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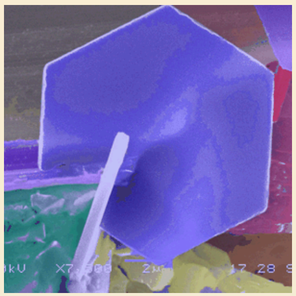



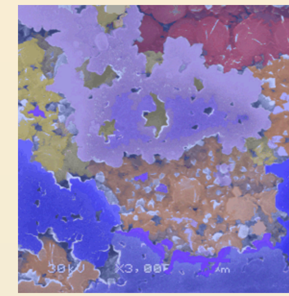

Anoxic Corrosion of Steel and Lead in Na-Cl ± Mg Dominated Brines and Effects on PA

DOE/EPA Technical Exchange; November 14-15, 2012; Carlsbad, NM

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

U.S. DEPARTMENT OF ENERGY NNSA National Nuclear Security Administration

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)

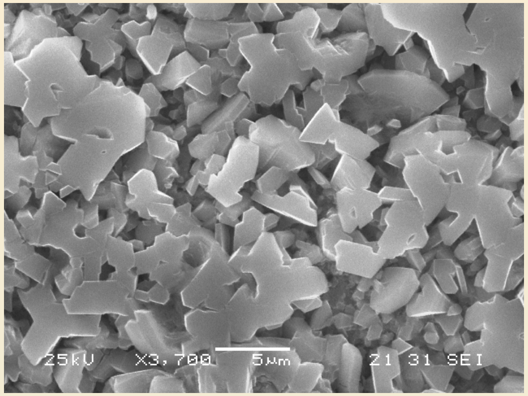
Sample Analysis

- 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

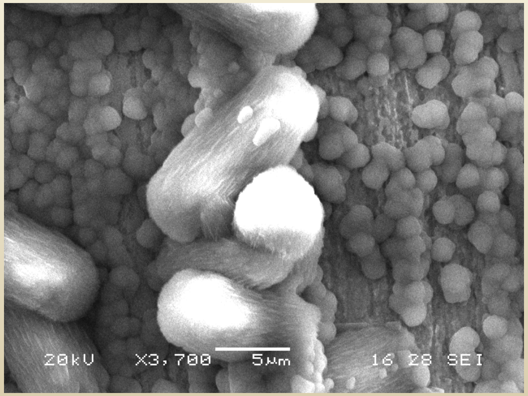
Typical Appearance of Steel Coupons

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



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.			

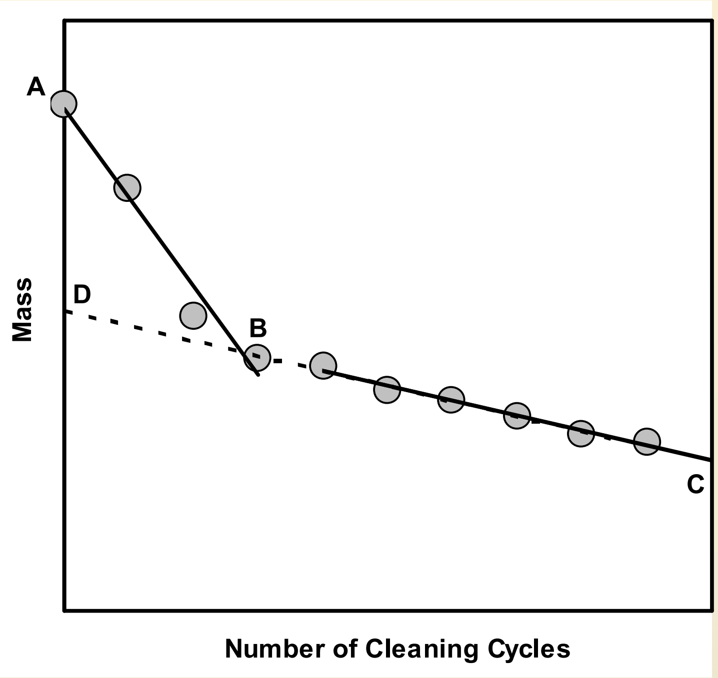
- After 2 minutes, removed, scrubbed, rinsed in DI water followed by ethanol
- Coupon weighed
- Repeat process for 5 to 10 cycles

Weight Loss Graphical Analysis

AB – Removal of corrosion product and base metal

BC – Removal of base metal only

D – Projected final weight



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

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)

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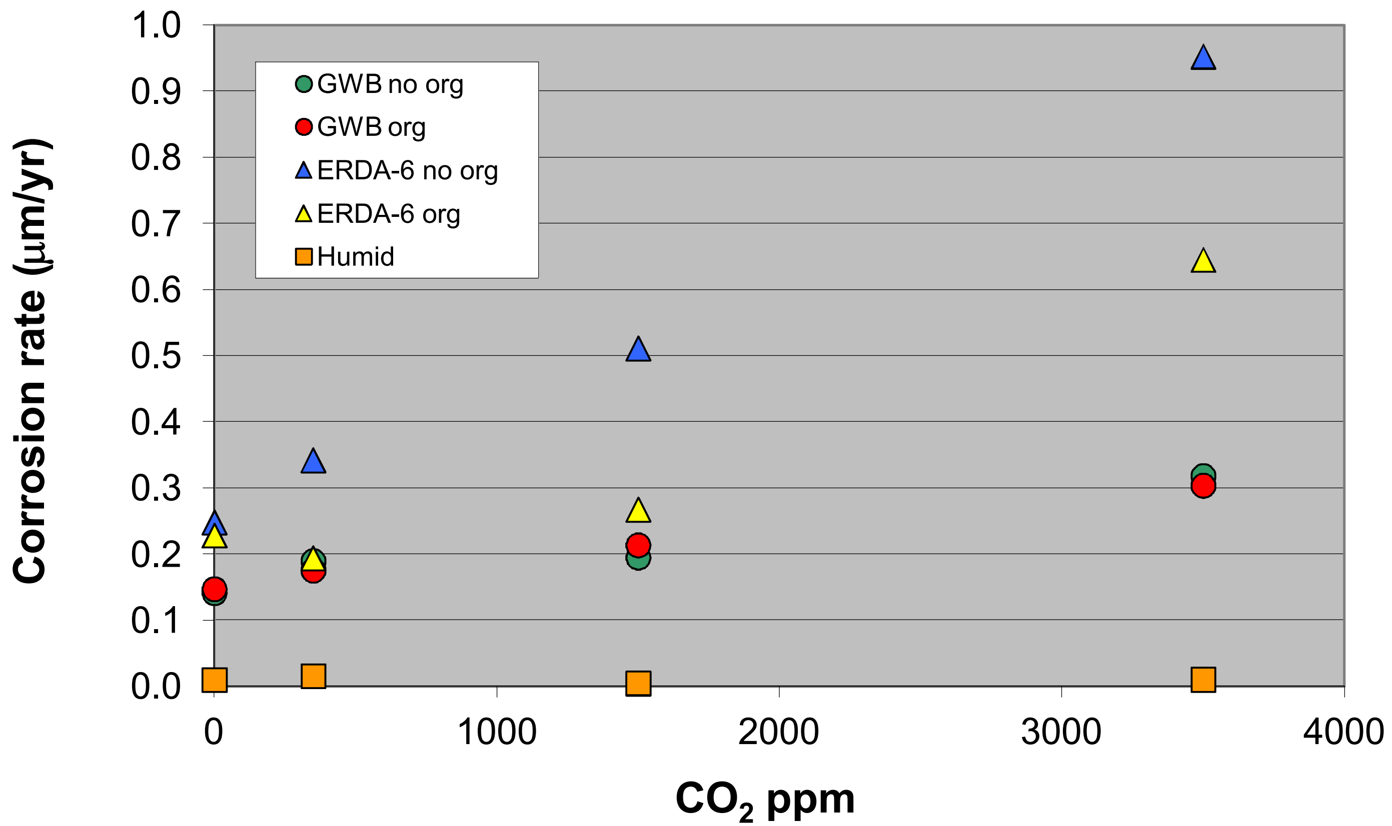

Fe Corrosion Rates with Time

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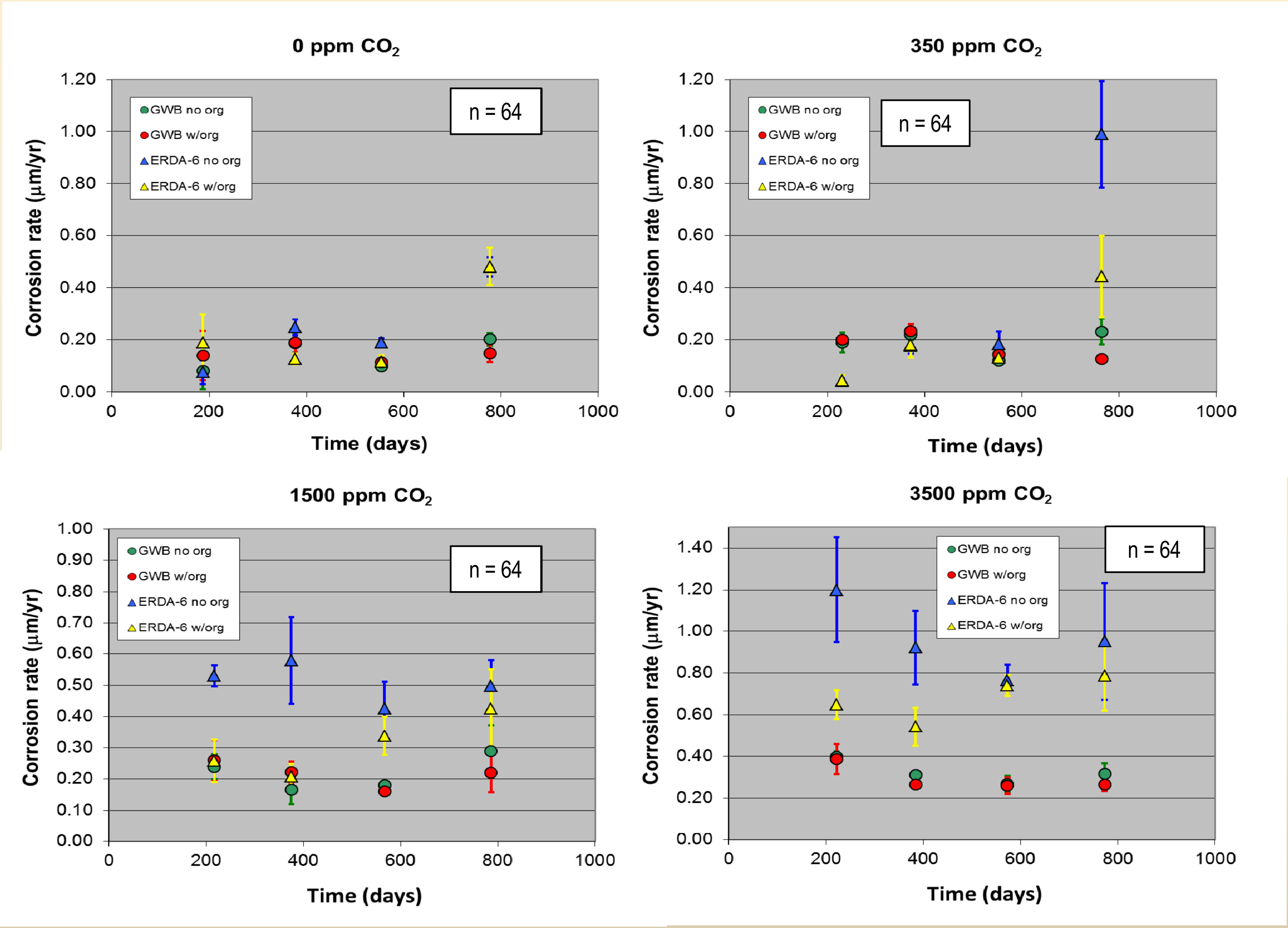


Gas Generation in PA

$$q_{rgc} = \left(R_{ci} S_{b,eff} + R_{ch} S_{g}^{*}\right) D_s \rho_{Fe} X_c \left(\mathrm{H}_2 \middle| \mathrm{Fe}\right) M_{\mathrm{H}_2}$$

q_{rgc} - H_2 gas generation rate due to corrosion ($kg/m^3/s$)

D_s - surface area concentration of steel in the repository (m^2 / m^3)

M_{H2} - molecular weight of H_2 (kg/mol)

R_{Ci} - inundated corrosion rate in the absence of CO_2 (m/s) [CORRMCO2]

R_{Ch} - corrosion rate under humid conditions (m/s) [HUMCORR]

$S_{b,eff}$ - effective brine saturation due to capillary action in the waste materials

$X_C(H_2|Fe)$ - stoichiometric coefficient for gas generation due to corrosion of steel (mol H_2/mol Fe) [STOIFX]

ρ_{Fe} - molar density of steel (mol/m^3)

Current PA Parameters

- Current PA Corrosion Parameters

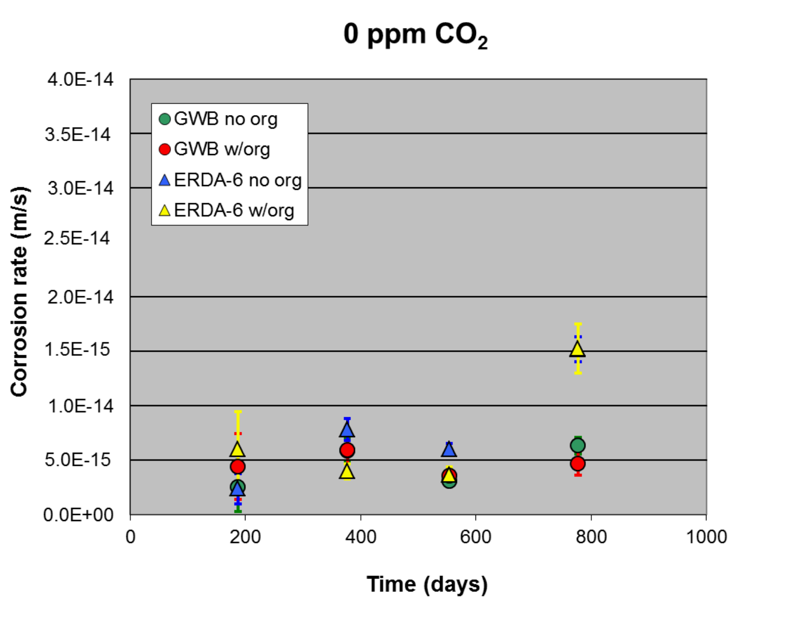
Parameter	Units	Description	Distribution Type	Distribution Parameters
CORRMCO2	m/s	Rate of anoxic steel corrosion under brine-inundated conditions with no CO_2 present	Uniform	Min = 0 Max = 3.17e-14
HUMCORR	m/s	Rate of anoxic steel corrosion under humid conditions	Constant	0
STOIFX	none	Stoichiometric coefficient for gas generation	Constant	1
Source: WIPP PA Parameter Viewer				

Updated PA Parameters

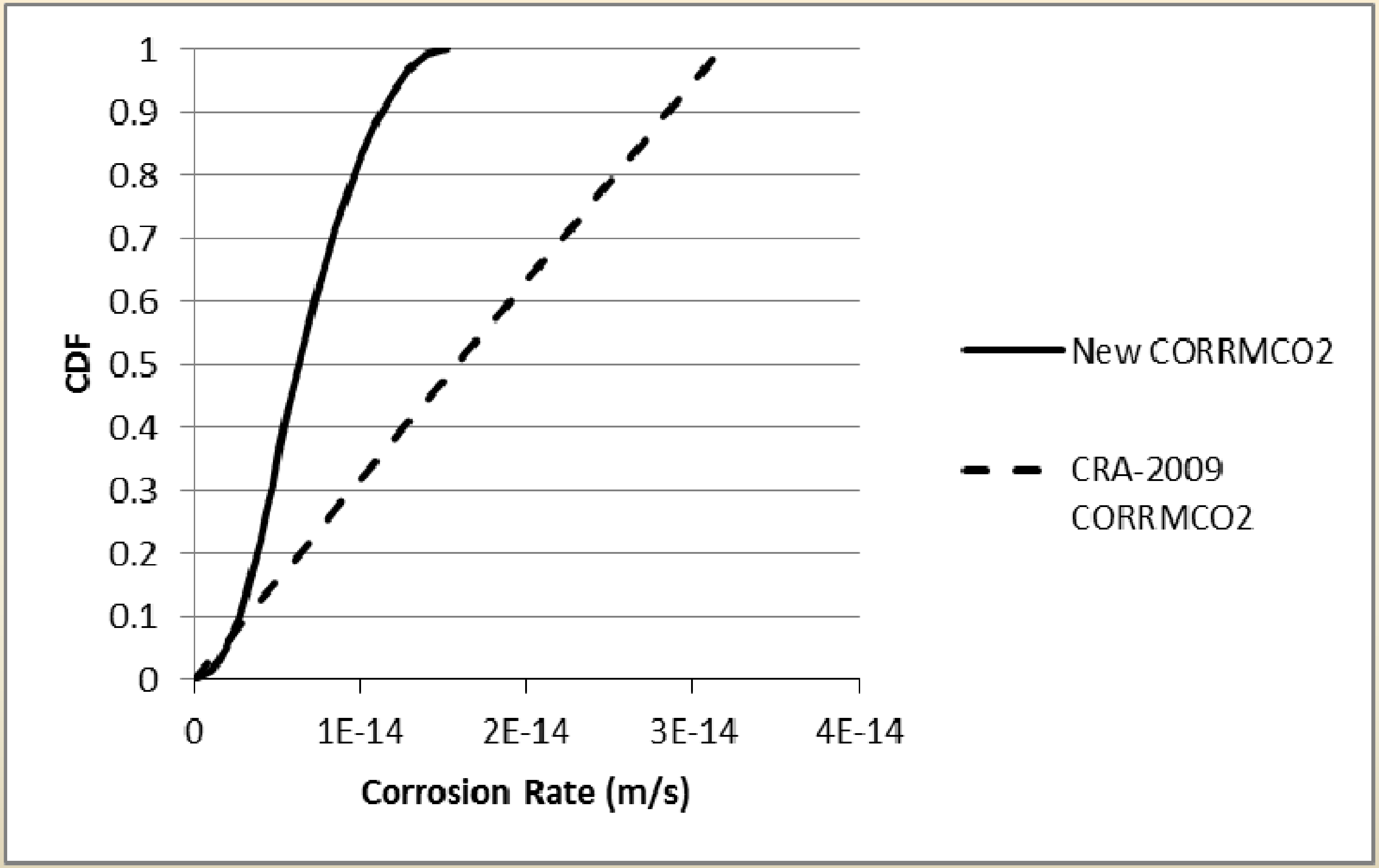
- Proposed PA Parameter Updates

Parameter	Units	Description	Distribution Type	Distribution Parameters
CORRMCO2	m/s	Rate of anoxic steel corrosion under brine-inundated conditions with no CO_2 present	Triangular	Min = 0 Max = 1.523e-14 Mode = 4.749e-15 Mean = 6.660e-15

  - HUMCORR and STOIFX remain unchanged



PA Parameters



Summary

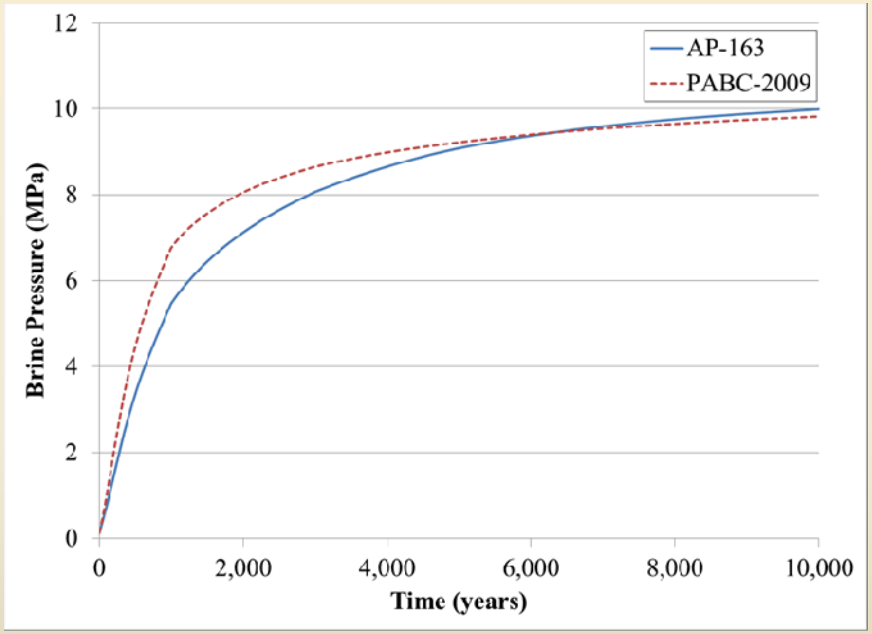
- Corrosion of Fe
  - ERDA-6 (NaCl-dominated) is more corrosive than GWB ($NaCl-MgCl_2$)
  - The presence of organics is important only for ERDA-6 (suppresses corrosion)
  - Corrosion increases with CO_2
- Steel subjected to humid conditions shows no evidence of corrosion
- No clear evidence of passivation for Fe at low CO_2 ppm
- Based on the new steel corrosion data it is suggested that the PA parameter CORRMCO2 be changed from a uniform to a triangular distribution with new values.

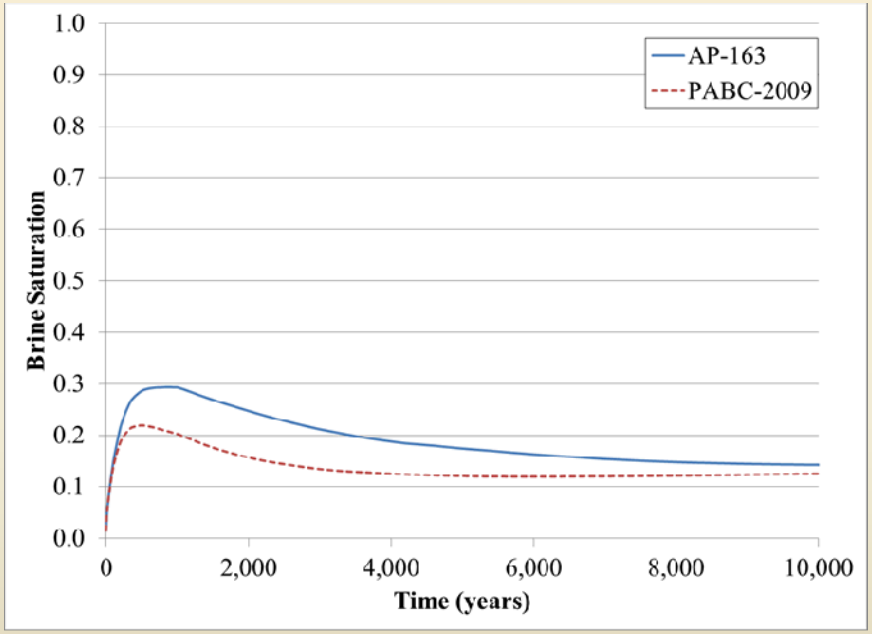
Effects of New Parameter on PA

Preliminary Results

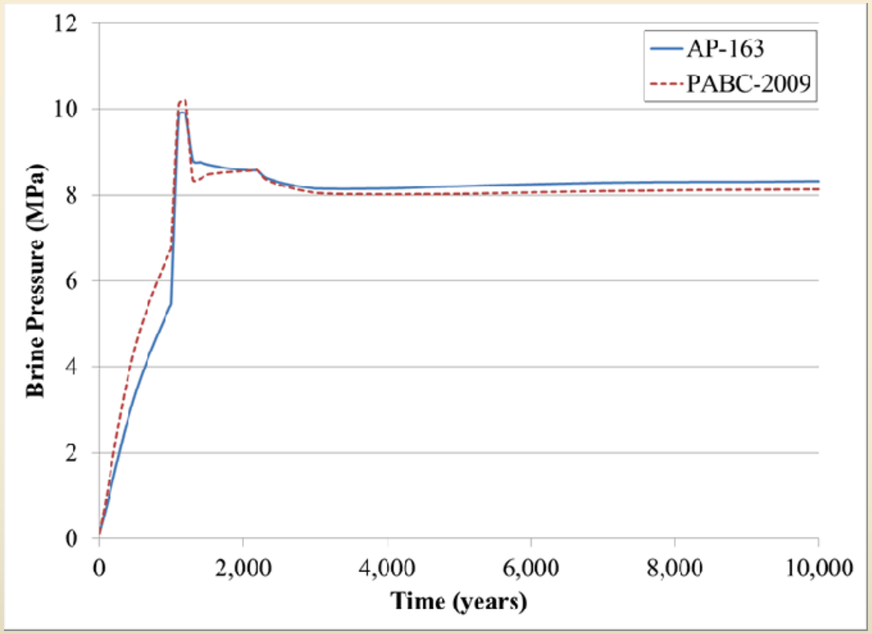
- Increase in saturations
- Pressure
  - Initially lower, then increases at later times or after intrusion
- Less overall waste material degradation, especially at earlier times

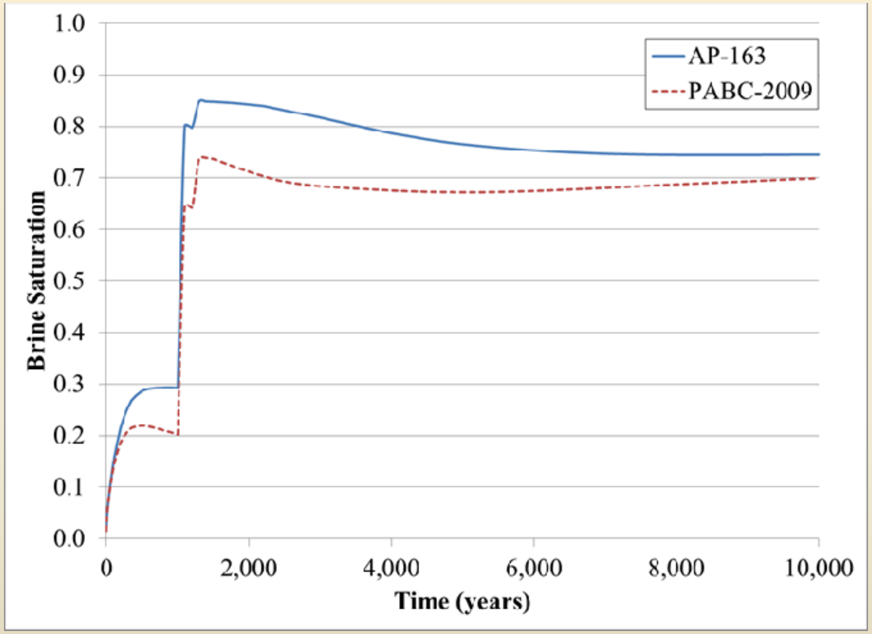
Undisturbed





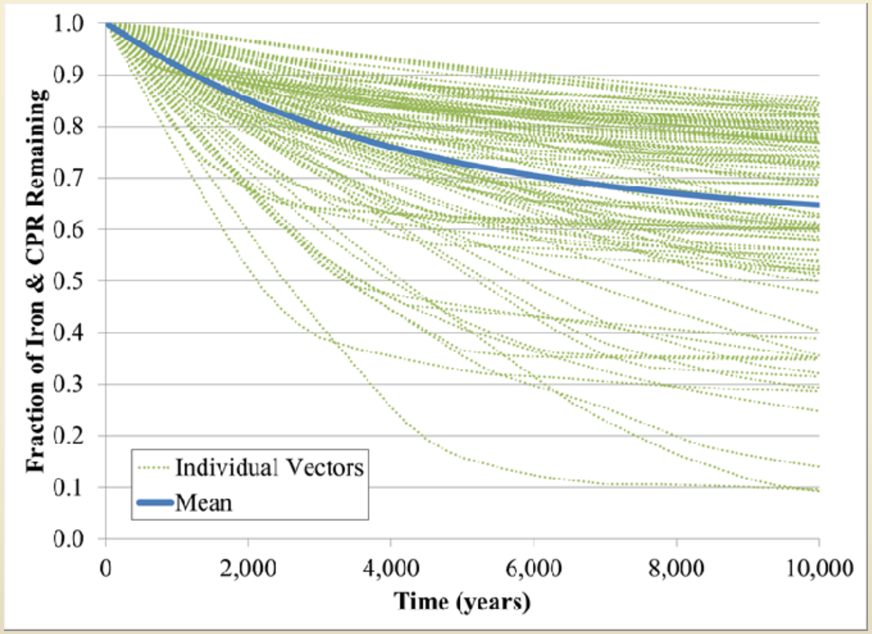
E1 Intrusion





Waste Material Degradation

AP-163



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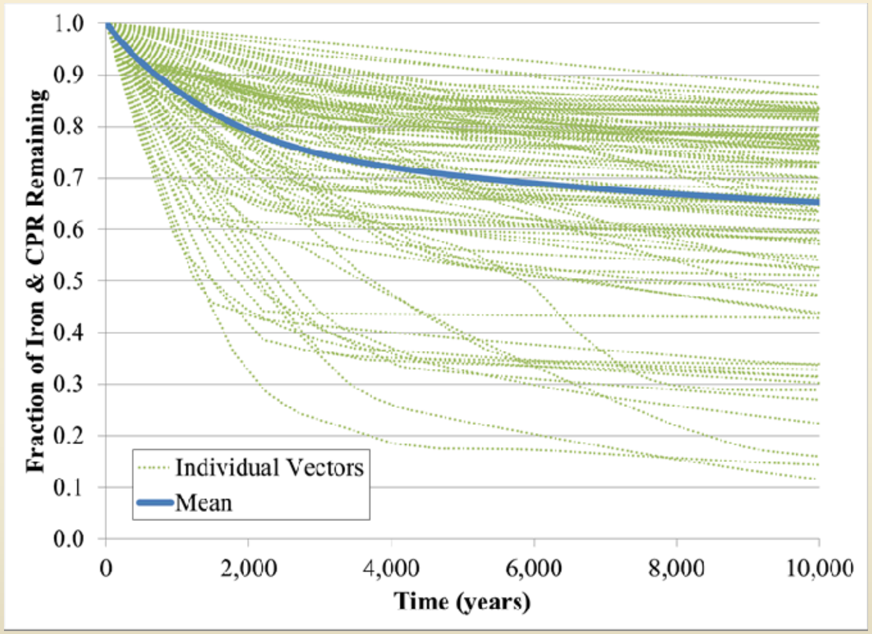


Supplemental Materials

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

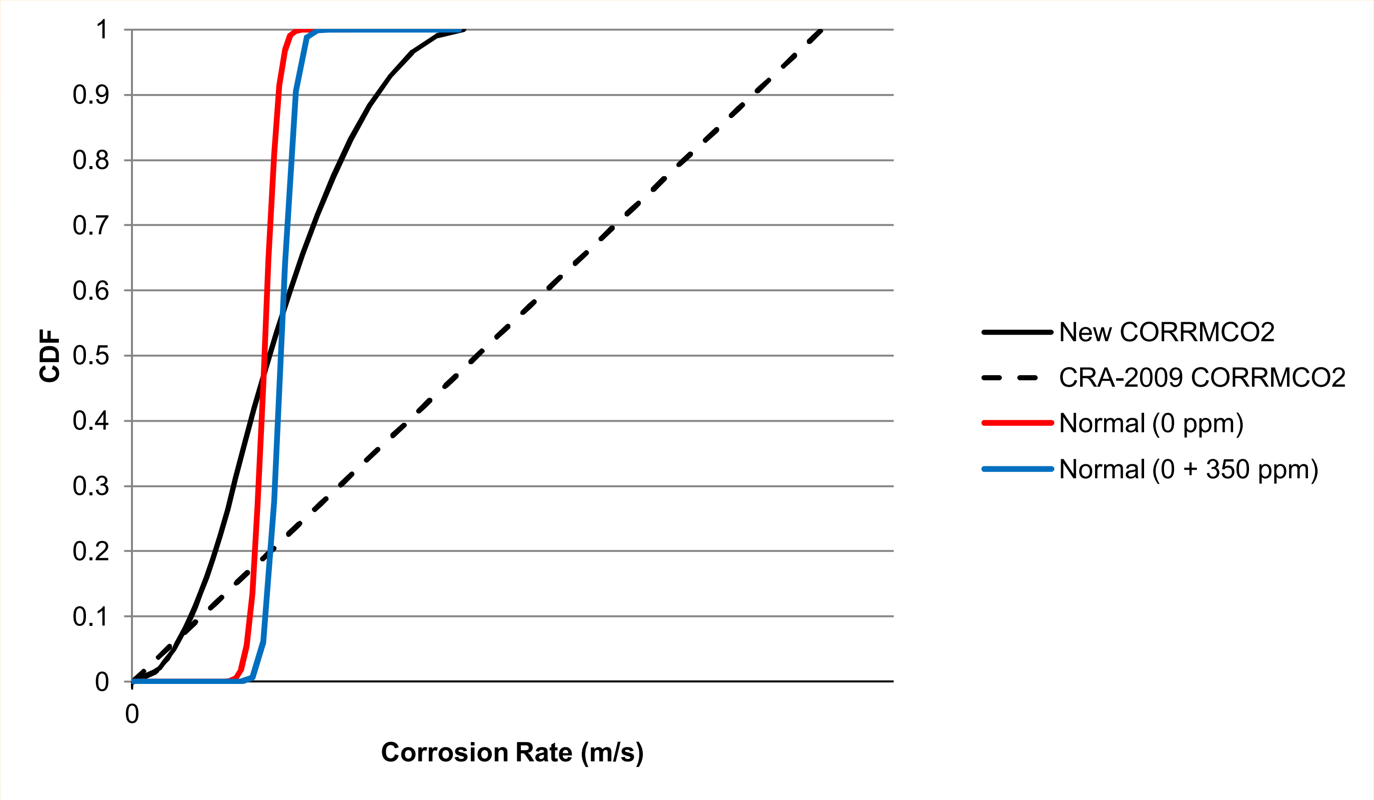
Element	Weight Percent
Ag	0.010
Bi	0.015
Cd	0.001
Cu	0.070
Fe	0.001
Ni	0.001
Pb	99.900
Sb+Sn+As	0.001
Zn	0.001

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)



Mean = 6.059E-15 m/s
Std. Error = 5.059e-16 m/s
n=64

Mean = 6.811E-15 m/s
Std. Error = 7.292e-16 m/s
n=124