



U.S. DEPARTMENT OF  
**ENERGY**

Nuclear Energy

---

---

Fuel Cycle Research & Development  
Separations/Waste Form Campaign

## **Waste Form Characterization Metallic Waste Forms**

ANL: Bill Ebert, Jeff Fortner, Terry Cruse

INL: Steve Frank

PNNL: Edgar Buck

SRNL: Luke Olson

WCU: David Shoesmith, Dmitrij Zagidulin, Jamie Noël

August 29, 2012 International Pyroprocess Research Conference

This work was supported by the U.S. Department of Energy,  
Office of Nuclear Energy, under Contract DE-AC02-06CH11357.



- **Develop radionuclide release model for metallic waste forms that**
  - Is based on mechanistic understanding of host phase corrosion and radionuclide release behavior
  - quantifies the effects of environmental variables on host phase corrosion and radionuclide release rates
  - can be used to calculate radionuclide source terms over long times for disposal system performance assessments
  - links composition to performance (product consistency) through phase assemblage to support waste acceptance
  
- **Objective of presentation is overview of approach and on-going work**



## Nuclear Energy

---

- **Interface with FCRD Separations Campaign for waste stream compositions from aqueous and pyrochemical reprocessing**



- **Formulate range of prototype waste forms for use in testing**
- **Evaluate waste form processing options and process controls**
- **Characterize phase assemblage and radionuclide distribution**
- **Measure waste form corrosion behavior and radionuclide release kinetics**
- **Develop mechanistically-based waste form degradation model to calculate radionuclide release**
- **Provide source terms for waste form performance in disposal environment**



- **Interface with disposal system models being developed in FCRD Used Fuel Disposition Campaign**

# Prototype Waste Form Materials Reference Alloy Waste Form (RAW)

Material	additives	%U	%Tc	Represented Wastes
Epsilon Waste Form	none	4		direct processing of fuel wastes
<b>RAW-1(Re) and RAW-1(Tc)</b>	<b>60% SS</b>	<b>0</b>	<b>2</b>	<b>low steel</b> high Mo
RAW-2(UTc)	60% SS	2.5	2.7	low Mo
RAW-4(UTc)a-d	SS 5-20% Zr	0-5	1-2	U & Tc for range of Zr/U ratios
EBR-II MWF	SS 15% Zr	11	<1	high SS
RAW-3(URe)	TBD	TBD	0	minimum added Zr (Olson)

Data base for wide range of RAW materials will be used to develop composition dependence term in degradation model.

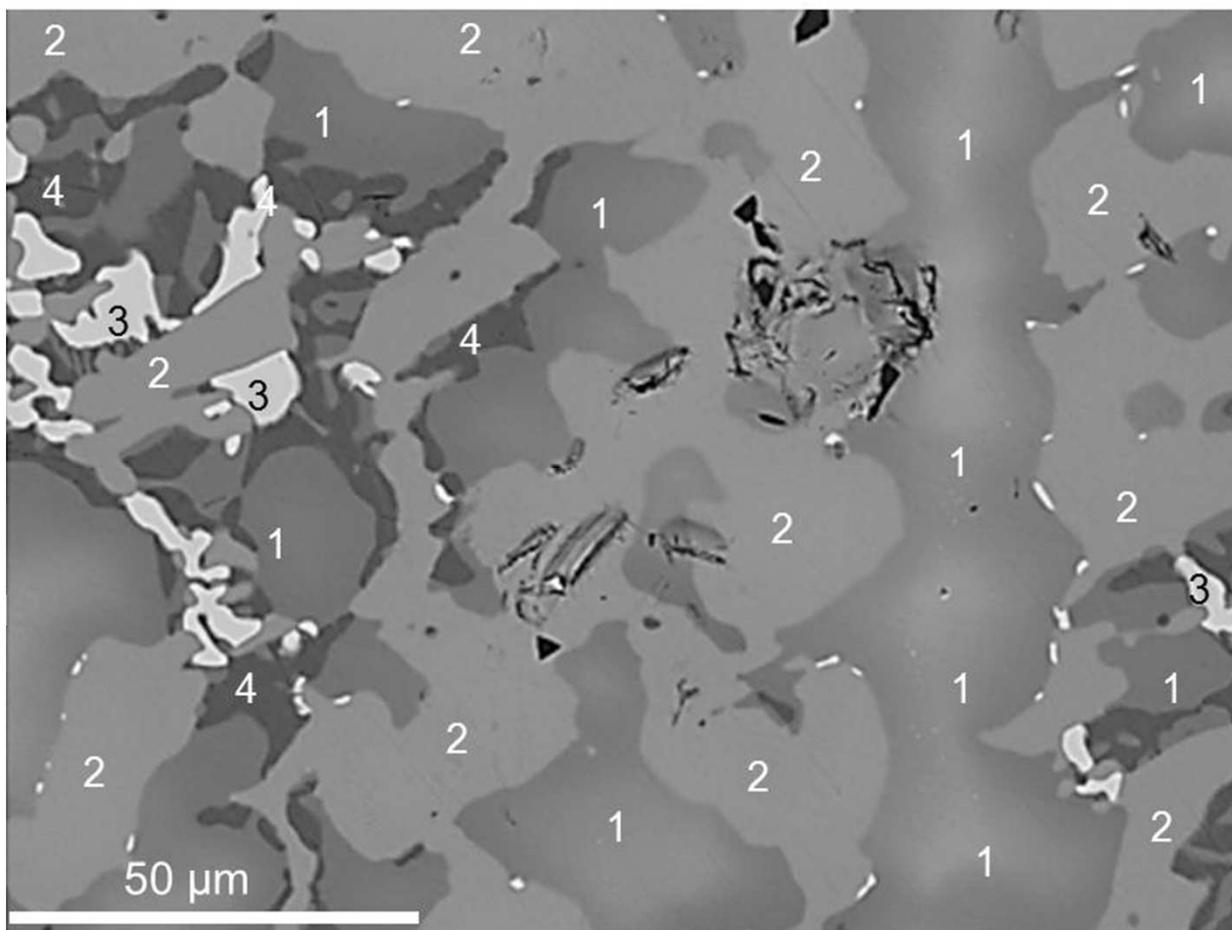


# RAW-1(Tc) and RAW-2(UTc) low steel Elemental Formulations

Waste + 60% Steel	RAW-1(Tc)	RAW-2(UTc)	Waste + 60% Steel	RAW-1(Tc)	RAW-2(UTc)
	mass %	mass %		mass %	mass %
Fe	38.61	37.64	Cd	excluded	excluded
Cr	11.02	10.74	Cu	0.105	0.10
Ni	7.41	7.22	Sn	excluded	excluded
Mo	12.49	4.68	Ag	excluded	excluded
Zr	12.30	10.08	W	0.066	0.06
Ru	7.61	11.73	Co	0.065	0.06
Pd	5.13	7.91	Se	excluded	excluded
Tc	2.50	3.85	V	0.030	0.03
U	—	2.52	C	0.027	0.03
Te	excluded	excluded	Sb	excluded	excluded
Rh	1.33	2.05	P	0.012	0.01
Mn	0.971	0.95	S	0.011	0.01
Si	0.306	0.30	As	0.006	0.01



## RAW-1(Tc): 4 constituent phases

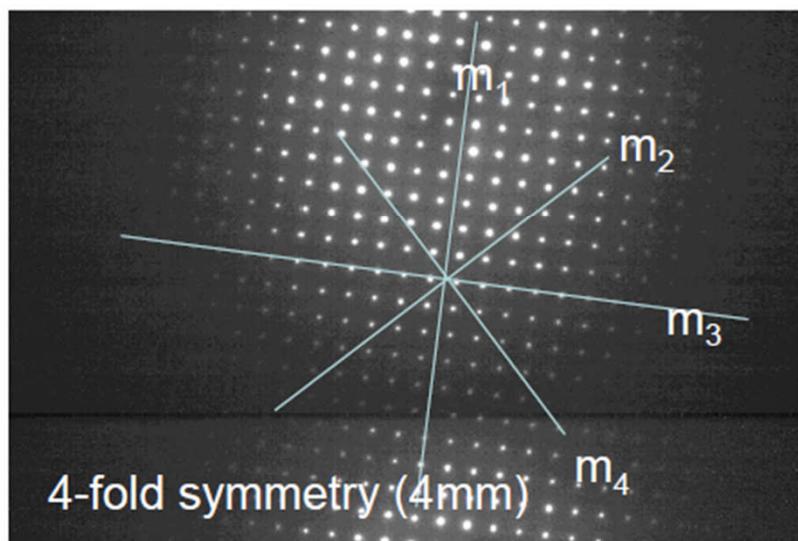
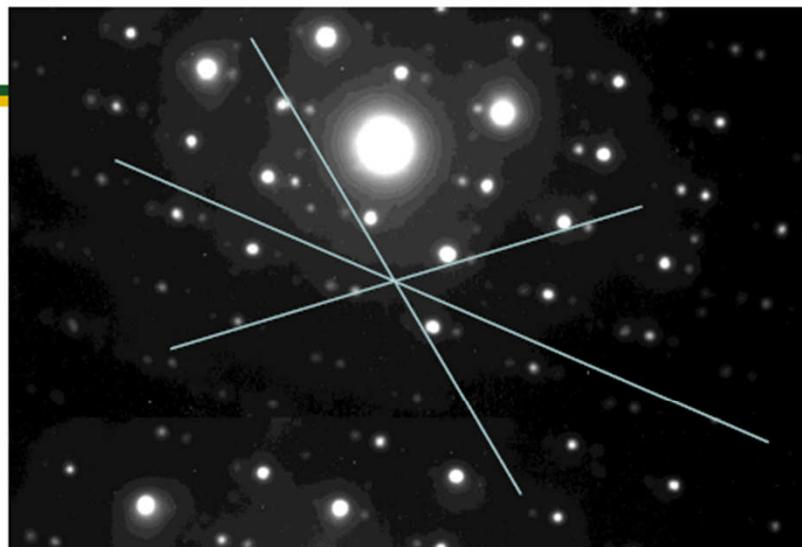
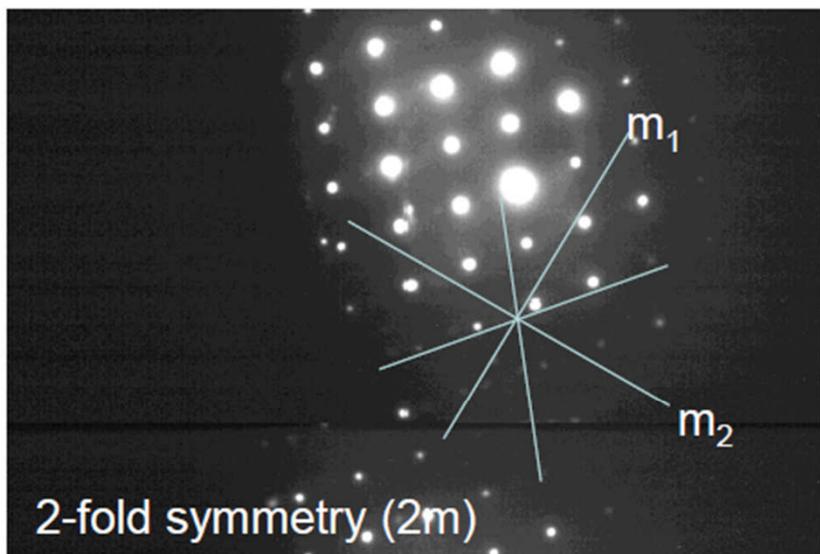


Reagent	Mass%
SS116L	60.0
Zr	12.3
Mo	12.5
Ru	7.6
Pd	5.1
Tc	2.5
Rh	1.3

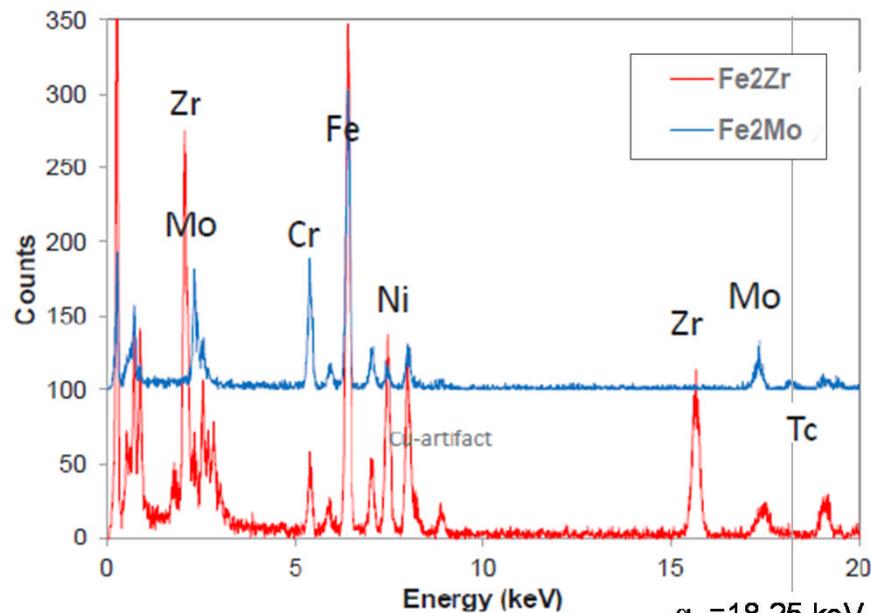
(1) MoCrTcFe <sub>2</sub>	50%
(2) ZrNiFe <sub>2</sub>	32%
(3) ZrPd <sub>2</sub>	4%
(4) Steel(Tc)	14%



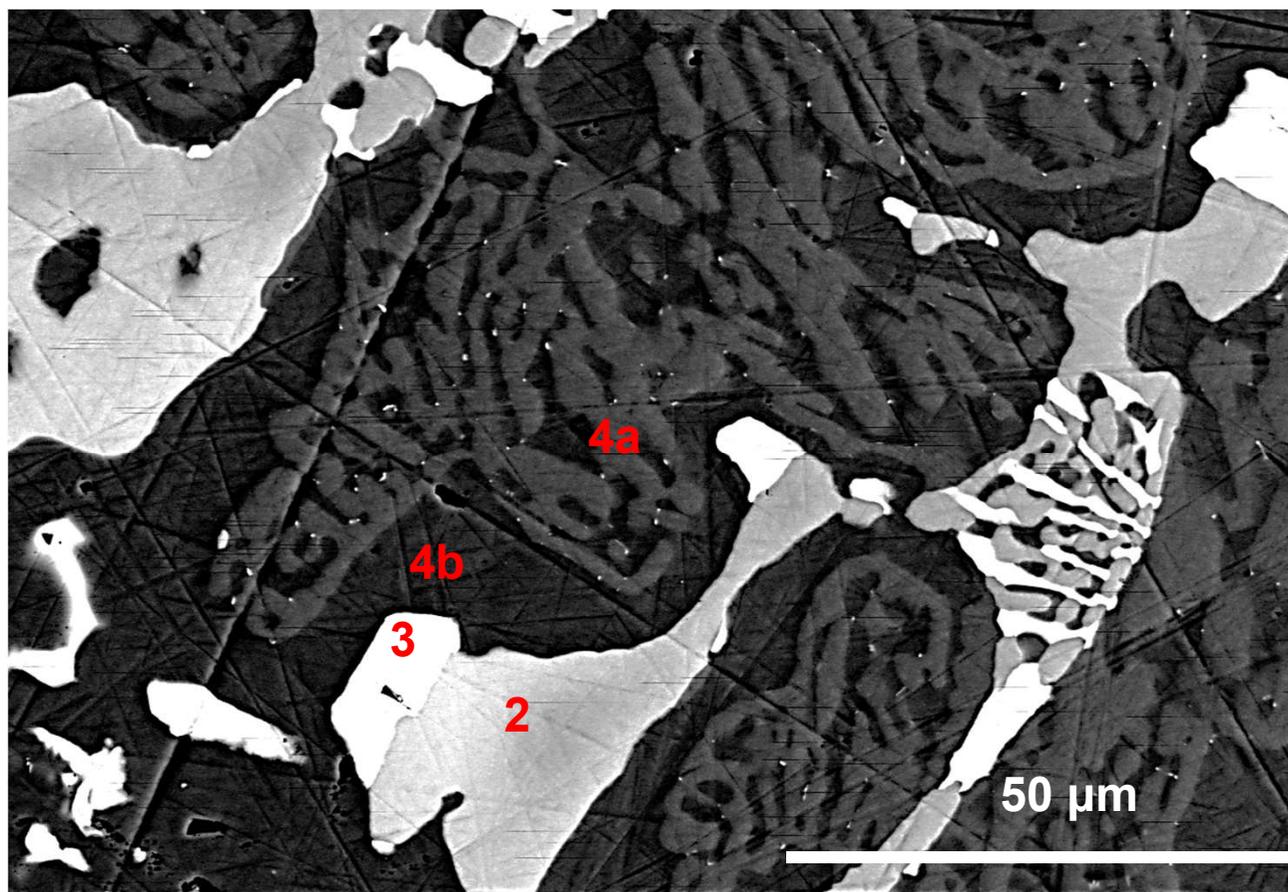
# Fe<sub>2</sub>Mo in RAW-1(Tc) Hosts Tc



Lattice parameter (a) ~8-9 Å



$\alpha_2 = 18.25$  keV  
 $\alpha_1 = 18.37$  keV



Reagent	Mass%
SS116L	59.9
Zr	9.7
Mo	3.2
Ru	11.3
Pd	7.6
Tc	3.7
Rh	2.0
U	2.5

1?	MoCr(Tc)Fe <sub>2</sub>
2	ZrNiFe <sub>2</sub> (U)
3	ZrNiPd <sub>2</sub> (U)
4a	steel(Ni, Tc)
4b	steel(Cr, Tc)



# Summary of Alloy Waste Form Development

- **Multiphase prototype alloy waste forms (RAW) form the same constituent phases in different relative amounts (function of Mo content?)**

	High Mo	Low Mo	
MoFe <sub>2</sub> intermetallic	50%	absent?	host phase for Tc
ZrFe <sub>2</sub> intermetallic	32%	major	major host phase for U and TRU
ZrPd <sub>2</sub> intermetallic	4%	minor	minor host phase for U
steel solution phase	14%	major	host phase for Tc

- **Oxidation behavior of RAW materials is being modeled**
- **Electrochemical characterizations of constituent phase corrosion behavior**
- **Effects of environmental variables being measured**
  - Initial measurements with Cl<sup>-</sup> (expected to have the greatest effect)
  - Measuring release of Tc for comparison with release behavior in immersion tests
  - Future measurements with H<sub>2</sub>O<sub>2</sub> etc.



# Alloy Waste Form: Conceptual Model and Approach

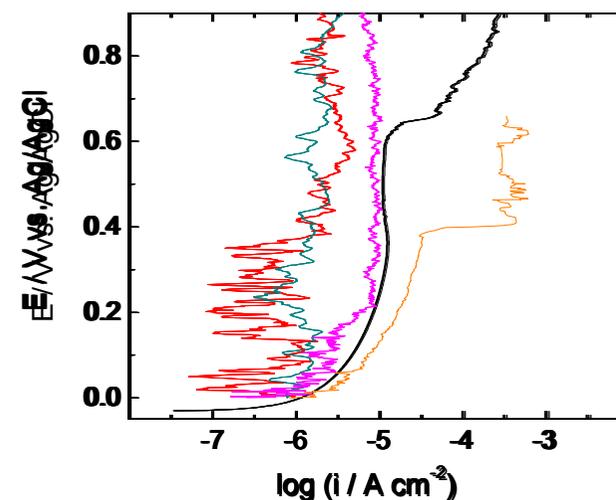
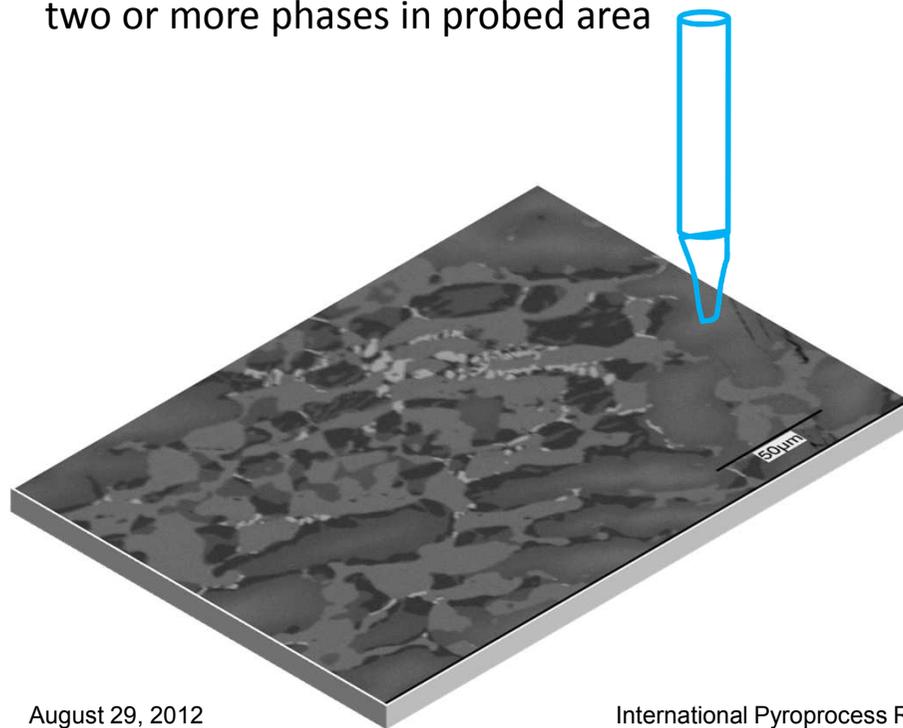
- **Two-step mechanism: oxidation of metal followed by dissolution of oxide**
- **Radionuclide release rate = oxidation rate of host  $\times$  oxide dissolution rate factor**
- **Conducting immersion corrosion experiments to provide data quantifying long-term effects of oxide layer on oxidation rate and release rate**
- **Calculating oxidation rate from electrochemical measurements following approach developed by Anderko for steels based on mixed potential theory and electrode kinetics**
- **Conducting electrochemical experiments to quantify model parameters for oxidation step**
- **Tracking changes in surface and measuring releases to solution during electrochemical experiments to link response to phases and long-term immersion behavior**
- **Measuring effects of environmental variables on oxidation and dissolution rates**



# Microelectrochemical Technique electrode anodic polarization



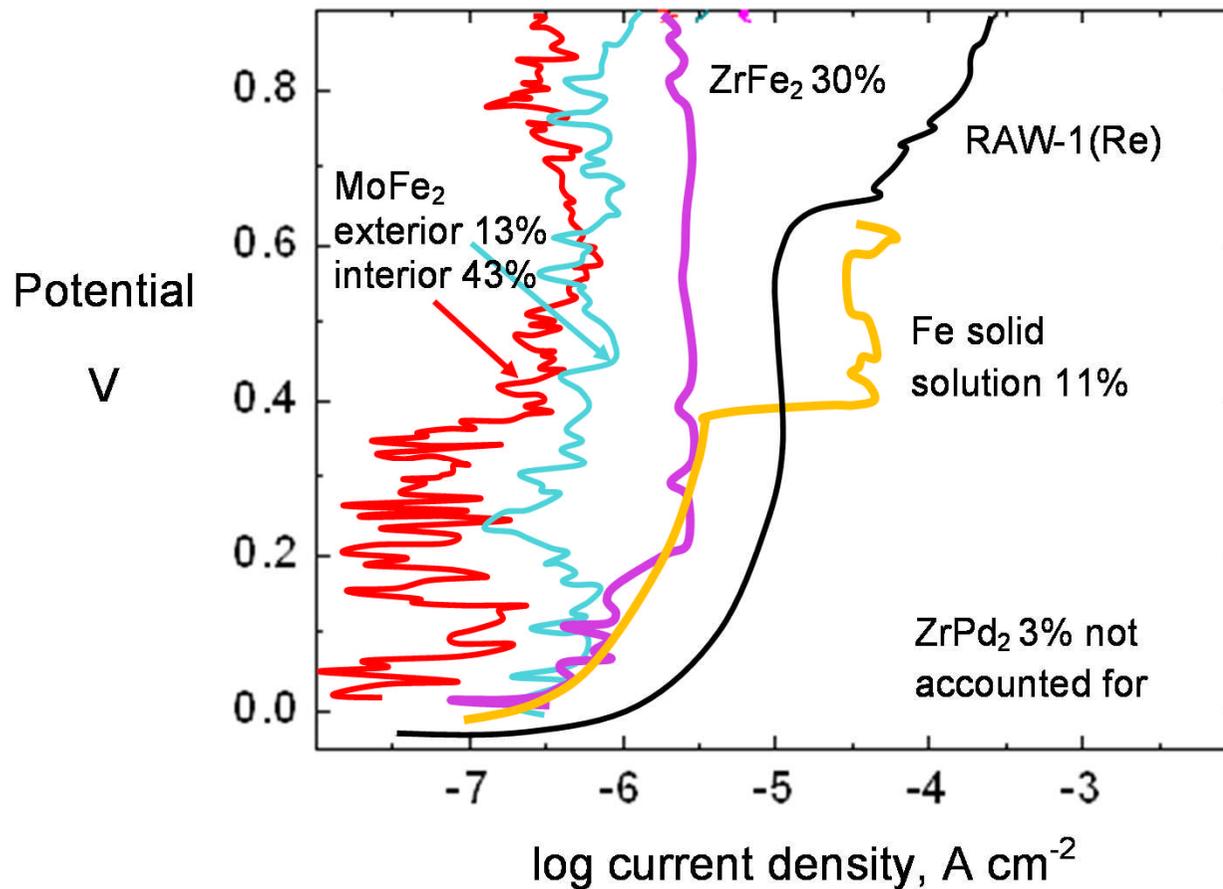
- Microelectrochemical cell (MEC) measures response of small area of sample 20-100  $\mu\text{m}$  diameter
- Polarization shown for MEC located on individual phases in RAW-1(Re)
- Future studies will address galvanic coupling in RAW-1(Tc) by including two or more phases in probed area



1. Full surface
  2.  $\text{MoFe}_2$  (interior)
  3.  $\text{MoFe}_2$  (exterior)
  4.  $\text{ZrFe}_2$
  5. steel
- RAW-1(Re)
  - Working surface of MEC cell is 30  $\mu\text{m}$  diameter
  - 0.1 mM NaOH solution
  - Potential scan rate 1 mV/s
  - Sample repolished between runs



## Area-Weighted Responses (anodic branches)



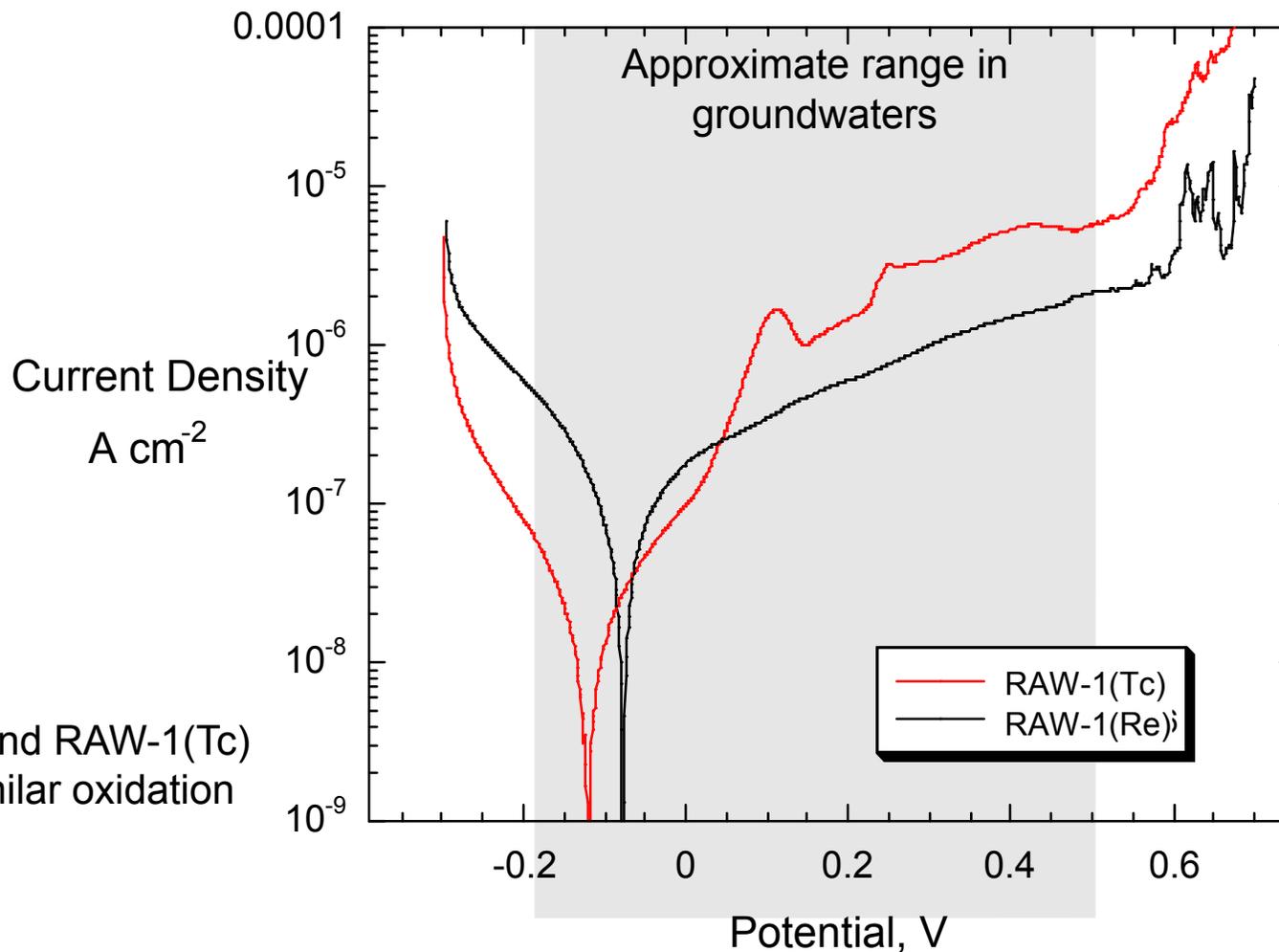
Area-weighted sum of responses of constituent phases sufficiently similar to overall response (offset of steel response).

Relate measured bulk response  $I_{RAW}$  to sum of responses from  $N$  constituent phases with each phase modeled as homogeneous material contributing  $I_j$ .

$$I_{RAW} = \sum_{j=1}^N W_j I_j$$



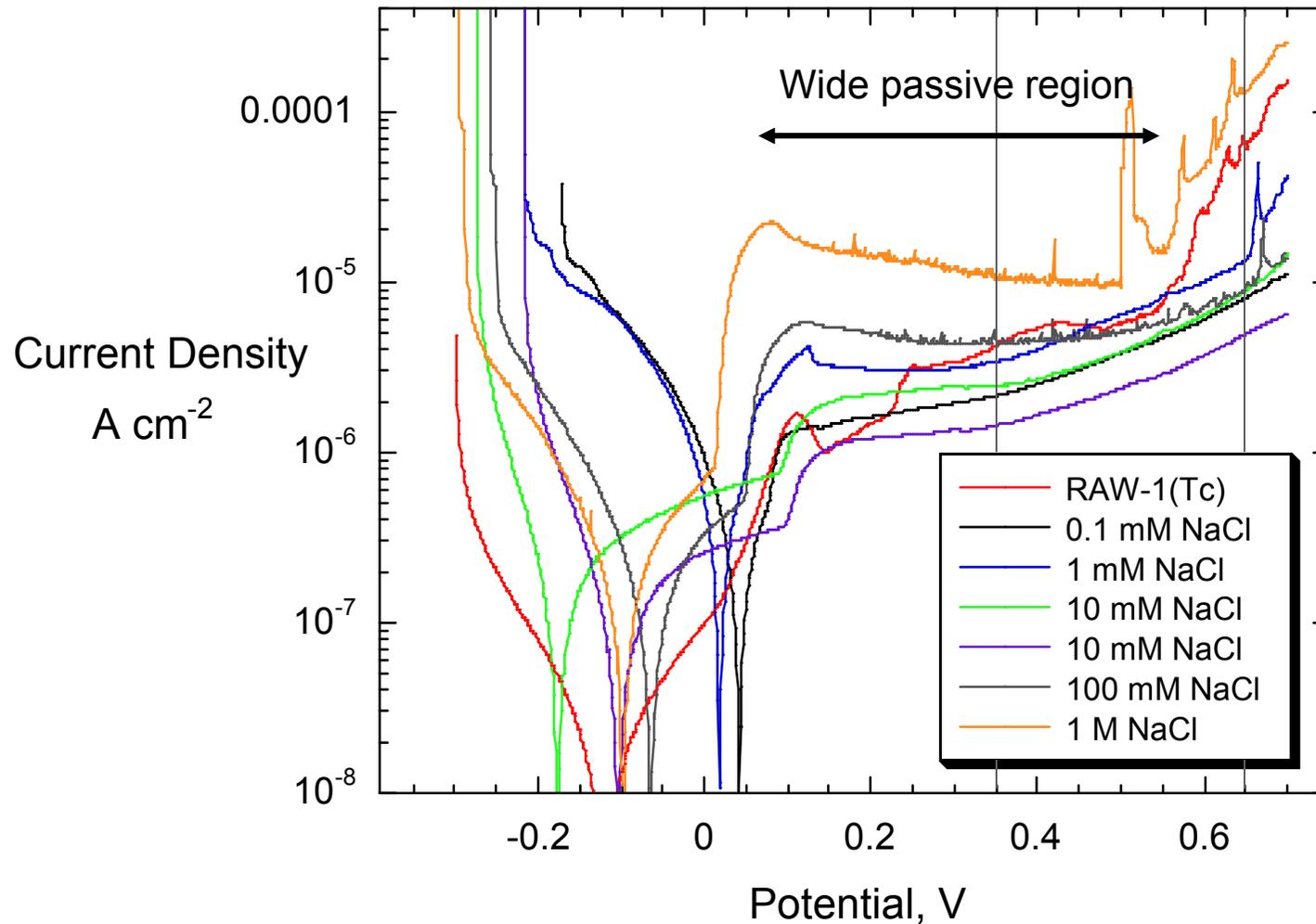
# Potentiodynamic Scans in Argon-purged 0.1 mM NaOH



RAW-1(Re) and RAW-1(Tc)  
have very similar oxidation  
behaviors

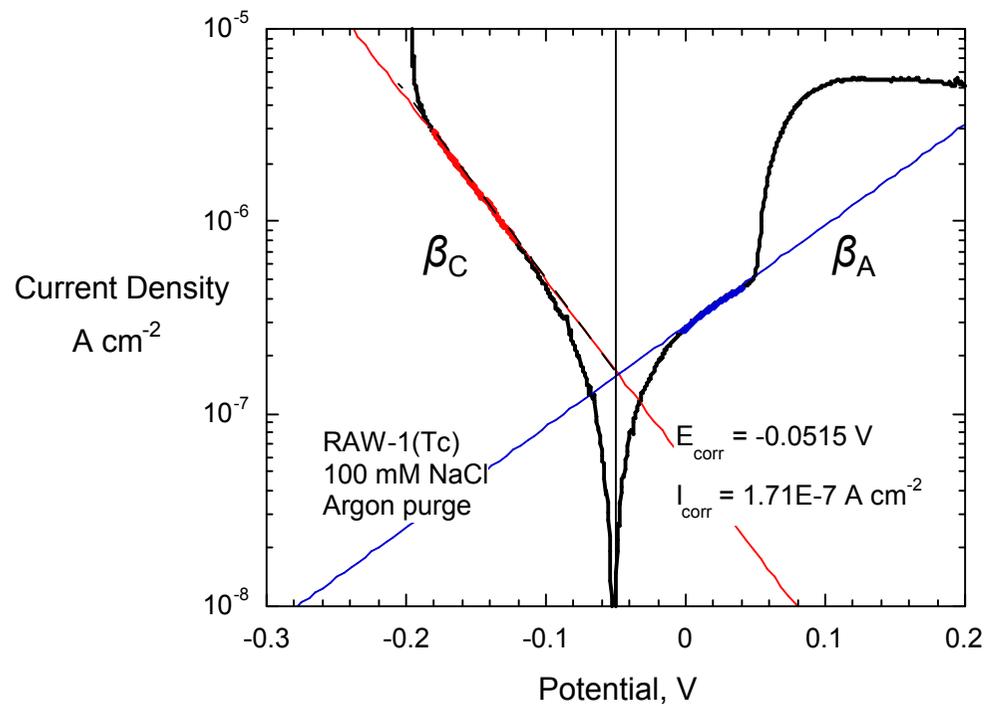


## RAW-1(Tc) in NaCl solutions at pH 9.5

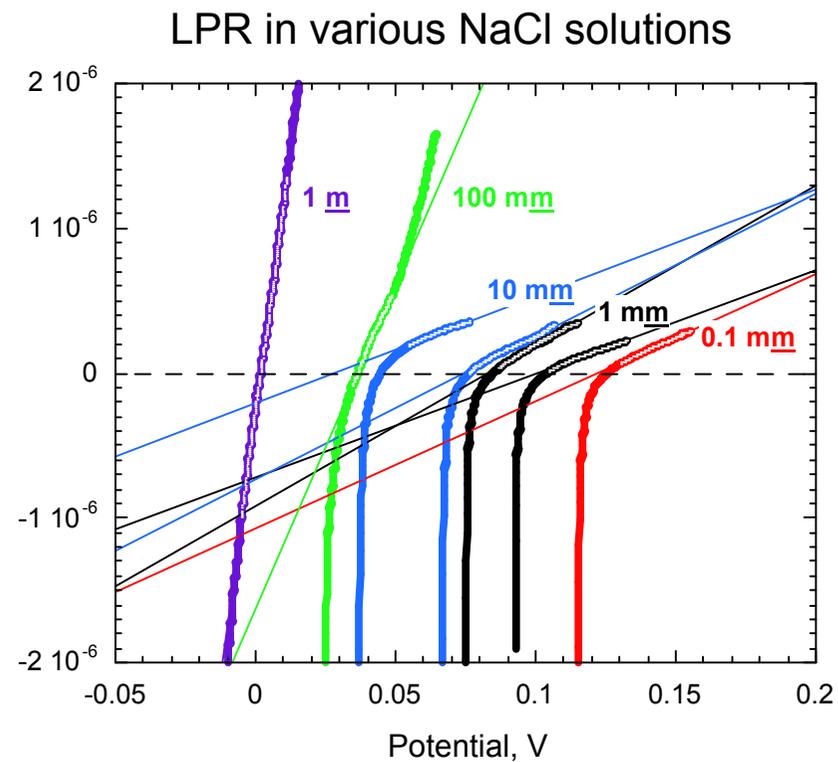


$$\frac{M}{t} = \frac{i_{corr} 25.46}{F}$$

Will measure in 10 M NaCl last because it will likely ruin electrode



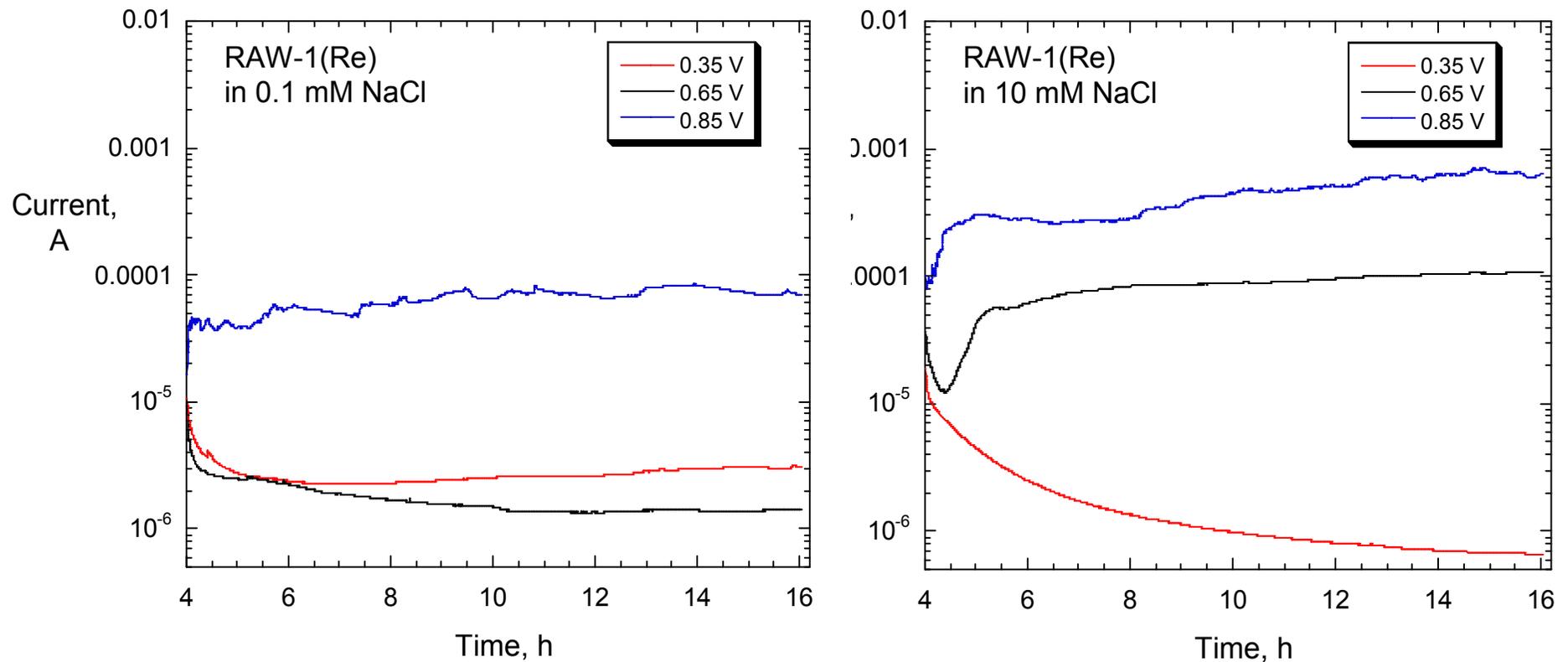
### Tafel Analysis



### Linear Polarization Resistance Analysis



# “Steady State” Effects of Cl<sup>-</sup> Change in concentration at constant potential



Will add a terms to existing model for potential dependence to quantify dependence of Tc release rate on Cl<sup>-</sup> and other solutes.

Same tests in progress with RAW-1(Tc), including measurement of [Tc] in solution.



## Examine Surface Before and After Electrochemical Tests to ID Active Phases



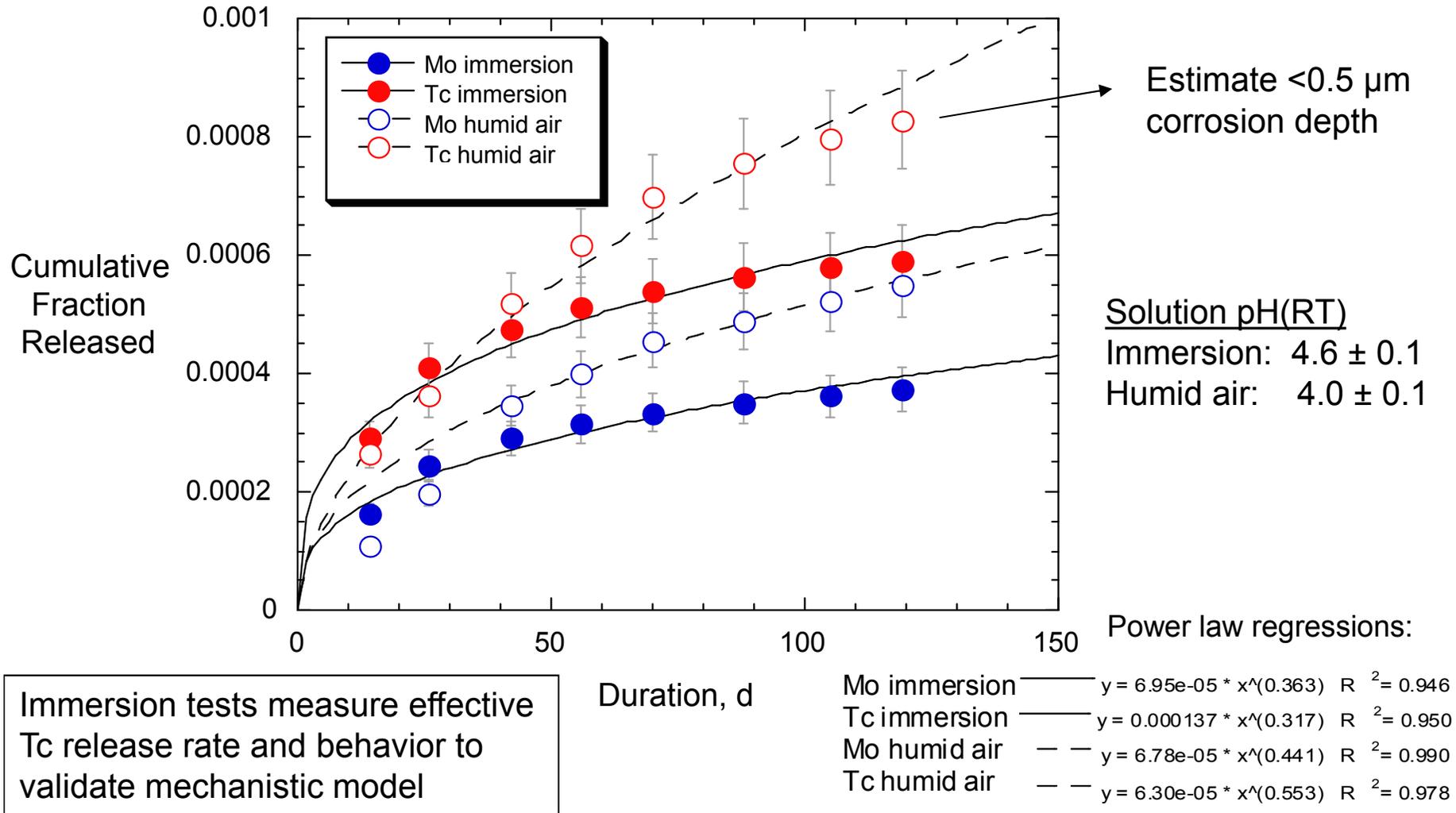
Before Electrochemical  
Measurements



After Electrochemical  
Measurements

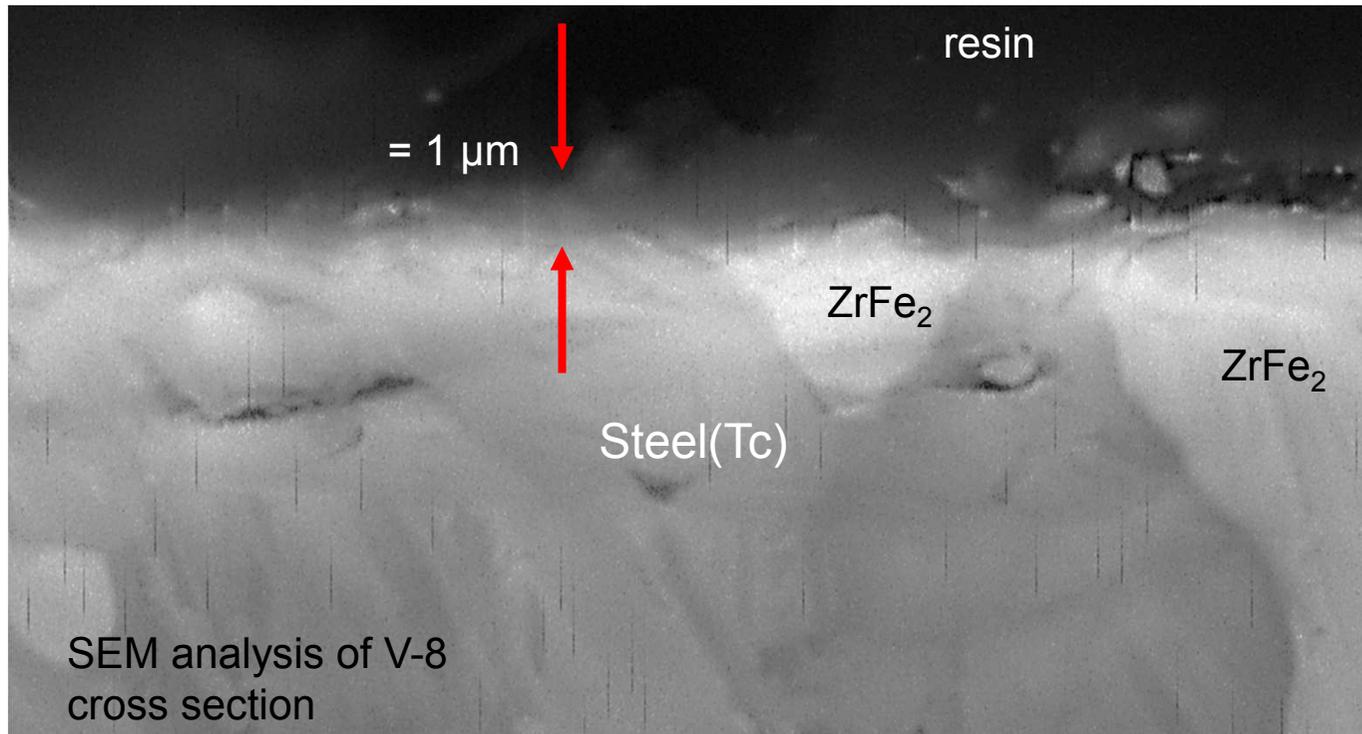


# Release of Tc and Mo from RAW-1(Tc) (electrically isolated; 200 °C)





## SEM Cross Section of RAW-1(Tc) after 119 days in humid air at 200 °C



Oxide layer  
composition  
mostly uniform

Corrosion  
appears to be  
uniform...no  
obvious pitting  
at phase  
boundaries

Utilizing measurements of electrochemical behavior, release to solution, and microscopic analyses to develop and parameterize a degradation model for steel-based alloy waste forms.