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Title: Development of Technetium Alloy Waste Forms for Advanced Nuclear Energy Cycles

Author(s): Gordon D. Jarvinen, Kristy M. Long, David G. Kolman, David P. Moore, Christopher D. Taylor, George S. Goff, Michael R. Cisneros, Rowena R. Gibson, Kenneth R. Czerwinski, Frederic Poineau, Edward Mausolf, Maryline Ferrier

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Development of Technetium Alloy Waste Forms for Advanced Nuclear Energy Cycles

G.D. Jarvinen[1], K.M. Long[2], D.G. Kolman[2], D.P. Moore[3], C.D. Taylor[3], G.S. Goff[4], M.R. Cisneros[4], R.R. Gibson[4], K.R. Czerwinski[5], F. Poineau[5], E. Mausolf[5], M. Ferrier[5]

1 G.T. Seaborg Institute, 2 Manufacturing Engineering & Technology Division, 3 Materials Science & Technology Division, 4 Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87545; 5 Radiochemistry Program, University of Nevada, Las Vegas, Las Vegas, NV 89154-4009

Abstract

The Fuel Cycle Technologies (FCT) Program within the Office of Nuclear Energy of the U.S. Department of Energy is charged with developing nuclear fuel cycle options that improve use of actinide resources, responsibly manage wastes, improve safety, and limit proliferation risk. Technetium is a fission product of particular concern for disposal in a repository because of its high fission yield, long half-life, and high solubility and mobility in groundwater as pertechnetate. For example, modeling studies for the former Yucca Mountain repository site indicated that technetium would be an important dose contributor after closure of the repository, especially in the first 10,000 years [1]. The FCT Program is investigating a range of potential repository environments for ultimate disposal of fission products including technetium from advanced nuclear fuel recycling schemes.

Among the separation process options that have been studied under the FCT Program and its predecessors is the UREX (uranium extraction) process. In this process used light water reactor fuel is chopped and dissolved in nitric acid and uranium and technetium are selectively extracted from the aqueous phase using tributylphosphate in a hydrocarbon diluent. The U and Tc are back extracted to give a product stream of uranyl nitrate and pertechnetate in dilute nitric acid (~0.01 M).

We evaluated a range of commercial anion exchange resins to selectively remove TcO_4^- in surrogate UREX product streams and found that an anion exchange extraction chromatographic (EC) material from Eichrom Industries, Inc., called Weak Base EC™ resin had the best properties for recovering TcO_4^-. The resin allowed reasonable loadings of Tc from the uranyl nitrate solutions and the TcO_4^- eluted sharply from the loaded column with 1 M ammonium hydroxide. The concentrated NH_4TcO_4 solution can be heated with a reductant to remove the water and produce a technetium metal product for alloying.

Among the potential waste forms for technetium, metal alloys are an initial focus in the FCT program because of work done at the Idaho National Laboratory for developing waste forms for the various residues produced during processing of the fuel and blanket alloys from the Experimental Breeder Reactor-II [2]. To minimize the number of waste forms, the FCT program is evaluating the potential advantages of metal alloy waste forms that combine the separated Tc stream from UREX processing, the undissolved solids from the dissolution of the fuel, and the transition metal fission products in the raffinate of other potential extraction process such as the TRUEX process that could be used to recover the minor actinides from the UREX raffinate. Iron or stainless steel would be added to reduce most metal oxides, decrease the melting point of the alloy, and provide robust alloy phases to accommodate the fission product metals.

Samples of alloys containing representative amounts of the major fission product metals combined with stainless steel or iron have been prepared. The alloys and their corrosion behavior in a range of aqueous environments are being characterized using a variety of techniques including scanning electron microscopy, elemental mapping, x-ray diffraction, Auger spectroscopy, potentiodynamic polarization tests, and electrochemical impedance spectroscopy (EIS). For example, study of binary Fe-Tc alloys was initiated to compare this simpler system with iron rich phases found in more complex alloys. A narrow window of passivity for the alloys was predicted for some aqueous conditions, but not observed in potentiodynamic studies. Liquid scintillation counting of solutions from electrochemical dissolution tests indicate a preferential dissolution of iron. Kinetic Monte Carlo simulations of dissolution of Fe-Tc alloys also predict an enrichment of Tc on the surface of the alloys consistent with the experimental results.

Key words: Technetium, Separation, Extraction, Alloy, Waste

References

1. B.W. Arnold, S.P. Kuzio, B.A. Robinson, *J. Contaminant Hydrology*, 62-63 (2003) 401.

2. S.G. Johnson, D.D. Keiser, S.M. Frank, T. DiSanto, M. Noy, *Scientific Basis for Waste Management XXIII*, Materials Research Society, Boston MA, (1999).

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Los Alamos National Laboratory

K.R. Czerwinski, F. Poineau, E. Mausolf and M. Ferrier
University of Nevada, Las Vegas

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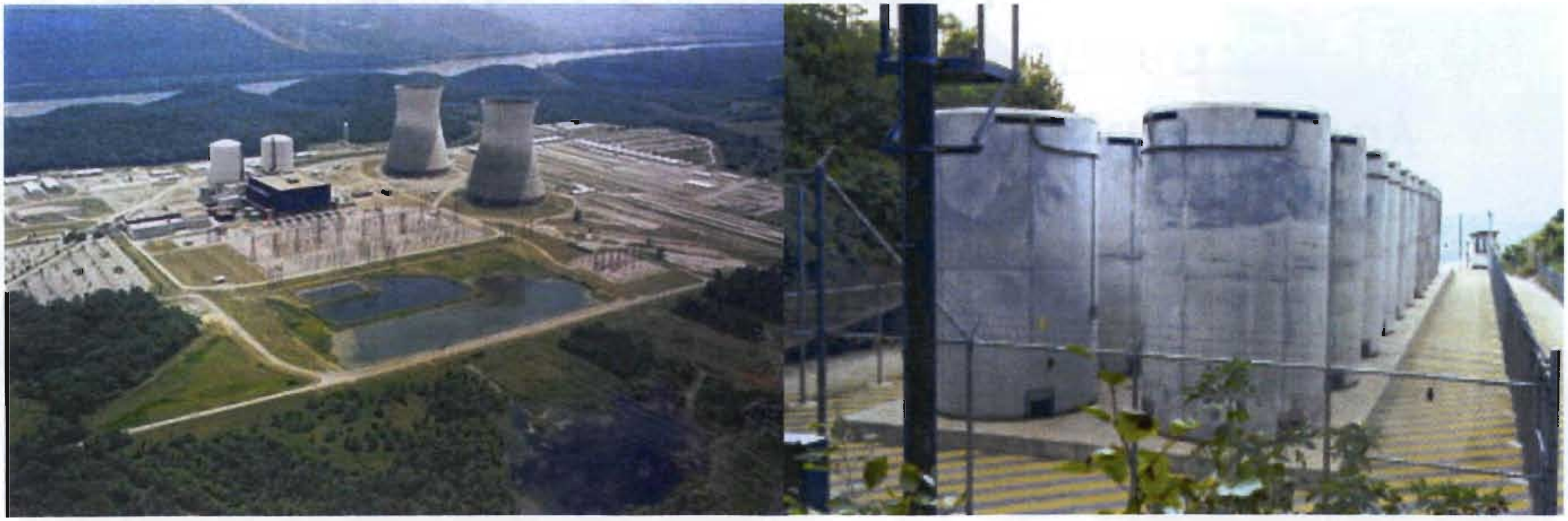
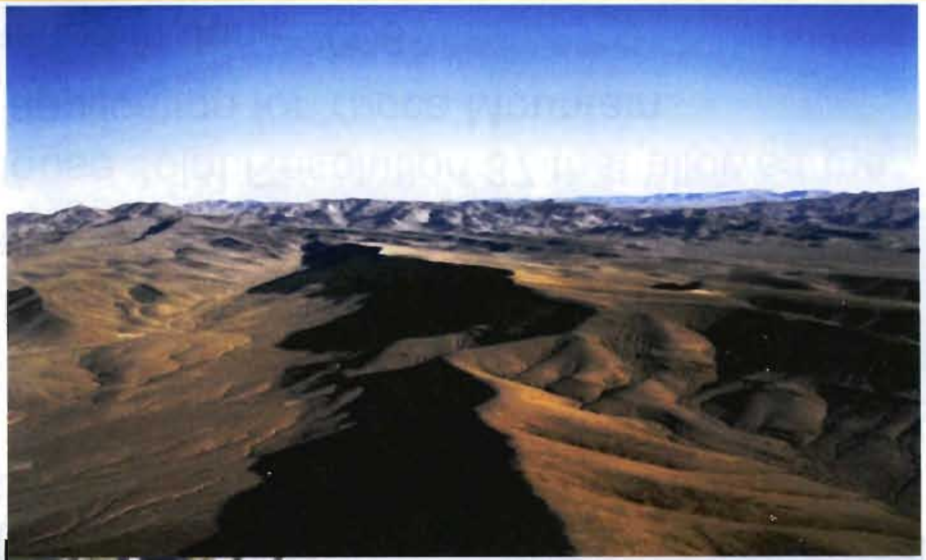
Nuclear Power Use in the U.S.

1) The U.S. has 104 operating LWRs supplying ~20% of electricity use. Most existing reactors are applying for license extensions with the Nuclear Regulatory Commission (NRC) and many extensions have been approved.
2) Energy Policy Act of 2005 included incentives for new nuclear power plants and in 2009 President Obama announced the first award of $8.3 billion in loan guarantees for construction of two nuclear power plants at the Vogtle site in the state of Georgia. The NRC recently approved the first combined construction and operating license for these two AP1000 plants (Feb. 9, 2012).
3) What to do with the used LWR fuel? (~65,000 MT accumulated to date)



Once-through Fuel Cycle Planned in U.S.

U.S. policy has planned for direct disposal of spent commercial nuclear fuel in a geological repository that can control the release of the radioactive byproducts in the spent fuel for a million years – a “once-through” or “open” cycle.



Brief History of Used Nuclear Fuel Disposition in the U.S.

- U.S. Congress in 1982 passed the Nuclear Waste Policy Act that required the Department of Energy (DOE) to site, build and operate a geological repository for high-level nuclear waste.
- In 1983 the DOE selected nine locations for study as potential repository sites and a preliminary report was prepared in 1985.
- The President approved three sites for intensive site characterization: Hanford, Washington (basalt), Deaf Smith County, Texas (salt), Yucca Mountain, Nevada (volcanic tuff).
- Congress amended the Nuclear Waste Policy Act in 1987 and directed the DOE to study only Yucca Mountain.
- In 2002 President Bush signed House Joint Resolution 87 that allowed the DOE to proceed with the license application for Yucca Mountain.
- The license application was submitted in June 2008.
- Work on the Yucca Mountain license application suspended in 2009. A "blue-ribbon" panel has been chosen in 2010 to recommend how the U.S. should proceed on disposition of used nuclear fuel.

Blue Ribbon Commission on America's Nuclear Future

- Established in 2009 by Secretary of Energy, 15 distinguished members, recommendations to be presented within two years.
- Charter of the Blue Ribbon Commission (BRC):

"Conduct a comprehensive review of policies for managing the back end of the nuclear fuel cycle, including all alternatives for the storage, processing, and disposal of civilian and defense used nuclear fuel, high-level waste, and materials derived from nuclear activities."

Subcommittees

Reactor and Fuel Cycle Technology
Transportation and Storage
Disposal
Ad hoc subcommittee on commingling of defense and civilian wastes

- Final report of the BRC delivered to the Secretary of Energy, Jan. 26, 2012. The Executive Summary begins:

"**America's nuclear waste management program is at an impasse.**"

U.S. DEPARTMENT OF
ENERGY
Nuclear Energy

Recommended Elements of a New Strategy for Nuclear Waste Management

1. A new, consent-based approach to siting future nuclear waste management facilities.
2. A new organization dedicated solely to implementing the waste management program and empowered with the authority and resources to succeed.
3. Access to the funds nuclear utility ratepayers are providing for the purpose of nuclear waste management.
4. Prompt efforts to develop one or more geologic disposal facilities.
5. Prompt efforts to develop one or more consolidated storage facilities.
6. Prompt efforts to prepare for the eventual large-scale transport of spent nuclear fuel and high-level waste to consolidated storage and disposal facilities when such facilities become available.
7. Support for continued U.S. innovation in nuclear energy technology and for workforce development.
8. Active U.S. leadership in international efforts to address safety, waste management, non-proliferation, and security concerns.

Mission of the Department of Energy's Office of Nuclear Energy (NE)

- Office of Nuclear Energy's primary mission is to advance nuclear power as a resource for the U.S.

- Department of Energy Strategic Goal: reduce CO_2 emissions by 80% by the year 2050.

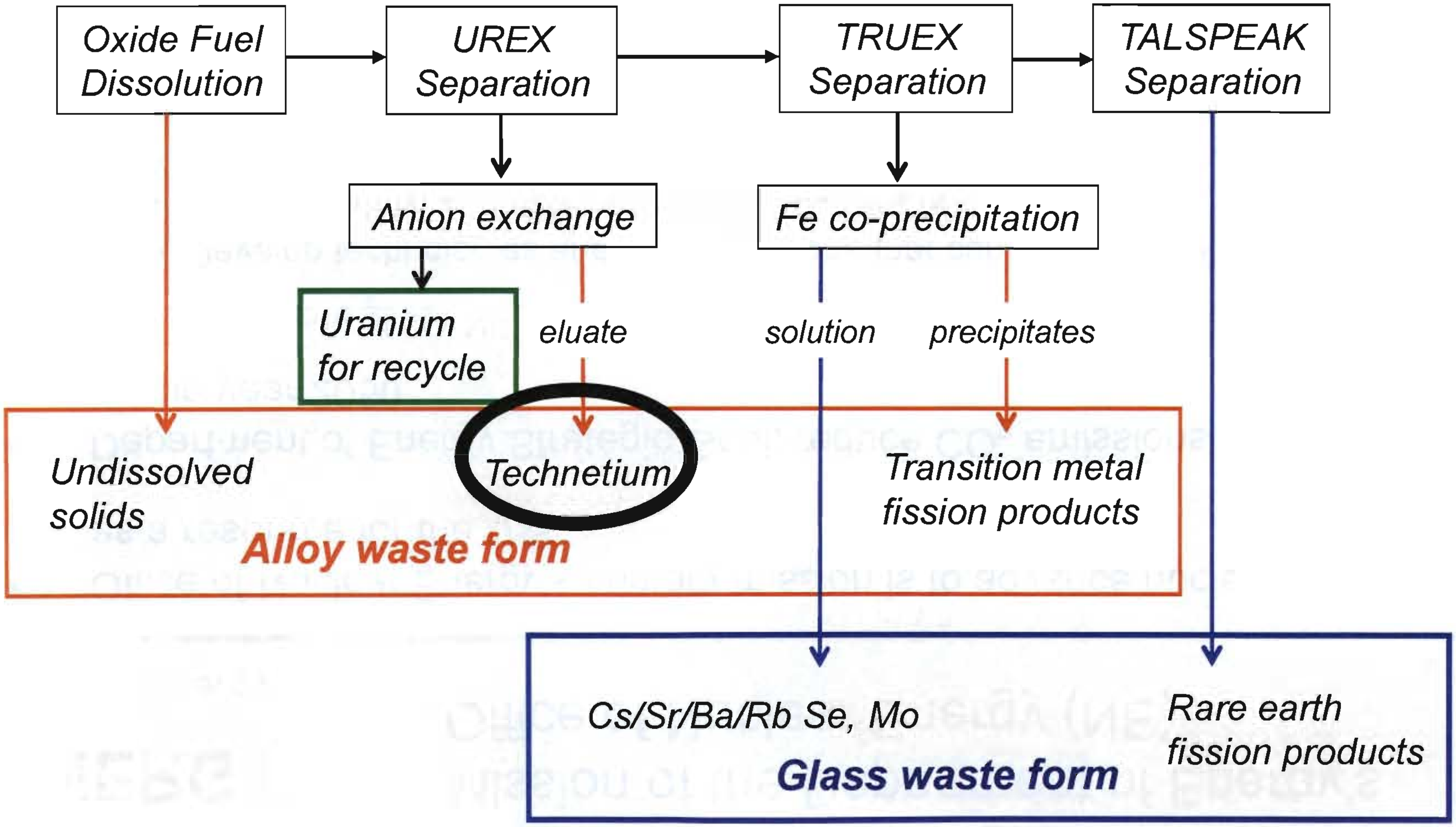
<u>Research Objectives of the NE Research and Development Roadmap:</u>

1) Develop technologies and other solutions that can improve the reliability, sustain the safety, and extend the life of current reactors.
2) Develop improvements in the affordability of new reactors to enable nuclear energy to help meet the Administration's energy security and climate change goals.
3) Develop sustainable fuel cycles.
4) Understand and minimize the risks of nuclear proliferation and terrorism.

- The **Fuel Cycle Technologies** (FCT) Program within NE is charged with developing nuclear fuel cycle options that improve use of actinide resources, responsibly manage wastes, improve safety, and limit proliferation risk.

Example of LWR Used Fuel Separations Scheme and Proposed Waste Forms

- Alloys of Tc and other fission product metals with SS under investigation



Oxide Fuel Dissolution

UREX Separation

TRUEX Separation

TALSPEAK Separation

Anion exchange

Fe co-precipitation

Uranium for recycle

eluate

solution

precipitates

Undissolved solids

Technetium

Transition metal fission products

Alloy waste form

Cs/Sr/Ba/Rb Se, Mo

Rare earth fission products

Glass waste form

Technetium is a Long-term Threat to the Biosphere

- The long half-life of ^{99}Tc ($t_{1/2} = 2.13 \times 10^5$ years) and its high mobility and solubility as pertechnetate create a long-term threat to the biosphere.

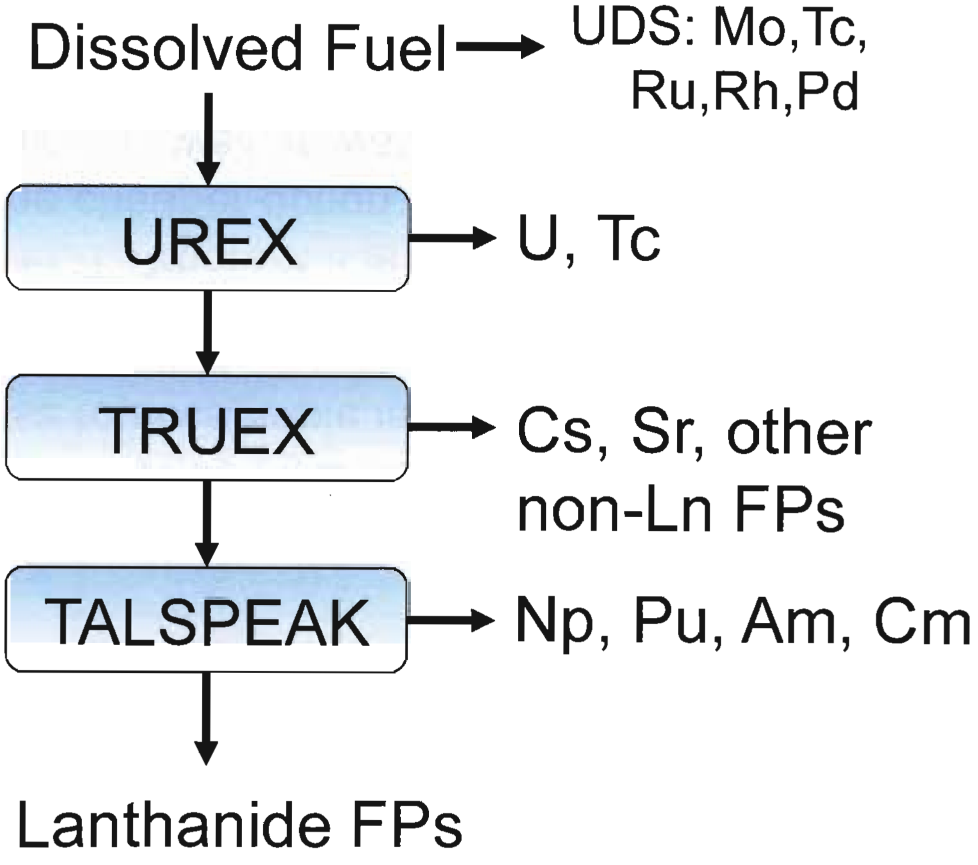
- Two primary methods for managing the long-term hazard of Tc have been considered: transmutation to Ru or using a robust waste form/ repository system to control release to acceptable levels over a long period of time (~1 million years)

- Systems analysis work within the FCT Program indicates that the Tc waste form-repository system is the cheaper option. The JAEA and CEA have investigated transmutation as well as waste forms.

- The Tc release rate from the waste package is an important input into any repository model. Therefore, the dissolution rate and mechanisms of key radionuclides from waste forms must be characterized. For example, Tc was found to be a key dose contributor at long times in Yucca Mountain repository modeling.

Tc Recovery from UREX Product Stream

- UREX process uses TBP in hydrocarbon solvent to recover U, Tc together (>95% of Tc).
- U(VI) and TcO_4^- are back extracted into ~0.01 M HNO_3 ([U] = 50-100 g/L, [Tc] = 66-132 mg/L for 60 GWd/MTIHM burn-up).
- Epsilon or five-metal alloy found in the undissolved solids (UDS) contains remaining Tc and this amount increases with fuel burn-up
- Separation of Tc into two compact streams enables enhanced waste form options for Tc relative to direct disposal in used fuel



Dissolved Fuel → UDS: Mo,Tc, Ru,Rh,Pd

UREX → U, Tc

TRUEX → Cs, Sr, other non-Ln FPs

TALSPEAK → Np, Pu, Am, Cm

Lanthanide FPs

Recovery of Pertechnetate with Weak-Base Anion Exchange Resins

- Pertechnetate, TcO_4^-, (and perrhenate, ReO_4^-) are large anions with relatively low free energies of hydration compared to common aqueous anions. They bind strongly to anion exchangers, but can be difficult to recover in concentrated form.
- Uranyl nitrate product solution from UREX has nitrate concentration ~400-600 times the TcO_4^- concentration; competition from NO_3^- limits loading capacity and makes direct pyrolysis/steam reforming of loaded resin to form metal more costly than loading-elution-conversion route
- Reillex HP, a weak-base polyvinylpyridine polymer, showed the best loading and elution properties in screening of commercial ion exchangers; ammonium hydroxide eluant (vs NaOH) has the advantage of being recyclable by distillation.
- Reillex HP was used in initial demonstration tests and deployed in a test run with used fuel at ORNL to recover Tc from 50 liters of UREX product solutions.

Eichrom Weak-Base Extraction Chromatographic Resin

- An extraction chromatographic resin containing a weak-base amine compound from Eichrom Industries (Weak Base EC resin) was also tested. The resin beads are coated with a tertiary amine with straight-chain alkyl groups of 8-10 carbon atoms.

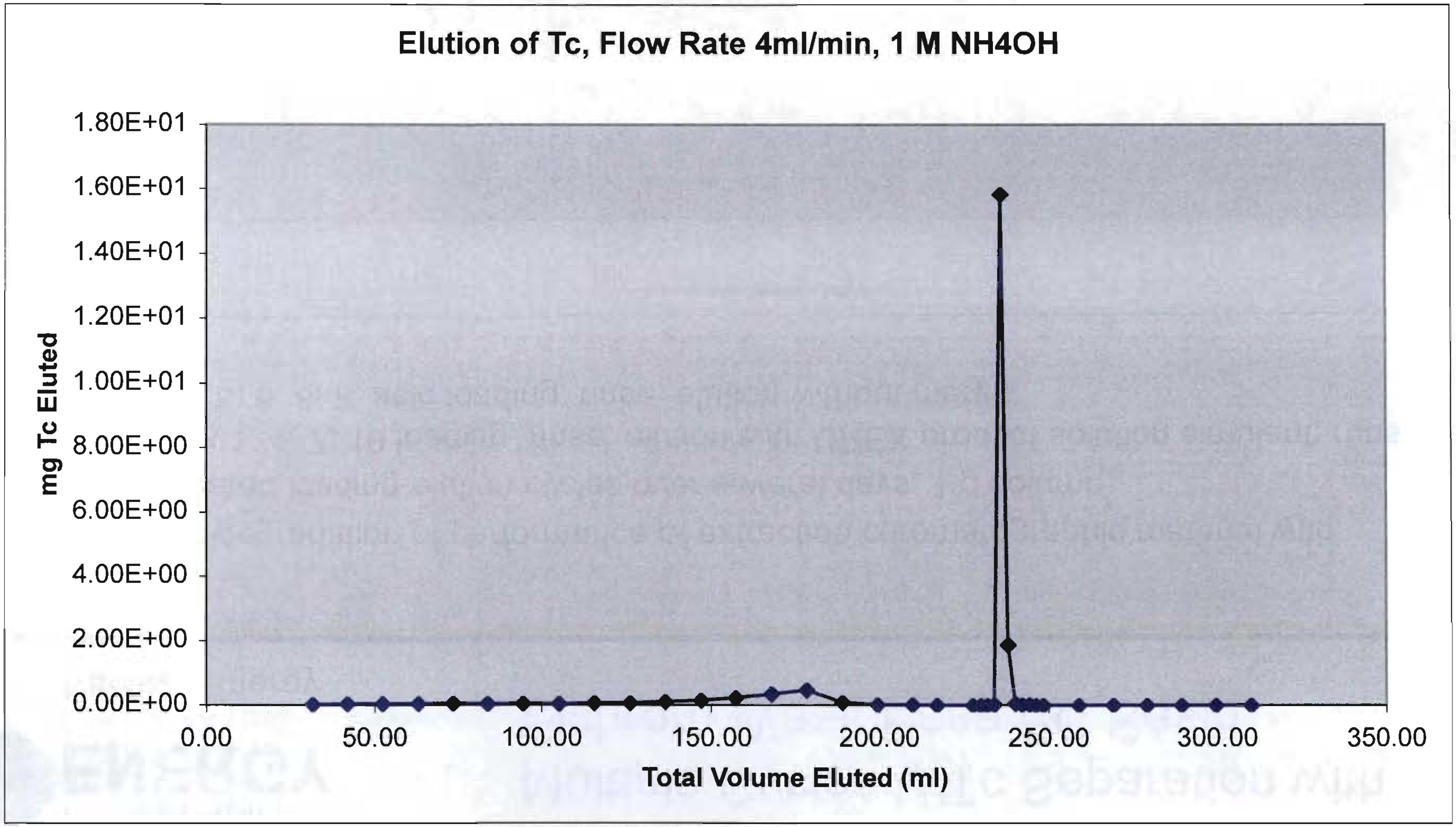
- The Weak Base EC material showed a 30-40% higher loading capacity than the Reillex resin in tests with ReO_4^- and substantially sharper elution peaks using the same ammonium hydroxide solutions used with the Reillex HP elution. The Eichrom material was then tested with Tc/U solutions.

- Ran column test with 150 ml uranyl nitrate solution (100 g/L U) with NH_4TcO_4 (132 mg/L Tc) in 0.01 M nitric acid. One gram column (~2.2 mL bed volume) and flow rate of 4 mL/min. Near the elution peak 2 mL volumes were collected for liquid scintillation counting.

- Loading of Tc ~30% higher than Reillex HP and nearly all Tc eluted from column in ~2 CV vs ~15 CV with HP.

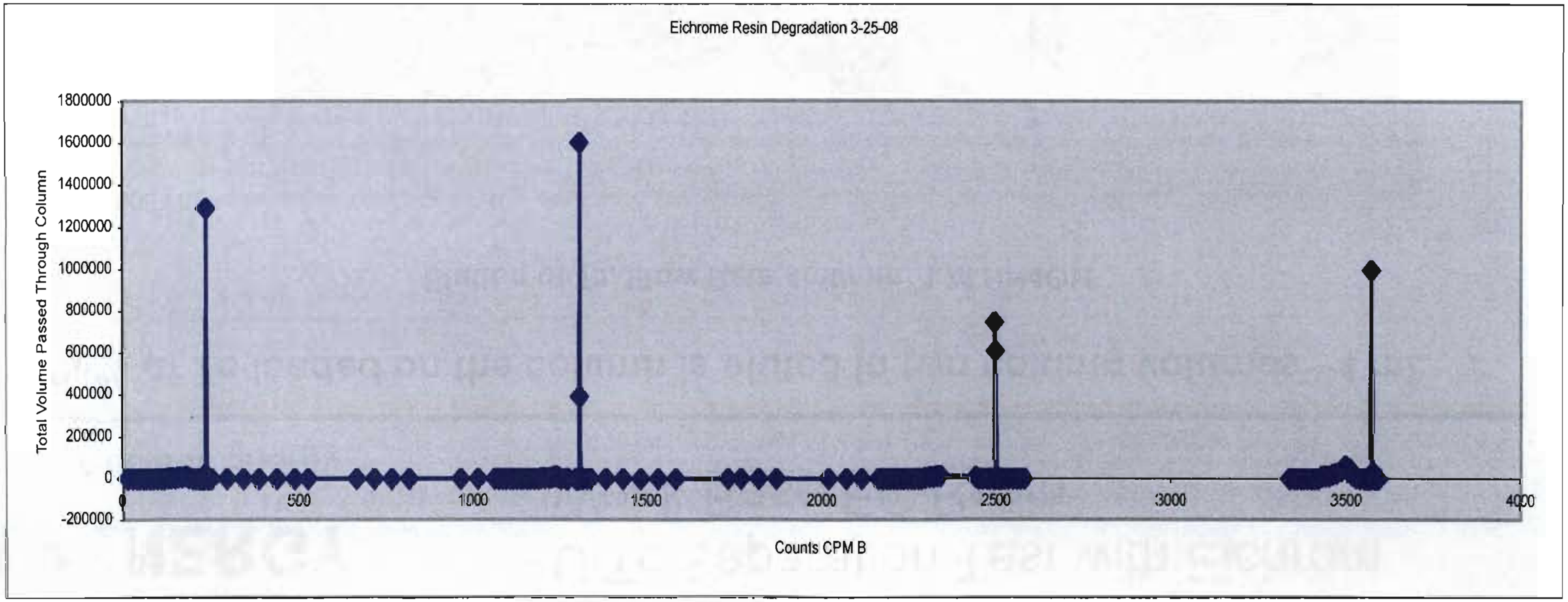
U/Tc Separation Test with Eichrom Weak Base EC Resin

96% of Tc loaded on the column is eluted in two column volumes ~4 mL



Multiple Cycles U/Tc Separation with Eichrom Weak Base EC Resin

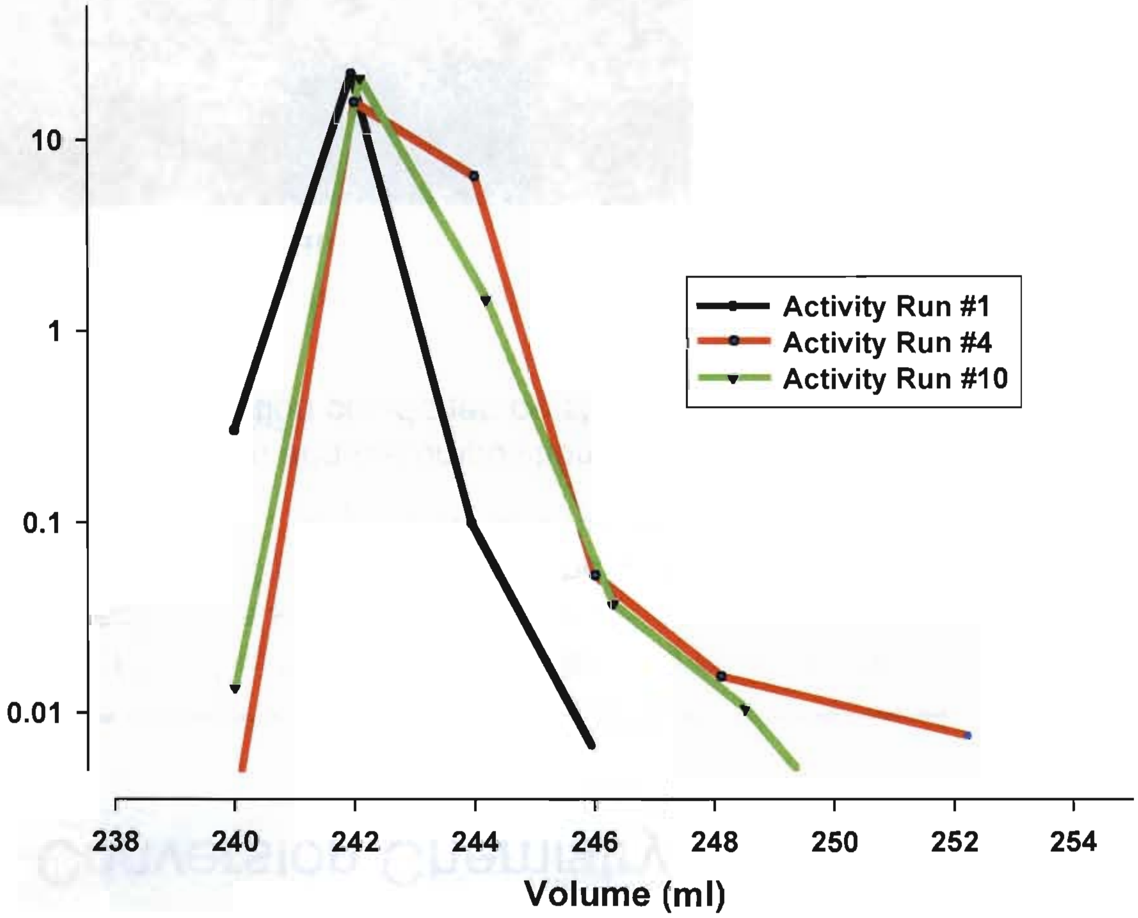
- Test degradation of performance of extraction chromatographic material with repeated loading-elution cycles over several days, 1 g column
- Runs 1, 4, 7, 10 loading, rinse, elution with UREX product solution simulant; runs 2, 3, 5, 6, 8, 9, acid loading, rinse, elution without metals



Multiple Cycles U/Tc Separation with Eichrom Weak Base EC Resin

- No significant difference in loading or elution between runs 1, 4 and 10 (run 7 - column left loaded overnight before elution and elution peak very broad due to diffusion)
- The extraction chromatographic material appeared quite stable in these initial tests although the tertiary amine compound is not chemically bonded to the polymer support.

Elution of Tc, Flow Rate 4 ml/min, 1M NH_4OH



Conversion Chemistry

- To simplify the conversion chemistry the direct thermal evaporation and reduction of the ammonium nitrate - ammonium pertechnetate solution eluted from IX column is being tested. Thermal decomposition at 150-300 °C using added compounds to reduce nitrate and pertechnetate were tested including sugar, formic acid, and high-boiling ethanolamines.
- Triethanolamine gave the smoothest reduction and decomposition of the compounds tested. The black residue from the evaporation-reduction could then be steam reformed under a slow Ar-H_2O flow at 900 °C to give Tc metal.
- Ammonium hydroxide was added to the uranyl nitrate product solution to precipitate “yellow cake” that was converted to U_3O_8 at 800 °C in air.

Conversion Chemistry

A demonstration test was run with 500 ml of surrogate UREX solution with 100 g/L U and 132 mg/L Tc using the Eichrom Weak Base EC resin. Very good separation of U and Tc was achieved with 98% recovery of the U and 96% recovery of the Tc (63.4 mg). XRD indicates only U_3O_8 and Tc metal in the solids.

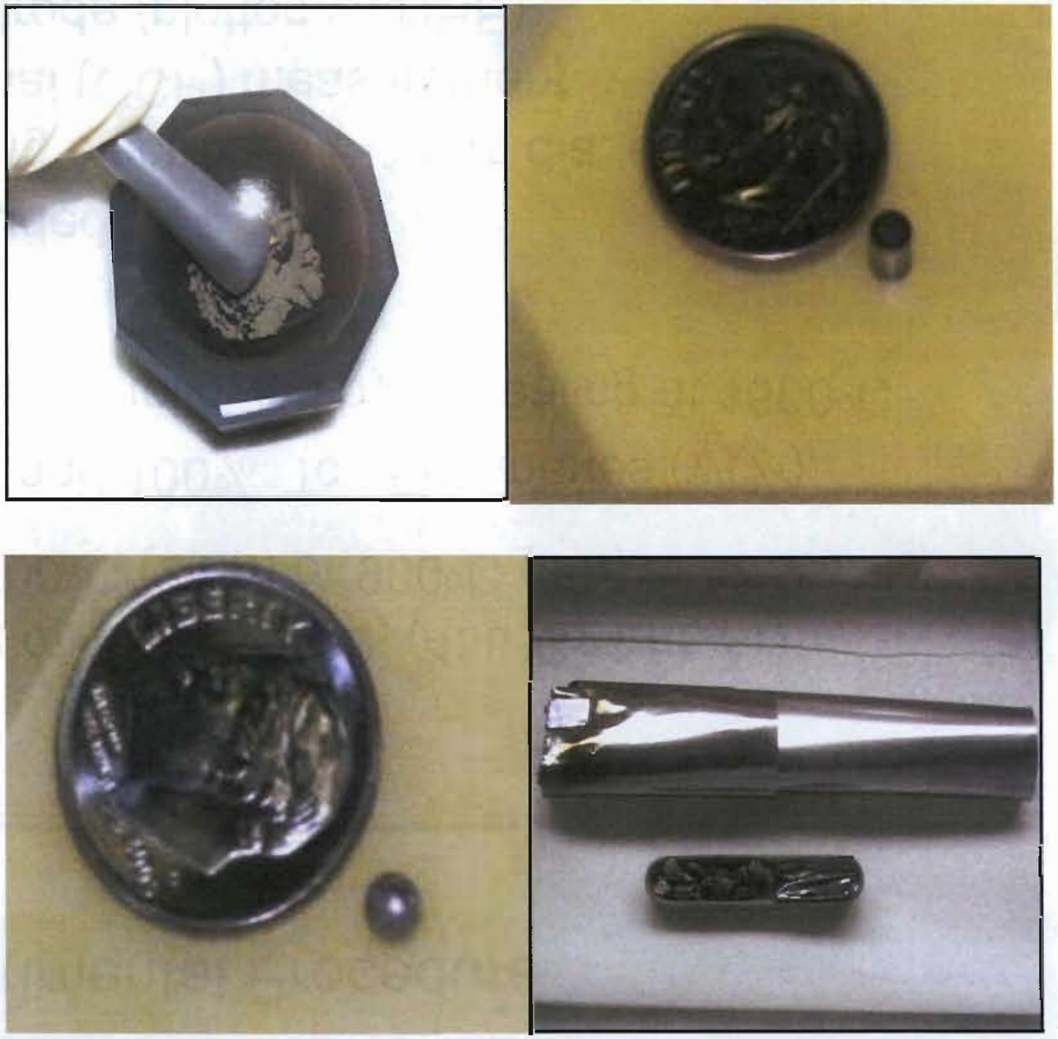
In a large scale process a rotary furnace or spray into a hot gas would be a more likely unit operation to perform the initial nitrate destruction and pertechnetate reduction than evaporation and thermal decomposition in an open vessel.

Metal Alloy Waste Form Development for Tc and other Transition Metal Fission Products

- A Metal Waste Form (MWF) has been developed at the Idaho (INL) and Argonne (ANL) National Laboratories for the cladding and anode residue from the electrometallurgical processing of the metal fuel from the EBR-II Reactor. The most studied composition consists of stainless steel from the cladding and 15 wt% Zr combined with up to 4 wt% noble metal fission products (including up to 2 wt% Tc). The MWF has undergone extensive qualification and testing for acceptance at the formerly proposed Yucca Mountain repository. This forms the basis for some initial metal alloy waste form compositions based on iron or stainless steel.
- Another group of alloy compositions is based on the epsilon phase found in used fuel that is known to resist dissolution in hot nitric acid and appeared to remain intact in the irradiated uranium oxide material in the Oklo reactors in Gabon.
- While no specific repository site is currently under study in the U.S., the durability of potential waste forms for various used fuel processing schemes will be evaluated under a wide range of groundwater conditions.
- A larger multi-lab team is examining a variety of alloy compositions. At LANL and UNLV we have concentrated on the fundamental behavior of Tc-Fe and Tc-Mo binary alloys using electrochemical and surface science diagnostics and modeling.

Preparation of Technetium Waste Form Samples

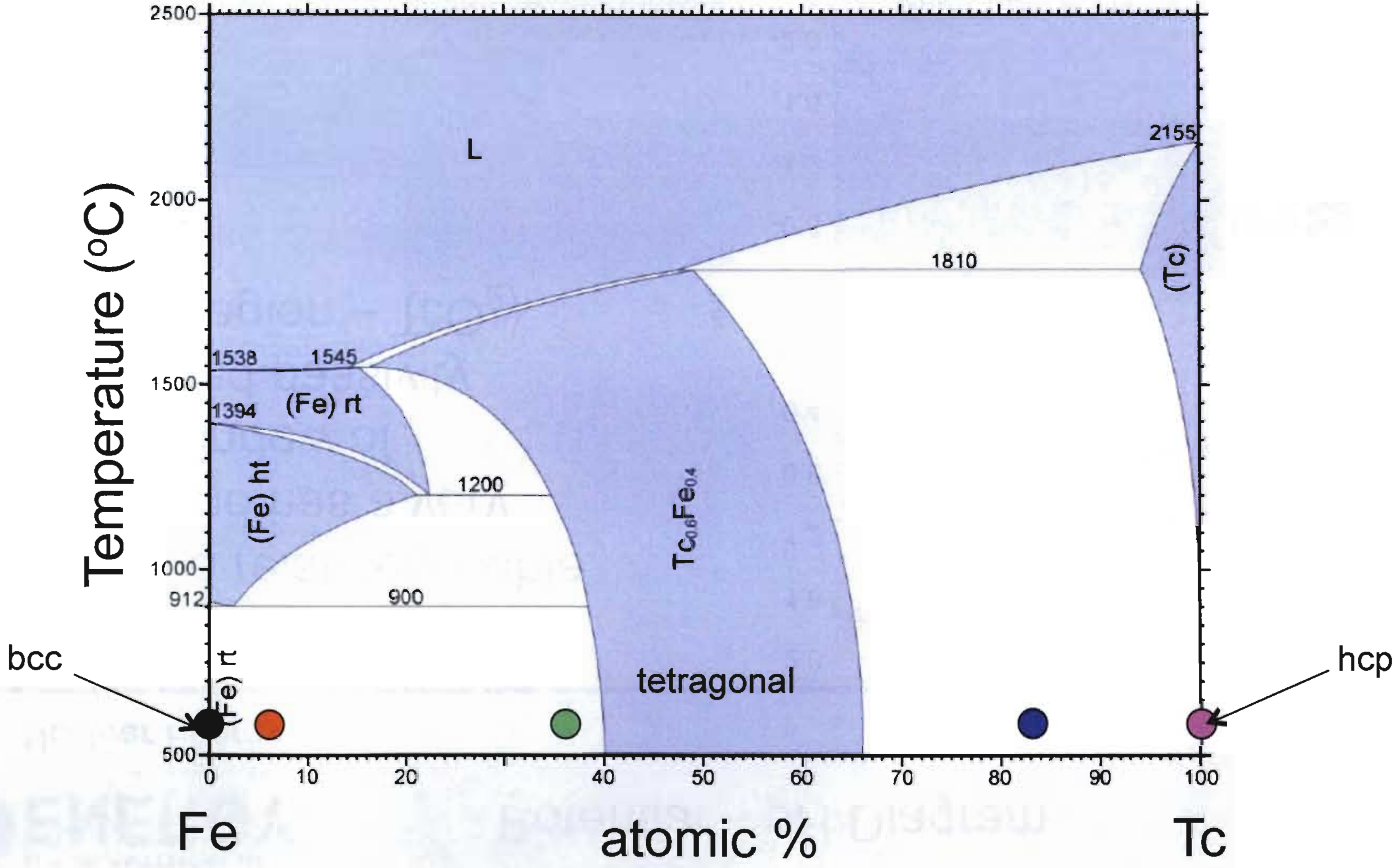
Metal powders are ground together often using hexane or methanol as a wetting agent. Pellets are pressed in a metal die. The pellets are sintered or melted in a furnace or with an arc melter. The solid products are characterized by XRD, SEM, electron microprobe and other techniques. The corrosion behavior of the alloys in a range of aqueous solution is studied with electrochemical techniques.



Experimental Procedure

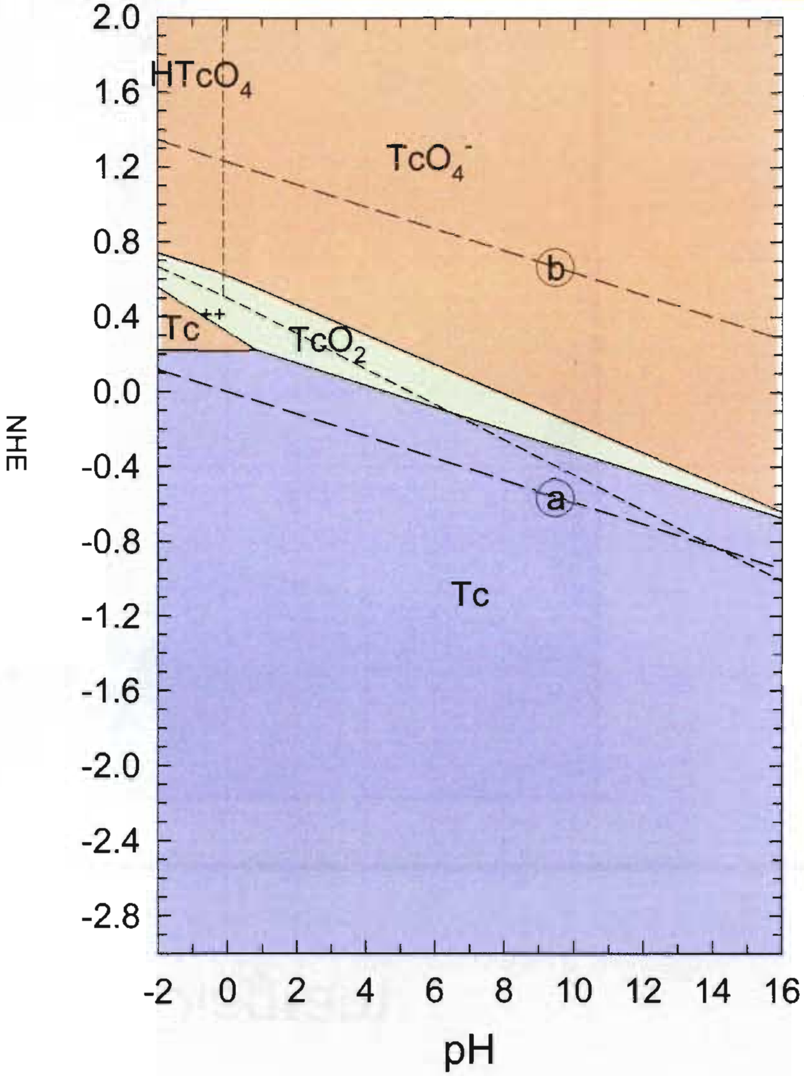
- Tc metal produced by
  - Thermal decomposition of TcO_4^- to TcO_2 (450°C, 1 hr, Ar)
  - Reduction TcO_2 to Tc (700°C (24 h) or 900°C (4 h) in Ar/5% H_2)
- Alloys: 0%, 10%, 50%, 90% and 100% Tc - Fe binaries (wt%). Alloys were made by arc-melting followed by annealing at 1600°C for 4 hours.
- Electrochemical testing included:
  - <100 mg Tc alloy working electrodes (~1 mm dia. electrode)
  - 4 h Open Circuit Potential (OCP) measurement
  - Ag/AgCl reference electrode (plotted vs NHE)
- Ambiently aerated 10^{-4} M H_2SO_4

Tc - Fe Phase Diagram



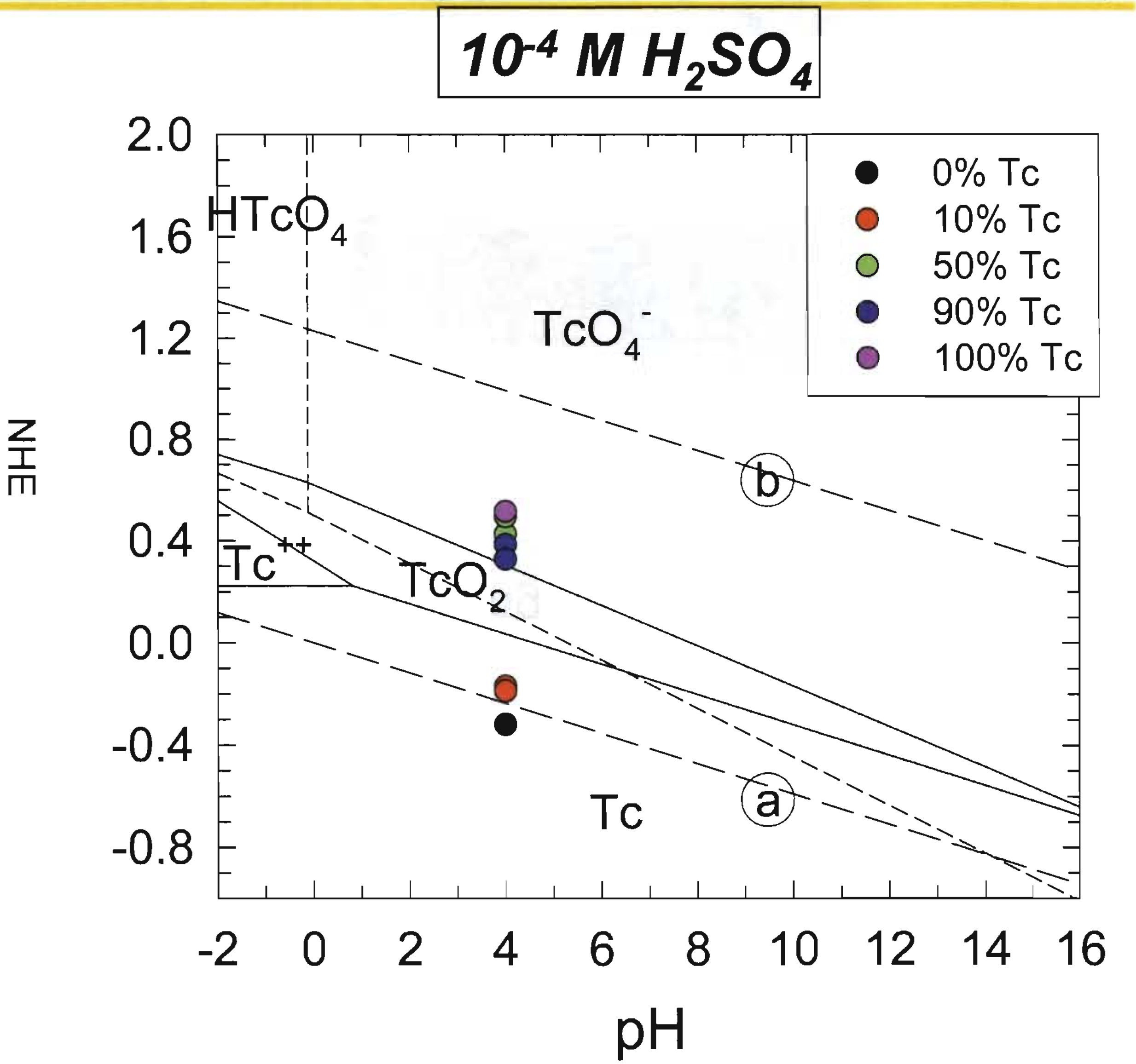
Potential – pH Diagram

- Tc is a relatively noble metal and has a very small window of presumed passivity (green region – TcO_2)



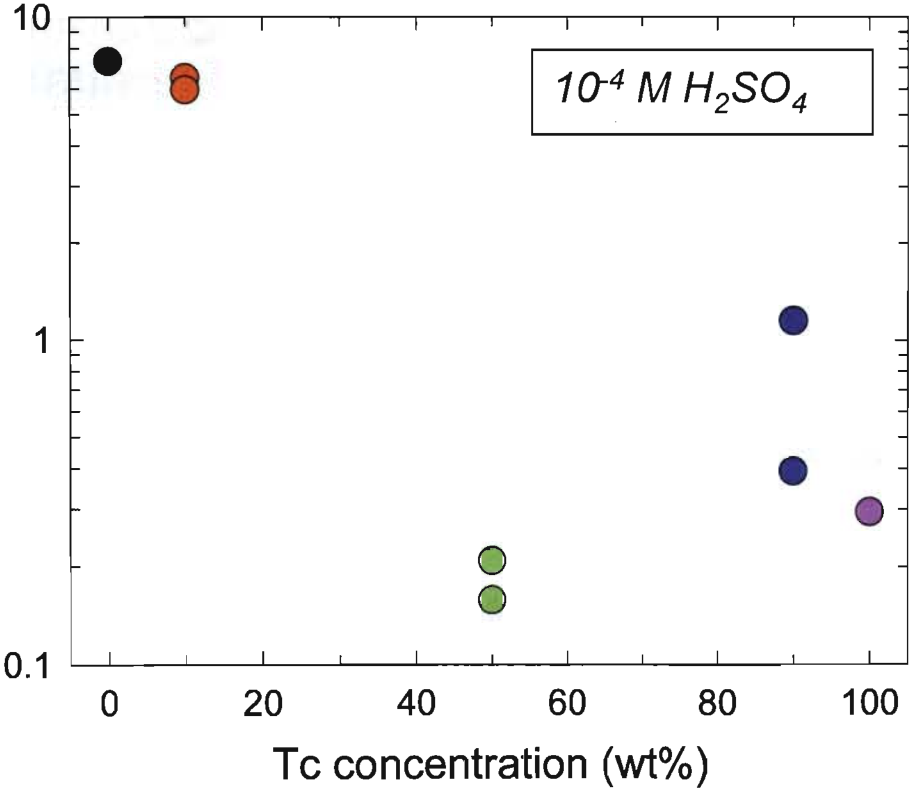
Open Circuit Potential

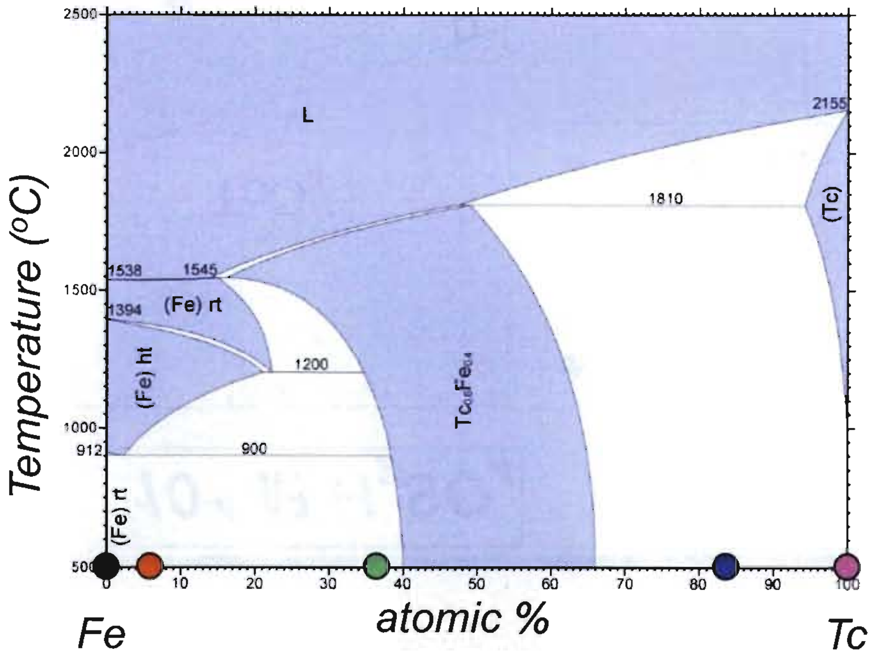
- OCPs span immune, passive and corrosion regimes
- Increasing Tc generally increases the OCP



Corrosion Rates

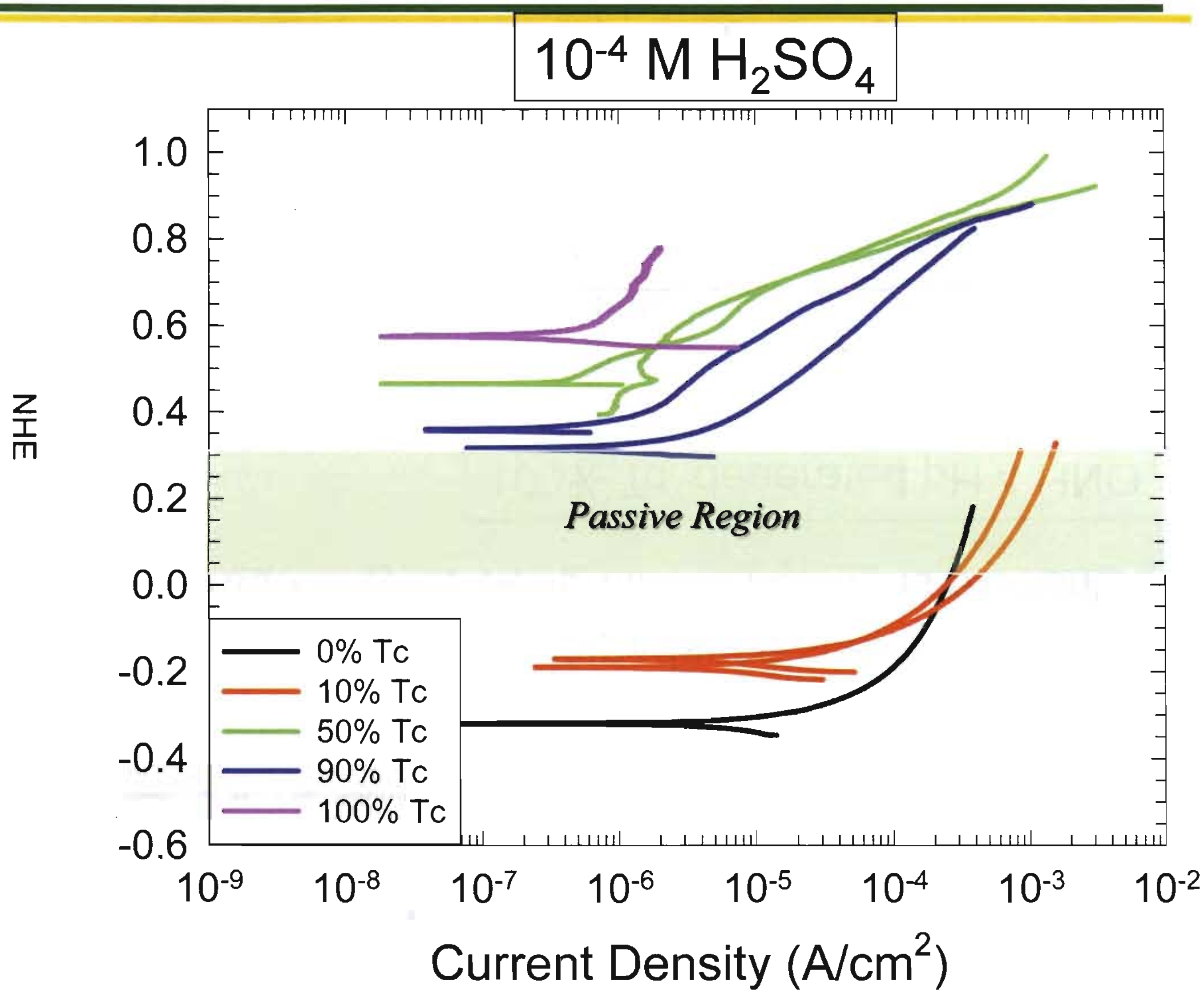
- Corrosion rate measured from linear polarization resistance is a minimum at 50% Tc
- Chemical / microstructural effects of alloying are apparent.





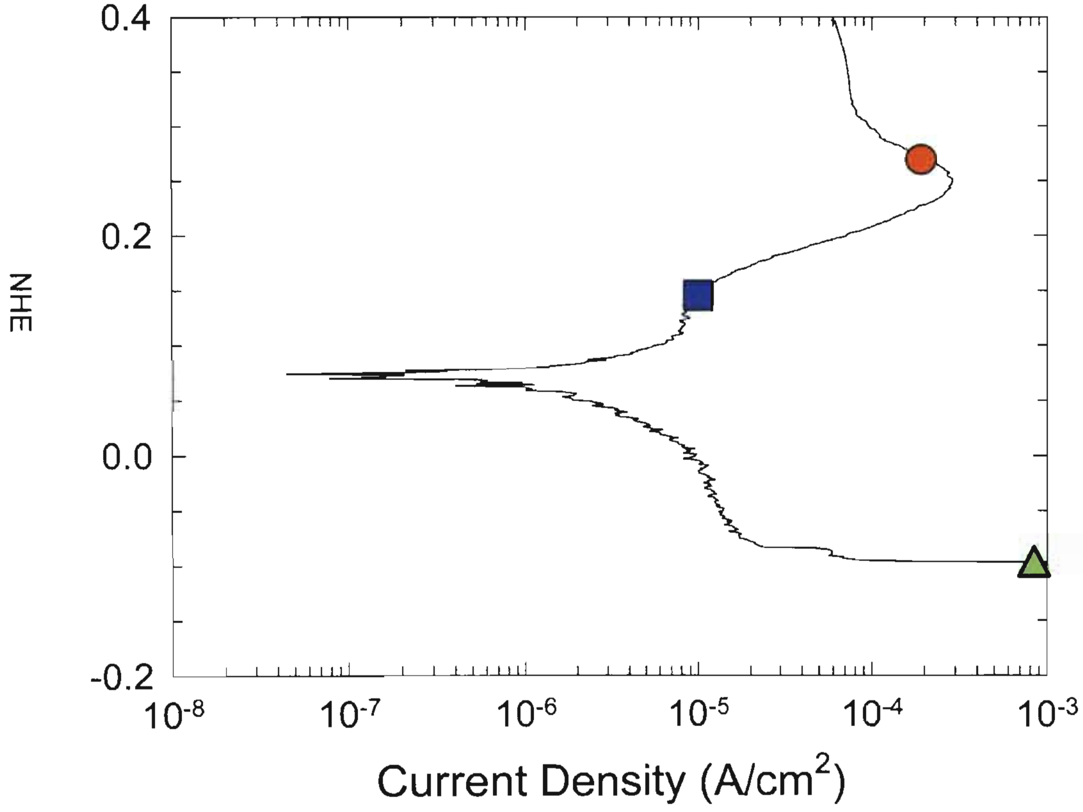
Anodic Polarization

- 0% and 10 % Tc tests appear IR_s limited ($R_s \approx$ 100 kΩ from EIS)
- No passivity observed
- Low i_{corr}

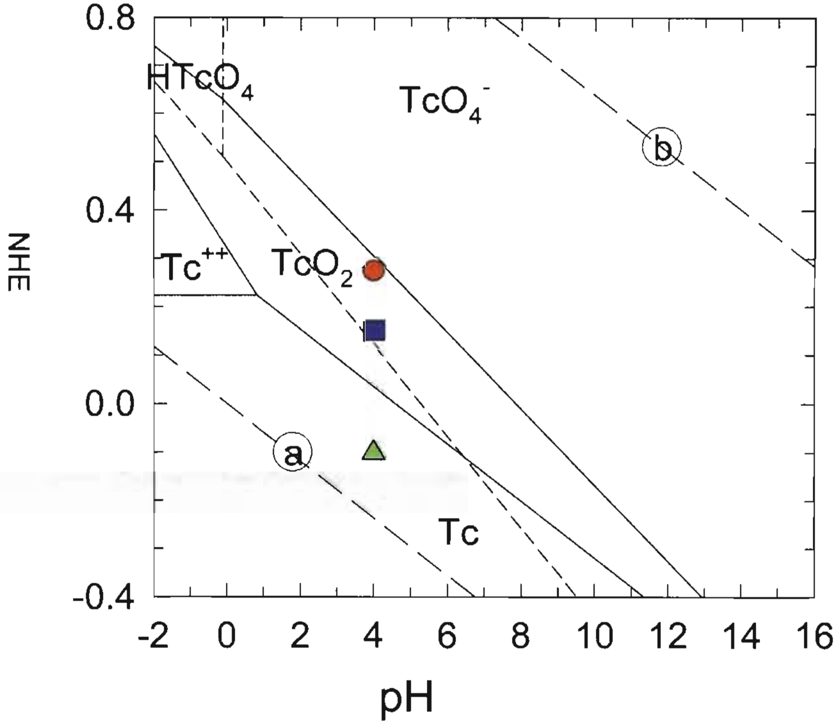


Oxide Film

- Abrade 100% Tc sample → EIS at -0.1V_{NHE}, 0.15V_{NHE}, 0.27V_{NHE}
- EIS: Two or more time constants present in impedance spectra and diffusional impedance at low frequency so nonpassivating film is present?

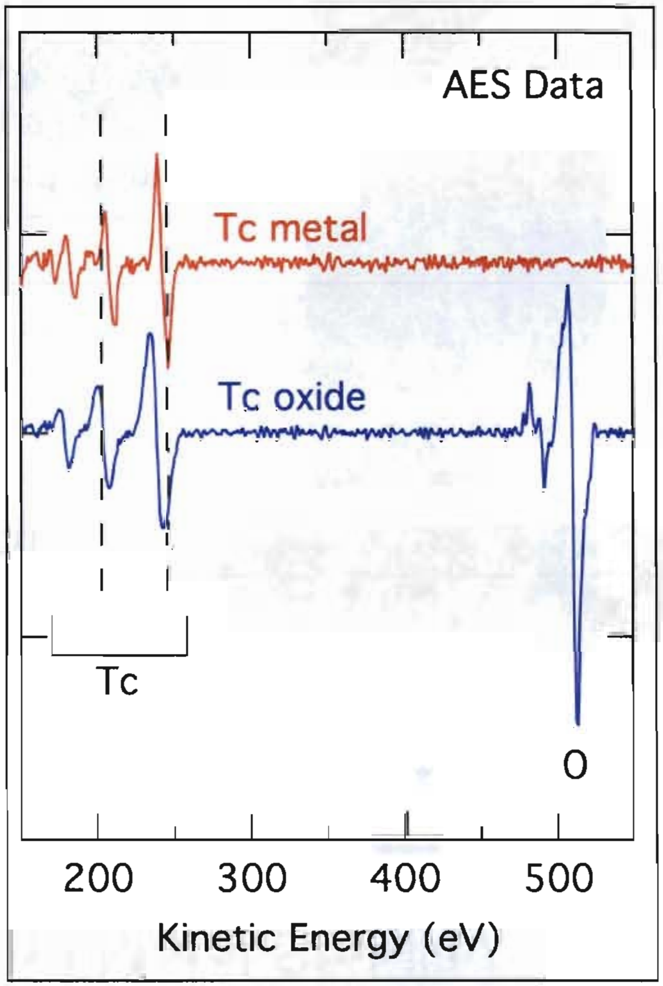


100% Tc, deaerated pH 4 HNO_3



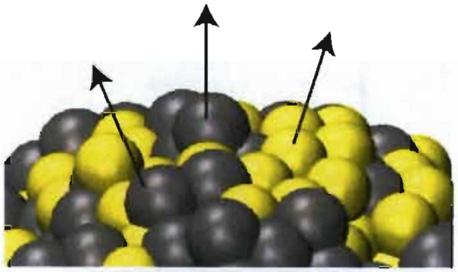
Oxide Film

- **100% Tc oxidation by O_2 exposure:**
  - Controlled oxidation by low-level oxygen (O_2) exposures for “pure” oxide surfaces.
  - Tc oxide peaks broaden, show some sub-structure, and shift to lower energy.
  - Indicates formation of a nominal TcO_2 oxide layer on the metal surface based on relative peak heights, positions, and peak shapes/structure.
- **Discrepancy between air oxidation and aqueous electrochemistry and / or TcO_2 is not passivating.**

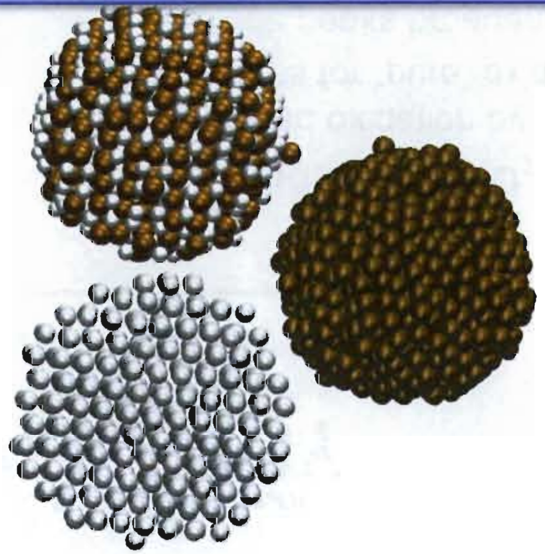


Tc - Fe Alloys: Nearest-neighbor Interactions and Metal Stability

- Fundamentally, corrosion involves rupture of metal-metal bonds:
  - at metal/oxide interface
  - at metal/environment interface
- Energy required is a function of local composition and ordering of atoms (concept of local cohesive energy)

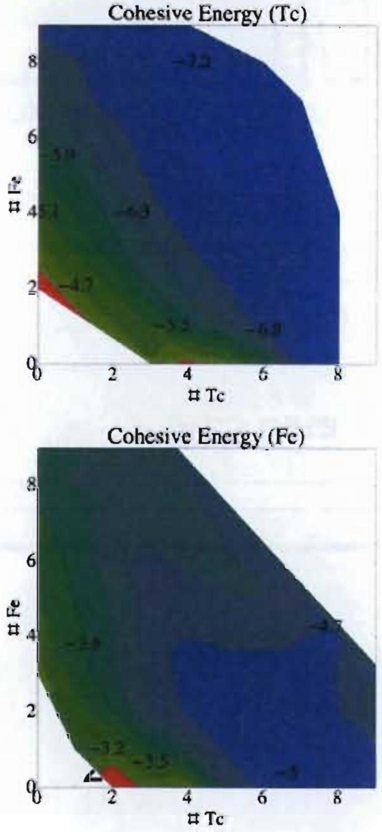


Generate hypothetical configurations of Tc/Fe



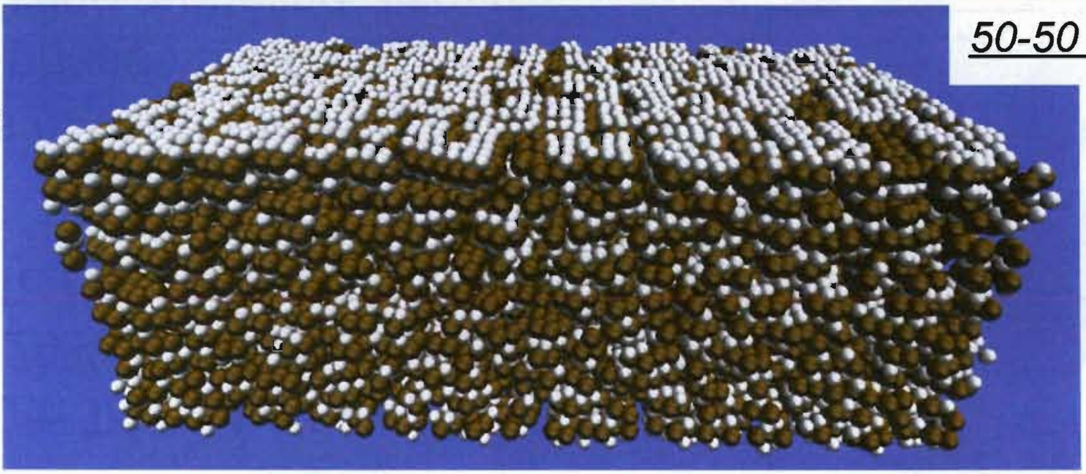
Modified embedded atom method computes local cohesive energies for Tc/Fe

Decompose structures to determine cohesive energy links to local structure



Kinetic Monte Carlo: Sample Outputs

1000 steps

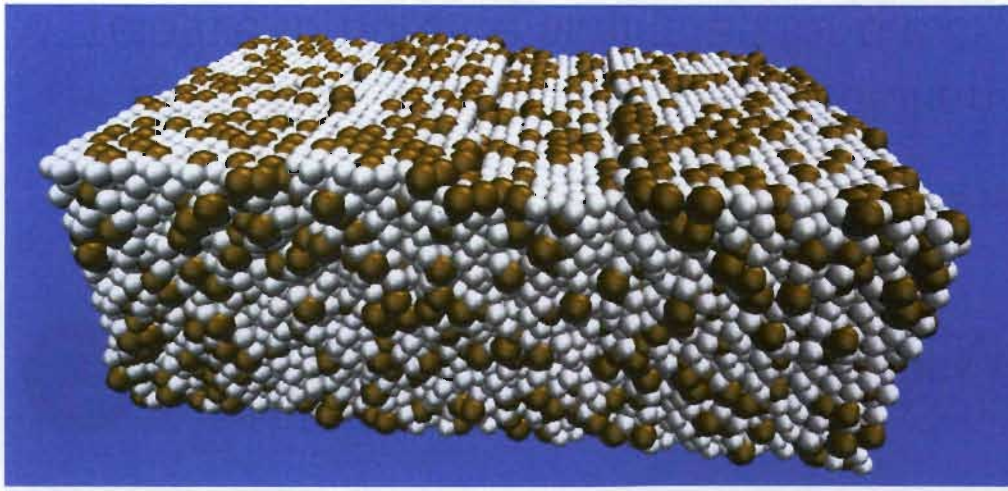


50-50 Fe/Tc hcp, ordered

*Island formation,
uniform dissolution*

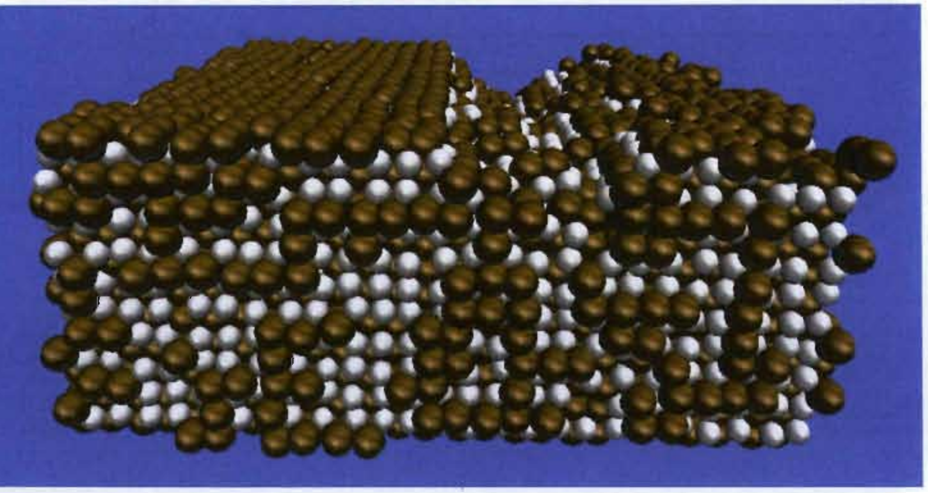
50-50 Fe/Tc hcp, disordered

*Uniform dissolution,
step edge mechanism*



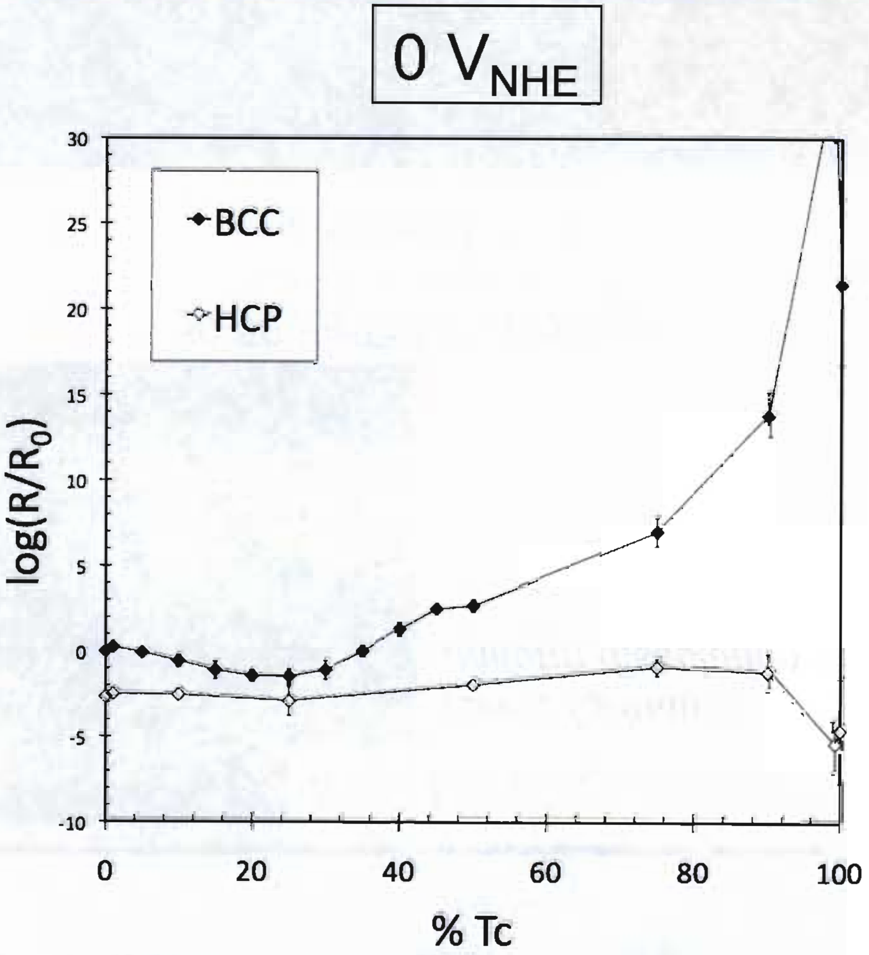
50-50 Fe/Tc bcc, ordered

*Crystallographic
pitting "channeling"*



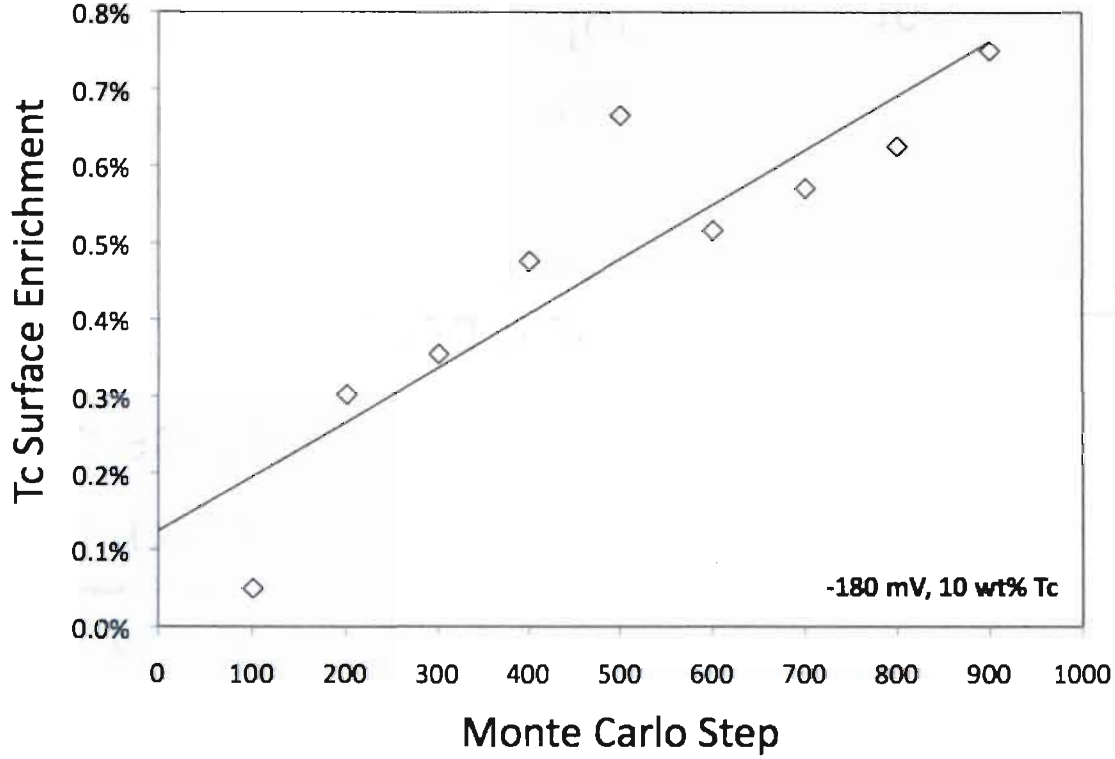
Kinetic Monte Carlo: Sample Outputs

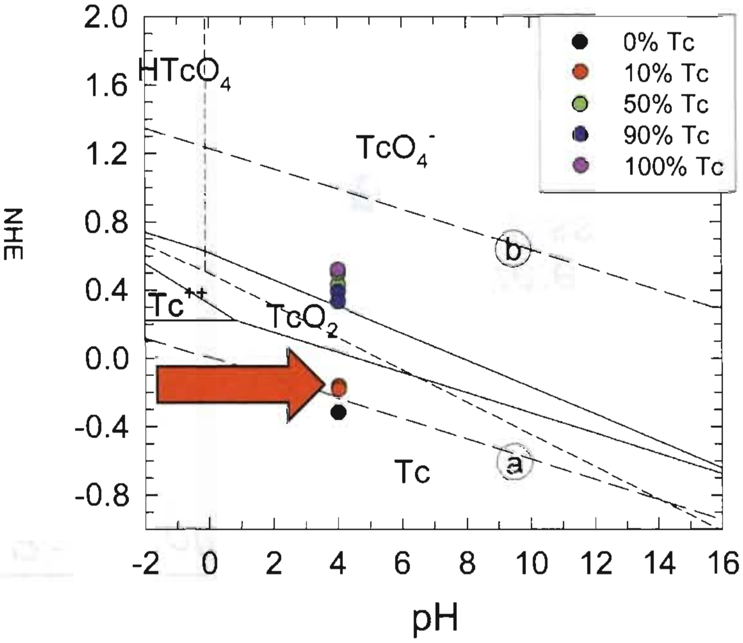
- Corrosion rates for active dissolution relative to pure Fe simulated for b.c.c. and h.c.p. type phases with varying Tc:Fe compositions
- Results
  - ➢ optimum Tc content exists (around 20% Tc) for b.c.c. phase
  - ➢ h.c.p Tc corrodes slower than b.c.c. Fe
- Simulations of other ordered and intermetallic phases are being performed. Oxide modeling also in progress.



Kinetic Monte Carlo: Sample Outputs

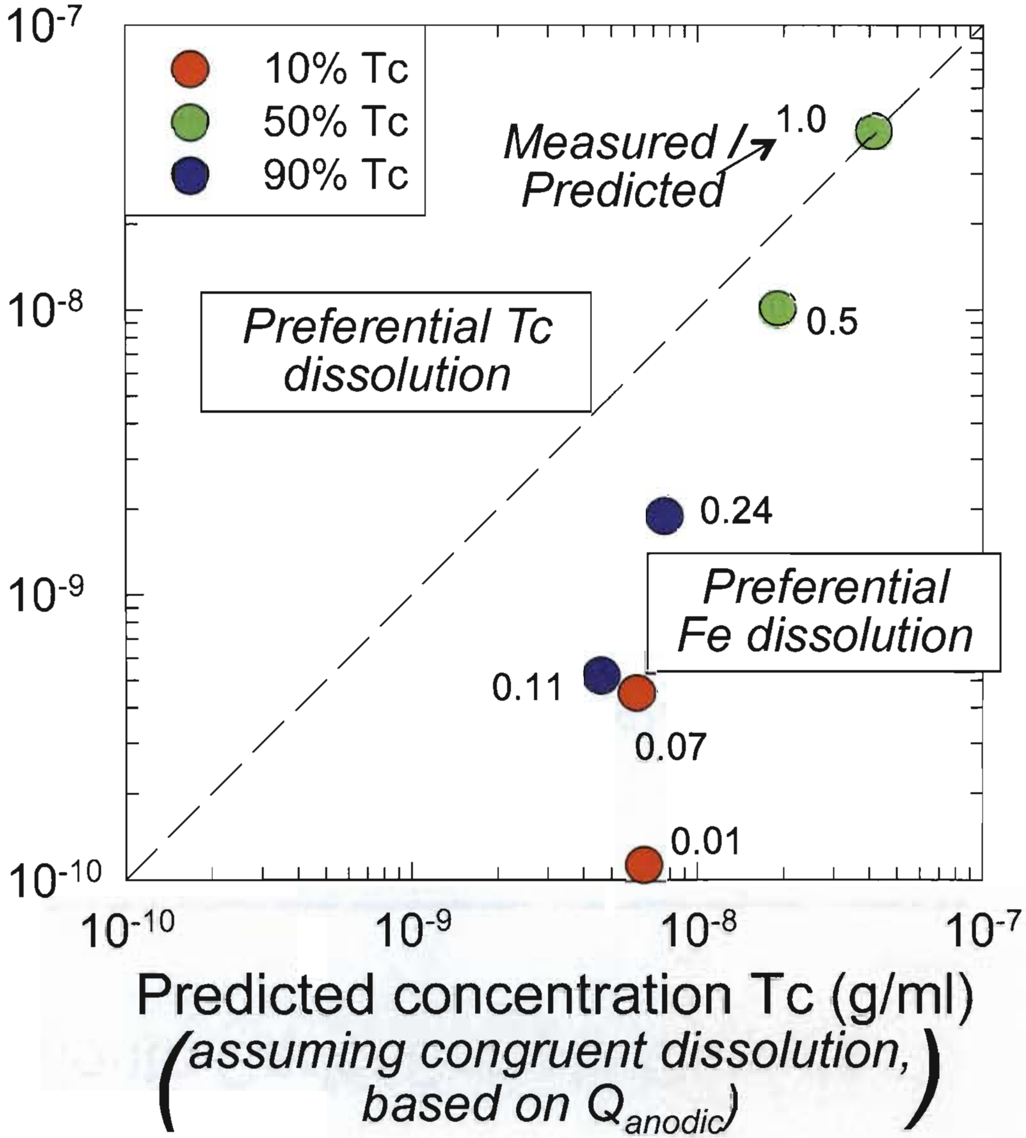
- For 10% Tc at -0.180V_{NHE}, Tc surface enrichment is predicted





Tc Concentration Measurements

- Preferential Fe dissolution
- Q measured from anodic polarization tests (Tc/Tc^{4+}, Fe^{2+}/Fe^{3+}). Potentiostatic tests are needed for increased accuracy.



Conclusions

- Electrochemistry, surface science and modeling of Tc – Fe alloys exposed to 10^{-4} M H_2SO_4 and other aqueous solutions (e.g. 10^{-4} M NaOH) is underway.
- Passivity was not observed from anodic polarization or EIS data. EIS indicated the presence of a non-passivating film. High-vacuum surface science revealed the presence of TcO_2.
- Corrosion rates were found to be minimized at intermediate Tc concentrations. Although passivity was not observed, the corrosion rate of Tc-Fe alloys is relatively low.
- Data were in agreement with preliminary atomistic modeling results.
- Preliminary measurements indicate that Fe dissolves preferentially.

Future Work

- Electrochemical measurements of Tc-Mo and Fe-Tc-Mo alloys in progress.
- Theoretical analysis of these alloys and dissolution mechanisms is in progress. Oxide surface phases to be added in the future analysis.
- Prepare and characterize alloys with Tc and additional epsilon phase metals (Mo, Ru, Rh, Pd)
- Use various aqueous dissolution protocols (e.g., modified ANSI 16.1) to assess robustness of waste forms and further develop mechanistic understanding of dissolution processes in most promising alloy compositions.
- Rate of dissolution of waste forms is input to the larger-scale models for the repository assessment being developed in another part of the Fuel Cycle Technologies Program.

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Development of Technetium Alloy Waste Forms for Advanced Nuclear Energy Cycles

G.D. Jarvinen[1], K.M. Long[2], D.G. Kolman[2], D.P. Moore[3], C.D. Taylor[3], G.S. Goff[4], M.R. Cisneros[4], R.R. Gibson[4], K.R. Czerwinski[5], F. Poineau[5], E. Mausolf[5], M. Ferrier[5]
1 G.T. Seaborg Institute, 2 Manufacturing Engineering & Technology Division, 3 Materials Science & Technology Division, 4 Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87545; 5 Radiochemistry Program, University of Nevada, Las Vegas, Las Vegas, NV 89154-4009

Introduction

The U.S. currently has 104 operating light water reactors providing about 20% of the nation's electricity. Most of these reactors are applying for license extensions to the U.S. Nuclear Regulatory Commission. Many extensions have been approved. However, no licenses to build a new reactor had been approved for over 30 years until February 9, 2012 when the NRC granted the first combined construction and operating license for two new AP1000 reactors at the Vogtle site in the state of Georgia. Additional license applications are in progress. The potential for nuclear power to provide a greater share of the energy needs in the U.S. is increasing, but difficulties with the management of the growing stock of used fuel from commercial reactors in the U.S. is continuing to slow the growth of nuclear energy.

The current policy in the U.S. for the disposition of used nuclear fuel is to directly dispose of the fuel after it is removed from the reactor and allowed to "cool" for a number of years. Under the amendments to the Nuclear Waste Policy of 1987, a repository site at Yucca Mountain in the state of Nevada was under study for disposal of the used commercial fuel and fuel and high-level radioactive wastes from nuclear weapons programs. A license application to approve the suitability of the Yucca Mountain site for used fuel disposal was submitted to the NRC in 2008. However, in 2009 the current administration in the U.S. decided to try to withdraw the application. A panel was appointed by the U.S. Secretary of Energy in 2009 with 15 distinguished members to make recommendations on how the U.S. should proceed with high-level nuclear waste management, "The Blue Ribbon Commission on America's Nuclear Future." This BRC panel submitted its final report on January 26 of this year (www.brc.gov). The BRC had eight major recommendations that are briefly listed here:

1) A new, consent-based approach for siting future nuclear waste management facilities.
2) A new organization dedicated solely to implementing the waste management program and empowered with the authority and resources to succeed.
3) Access to the funds nuclear utility ratepayers are providing for the purpose of nuclear waste management.
4) Prompt efforts to develop one or more geologic disposal facilities.
5) Prompt efforts to develop one or more consolidated storage facilities.
6) Prompt efforts to prepare for the eventual large-scale transport of spent nuclear fuel and high-level waste to consolidated storage and disposal facilities when such facilities become available.
7) Support for continued U.S. innovation in nuclear energy technology and for workforce development.
8) Active U.S. leadership in international efforts to address safety, waste management, non-proliferation, and security concerns.

The BRC supported continuing research into advanced nuclear fuel cycles and that responsibility resides within the U.S. Department of Energy (DOE). The Fuel Cycle Technologies (FCT) Program within the Office of Nuclear Energy of the DOE is charged with developing nuclear fuel cycle options that improve use of actinide resources, responsibly manage wastes, improve safety, and limit proliferation risk. Among the fission products in used nuclear fuel technetium is a fission product of particular concern for disposal in a repository because of its high fission yield, long half-life, and high solubility and mobility in groundwater as pertechnetate. For example, modeling studies for the former Yucca Mountain repository site indicated that technetium would be an important dose contributor after closure of the repository, especially in the first 10,000 years [1]. Since there is currently no specific repository site under investigation within the U.S., the FCT Program is investigating a range of potential repository environments for ultimate disposal of fission products including technetium from advanced nuclear fuel recycling schemes.

Anion exchange for technetium recovery

Among the separation process options that have been studied under the FCT Program and its predecessors is the UREX (uranium extraction) process. In this process used light water reactor fuel is chopped and dissolved in nitric acid and uranium and technetium are selectively extracted from the aqueous phase using tributylphosphate in a hydrocarbon diluent (acetohydroxamic acid is used to keep plutonium and neptunium in the aqueous phase). The U and Tc are back extracted to give a product stream of uranyl nitrate and pertechnetate in dilute nitric acid (~0.01 M). The technetium concentration relative to U depends on the burn-up of the fuel and the amount of technetium that is incorporated into the epsilon metal phase (principally Mo, Ru, Tc, Rh and Pd) that is part of the undissolved solids from the dissolver operation.

In the UREX product stream, the technetium occurs as the anion pertechnetate, TcO_4^-, and uranium(VI) nitrate is found as the aquo uranyl dication, UO_2^{2+}, with a smaller amount of $UO_2(NO_3)^+$, and very small amounts of higher nitrate complexes. An anion exchange resin provides a potentially good approach for separating TcO_4^- from the cationic uranium species. However, the uranyl nitrate solution contains high concentrations of the free nitrate anion relative to the TcO_4^- (~400-600 times depending on the amount of nitrate bound to the uranyl dication and the concentration of TcO_4^-) and the nitrate competes with TcO_4^- for sites on an anion exchange resin.

We evaluated a range of commercial anion exchange resins, especially weak-base anion exchangers, for pertechnetate binding and elution in surrogate UREX product streams. These tests indicated that the most promising commercial resin for a loading-elution process was Reillex HP^{TM}, a weak-base anion exchanger built from a vinylpyridine-divinylbenzene copolymer. The most useful eluant solution was ammonium hydroxide because it can be recovered and recycled by evaporation to give a concentrated product solution. Results from testing of Reillex HP^{TM} to recover TcO_4^- from a surrogate UREX U/Tc product solution were reported [2]. As noted above, the large molar excess of nitrate present in the UREX product solution competes for the anion exchange sites on the resin and limits the loading of pertechnetate to about 2-3% of the theoretical capacity of the technetium for the Reillex HP^{TM} resin.

The uranyl nitrate solution resulting after the removal of the TcO_4^- by the anion exchange column can be treated with ammonium hydroxide to precipitate "ammonium diuranate." The bright yellow precipitate is collected by filtration, dried and then calcined to U_3O_8 that can be stored for eventual recycle. Any technetium contamination of the uranium was shown to be very low [2].

Recently, a new anion exchange extraction chromatographic (EC) material has become available from Eichrom Industries, Inc., called Weak Base EC^{TM} resin. This resin incorporates a tertiary amine mixture into the resin bead support. We obtained quantities of the material from Eichrom to compare with Reillex HP. Figure 1 shows the loading and elution profile of a one-gram column of the Weak Base EC^{TM} material with a surrogate U/Tc UREX product solution. The surrogate solution had a volume of 150 mL with uranyl nitrate and ammonium pertechnetate dissolved in 0.01 M nitric acid to give a U concentration of 100 g/L and a Tc concentration of 132 mg/L. The plot in the figure shows the total amount of Tc (mg) in each fraction collected versus the total volume of solution passed through the 1 cm diameter column. The 150 mL of feed solution was followed by 50 mL of deionized water wash, and then 100 ml of 1 M ammonium hydroxide to elute the sorbed Tc. Under the conditions used in this test, breakthrough to about 20% of the feed concentration was observed during the water wash.

The elution of the TcO_4^- with 1 M ammonium hydroxide showed that 96% of the TcO_4^- on the column was recovered in 3-4 column volumes. This is substantially better than TcO_4^- elution from loaded Reillex HP^{TM} where about 18-20 column volumes are required to remove the loaded technetium. The Weak Base EC^{TM} resin also exhibits a capacity 30-40% higher than Reillex HP^{TM}.

The tertiary amines in the Eichrom Weak Base EC^{TM} resin are not chemically bonded to the polymer structure as are the cationic sites are in the Reillex resin or other typical anion exchange resins. The tertiary amines and their protonated ammonium salts have low solubility in aqueous solutions, but with repeated use the amine is expected to be slowly lost into the aqueous solution flowing through the column resulting in a loss of capacity. Some tests were performed with the Weak Base EC^{TM} resin to observe how quickly the capacity degrades.

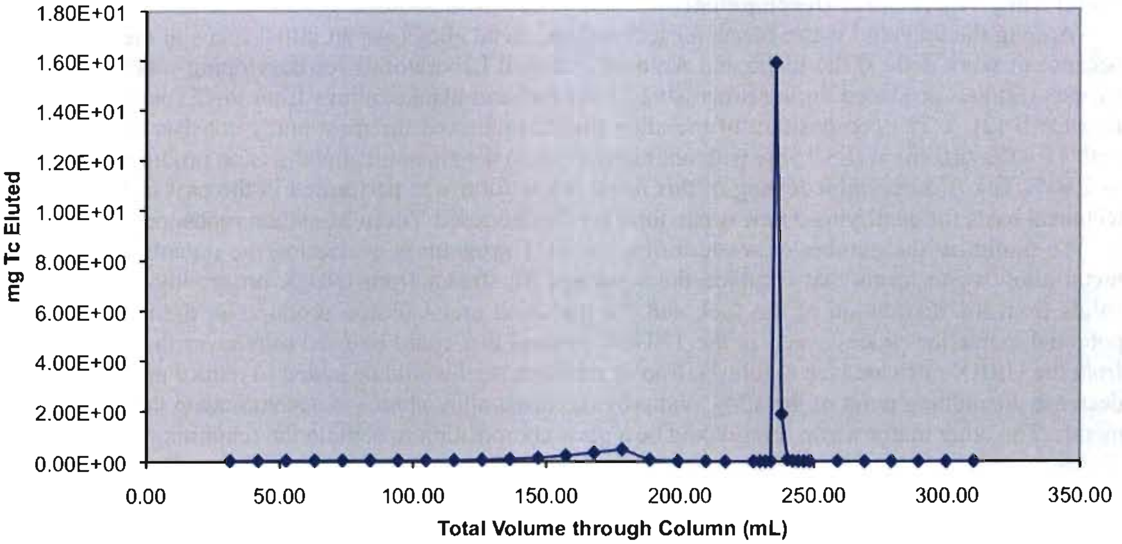

Figure 1. Loading-elution profile for a one-gram column of Weak Base EC resin loaded with a surrogate UREX product solution

A series of 10 loading, wash and elution cycles using a one-gram column of the Weak Base EC^{TM} resin was performed to provide an initial assessment of the durability of this material. The sequence used on cycles 1, 4, 7 and 10 was first protonation of the amine using 50 mL of 2 M nitric acid, washing with 50 mL of DI water, loading with 150 mL of U/Tc solution (100 g/L U and 0.132 g/L Tc in 0.01 M nitric acid), washing with 50 mL of DI water, eluting with 150 mL of 1 M ammonium hydroxide and washing with 50 mL DI of water. In this series only runs 1, 4, 7, and 10 used U and Tc to reduce radioactive waste. The other six cycles used a sequence consisting of 50 mL of 2 M nitric acid, 50 mL DI water wash, 150 mL of 1 M ammonium hydroxide and 50 mL of DI water wash.

The total loading of technetium on cycles 1, 4, 7, and 10 were the same within experimental error. Within the limitations in resolution of the peak imposed by the 2 mL volume of the fractions collected during the elution, the peaks were quite similar. This initial assessment indicates that the EC resin is certainly durable enough to be considered for process testing.

The ammonium pertechnetate product elutes from the anion exchange resin column along with a considerable molar excess of ammonium nitrate (~25-50:1). The conversion of the pertechnetate eluted from the anion exchange column to metal has been accomplished by concentrating the solution using evaporation at reduced pressure, followed by addition of excess tetrabutylammonium hydroxide or bisulfate, TBA[OH] or TBA[HSO_4], to precipitate tetrabutylammonium pertechnetate, TBA[TcO_4]. The TBA[TcO_4] is then converted to the metal by pyrolysis and steam reforming under a nitrogen or argon atmosphere humidified by bubbling through water [2]. Technetium metal can also be prepared directly from $NH_4[TcO_4]$ or anion exchange resin beads loaded with TcO_4^- by this pyrolysis and steam reforming route [3]. To further simplify the conversion chemistry, addition of reductant species such as sugar, formic acid and high-boiling alkanol amines to the eluant solution, followed by evaporation of the ammonium hydroxide and thermal decomposition of the solid was investigated. Triethanolamine was found to give to the most gradual and controlled decomposition of the nitrate between 150-300 C. The black residue could then be steam reformed at 900 C in a slow stream of Ar saturated with water vapor to give a pure Tc metal product.

A demonstration test was run with 500 mL of a surrogate UREX product solution with 100 g/L U and 132 mg/L Tc using the Eichrom Weak BaseTM EC resin. Very good separation of U and Tc was achieved with 98% recovery of the U and 96% recovery of the Tc.

Metal Alloy Waste Form Development

Among the potential waste forms for technetium, metal alloys are an initial focus in the FCT program because of work done at the Idaho and Argonne National Laboratories for developing waste forms for the various residues produced during processing of the fuel and blanket alloys from the Experimental Breeder Reactor-II [2].). The composition of the alloy that has received the most study consists of stainless steel with 15 wt% zirconium (SS/15Zr) with additions of up to 4 wt% noble metal fission products (including up to 2 wt% Tc). Considerable testing of this metal waste form was performed in the past to form the initial technical basis for qualifying a new waste form for the proposed Yucca Mountain repository [4,5].

To minimize the number of waste forms, the FCT program is evaluating the potential advantages of metal alloy waste forms that combine the separated Tc stream from UREX processing, the undissolved solids from the dissolution of the fuel, and the transition metal fission products in the raffinate of other potential extraction process such as the TRUEX process that could be used to recover the minor actinides from the UREX raffinate (see Figure 1). Iron or stainless steel would be added to reduce most metal oxides, decrease the melting point of the alloy, and provide robust alloy phases to accommodate the fission product metals. The other major waste form would be a glass composition to contain the remaining fission products.

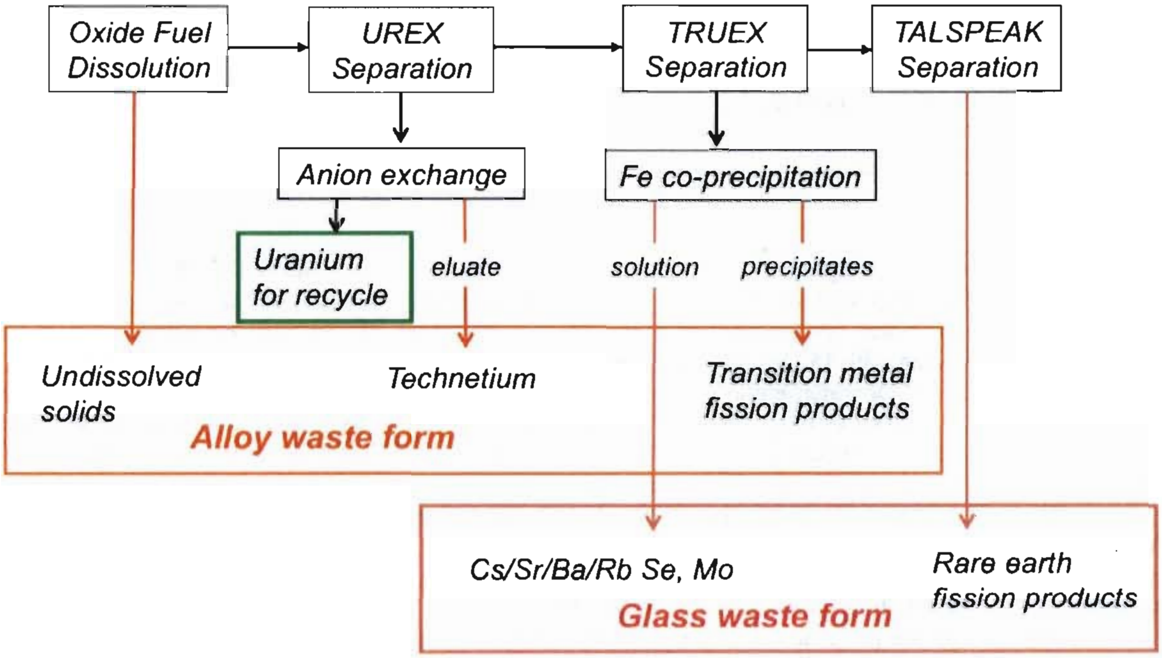

Figure 1. Example conceptual flowsheet for LWR used fuel separations and waste forms.

A larger multi-laboratory team is examining a variety of alloy waste form compositions. At LANL and UNLV we have initially focused on the fundamental behavior of Tc-Fe and Tc-Mo binary alloys. This work is investigating the corrosion behavior of these alloys across a wide range of aqueous environments in order to determine release rates and mechanisms. Theoretical surface science and modeling work has also been performed to provide basic understanding of the materials/environment interface. Initial studies on Tc and Tc - Fe alloys will be reported here. The electrochemical behavior of behavior of pure Tc, 90 wt% Tc – 10 wt% Fe, 50 wt% Tc – 50 wt% Fe, 10 wt% Tc – 90 wt% Fe, and pure Fe was examined.

Tc metal was produced by thermal decomposition of NH_4TcO_4 to TcO_2 at 450 °C for 1 hr in Ar. TcO_2 was converted to Tc metal in Ar - 5 % H_2 using a two-step furnace cycle (700 °C for 24 hours followed by 900 °C for 4 hours). Fe - Tc alloys were made by arc-melting followed by annealing at 1600 °C in an Ar-atmosphere resistance furnace. 0 wt%, 10 wt%, 50 wt%, 90 wt% and 100 wt% Tc alloys were prepared.

Specimens were mounted in epoxy and polished to 600-grit finish. The polished samples were ultrasonically cleaned in ethanol for five minutes. Crevice corrosion between the metal and the epoxy mount was not apparent following testing. The exposed metal surface area varied between 0.002 and 0.007 cm^2 depending on the individual sample.

Solutions were composed of reagent-grade chemicals and distilled, deionized, 18-MΩ water.

Solutions were room temperature - self-heating of the materials from radioactive decay was considered negligible. Solutions were neither actively aerated nor deaerated. A commercially available, computer-controlled potentiostat and frequency response analyzer were used to perform the electrochemical measurements. The electrochemical cell was a 100-mL flask incorporating a Ag/AgCl reference electrode and a platinized-niobium mesh counter electrode. Potentials are plotted vs. NHE.

Prior to polarization, working electrodes were immersed in solution for four hours and the open circuit potential monitored. Potentiodynamic polarization tests used a scan rate of 0.1 mV/s. Electrochemical impedance spectroscopy used a 10-mV rms AC voltage signal applied at frequencies between 100 kHz and 10 mHz using potentiostatic control. Impedance data fitting was performed with complex nonlinear least squares circuit fitting software. Linear polarization resistances were fit between $-20\ mV_{OCP}$ and $+20 mV_{OCP}$. Most tests were replicated to assess the reproducibility of the results. Corrosion rates (mils per year) are calculated from fitting of i_{corr}.

Open circuit potentials for the different materials measured in 10^{-4} M H_2SO_4, superimposed on the potential - pH diagram for technetium, are shown in Figure 3. It can be seen that measured OCP at 4 hours spans the active, passive and immune regions for Tc. Increasing Tc concentration generally increases the OCP, with a large increase in OCP between 10% Tc and 50% Tc.

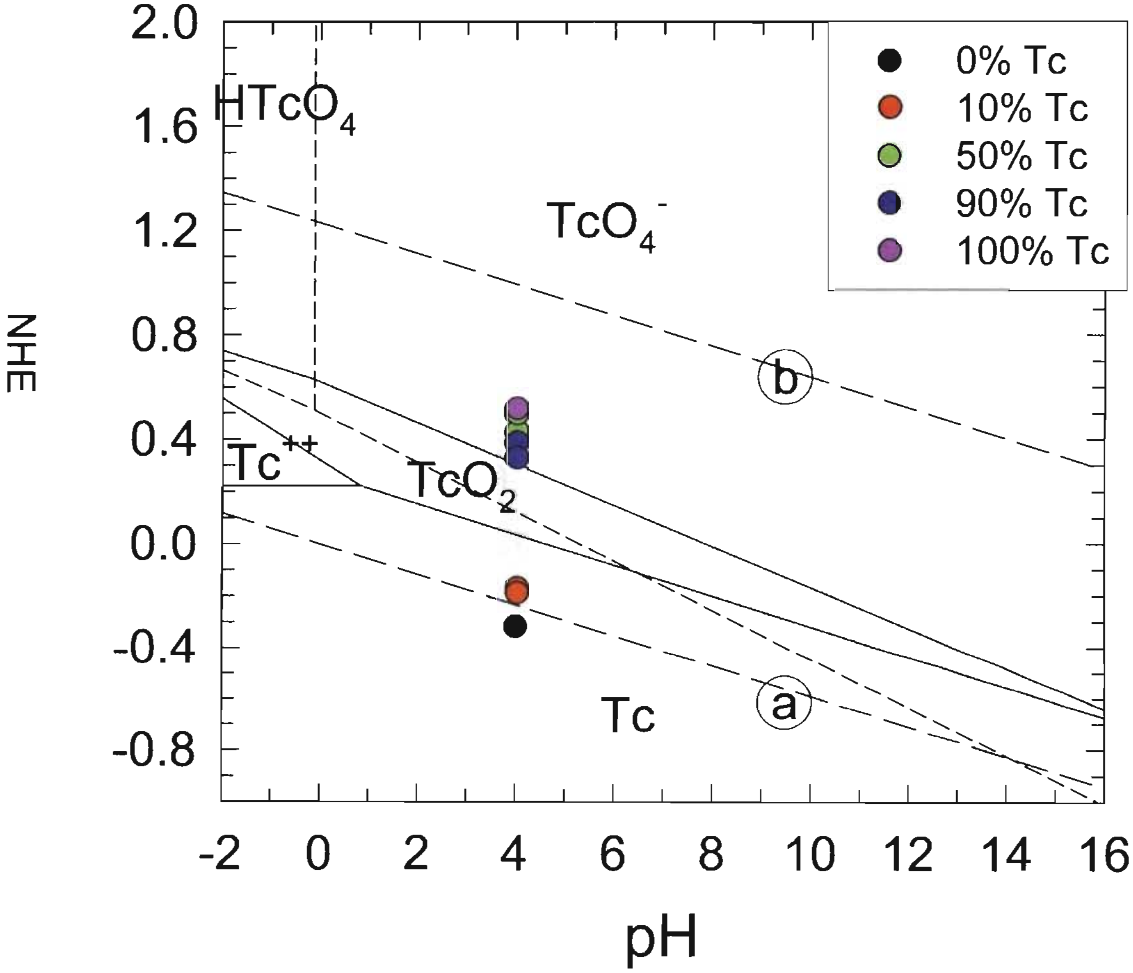

Figure 3. Open circuit potentials of the metal alloys measured in 10^{-4} M H_2SO_4.

Figure 4 shows corrosion rates derived from linear polarization resistance measurements. The corrosion rate for 10 wt% Tc is relatively similar to that of pure Fe. However, a dramatic decrease in corrosion rate occurs between 10 and 50 wt% Tc. It appears that both chemical and microstructural effects play a role in the corrosion of these alloys. Addition of Tc to Fe is beneficial to corrosion resistance, however, beyond 50 wt%, the benefit is reduced.

Potentiodynamic polarization data are shown in Figure 5. The passive region from the potential - pH diagram is overlaid on the data for reference. Replicate tests indicate good reproducibility. Although corrosion rates are relatively low, no passivity is observed for any of the materials. The 0 and 10% Tc tests appear to be IR-limited based on linear V-I plots (not shown). For these samples, the solution resistance was approximately 100 kW, as determined from EIS. Note that passivity cannot be definitively precluded for the 10 wt% Tc sample because significant ohmic loss in solution may prevent polarization of the sample into the passive region. However, given the lack of passivity observed in other Tc-containing materials, passivity appears to be unlikely. In summary, passivity is predicted for Tc, but was not observed.

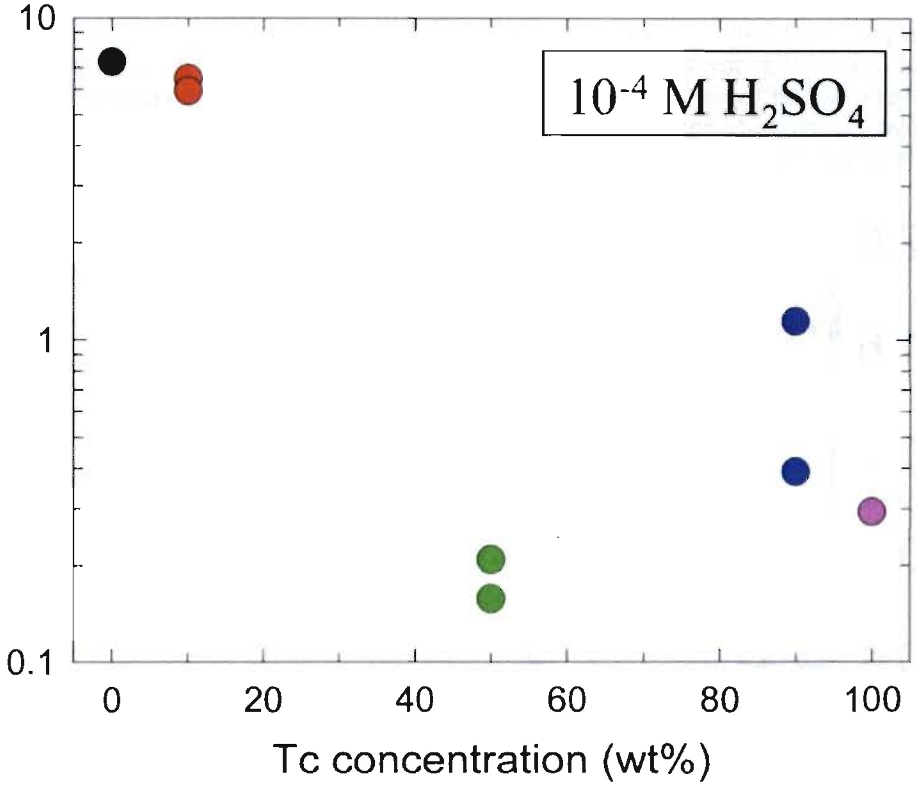

Figure 4. Corrosion rates measured from linear polarization resistance measurements.

A more complex test was performed to confirm the lack of passivity. A pure Tc sample was exposed to deaerated (argon) in pH 4 HNO_3. The sample was potentiostated to the immune region (−0.1 VNHE) and abraded in-situ while polarization was held. EIS was then performed. The sample was then polarized to the passive region (0.15 VNHE) at a rate of 0.1 mV/s and EIS performed again. Finally, the sample was polarized to a more noble potential in the passive region (0.27 VNHE) at a rate of 0.1 mV/s and was EIS performed. The potentials where EIS was performed are overlaid on the potential - pH diagram in Figure 6. Impedance results were difficult to interpret. However, two or more time constants were observed to be present in the impedance spectra and a diffusional impedance was observed at low frequency. So it appears that some nonpassivating film is present on Tc at these potentials. Additional work is necessary in to confirm the structure and composition of this oxide.

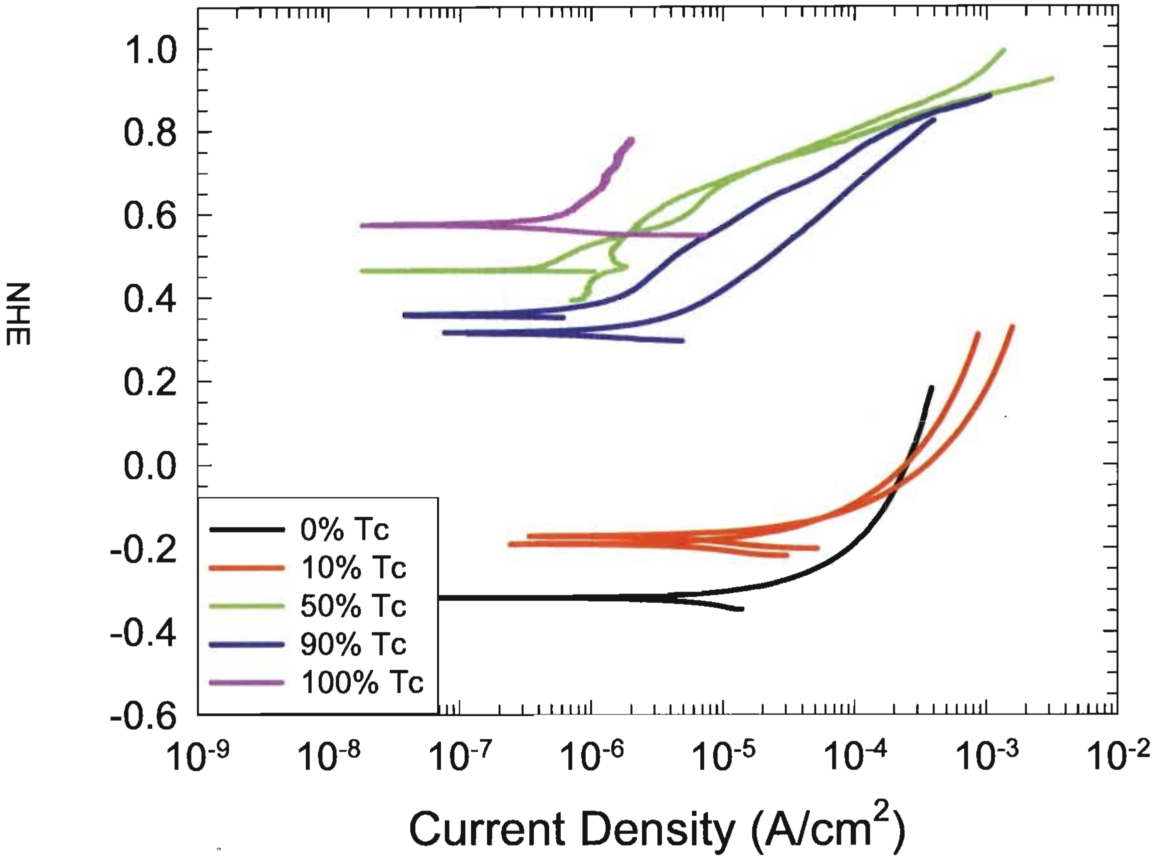

Figure 5. Potentiodynamic polarization data for metal samples exposed to 10^{-4} M H_2SO_4.

High-vacuum tests were performed in order to examine oxidation of a technetium metal surface. A Tc sample was introduced into a high-vacuum chamber and sputter cleaned. The sample was the exposed to a few monolayers of O_2 gas and an auger-electron spectrum acquired. The results are shown in Figure 6. Based on relative peak heights, positions, and peak shapes/structure formation of a nominal TcO_2 layer is indicated. Because TcO_2 is thought to be passivating (the green region in Figure 1), either TcO_2 does not form in solution or TcO_2 is not passivating as believed.

In order to assess the relative amounts of Fe and Tc dissolution, solutions was analyzed for Tc by liquid scintillation counting. The results (Figure 7) showed that less Tc was in solution than would be predicted if congruent dissolution occurred. Therefore, it can be concluded that Fe preferentially dissolves from the binary alloys. Note that these results represent the integral of dissolution over the potential range used in the potentiodynamic tests and that the ratio of Fe : Tc dissolution almost certainly varies as a function of potential.

A combined DFT and modified embedded atom method modeling studey was used to corroborate the experimental findings [6]. A kinetic Monte Carlo simulation computation of 10 wt% Tc at −0.18 V versus NHE predicts surface enrichment of Tc. This is consistent with the preferential Fe dissolution that was observed.

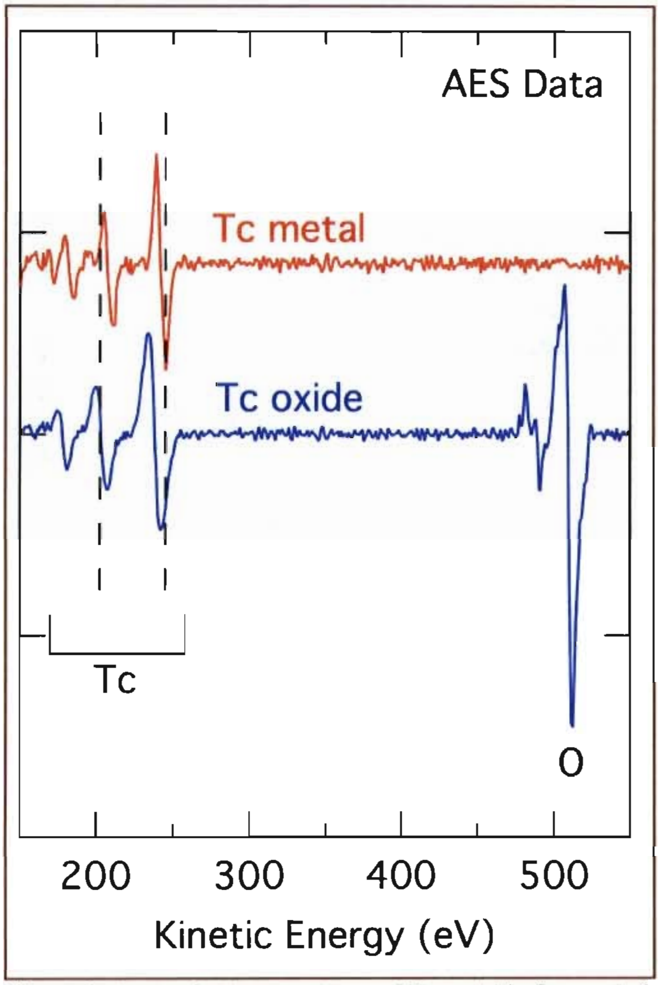

Figure 6. Auger electron spectrum of Tc metal before and after exposure to O_2.

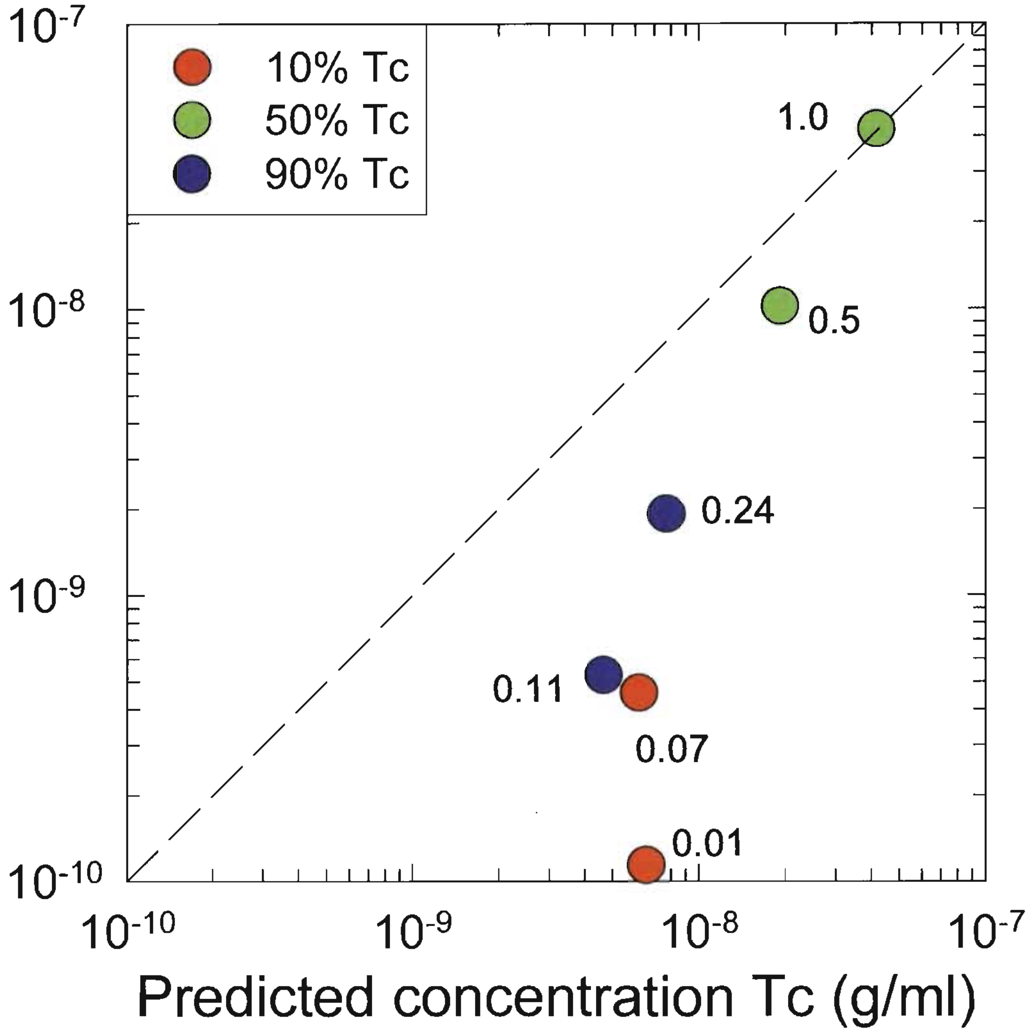

Figure 7. Measured Tc concentration in solution vs. predicted concentration base upon congruent dissolution of Fe and Tc and total current passed during the dissolution.

Metal samples containing iron and 0, 10, 50 90 and 100 wt% Tc were exposed to dilute H_2SO_4 solutions. The results indicate that corrosion rates are relatively low for the 50, 90 and 100 wt% materials, even though passivity is not observed. Corrosion rates were minimum at intermediate Tc concentrations, suggesting both chemical and microstructural effects of alloying. The presence of a nonpassivating film was inferred from EIS spectra. High-vacuum measurements indicate the formation of TcO_2, therefore, there is either a difference in the film formed in solution from that in high-vacuum or TcO_2 is not passivating. LSC measurements and modeling simulations indicate that Fe preferentially dissolves in these Fe-Tc binary materials.

Further work continues with other solution conditions for the Fe-Tc materials. A series of Mo-Tc and Fe-Mo-Tc materials have been prepared and will also be investigated. Ultimately, the understanding of the dissolution mechanism of the metal alloys will be integrated into the larger-scale transport models for radionuclides from various repository environments.

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