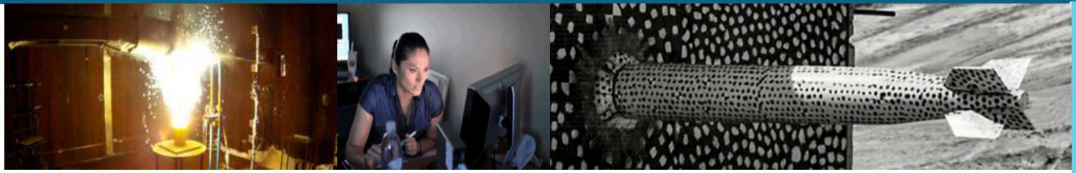
SAND2019-6994C

Research Topics at Sandia National Laboratories



PRESENTED BY

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Mineral Fragment Colloids Related to Engineered Barrier (MgO): Experimental Determination

Introduction:

- Hydration and carbonation products of MgO in WIPP may provide mineral fragment colloids that could potentially increase actinide solubility and mobility.

Objective:

- To determine experimentally the absence or presence of colloids related to the hydration and carbonation products of the engineered barrier MgO.
- To investigate the absence or presence of mineral fragment colloids by using the method of ultrafiltration.

Results:

- Systematic experimental work demonstrates the absence of mineral fragment colloids produced by hydration and carbonation of the WIPP engineered barrier MgO in the WIPP brines, by two independent experimental approaches.
- The absence of mineral fragment colloids in the WIPP brines is due to the high concentrations of mono and divalent ions which neutralize any mineral fragment colloids causing them to coagulate and fall out of solution.

Am(III)/Nd(III) Interactions with Borate: Experimental Investigations of $Nd(OH)_3$(micro cr) Solubility in Mixtures of NaCl and $MgCl_2$ in Equilibrium with Borax

- Introduction:
- The Am(III) analog, Nd(III) can form stable aqueous complexes with borate, and thus increase its solubility.
- Objective:
  - To measure solubility of $Nd(OH)_3$(micro cr) in mixtures of NaCl + $MgCl_2$ saturated with borax ($Na_2B_4O_7 \bullet 10H_2O$) at 25°C in long-term experiments
- Results:
  - In this work, we have conducted solubility measurements regarding Nd(OH)3(micro cr) in mixtures of NaCl and $MgCl_2$ saturated with borax at 25°C.
  - Our results indicate that in the NaCl-dominated brines, the presence of borate increases Nd(III) concentrations.
  - Our results indicate that in the $MgCl_2$-dominated brines, the presence of borate decreases Nd(III) concentrations.

Equilibrium Constants for $AmHB_4O_7^{2+}$ and $AmB_9O_{13}(OH)_4(cr)$

- Introduction:
  - Recent experimental work indicates that borate could form a relatively strong complex with Nd(III) ($NdHB_4O_7^{2+}$, log $\beta_1 = 4.99 \pm 0.30$) at 25°C, an analog to Am(III), thus increasing solubility. Borate has a relatively high concentration in WIPP brines, up to ~0.2 m.

- Objective:
  - To evaluate the formation constant for $AmHB_4O_7^{2+}$ to be consistent with the WIPP borate model based on the raw solubility data.

- Results:
  - Speciation calculations using the formation constant obtained in this work at a constant concentration of borate of 0.16 mol•kg–1 indicate that:
    - In low concentrations of NaCl such as 0.1 mol•kg–1, $AmHB_4O_7^{2+}/NdHB_4O_7^{2+}$ is a dominant species from pHm 6 to pHm 9. Above pHm 9, hydroxyl species dominate.
    - In high concentrations of NaCl such as 3.2 mol•kg–1, $AmHB_4O_7^{2+}/NdHB_4O_7^{2+}$ is a dominant species from pHm 6.4 to pHm 8.4. Below pHm 6.4, Am^{3+}/Nd^{3+} is a dominant species. Above pHm 8.4, hydroxyl species dominate.
  - In the presence of borate, $AmHB_4O_7^{2+}/NdHB_4O_7^{2+}$ is expected to be important in solutions with low concentrations of Na+ and in neutral to mildly alkaline pH.

Experimental Determination of Solubility Constants of Saponite at Elevated Temperatures in High Ionic Strength Solutions

➢Introduction:

Brines associated with salt formations usually have high concentrations of magnesium, as exemplified by the examples.

When high level waste (HLW) glass is corroded in Mg-rich solutions, Mg-containing clay minerals such as saponite, $Mg_4Al_2Si_2O_{10}(OH)_2 \cdot 4H_2O$, form.

When saponite forms it may impact the near-field chemistry of a geological repository in salt formations:

- Governing the chemical compositions, including hydrogen ion concentrations, of the resulting solutions
- Forming protective layer on surfaces of HLW glass, preventing or reducing the further corrosion of HLW glass

➢Objective:

- To synthesize saponite according to the well-established procedure (Shao and Pinnavaia, 2010).
- To investigate solubility constants of saponite at elevated temperatures.

➢Preliminary Results:

$$Na_{0.3}Mg_{3.85}Al_2Si_2O_{10}(OH)_2 \bullet 4H_2O + 2H_2O(l) = 0.3Na^{+} + 3.85Mg^{2+} + 2Al(OH)_4^{-} + 2H_2SiO_4^{-2} + 2OH^{-}$$

log Q = -29.75 ± 0.75 (2σ) for data at 80°C

In the near future, the following will be reported:

- Experimental results from undersaturation experiments
- Extrapolation of equilibrium quotients to infinite dilution using the Pitzer and Specific Ion Interaction Theory (SIT) models

Solubility and iron colloid studies:

- Fe^{+2} – $EDTA^{-4}$
- Fe^{+2} – $Oxalate^{-2}$ (Humboldtine)
  - Mg^{+2} – $Oxalate^{-2}$ (Glushinskite)
- Mackinawite (Fe^{+2} – S^{-2})
- Vivianite (Fe^{+2} – PO_4^{-3})
- Siderite/Chukanovite (Fe^{+2} – CO_3^{-2})
- Hibbingite/Ferrous Iron Hydroxide (Fe^{+2} – OH^- - Cl^-)
- Ferric iron model being sought.

Thermodynamic Database Update for WIPP Geochemical Modeling

- Introduction:
  - Selected parameters of the WIPP EQ3/6 thermodynamic database, DATA0.FM1, were updated for use in the 2019 recertification, CRA-2019.
- Objective:
  - Both lead and iron have significant masses in the WIPP repository, and neither had been included in previous recertifications until CRA-2019. The addition of lead and iron models, and updates to some of the organic systems was the primary objective of creating the new WIPP database DATA0.FM4.
- Results:
  - Both the actinide baseline solubility model and the actinide uncertainty analysis were completed for the CRA-2019 PA using the new database. The baseline solubility model was updated to include lead (PbO) and iron ($Fe(OH)_2(s)$) reactants. The addition of lead had virtually no impact on the actinide solubility, the data set added to DATA0.FM4 did not include Pb – organic complexes. While the inclusion of iron had only minor effects on the actinide solubility, it had a much greater impact on the carbonate system which required a re-evaluation of assumptions from past models.

Reevaluation of Actinide(IV)-Humic Complexation in the WIPP Performance Assessment

Abstract:

The legacy humic colloid model for tetravalent actinides (Th(IV), U(IV), Np(IV), and Pu(IV)) in the performance assessment (PA) of the Waste Isolation Pilot Plant (WIPP) is highly conservative. The model structure is feasible, but substantial reductions are needed for two constants, PHUMSIM and PHUMCIM, that represent the equilibrium aqueous concentration ratio of humic-bound An(IV) to non-colloidal An(IV) for the Salado and Castile formations. In the WIPP PA model, both constants are set at 6.3 based on observed colloidal partitioning of Th(IV) in seawater. Humic partitioning in WIPP brines is expected to be significantly lower than in seawater because the pH of WIPP brines (~9) is higher, concentrations of competing cations (e.g., Mg^{2+}) are higher, and concentrations of aqueous humic substances may be lower.

In this work, competitive humic complexation is simulated under WIPP conditions. The resulting PHUMSIM and PHUMCIM values are calculated to be well below 0.01. These values would reduce mobile An(IV) concentrations in the WIPP PA by as much as 85%.

Steel Corrosion in the Waste Isolation Pilot Plant, Carlsbad, NM

Areas of Impact:

1. Redox conditions after repository closure
2. Consumption of microbially produced CO_2
3. Formation of actinide/organic ligand complexes
4. Hydrogen gas generation

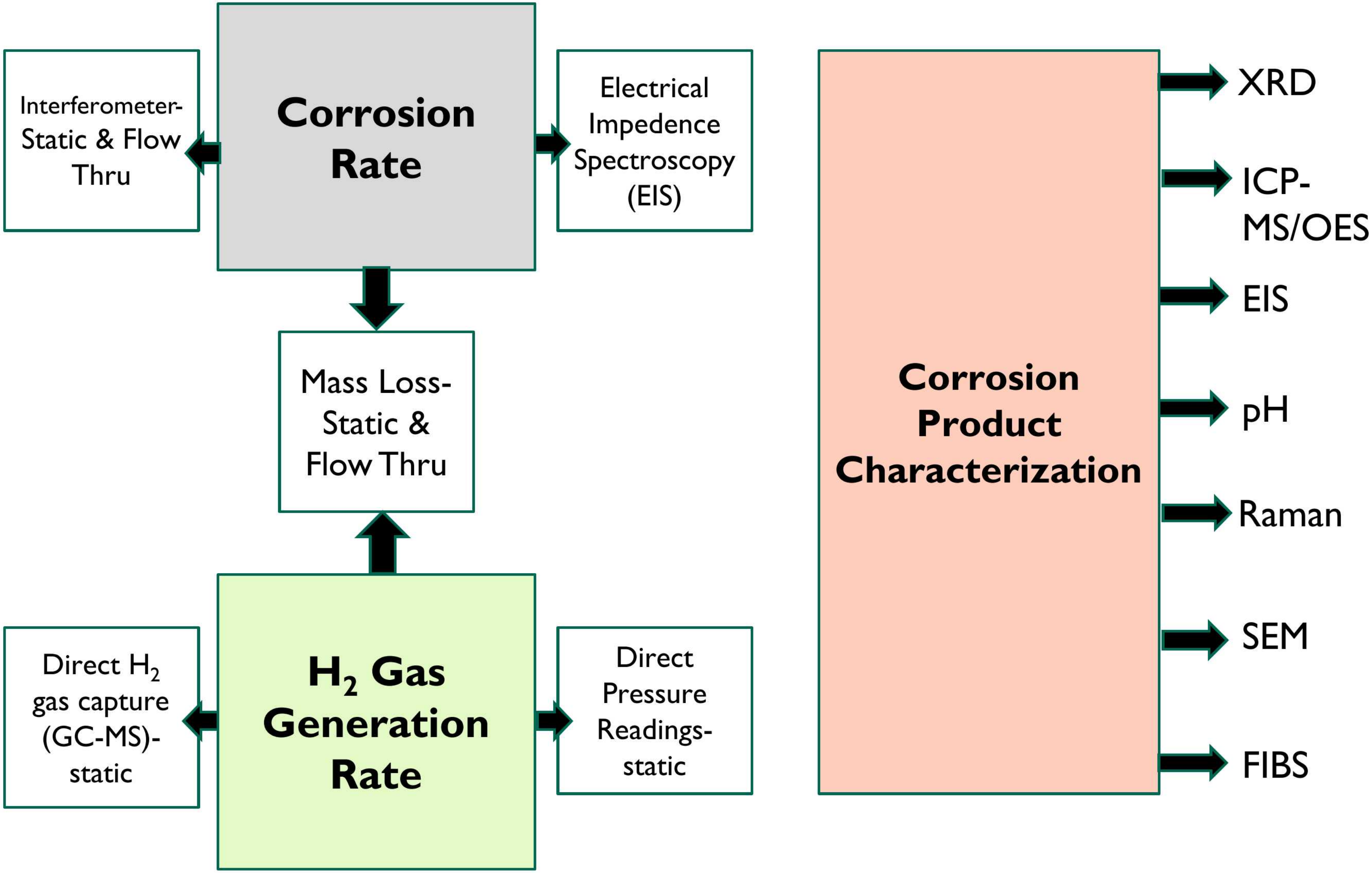
Performance Assessment Corrosion Parameters:

- *CORRMCO2*-Inundated Corrosion rate without CO_2 present
- *HUMMCORR*-Corrosion rate under humid conditions
- *STOIFX*-gas generation stoichiometric coefficient

After O_2 consumption, corrosion mechanics are:

1. $Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2$
2. $3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$
3. $2Fe(OH)_2 + Cl^- + H^+ \rightarrow Fe(II)_2(OH)_3Cl(cr) + H_2O$
4. $2Fe(cr) + 3H_2O(l) + Cl^- + H^+ = Fe(II)_2(OH)_3Cl(cr) + 2H_2(g)$
5. $6\,Fe + CO_2 + 15\,H_2O \rightarrow Fe(III)_2Fe(II)_4(OH)_{12}CO_3 \cdot 2H_2O + 7\,H_2$
6. $Fe + H_2O + CO_2 \rightarrow FeCO_3 + H_2$
7. $3Fe(OH)_2 \rightarrow Fe_3O_4 + H_2 + H_2O$
8. $Fe + H_2S \rightarrow FeS + H_2$

Steel Corrosion Research Route



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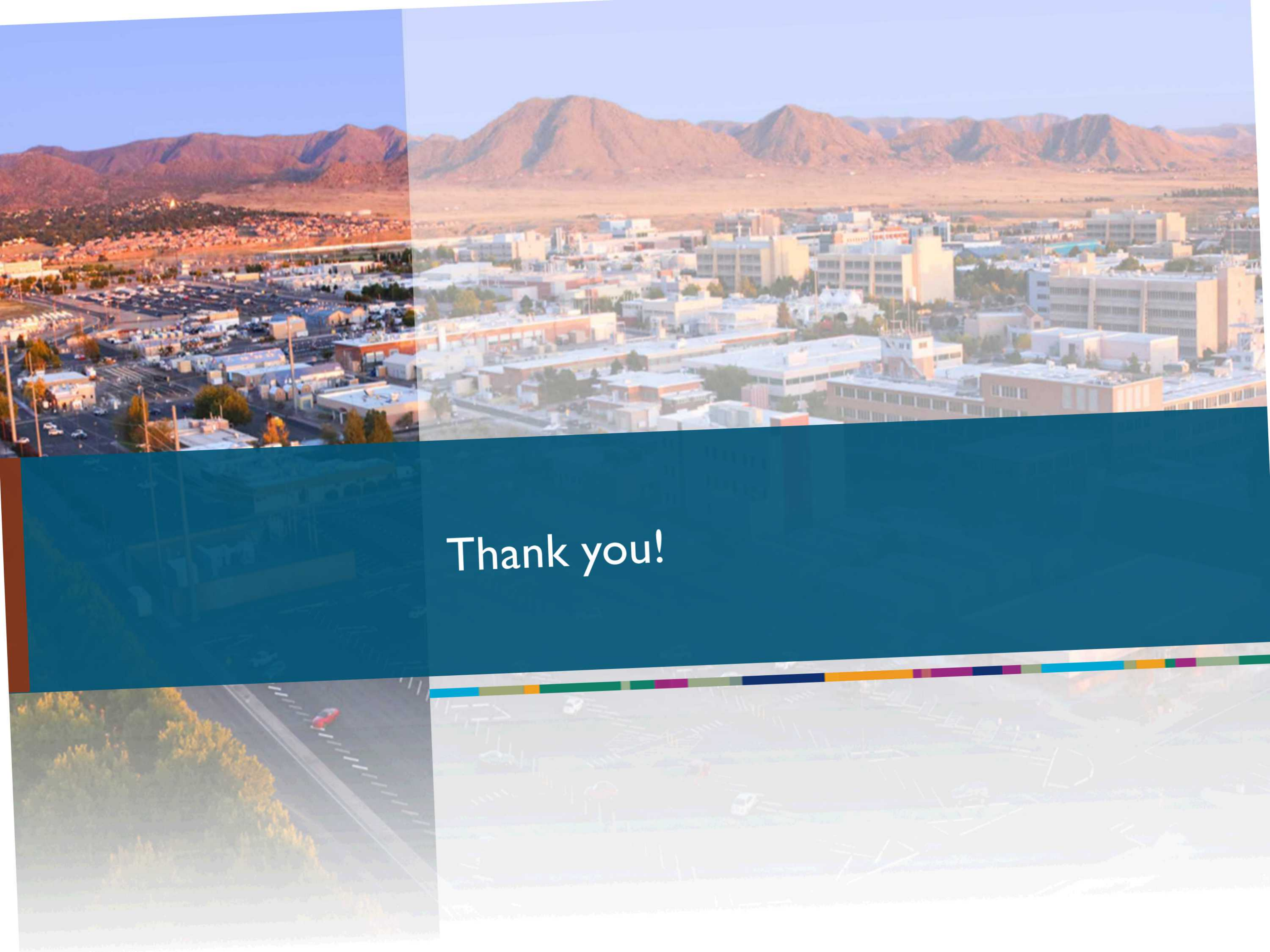

Thank you!