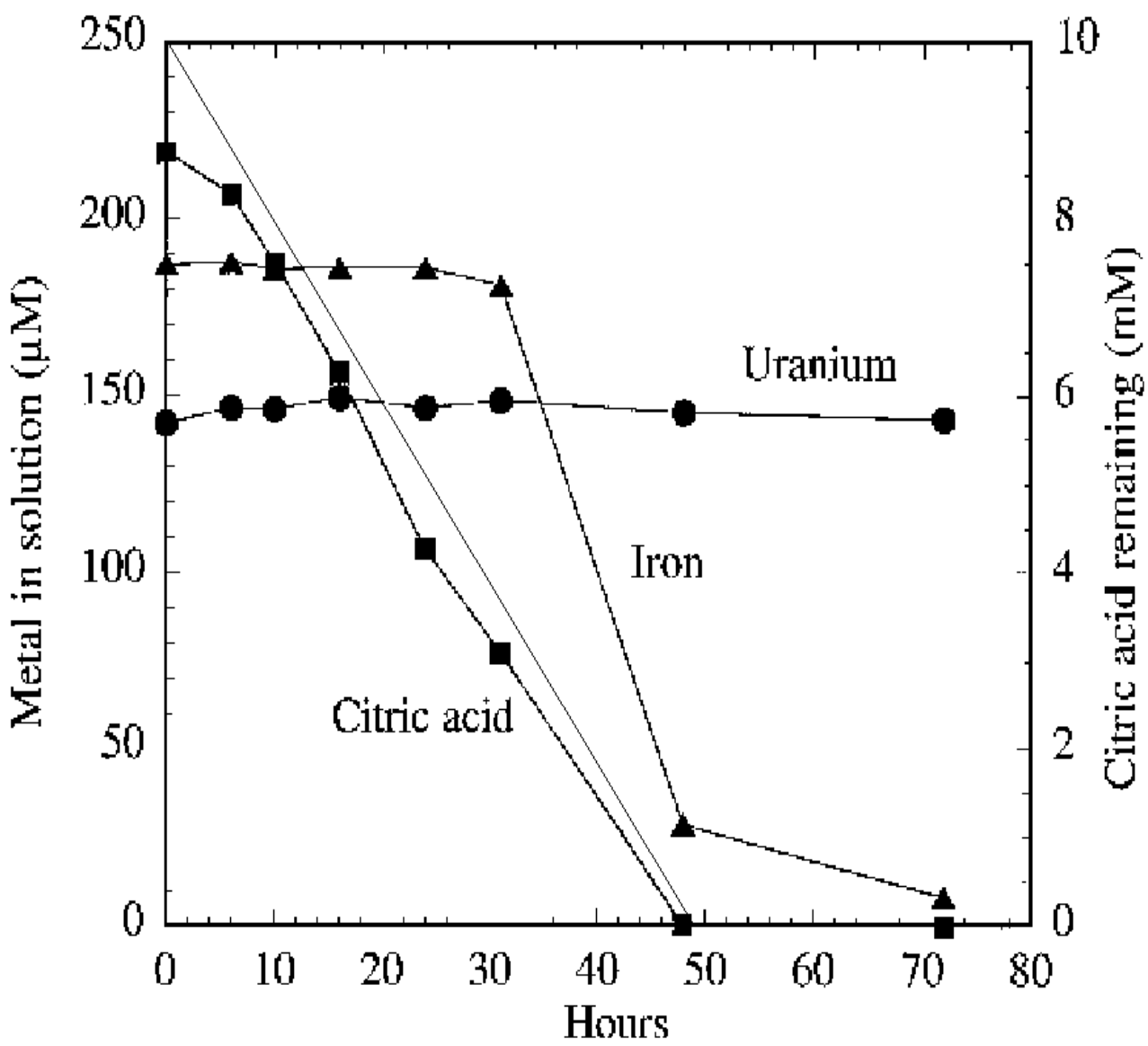
Sample	Atom	N	R(Å)	σ^2	F
Ferrihydrite	U-O$_{ax}$	2.0	1.79	0.001	0.15
	U-O$_{eq1}$	3.0	2.35	0.004	0.01
	U-O$_{eq2}$	2.0	2.54	0.040	0.02
	U,Fe	1.0	3.42	0.010	0.01
Magnetite	U-O$_{ax}$	2.0	1.78	0.001	0.01
	U-O$_{eq1}$	1.9	2.35	0.007	0.02
	U-O$_{eq2}$	1.8	2.43	0.004	0.01
Lepidocrocite	U-O$_{ax}$	2.0	1.82	0.004	0.03
	U-O$_{eq}$	3.1	2.33	0.015	0.01
	U-Cl	0.7	2.65	0.005	0.01
	U,U	1.1	4.14	0.0025	0.01

Coordination number (N), interatomic distance (R), disorder parameter (σ^2), and goodness of fit parameter (F).

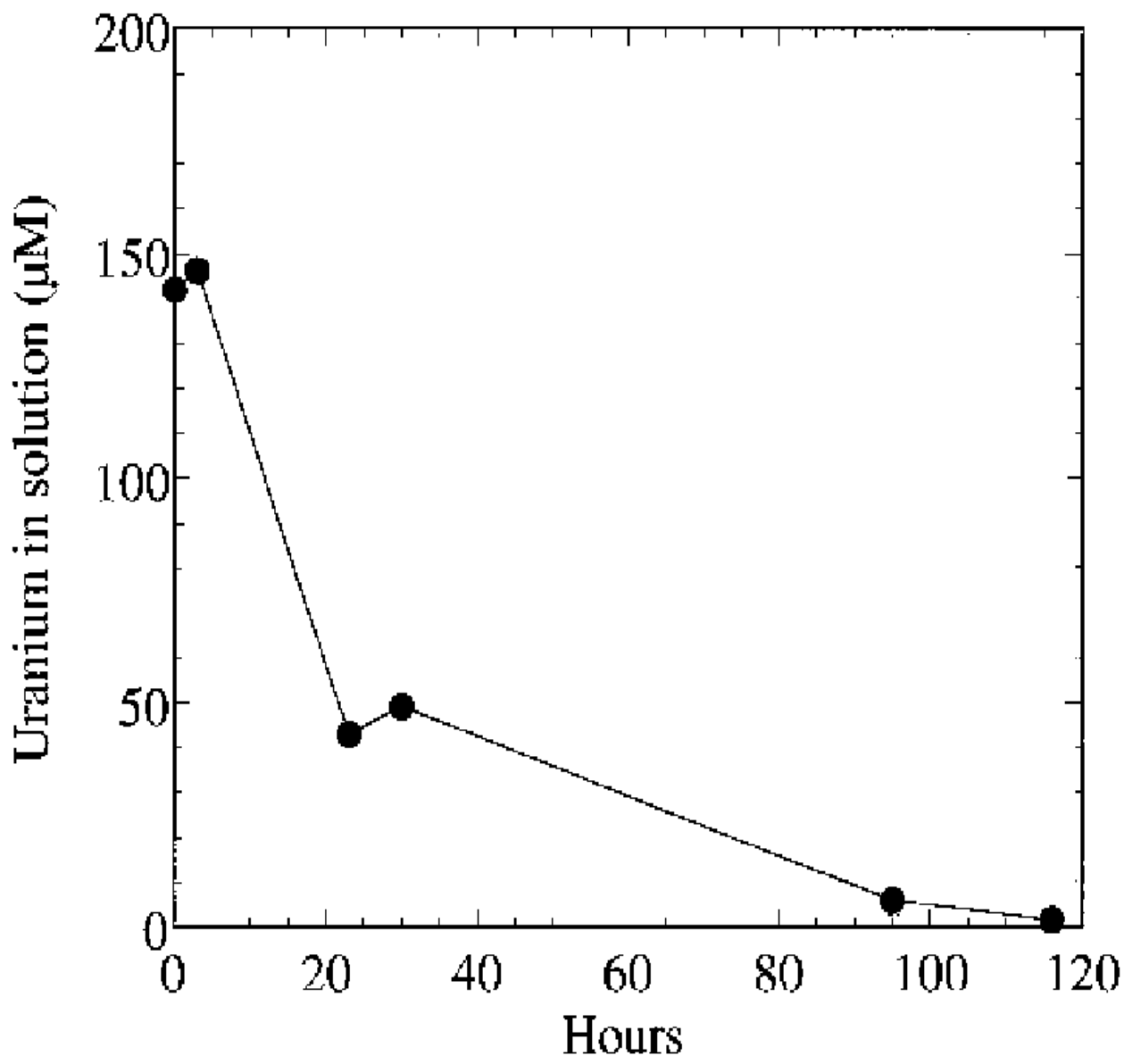
Extraction of Uranium From Iron Oxides by Citric Acid



Uranium was completely extracted from lepidocrocite and magnetite by citric acid, whereas it was partially extracted from ferihydrite (80%). The rate of extraction of U was dependent upon its association with the oxide.



Fate of Citric Acid, Iron, and Uranium During Biodegradation of Citric Acid Solution



Fate of Uranium During Photodegradation of Citric Acid Solution

Summary

- Ferrihydrite, lepidocrocite, and magnetite were the predominant oxides found on corroded low carbon steel surfaces.
- Uranium was associated with ferrihydrite as a bidentate complex with iron [$U(\mu_2\text{-}O)Fe$]; as uranium hydroxochloro species with lepidocrocite; and uranium hydroxide [$UO_2(OH)_2$] in magnetite.
- Both U(4+) and U(6+) oxidation states were detected on corroded steel surfaces. Uranium was bound to oxide surface as well as occluded in the oxide matrix.
- The efficiency of extraction of U from the oxides by citric acid was dependent upon the nature of uranium association with the oxide.
- Biodegradation of citric acid solution removed excess citric acid and Fe from the extract; U was recovered as uranium trioxide [$UO_3 \cdot 2H_2O$] by photodegradation.