NRC Form 390A
(12-2003)
NRCMD 3.9

U.S. NUCLEAR REGULATORY COMMISSION

RELEASE TO PUBLISH UNCLASSIFIED NRC CONTRACTOR SPEECHES, PAPERS, AND JOURNAL ARTICLES

(Please type or print)

1. TITLE (State in full as it appears on the speech, paper, or journal article)
Evolution of Fluid Chemistry Inside a Waste Package Due to Carbon-Steel and Simulated High-Level Waste Glass Corrosion

2. AUTHOR(s)
Xihua He, Paul Bertetti, and David Pickett

3. NAME OF CONFERENCE, LOCATION, AND DATE(s)
Materials Science & Technology 2007 Conference and Exhibition
Detroit, MI September 16-20, 2007

4. NAME OF PUBLICATION
Materials Science & Technology 2007 Conference

5. NAME AND ADDRESS OF THE PUBLISHER
The Minerals, Metals & Materials Society
184 Thorn Hill Road
Warrendale, PA 15086-7514

TELEPHONE NUMBER OF THE PUBLISHER
(724) 776-9000

6. CONTRACTOR NAME AND COMPLETE MAILING ADDRESS (*Include ZIP code*)
Center for Nuclear Waste Regulatory Analyses
Southwest Research Institute
6220 Culebra Rd.
San Antonio, TX 78238

TELEPHONE NUMBER OF THE CONTRACTOR
(210) 522-5194 (X. He)

YES	NO	7. CERTIFICATION (ANSWER ALL QUESTIONS)		
	X	A. COPYRIGHTED MATERIAL – Does this speech, paper, or journal article contain copyrighted material? If yes, attach a letter of release from the source that holds the copyright.		
	X	B. PATENT CLEARANCE – Does this speech, paper, or journal article require patent clearance? If yes, the NRC Patent Counsel must signify clearance by signing below.		
		NRC PATENT COUNSEL *(Type or Print Name)*	SIGNATURE	DATE
X		C. REFERENCE AVAILABILITY – Is all material referenced in this speech, paper, or journal article available to the public either through a public library, the Government Printing Office, the National Technical Information Service, or the NRC Public Document Room? If no, list below the specific availability of each referenced document.		
		SPECIFIC AVAILABILITY		
	X	D. METRIC UNIT CONVERSION – Does this speech, paper, or journal article contain measurement and weight values? If yes, all must be converted to the International System of Units, followed by the English units in brackets, pursuant to the NRC Policy Statement implementing the Omnibus Trade and Competitiveness Act of 1988, Executive Order 12770, July 25, 1991.		

8. AUTHORIZATION

The signatures of the NRC project manager and the contractor official certify that the NRC contractor speech, paper, or journal article is authorized by NRC, that it has undergone appropriate peer review for technical content and for material that might compromise commercial proprietary rights, and that it does not contain classified, sensitive unclassified, or nonpublic information. (NRC MD 3.9, Part II(A)(1)(d))

A. CONTRACTOR AUTHORIZING OFFICIAL *(Type or print name)*	SIGNATURE	DATE
Gordon W. Wittmeyer, Assistant Director	Gordon Wittmeyer	7/30/07
B. NRC RESPONSIBLE PROJECT MANAGER *(Type or print name)*	OFFICE/DIVISION	MAIL STOP

TELEPHONE NUMBER	E-MAIL I.D.	Did you place the speech, paper, or journal article in ADAMS? YES ☐ NO ☐ If so, provide the ADAMS Accession No. (Use Template OCIO 099)

SIGNATURE	DATE

PRINTED ON RECYCLED PAPER

Attachment 1

Checklist for Implementing the Guidelines on Technical Publications and Presentations

Date	Initials	Action
General Planning and Scheduling		
7/20/07	[illegible]	CNWRA Manager (for CNWRA initiated publications) or NRC Branch-Chief (for NRC initiated publications) concurrence of no anticipated impact on assigned or anticipated tasks.
7/20/07	[illegible]	CNWRA Manager (for CNWRA initiated publications) or NRC Branch-Chief (for NRC initiated publications) approval of planned technical and programmatic scope of paper or presentation.
7/30/07	XH	CNWRA manager/author Informally discusses with NRC Branch Chief or designee on planned scope; this may be done on telephone or via email.
7/30/07	XH	Acknowledgment of staff member that paper or presentation may be later withheld from publication for programmatic reasons.
Materials Generally Unsuitable for Inclusion		
7/20/07	[illegible]	CNWRA Manager (for CNWRA initiated publications) or NRC Branch-Chief (for NRC initiated publications) review and determination that the document contains no information that is unsuitable for inclusion. [In most cases, the review will stop at this point.]
		If needed, NRC programmatic review and determination that the document contains no information that is unsuitable for inclusion.
		If needed, NRC OGC review and determination that the document contains no information that is unsuitable for inclusion.
Decision and Agreement on Constraints		
		Acknowledgment of staff member that—despite approval—the paper or presentation may be later withheld for programmatic reasons.
		Acknowledgment of staff member of any constraints imposed on discussions about and/or oral presentation of the document.
		NRC Deputy Director or designee High-Level Waste Repository Safety

G:\BSagar\HLWRS Board Meetings\Guidelines on Publications and Presentations Rev1.wpd

Evolution of Fluid Chemistry Inside a Waste Package Due to Carbon Steel, Stainless Steel, and Simulated High-Level Waste Glass Corrosion

Xihua He, David Pickett, Paul Bertetti, and Vijay Jain[1]
Center for Nuclear Waste Regulatory Analyses
Southwest Research Institute®
San Antonio, Texas, U.S.A.

CNWRA
A center of excellence in earth sciences and engineering TM

MS&T 2007
Detroit, Michigan
September 16–20, 2007

[1] Now at Washington Group International

Outline

- Background
- Objectives
- Experiments
  - Carbon Steel and Glass Immersion
  - Neptunium Sorption
  - Stainless Steel Immersion
- Results
- Summary

Background

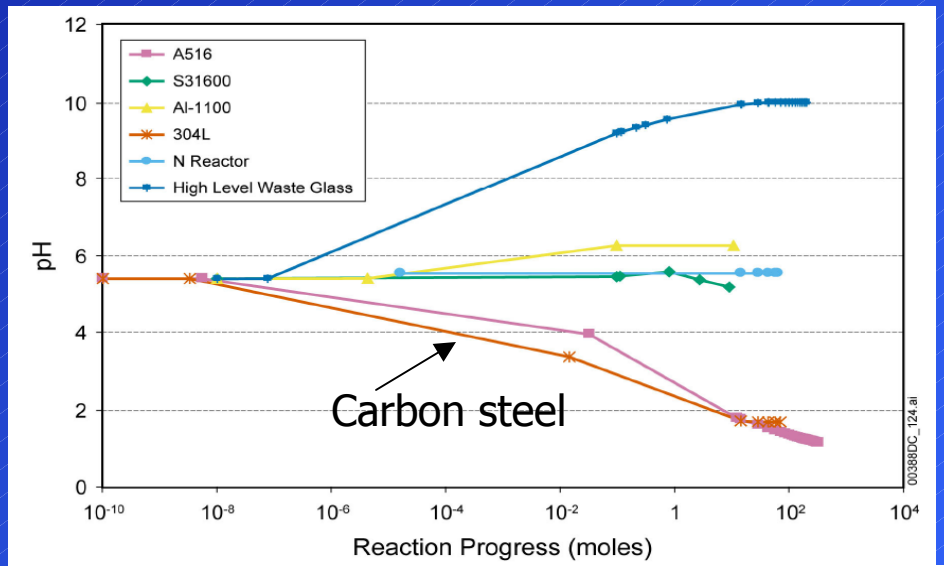
(Modified from U.S. DOE, Yucca Mountain Science and Engineering Report, Rev 1, 2002)

- The waste package would be an important engineered barrier controlling the release of radionuclides from the potential repository at Yucca Mountain
- Penetration of the waste package may allow seepage water to enter and contact the waste forms

- Reactions with in-package components are expected to affect water chemistry, which affects waste form degradation and radionuclide release (e.g., Pu and Np)
- Steel corrosion products may retard release of radionuclides such as Np
- A newer DOE canister design eliminates most carbon steel internal components

DOE In-Package Chemistry Model Abstraction

- Corrosion of A516 carbon steel leads to pH values of 1.5 to 2, due to
  - oxidation of elemental sulfur
  - large quantity and high corrosion rate of steel
- Multicomponent models predict minimum pH of ~4
- Surface complexation model predicts that the pH will be buffered at 7.3 to 8.1



Evolution of pH and Reactants for Codisposal Waste Packages under 1.5-L/yr Seepage-Dripping Conditions and 10% Fuel Exposure at 25°C

(Bechtel SAIC Company, LLC. Technical Basis Document No. 7: In-Package Environment and Waste Form Degradation and Solubility, Rev 1, 2004)

Objectives

- Conduct independent analysis of in-package chemistry to
  - Reduce uncertainty in possible range of chemistries on corrosion of steels and glass waste form
  - Provide insights into DOE in-package chemistry abstraction
- Experimentally determine the evolution of the chemical composition and pH of the fluid inside the waste package due to corrosion of carbon steel and stainless steel samples starting with expected groundwater compositions
- Characterize the corrosion products by particle size distribution, mineral phases, and neptunium sorption

Experiments

- Materials: A516 carbon steel, 316L stainless steel, and simulated SRS-202G high-level waste glass

Chemical Composition (Weight Percent)											
	Fe	Cr	Ni	Mo	V	Al	Mn	Si	P	S	C
A516 Carbon Steel (Heat D84944)	Bal	0.02	NA	<0.01	<0.01	0.021	0.90	0.30	0.011	0.011	0.18
316L Stainless Steel Heat P80746	Bal	16.35	10.04	2.07	NA	NA	1.58	0.49	0.026	0.018	0.014

Simulated high-level waste glass: Al_2O_3 (5.81), B_2O_3 (10.32), BaO (0.03), CaO (1.08), Cr_2O_3 (0.41), CuO (0.12), Fe_2O_3 (9.27), K_2O (3.28), La_2O_3 (0.02), Li_2O (3.44), MgO (1.70), MnO_2 (1.54), MoO_3 (0.01), Na_2O (15.33), Nd_2O_3 (0.01), NiO (0.95), P_2O_5 (0.32), PbO (0.04), SiO_2 (44.46), SnO (0.02), TiO_2 (0.13), UO_3 (1.61), ZnO (0.01), and ZrO_2 (0.08)

Experiments—continued

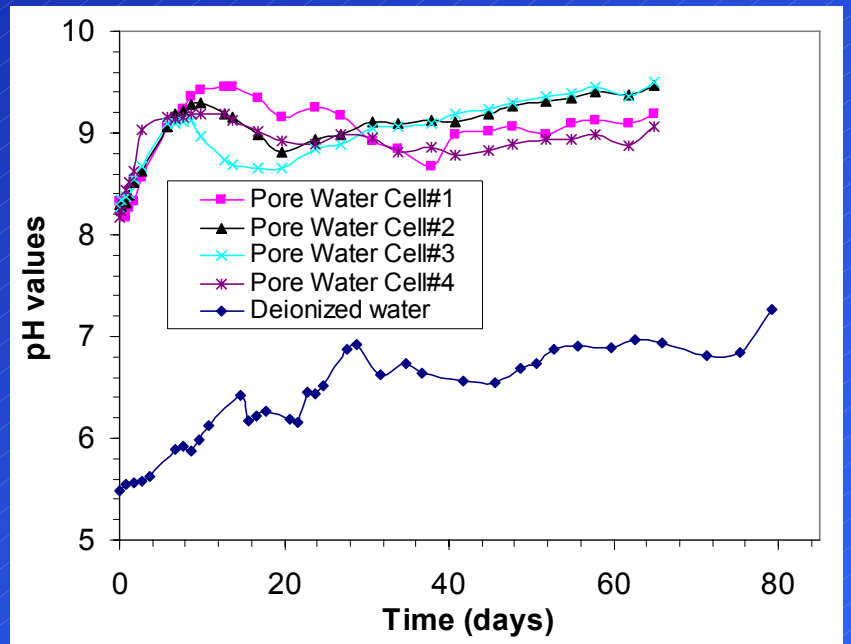
- Solution: simulated sodium-pore water

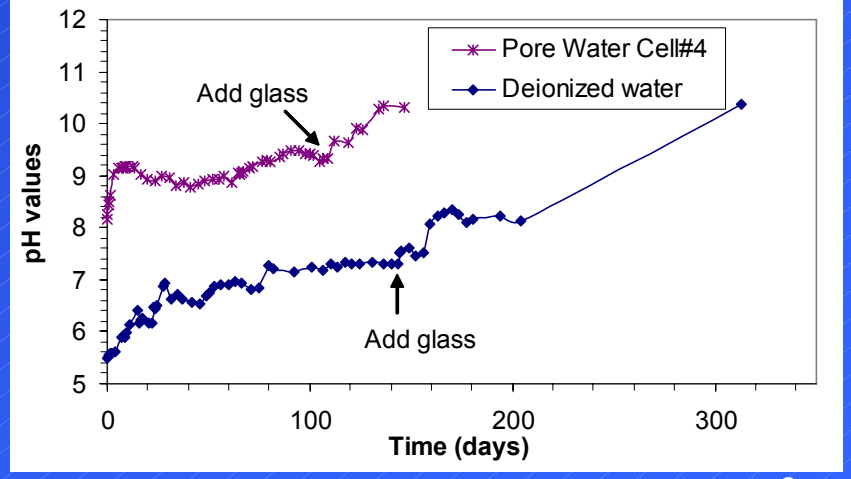
Chemical Composition of Simulated Sodium-Pore Water										
Species	Ca^{2+}	K^{+}	Mg^{2+}	Na^{+}	SO_4^{2-}	NO_3^{-}	Cl^{-}	F^{-}	HCO_3^{-}	pH
Content (mg/L)	18.1	6.16	3.37	120	31.3	0.42	24.2	6.15	299	8.48

- Test solution volume : surface area of carbon steel/stainless steel = 13.7 mL/cm^2
- Temperature: 60 °C
- Tests: Immersion in glass cell lined with polytetrafluoroethylene

In-Package Chemistry: pH During Carbon Steel Corrosion in Simulated Sodium-Pore Water

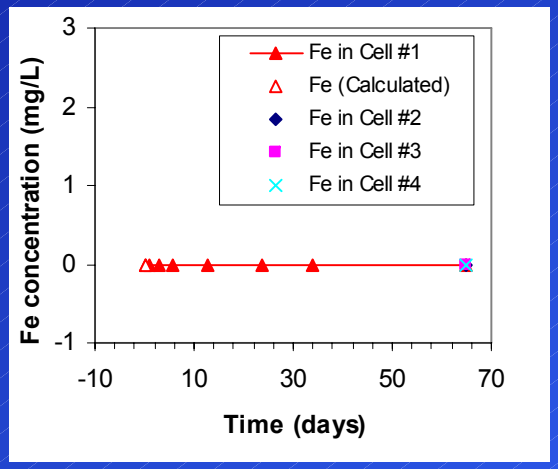
- High pH (>9) seen in simulated pore waters; moderate pH in deionized water
- In both cases, the pH values were higher than predicted by DOE model
- Addition of glass increased the pH further

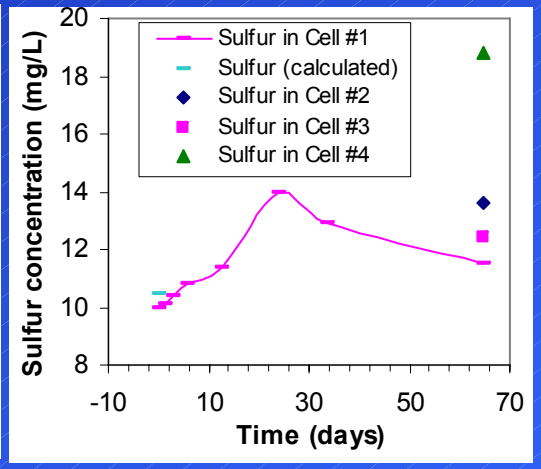


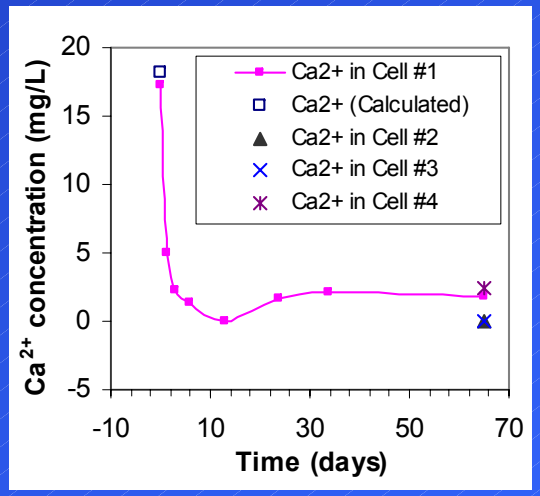


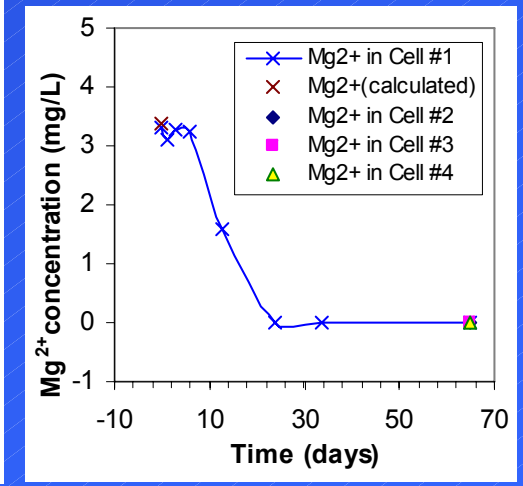
In-Package Chemistry: Chemical Composition During Carbon Steel Corrosion

- No soluble iron detected in solution
- Sulfur concentration increased during the first 20 days, but it decreased with time
- Calcium and magnesium decreased with time





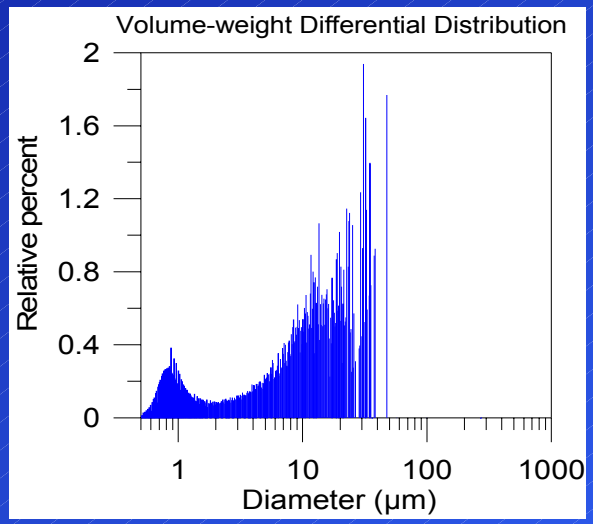


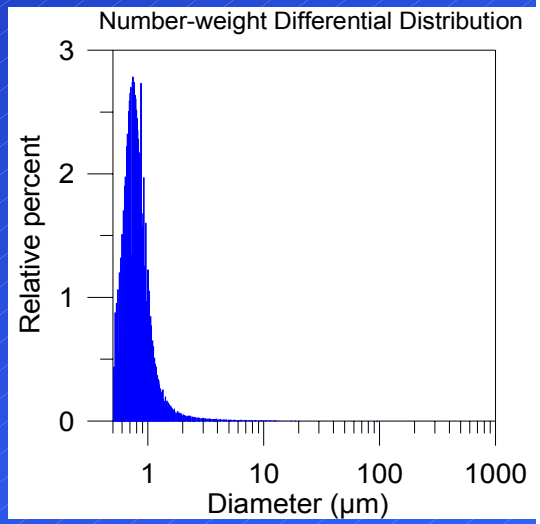


In-Package Chemistry: Carbon Steel Corrosion Products

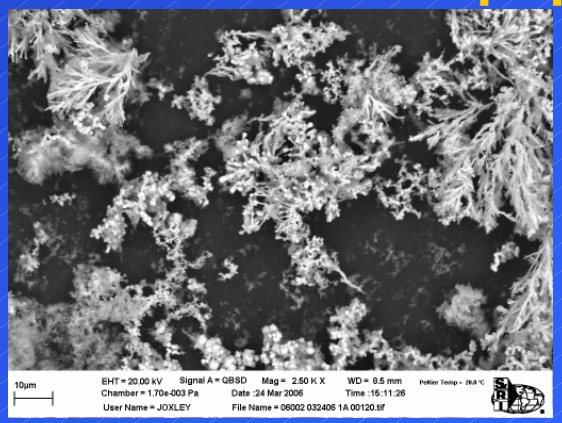
- Most particles ranged from 0.5 to 3 µm
- Small number of large particles contributed significant mass and volume
- The corrosion products tended to agglomerate
- XRD showed that the corrosion products were primarily magnetite

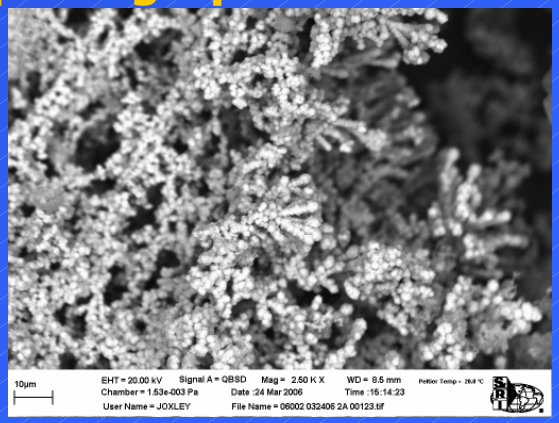
Size distribution analysis in micron range





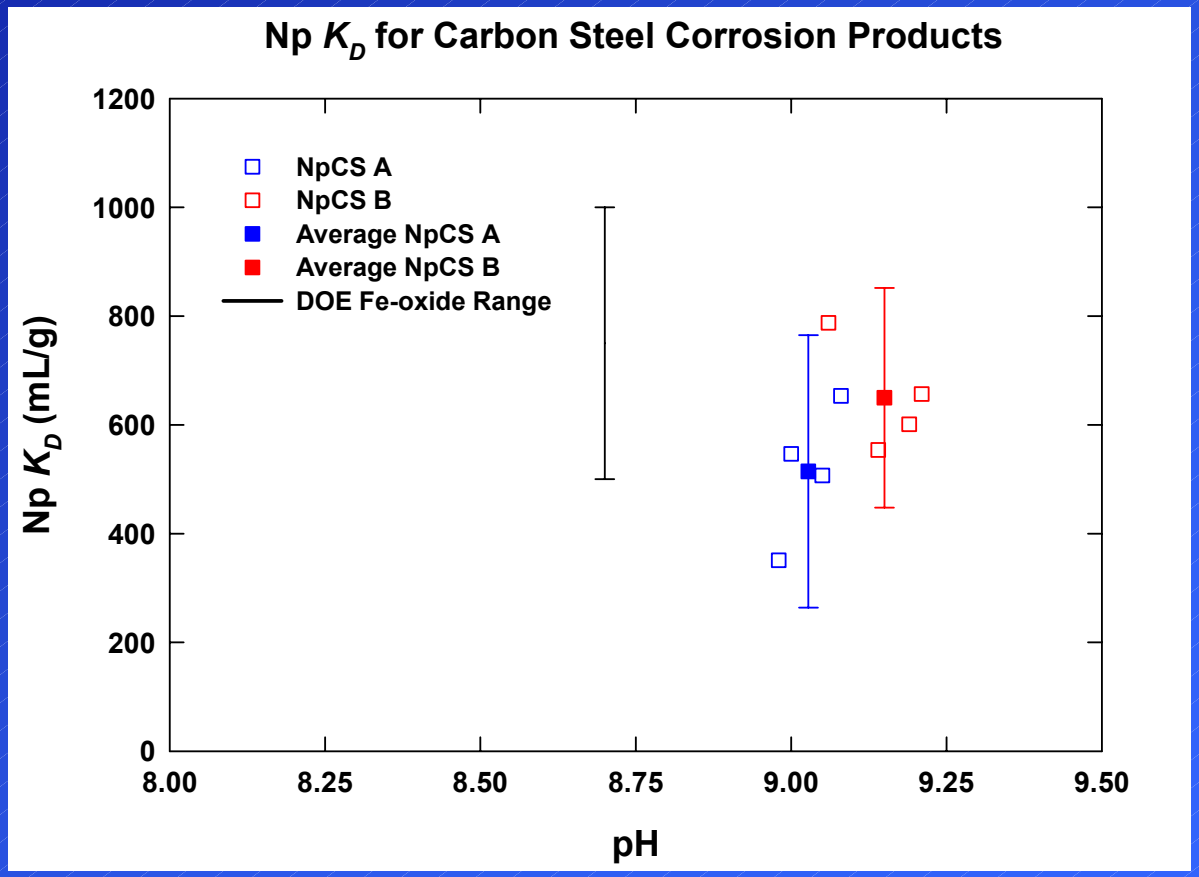
Environmental-Scanning Electron Microscope photographs





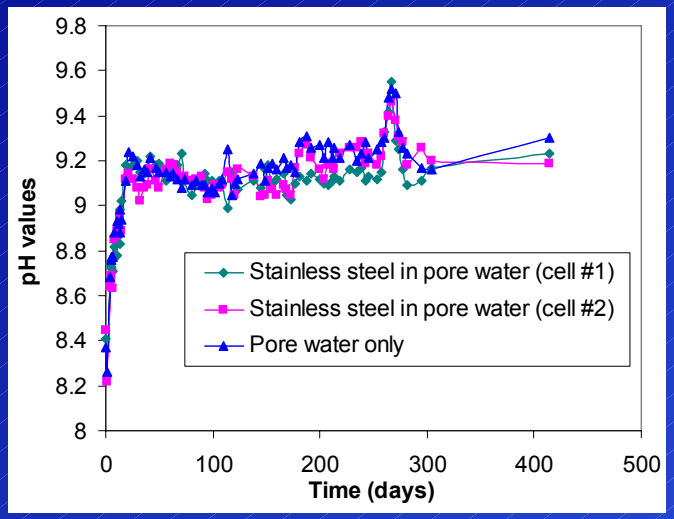
In-Package Chemistry: Neptunium Sorption on Carbon Steel Corrosion Products

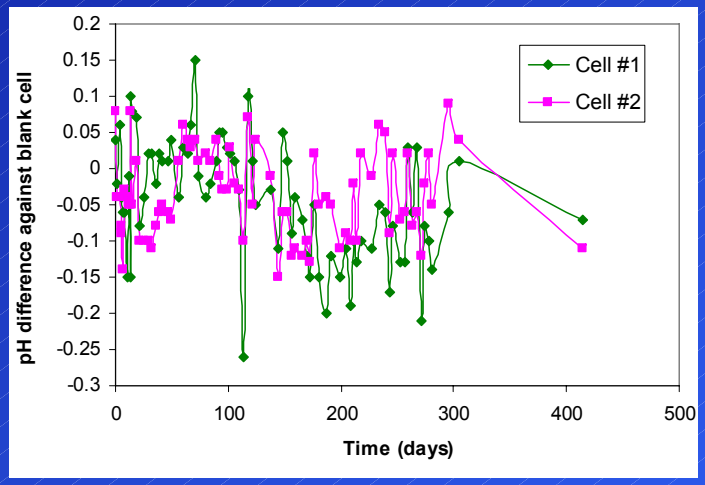
- K_D—Magnitude of sorption of an element or species onto a given substrate
- Corrosion products showed substantial sorption of neptunium; however, calcite may also contribute to the sorption



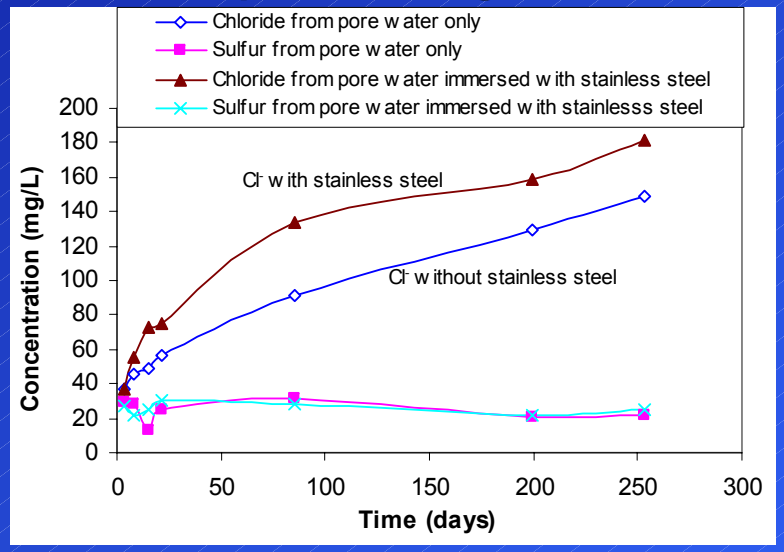
Tests are underway to determine neptunium sorption on calcite-free corrosion products

In-Package Chemistry: Stainless Steel Corrosion in Simulated Pore Water





- Little pH change and no visible corrosion were observed



- The chemical composition evolution of pore water immersed with stainless steel is similar to that of pore water with no stainless steel
- Cl^- concentration increase could be due to Cl^- leaching from pH probe

Summary

- Carbon steel corrosion processes increased the pH of the solution from near neutral to alkaline (pH>9), accompanied by the formation of iron-bearing corrosion product precipitates.
- Adding simulated high-level waste glass to the corroding carbon steel solution caused a further increase in pH.
- Stainless steel immersion produced little pH change, and corrosion was limited.
- No pH decrease was observed. The measured pH values were higher than predicted by DOE model.

Future Work

- Continue to conduct immersion tests of stainless steel specimens; tests may be extended to borated stainless steel, which is specified in the newer DOE canister design.
- Evaluate the presence of colloids due to carbon steel and stainless steel corrosion with improved methods.
- Study the corrosion products of carbon steel and stainless steel using *in-situ* Raman Spectroscopy.
- Model the chemical evolution of the experimental solutions during steel corrosion.

Disclaimer

- This presentation was prepared to describe work performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) for the U.S. Nuclear Regulatory Commission (NRC) under Contract No. NRC–02–02–012. The activities reported here were performed on behalf of the NRC Office of Nuclear Material Safety and Safeguards, Division of High-Level Waste Repository Safety. This presentation is an independent product of the CNWRA and does not necessarily reflect the view or regulatory position of the NRC.