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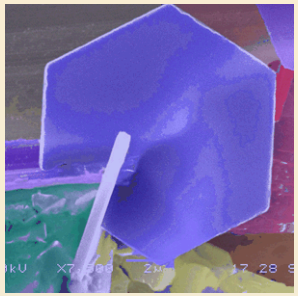



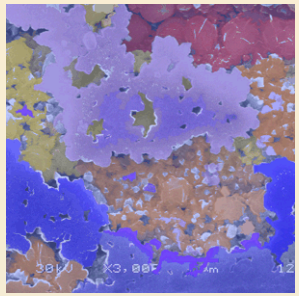

Anoxic Corrosion of Steel and Lead in Na-Cl ± Mg Dominated Brines

International High-Level Radioactive Waste Management

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U.S. DEPARTMENT OF ENERGY

NNSA Nuclear National Security Administration

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Purpose and Scope

- Determine Fe Corrosion Rates for use in PA H_2 Gas Generation Model

- Determine what corrosion products are likely to form
  - Kinetics of Fe and Pb corrosion
  - Potential for passivation of metal surfaces

- Determine the extent to which Fe and Pb consume CO_2
  - Potential for Fe and Pb to support MgO as engineered barrier

- Work conducted under:
  - TP 06-02 *Iron and Lead Corrosion in WIPP-Relevant Conditions*
  - AP-159 *Determination of Gas Generation Rates from Iron/Lead Corrosion Experiments*

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 submersed
- Four time segments (6, 12, 18 and 24 months)
- Experiments are being performed in a flow-through system designed to maintain above environmental conditions
- 864 total samples (432 steel, 432 lead)

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
- Determination of updates to corrosion rate parameters

Typical Appearance of Steel Coupons

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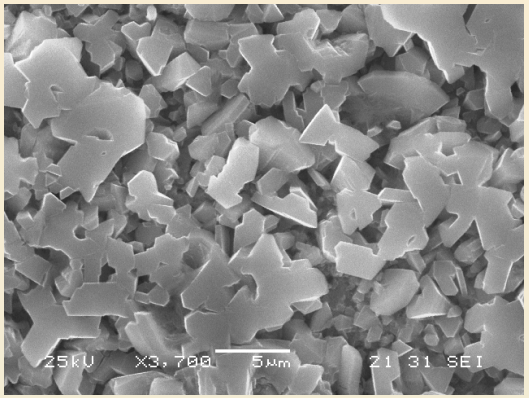
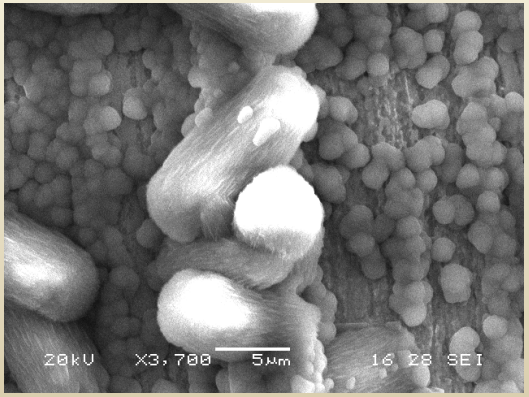
Coupon 021
24 month exposure, 0 ppm CO_2, ERDA-6 no organics

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

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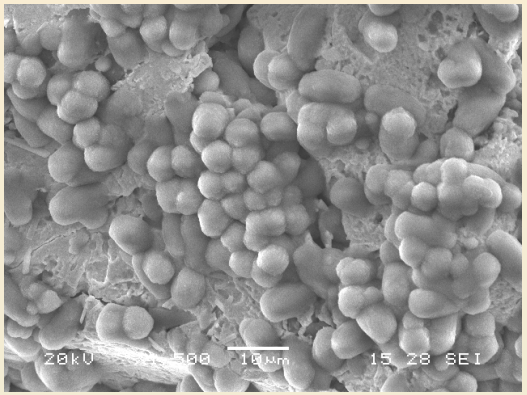
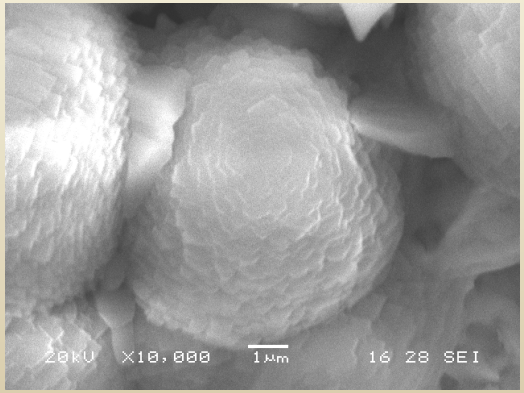
Coupon L451
6 month exposure, 3500 ppm CO_2, ERDA-6 with organics

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



Coupon L313
6 month exposure, 1500 ppm CO_2, ERDA-6 no organics



Possible Corrosion Products

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	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

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- 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.

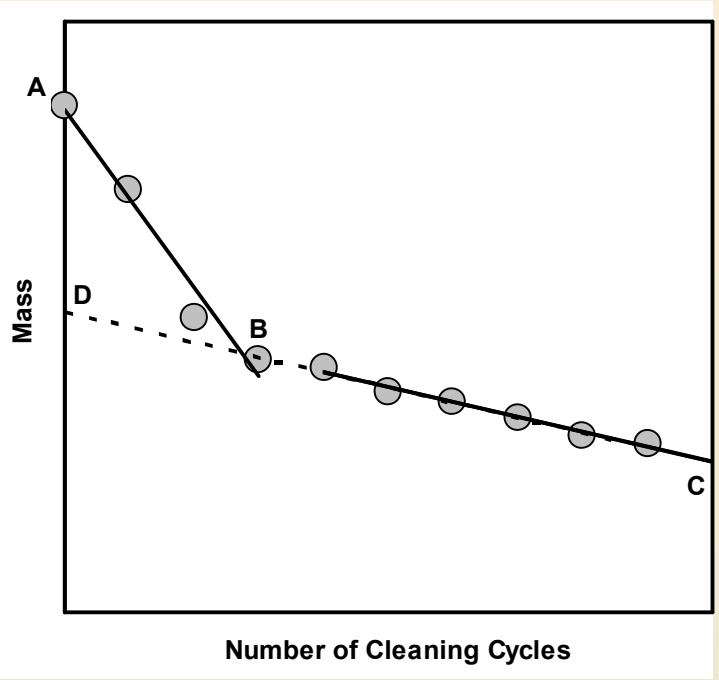
- After 2 minutes, removed, scrubbed, rinsed in DI water followed by ethanol
- Coupon weighed
- Repeat process for 5 to 10 cycles

Weight Loss Graphical Analysis

AB – Removal of corrosion product and base metal

BC – Removal of base metal only

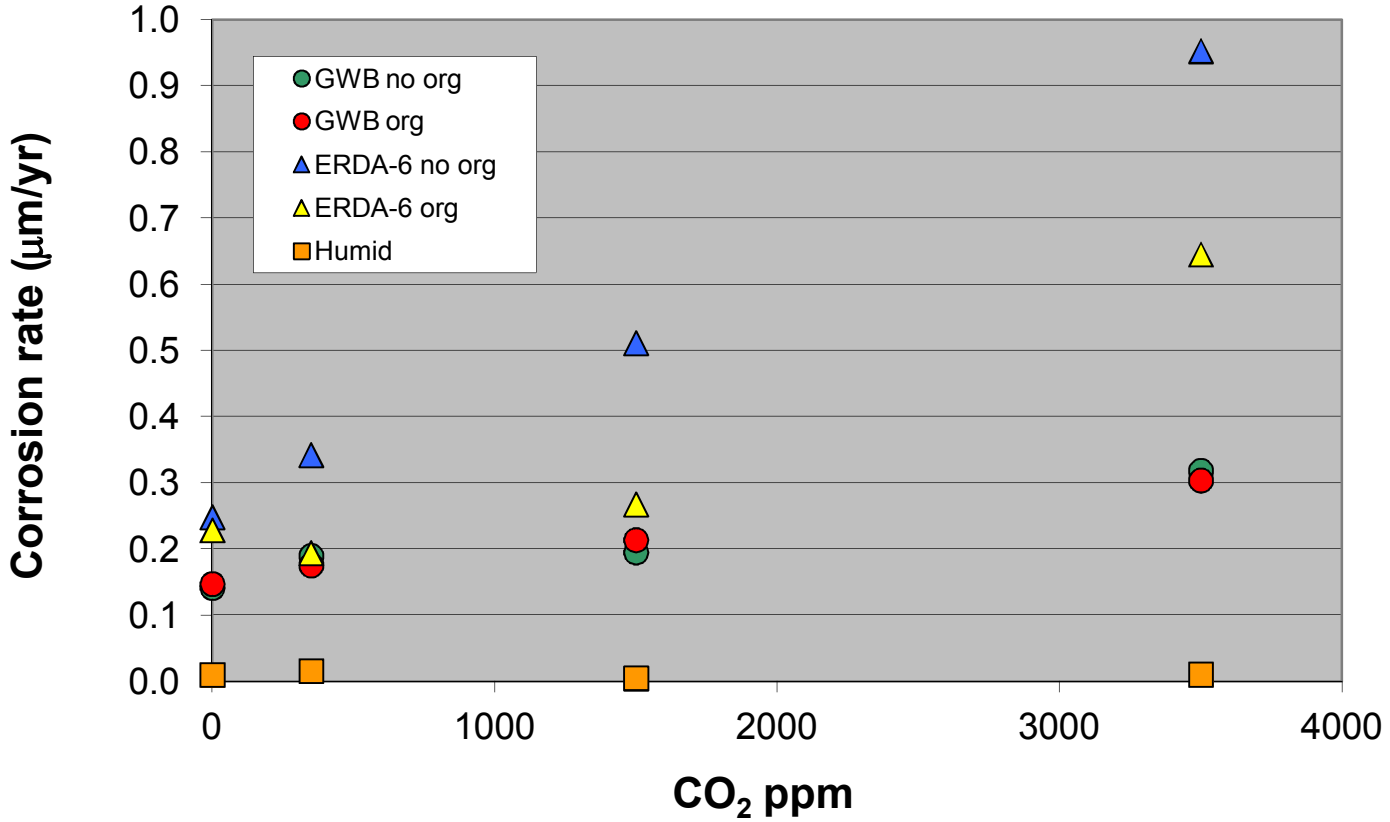
D – Projected final weight



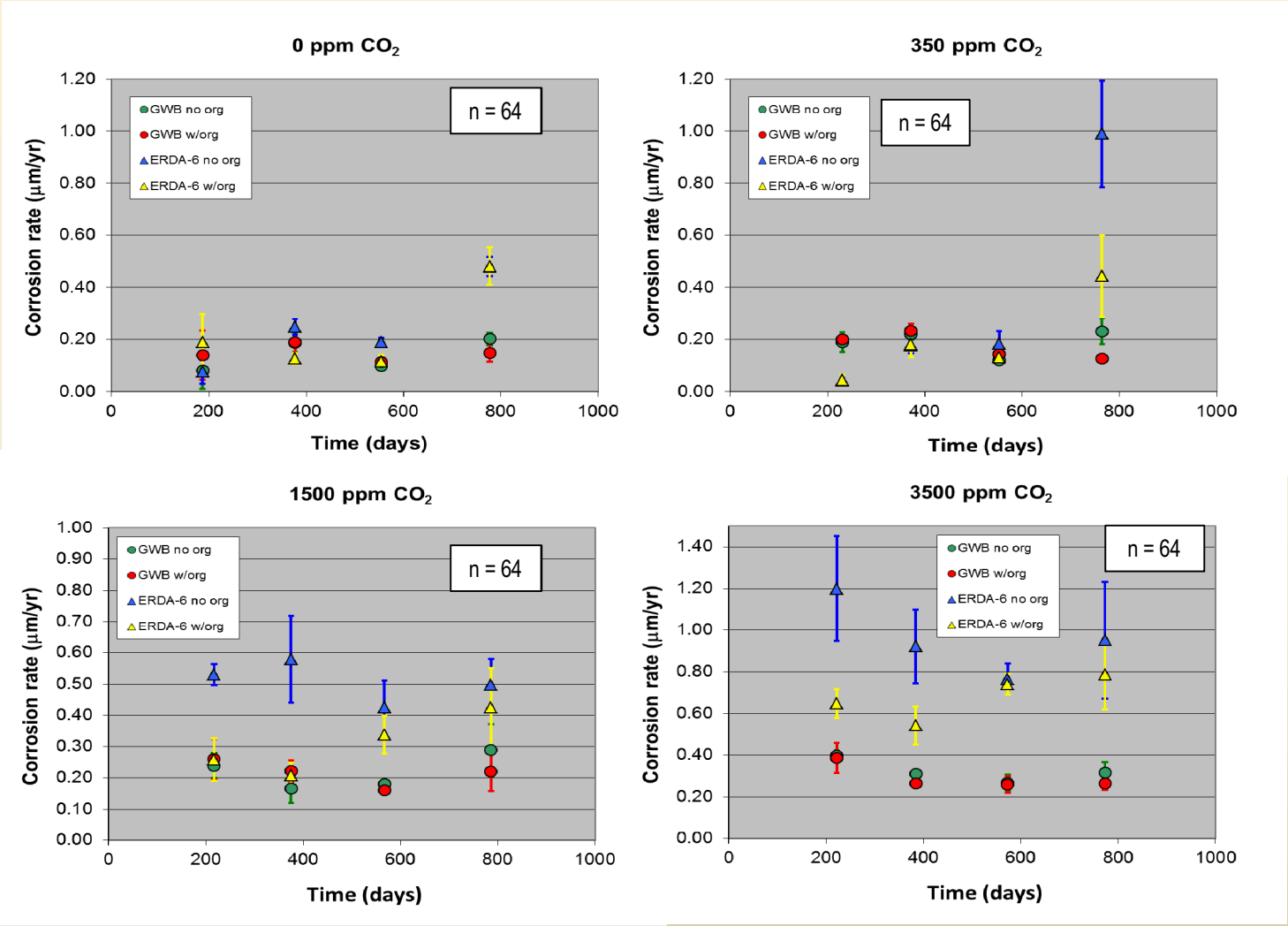
$$rate(\mu m / yr) = \frac{W \times 87.6}{SA \times t \times \rho} \times 1000$$

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

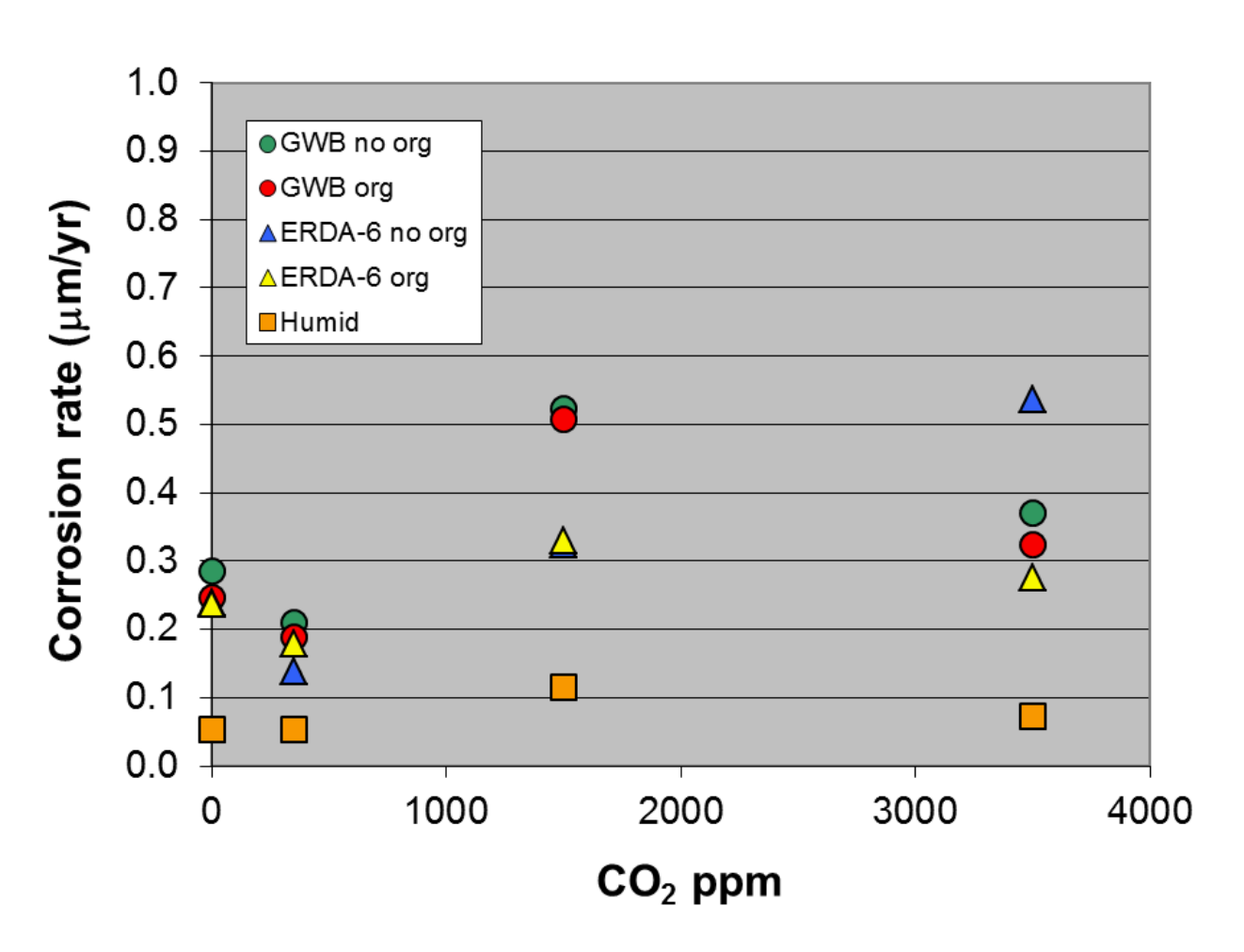
Corrosion Rates for Fe Coupons (All results)



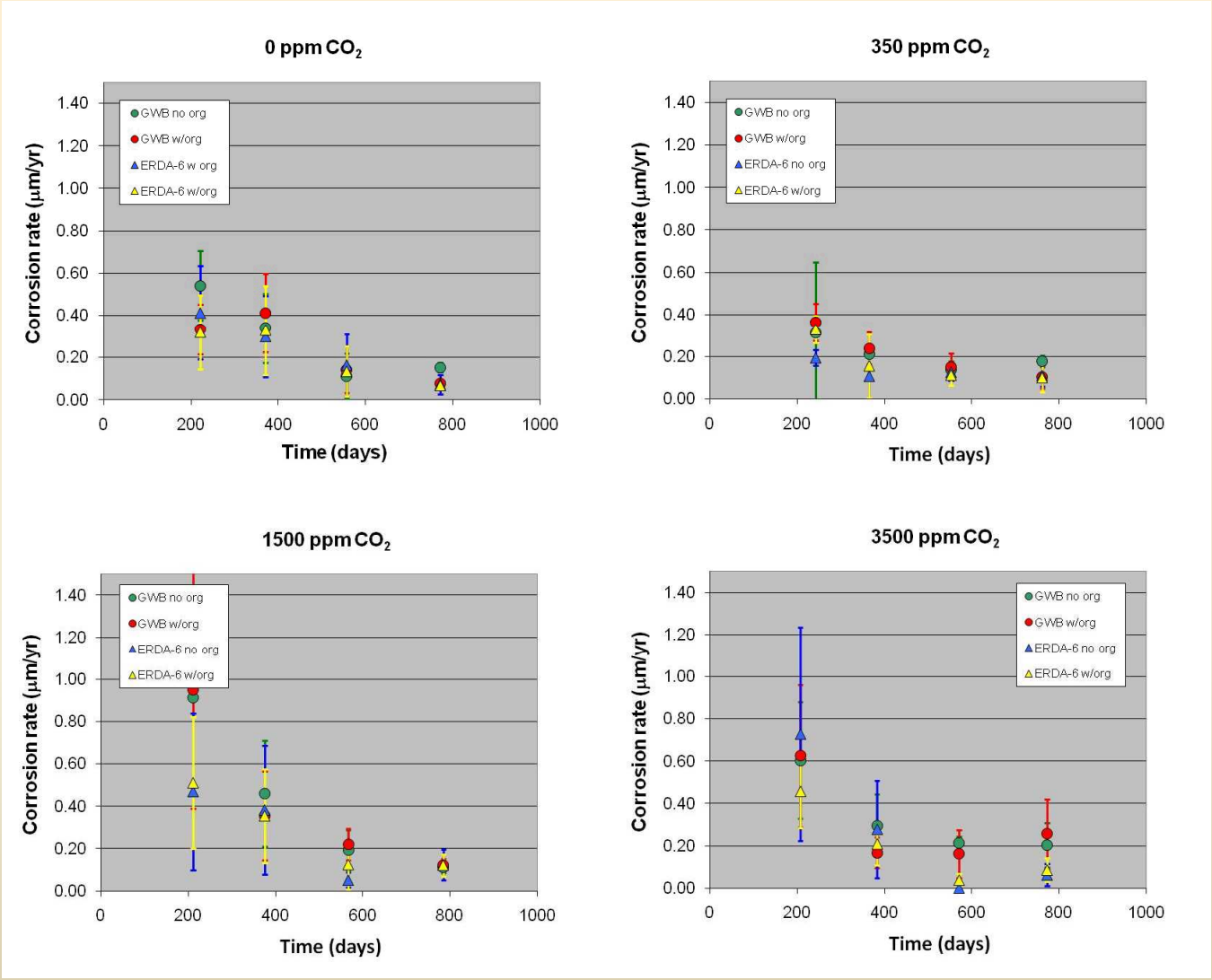
Fe Corrosion Rates with Time



Corrosion Rates for Pb Coupons (All results)



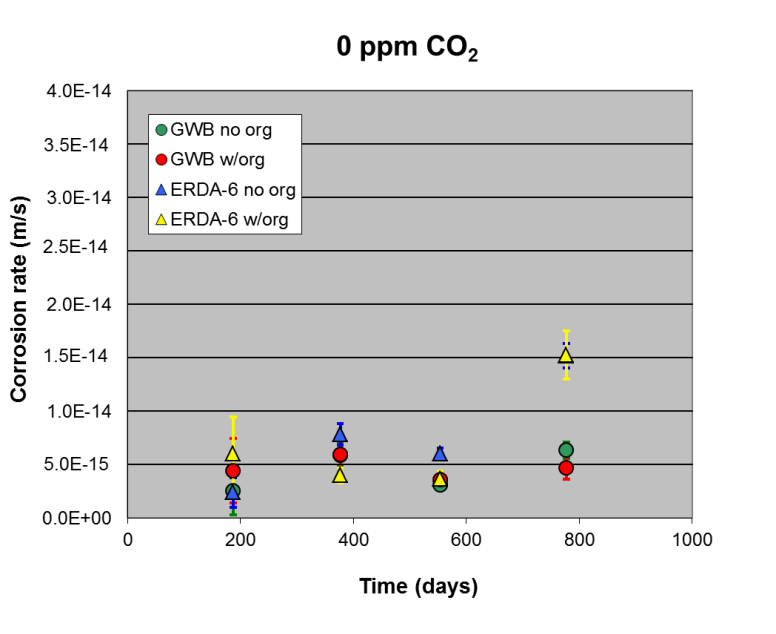
Corrosion Rates for Pb Coupons



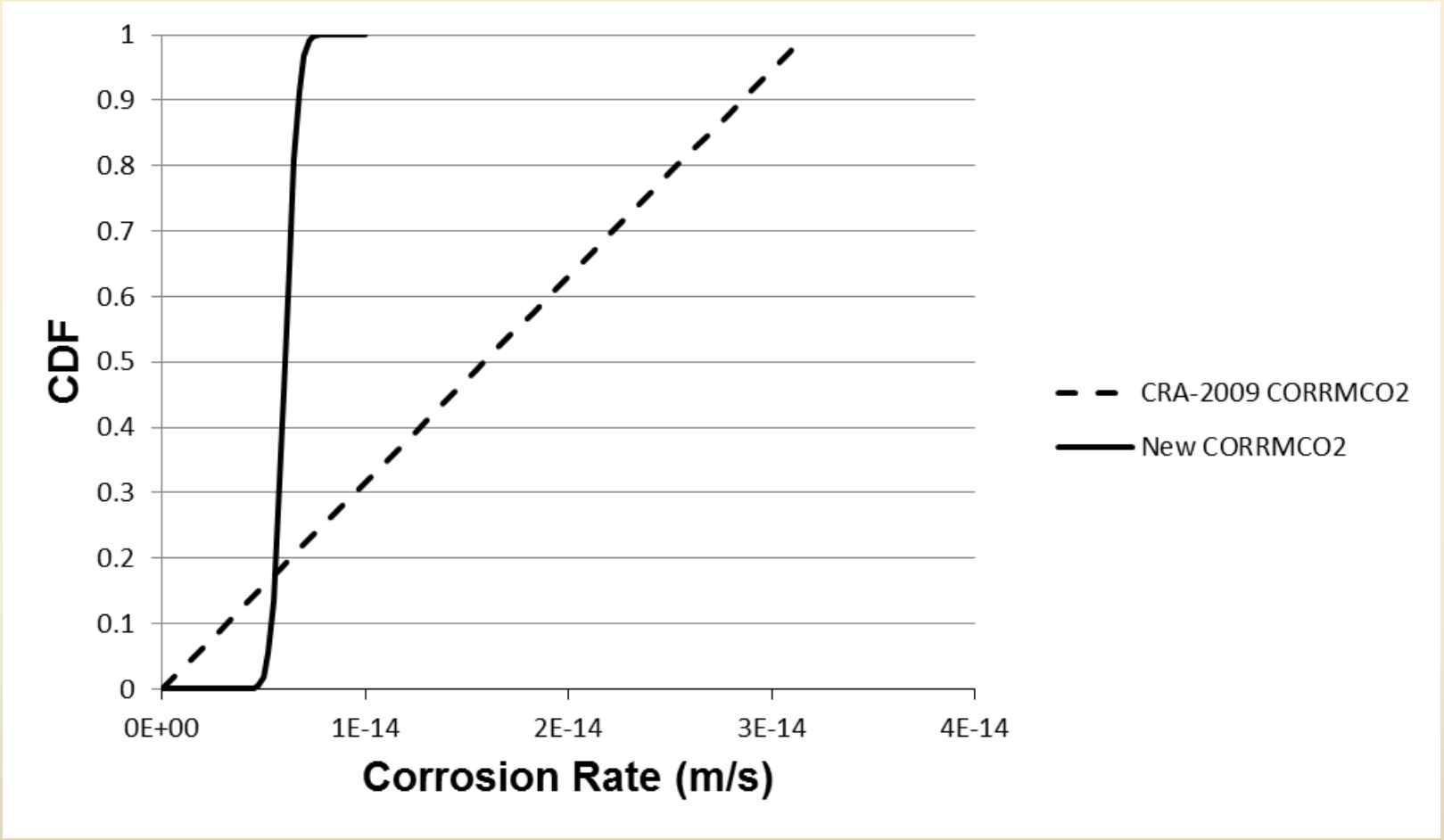
Updated PA Parameters

- Proposed PA Parameter Updates

Parameter	Units	Description	Distribution Type	Distribution Parameters
CORRMCO2	m/s	Rate of anoxic steel corrosion under brine-inundated conditions with no CO_2 present	Student-t (n = 64)	Mean = 6.059e-15 σ = 4.047e-15 SE = 5.059e-16



PA Parameters



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
- Steel and Lead subjected to humid conditions shows no evidence of corrosion
- No clear evidence of passivation for Fe at low CO_2 ppm
- Passivation of Pb may be occurring at all P_{CO2}
- Based on the new steel corrosion data it is suggested that the PA parameter CORRMCO2 be changed from a uniform to a Student's-t distribution with new values.

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Supplemental Materials

Coupon Compositions

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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)