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

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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

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 overpessure 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

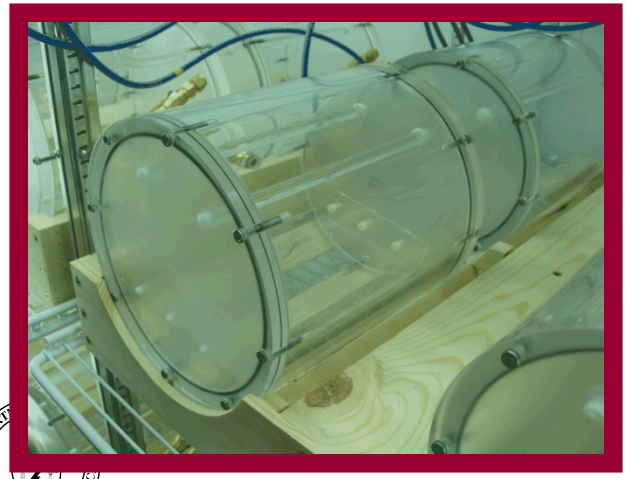
- WIPP-relevant environmental conditions
  - Temperature: 26°C
  - Relative humidity: approx. 72%
  - Atmosphere:
    - N_2, N_2 + CO_2, N_2 + H_2S, or N_2 + CO_2 + H_2S
    - Anoxic: < 1 ppm O_2
  - Brine compositions:
    - ERDA-6 ± organics (EDTA, citrate, acetate, oxalate)
    - GWB ± organics (EDTA, citrate, acetate, oxalate)
- Materials:
  - Iron – ASTM A1008 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

Mixed-Flow Gas Control System (MFGCS)

- Designed to maintain desired environmental conditions in a flowing-gas setup

- Continuous monitoring of gas flow rates and compositions with data acquisition software
  - Alarms if gas flow rates/compositions or RH outside accepted tolerances
  - Logs monitoring data to hard drive
  - Monitors supply gas pressures

Mixed Flow Gas Control System (MFGCS)



Test Matrix (CO_2)

- Two material types
  - Carbon steel (A1008) and lead (QQ-L-171e)
- Four brine compositions
  - ERDA-6 with or without organics, GWB with or without organics
- 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
- No experiments involving H_2S are currently underway

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)

Typical Appearance of Steel Coupons

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

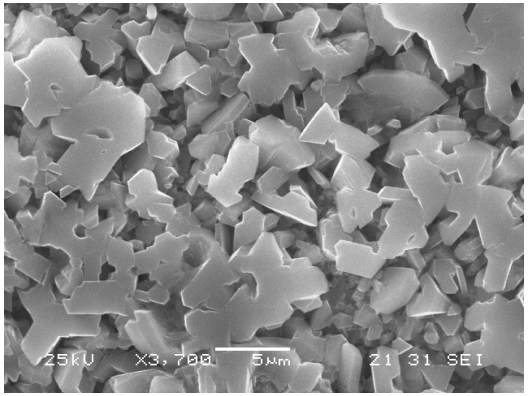
Before

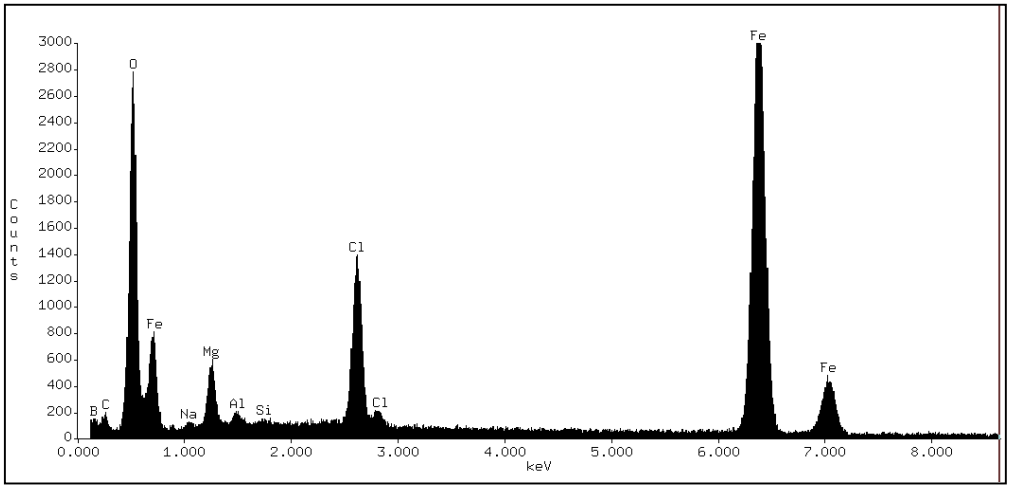
After

EDS of Fe Corrosion Products

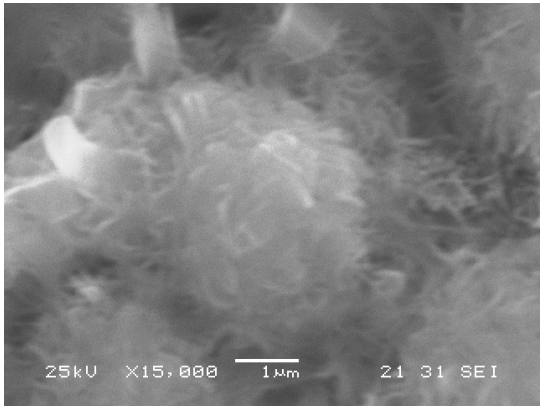
Coupon 104

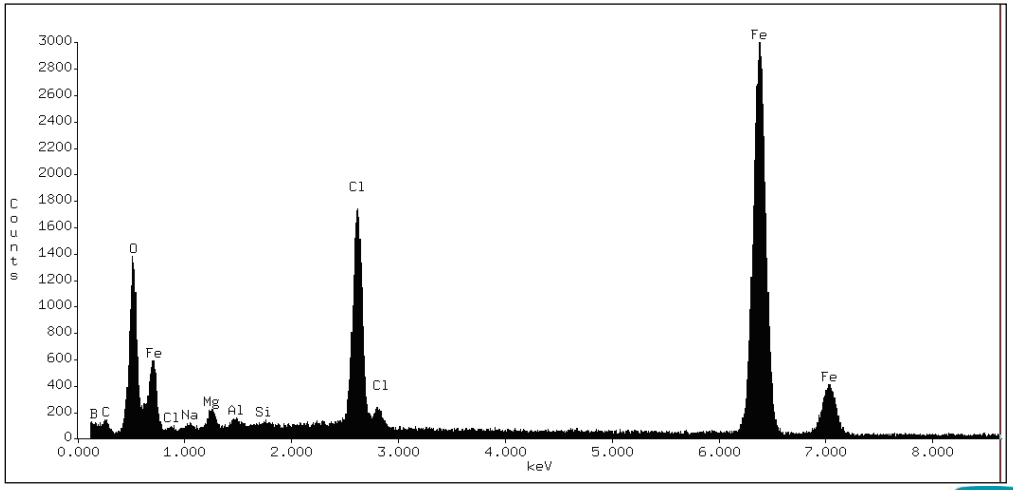
Green Corrosion Product





Hazy Corrosion Product





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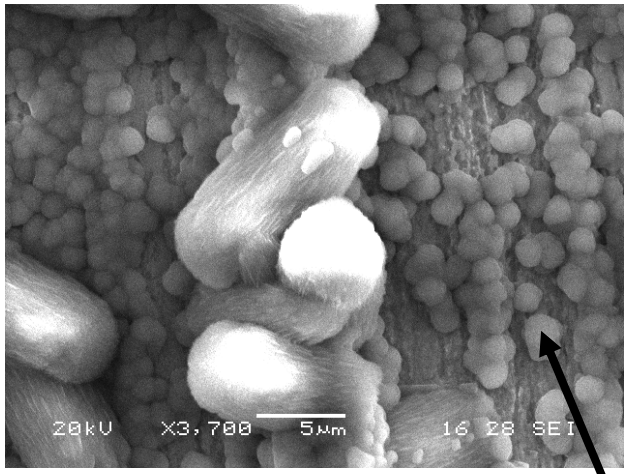
Typical Appearance of Steel Coupons

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

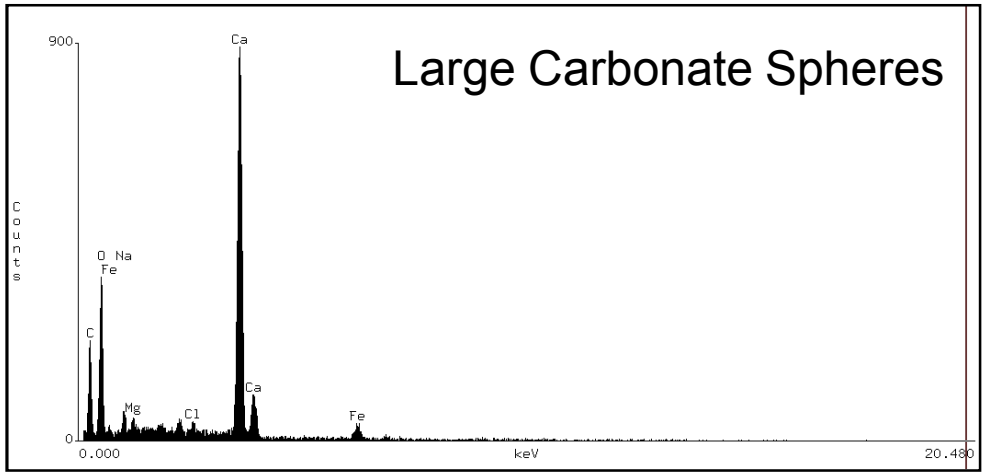
Before

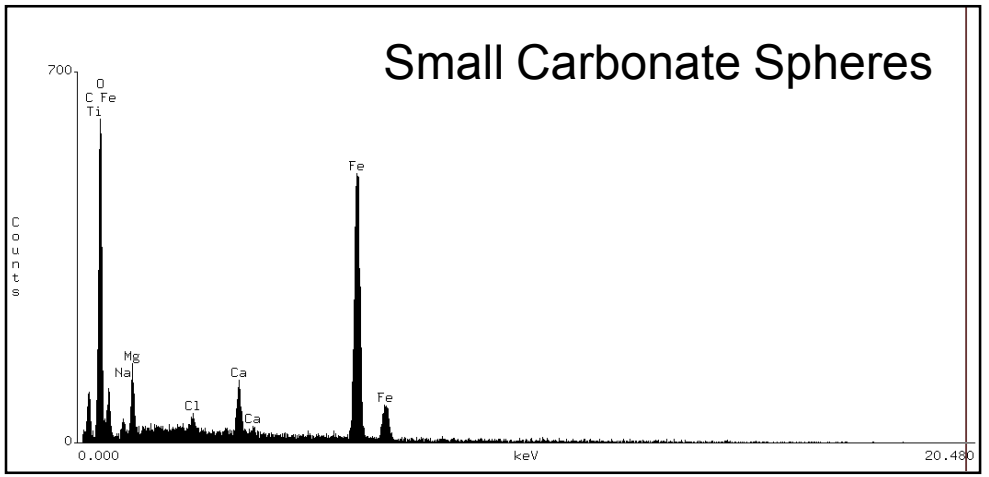
After

EDS of carbonate Corrosion Products



Coupon 327





Typical Appearance of Lead Coupons

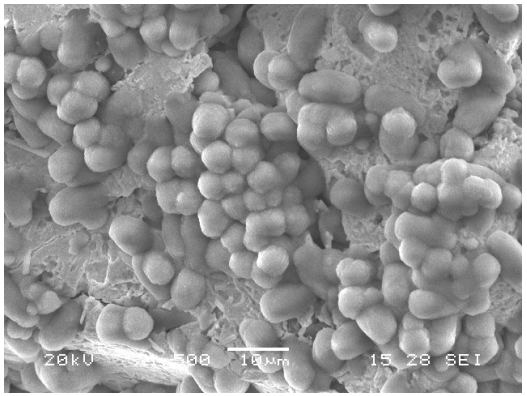
Coupon L451
6 month exposure, 3500 ppm CO_2, ERDA-6 w/ organics

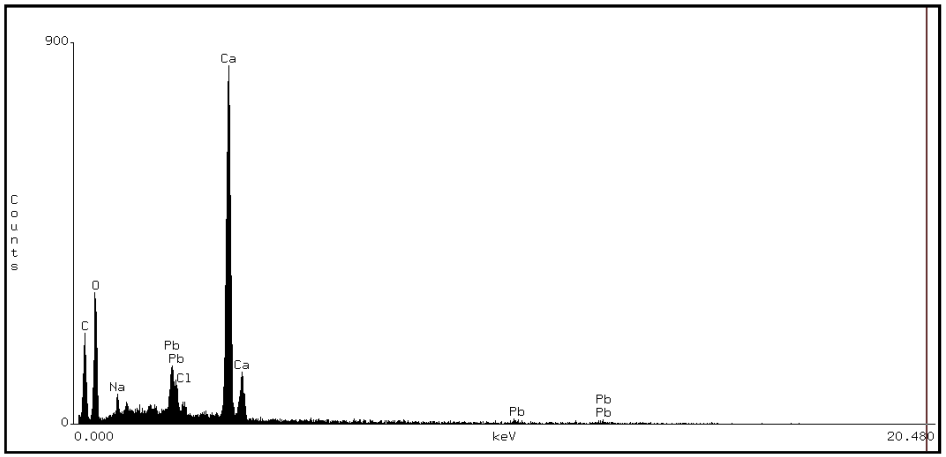
Before

After

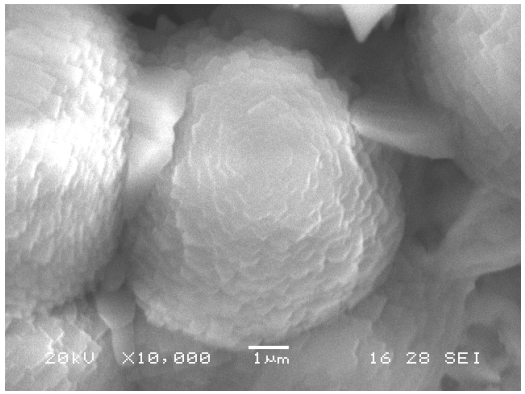
EDS of Pb Corrosion Products

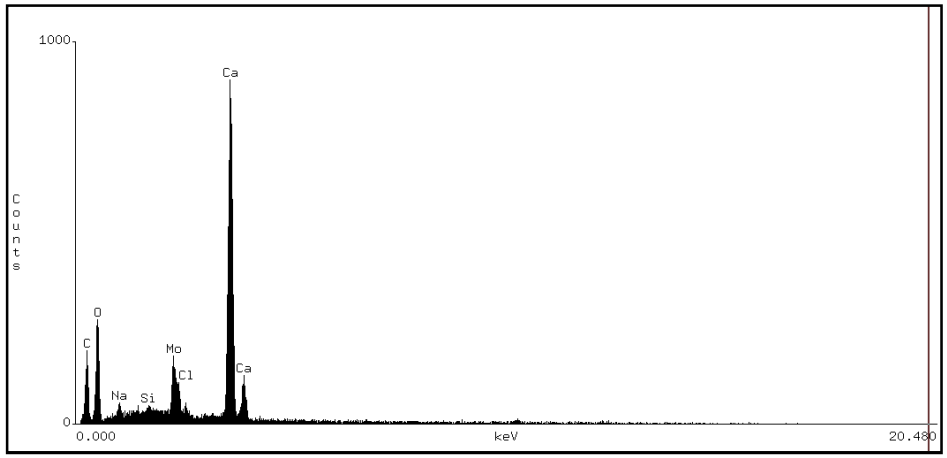
Coupon L451





Coupon L313





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Weight Loss Determination

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

Material	Chemical	Time	Temp.	Source[1]
Iron (Fe)	concentrated HCl + 50 g/L $SnCl_2$ + 20 g/L $SbCl_3$	25 min max.	Cold	A
	500 mL conc. hydrochloric acid (HCl) 3.5 g hexamethylene tetramine Reagent water to make 1000 mL	10 min	20 to 25 ºC	B
Lead (Pb)	250 g ammonium acetate (CH_3COONH_4) Reagent water to make 1000 mL	5 min	60 to 70 ºC	B
[1]Source: A, NACE Standard TM0169-2000; B, ASTM G 1 – 03.				

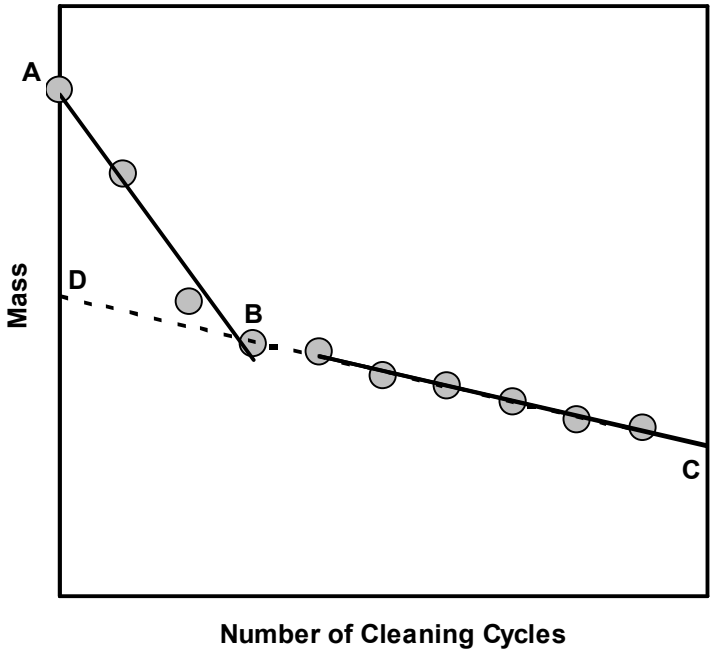
- **After 2 minutes, removed, scrubbed, rinsed in DI water followed by ethanol**
- **Coupon weighed**
- **Repeat process for 5 to 10 cycles**

Weight Loss Graphical Analysis

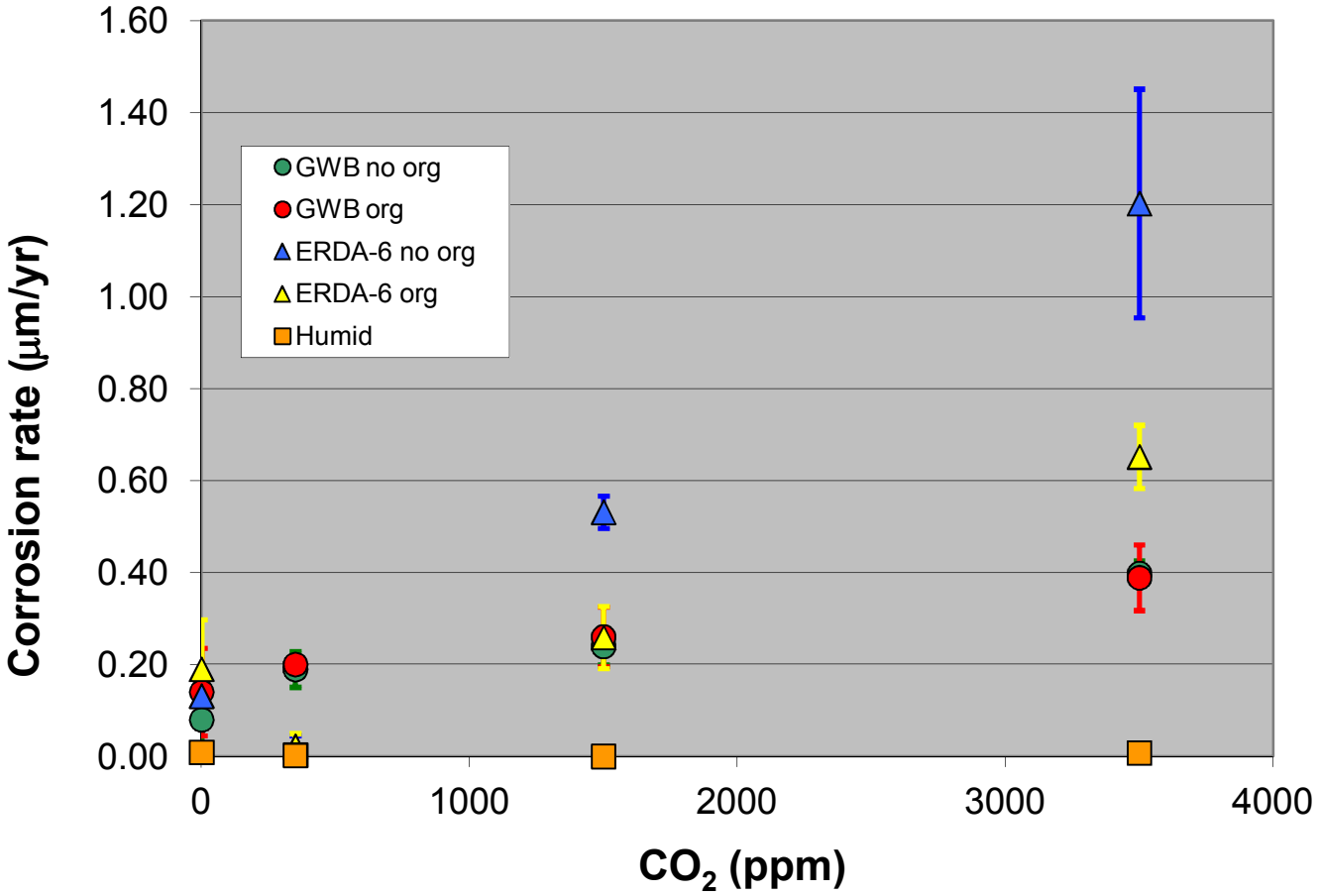
AB – Removal of corrosion product and base metal

BC – Removal of base metal only

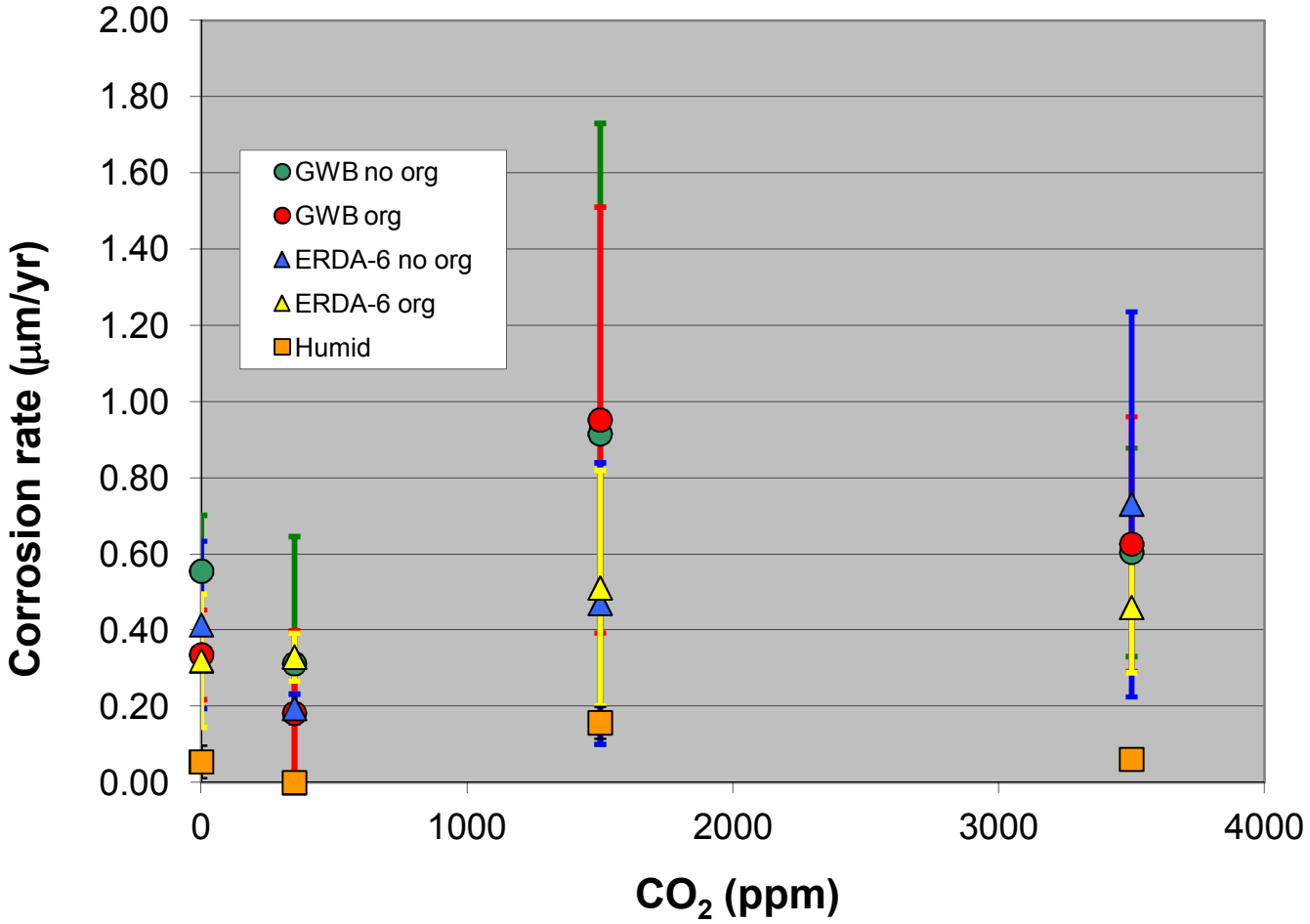
D – Projected final weight



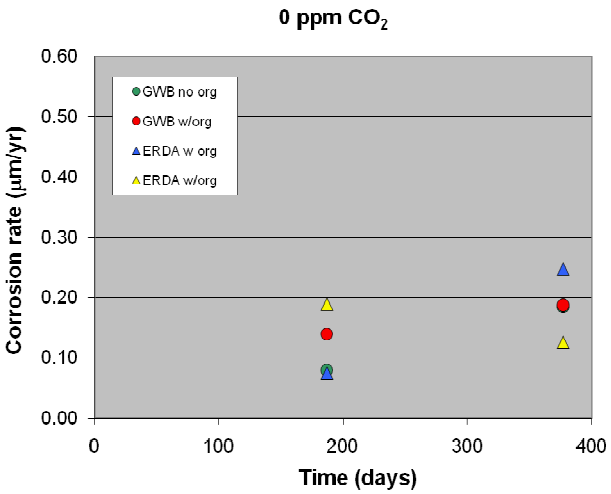
Corrosion Rate for Fe Coupons

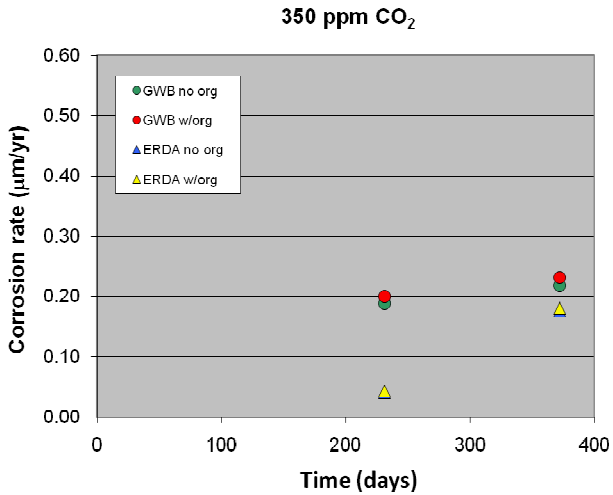


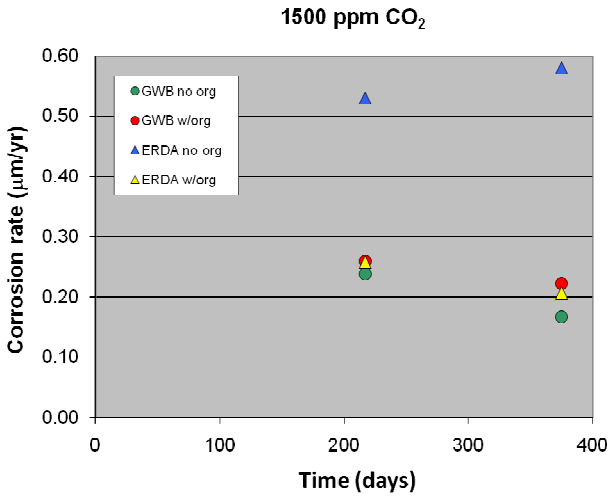
Corrosion Rate for Pb Coupons

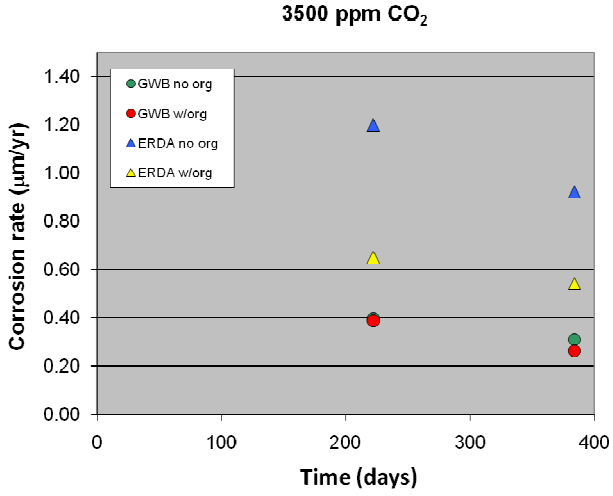


Corrosion Rate for Fe Coupons









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 may be occurring at high P_{CO2}

References

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