National Analytical Management Program (NAMP)
Savannah River National Laboratory
U.S. Department of Energy Savannah River

Radiochemistry Webinars

Nuclear Fuel Cycle Series
Nuclear Waste Management –Application to Technetium

In Cooperation with our University Partners

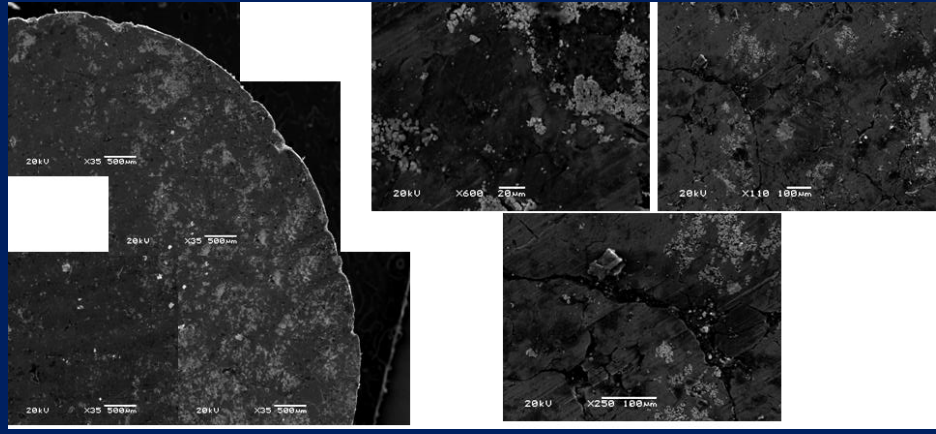
Meet the Presenter…

Dr. Edward Mausolf

Dr. Edward Mausolf is an Associate Research Chemistry Department at the University of Nevada, Las Vegas (UNLV), and a joint appointee Scientist with the Pacific Northwest National Laboratory within the National Security Directorate. He received his Ph.D. in Radiochemistry in 2013 from UNLV, with a research emphasis on the investigation of nuclear reprocessing of uranium and the development of advanced technetium waste forms.
His current research is focused on the development of accident tolerant nuclear fuels. Dr. Mausolf has a patent pending on methods designed to reprocess nuclear waste within the reactor while under operation, with a secondary emphasis on the stabilization of fuel for use in intermediate storage, or direct geological disposal of used nuclear fuel. His expertise in the nuclear fuel cycle provides significant knowledge around fuel forms, fuel separations, and various characterization techniques such as microscopy, corrosion, and inorganic hard-synthesis techniques, which is leveraged through innovative strategies to develop intellectual property from his research.

Contact Information: Dr. Edward Mausolf
mausolfe@unlv.nevada.edu

UNLV



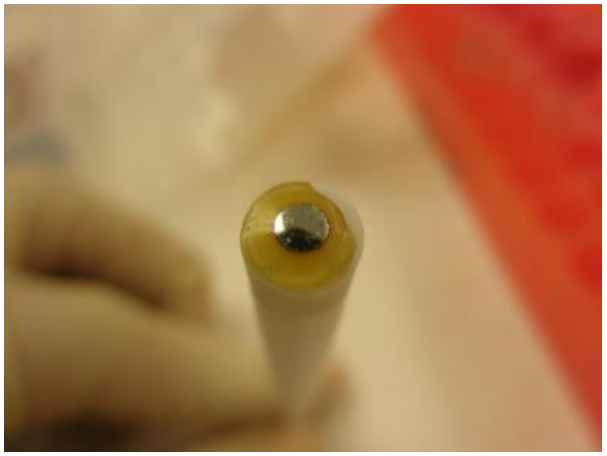
Nuclear Waste Management- Application to Technetium

Dr. Edward Mausolf
Pacific Northwest National Laboratory
University of Nevada Las Vegas

National Analytical Management Program (NAMP)

TRAINING AND EDUCATION SUBCOMMITTEE

Outline

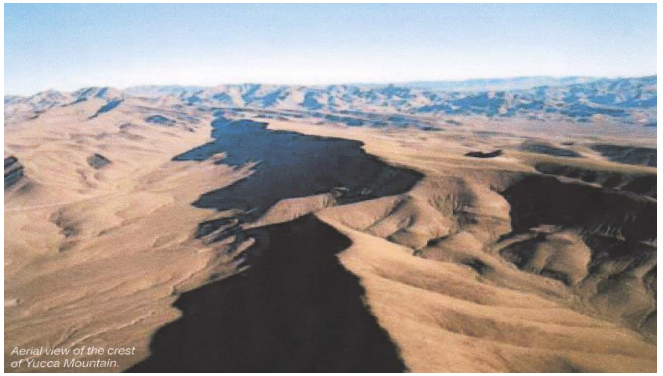


- Introduction
- Nominal composition of used fuel
  - The Fe-solid solution; single phase of the metal alloy
- Synthesis of Tc metal and alloys
  - Solid phase
  - Electrodes
- Electrochemical Techniques and Interpretation of Data
  - Electrodes and evaluated electrochemically
- Results and conclusions

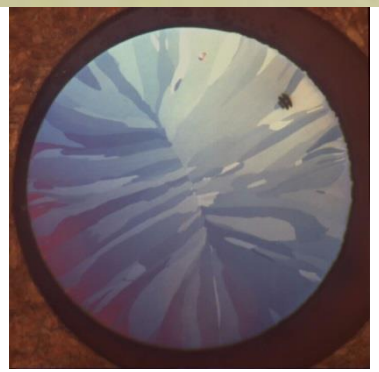
Technetium is a Long-term Threat to the Biosphere

- Technetium is a key dose contributor in a generic repository modeling if TRU elements are greatly reduced by advanced recycling. The long half-life of 99Tc (t1/2 = 2.14 x 105 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 threat of 99Tc to the biosphere have been considered:
  - Transmutation to 100Ru or
  - Using a robust waste form/repository system to control release to acceptable levels over a long period of time (~1 million years).

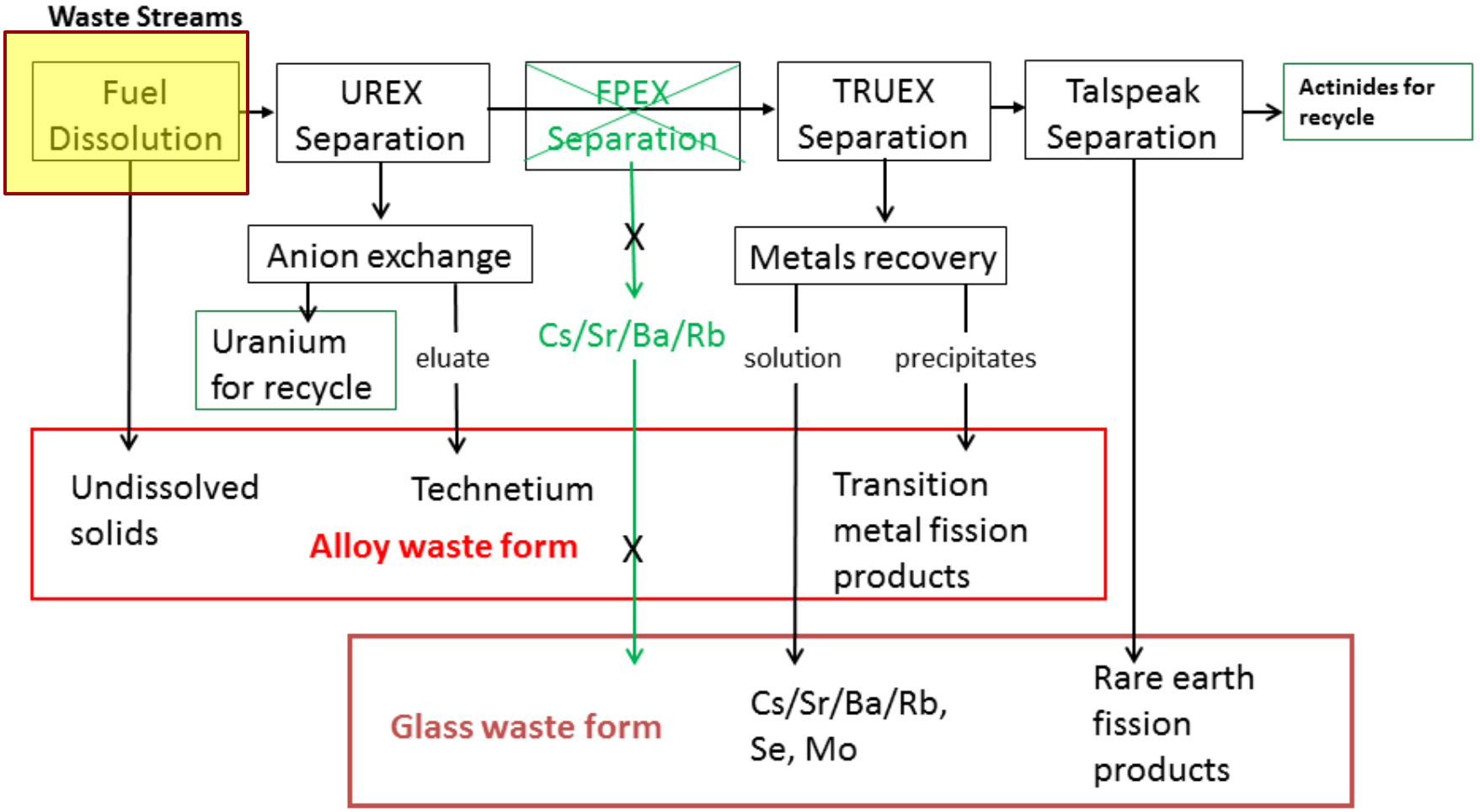


TcZr Waste-Form



Microscopic cross section of irradiated Tc target
Konings et al., http://www.nea.fr/html/pt/docs

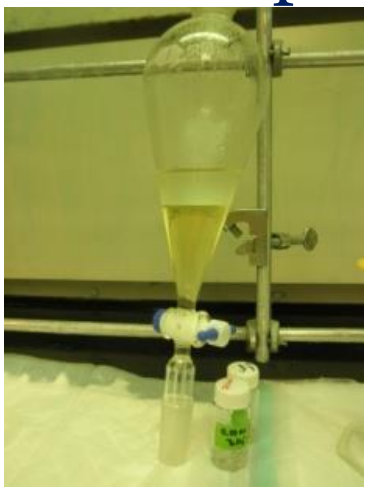
Tc Waste streams



Separations

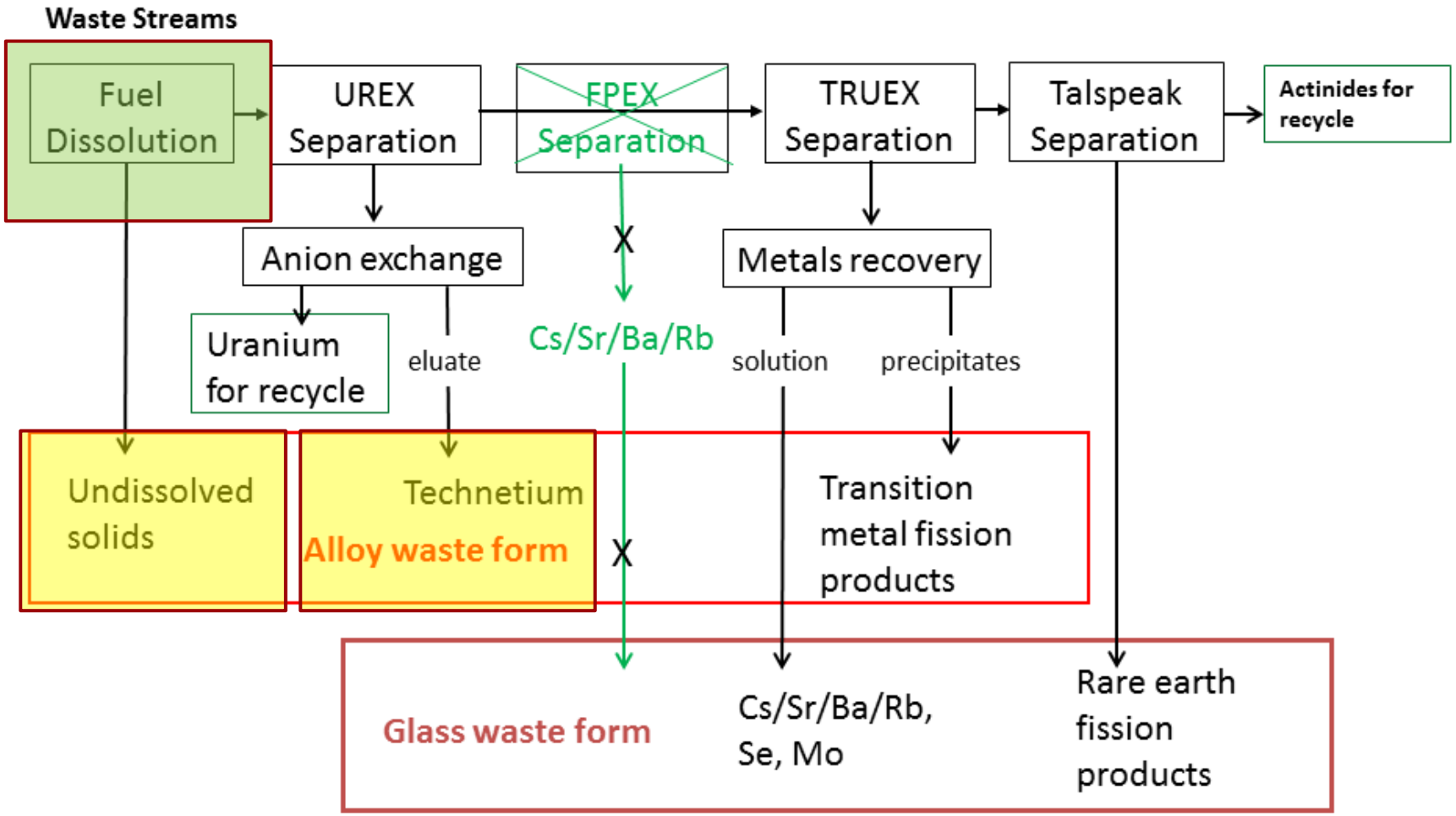
- Traditionally, dissolution of Tc occurs in high concentrations of nitric acid.
- Some Tc is also found “un-dissolved” in the UDS.
- Tc(VII) is extracted with U(VI) into an organic phase then isolated.
- Tc can be isolated by anion exchange, liquid-liquid extraction, precipitation, volatilization and/or distillation, and electrochemical separation.

Before U Extraction



After U Extraction

Tc Waste streams



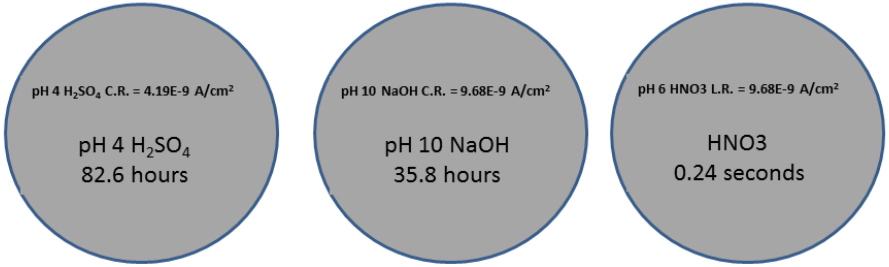
Introduction

- Most Tc generated found in liquid phase
  - Can vary with burnup and UO2+x
- Nominal Tc distribution
  - Total Tc = 1.04 kg
    - Undissolved solids (UDS) ~ 26%
      - Tc(VII) ~ 74%

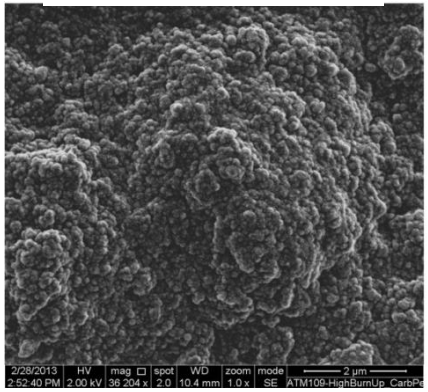
Nominal Metals Contents of Waste Streams kg/1000 kg fuel (51 MWd/MT 20-year cooled)

Element	UDS waste (to alloy WF)	Tc waste (to alloy WF)	TRUEX waste (to alloy WF)	TRUEX waste (to glass WF?)
Fe	0	may be added to recover Tc	may be added to recover dis. metal	0
Zr	1.86 *as oxide*	0	3.78 *as oxide*	0
Mo	4.75	0	0	0.36
Tc	0.27	0.87 *reducible*	0	0
Ru	1.64 *in ε-phase*	0	1.65	0.20
Rh	0.24	0	0.37	0.00
Pd	0.68	0	1.29 *reducible*	0.38
Ag	0.05 *reducible*	0	0.05	0.01
Sn	0	0	0.14	0.01
Total from fuel	*9.50 kg*	*0.87 kg*	*7.27 kg*	*0.96 kg (+Cs/Sr/Ba/Rb)*

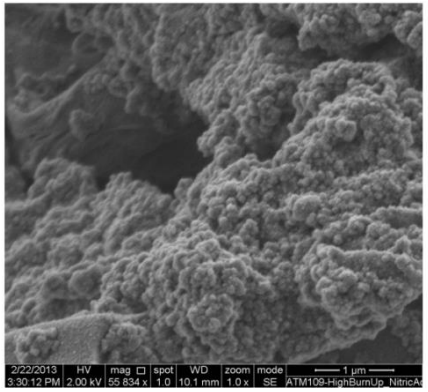
Epsilon metal characterization



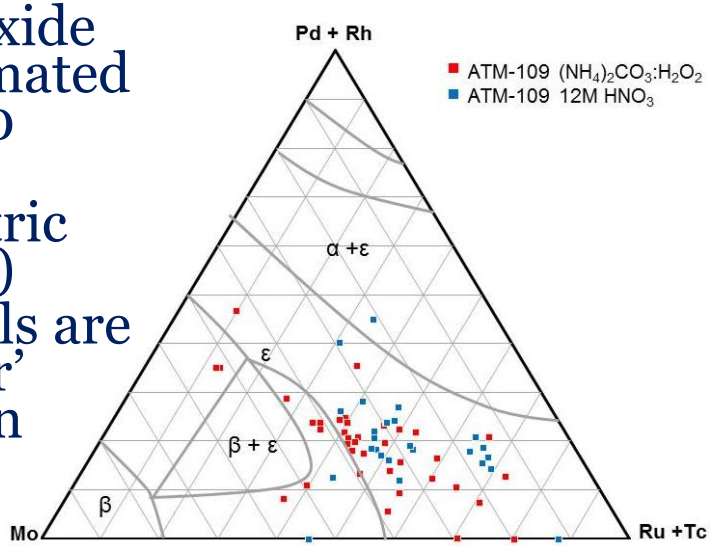
Ammonium carbonate (pH 10)

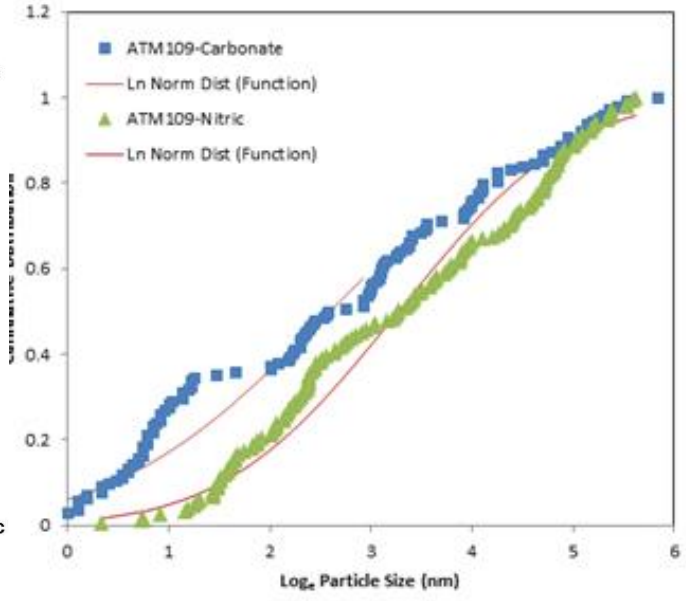


12M HNO3



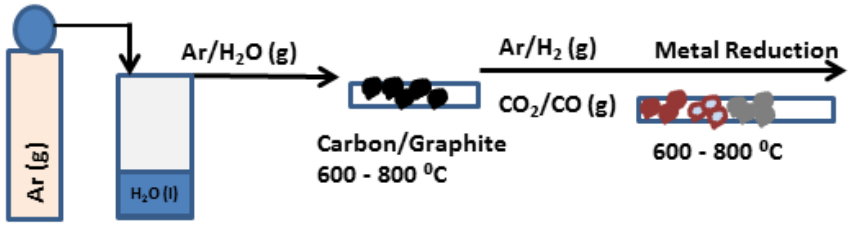
- Tc corrosion behavior in ammonium carbonate- peroxide (unknown) estimated lifetime in pH 10 NaOH
- Compared to nitric acid (6M HNO3)
- All epsilon metals are surviving 'longer' than predicted in both systems

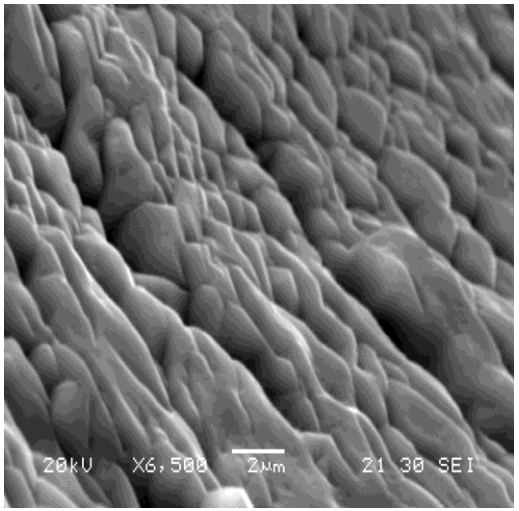


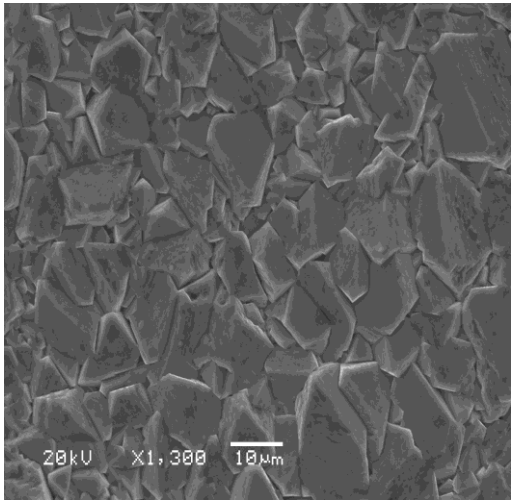


Tc Metal Isolation

- Tc isolated from solution must be converted to metal
  - Thermal Reduction
  - H2(g), steam reformation
- Chemical Reduction
  - NaBH4/Zn in boiling HCl
- Electrochemical Reduction
  - 1 M H2SO4at high current densities (1 A/cm2)
- Examine Tc metal
  - Benchmark
  - Potential waste form

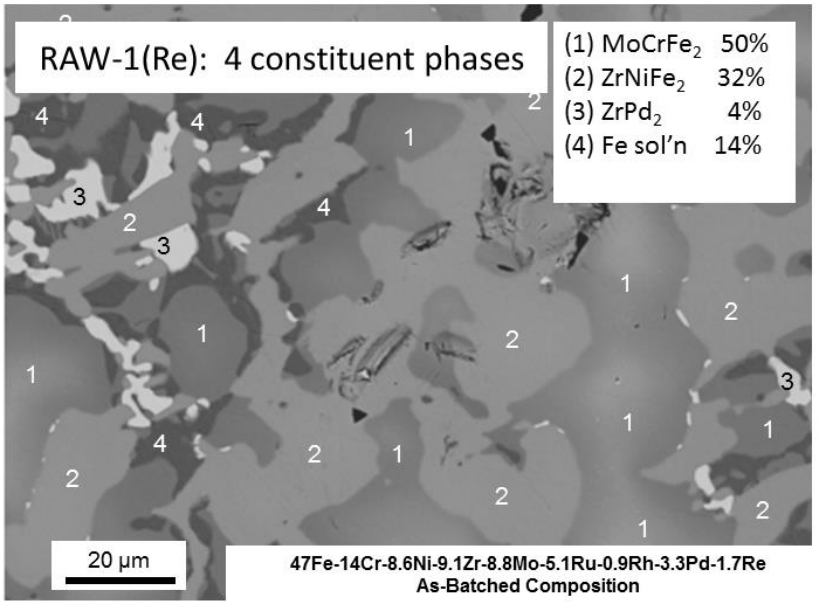


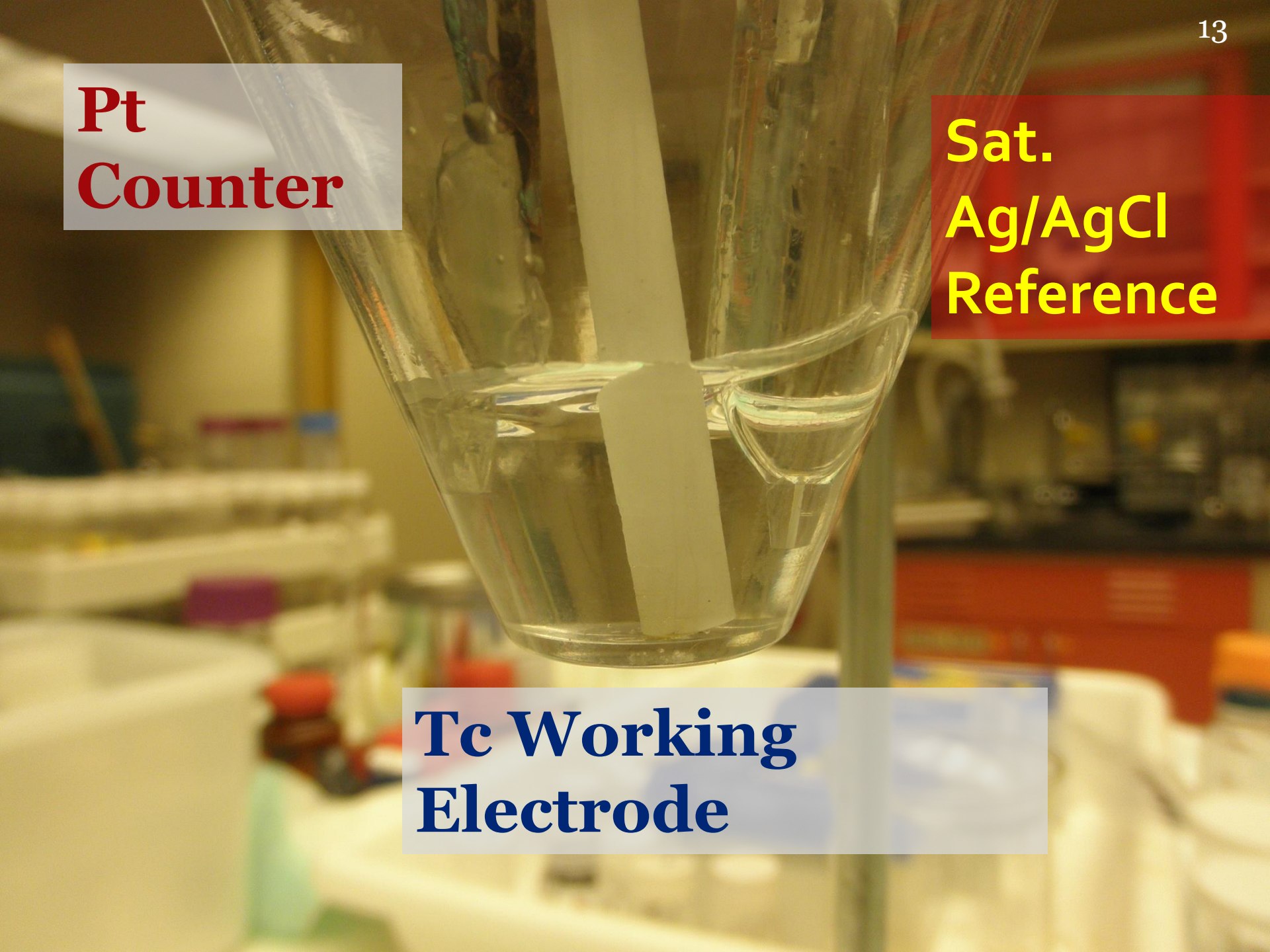




Iron solid solution: Proposed Waste Form

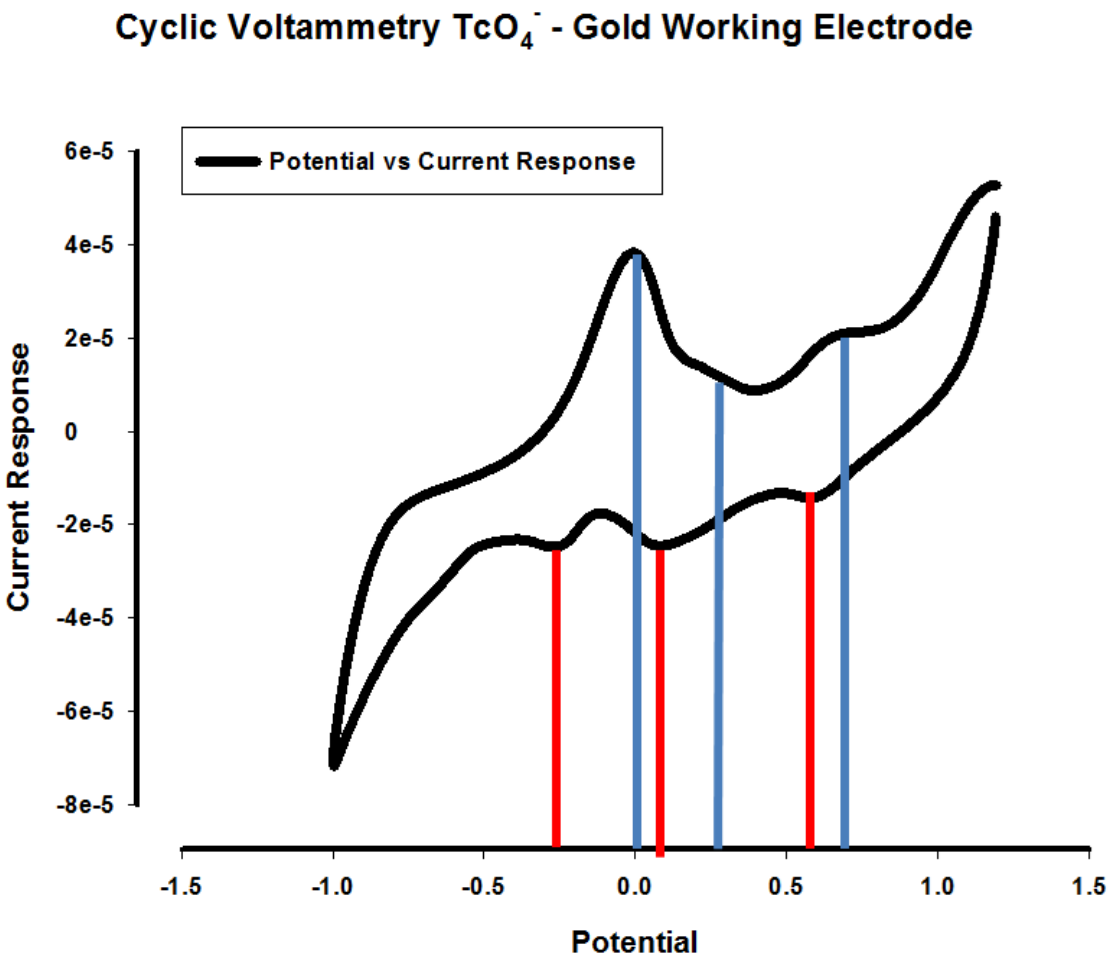
- Fe metal as major component of waste form
  - Provides low melting point
  - High solubility of metal fission elements
  - Utilization of fast reactor cladding for waste form
- Fe based phases from fission elements can be generated
- 14 % of total phases are Fe solid solutions
  - Tc incorporates into Fe phase
  - Galvanic coupling effects
  - Examine Tc loading capacity




Pt
Counter
Sat.
Ag/AgCl
Reference
Tc Working
Electrode

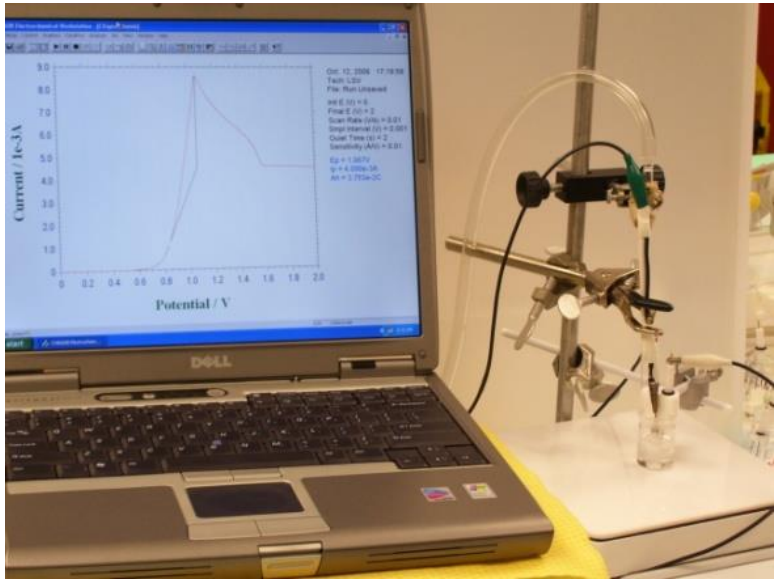
Cyclic voltammetry of Tc(VII)

- Multiple peaks associated with oxidation and reduction
  - KTcO4 in DI H2O
  - Au – W.E.
  - Pt Foil – C. E.
  - Sat. Ag/AgCl – R. E.
- Insight into corrosion behavior is limited by this traditional technique



Experimental conditions

- Metals
  - Tc metal
  - Tc alloys
    - 1-8 % by atom in Fe
    - 2-10 % by mass in Stainless Steel (316 SS) and Zr
      - 85 % SS/ 15 % Zr
- Imaging
  - SEM/EDX
- Various Solutions
  - HCl, H_2SO_4, HNO_3, NaOH, NaCl
- Electrochemistry of systems

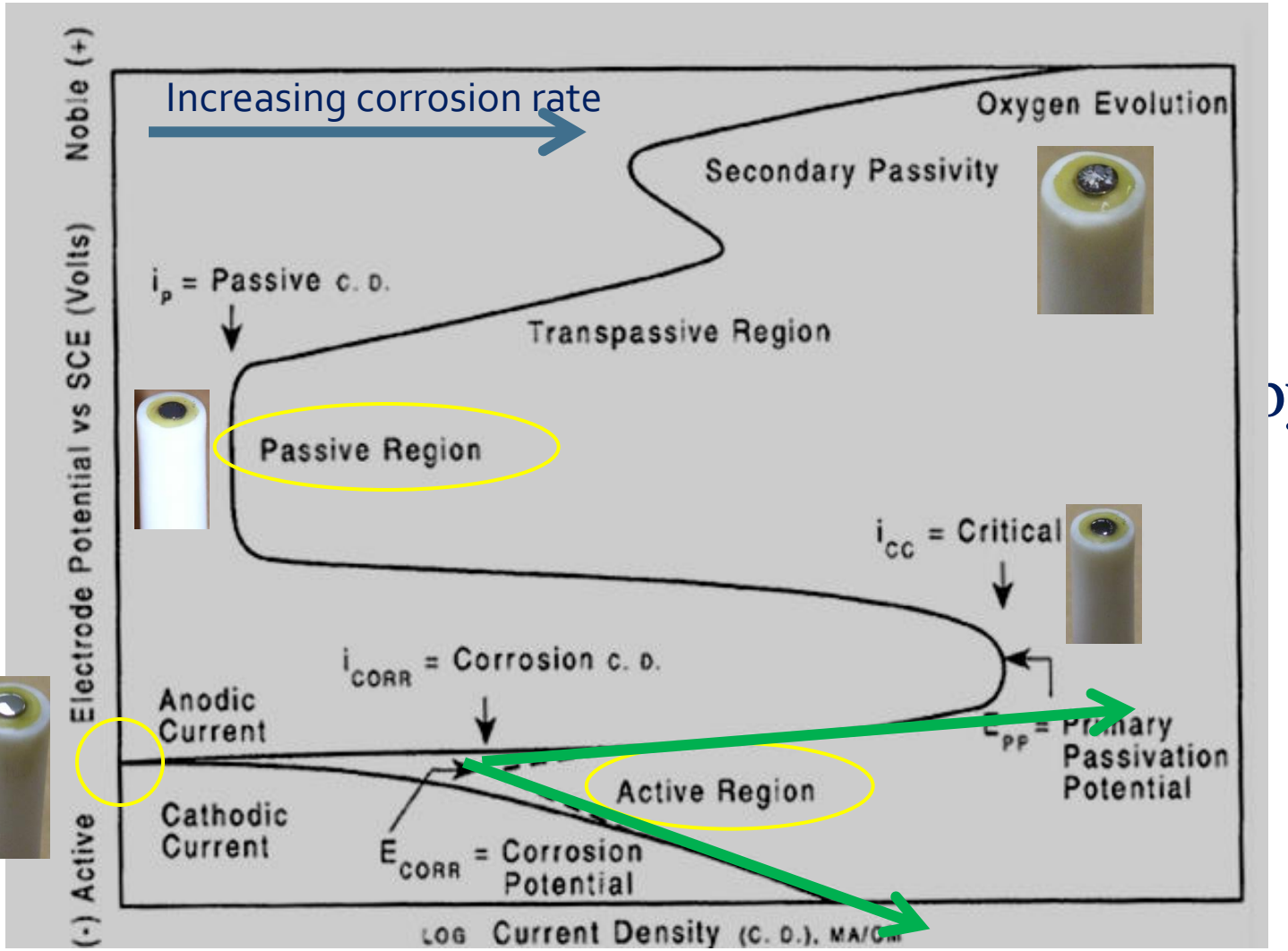


Solution	Composition
Acidic	1E-4M H_2SO_4
Acidic Brine	1E-4M H_2SO_4 + 0.01M NaCl
Basic	1E-4M NaOH
Basic Brine	1E-4M NaOH + 0.01M NaCl
Brine	0.01M NaCl
Neutral	0.2M Borate Buffer

Electrochemical Techniques

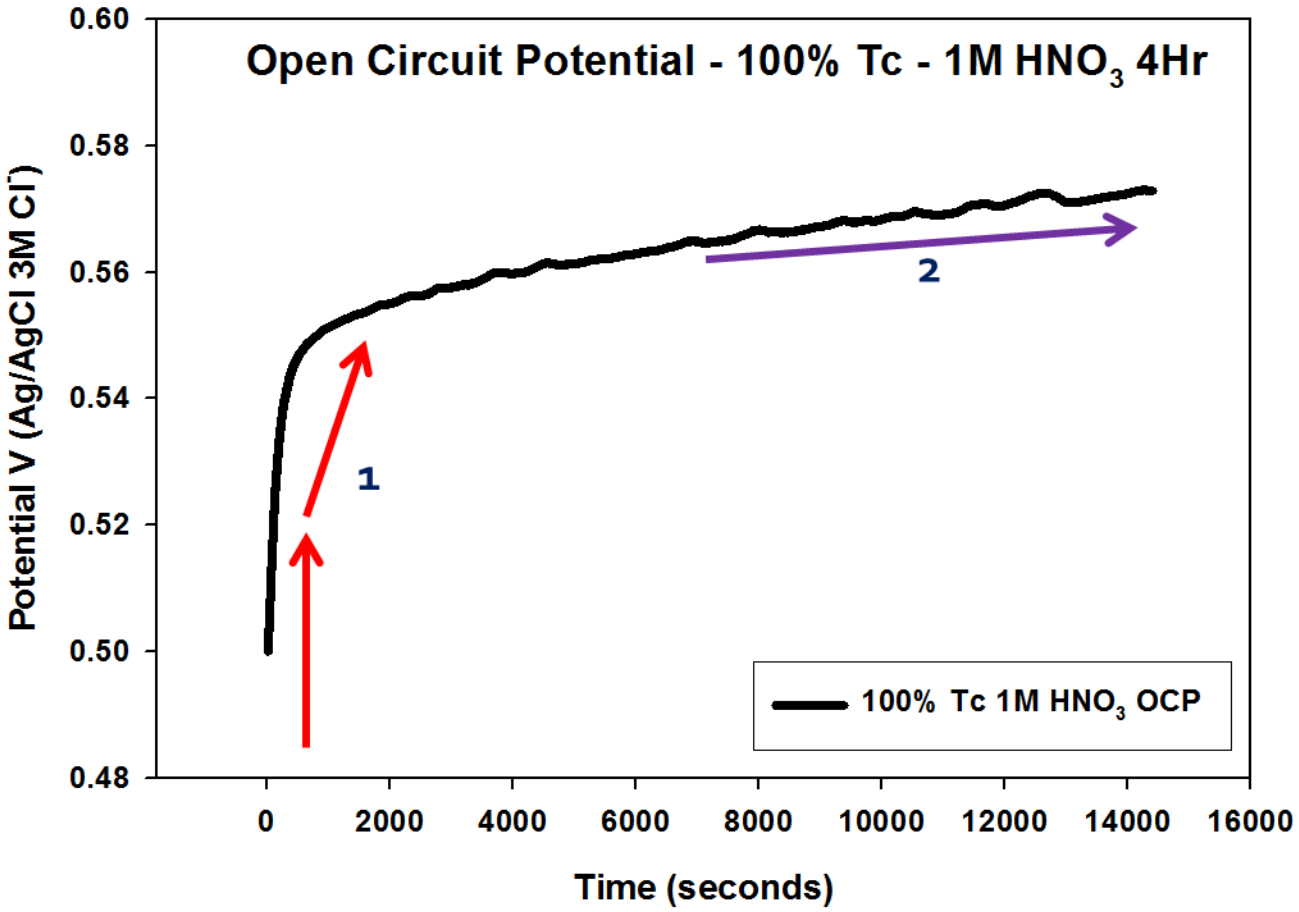
- Open Circuit Potential (OCP)
  - States of corrosion
    - Active: No formation of different phase during corrosion
    - Passive: Formation of different phase during corrosion (i.e., oxide layer)
  - Potential where corrosion dominates
- Linear Polarization Resistance (LPR) and the Tafel plot
  - Instantaneous corrosion rates at examined potential regions
    - Potential identification of passivity
- Electrochemical Impedance Spectroscopy (EIS)
  - A corrosion probing tool using equivalent circuit modeling
  - Potentials more electropositive than OCP
- Bulk Electrolysis (BE)
  - Examine release behavior from metal above OCP
    - Real material leach rate

Electrochemical Techniques



Open circuit potential

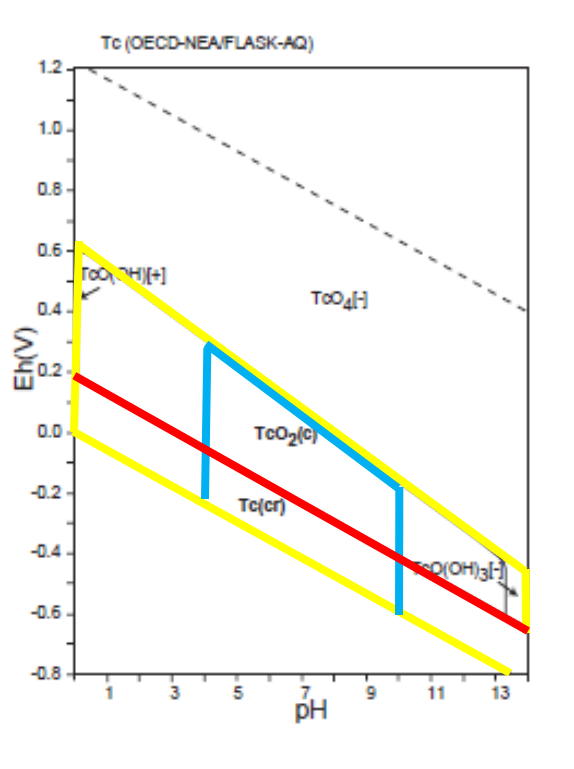
- Describes active or passive state of a metal
  - No outside applied potential
  - Measure between components of cell
  - Provide sample potential relative to reference
- Increase in potential with time indicates passive corrosion

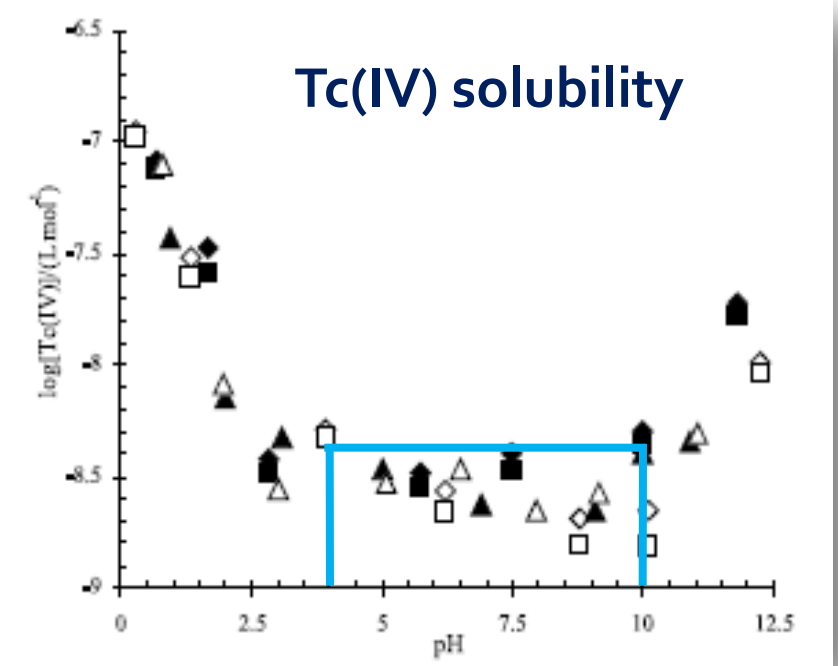


1. Rapid rise in OCP is observed with Tc metal in 1M HNO_3
2. Equilibrium partially indicated by small potential (E) changes

Open circuit potential

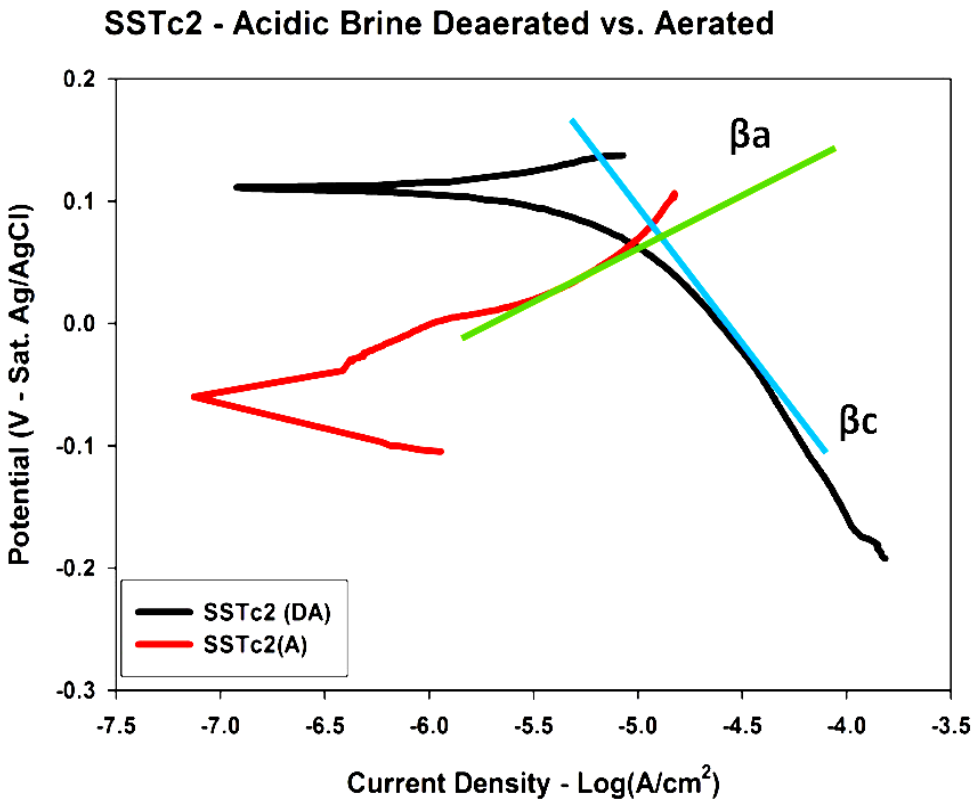
- Shows stability of dominant phases in Eh/pH diagram
  - provides little insight into corrosion kinetics





Linear Polarization and the Tafel Plot

- Floating OCP for 4 hrs
- Polarization
  - -30 mv to +300 mV, non-deaerated solution
  - +30 mV to -300 mV, deaerated solution
  - Scan rate = 0.1 mV/sec
- RP value determined by Tafel constants from de-coupled polarization curves
  - Reported in Ω, or Ω•cm-2



Effect of radical O_2* formation should be minimized on the cathodic reaction, therefore predicting Tafel constant sshould be better estimated of corrosion rate.

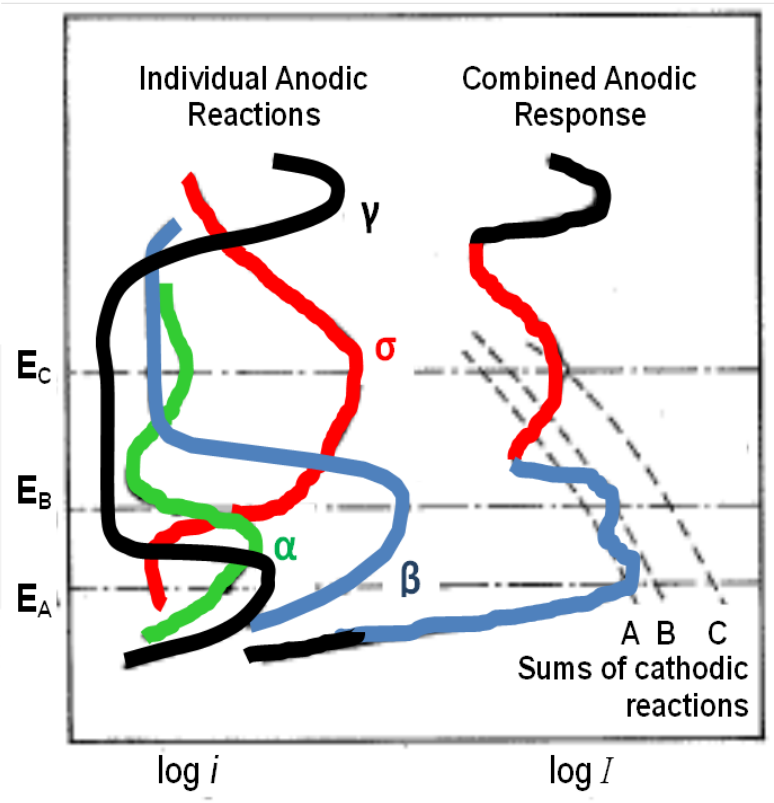
Linear polarization resistance (LPR) measurements

- Anodic and cathodic polarization curves evaluated following stabilization in OCP

$$R_P = \frac{dE}{dI} \quad as\ dE \rightarrow 0$$

Where:

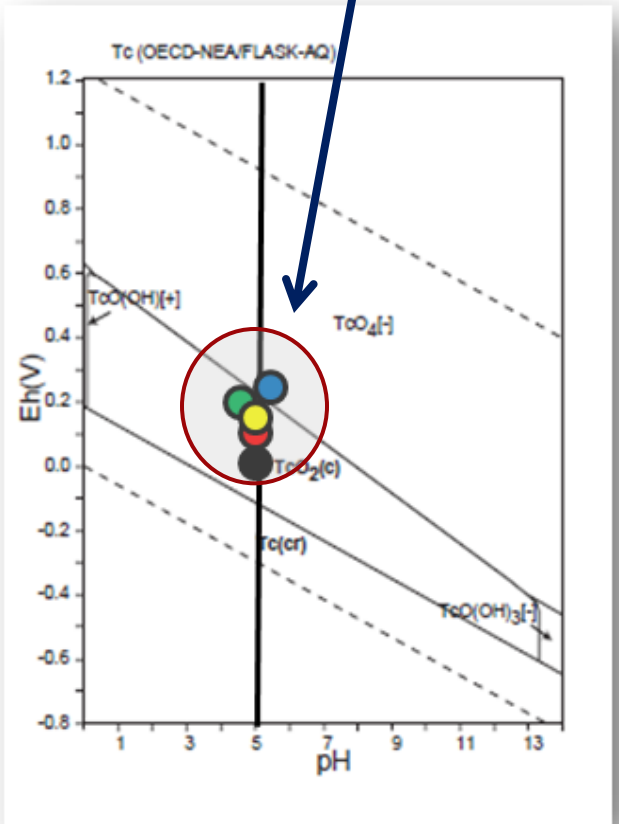
$$E = \frac{I\beta_a\beta_c}{I_{corr}(\beta_a + \beta_c)\ln 10} + E_{corr}$$



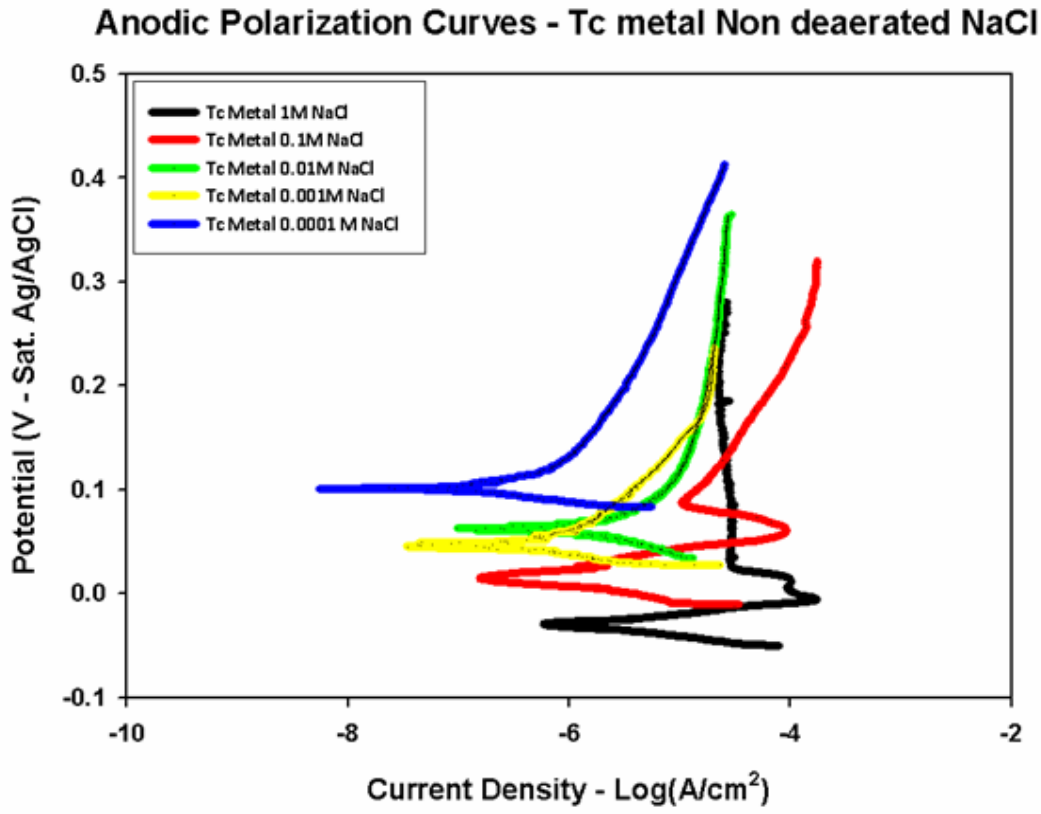
The Stern-Geary equation predicts that for $E > E_{CORR}$ the anodic reaction predominates and for $E < E_{CORR}$ the cathodic reaction predominates.

Tc metal LPR – Sodium Chloride

Tc(IV) will dominate, kinetically limited



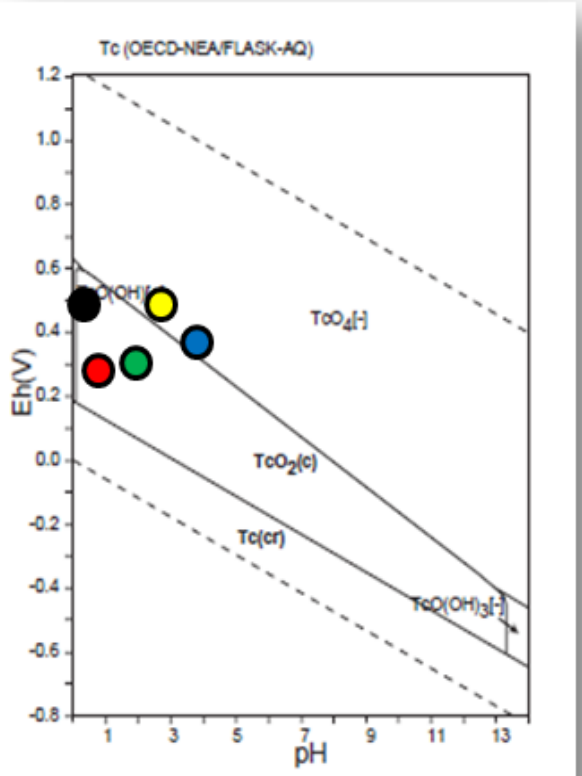
	Tc Metal			
	Rp - Ω	Corr Rate A/cm2	OCP Sat. Ag/AgCl	OCP NHE
1M NaCl	24122	5.838E-04	-0.029	0.168
1E-1M NaCl	112346	1.559E-04	0.015	0.212
1E-2M NaCl	76334	9.624E-05	0.063	0.260
1E-3M NaCl	235380	4.688E-05	0.049	0.246
1E-4M NaCl	473488	5.488E-06	0.101	0.298

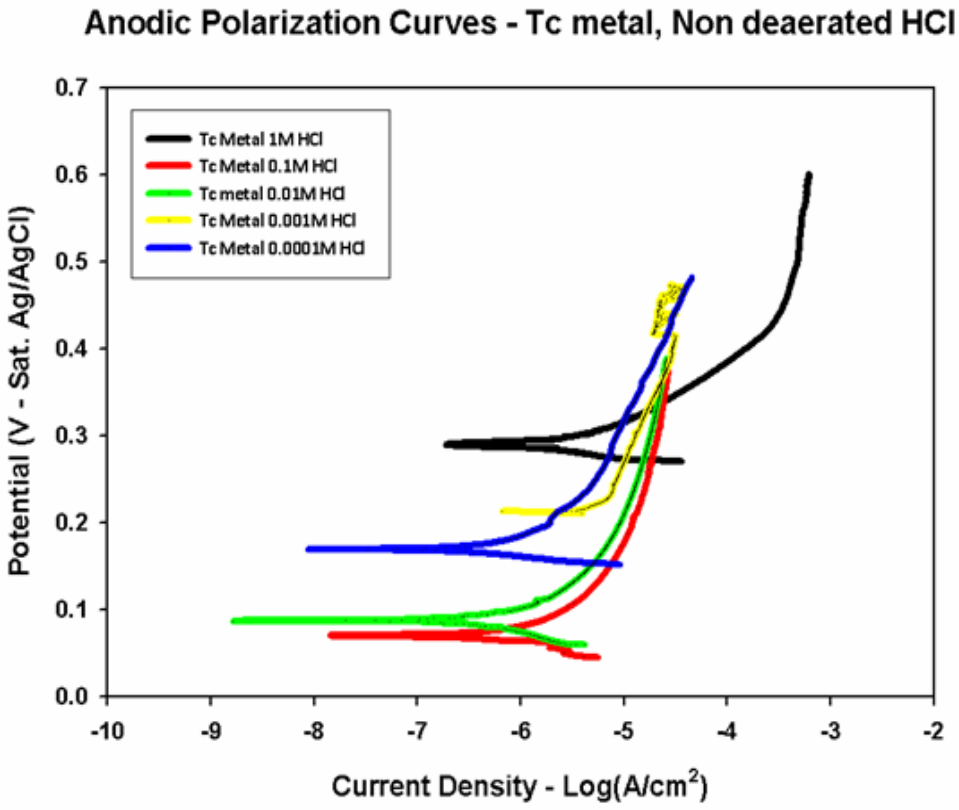


Tc metal LPR – Hydrochloric Acid

- Tc is "immune" to release in reducing acids

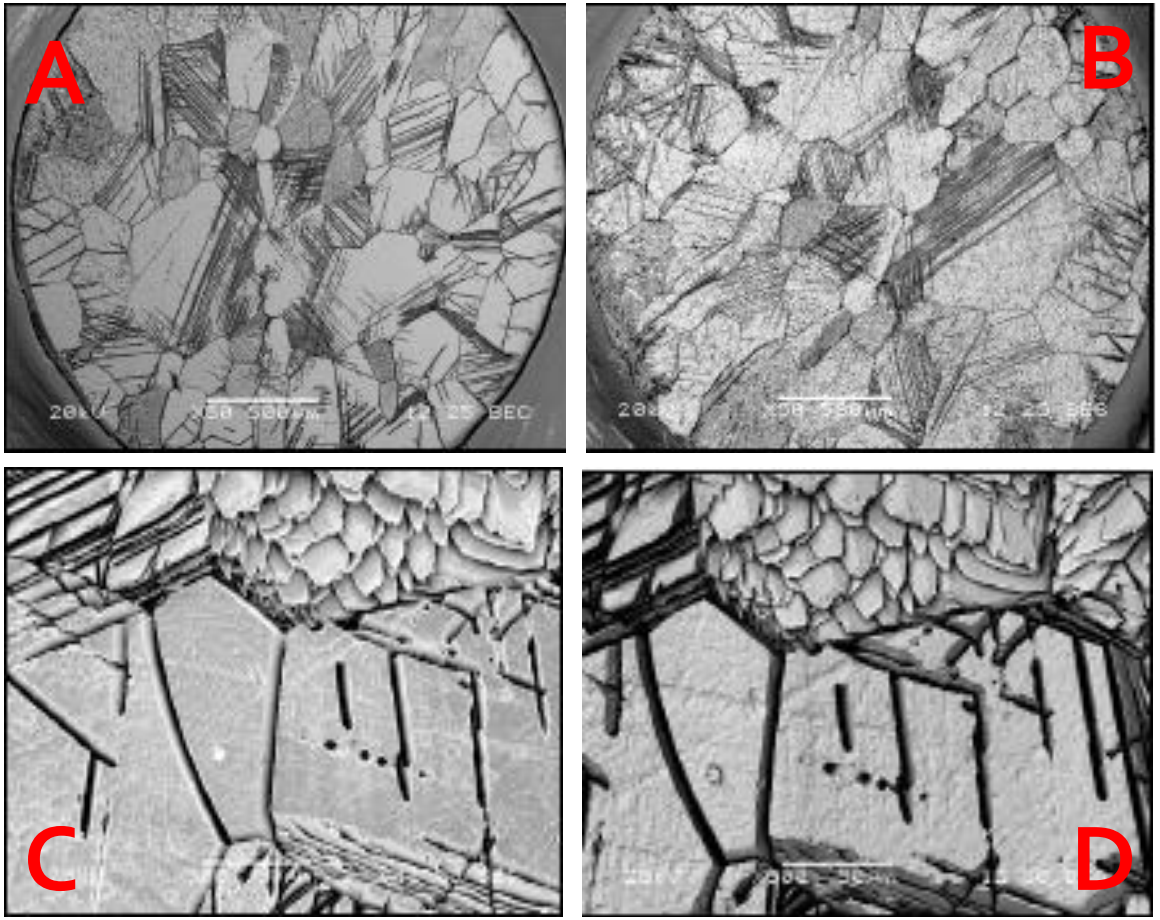
	Tc Metal			
	Rp - Ω	Corr Rate A/cm2	OCP Sat. Ag/AgCl	OCP NHE
1M H_2SO_4	311727	9.648E-05	0.319	0.516
1E-1M H_2SO_4	103578	2.617E-04	0.431	0.628
1E-2M H_2SO_4	183538	4.355E-04	0.360	0.557
1E-3M H_2SO_4	1060000	6.077E-05	0.177	0.374
1E-4M H_2SO_4	520000	4.164E-06	0.378	0.575





SEM - Tc metal, 1 and 2M HCl

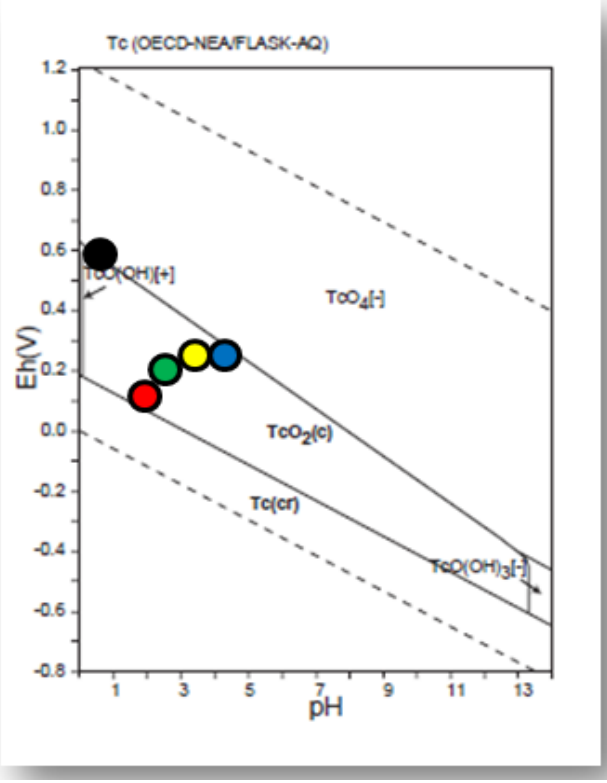
- Bulk Electrolysis
  - **A/C**
    E = [+0.6 V Ag/AgCl]
  - 1M HCl
  - **B/D**
    E = [+0.6 V Ag/AgCl]
  - 2M HCl

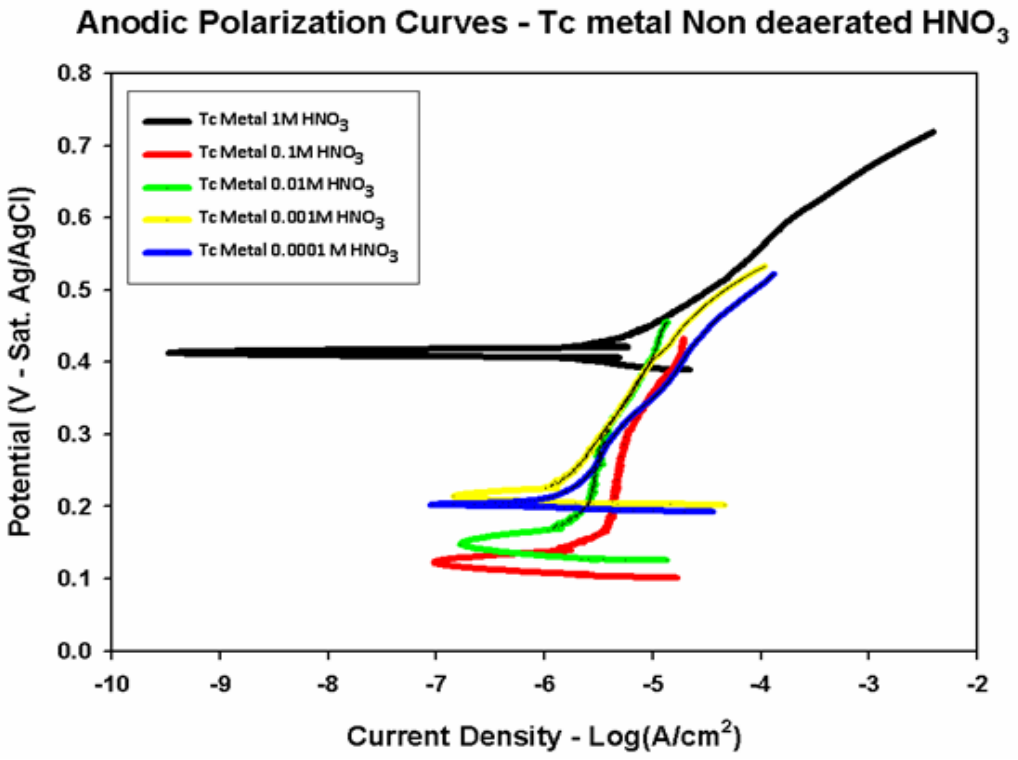


Tc metal LPR – Nitric Acid

- At or below 1M HNO3, Tc metal corrodes slowly but passive states or adsorption is observed

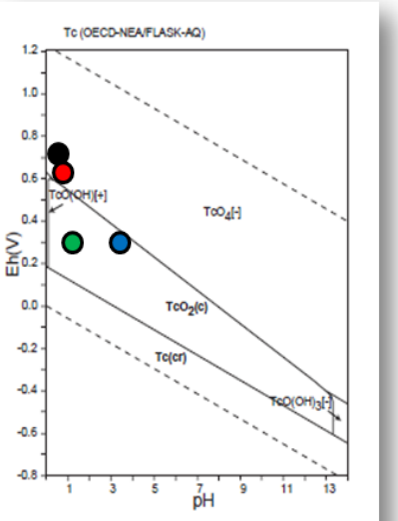
	Tc Metal			
	Rp - Ω	Corr Rate A/cm2	OCP Sat. Ag/AgCl	OCP NHE
1M HNO_3	76608	1.928E-03	0.412	0.609
1E-1M HNO_3	217687	9.367E-05	0.122	0.319
1E-2M HNO_3	251708	1.672E-04	0.147	0.344
1E-3M HNO_3	238870	1.447E-04	0.214	0.411
1E-4M HNO_3	256654	9.213E-05	0.202	0.399

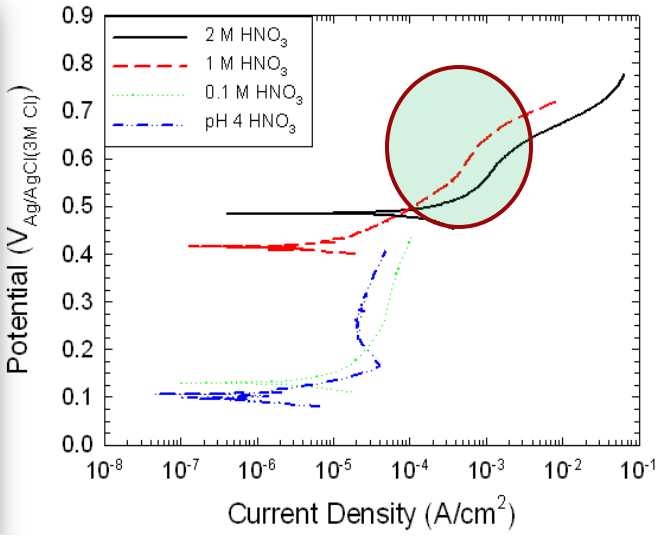


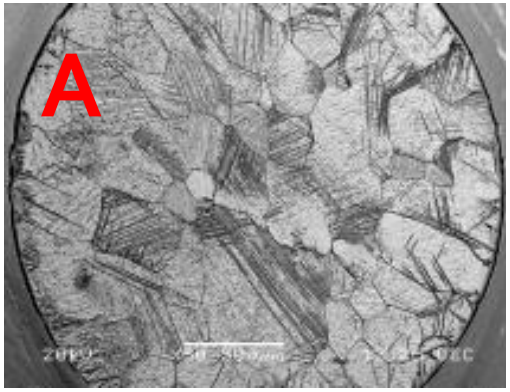


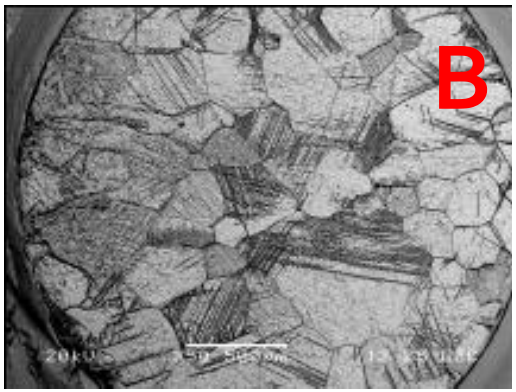
SEM- Tc metal 1M HNO3

- Bulk electrolysis
  - E = [1.0 V Ag/AgCl]
  - t = 5 min
- Post BE
  - A E = [+0.6 V Ag/AgCl
  - 1M HNO3
  - B E = [+0.6 V Ag/AgCl]
  - 2M HNO3





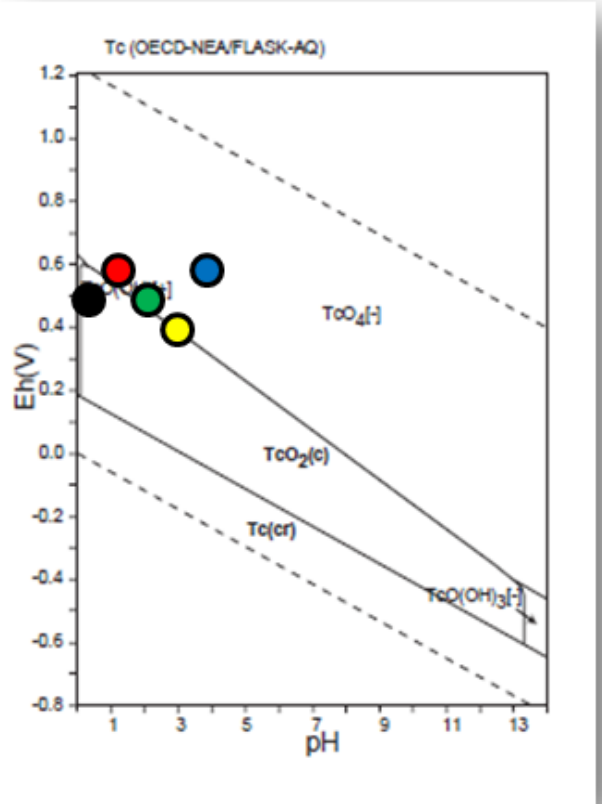


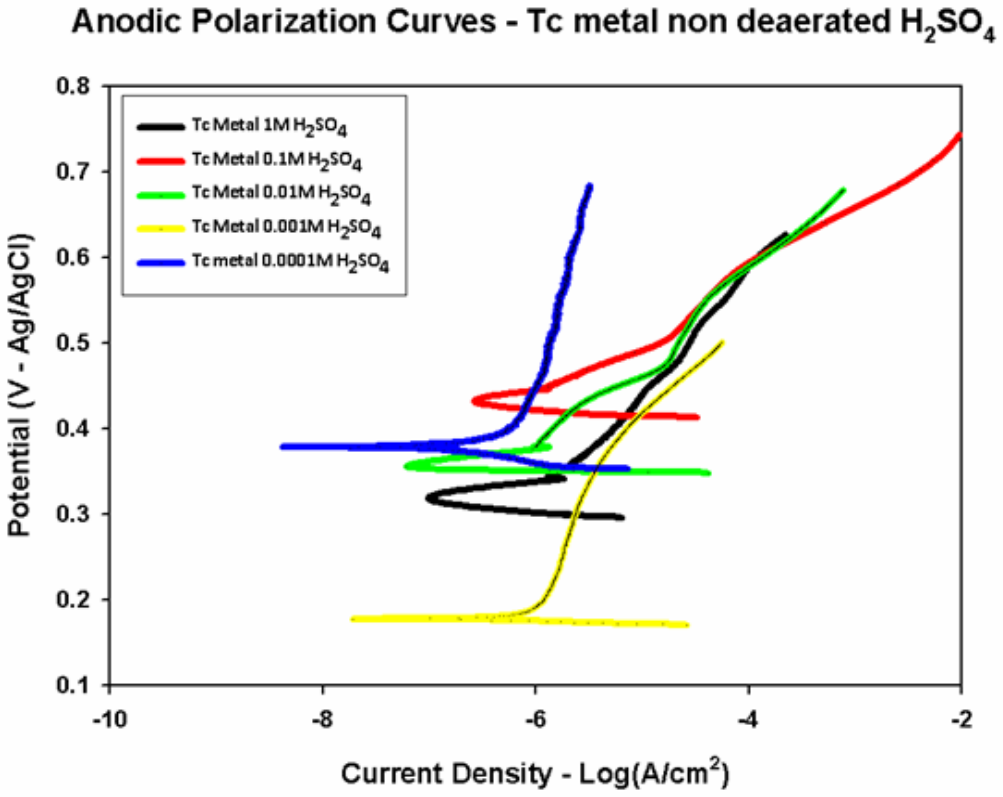


Tc metal – Sulfuric Acid

- Tc metal is much more stable in H_2SO_4, hence deposition qualities of solution

	Tc Metal			
	Rp - Ω	Corr Rate A/cm2	OCP Sat. Ag/AgCl	OCP NHE
1M H_2SO_4	311727	9.648E-05	0.319	0.516
1E-1M H_2SO_4	103578	2.617E-04	0.431	0.628
1E-2M H_2SO_4	183538	4.355E-04	0.360	0.557
1E-3M H_2SO_4	1060000	6.077E-05	0.177	0.374
1E-4M H_2SO_4	520000	4.164E-06	0.378	0.575

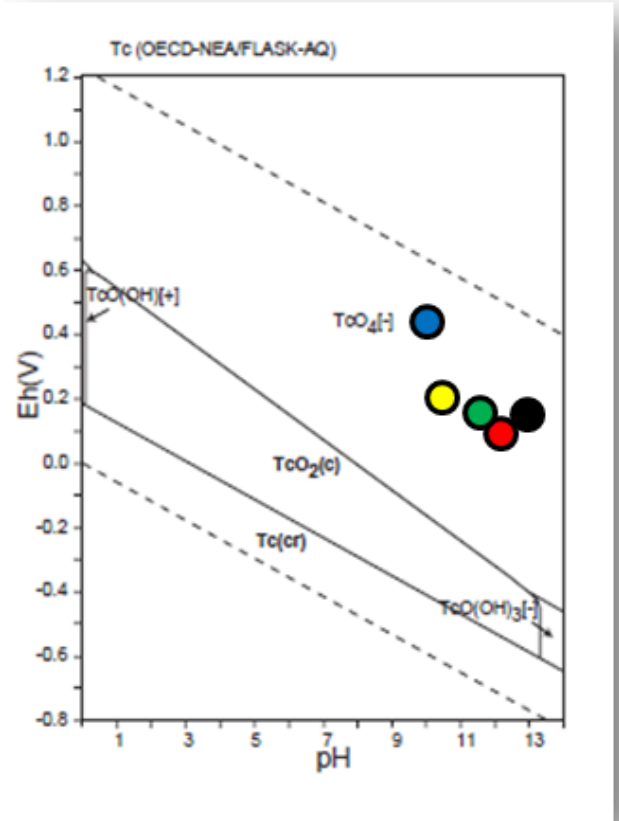


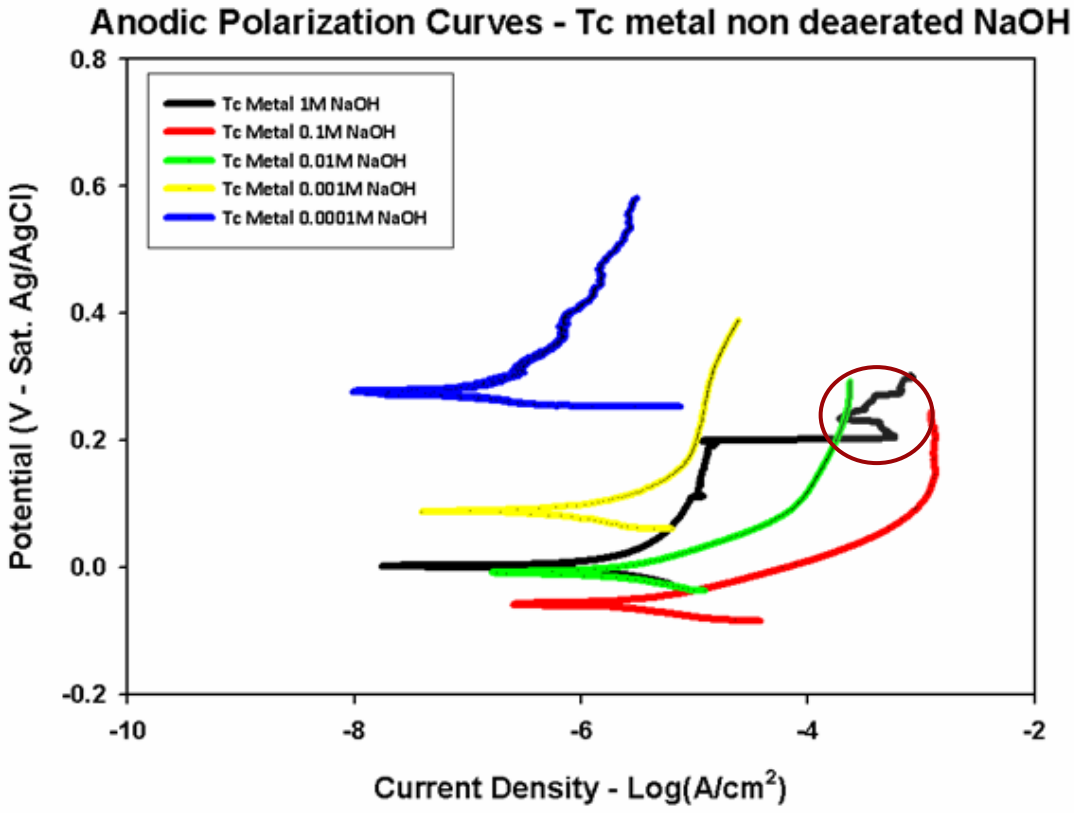


Tc metal – Sodium hydroxide

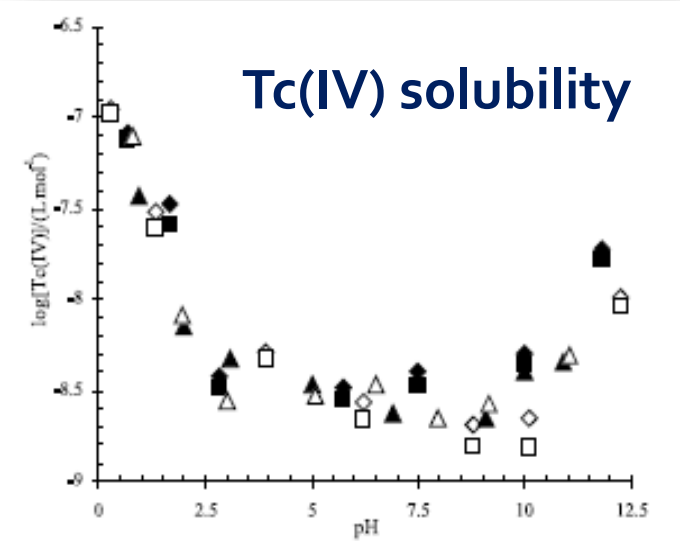
- Observe Tc breakdown in 1M NaOH. Active corrosion of Tc, but passivity and preferential Tc(IV) redox limits Tc(VII) formation under these conditions

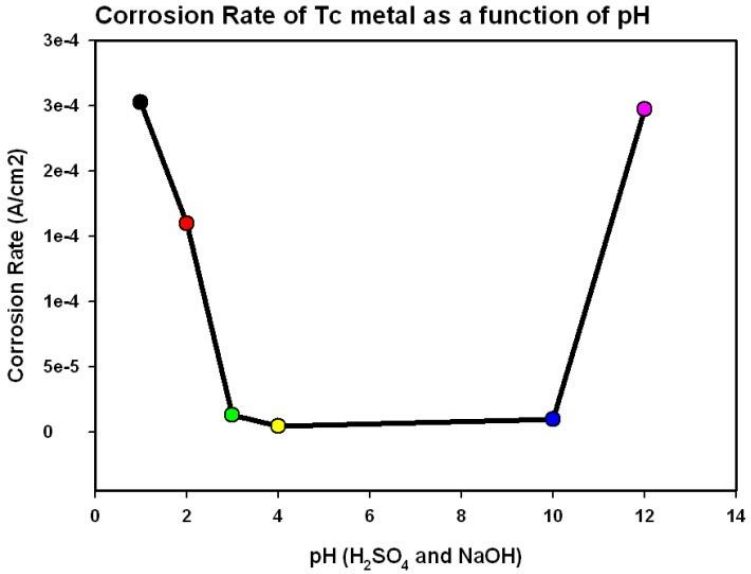
	Tc Metal			
	Rp - Ω	Corr Rate A/cm2	OCP Sat. Ag/AgCl	OCP NHE
1M NaOH	116315	9.562E-07	0.002	0.199
1E-1M NaOH	43923	1.368E-05	-0.059	0.138
1E-2M NaOH	73331	9.824E-06	-0.008	0.189
1E-3M NaOH	185905	2.134E-06	-0.087	0.110
1E-4M NaOH	1640000	5.290E-07	0.277	0.474





Effect of pH on corrosion – non complexing solution conditions





Corrosion rate as a function of pH mimics Tc(IV) solubility shape. Both may be used to estimate life-time of each phase.

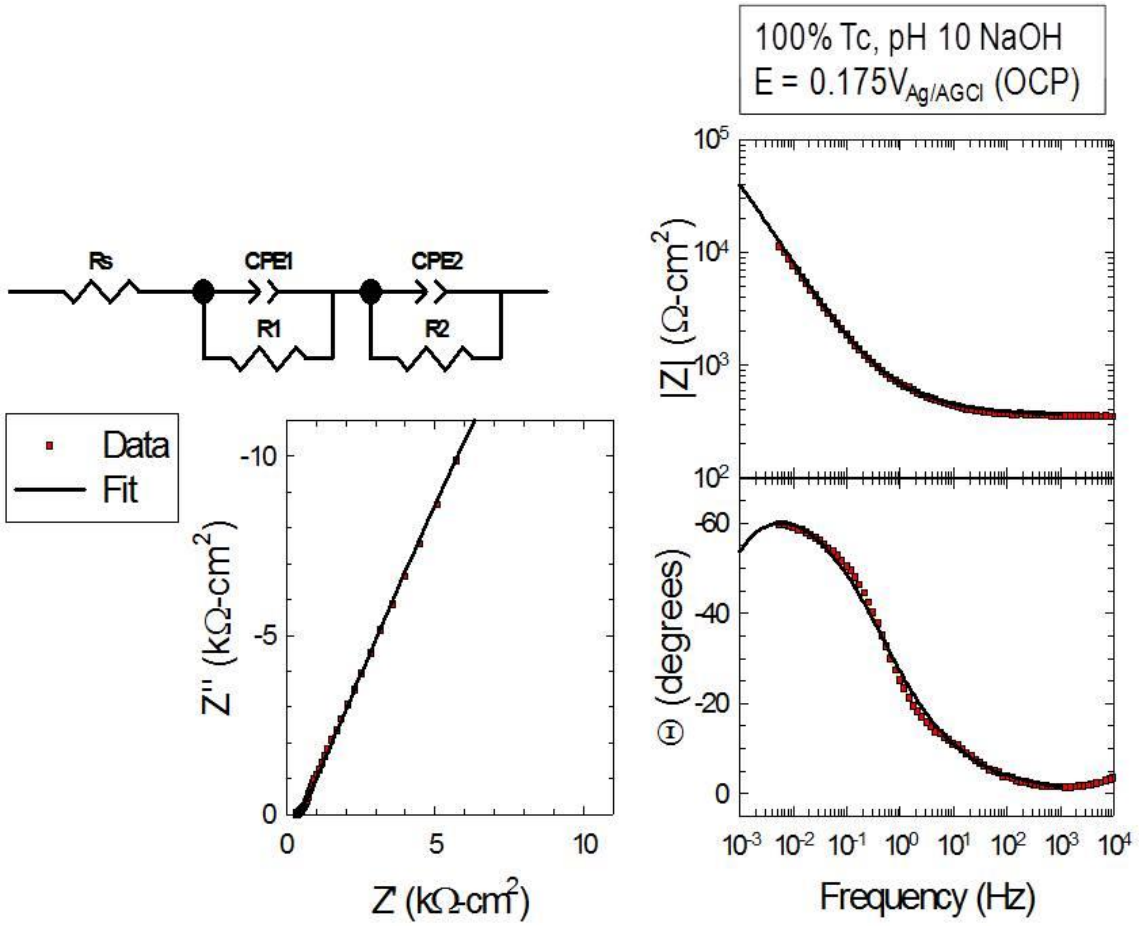
As metal degrades, if Tc(IV) stability region is observed, the dissolution rate of Tc(IV) may be evaluate.

Layers may be electrodeposited representing uniform corrosion from these solutions where the metal is not to be studied

Electrode: Tc Metal		
Media	Corrosion Rate (A/cm2)	OCP
pH 1	2.527E-04	0.728
pH 2	1.594E-04	0.657
pH 3	1.296E-05	0.474
pH 4	4.193E-06	0.675
pH 10	9.607E-06	0.574
pH 12	2.469E-04	0.238

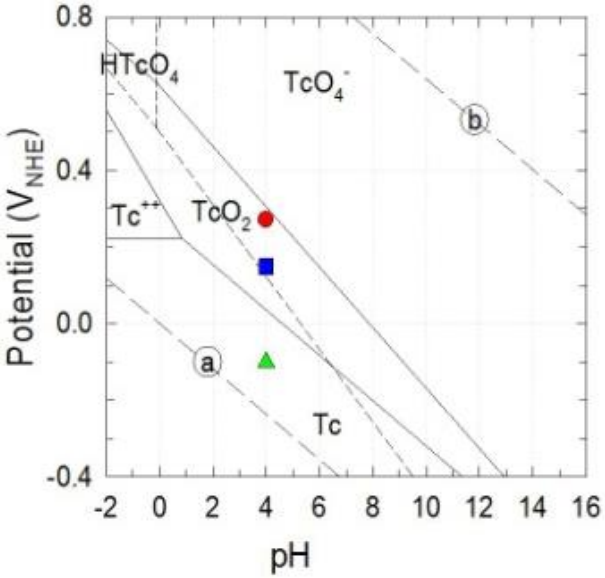
Limited EIS – Tc metal pH 10 NaOH

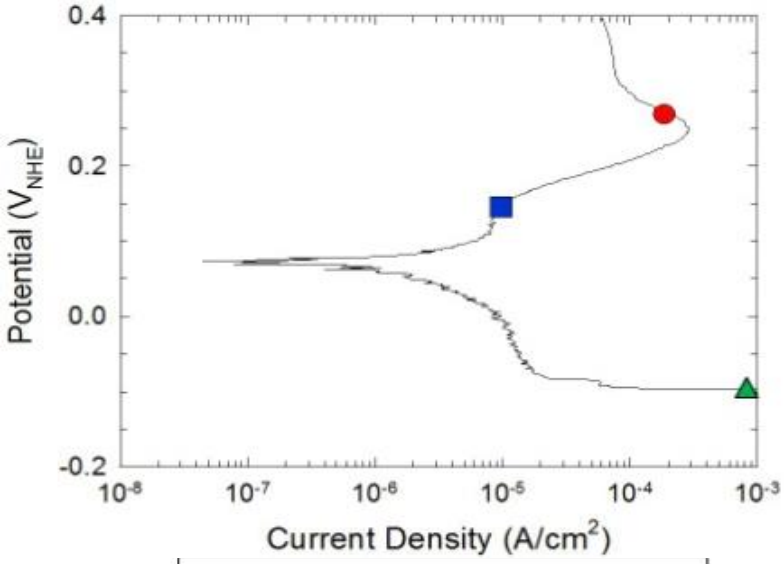
- Fit to a 2-resistor equivalent circuit
- Two time constants observed
  - Layer formation
    - Oxide
    - Adsorption of OH^-

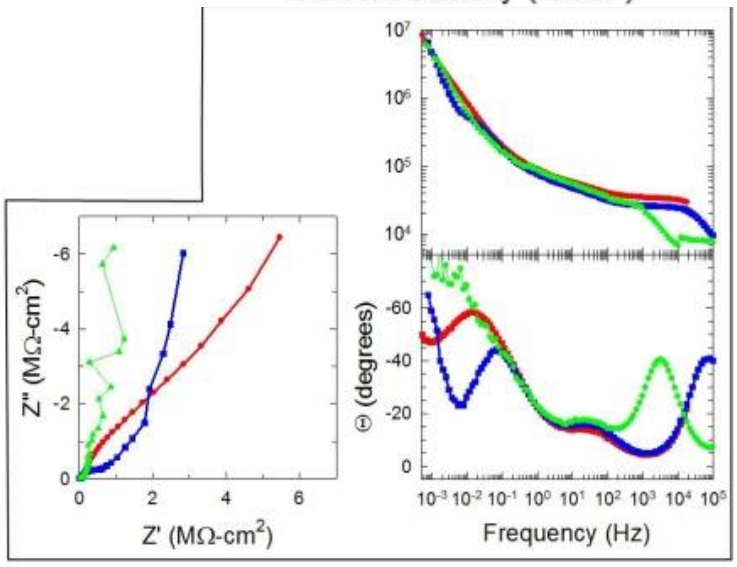


Limited EIS – Tc Metal pH 4 HNO3

- 3 regions of Tc stability evaluated
  - Tc Immunity
  - Tc(IV)
  - Tc(IV/VII)



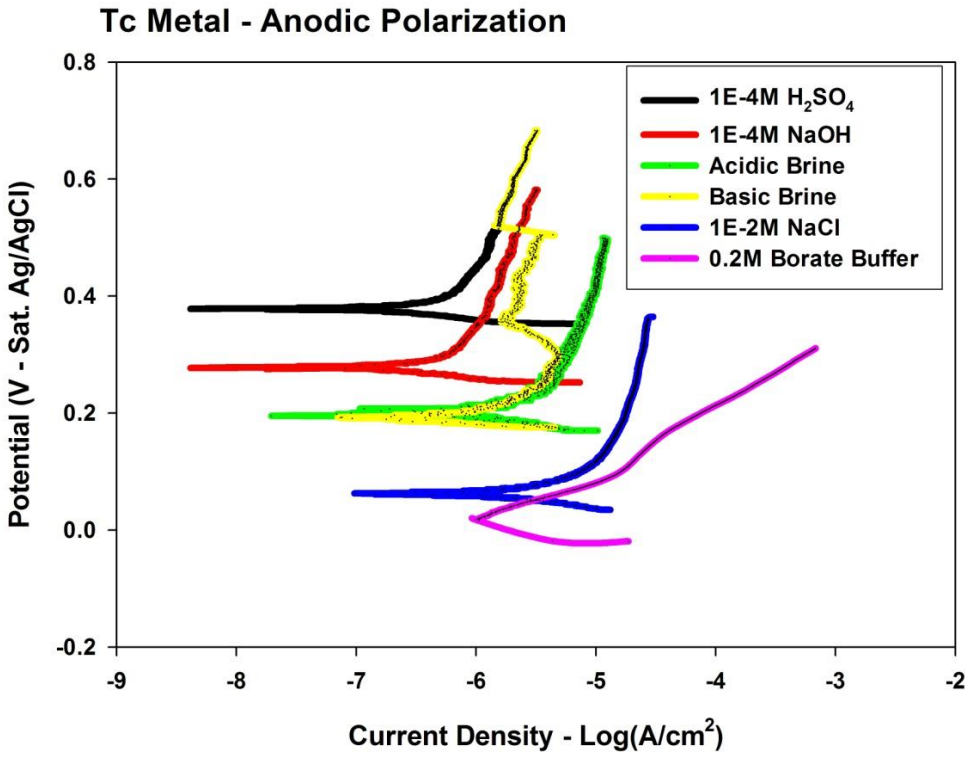




Increases in impedance observed as potential is ramped (EIS Red > Blue > Green lines)

Tc Metal in the Environmental Solution Set

- Tc is not readily attacked by Cl^-
- Passivity is observed in the basic brine solution
  - Similar unknown layers exist in all other solutions at higher potentials
- Data suggests nobility of Tc within the environments

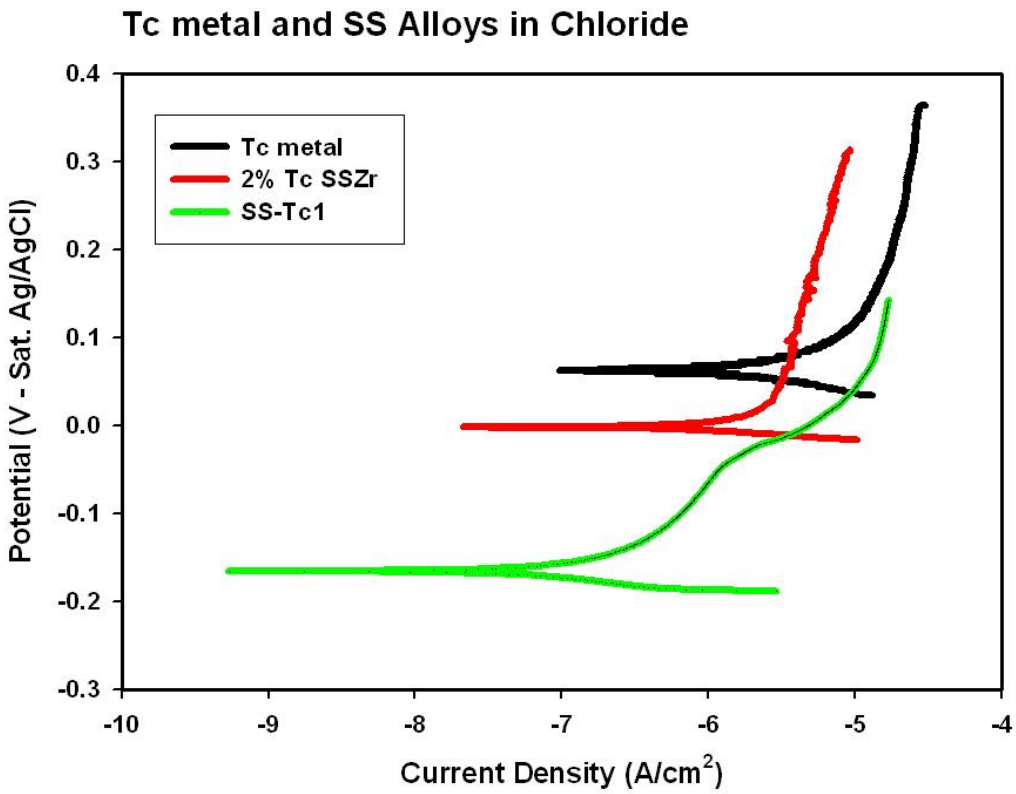


Tc Metal - 0.05463 cm²

	Rp - Ω	Corr Rate A/cm2	OCP Sat. Ag/AgCl	OCP NHE
1E-4M H2SO4	494527	4.165E-06	0.378	0.575
1E-4M NaOH	1360000	9.558E-06	0.276	0.473
Acidic Brine	152551	1.948E-05	0.195	0.392
Basic Brine	248866	7.383E-05	0.192	0.389
1E-2M NaCl	78585	9.624E-05	0.063	0.26
0.2M Borate Buffer	190000	9.944E-04	0.018	0.215

Effects of alloying Tc

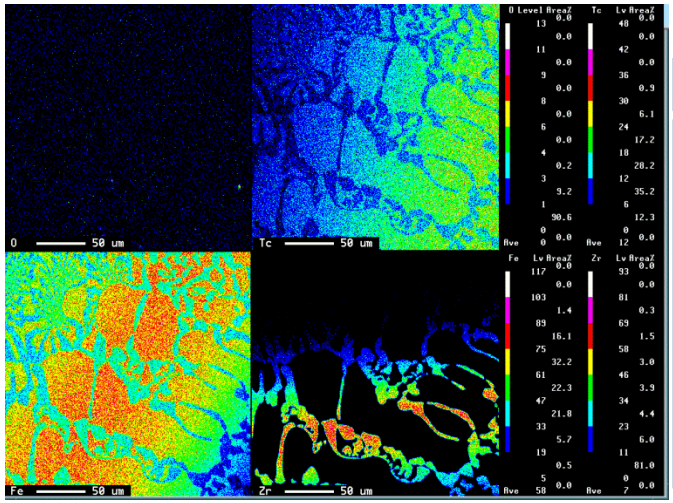
- The OCP of a host material is decreased in both the SS/Zr intermetallic and Fe solid solution, stainless material.
  - In all cases, Tc does not reside in the immunity region, unfortunately.



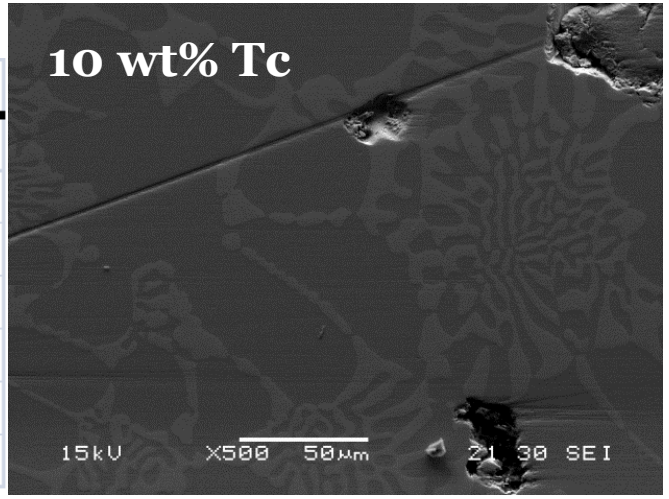
LPR in 0.01M NaCl

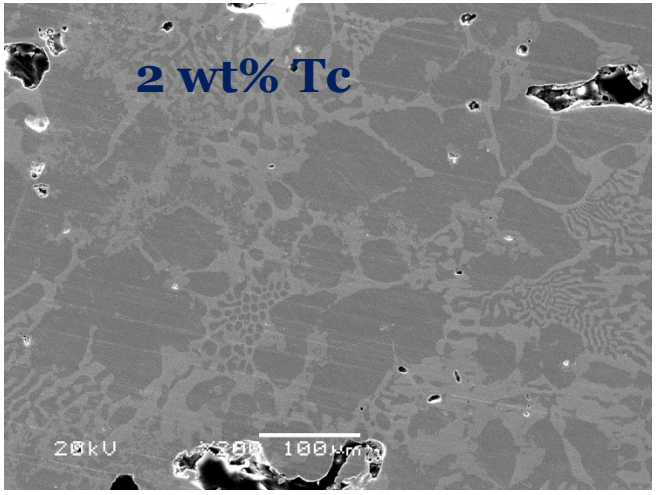
It should be noted that Tc is more noble than either phase

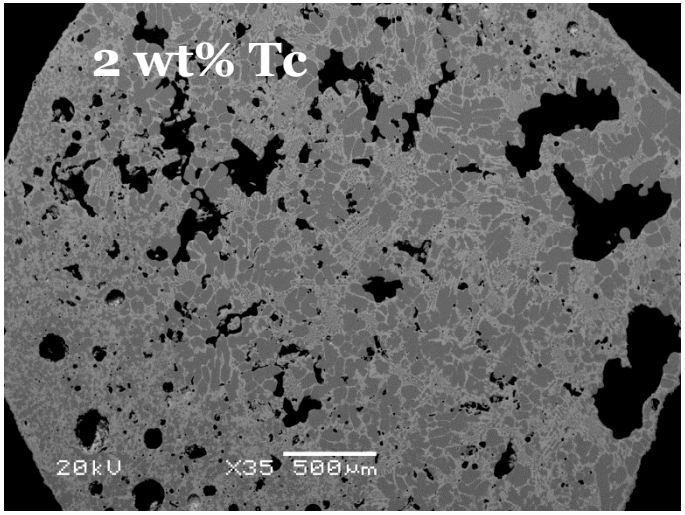
Tc in SS_{85}-Zr_{15}



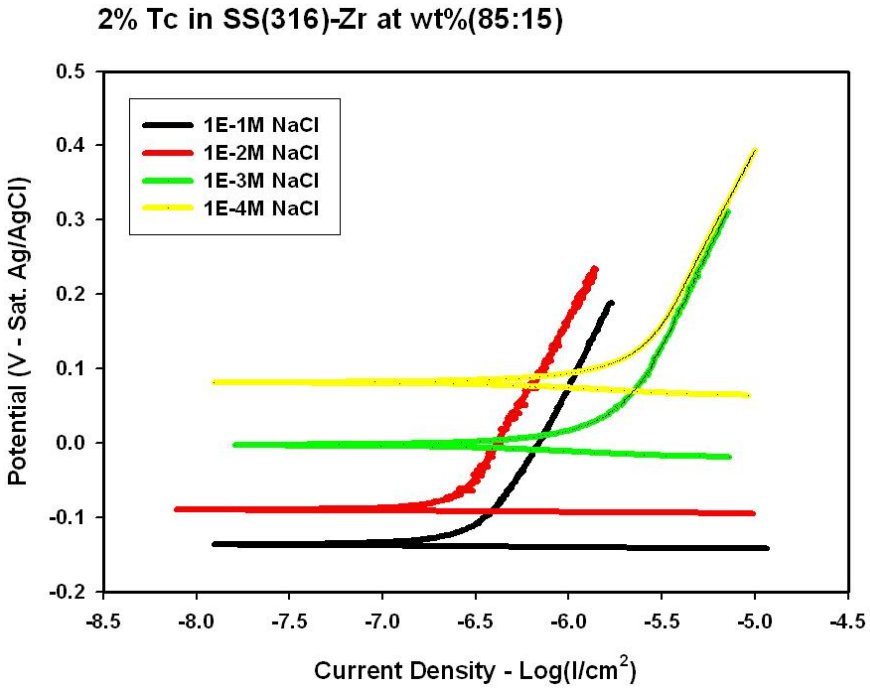
Element	Dark Phase	Light Phase
Zr	0%	29%
Fe	64%	37%
Tc	11%	8%
Cr	18%	4%
Mo	2%	2%
Ni	7%	17%
Total	100.7	96.60%

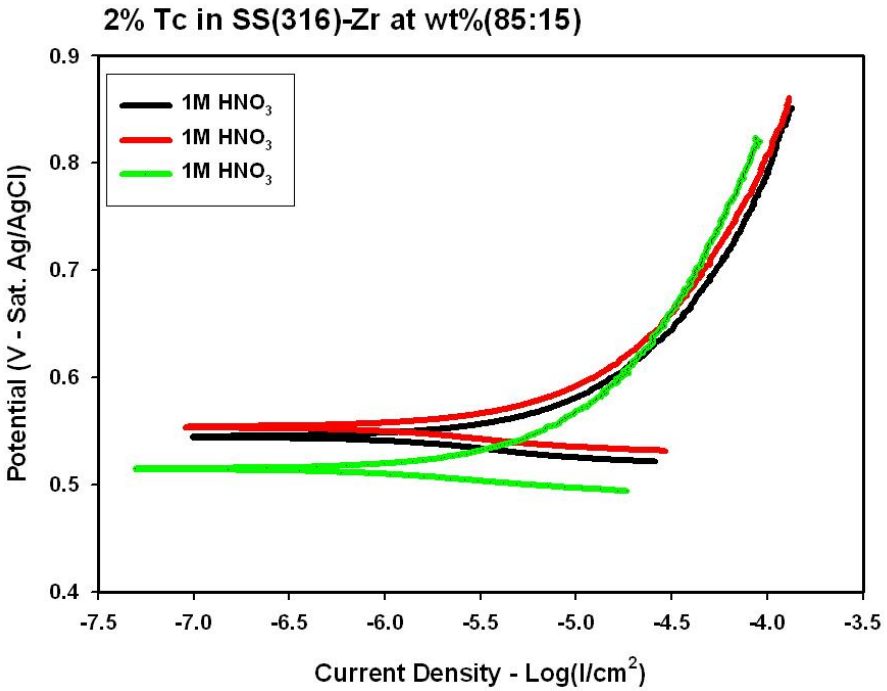






2 wt% Tc SSZr in HNO_3 and Cl^-





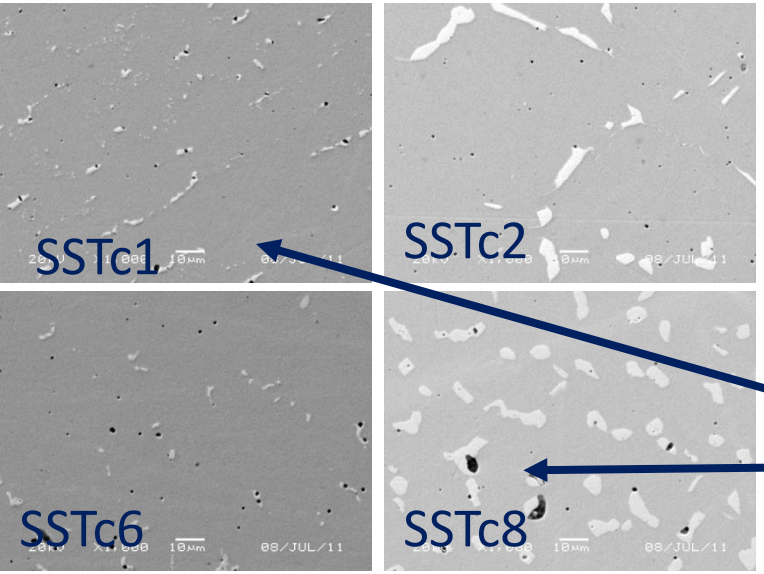
Alloy appears to be little effected by the presence of chloride on corrosion behavior, similar to Tc.

Semi-passive state is unchanged

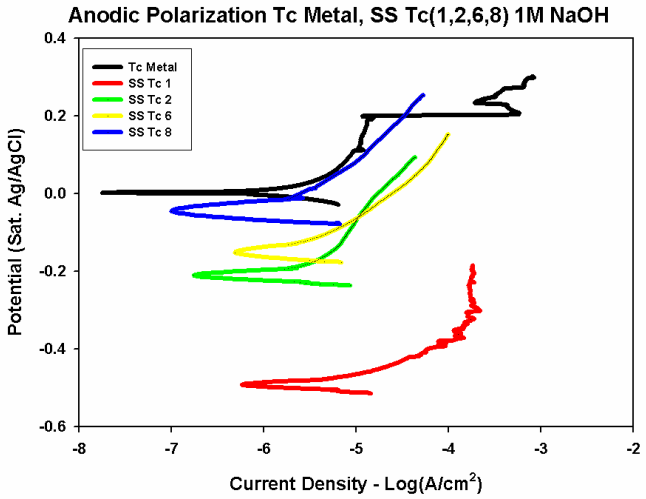
Replicate experiments after polishing many times shows the behavior of the alloy is essentially unchanged over a period of 1 year.

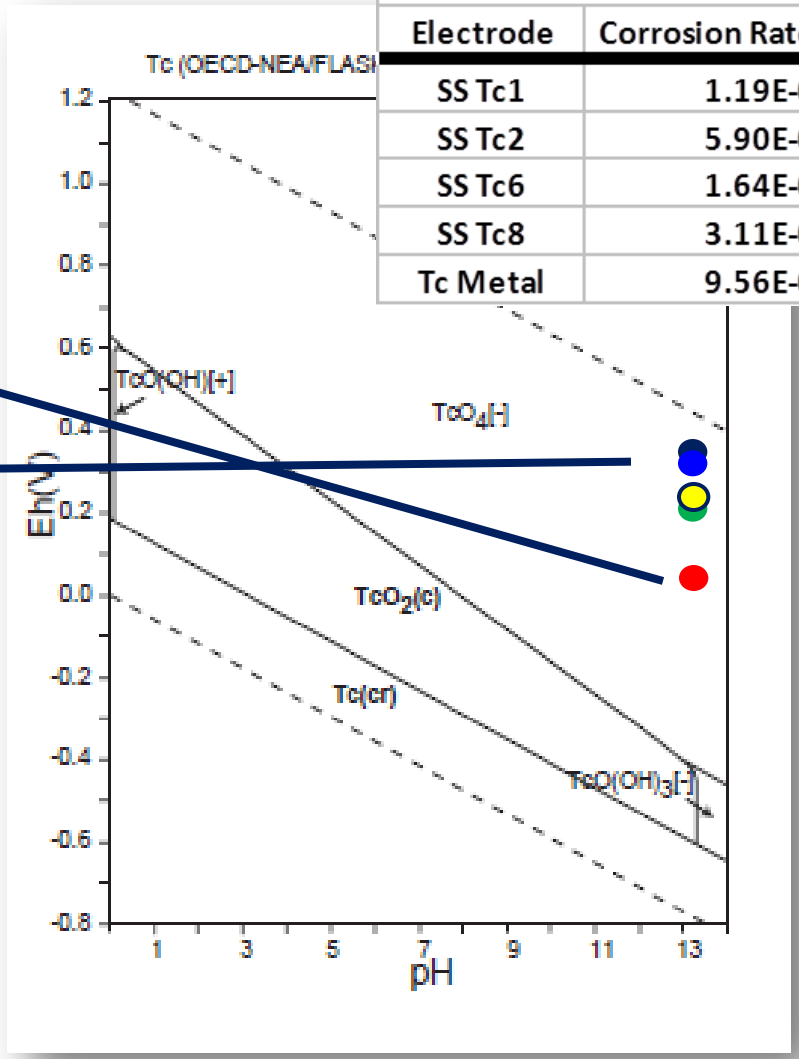
Suggests a single phase alloy may not be required to host radioelements

Fe-solid solutions – LPR 1M NaOH



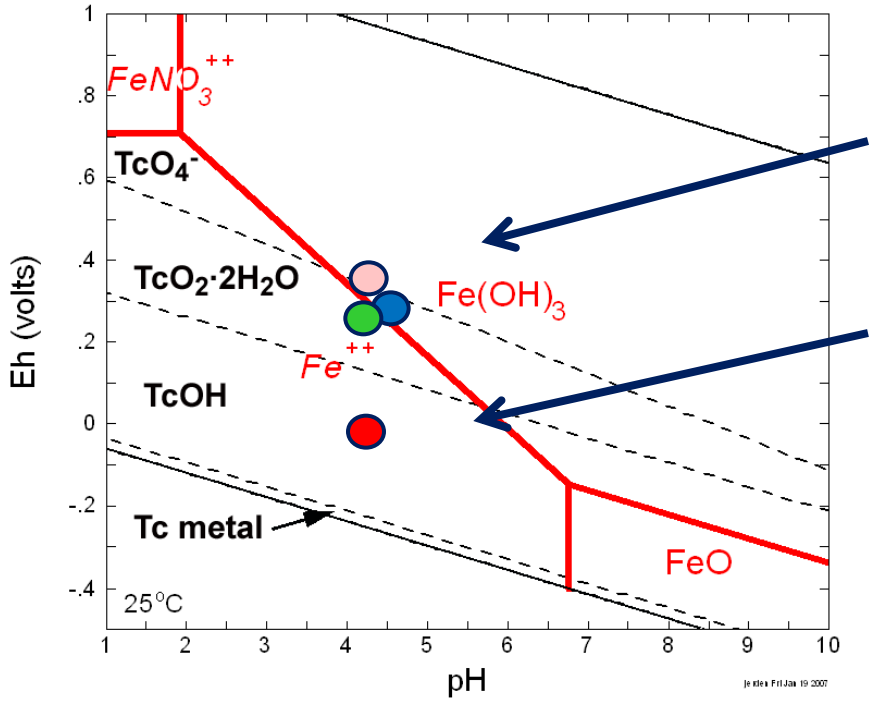
1M NaOH		
Electrode	Corrosion Rate (A/cm2)	OCP vs NHE
SS Tc1	1.19E-05	-0.296
SS Tc2	5.90E-06	-0.014
SS Tc6	1.64E-05	0.045
SS Tc8	3.11E-06	0.152
Tc Metal	9.56E-07	0.198





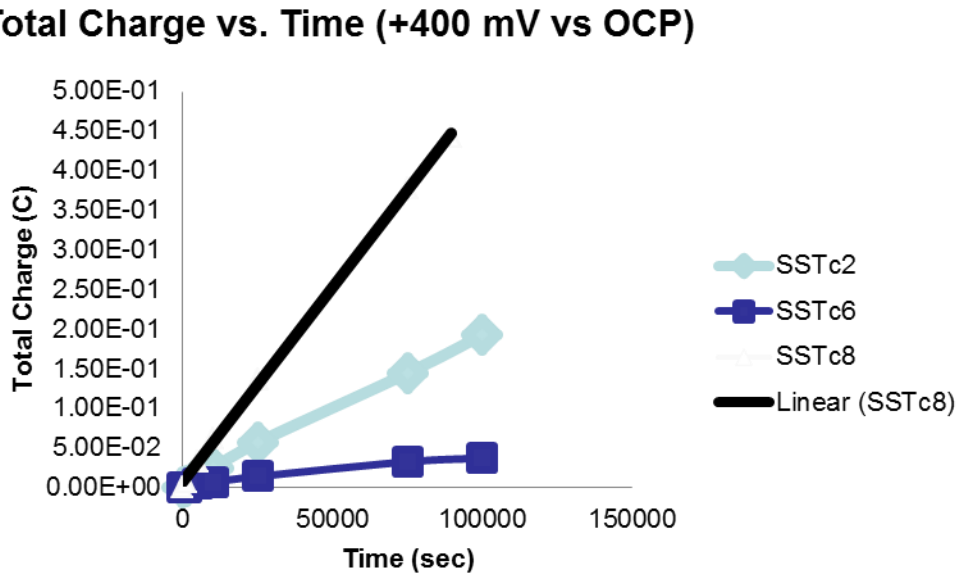
Release of Tc from materials

SSTc1,2,6,8 – Eh(V, NHE) vs pH,
Acidic Brine (0.01M NaCl + 1E-4m H_2SO_4), Electrochemical Leach



SSTc2 OCP = 0.3042 V NHE
SSTc6 OCP = 0.2729 V NHE
SSTc8 OCP = 0.2273 V NHE

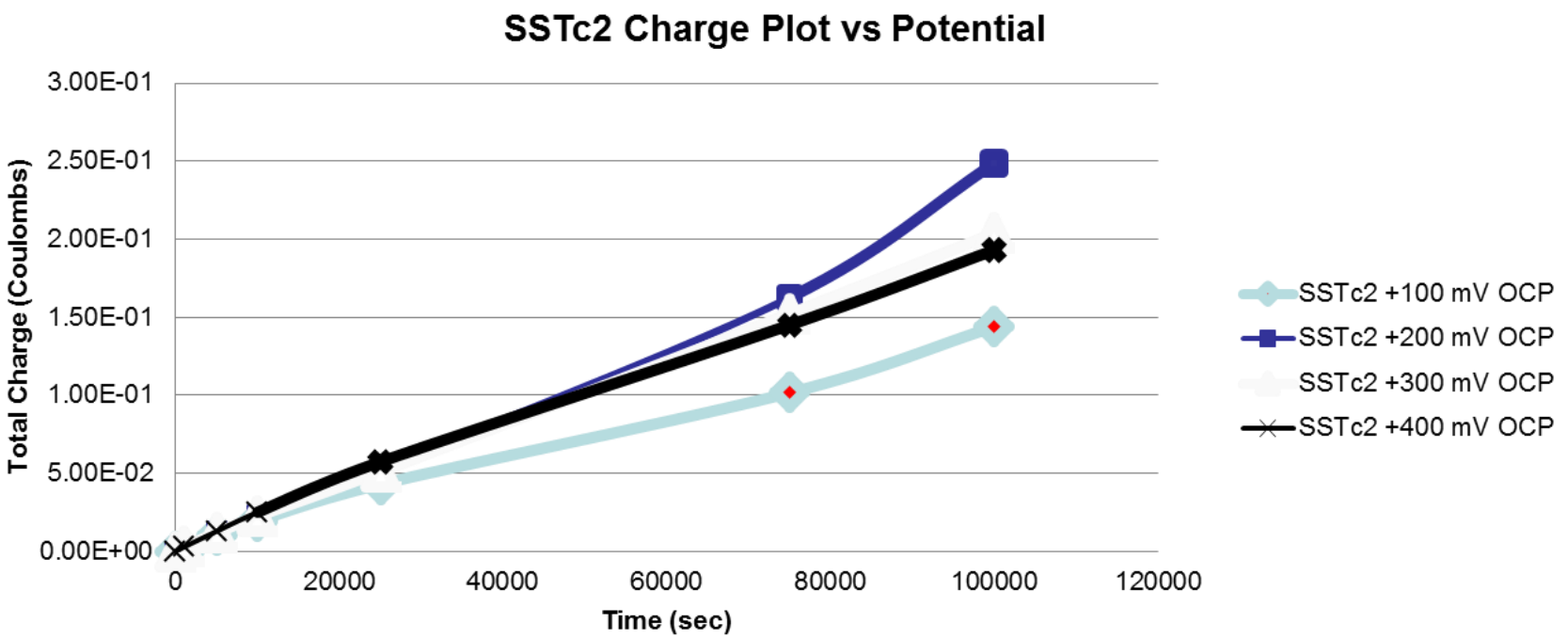
SSTc1 OCP = -0.0606 V NHE



- Rate of corrosion can be correlated to total current expelled from alloy at corroding potentials
- No soluble forms of Tc are present; LS counting suggests that Tc is held in alloy effectively

Bulk Electrolysis

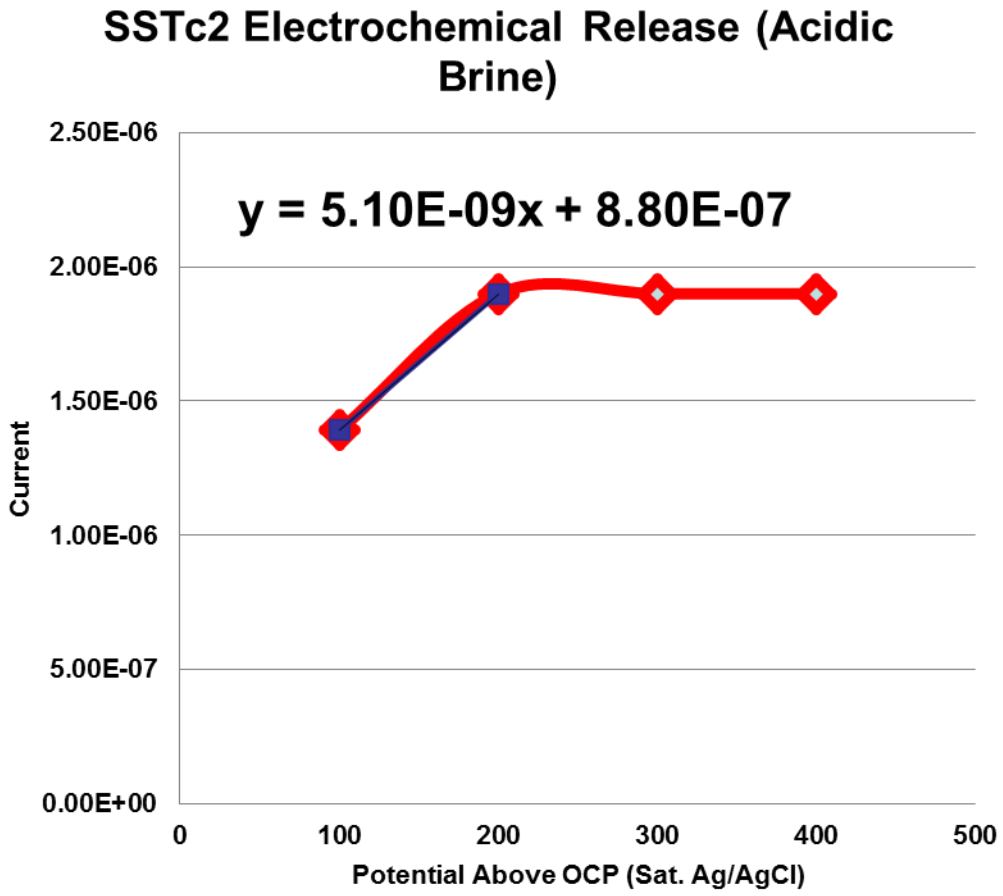
SSTc2 – Constant Current Plots in Acidic Brine (1E-4M H_2SO_4 + 0.01M NaCl)



- At elevated potentials, constant current is experienced indicating that passive regions are formed on surface of sample at higher potentials.
- Each test resulted in no detectable Tc by LS counting (DL ~ 1E-8M)

Bulk Electrolysis

SSTc2 – Constant Potential, Current/Plot Slope vs. Potentials above OCP



SSTc2 - +100, +200, +300, +400 mV vs. OCP

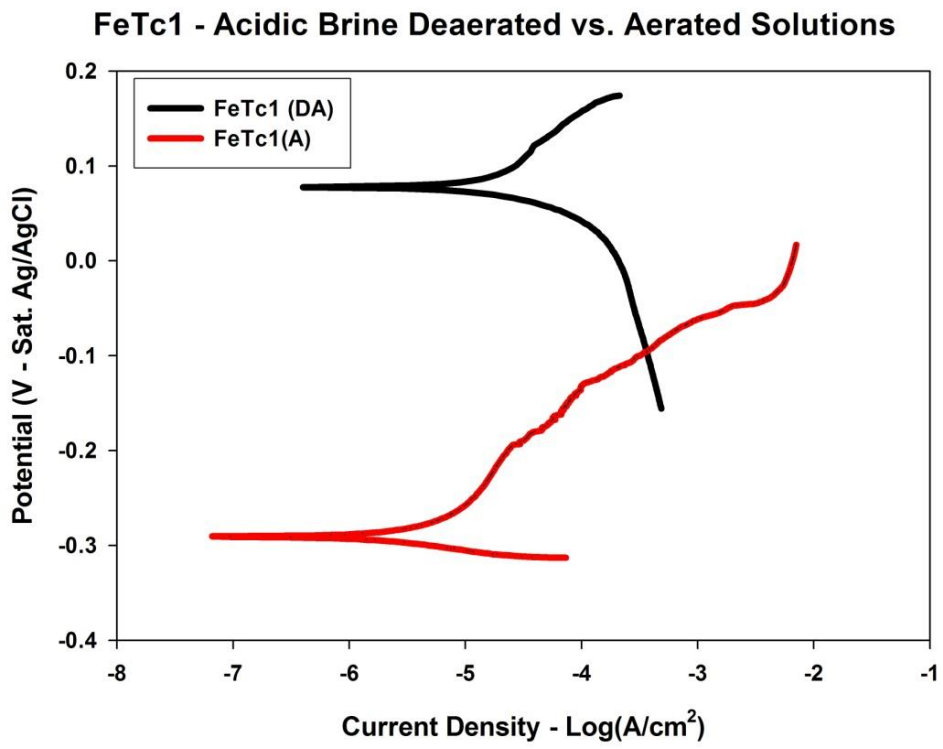
Instantaneous current plot versus potential

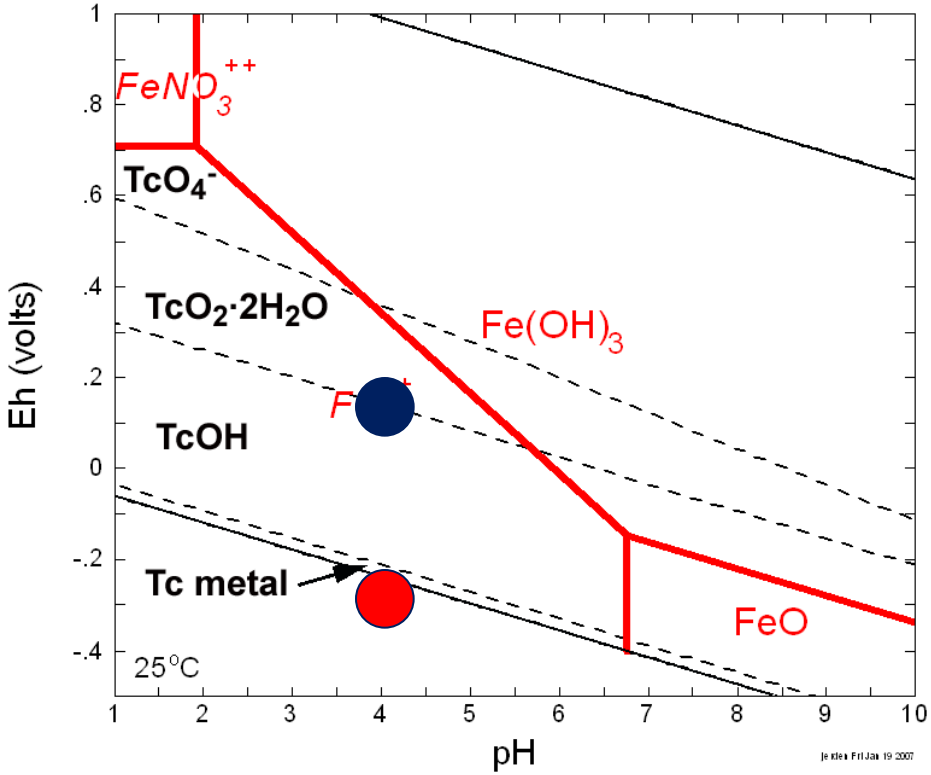
I_{CORR} ~ 1E-7 to 1E-6 A/cm²

Constant potential
I_{CORR}8.80E-7 A/cm²

FeTc1 – Acidic Brine LPR (DA vs A)

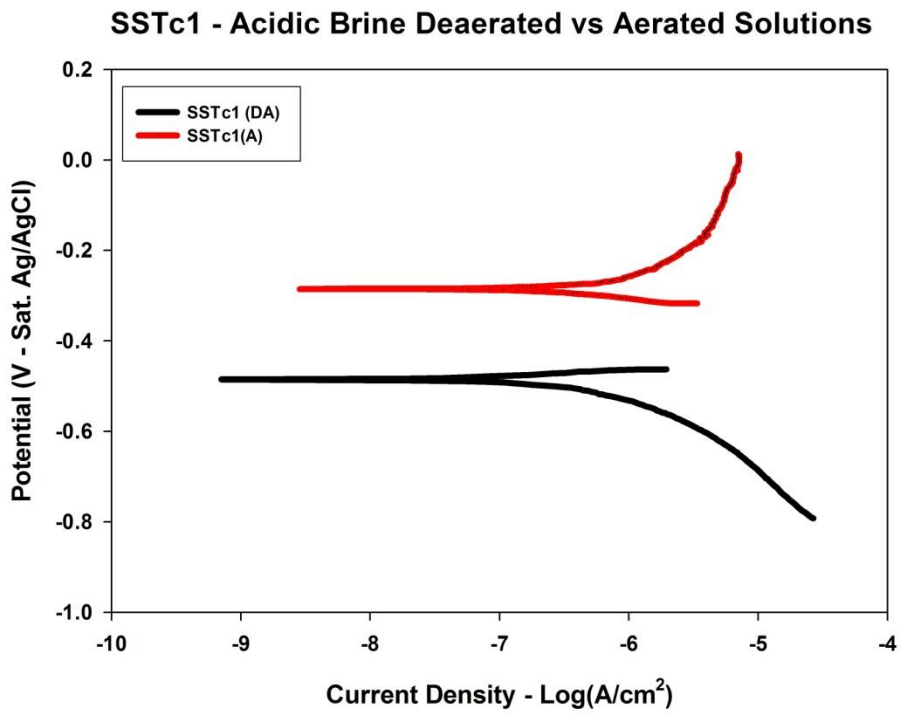
- Stainless aducts such as Cr are missing in Fe(Tc1); SSTc1 homologue
- Cl^- removes passivity effects

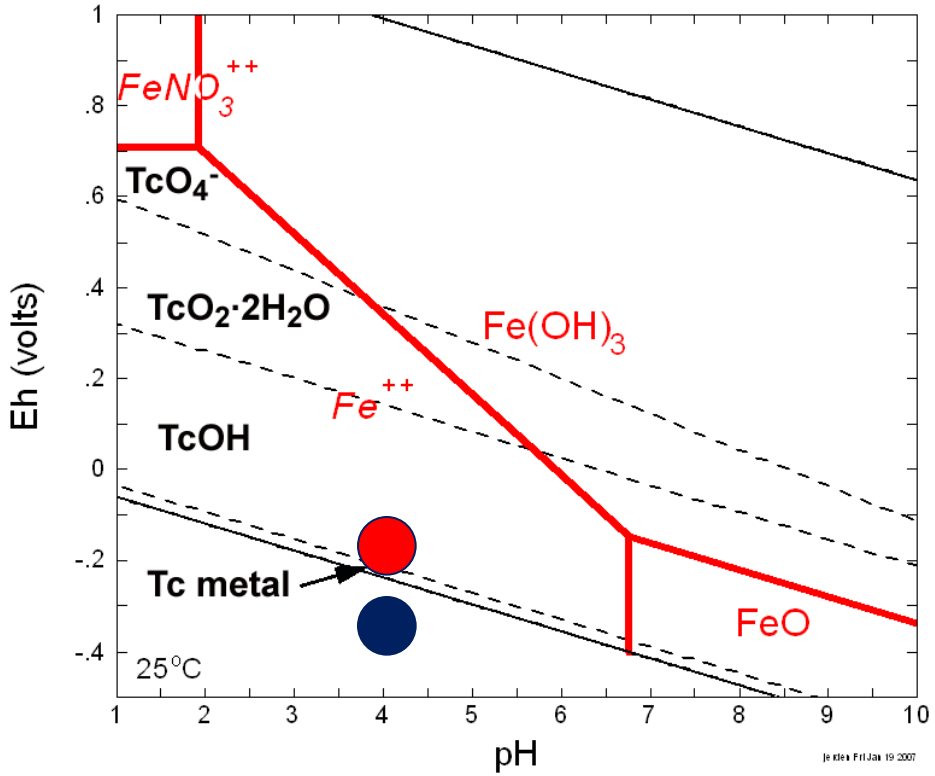




SSTc1 - Acidic Brine LPR (DA vs A)

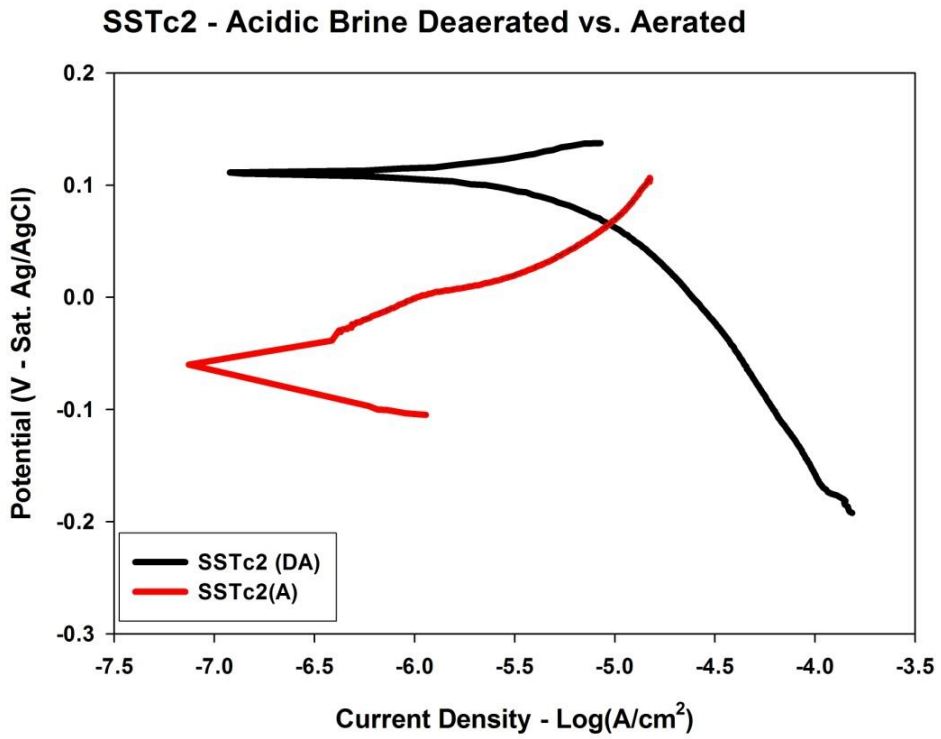
- SSTc1 – Removal of O_2 makes material immune
- Cl^- does not effect initial passivity under these conditions

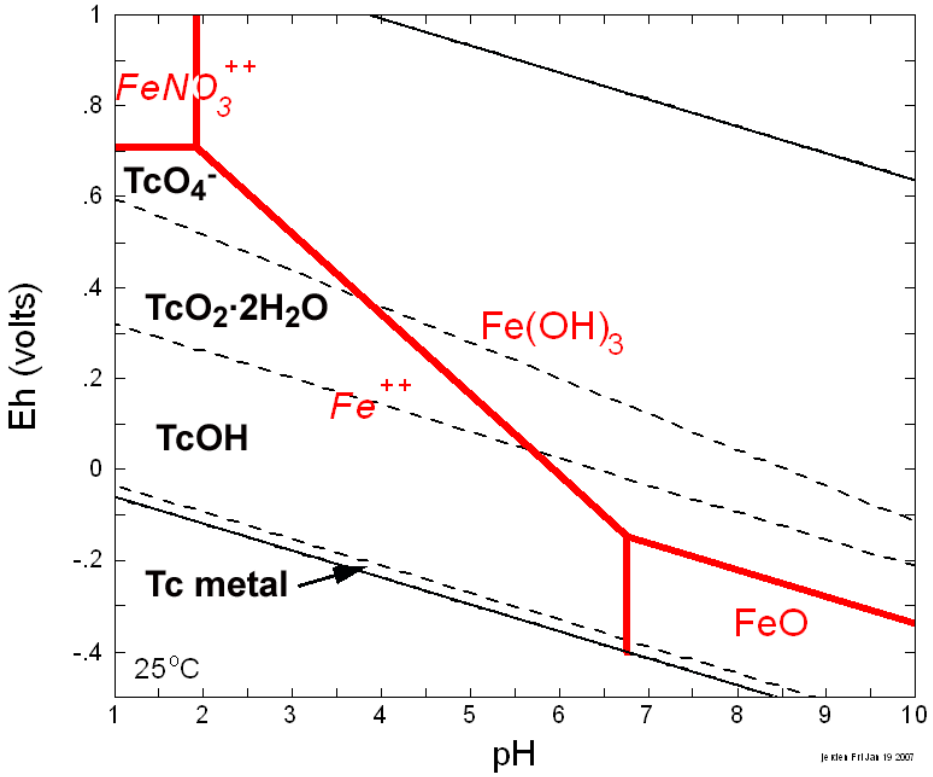




SSTc2 - Acidic Brine LPR (DA vs A)

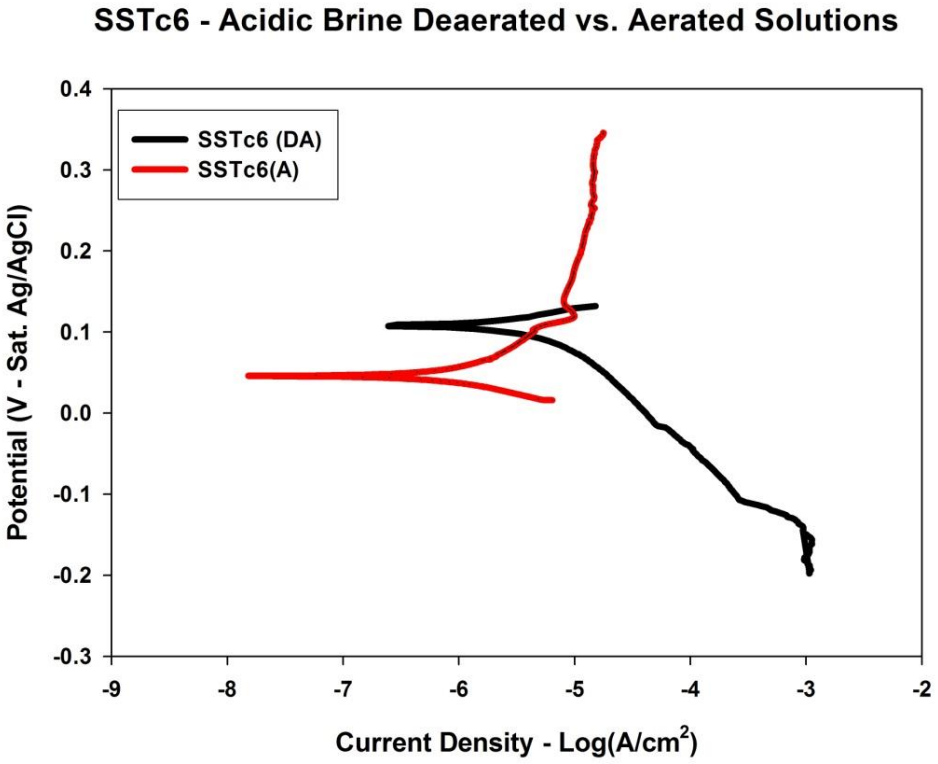
- Nobility of phase increases

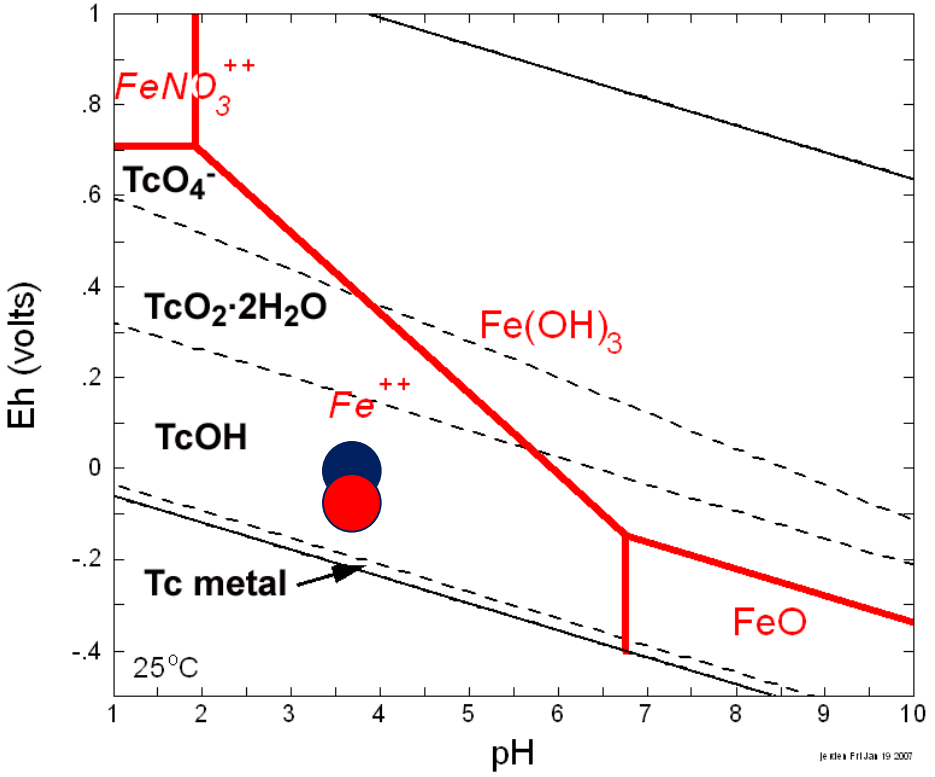




SSTc6 – Acidic Brine LPR (DA vs A)

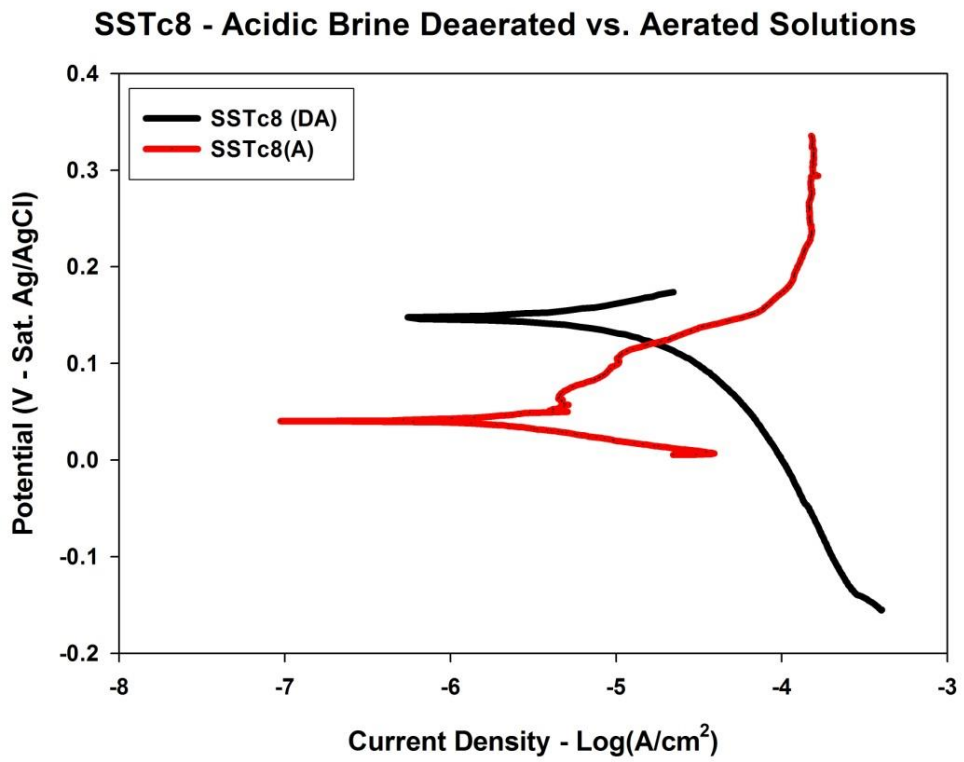
- OCP separation as more Tc is introduced becomes less

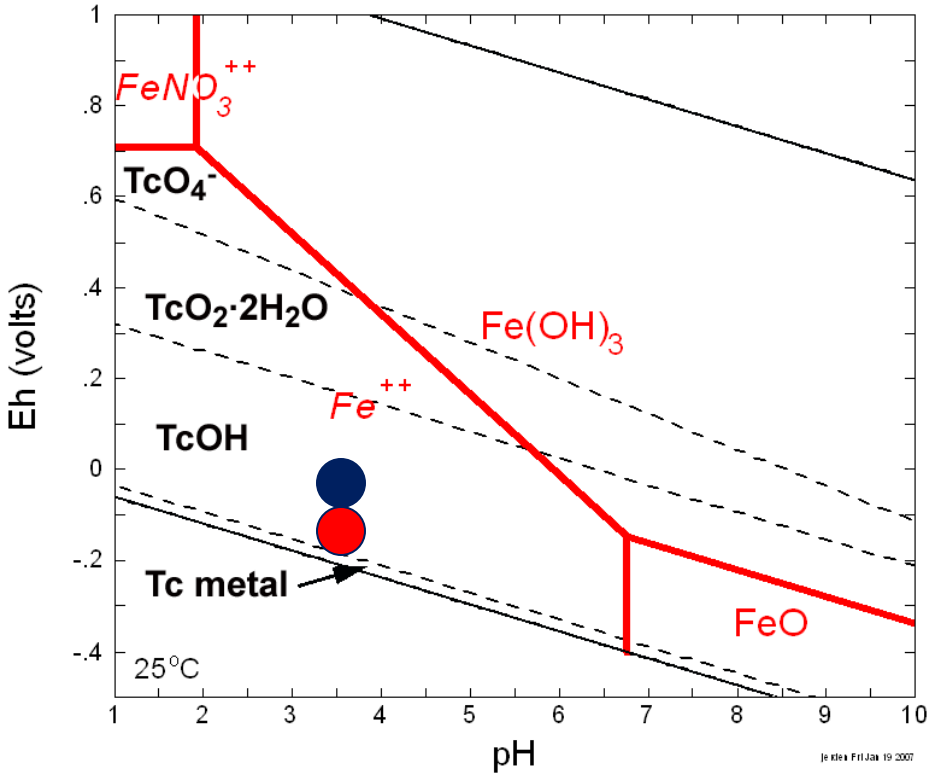




SSTc8 – Acidic Brine LPR (DA vs A)

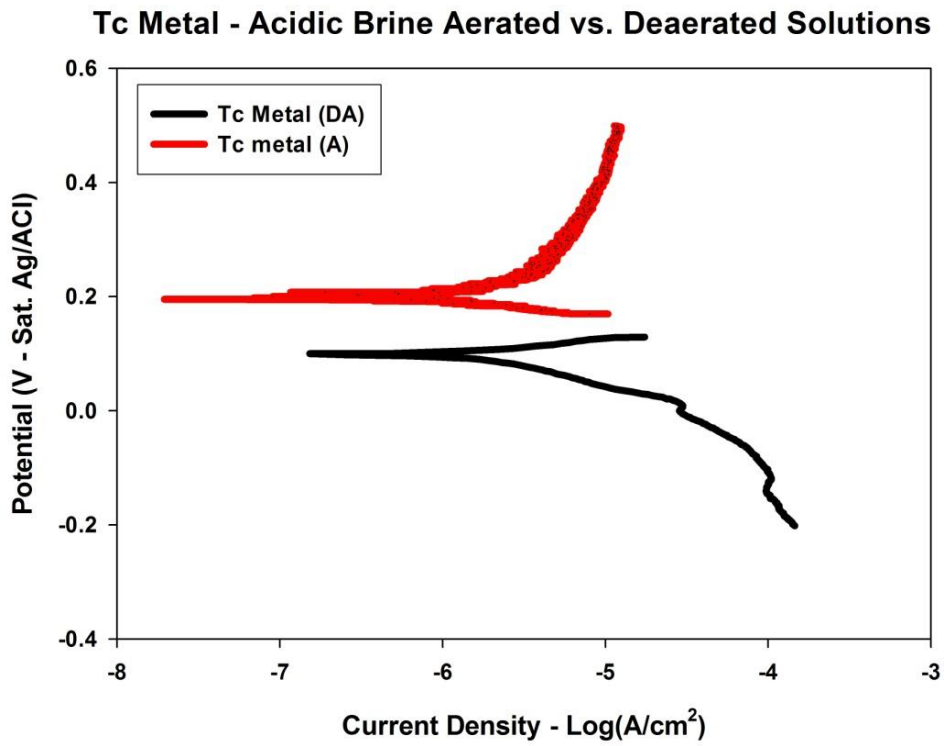
- OCP separation as more Tc is introduced becomes less

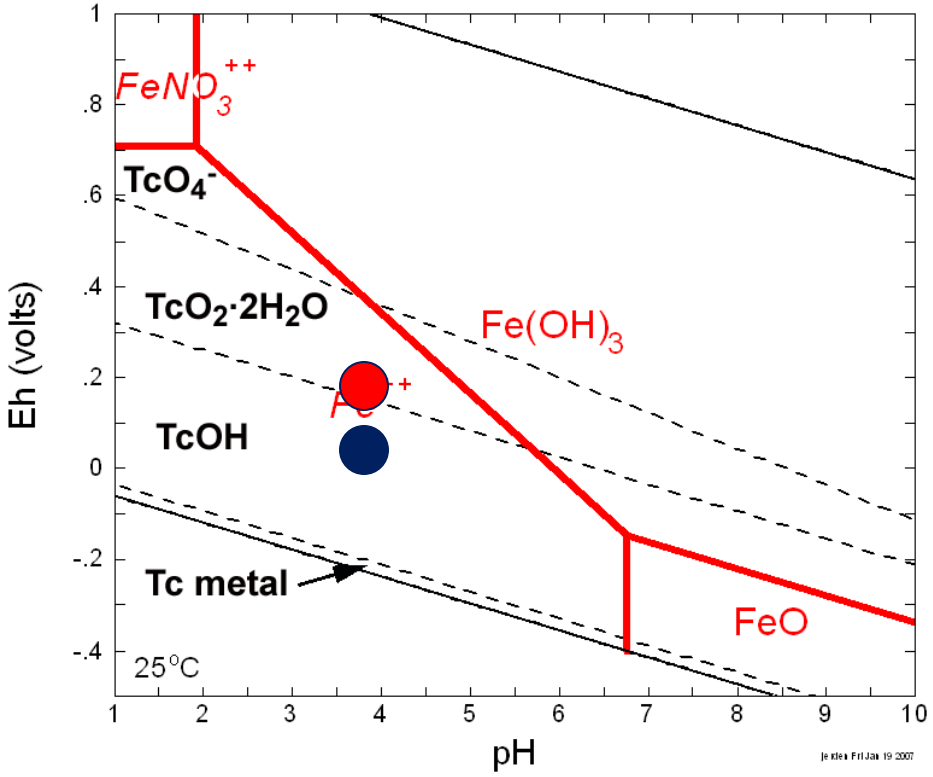




SSTc8 – Acidic Brine LPR (DA vs A)

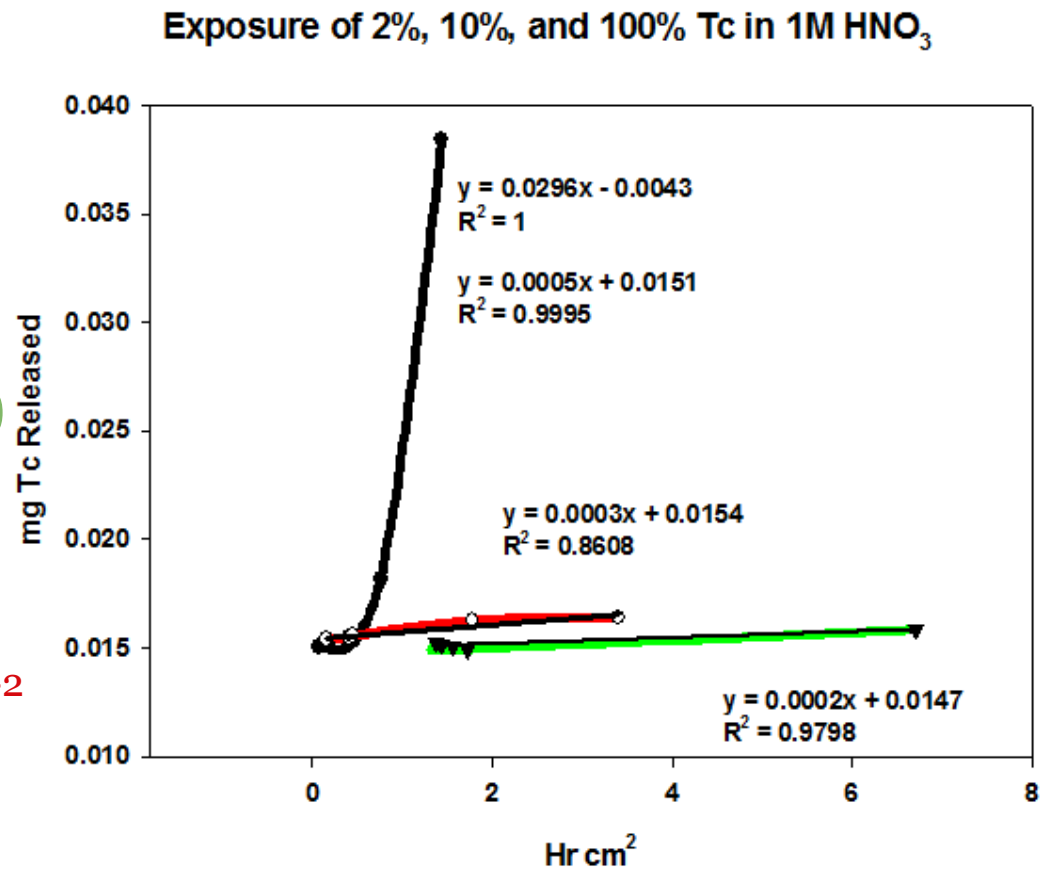
- OCP separation as more Tc is introduced becomes less





Experimental – 1M HNO3 2%, 10%, and 100% Tc

- 100% Tc
  - Initial
    ~1E-4 mg Tc hr-1 cm-2
    (1.01E-9 mol Tc hr-1 cm-2)
  - Final
    0.0296 mg Tc hr-1 cm-2
    (2.99E-7 mol Tc hr-1 cm-2)
- 10% Tc – SS85Zr15
  3E-4 mg Tc hr- cm-2
  - Normalized Release Rate
    ~ 3.03E-8 mol Tc hr^{-1} cm^{-2}
- 2% Tc SS85Zr15
  2E-4 mg Tc hr-1 cm-2
  - Normalized Release Rate
    ~ 1.01E- mol Tc hr^{-1} cm^{-2}



Experimental – 1M HNO3 2%, 10%, and 100% Tc

- 100% Tc
  - Initial
    ~1E-4 mg Tc hr-1 cm-2
    (1.01E-9 mol Tc hr-1 cm-2)
  - Final
    0.0296 mg Tc hr-1 cm-2
    (2.99E-7 mol Tc hr-1 cm-2)
- 10% Tc – SS85Zr15
  3E-4 mg Tc hr- cm-2
- Normalized Release Rate
  ~ 3.03E-8 mol Tc hr^{-1} cm^{-2}
- 2% Tc SS85Zr15
  2E-4 mg Tc hr-1 cm-2
- Normalized Release Rate
  ~ 1.01E-7 mol Tc hr^{-1} cm^{-2}

	Release Rate (mols Tc cm^{-2} hr^{-1})		
Electrode	**2.25 hr**	**69.33 hr**	**Noramlized (Tc)**
Tc Metal	3.46E-08	8.91E-09	8.91E-09
FeMoTc	2.78E-07	1.45E-07	1.45E-05
FeTc1	4.17E-07	1.05E-07	1.05E-05
SS316_Tc1	2.61E-08	1.24E-09	1.24E-07
SS613_Tc2	2.62E-08	1.12E-09	5.60E-08
SS316-Tc6	3.23E-08	2.36E-09	3.93E-08
SS316_Tc8	2.78E-08	1.20E-09	1.50E-08
SSZr 10%Tc	1.34E-07	1.37E-08	1.37E-07
SSZr 2%Tc	6.49E-09	3.85E-10	1.93E-08

Effect of aeration and true release rates of Tc

- True release rates of Tc, in current density are orders of magnitude lower than that observed in LPR data

Tc Metal Only - De-aerated HCl and HNO_3

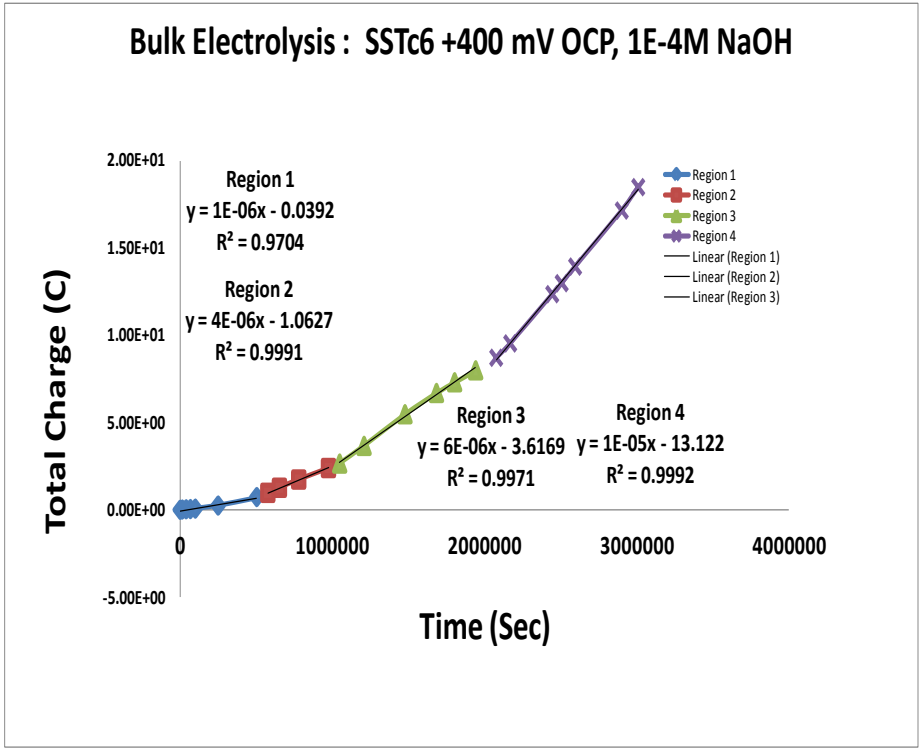
Media	Deaearted HCl		Deaerated HNO_3	
	mols Tc cm^{-2} hr^{-1}	(A cm^{-2})	mols Tc cm^{-2} hr^{-1}	(A cm^{-2})
pH 2.5	3.81E-10	1.58E-14	9.70E-10	4.02E-14
pH 1	2.25E-10	9.33E-15	1.29E-09	5.35E-14
0.1M	4.37E-10	1.81E-14	1.00E-08	4.15E-13
1M	4.50E-10	1.87E-14	2.00E-08	8.29E-13
2M	9.81E-10	4.07E-14	4.00E-08	1.66E-12
6M	2.05E-09	8.50E-14	8.63E-05	3.58E-09

Tc metal and Alloys - Aerated HNO_3

Electrode	Norm. Rel Rate	Current Density (CD)
	mols Tc cm^{-2} hr^{-1}	(A cm^{-2})
Tc Metal	8.91E-09	3.69E-13
	2.99E-07	1.24E-11
FeMoTc	1.45E-05	6.01E-10
FeTc1	1.05E-05	4.35E-10
SS316_Tc1	1.24E-07	5.14E-12
SS316_Tc2	5.60E-08	2.32E-12
SS316_Tc6	3.93E-08	1.63E-12
SS316_Tc8	1.50E-08	6.22E-13
SSZr 10%Tc	1.37E-07	5.68E-12
	3.03E-08	1.26E-12
SSZr 2%Tc	1.93E-08	8.00E-13
	1.01E-07	4.19E-12

SSTc6 Bulk Electrolysis 1E-4M NaOH

- Open Circuit Potential evaluated
- Potential (V) vs Sat. Ag/AgCl
  - +400 mV vs OCP applied
- Solution volume
  - 15 mL
- Time
  - ~ 3,010,000 sec
  - (836 hr)
- Total Charge (C)
  - 18.485 C
- End Current
  - +1.9145 E-7 A Instantaneous
  - Total amperage: 9.882E-2
- Approximate Tc concentration
  - Below 1.686E-7 M Tc
  - Background = 18 CPM
  - Raw Counts = 52



Assuming uniform release of Tc, total mols ~ 2.529E-9
Tc release rate: 3.025E-12 mols per hr
Time = 3,010,000 sec
Tc Current: 1.25E-16 Amps
Compare Tc metal ~ 1-2 orders of magnitude greater release from bare metal

SSTc6 Bulk Electrolysis 1E-4M NaOH

- Open Circuit Potential evaluated
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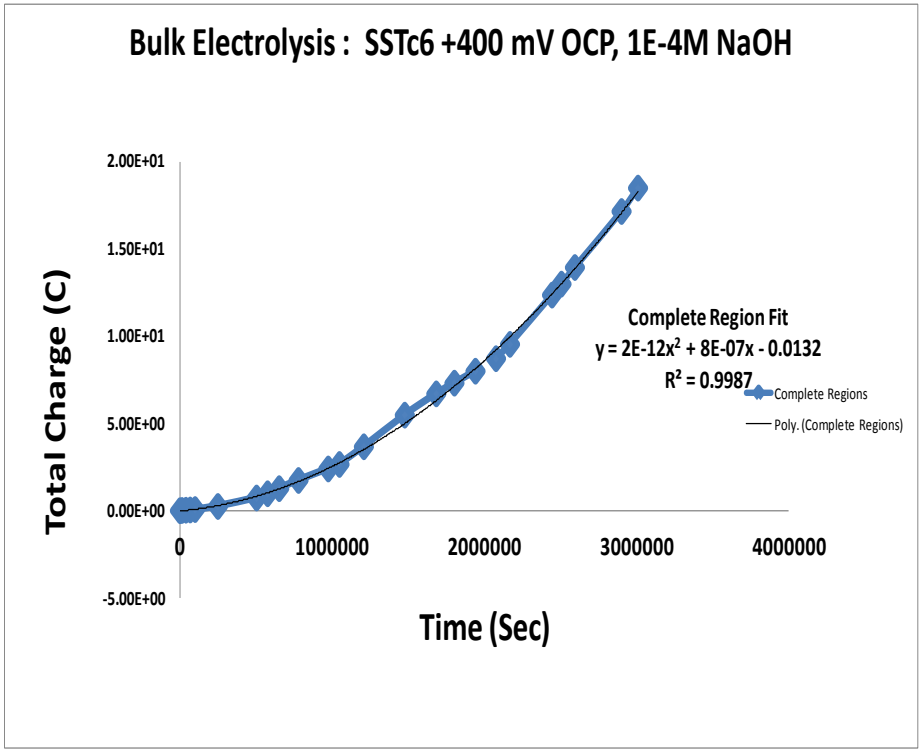

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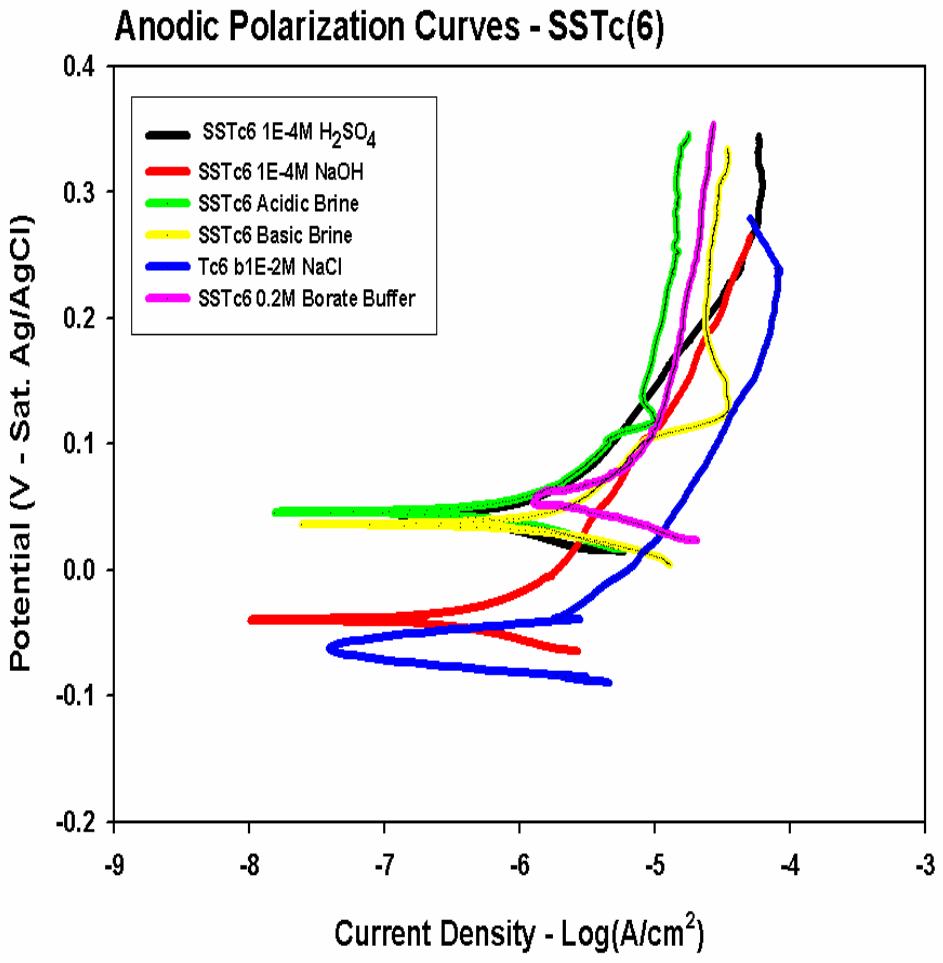
SSTc6 Bulk Electrolysis 1E-4M NaOH and Environmental Solution Set



Conclusion/Future Work

- In all alloys, 2% Tc addition creates more noble materials, though Tc is the most noble.
- Tc corrosion rate is little changed by environment solutions and Cl^-
- Tc is considered a low-corroding material relative to other active metals
  - Tafel constants should be evaluated and be input with correction factors relative to Tc release rate
  - This simplifies the "model" of corrosion….Tc doesn't and the host phase does until galvanic protection fails.
- Metal alloys can be recycled
- Metal alloys can be produced direct from sequeterization of TcO_4^- using metal amines
- Tc isolation using electrochemical techniques linked to potential ranges appropriate for TcO_2 & Tc metal deposition

Study 1: Formation of $Co[(NH_3)_6](TcO_4)_3$

Starting compound is insoluble in MeOH, Acetone, and CH_2Cl_2

Ending compound is slightly-soluble in DI H_2O and MeOH

Used 0.2272 g $[Co(NH_3)_6]Cl_3$

Tc metal = 200 mg, with 2% excess TcO_4^-
Tc concentrations determined by LSC

Formation of precipitate is immediate
0.2576 g recovered
yield: 46.6%

Estimated Solubility
Made solution: 0.0989 g in 1 mL DI H_2O 26 °C

Estimated Solubility of Co-Tc Compound: 0.40 mg per mL (quantified by LSC)

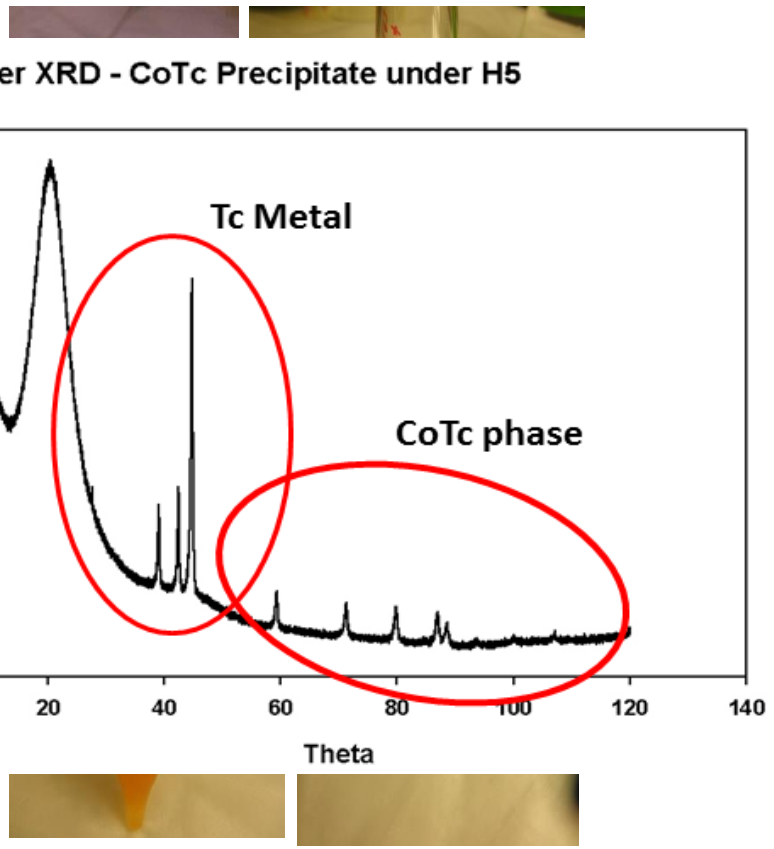


Figure X: Hexamminecobalt(III) chloride in 10 mL of water and precipitation after inclusion of pertechnetate

Study 2. Electrodeposition of Tc

- Tc deposits on Cu in sulfuric acid…

Electrodeposition of Tc from $KTcO_4$ in water

0.32M H_2SO_4 + 0.7M Oxalic acid

0.7M Oxalic acid (right) on Cu for 500 sec

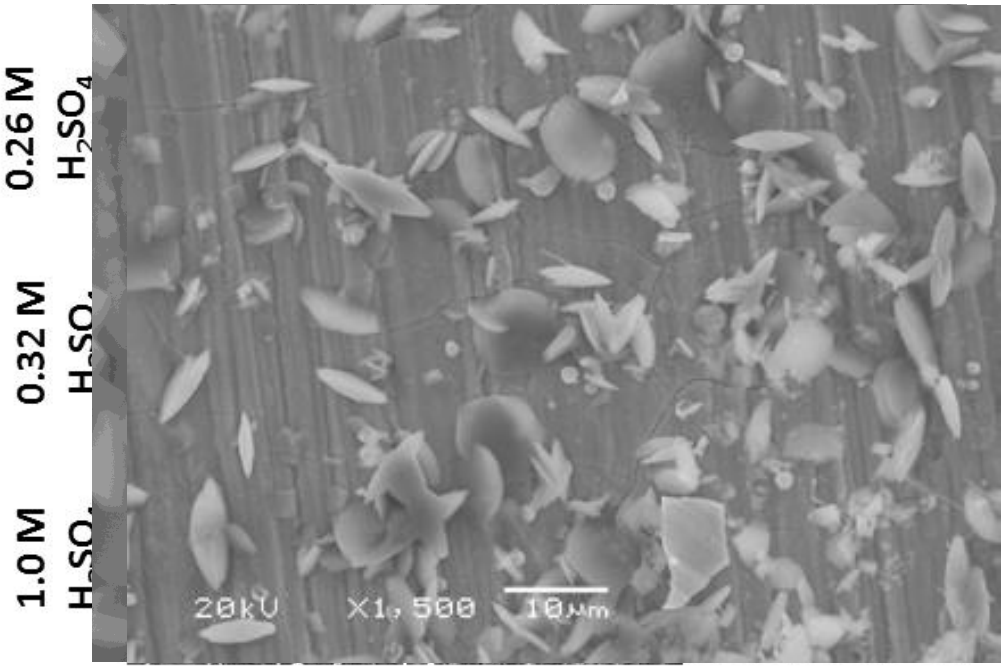


Figure X. Insert Tc electrodeposition images from solution on Cu…..

Study 3: Lifetime Assumptions

	Tc metal	SS(Tc2 wt%)Zr	SS(Tc1.34 wt%)
1. The dimensions of the exposed surface area of each alloy is:	3136 cm^2	54 756 cm^2	70 225 cm^2
2. The instantaneous corrosion rate of each material is:	1.74E-6 A/cm^2	1.54E-6 A/cm^2	1.81E-8 A/cm^2
3. The instantanesous corrosion rate - Coulombs over the face:	5.46E-03	8.43E-02	1.27E-03
3. The number of electrons per coulomb:	6.24E+18		
4. The number of electrons required to release an atom:	7	3	3

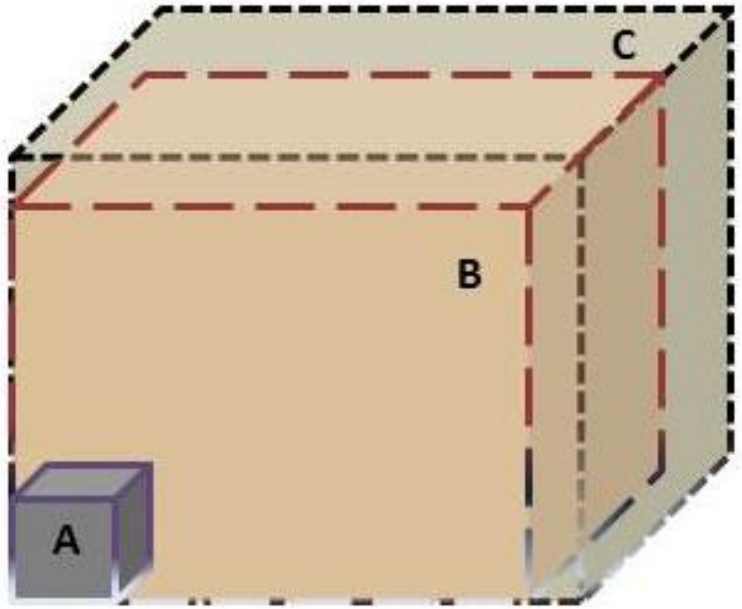
Waste Form Predictions - Lifetime

- Anion exchange decontaminates uranium from technetium with separation factors great enough to reuse U or directly dispose of the material.
- Accompanying nitrate has successfully been removed from the elution stream in the presence of the carbon sources triethanol amine and D,L-ascorbic acid while simultaneously generating a phase that is reducible to generate Tc metal
- The generated Tc metal can suitably be placed in a metallic host phase and characterized by a variety of methods
- Alloying Tc will dramatically increase the waste loading volume of materials

  2000 kg Tc ~ 0.174 m^3

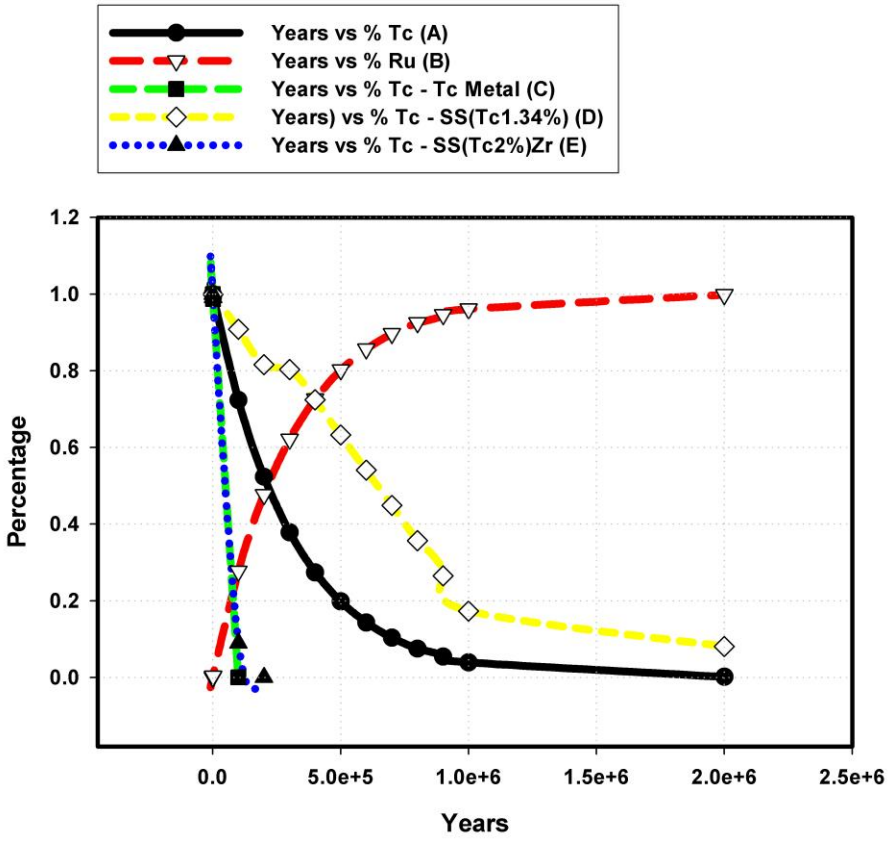
  SS(Tc2%)Zr ~ 12.73 m^3

  SS(Tc1.34%) ~ 18.5 m^3
- Lowering the corrosion rate of the bulk will dramatically influence the life-time of the host phase. The trade off is the increase in surface area of the "waste package"



Lifetime Approximation

With many assumptions being made, the estimated life-time of Tc metal, SS(Tc2%)Zr and SS(Tc1.34%) based on LPR data, it can be expected that the direct corrosion rate of each material will not live longer than 80,000 yrs (100% Tc), 100,000 yrs (SS(Tc2%)Zr, and 1,000,000 yrs (SS(Tc1.34%)



Lifetime approximation corrections relative to Metal Waste form conceptual model

- 2% Tc in SS_{85}/Zr_{15} placed in H2O over a period of 4 years as of Feb 2014 – still in water
- Sample counted by LSC (100 µL, DL 1E-9 M Tc)
- Solution Volume 0.05L → mols Tc 5E-11
- Atoms Tc ~ 3.011E13
- Electrons ~ 4/release ~ 1.2044E14
- Coulombs @ 0.01M NaCl 1.54E-6 A/cm²
- 97.13 C (2% Tc ~ 1.94 C) = 1.046E-4M
- Lifetime extension (10,000 – 100,000 in pure water)

Bare surface oxidation rate **moderated by passivation** **and dissolution affinity**

$$FR(T,RN) = B(Eh,T,pH) \times P(Cl^-) \times D(T,RN)$$

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