Aqueous Electrochemical Mechanisms in Actinide Residue Processing

D. E. Morris[1], C. J. Burns[1], W. H. Smith[1], and D. L. Blanchard, Jr.[2]

1 Seaborg Institute for Transactinium Science
Los Alamos National Laboratory
2 Pacific Northwest National Laboratory

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INTRODUCTION

The US Department of Energy is faced with the stabilization and disposition of many metric tons of plutonium- and uranium-bearing residue materials resulting from 50+ years of nuclear weapons production activities. These materials are presently in storage at sites throughout the weapons production complex. They pose an immediate potential threat due to instability and degradation, and a long-term problem because the volume of material to be disposed may exceed projected repository capacities. Mediated electrochemical oxidation / reduction (MEO/R) processes [1] for dissolution of the actinide material from these residues are one approach for stabilization / volume reduction. These are low temperature, ambient pressure processes, they can be highly selective for the actinides (i.e., no substrate degradation occurs), and they can be used for many categories of residue materials with little or no modification. Some questions remain concerning the details of the e^- - transfer mechanisms through which these processes act, and how the processes might be optimized to maximize efficiency while minimizing secondary waste. In addition, further research is merited to extend the range of applicability of these electrochemical methods to other residue and waste streams. Recent advances in the study of heterogeneous e^- - transfer in transition-metal oxide solids [2] provided a new framework within which these studies are being conducted.

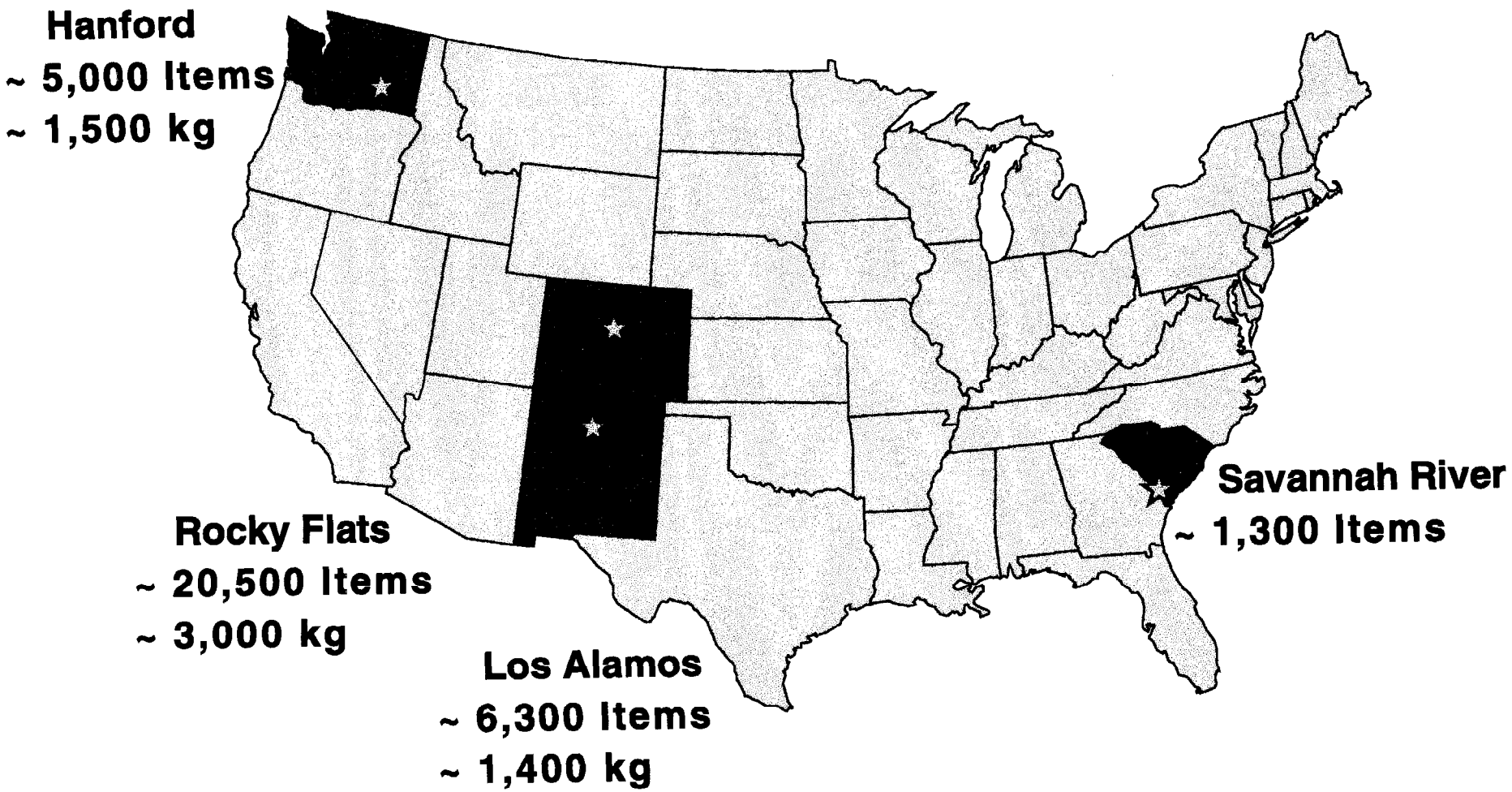
OBJECTIVES

- Determine the potential windows for oxidation / reduction of colloidal actinide oxides and actinide-bearing oxide substrates and the e^--transfer kinetic parameters that govern the current - overpotential characteristics

- Develop adaptations of mediation schemes and applications of co-mediation reagents for oxidative and reductive dissolution based on complexation of the surface-bound or solid-phase actinides and/or the dissolved redox mediator

- Conduct bench-scale tests of new MEO/R schemes on actual residue materials.

Major Plutonium Residue Holdings within the DOE Complex



Rocky Flats Residue Inventory (Partial)

Residue Class	Mass of Pu (kg)	Bulk Mass (kg)
Graphite	25	19500
Pyrochemical Salts	1000	13778
Combustibles	64	12800
Incinerator Ash	535	10690
Ceramic Crucibles	166	9760
Heels	178	8940
Plastic Filters	60	5900
Sand, Slag, & Crucible	215	5340
Firebrick	90	3010
Sludge	3.4	610
Resins	2.1	210

Materials & Systems

Solid Substrates*

- SiO_2 - Degussa Aerosil 200
- TiO_2 - Degussa P25
- Pure U and Pu Oxide Phases
- Incinerator Ash (from existing inventories at Rocky Flats and LANL)

Soluble Redox Mediators

- Oxidants - Ce(IV) / Ag(II) / Co(III)
- Reductants - Fe(II) / Sn(II) / V(III) / Eu(II)
- Complexes of these metals with ligand systems that perturb metal E^0s

Complexants for Enhanced Surface Dissolution / Solution Stabilization

* Previous characterization work [3] has shown that incinerator ash samples contain silicates and silicotitanates

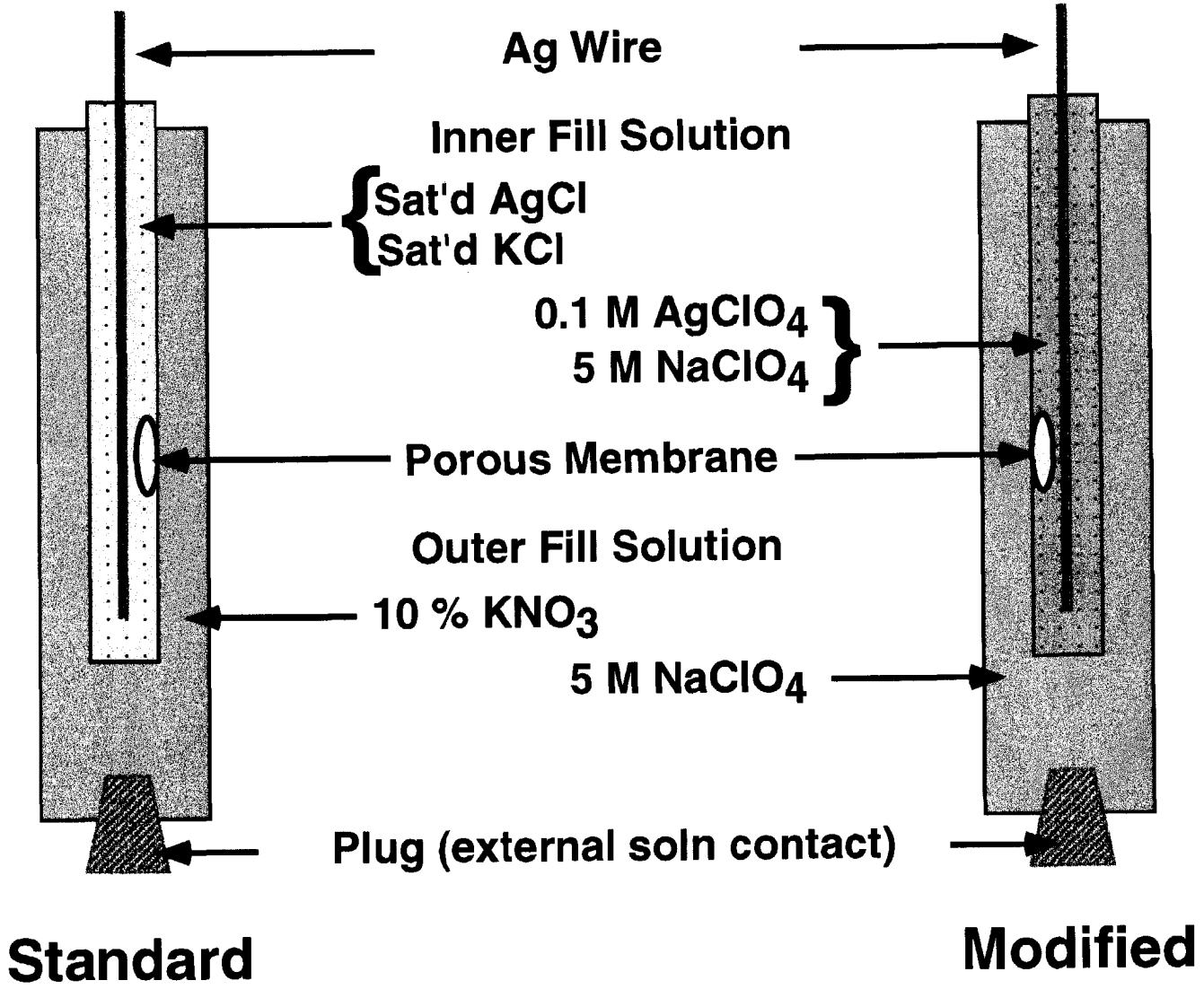
Redox potentials of mediator species: Ligand dependence

		$E_{1/2}$ (V)
Ce(+4/+3):	Ce(+4) aquo	+1.20 (SCE)
	Ce(SALEN)$_2$	-0.68 (SCE)
	Ce(5-BrSALEN)$_2$	-0.52 (SCE)
	Ce(5-MeOSALEN)$_2$	-0.78 (SCE)
	Ce(SALOPHEN)$_2$	-0.53 (SCE)
	$K_{11}[Ce(PW_{11}O_{39})_2]$	+ 0.424 (Ag/Ag^+)
Fe(+3/+2):	Fe(+3) aquo	+0.53 (SCE)
	$Fe(SALEN)^+$	-0.62 (SCE)
	$FeCp_2^+$	+0.31 (SCE)
Co(+3/+2):	Co(+3) aquo	+1.60 (SCE)
	$Co(SALEN)^+$	+0.16 (SCE)
	$CoCp_2^+$	-0.87 (SCE)
	$Co(C_5Me_5)_2^+$	-1.48 (SCE)
	$Co(C_5H_4CO_2H)_2^+$	-0.43 (SCE)

refs: Wester et al, *Inorg. Chem.* 1985, 24, 4435; Puxeddu et al, *J. Chem. Soc., Dalton Trans.* 1977, 2327; Costa et al, *Collect. Czech. Chem. Commun.* 1971, 36, 1065; Haraguchi, et al, *Inorg. Chem.* 1994, 33, 1015; El Murr et al, *Can. J. Chem.* 1976, 54, 3350; Koelle et al, *Angew. Chem. Int. Ed. Engl.* 1980, 19, 640.

SALEN = *N,N'*-ethylenebis(salicylideneamine)
SALOPHEN = *N,N'*-phenylenebis(salicylideneamine)

Double Junction Reference Electrode Design



Problems with Standard Reference Electrodes

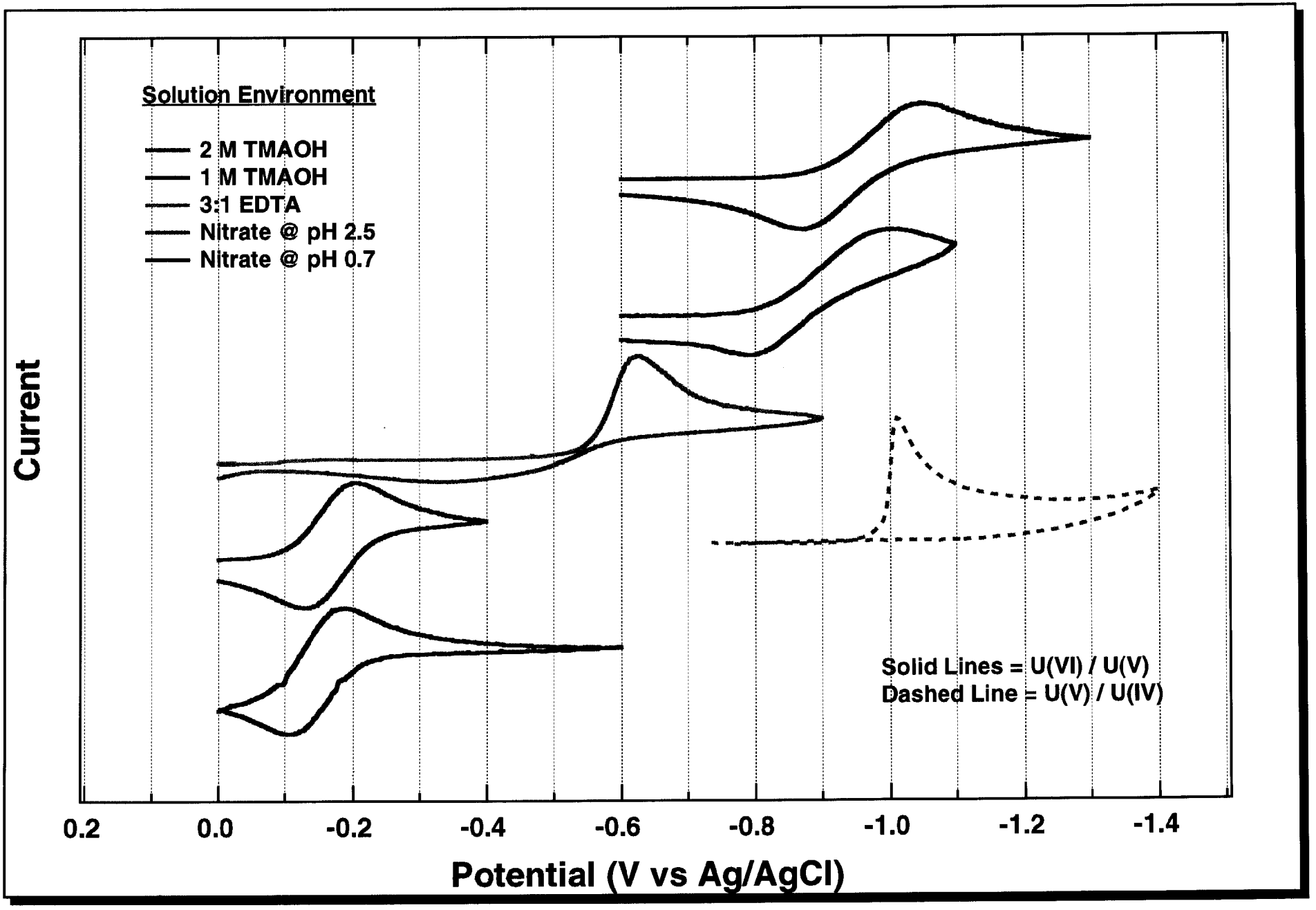
- Determination of stability constants requires very accurate potential shift measurements, on the order of 1 - 2 mV

- Reference electrode potentials drift due to changes in liquid junction as a result of differing ion migration rates in strongly acidic media

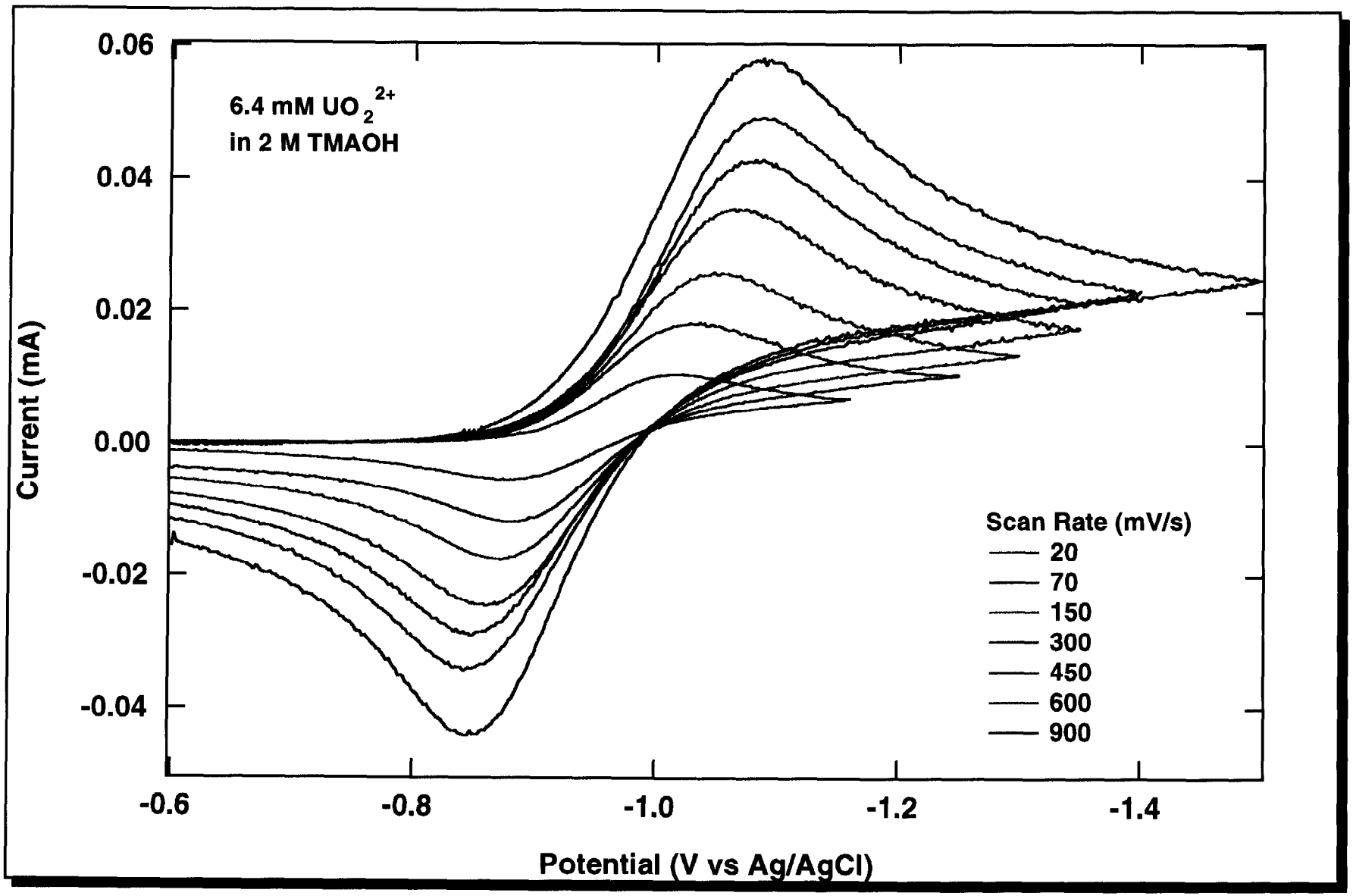
- Precipitation of salts occurs at the interface between the reference electrode and the test solution from exceeding salt solubility in strongly ionic media results in electrical short circuit

- Outer electrode filling solution must contain an ion that will not form a complex with plutonium since it is in contact with test solution

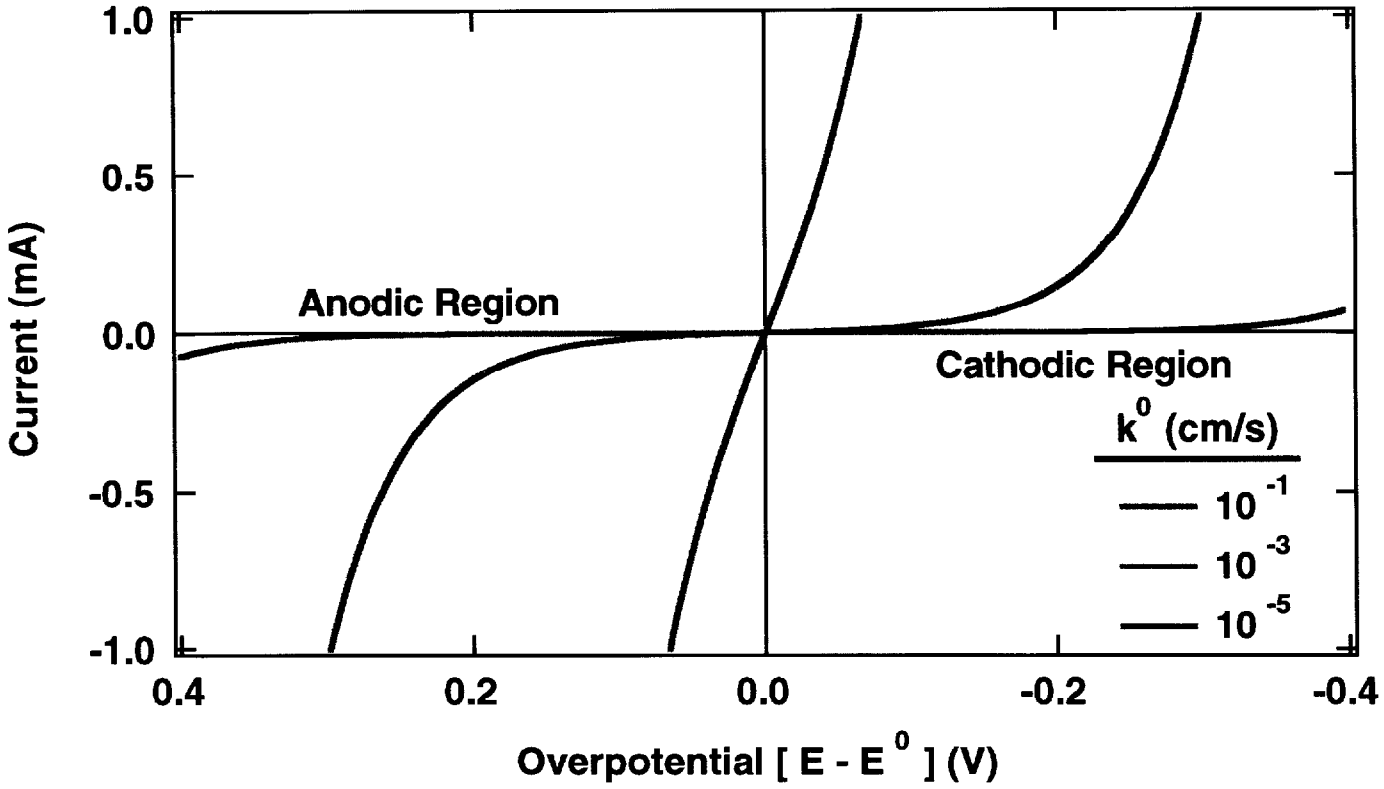
Uranyl Voltammetry in Aqueous Media

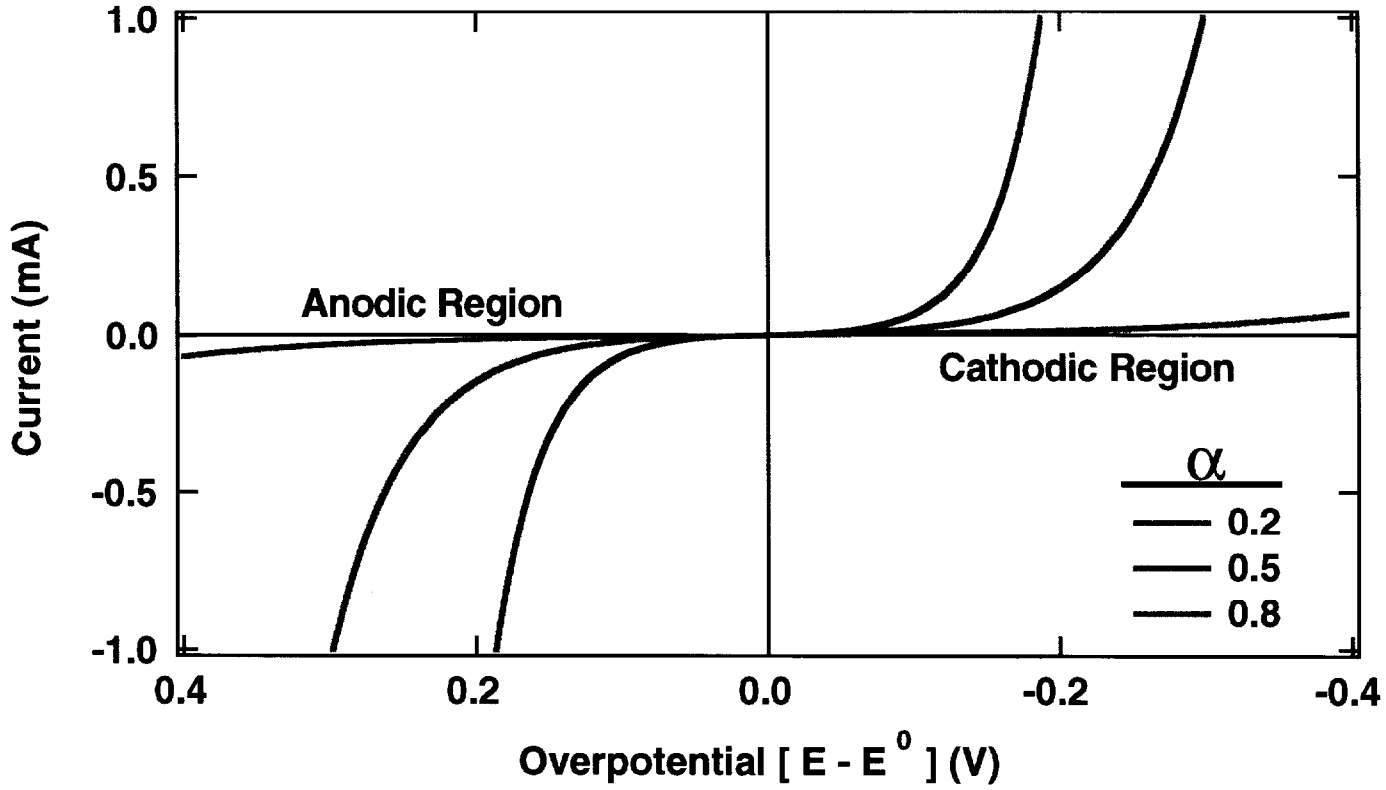


Voltammetric Manifestations of Slow Electron-Transfer Kinetics

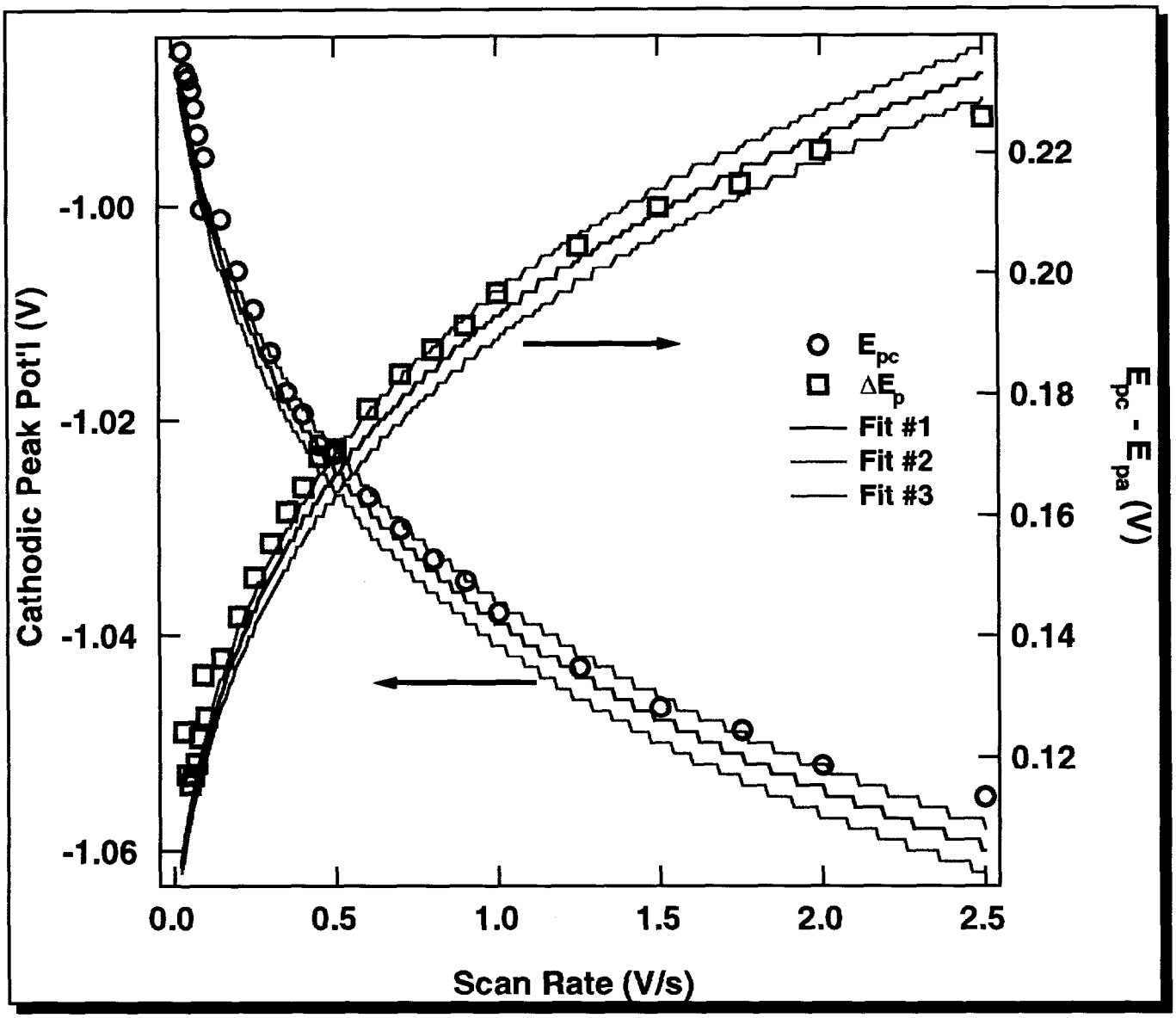


Effect of Electron-Transfer Kinetics on Current-Overpotential Characteristics





Electron-Transfer Kinetic Analysis by Digital Simulation



Fitting Parameters

$E_{1/2}$ = -0.935 V vs Ag/AgCl

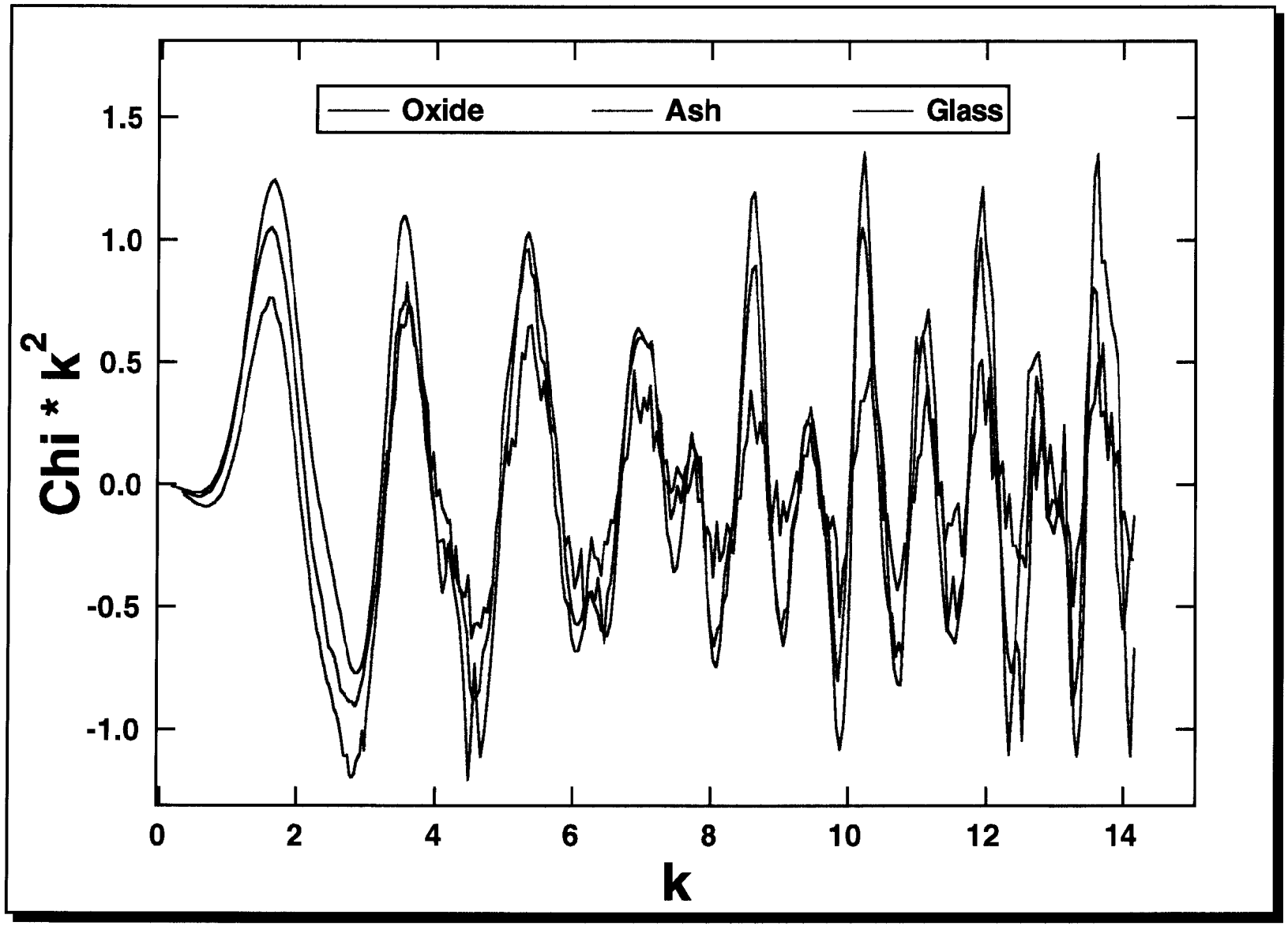
α = 0.50

Fit #1: k^0 = 0.0045 cm/s

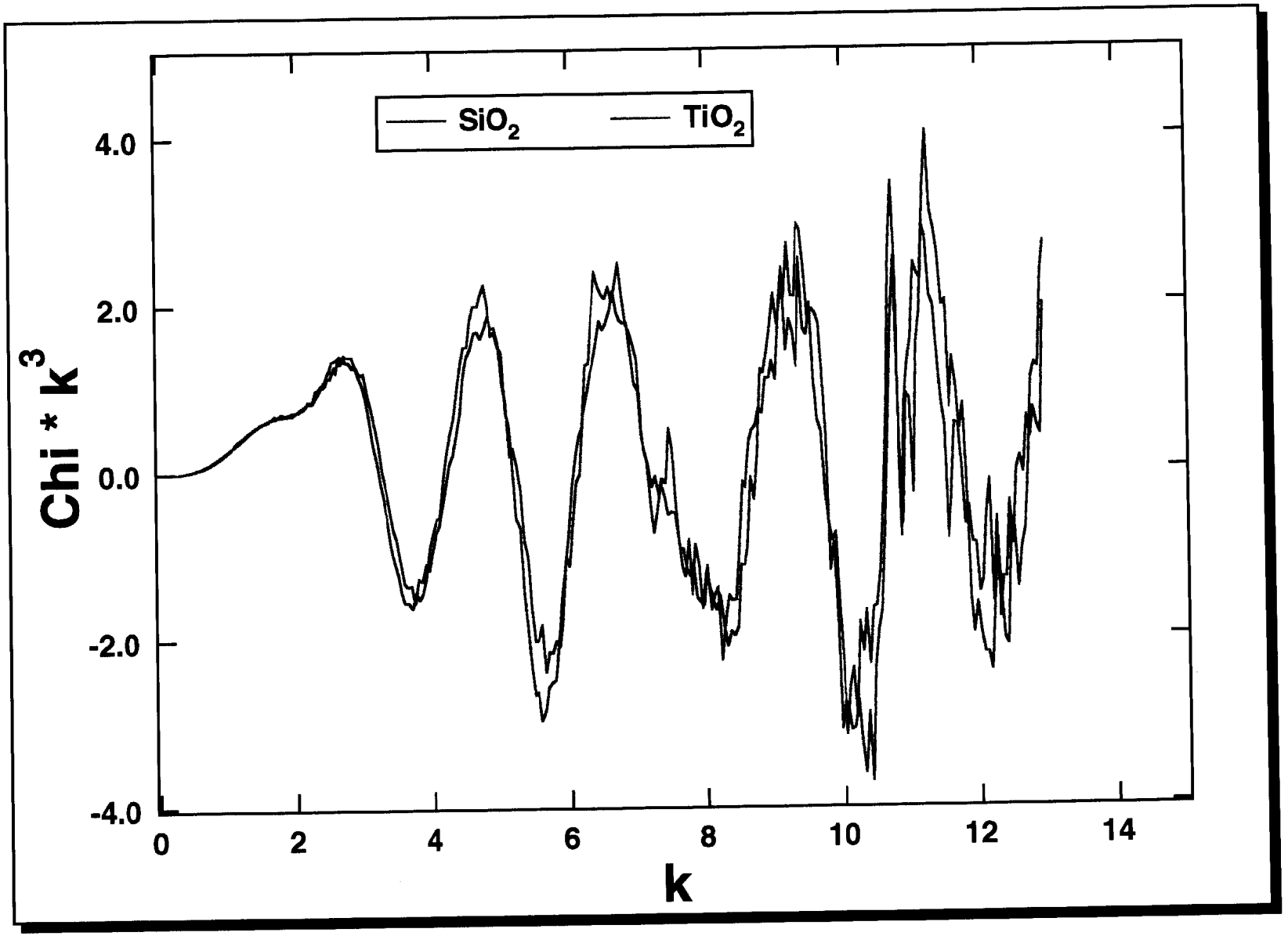
Fit #2: k^0 = 0.0043 cm/s

Fit #3: k^0 = 0.0047 cm/s

Plutonium L_{III} EXAFS Data for PuO_2, Calcined Rocky Flats Ash, and Simulated Waste Glass



Neptunium L_{III} EXAFS Data for Neptunyl on Silica and Titania



Work in Progress

- Sorption experiments with Pu(IV), U(VI), and Eu(III)
  - SiO_2 at pH ~ 2 and 5 g/L solid
  - TiO_2 at pH ~ 5 and 5 g/L solid
- Voltammetric studies
  - Pu(IV) oxidation on the oxide substrates at Pt anode
  - U(VI) and Eu(III) reduction on the oxide substrates at a Hg cathode

Future Work

FY 98 - 99

- Complete sorption experiments of actinides on SiO_2 and TiO_2 and characterize these solid phases by spectroscopy and microscopy
- Conduct heterogeneous electron transfer studies with these colloidal materials using potentiostatically-controlled metallic electrodes
- Begin heterogeneous electron transfer studies with colloidal materials and dissolved-phase redox mediators

FY 99 - 00

- Complete heterogeneous electron transfer studies with colloidal materials using potentiostatically-controlled metallic electrode
- Continue heterogeneous electron transfer studies with colloidal materials and dissolved-phase redox mediators
- Conduct studies of the effects of actinide complexing agents (surface and dissolved) on dissolution using metallic electrodes and dissolved redox mediators
- Conduct solution speciation and surface complexation studies of reactant systems with and without actinide complexants
- Initiate scale-up studies of new mediator systems using incinerator ash as the residue stream.

Other Potential Application Areas for MEO/R Methods

- Assessment of Corrosion Stability of Waste Forms (Glasses, Cements, Synroc, etc.) and Spent Nuclear Fuels

- Decontamination of Soils

- Facilities Decontamination / Decommissioning

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