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Anoxic Corrosion of Steel and Lead in Na-Cl ± Mg Dominated Brines

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NNSA National Nuclear Security Administration

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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

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

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Previous Work

- **Telander and Westerman (1993, 1997)**
  - Investigated gas generation (H_2) due to 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.
- **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

***Cellulose, plastic, and rubber materials**

Experimental Setup

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

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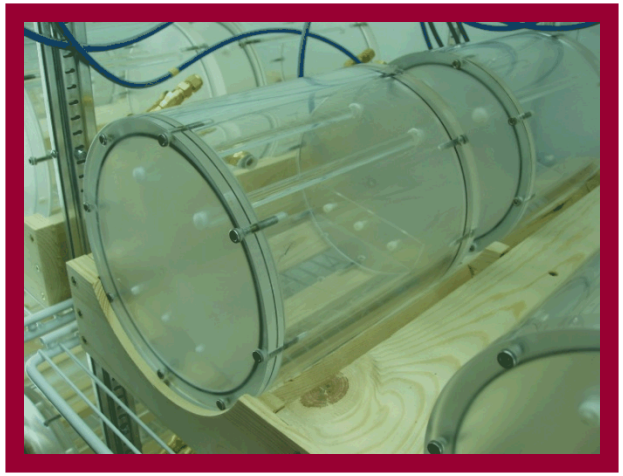
Mixed Flow Gas Control System (MFGCS)



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Test Matrix (CO_2)

- Two material types
  - Low-carbon steel (ASTM A1008) and chemical lead (QQ-L-171e)
- Four brine compositions
  - ERDA-6 with or without organics (NaCl-dominated brine)
  - GWB with or without organics (NaCl-, $MgCl_2$-dominated brine)
- Four atmospheres
  - N_2, N_2 + CO_2 (350 ppm, 1500 ppm, or 3500 ppm)
- Four time segments
  - 6, 12, 18 and 24 months
- Three sample positions
  - Atmospheric
  - Partially submerged
  - Fully submerged
- Three replicates for each sample
- Total of 432 samples for each metal type

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Sample Analysis

- Weight loss after removal of corrosion products
- Characterization of coupon surfaces
  - Before and after removal of corrosion products
  - SEM
- Characterization of corrosion products
  - XRD
  - SEM with EDS and EBSD
- Solution chemistry
  - pH
  - Major element concentrations
- Sample loading/unloading is being done in a VAC environmental glove box (<1 ppm O_2)

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Typical Appearance of Steel Coupons

Coupon 135
6 month exposure, 350 ppm CO_2, ERDA-6 w/ organics

Before

After

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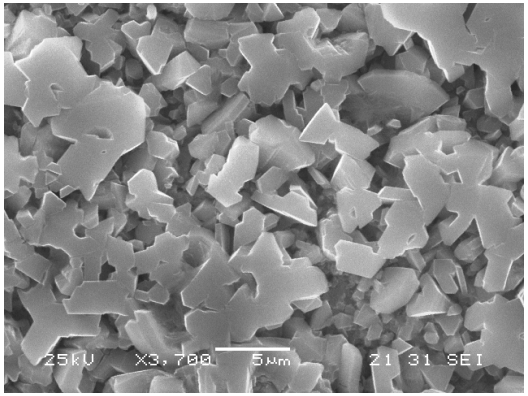
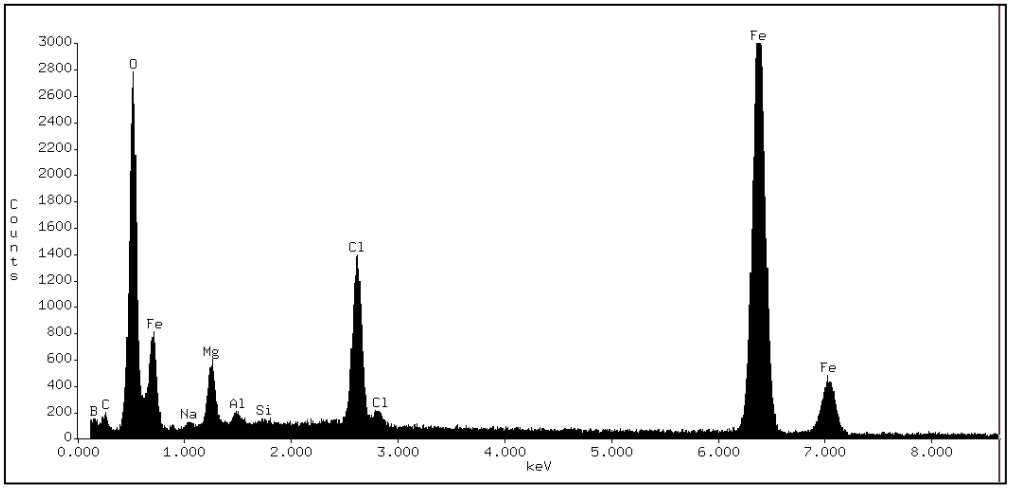
EDS of Fe Corrosion Products

Coupon 104

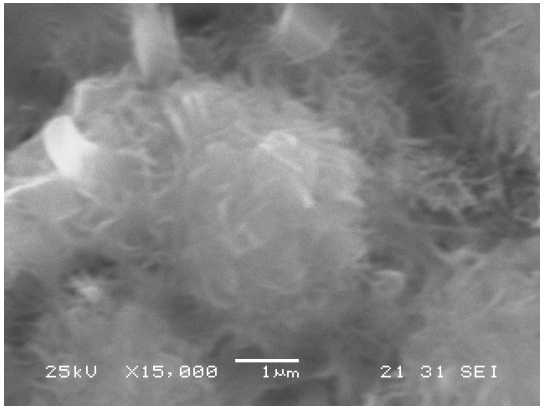
6 month exposure, 0 ppm CO_2, ERDA-6 no organics

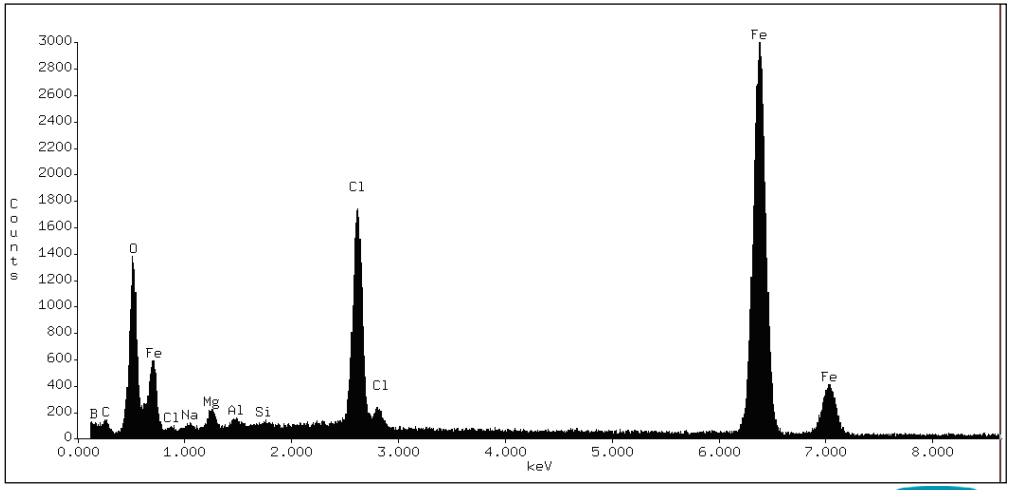
Green Corrosion Product





Hazy Corrosion Product





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Typical Appearance of Steel Coupons

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

Before

After

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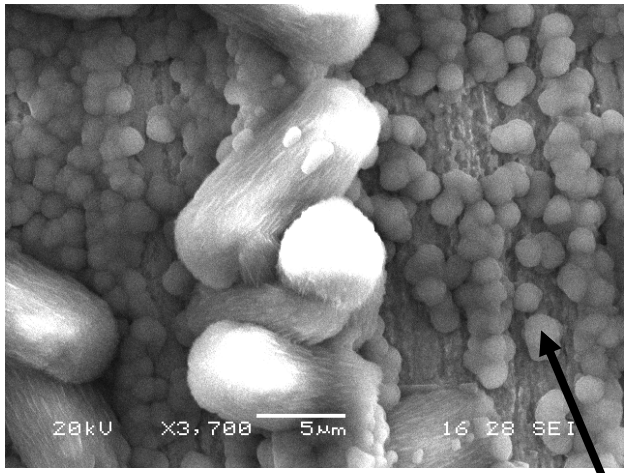
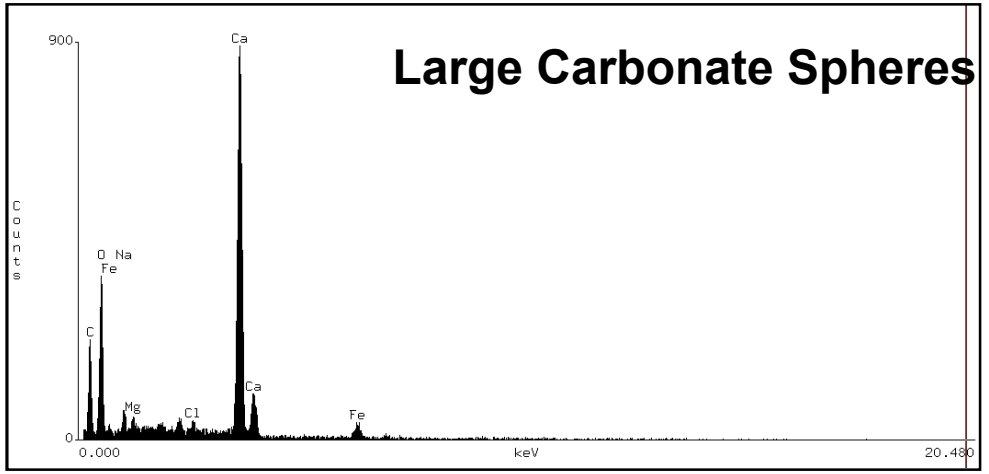
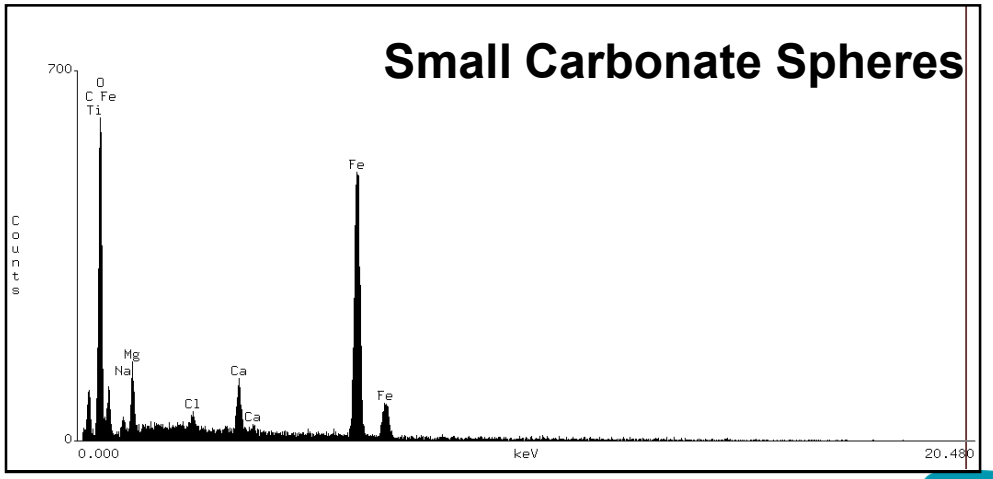
EDS of Carbonate Corrosion Products



Coupon 327





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Hypothetical Steel Corrosion Reactions

- **Low CO_2 conditions:**

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

- **High CO_2 conditions:**

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

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Typical Appearance of Lead Coupons

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

Before

After

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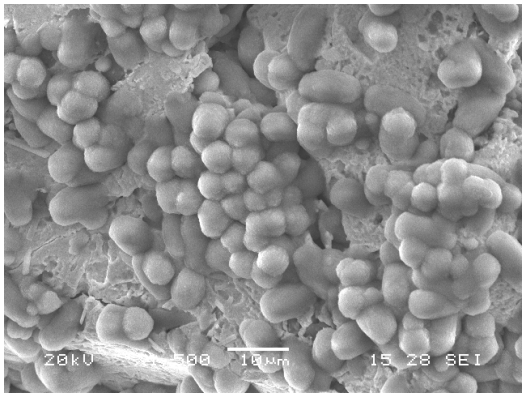
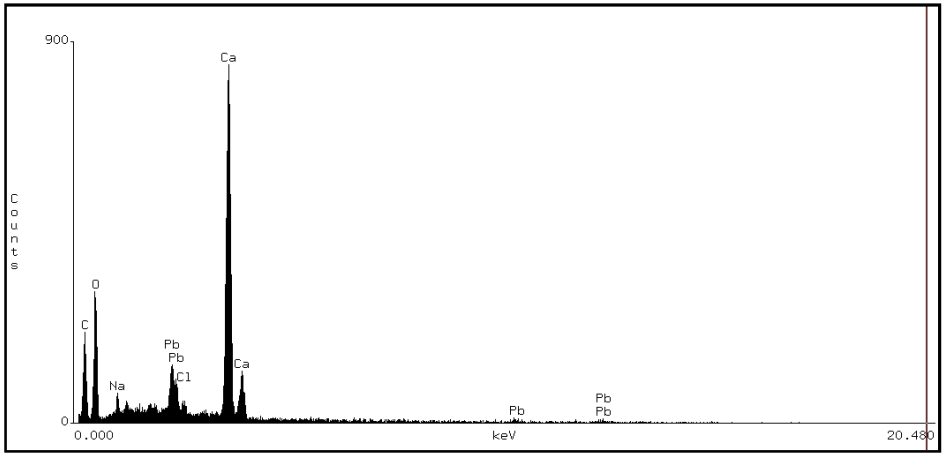
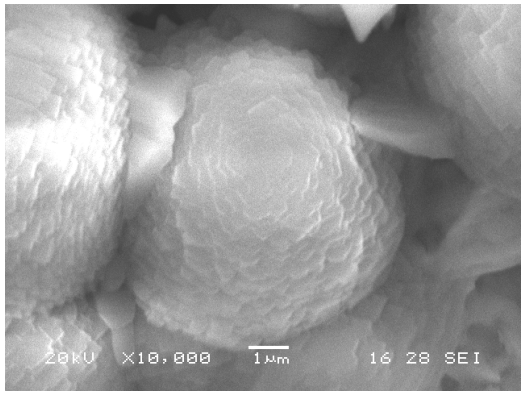
EDS of Pb Corrosion Products

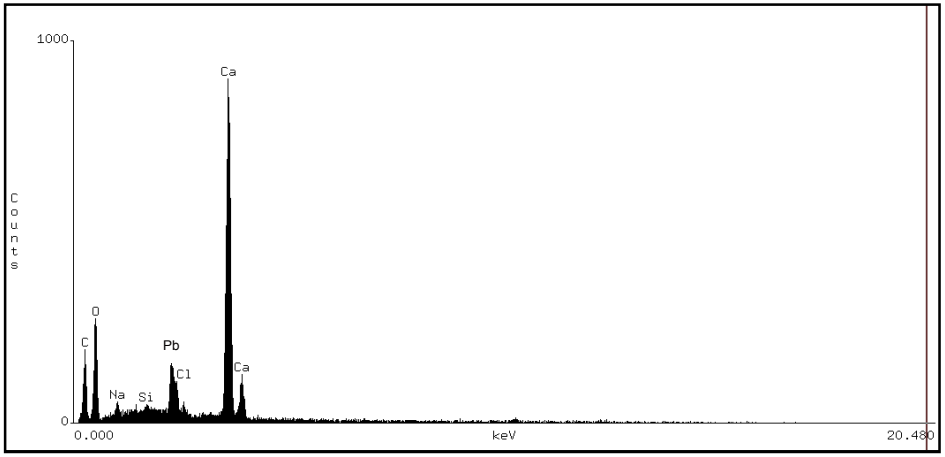
Coupon L451





Coupon L313*





*6 month exposure, 1500 ppm CO_2, ERDA-6 no organics

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Hypothetical Lead Corrosion Reaction

- High CO_2 conditions:

$$Pb(II)_{(s)} + CO_2 + H_2O \leftrightarrow PbCO_{3(s)} + H_2$$

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Weight Loss Determination

- **Coupon placed in cleaning solution for 2 minutes**

Material	Chemical	Time	Temp.
Iron (Fe)	500 mL conc. hydrochloric acid (HCl) 3.5 g hexamethylene tetramine Reagent water to make 1000 mL	10 min	20 to 25 ºC
Lead (Pb)	250 g ammonium acetate (CH_3COONH_4) Reagent water to make 1000 mL	5 min	60 to 70 ºC
Source: ASTM G 1 – 03			

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

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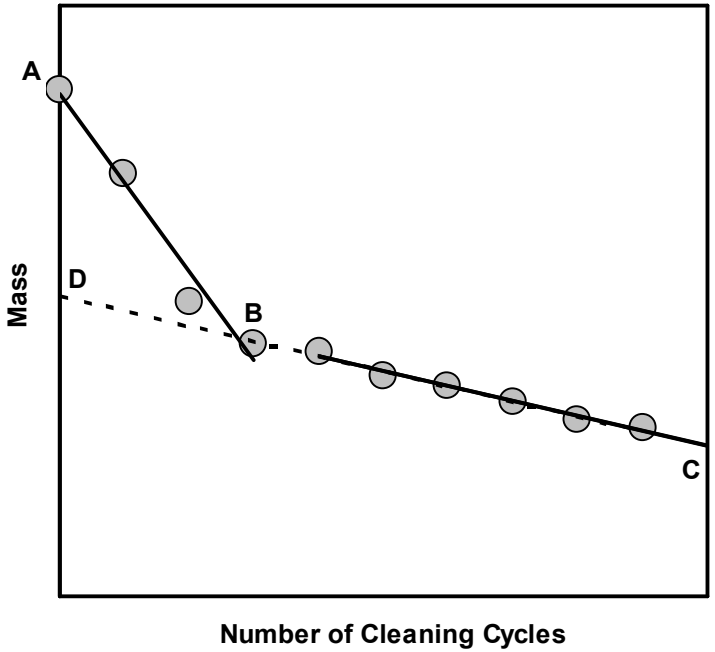
Weight Loss Graphical Analysis

AB – Removal of corrosion product and base metal

BC – Removal of base metal only

D – Projected final weight



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

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

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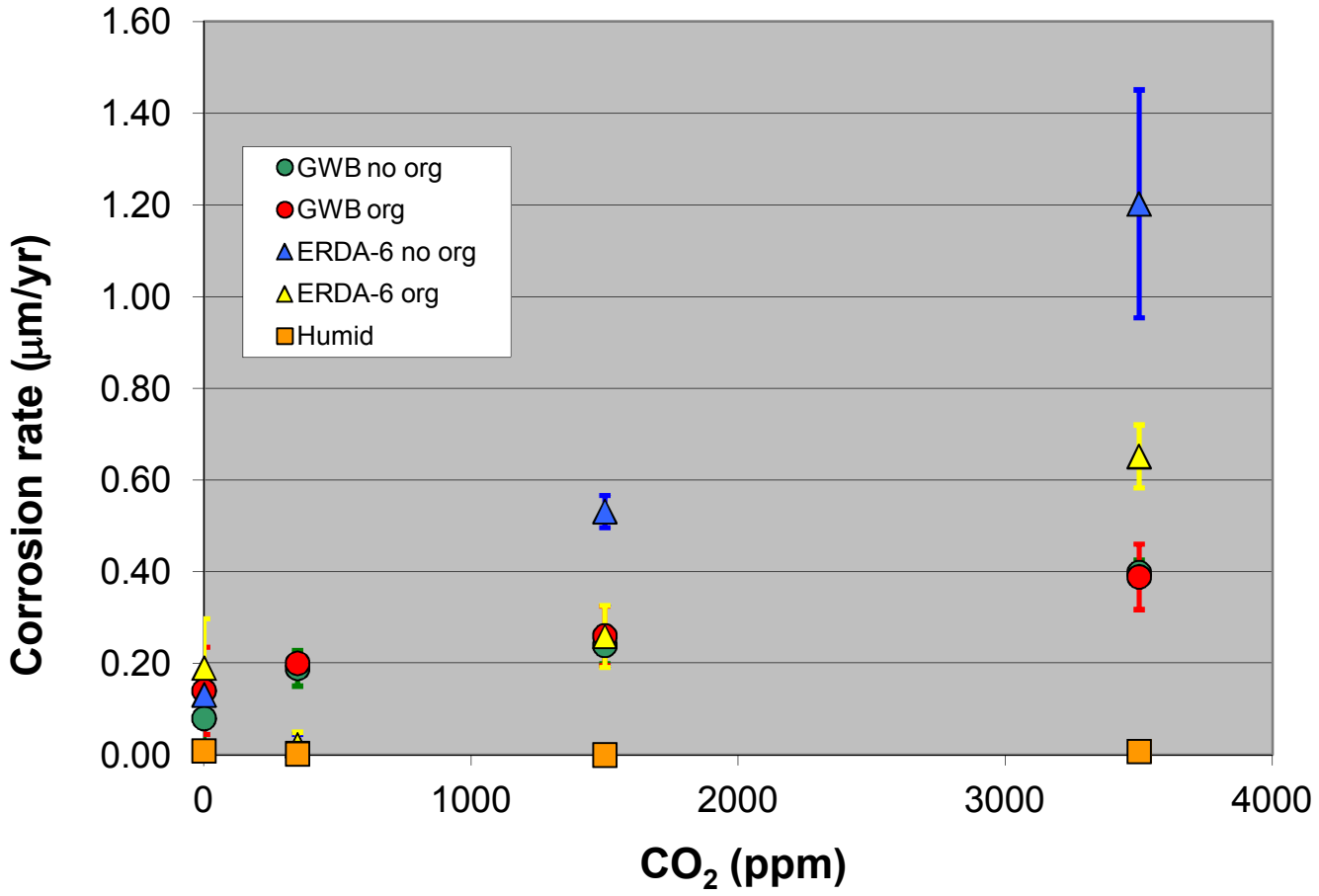
Corrosion Rates for Fe Coupons
(6 month results)



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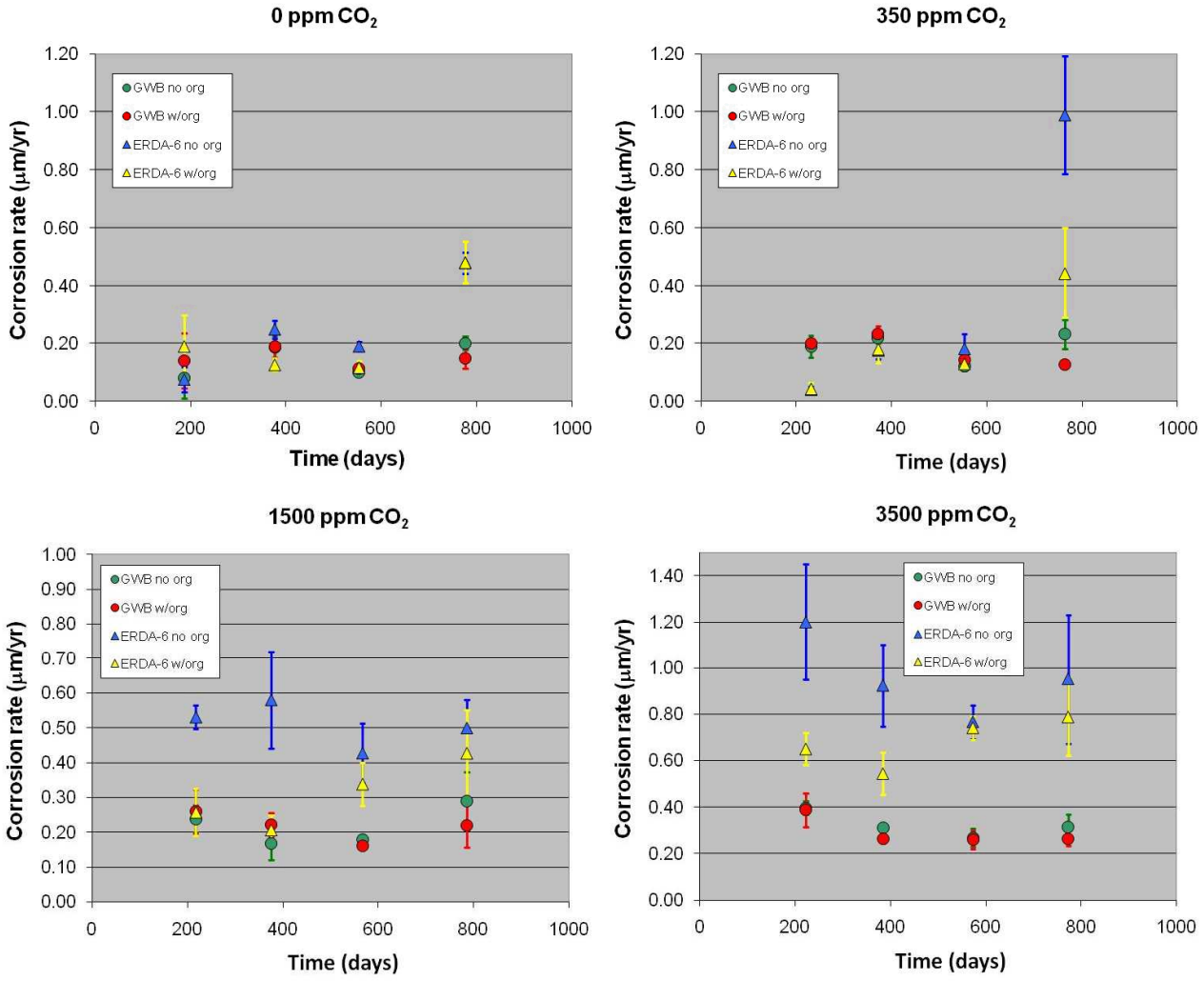
Corrosion Rates for Fe Coupons



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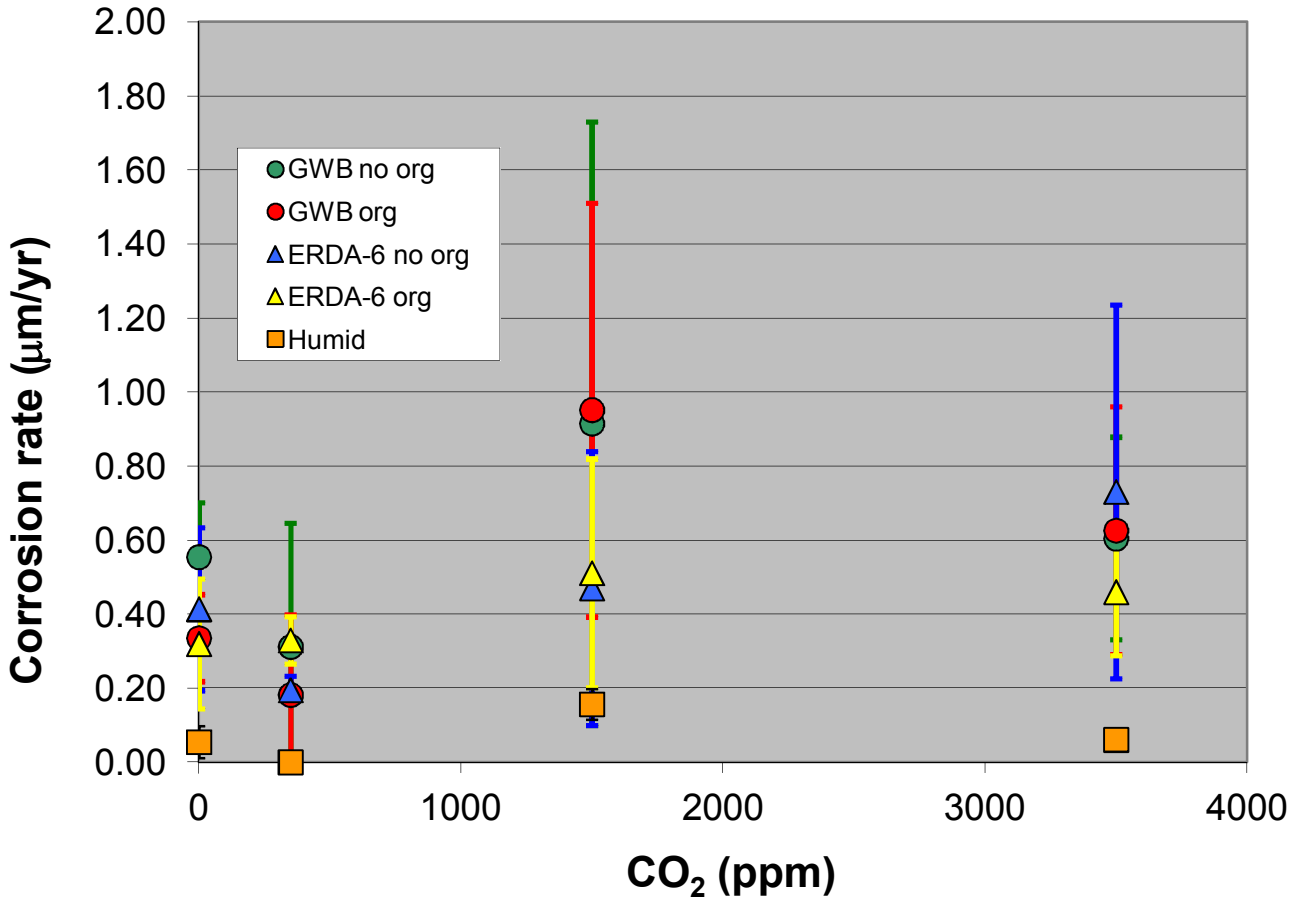
Corrosion Rates for Pb Coupons
(6 month results)



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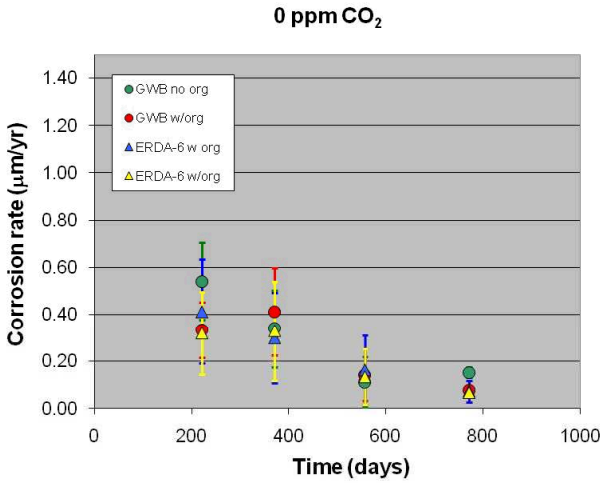
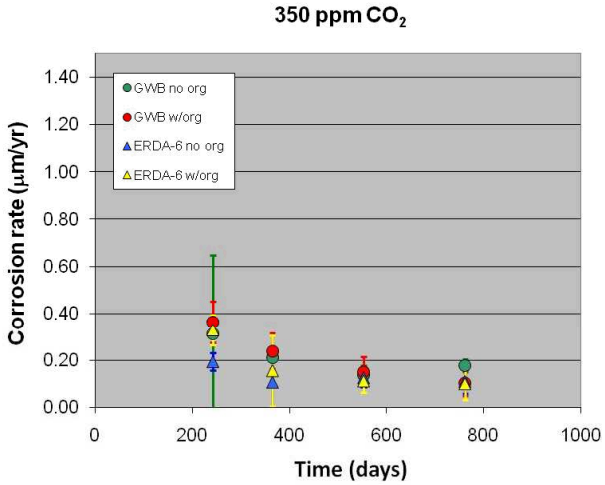
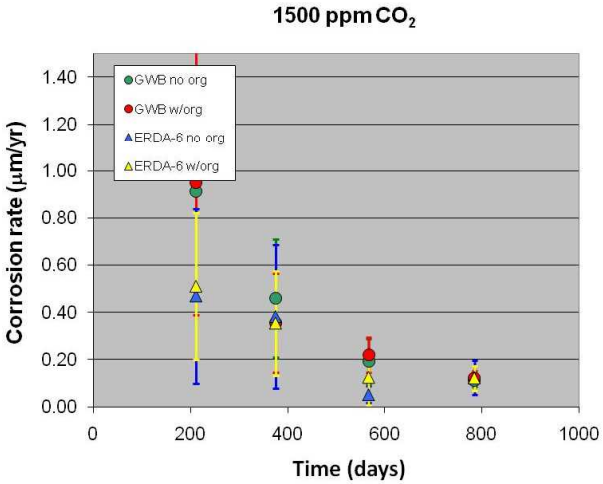
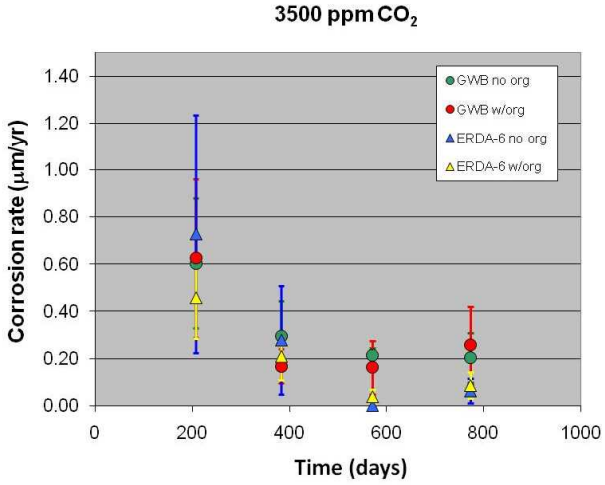
Corrosion Rates for Pb Coupons









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Summary

- Corrosion of Fe
  - ERDA-6 is more corrosive than GWB
  - 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
- Future experiments will be done with H_2S

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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)

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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)

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