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A PERFORMANCE MODEL FOR ALLOYED WASTE FORMS

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Outline

- Primary role of all waste form performance models for context (3)
- Conceptual/logical approach for alloyed waste form performance model (2)
- Experimental approach (5)
- Examples of experiments being conducted to support model development (12)

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Conceptual Approach for Waste Form Performance Models

- **Waste Form performance models provide the radionuclide source term values used in performance assessment (PA) calculations used to demonstrate long-term safety of engineered disposal systems to support NRC licensing.**
- **Primary measures of WF performance in disposal system are the mitigation of radionuclide release and the reliable predictability of that release.**
- **WF corrosion rate and RN release rate will change as corrosion layers form and environment changes throughout the regulated service life of a disposal system.**
- **A mechanistic understanding of the corrosion processes controlling radionuclide release is important for justifying the predictions of Waste Form performance models over very long disposal times…**

  …but implementing a detailed numerical model that takes all mechanistic processes into account explicitly is not necessary to make those predictions.
- **The prediction can be made using an empirical radionuclide source term model that captures effects of controlling process.**

General Approach for Developing a Waste Form Performance Model

Scientific Basis

- Individual process tests and models
- Coupled process tests and models
- Simulation tests and models
- Mechanistic description and model

Key effects →

Source Term Model

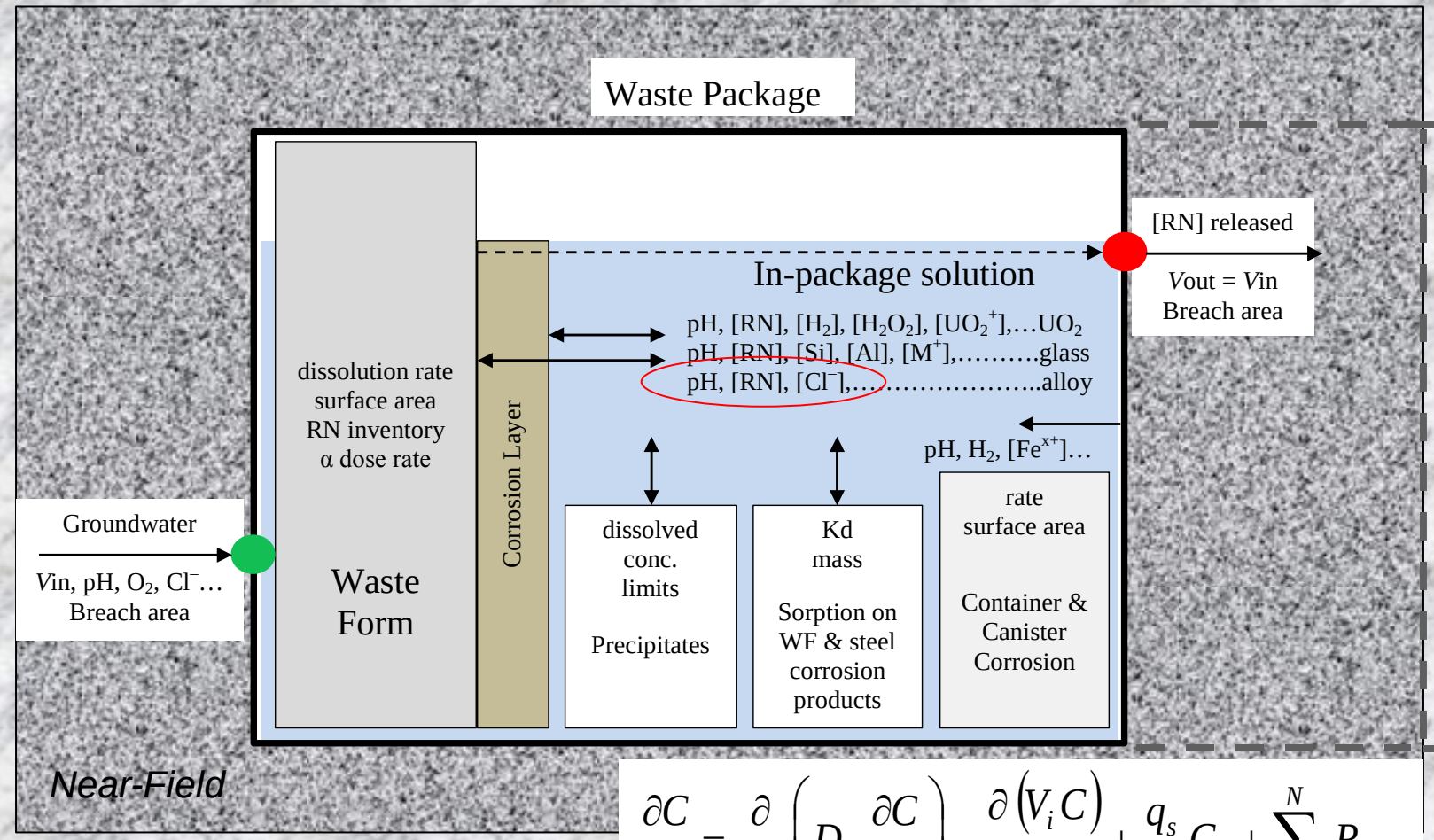
- Semi-empirical analytical expression
- Lumped parameters
- Empirical values
- Bounding values
- Interface with PA

WF models provide RN source terms for the reactive transport model used in PA:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial\left(V_i C\right)}{\partial x_i} + \frac{q_s}{\theta}C_s + \sum_{k=1}^{N} R_k$$

RN source term

Waste Forms in Waste Packages



$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial\left(V_i C\right)}{\partial x_i} + \frac{q_s}{\theta}C_s + \sum_{k=1}^{N} R_k$$

Host Rock

Alloyed Waste Form Performance Model

- **The alloy WF performance model was developed with the following objectives:**
  - Provide the radionuclide source term values needed by the PA model.
  - Be consistent with the underlying scientific bases for alloy corrosion and radionuclide release modes.
  - Be compatible with experimental methods used to derive model parameter values.

- **Testing and modeling done with a purpose:**
  - Gaining a mechanistic understanding of processes important to long-term behavior
  - Measuring RN release under range of possible environmental conditions and extent of waste form corrosion
  - Quantify effects of key environmental variables based on the measured sensitivities
  - Develop analytical representations for modeling long-term release behavior appropriate for upscaling laboratory results to full-scale waste forms
  - Integrate source term model with disposal system process models in PA

Alloy Waste Form Analytical Performance Model

- **Conceptual Oxidative-Dissolution Model**
  - Metallic constituents in multi-phase alloy composite are **oxidized** by reactions with groundwater
  - Steel-based alloy phases may **passivate** surface to slow oxidation
  - Oxide surface layers release RNs according to **solubilities (RN oxidation state)**

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

$$\frac{RN\ release\ rate}{A} = B\left(E, pH, T, etc.\right) \times P\left(E, Cl^{-}\right) \times D\left(T, RN, E\right)$$

(*E* = solution *Eh* + imposed potential)

- **Work in progress to develop expressions quantifying short-term and long-term effects of contributing processes**

calculated RN $\frac{rate}{A}$ x WF surface area x RN inventory in WF = RN release rate

Supporting Experiments

- **Generate data base of electrochemical responses for bare surface**
  - Prototype multi-phase alloys to represent range of waste form compositions
  - Standard solutions used to bound possible range of disposal conditions
  - Controlled concentrations of dissolved Cl^-, O_2, H_2O_2, etc.
  - Suite of standard electrochemical measurements
- **Hybrid electrochemical/corrosion experiments for passivation and RN release**
  - Detailed characterization of "long-term" corrosion behavior at important potentials
  - Measure Tc and U release kinetics and relate to electrochemical responses
  - Track changes in release kinetics over time due to passivation

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

Solution measurements

Electrochemical measurements

*Empirical calibration factor**

bare surface

passivating surface

*Difference between oxidation rate from corrosion current and measured Tc release

Potentiostatic/Immersion/Tafel/EIS Experiments to Parameterize Model

Tests provide form and values of *P*(*E,Cl*) and measure *FR*(*T,RN*) to derive *D*(*T,E,RN*)

Month-long potentiostatic experiments at various imposed potentials in standard solutions with different pH and [Cl^-] under controlled P(O_2) to measure **corrosion current** as corrosion layer forms

Interrupt test periodically to conduct electrochemical impedance spectroscopy (EIS) and Tafel measurements to characterize effects of surface corrosion and possible formation of **passivating layer** and sample solution for **analysis of Tc, U**, and elements in host alloys

Microscopic analyses of electrode before and after test to **identify active phases** and characterize **corrosion product phases** (e.g., for RN uptake)

Qualitative scratch test to evaluate self-healing of **passivation layer** and verify long-term benefit

Conduct experiments with several electrodes made from test alloys to use statistical averages for up-scaling local heterogeneities of test specimens to WF scale

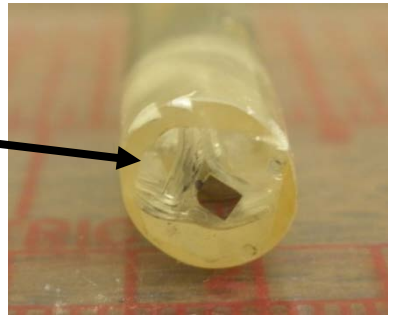
ANL Electrochemical Apparatus and Mini-electrode

Specimen is cut from ingot,

~1 cm x 1.5 mm x 1.5 mm

fixed in an acrylic resin, and fabricated into a mini-electrode that fits in an SEM

…and exposes ~2 mm^2 alloy surface area.



Experiments are run in a mini-electrochemical cell with ~20 mL solution…

(Aliquot of test solution removed for analysis is replaced by equal amount of fresh solution)

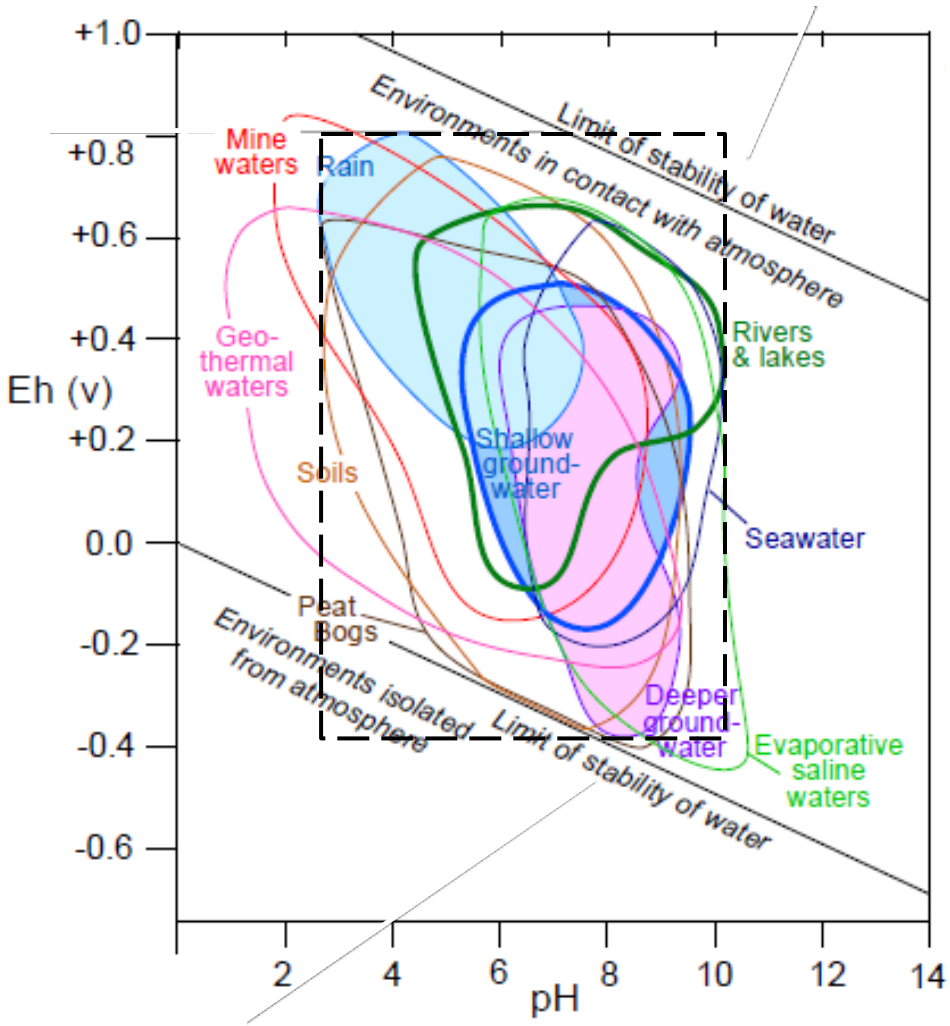
at various controlled temperatures and atmospheres.

Representative Alloyed Waste Form (RAW) Materials for Testing

Mass%

		RAW-1 (Tc)	RAW-2 (UTc)	RAW-3 (U)	RAW-4 (UTc)	RAW-5 (U)	EWF (Tc)
		Fuel Waste Constituents					
NM	Mo	11	3.2	1.8	—	—	20
NM	Ru	7.5	10.6	1.8	1	—	55
NM	Pd	5.1	7.6	1.8	—	—	10
NM	Rh	1.3	2.0	1.8	1	—	10
NM	Tc	2.4	3.7	—	1	—	5
NM	Re	—	—	3.2	—	—	—
	U	—	2.4	4.6	2	10	—
	Zr	12	9.7	3.3	15	15	—
		Metal Additives					
	316L	60.8	60.8	—	80	75	—
	HT-9	—	—	81.7	—	—	—
		Aqueous		*Pyro*			*epsilon*

Wide Range of Relevant Conditions



Generating data base of electrochemical responses for bare surfaces with suite of standard electrochemical measurements

6 prototype alloys to represent range of waste form compositions
- 316L-based
- HT9-based
- no steel

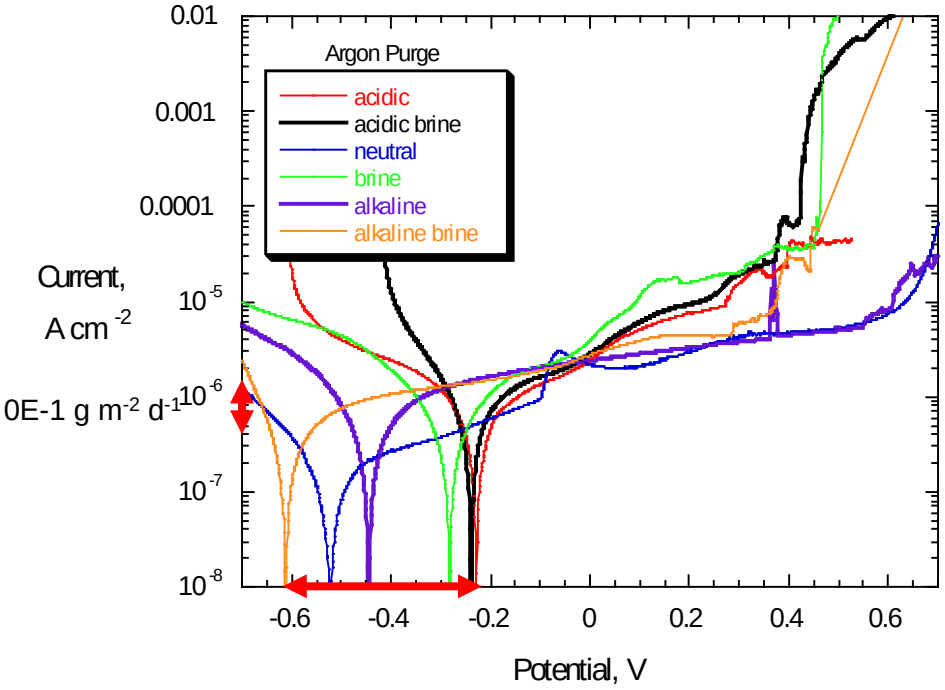
6 standard solutions used to bound possible pH range of disposal conditions
- acidic, acidic brine
- neutral, neutral brine
- alkaline, alkaline brine

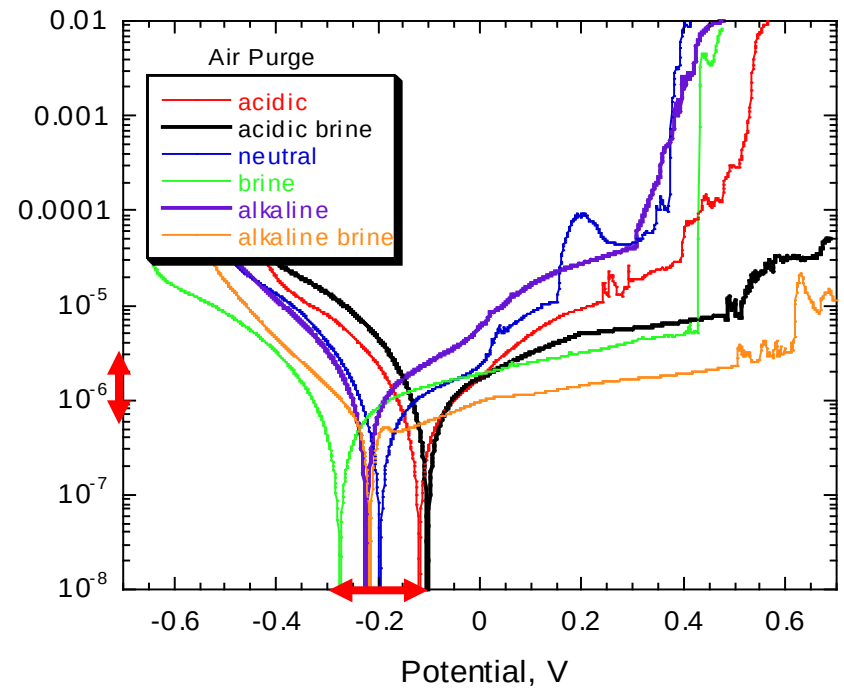
3 purge gases to impose larger Eh range
- air, argon, safe gas (3% H_2 in He)

Controlled concentrations of dissolved Cl^-, H_2O_2, etc. for chemical effects

from Railsback based on Baas-Becking

Bare Surface Potentiodynamic Measurements with RAW-5(U) 75SS-15Zr-10U





Narrow range of corrosion potentials (and corrosion currents) under a wide range of solution conditions; electrochemical measurements address $B(E, pH, T)$ term.

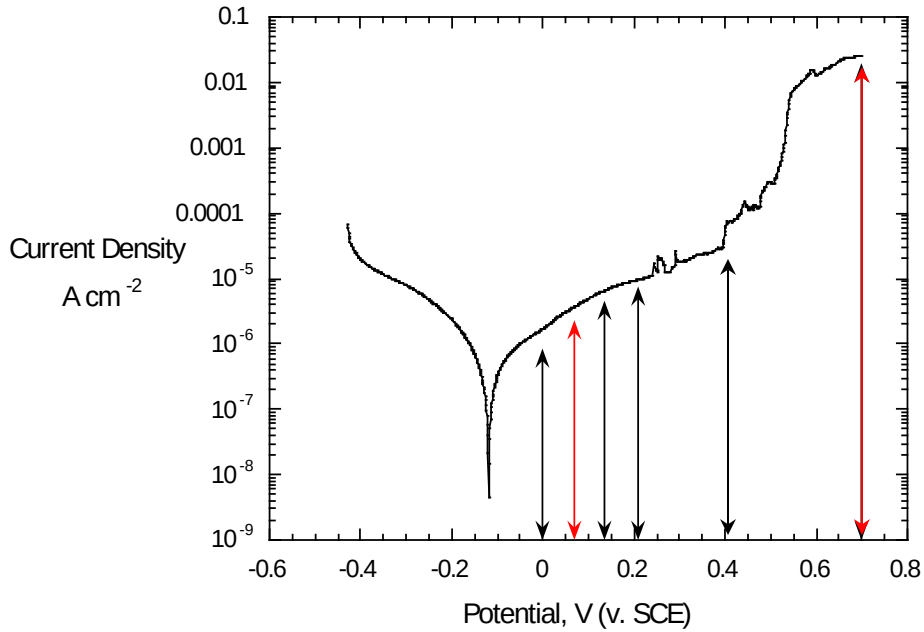
Bare surface characterizations completed for RAW-1, RAW-2, RAW-3, RAW-5, and EWF-1.

Voltages for Potentiostatic Hold Experiments to Evaluate Time Dependence

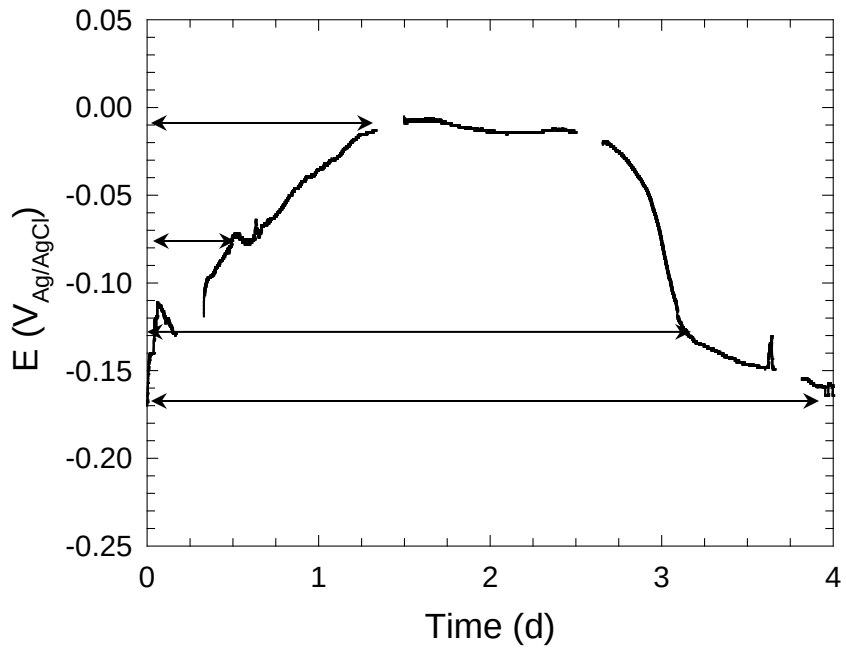
Potentiostatic experiments conducted at various imposed potentials to monitor corrosion current and RN release over time as corrosion layer forms.

Hold potentials selected based on behaviors measured in potentiodynamic scans and open circuit tests (e.g., range and change).

Potentiodynamic scan for RAW-5 in acidic brine

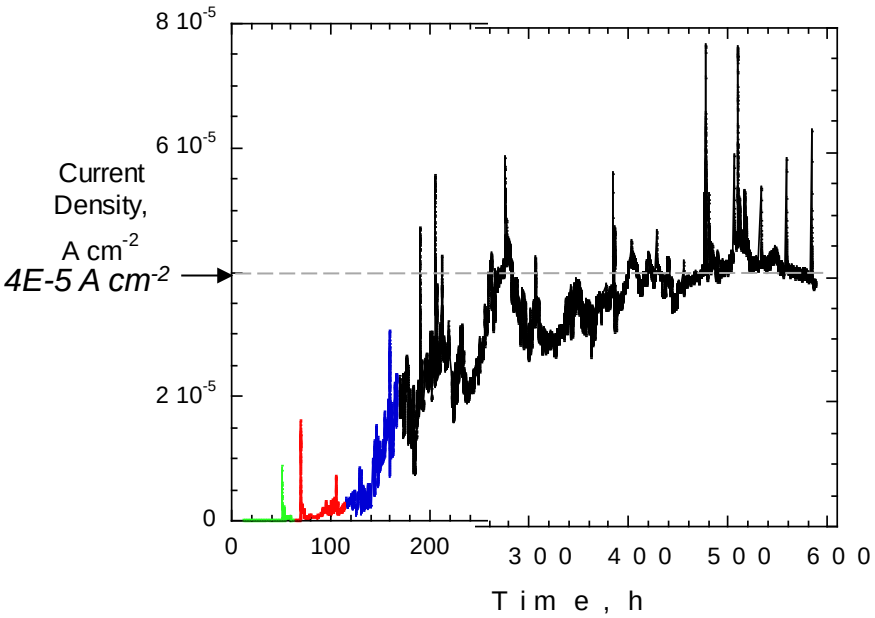


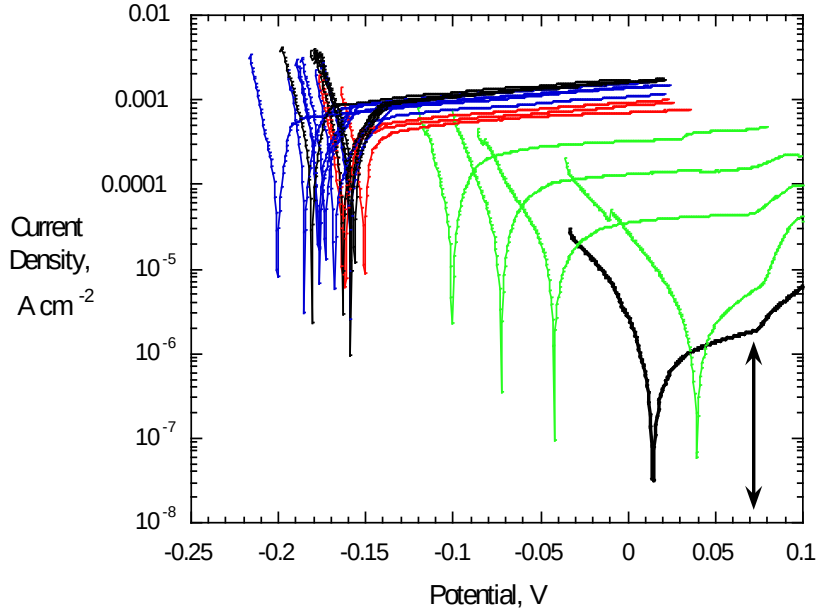
Open circuit tests with RAW-2 in acidic solution



RAW-5 in Acidic Brine at 70 mV (v. SCE)

0.1 mm H_2SO_4 + 0.1 mm NaCl at 30 °C

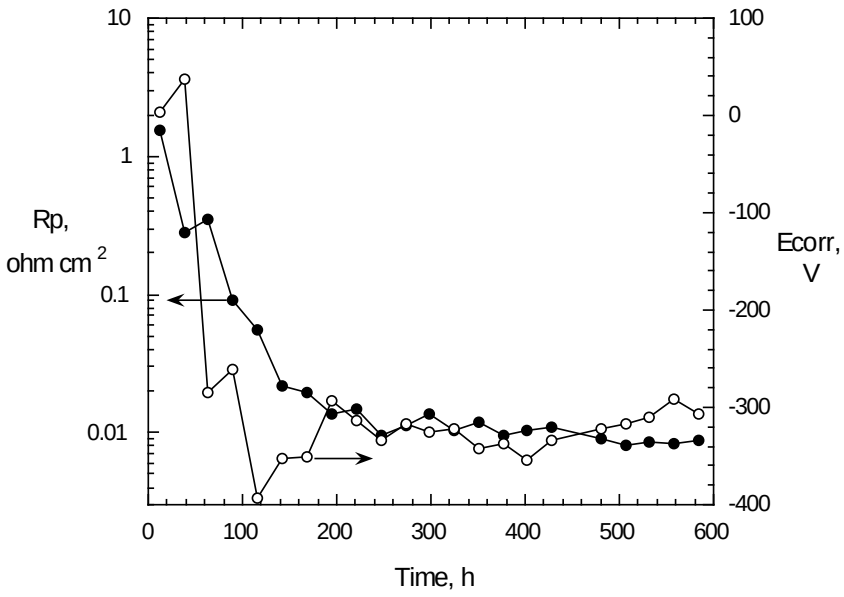


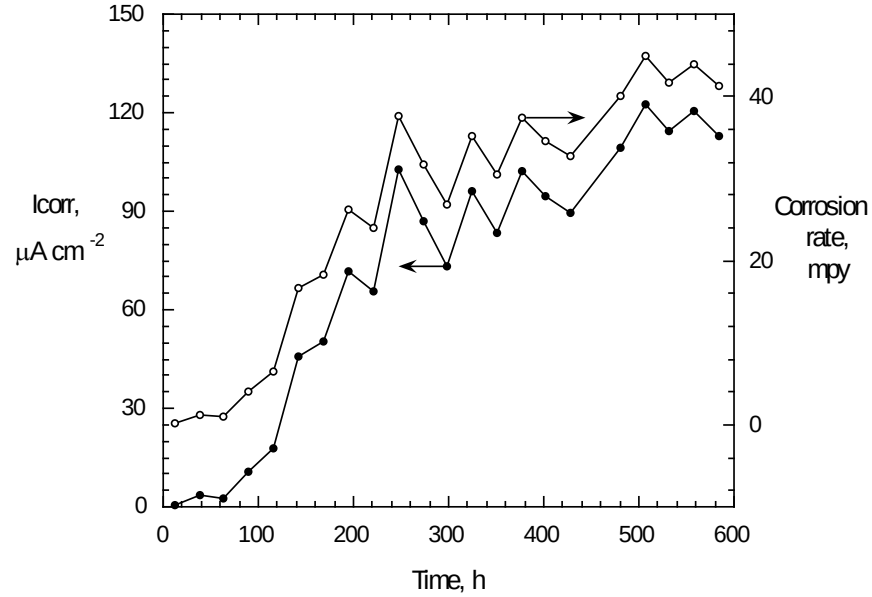


PotentioStatic at 70 mV.
Corrosion current increases then stabilizes

Tafel at OC.
Corrosion potential drifts cathodic then stabilizes

Evolution of Corrosion Characteristics of RAW-5



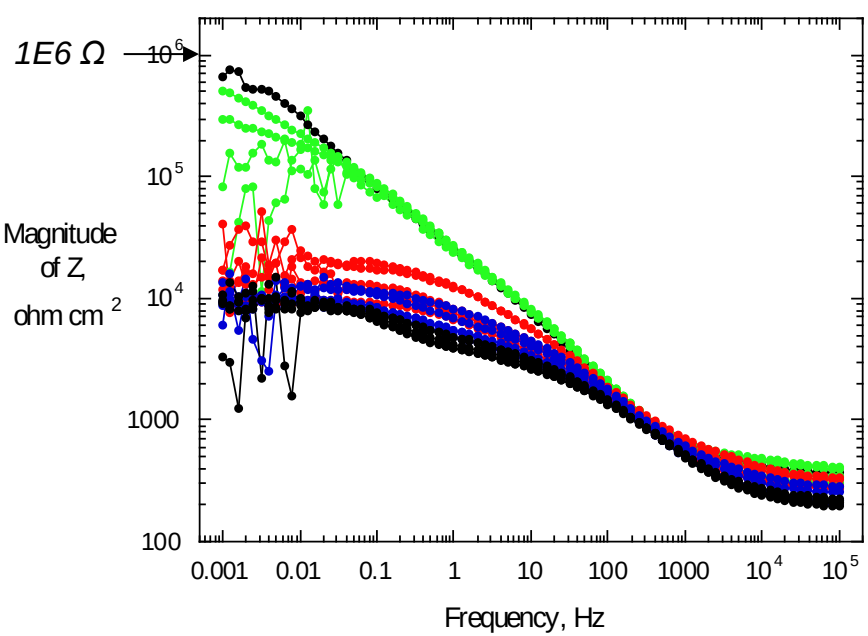


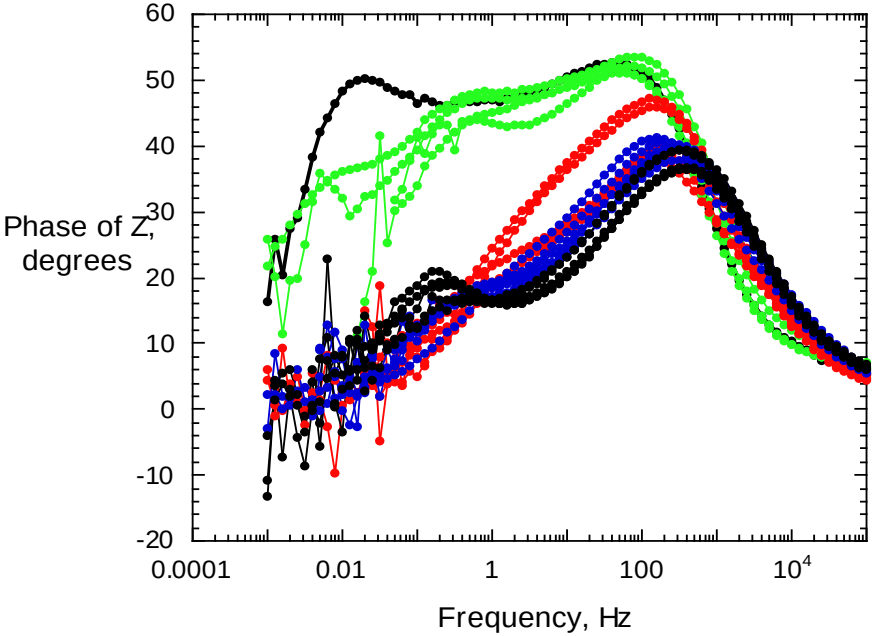
Tafel at OC.

Corrosion potential and polarization resistance (Rp) decrease then stabilize.

Corrosion current (Icorr) and corrosion rate increase with time then stabilize.

Evolution of Surface Properties on RAW-5



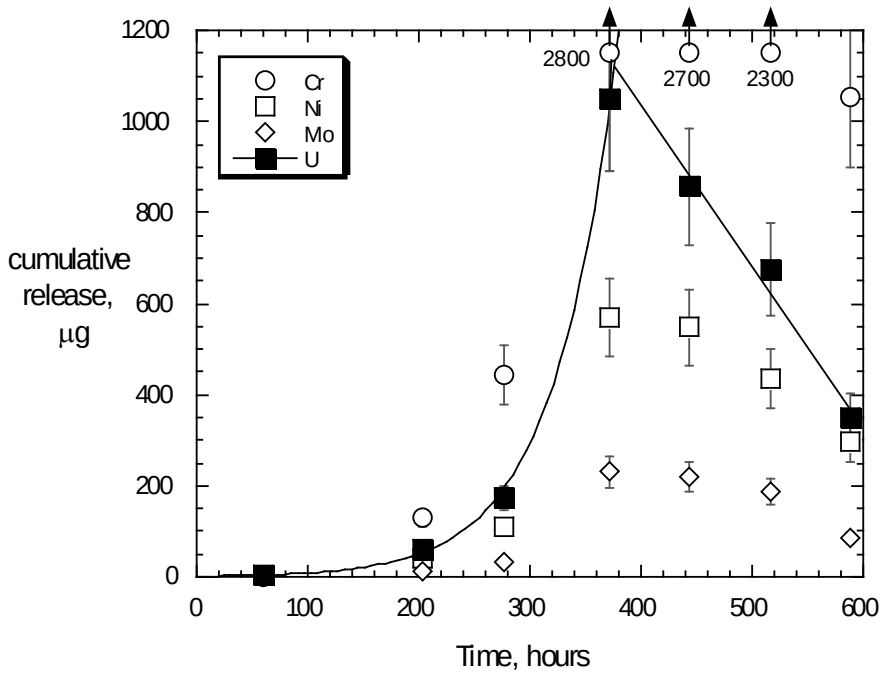


Electrochemical Impedance Spectroscopy at 70 mV.

Polarization resistance decreases from ~1 MΩ then stabilizes at ~10 kΩ.

Corrosion layer loses capacitive properties.

Release to Solution during Corrosion RAW-5 at 70 mV (v. SCE)

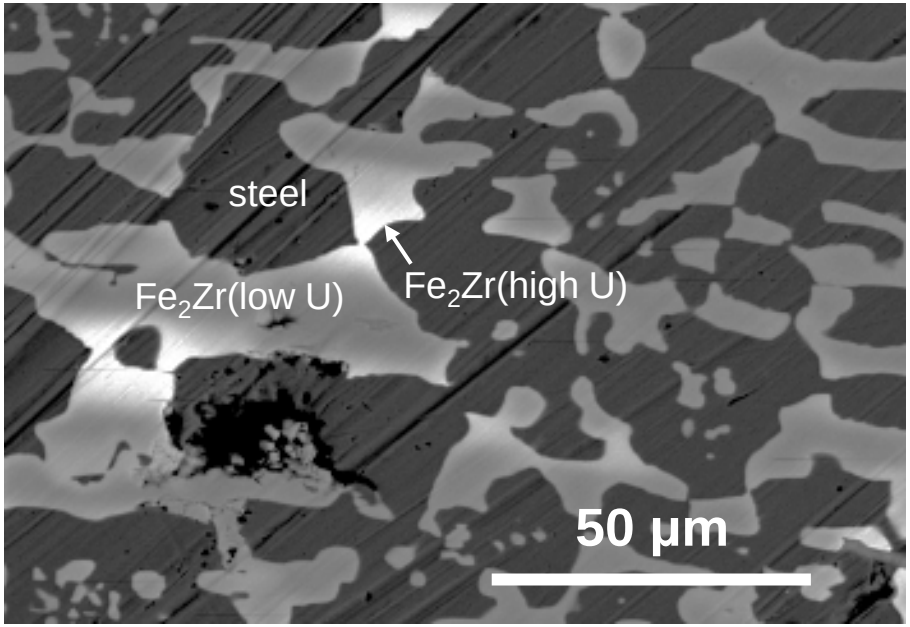


Periodic solution analysis by ICP-MS.
Releases adjusted for dilution during sampling (3-mL aliquot replaced by 3 mL acidic brine solution.)

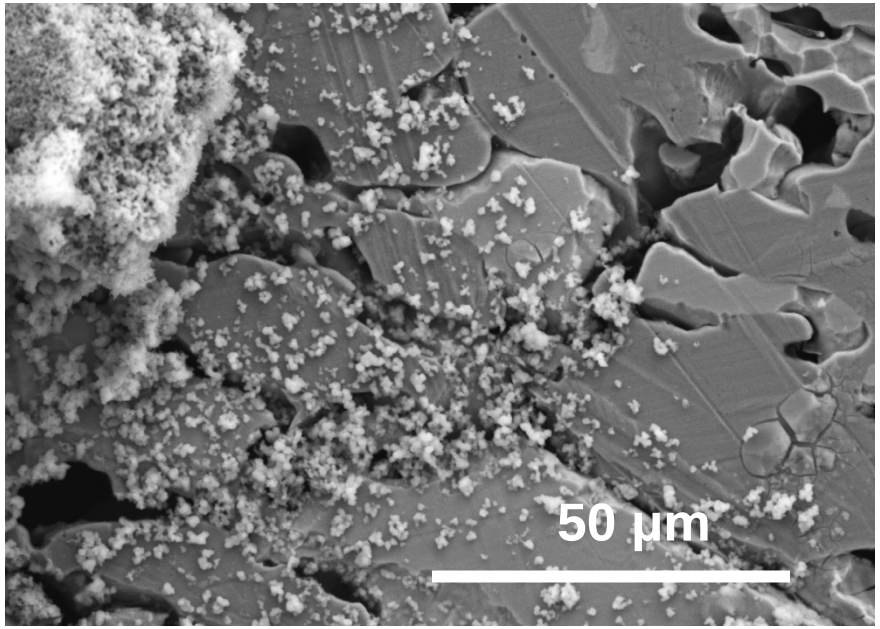
This test needed more frequent sampling and larger samples

Suspended solids after about 10 days (shown after agitation)

RAW-5(U) Corroded in Potentiodynamic Experiments in acidic brine at 70 mV

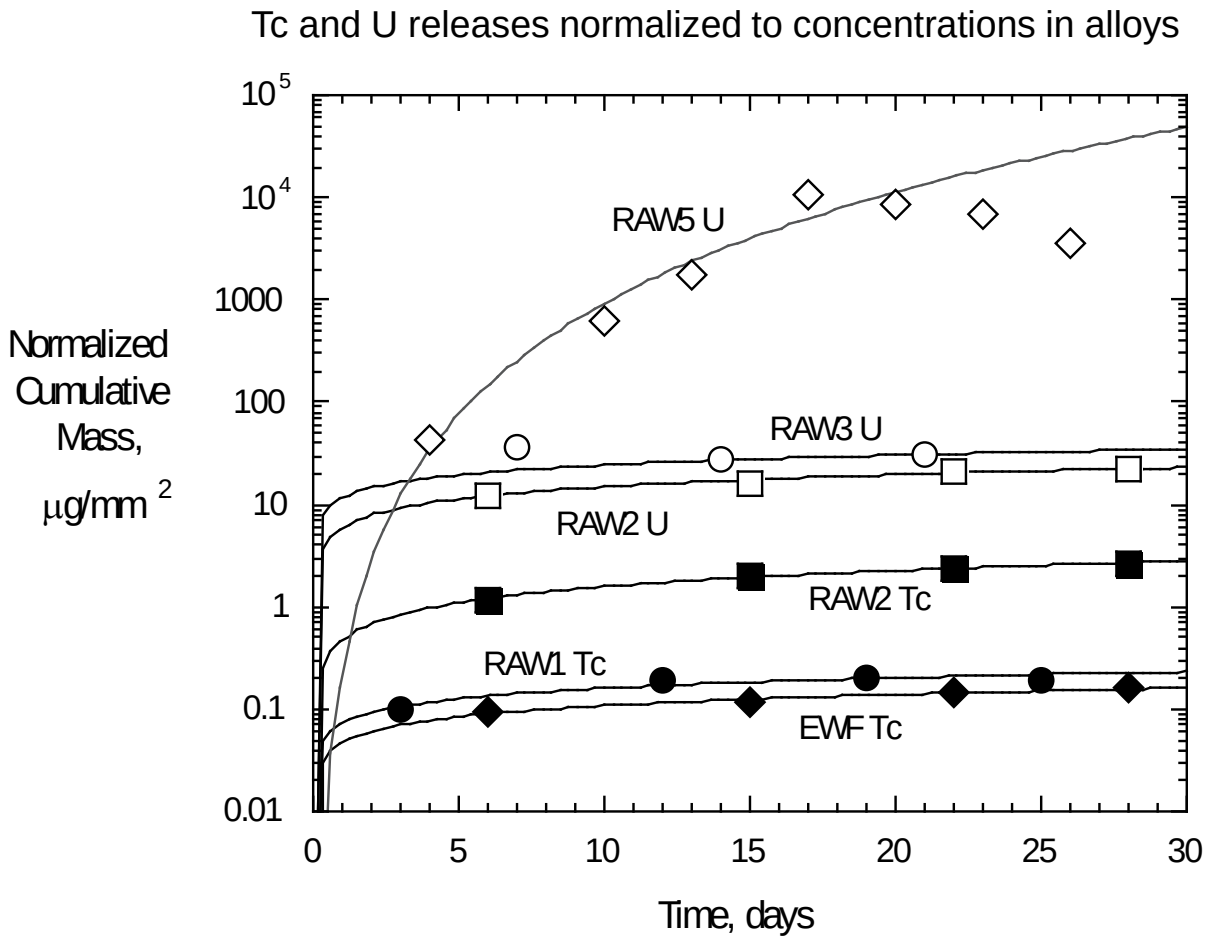


Surface microstructure prior to testing



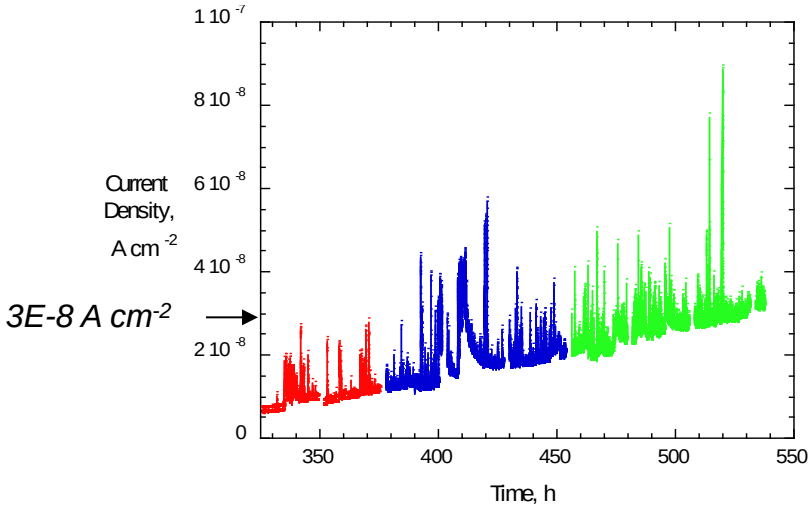
Corroded surface after test showing corrosion products and loss of Fe_2Zr(low U)

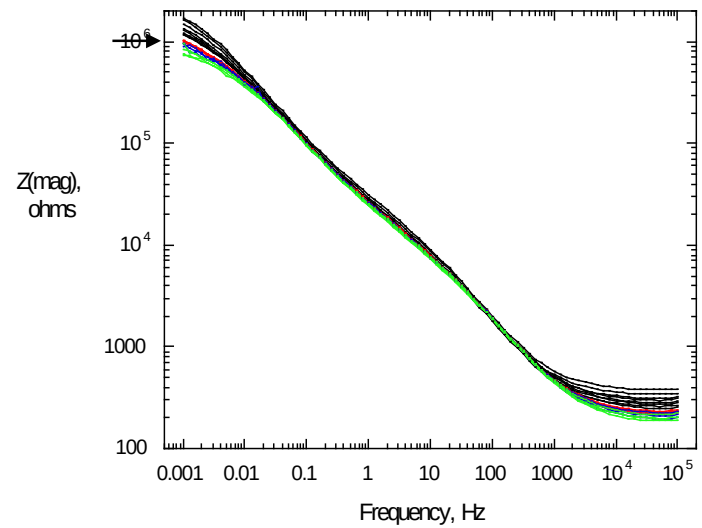
Tc and U Released in Acidic Brine at 70 mV (v. SCE)

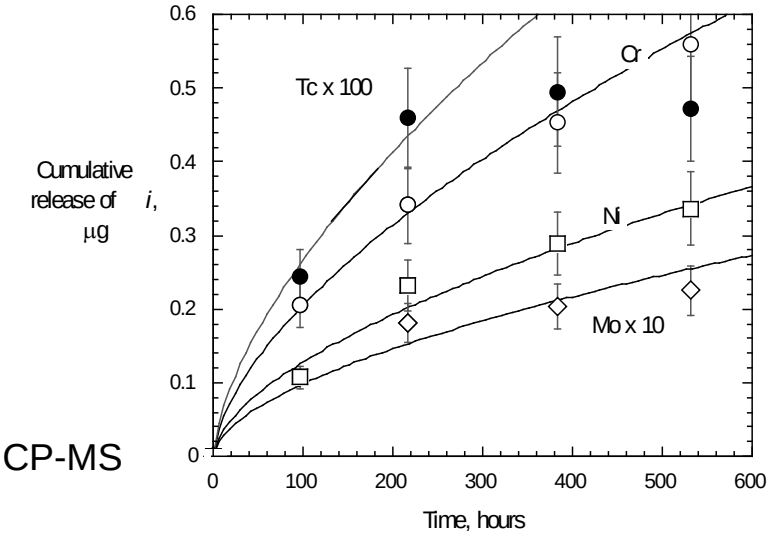


RAW-1 Corrosion in Acidic Brine

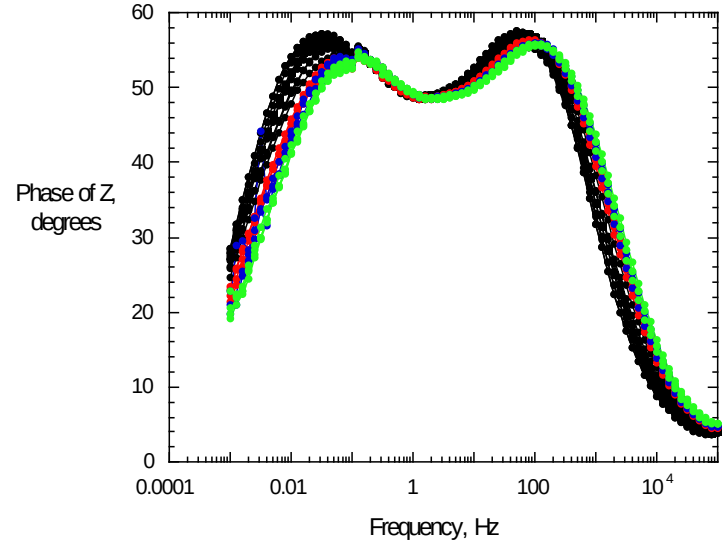
at 70 mV (v. SCE) 61SS-12Zr-26NM-2Tc



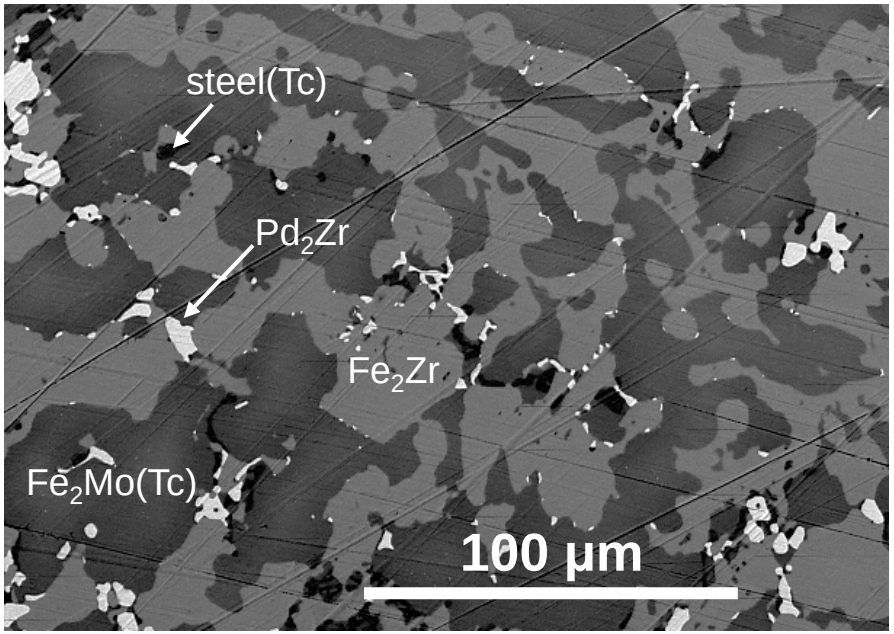




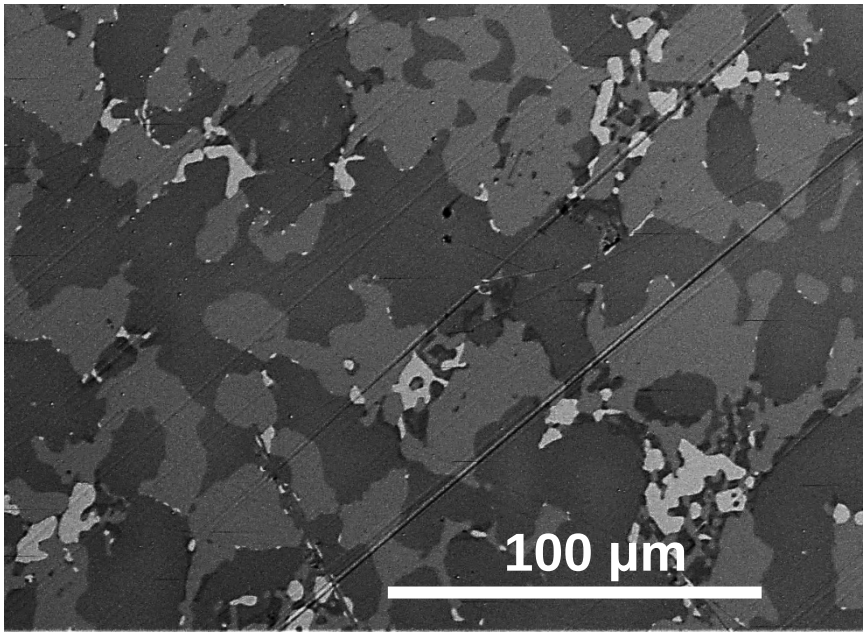
ICP-MS



RAW-1(Tc) Microstructure



Surface microstructure prior to testing



Surface after testing with no visible corrosion

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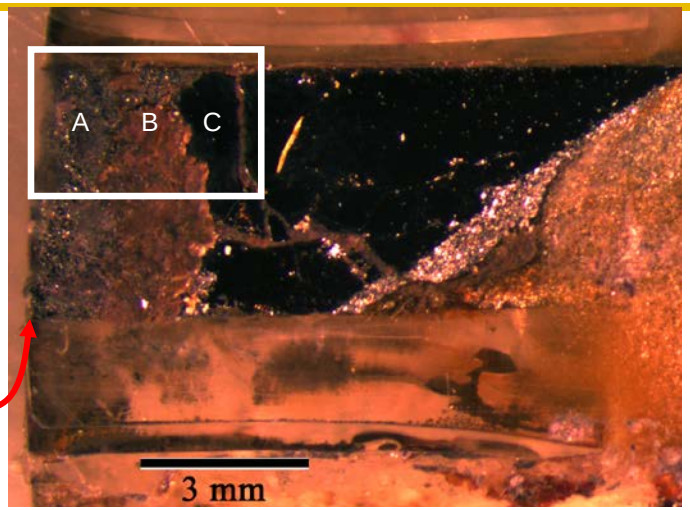
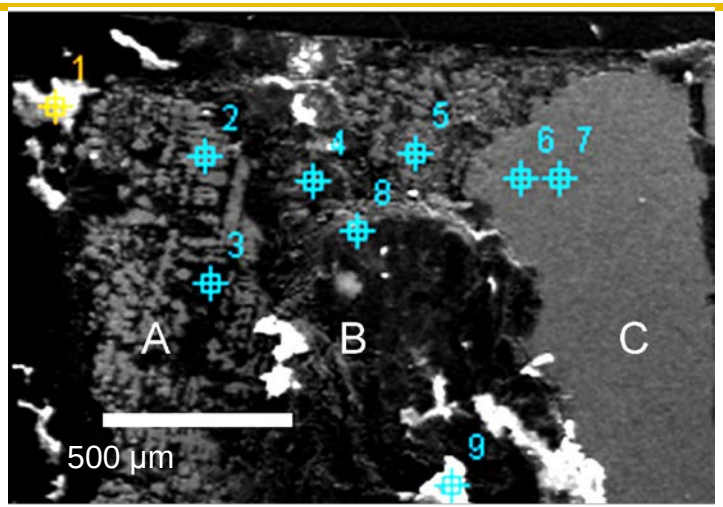
Cross-Sectioned RAW-1 Electrode
corroded at 700 mV in acidic brine

exposed surface on electrode





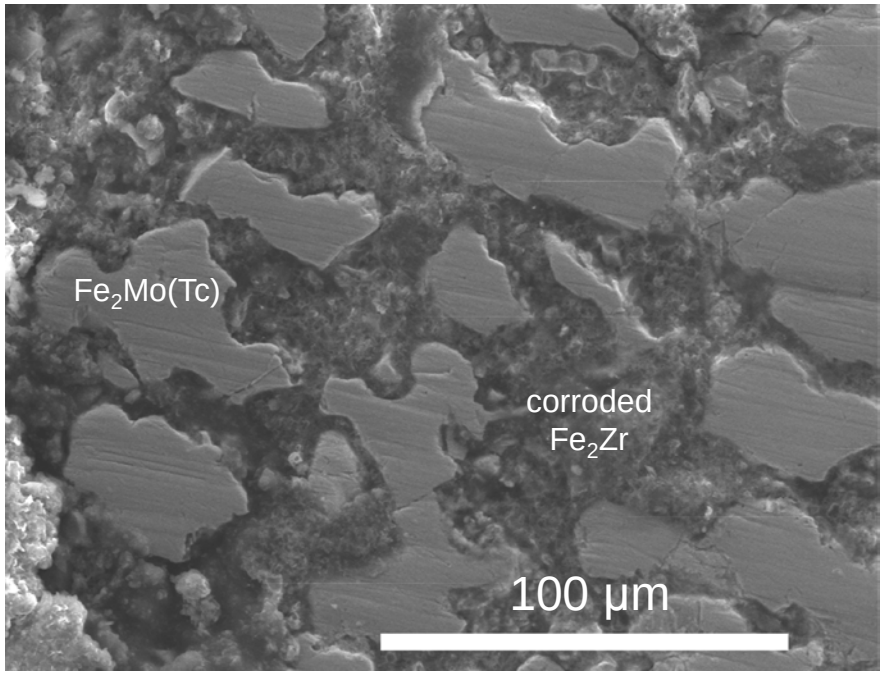
EDS atom fractions

	Spot	Cr	Fe	Ni	Zr	Mo	Tc	Ru	Rh	Pd
Corrosion layer	1	0.0	0.03	0.02	0.06	0.14	0.0	0.58	0.17	0.0
	2	0.18	0.46	0.04	0.01	0.19	0.048	0.06	0.00	0.00
	3	0.05	0.23	0.00	0.06	0.09	0.0	0.38	0.11	0.06
	4	0.20	0.55	0.04	0.01	0.11	0.033	0.05	0.01	0.01
	5	0.17	0.43	0.04	0.00	0.23	0.051	0.07	0.0	0.01
	8	0.01	0.45	0.05	0.00	0.0	0.0	0.33	0.14	0.03
	9	0.0	0.36	0.10	0.0	0.0	0.0	0.28	0.13	0.14
Alloy	6	0.03	0.31	0.12	0.30	0.05	0.004	0.10	0.03	0.06
	7	0.05	0.32	0.11	0.27	0.05	0.000	0.11	0.02	0.07
Volume fraction in bulk alloy: 0.52	Fe_2Mo	0.21	0.53	0.04	0.00	0.13	0.034	0.04	0.00	0.01
0.32	Fe_2Zr	0.05	0.40	0.15	0.22	0.03	0.007	0.08	0.02	0.05
0.13	steel	0.14	0.65	0.09	0.01	0.04	0.013	0.03	0.01	0.01
0.03	Pd_2Zr	0.01	0.05	0.13	0.22	0.0	0.0	0.01	0.03	0.54

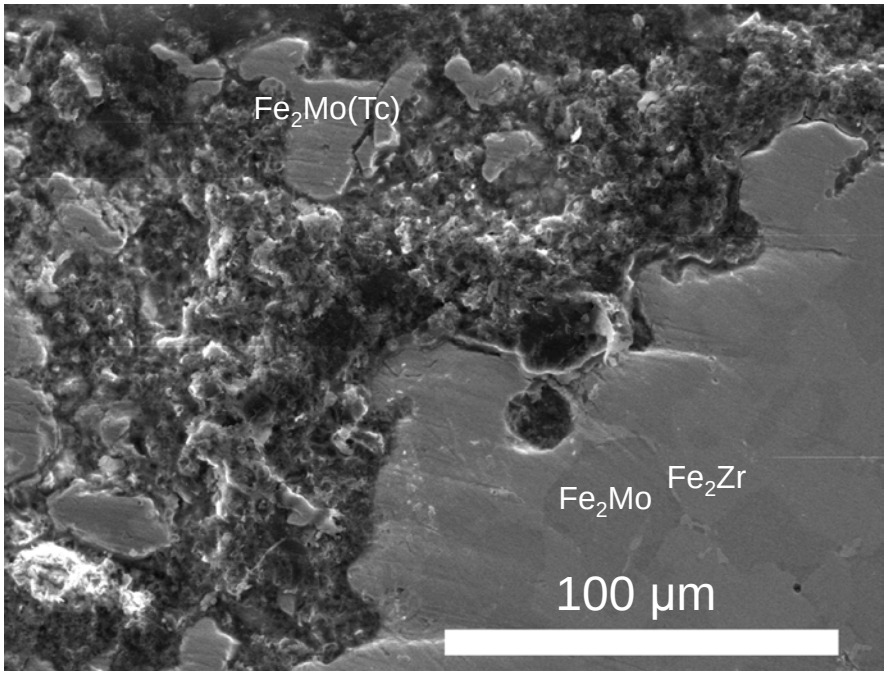
Corroded Fe_2Zr

RAW-1 Corrosion Layer
at 700 mV in acidic brine

Skeleton of Fe_2Mo in corroded layer (B)



Interface of corroded layer (B) and alloy (C)



No evidence of preferential corrosion at phase boundaries

Summary and Future Plan

- Modular approach to integrate all waste form radionuclide source term models into PA calculations has been developed; this is primary role of WF performance models and primary objective of WF testing program.
- Testing protocol developed in FY2013 to parameterize the semi-empirical analytical model for alloy waste form degradation has been successfully demonstrated.
- Initial tests with multi-phase alloys containing U and Tc to demonstrated approach were completed successfully and provide insights into long-term corrosion behavior.
- Tests continuing in various solutions and purge gases to generate data base to determine analytical dependencies on passivation and dissolution behaviors.
- Analytical model relates measured electrochemical effects of solution on oxidation of AWF to the dissolution of constituent phases and release of RNs; model provides spatial average for multi-phase waste forms. In progress.
- Methods to upscale parameterized model to full-size WF being developed.

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Acknowledgements

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