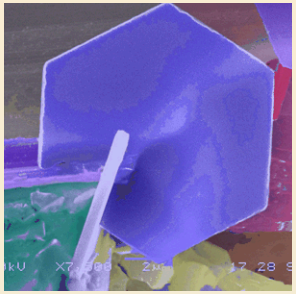
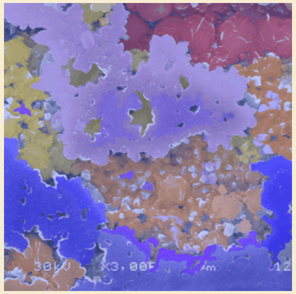
SAND2011-8206P

Sandia National Laboratories







Gas Generation due to Anoxic Corrosion of Steel and Lead in Na-Cl ± Mg Dominated Brines

ABC Salt Workshop; November 7 & 8, 2011; Karlsruhe, Germany

Gregory T. Roselle, PhD

Repository Performance Department, 6212

This research is funded by WIPP programs administered by the Office of Environmental Management (EM) of the U.S Department of Energy.

Purpose and Scope

- Determine the extent to which Fe and Pb consume CO_2 and H_2S^*
  - Potential for Fe and Pb to support MgO as engineered barrier
- Determine what corrosion products are likely to form
  - Kinetics of Fe and Pb corrosion
  - Potential for passivation of metal surfaces
  - Competition of CO_2 and H_2S^* in corrosion
- Determine H_2 Gas Generation Rates based on Corrosion Rates

*No H_2S experiments started yet due to ES&H and budget issues

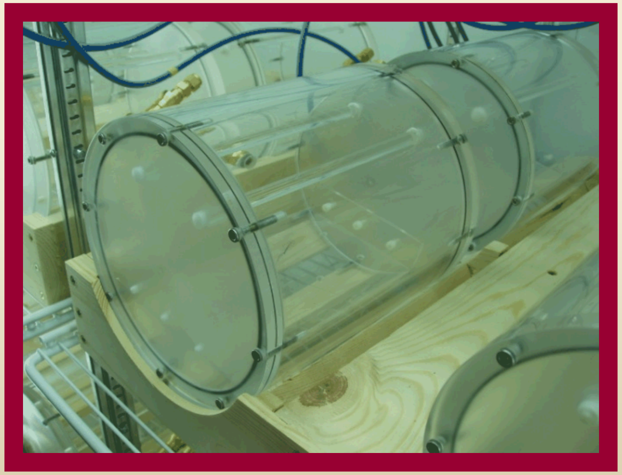
Previous Work

- Telander and Westerman (1993, 1997)
  - Investigated H_2 generation via corrosion of steels immersed in/or hanging above brine with overpressures of different gases (H_2, N_2, CO_2, H_2S)
  - Corrosion independent of H_2 overpressure
  - N_2 overpressure results in Fe-Mg hydroxide
  - CO_2 overpressure passivates with coating of Fe-Mg-CO_3
  - Addition of H_2S depassivates CO_3, H_2S alone passivates with FeS layer.
  - Used by Wang and Brush (1996) to derive gas generation parameters for WIPP Performance Assessment.
- Molecke et al. (1993)
  - Carbon steels and Pb exposed to Brine A in boreholes
  - No control of gas phases present (no CPR gases*, likely oxic conditions)
  - Significant corrosion seen (corrosion products not analyzed)
- Wang (2001)
  - Exposed steel coupons to ERDA-6 and G-Seep equilibrated with brucite
  - Produced green rust [Fe(II),Fe(III)]hydroxide

Experimental Setup

- WIPP-relevant environmental conditions
  - Temperature: 26°C
  - Relative humidity: approx. 72%
  - Atmosphere:
    - N_2 and N_2 + CO_2 (350 ppm, 1500 ppm, or 3500 ppm)
    - Anoxic: < 5 ppm O_2
  - Brine compositions:
    - ERDA-6 ± organics (NaCl-dominated brine)
    - GWB ± organics (NaCl-$MgCl_2$ dominated brine)
    - organics - EDTA, citrate, acetate, oxalate
- Materials:
  - Iron – ASTM A1008 low-carbon steel
  - Lead – QQ-L-171e Grade C chemical Pb
- Three sample positions: humid, partially submersed, fully inundated
- Experiments are being performed in a flow-through system designed to maintain above environmental conditions

Mixed Flow Gas Control System (MFGCS)



Sample Analysis

- Characterization of coupon surfaces
  - Before and after removal of corrosion products
  - SEM and digital photography
- Characterization of corrosion products
  - XRD
  - SEM with Energy Dispersive Spectroscopy (EDS)
- Weight loss after removal of corrosion products
- Determination of corrosion rates from weight loss data
- Calculation of H_2 gas generation rates from corrosion rates
- Changes in solution chemistry
  - pH and major elements

Typical Appearance of Steel Coupons

Coupon 021

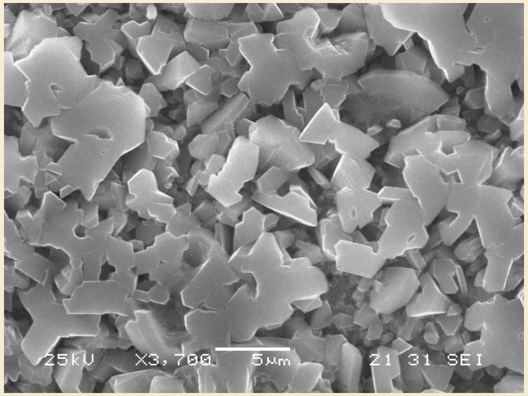
24 month exposure, 0 ppm CO_2, ERDA-6 no organics

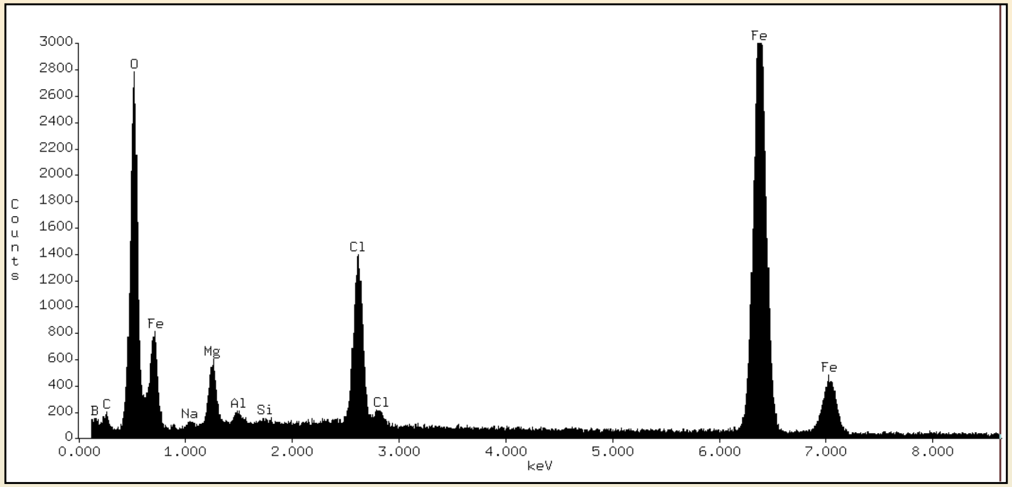
Before

After

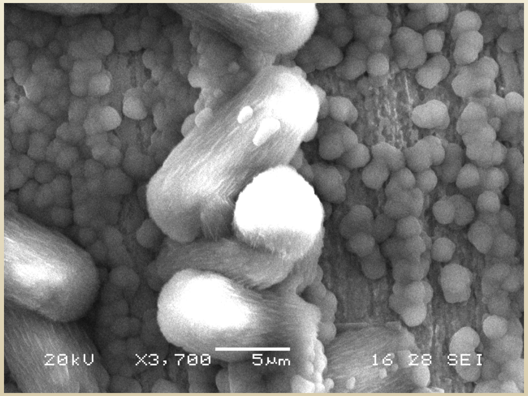
EDS of Steel Corrosion Products

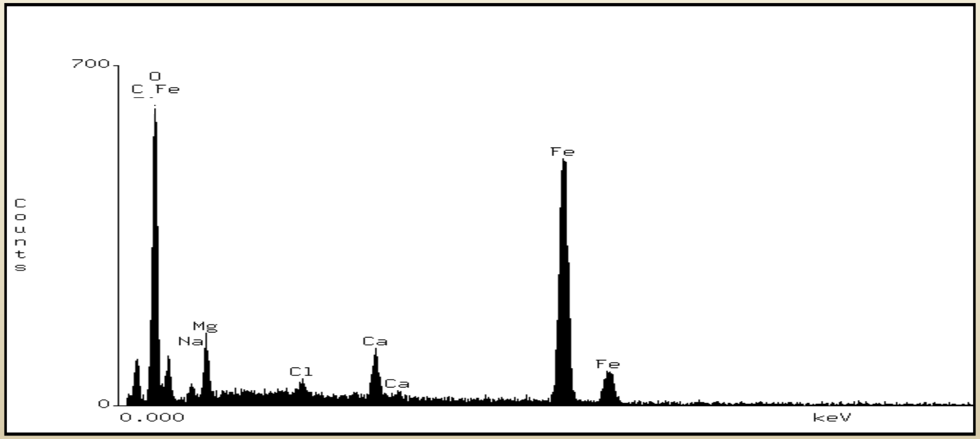
Coupon 104
6 month exposure, 0 ppm CO_2, ERDA-6 no organics





Coupon 327
6 month exposure, 1500 ppm CO_2, ERDA-6 w/ organics





Typical Appearance of Lead Coupons

Coupon L451

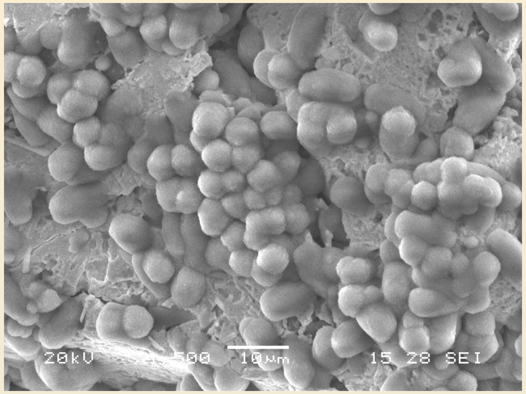
6 month exposure, 3500 ppm CO_2, ERDA-6 w/ organics

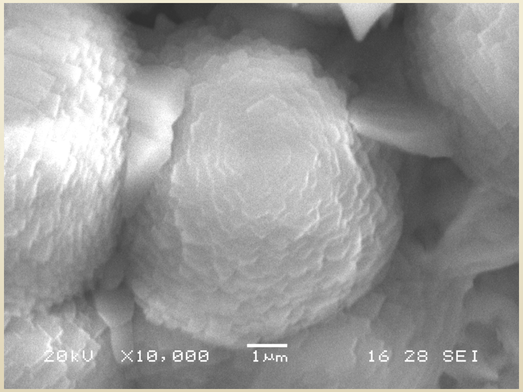
Before

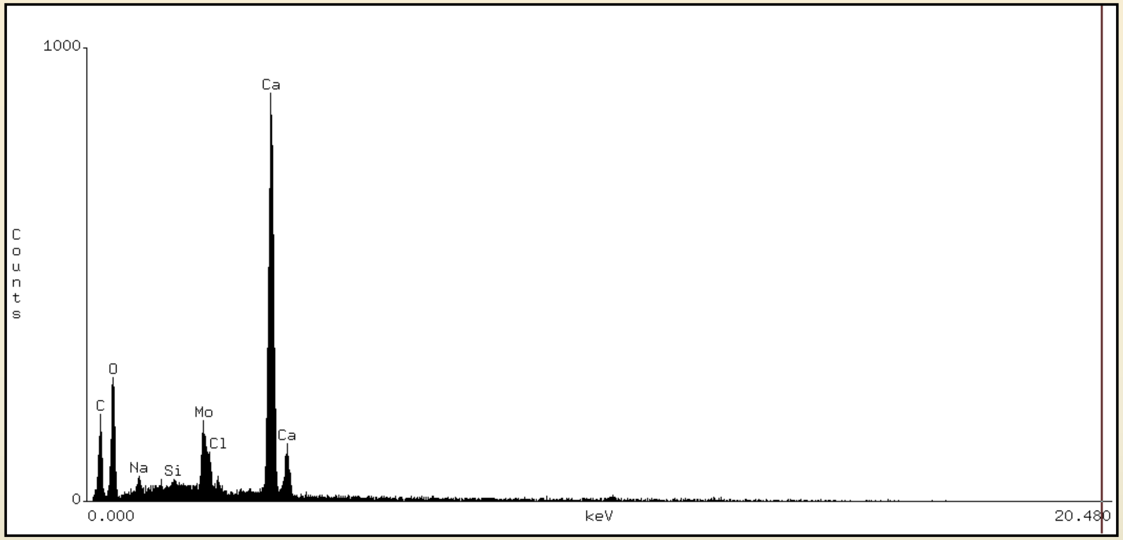
After

EDS of Lead Corrosion Products

Coupon L451
6 month exposure, 3500 ppm CO_2, ERDA-6 w/ organics







Possible Corrosion Products

	Steel		Lead	
Low CO_2 < ~1500 ppm	Amakinite Green Rust	$(Fe,Mg)(OH)_2$ $Fe(III)_2Fe(II)_4(OH)_{12}CO_3 \cdot 2H_2O$	N/A	N/A
High CO_2 > ~1500 ppm	Siderite Ankerite	$(Fe,Ca)CO_3$ $CaFe(CO_3)_2$	Cerussite Tarnowitzite	$PbCO_3$ $(Ca,Pb)CO_3$

Weight Loss Determination

- Coupon placed in cleaning solution for 2 minutes

Material	Chemical	Max. Time	Temp.
Iron (Fe)	500 mL conc. HCl 3.5 g hexamethylene tetramine Reagent water to make 1000 mL	10 min	20 to 25 ºC
Lead (Pb)	250 g ammonium acetate Reagent water to make 1000 mL	5 min	60 to 70 ºC
Source: ASTM G 1 – 03 *Standard Practice for Preparing, Cleaning and Evaluation Corrosion Test Specimens*. West Conshohocken, PA: American Society for Testing and Materials (ASTM) International.			

- After 2 minutes, removed, scrubbed, rinsed in DI water followed by ethanol
- Coupon weighed
- Repeat process for 5 to 10 cycles

Weight Loss Graphical Analysis

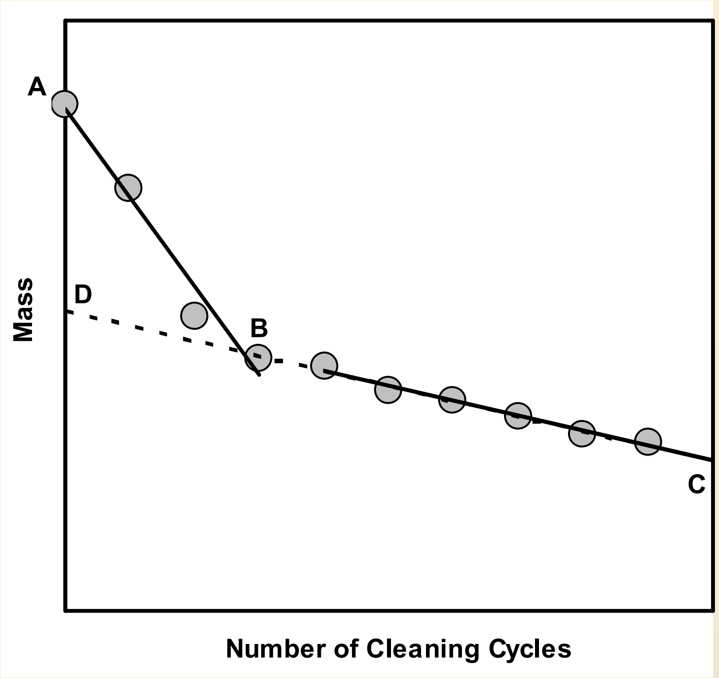
AB – Removal of corrosion product and base metal

BC – Removal of base metal only

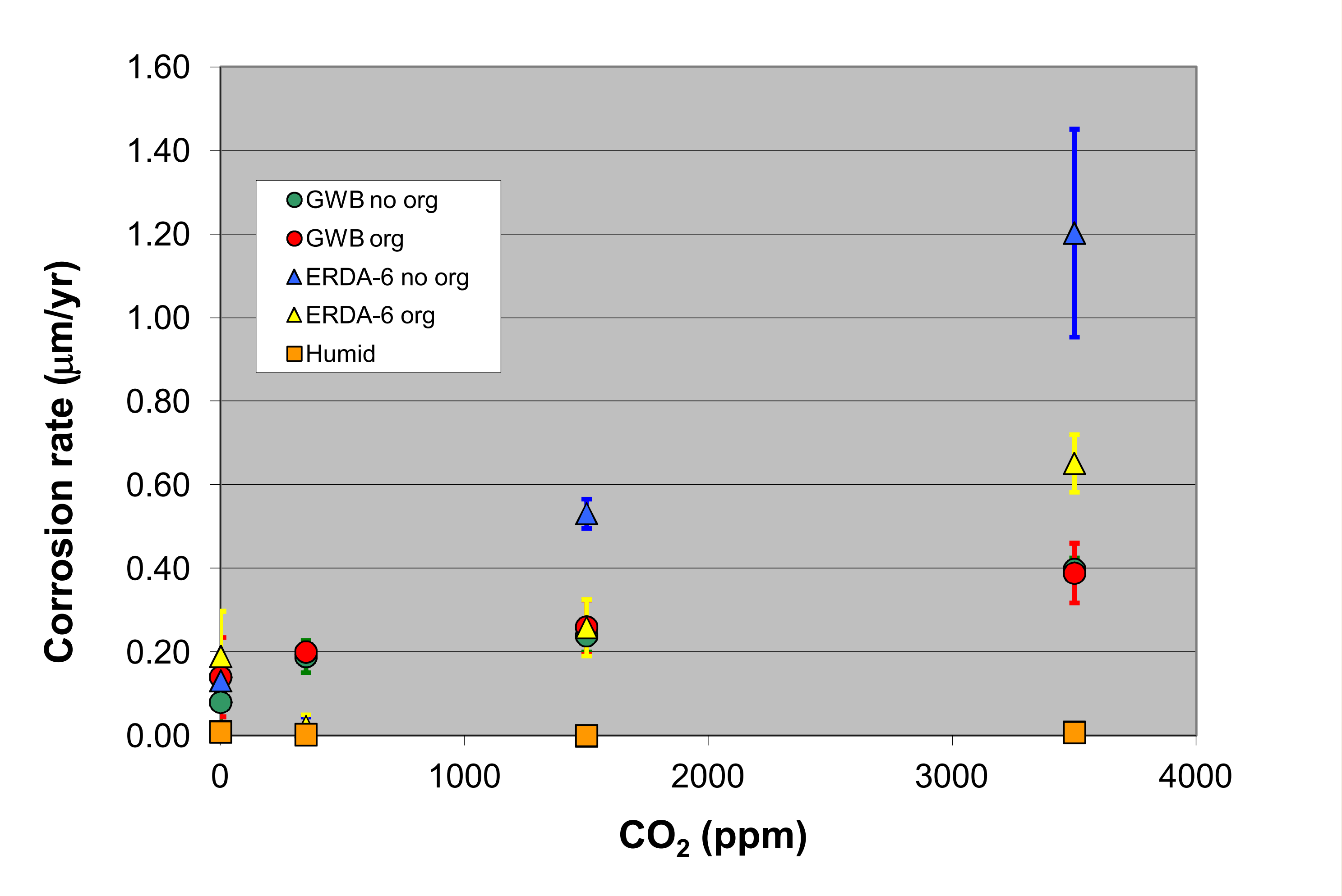
D – Projected final weight

$$rate(\mu m / yr) \equiv \frac{W \times 87.6}{SA \times t \times \rho} \times 1000$$

W - mass loss (mg)
SA - exposed surface area (cm^2)
t - exposure duration (hours)
ρ - metal density (g/cm^3)



Corrosion Rates for Fe Coupons (6 month results)



Gas Generation (H_2) Rates

- Identify possible corrosion reactions
- Convert corrosion rate (μm/yr) to molar rate (mol metal m^{-2} yr^{-1})
- Based on 1 μm corrosion of 1 m^2 metal plate (consumes 1 cm^3 metal):

$$\rho \ (g\ cm^{-3}) \times 1/M.W.\ (g\ mol^{-1}) = R\ (mol\ metal\ \mu m^{-1}\ m^{-2})$$

Example for 1 cm^3 Fe:

$$7.872\ g\ cm^{-3} \times 0.0179\ mol\ g^{-1} = 0.141\ mol\ Fe\ \mu m^{-1}\ m^{-2}$$

Example for 1 cm^3 Pb:

$$11.340\ g\ cm^{-3} \times 0.0048\ mol\ g^{-1} = 0.055\ mol\ Pb\ \mu m^{-1}\ m^{-2}$$

- Calculate H_2 generation rate based on stoichiometry of corrosion reaction.

Potential Corrosion Reactions

- Low CO_2 conditions:

$$Fe(II)(s) + 2\ H_2O \leftrightarrow Fe(OH)_2(s) + H_2$$

$$6\ Fe(II)(s) + CO_2 + 15\ H_2O \leftrightarrow Fe(III)_2Fe(II)_4(OH)_{12}CO_3\cdot 2H_2O(s) + 7\ H_2$$

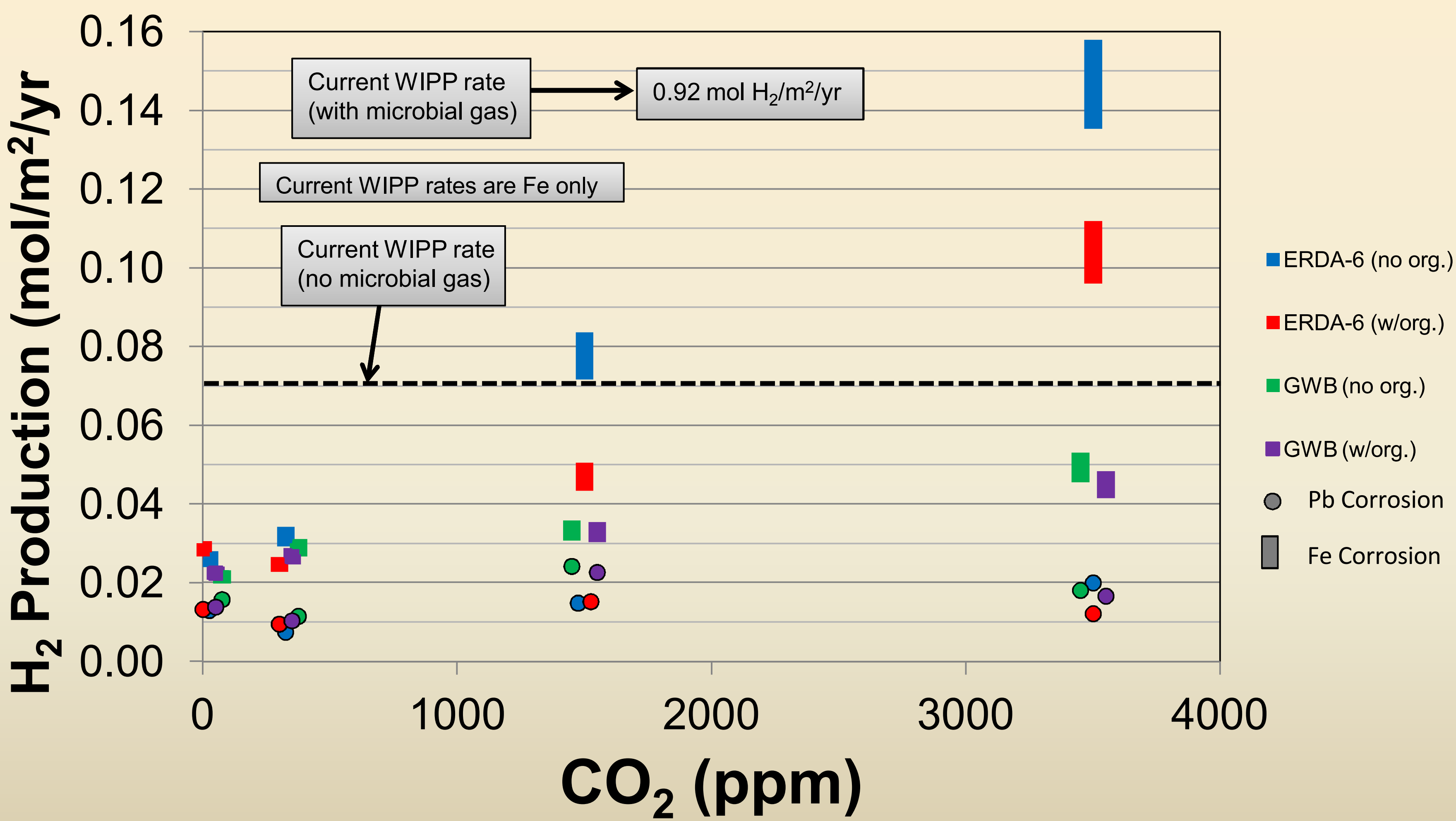
- High CO_2 conditions:

Above reactions plus:

$$Fe(II)(s) + CO_2 + H_2O \leftrightarrow FeCO_3(s) + H_2$$

$$Pb(II)(s) + CO_2 + H_2O \leftrightarrow PbCO_3(s) + H_2$$

H_2 Generation Rates
(Preliminary Estimates)



Summary

- Corrosion of Fe
  - ERDA-6 (NaCl-dominated) is more corrosive than GWB (NaCl-$MgCl_2$)
  - The presence of organics is important only for ERDA-6 (suppresses corrosion)
  - Corrosion increases with CO_2
- Corrosion of Pb
  - No clear trends apparent in corrosion rates
    - GWB may be more corrosive than ERDA-6
    - Further data required to support this hypothesis
- Passivation of Pb may be occurring at all P_{CO2}
- No clear evidence of passivation for Fe
- Initial H_2 gas generation rates are approx. 5 times lower than current values used in WIPP PA

Supplemental Materials

Coupon Compositions

Steel

Element	Weight Percent
Al	0.026
C	0.050
Ca	0.001
Cr	0.040
Cu	0.110
Fe	balance
Mn	0.250
Mo	0.010
N	0.009
Nb	0.003
Ni	0.040
P	0.006
S	0.005
Si	0.010
Sn	0.007
Ti	0.002
V	0.002

Source: Material Test Report for AE960 (ERMS 551552)

Lead

Element	Weight Percent
Ag	0.010
Bi	0.015
Cd	0.001
Cu	0.070
Fe	0.001
Ni	0.001
Pb	99.900
Sb+Sn+As	0.001
Zn	0.001

Source: Certificate of Compliance and Inspection Metal Coupon, Lot 32829 (ERMS 551551)

Brine Compositions

Total Elemental Concentration	GWB Concentration (molal)	ERDA-6 Concentration (molal)	GWB Concentration (molal)	ERDA-6 Concentration (molal)
Na^+	4.98	6.05	4.99	5.96
K^+	0.559	0.109	0.563	0.109
Li^+	5.05×10^{-3}	---	5.05×10^{-3}	---
Ca^{2+}	1.24×10^{-2}	1.28×10^{-2}	1.03×10^{-2}	1.22×10^{-2}
Mg^{2+}	0.635	0.121	0.663	0.179
Cl^-	6.30	6.00	6.24	5.98
Br^-	3.18×10^{-2}	1.24×10^{-2}	3.19×10^{-2}	1.24×10^{-2}
SO_4^{2-}	0.209	0.191	0.262	0.203
$B_4O_7^{2-}$	4.73×10^{-2}	1.77×10^{-2}	4.76×10^{-2}	1.77×10^{-2}
EDTA	---	---	8.85×10^{-6}	9.99×10^{-6}
Oxalate	---	---	3.38×10^{-4}	3.35×10^{-4}
Citrate	---	---	9.09×10^{-4}	9.04×10^{-4}
Acetate	---	---	1.19×10^{-2}	1.19×10^{-2}

Source: WIPP-FePb-3 p. 51, 52 (ERMS 550783)

References

Molecke, M.A., N.R. Sorensen, and G.G. Wicks. 1993. *Waste Isolation Pilot Plant Materials Interface Interactions Test: Papers Presented at the Commission of European Communities Workshops on In Situ Testing of Radioactive Waste Forms and Engineered Barriers*. SAND93-1055. Albuquerque, NM: Sandia National Laboratories.

Telander, M.R., and R.E. Westerman. 1993. *Hydrogen Generation by Metal Corrosion in Simulated Waste Isolation Pilot Plant Environments*: progress report for the period November 1989 through 1992. SAND92-7347. Albuquerque, NM: Sandia National Laboratories.

Telander, M.R., and R.E. Westerman. 1997. *Hydrogen Generation by Metal Corrosion in Simulated Waste Isolation Pilot Plant Environments*. SAND96-2538. Albuquerque, NM: Sandia National Laboratories.

Wang, Y. and Brush, L.H. 1996. *Estimates of Gas-Generation Parameters for the Long-Term WIPP Performance Assessment*. Memo to Martin S. Tierney, January 26, 1996. ERMS 231943. Carlsbad, NM: Sandia National Laboratories.

Wang, Z., R.C. Moore, A.R. Felmy, M.J. Mason, and R.K. Kukkadapu. 2001. "A Study of the Corrosion Products of Mild Steel in High Ionic Strength Brines," *Waste Management*. Vol. 21, 335-341.