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US/ German Workshop on Salt Repository

Overview of WIPP Geochemistry

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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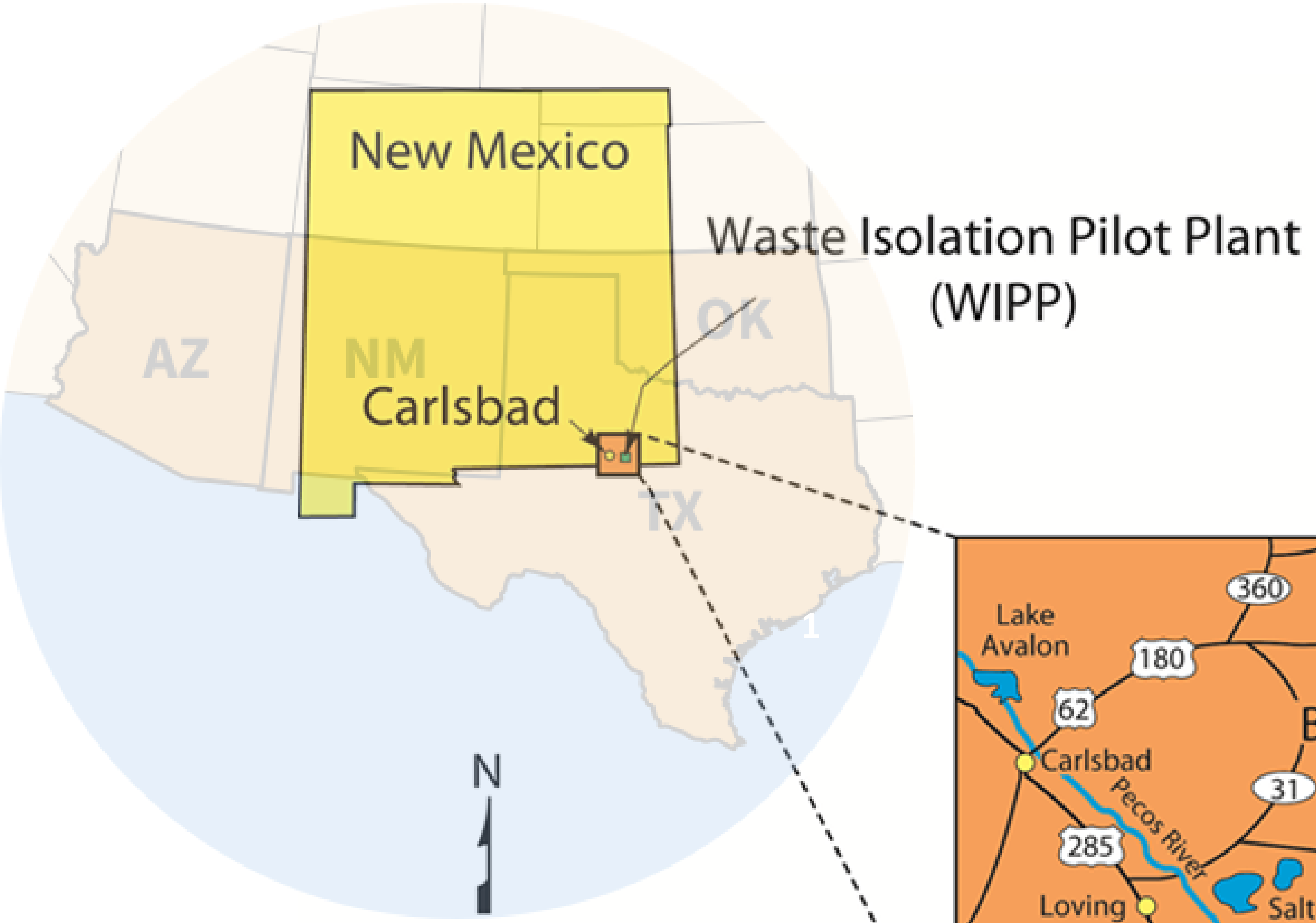
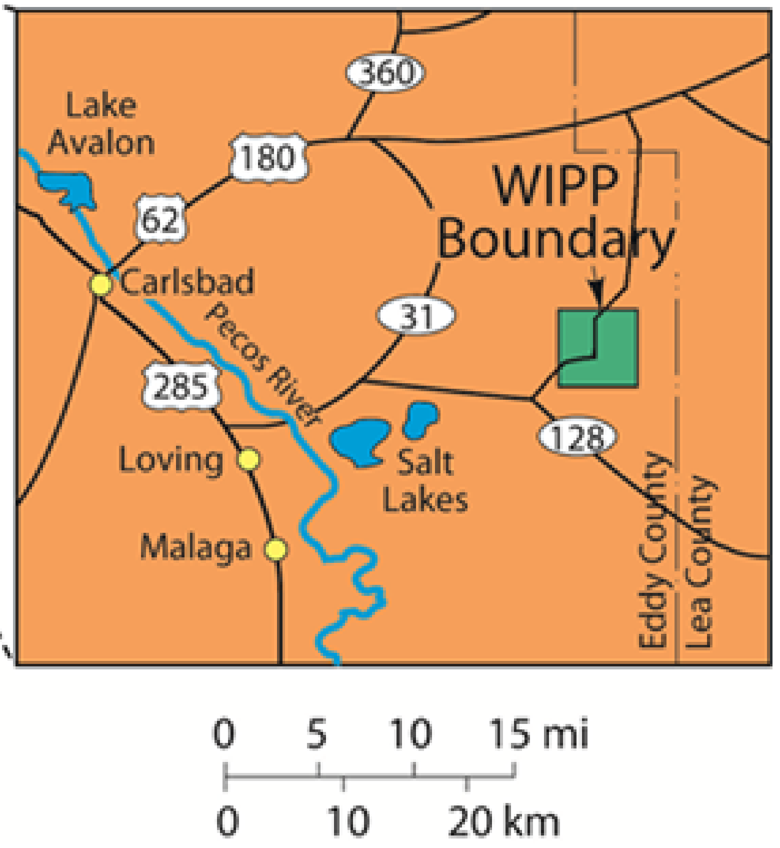
Outline

- Introduction to Waste Isolation Pilot Plant (WIPP)
- Geology of Repository
- Repository Chemistry at SNL
  - MgO Engineered Barrier
  - Metal Corrosion & Gas Generation
  - Solubility & Complexation
- Future Directions of Geochemistry at SNL
  - Metal Corrosion
  - MgO Hydration/Carbonation
  - Mineral Fragment Colloids
  - Solubility & Complexation
  - Thermodynamic Database Development for Repositories and other Geological Research
- Discussion

Introduction to Waste Isolation Pilot Plant (WIPP)



https://www.fws.gov/about/region/southwest

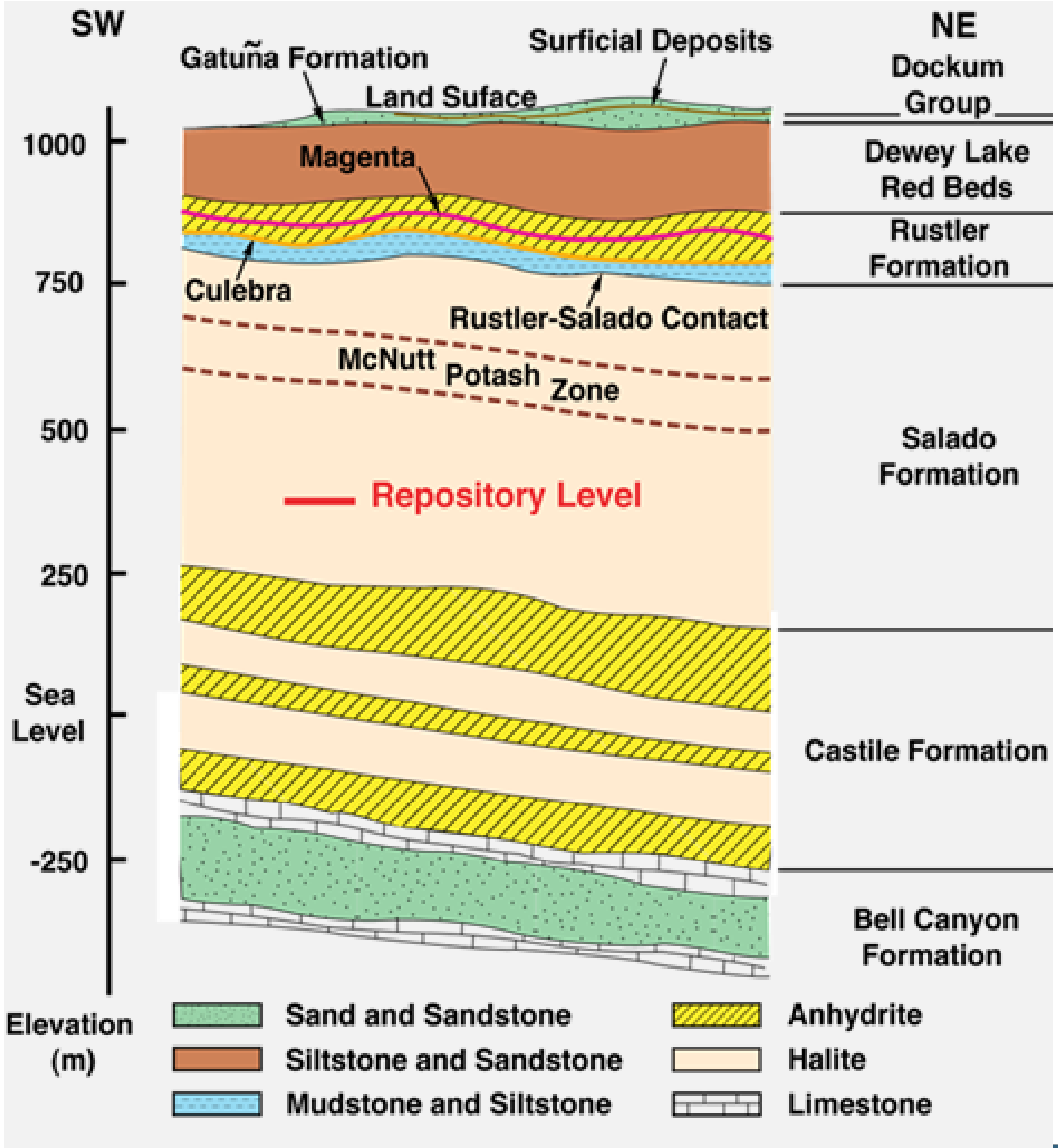


Hammond & Zeitler, 2017

- In 1979, Congress authorized the U.S. Department of Energy's (DOE) to WIPP.
- Congress limited WIPP to the disposal of defense-generated TRU wastes.
- In 1998, the U.S. Environmental Protection Agency (EPA) certified WIPP for safe, long-term disposal of transuranic (TRU) wastes.
- WIPP received first waste shipment in 1999.
- The disposal rooms are 2,150 feet (655 m) underground in a bedded salt formation of the Delaware Basin.
- Rock salt heals its own fractures because of its plastic quality. Once intact, the salt is essentially impermeable and does not contain flowing groundwater.

Geology of Repository - Mineralogy

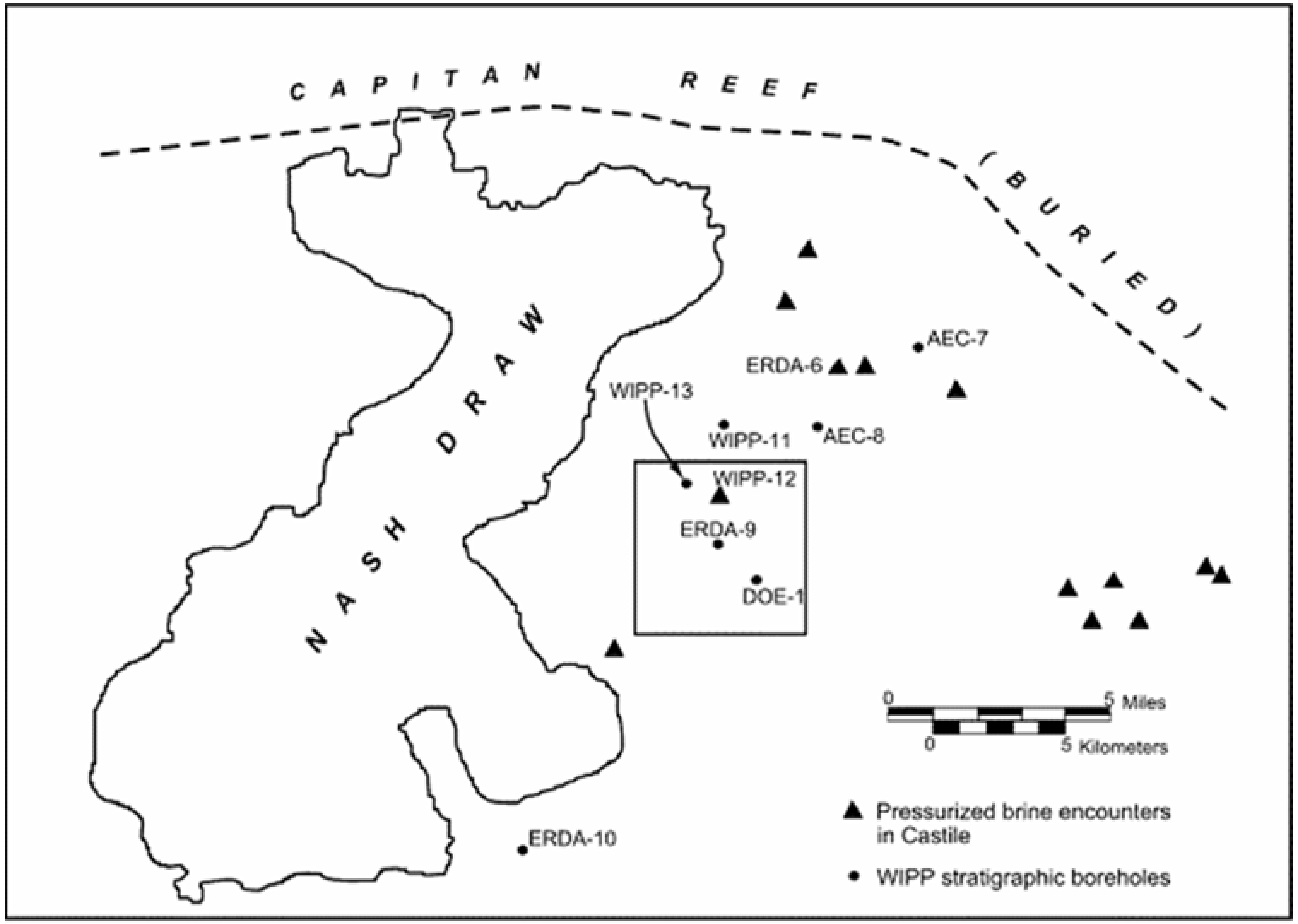
Geologic cross section of WIPP site The repository sits 655 m (2150 ft) below ground surface (HYDRO-2 DOE, 2019).



Mineral	Formula	Occurrence and Abundance
Amesite	$(Mg_4Al_2)(Si_2Al_2)O_{10}(OH)_8$	S, R
Anhydrite	$CaSO_4$	CCC, SSS, RRR (rarely near surface)
Calcite	$CaCO_3$	S, RR
Carnallite	$KMgCl_3 \bullet 6H_2O$	SS
Chlorite	$(Mg,Al,Fe)_{12}(Si,Al)_8O_{20}(OH)_{16}$	S, R
Corrensite	mixed-layer chlorite and smectite	S, R
Dolomite	$CaMg(CO_3)_2$	RR
Feldspar	$(K,Na,Ca)(Si,Al)_4O_8$	C, S, R
Glauberite	$Na_2Ca(SO_4)_2$	C, S (never near surface)
Gypsum	$CaSO_4 \bullet 2H_2O$	CCC (only near surface), S, RRR
Halite	$NaCl$	CCC, SSS, RRR (rarely near surface)
Illite	$K_{1-1.5}Al_4[Si_{7-6.5}Al_{1-1.5}O_{20}](OH)_4$	S, R
Kainite	$KMgClSO_4 \bullet 3H_2O$	SS
Kieserite	$MgSO_4 \bullet H_2O$	SS
Langbeinite	$K_2Mg_2(SO_4)_3$	S
Magnesite	$MgCO_3$	C, S, R
Polyhalite	$K_2Ca_2Mg(SO_4)_4 \bullet 2H_2O$	SS, R (never near surface)
Pyrite	FeS_2	C, S, R
Quartz	SiO_2	C, S, R
Serpentine	$Mg_3Si_2O_5(OH)_4$	S, R
Smectite	$(Ca_{1/2},Na)_{0.7}(Al,Mg,Fe)_4(Si,Al)_8O_{20}(OH)_4 \bullet nH_2O$	S, R
Sylvite	KCl	SS

C = Castile, S = Salado, R = Rustler, 3 letters = abundant, 2 letters = common, 1 letter = rare

Geology of Repository – Brine Compositions



Chaturvedi, L. and Neill, R.H. 2000

Ion or property	GWB Brine Composition	ERDA-6 Brine Composition
$B(OH)_3$	158 mM	63 mM
Na^+	3.53 M	4.87 M
Mg^{2+}	1.02 M	19 mM
K^+	0.467 M	97 mM
Ca^{2+}	14 mM	12 mM
SO_4^{2-}	177 mM	170 mM
Cl^-	5.86 M	4.8 M
Br^-	26.6 mM	11 mM
Total Inorganic C (as HCO_3^-)	16 mM^D	16 mM
pH	7.0	6.17
Ionic Strength (M)	7.44	5.32

Appendix GEOCHEM: CRA 2019

Repository Chemistry: MgO Engineered Barrier

Source: DOE CBFO

- Hydration

  $MgO(s) + H_2O \text{ (aq or g)} \rightleftharpoons Mg(OH)_2(s)$

- Carbonation

  $5Mg(OH)_2(s) + 4CO_2(g) \rightleftharpoons Mg_5(CO_3)_4(OH)_2(s) \cdot 4H_2O$

  $MgO(s) + CO_2 \text{ (aq or g)} \rightleftharpoons MgCO_3(s)$

- MgO on Colloidal An Concentration

  $Mg(OH)_2(s)$

  $Mg_5(CO_3)_4(OH)_2 \bullet 4H_2O$ (Hydromagnesite)

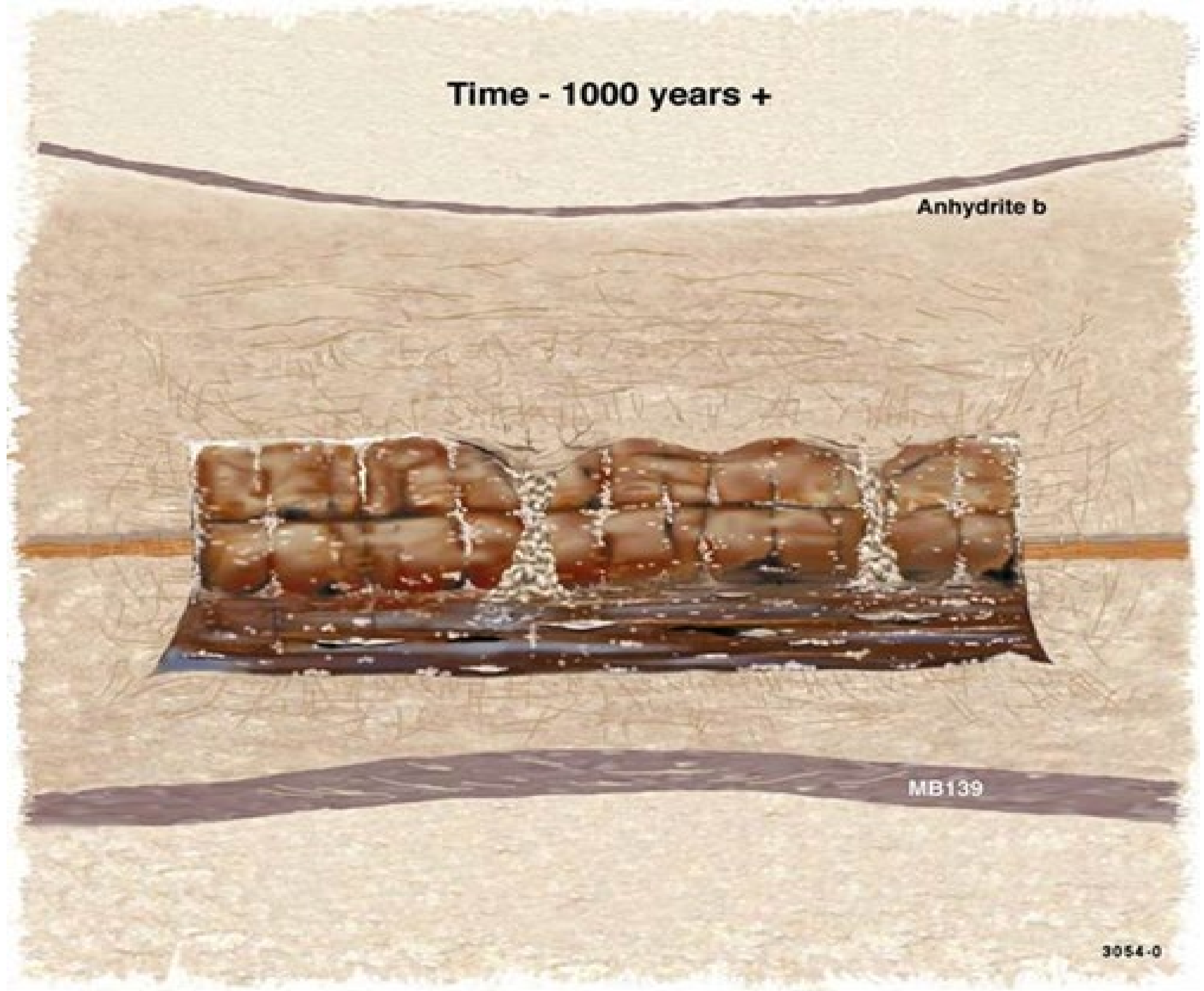
  $Mg_3Cl(OH)_5 \bullet 4H_2O$ (Phase 5)

Appendix GEOCHEM: CRA 2019

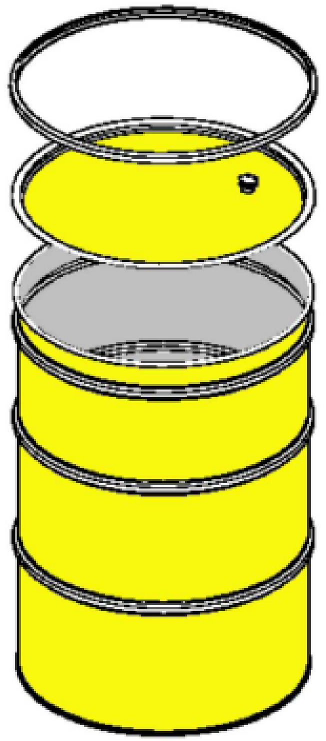
Repository Chemistry: Metal Corrosion & Gas Generation

Metals: Iron and Lead

Creep Closure & Waste



Todd Zeitler



Iron Corrosion Reactions

$Fe(s) + 2H_2O(l) \rightarrow Fe(OH)_2(s) + H_2(g)$

$Fe(s) + H_2S(g) \rightarrow FeS(s) + H_2(g)$

$Fe(OH)_2(s) + H_2S(g) \rightarrow FeS(s) + 2H_2O(l)$

$3Fe(s) + 4H_2O(l) \rightarrow Fe_3O_4(s) + 4H_2(g)$

Lead Corrosion Reactions

$PbO(s) + H_2O(l) \rightarrow Pb(OH)_2(s)$

$Pb(s) + H_2O(l) \rightarrow PbO(s) + H_2(g)$

These reactions subject to chemical conditions, availability of H_2O and H_2S, and standard free energy change.

$dG = dG° + RT \ln Q$, when $Q << 1$, $dG < 0$,; when $Q >> 1$, $dG > 0$

Appendix GEOCHEM: CRA 2019

Repository Chemistry: Solubility & Complexation

WIPP Minerals

Waste (An, Fe, Pb, Organics)

CO_2, H_2S

Brine composition
H^+, Na^+, K^+, Mg^{2+}, Ca^{2+}
OH^-, Cl^-, CO_3^{2-}, SO_4^{2-}, Borate

Mineral phases

- Dissolution Reactions for Salado and Castile Minerals.
- Dissolution Reactions for MgO Solids.
- Reactions with Organic Ligands Implemented in the WIPP Chemical Conditions Conceptual Model.
- Reactions with Borate Implemented in the WIPP Chemical Conditions Conceptual Model.
- Reactions with Lead Implemented in the WIPP Chemical Conditions Conceptual Model.
- Reactions with Iron Implemented in the WIPP Chemical Conditions Conceptual Model.

https://www.mining-technology.com/news/underground-ventilation-system-unveiled-wipp/

https://commons.wikimedia.org/wiki/File:Rock_salt_%28halitite%29_%28Lower_Member,_Salado_Formation,_Upper_Permian;_WIPP_Storage_Level,_New_Mexico,_USA%29_%2816656329020%29.jpg

Repository Chemistry: Solubility & Complexation

Dissolution Reactions for Salado and Castile Minerals Implemented in the WIPP Chemical Conditions Conceptual Model

$Na_2SO_4{\bullet}10H_2O$(mirabilite) ↔ $2Na^+ + SO_4^{2-} + 10H_2O$	$K_8H_4(CO_3)_6{\bullet}3H_2O(s) + 2H^+$ ↔ $8K^+ + 6HCO_3^- + 3H_2O$
Na_2SO_4(thenardite) ↔ $2Na^+ + SO_4^{2-}$	$KNaCO_3{\bullet}6H_2O(s) + H^+$ ↔ $K^+ + Na^+ + HCO_3^- + 6H_2O$
$Na_3H(SO_4)_2$ (s) ↔ $Na^+ + H^+ + 2SO_4^{2-}$	$K_2NaH(CO_3)_2{\bullet}2H_2O$(K-trona) $+ H^+$ ↔ $2K^+ + Na^+ + 2HCO_3^- + 2H_2O$
$NaK_3(SO_4)_2$(aphthitalite, glaserite) ↔ $Na^+ + 3K^+ + 2SO_4^{2-}$	$CaCl_2{\bullet}4H_2O(s)$ ↔ $Ca^{2+} + 2Cl^- + 4H_2O$
$Na_2Ca(SO_4)_2$(glauberite) ↔ $2Na^+ + Ca^{2+} + 2SO_4^{2-}$	$Ca_4Cl_2(OH)_6{\bullet}13H_2O(s) + 6H^+$ ↔ $4Ca^{2+} + 2Cl^- + 19H_2O$
$Na_4Ca(SO_4)_3{\bullet}2H_2O$(labile salt) ↔ $4Na^+ + Ca^{2+} + 3SO_4^{2-} + 2H_2O$	$Ca_2Cl_2(OH)_2{\bullet}H_2O(s) + 2H^+$ ↔ $2Ca^{2+} + 2Cl^- + 3H_2O$
$KHSO_4$ (mercallite) ↔ $K^+ + SO_4^{2-} + H^+$	$CaCO_3$(aragonite) $+ H^+$ ↔ $Ca^{2+} + HCO_3^-$
KCl (sylvite) ↔ $K^+ + Cl^-$	$CaCO_3$(calcite)$^B + H^+$ ↔ $Ca^{2+} + HCO_3^-$
$K_8H_6(SO_4)_7$(misenite) ↔ $8K^+ + 6H^+ + 7SO_4^{2-}$	$CaMg(CO_3)_2$ (dolomite) ↔ $Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$
K_2SO_4(arcanite) ↔ $2K^+ + SO_4^{2-}$	$CaNa_2(CO_3)_2{\bullet}5H_2O$(gaylussite) $+ 2H^+$ ↔ $Ca^{2+} + 2Na^+ + 2HCO_3^- + 5H_2O$
$K_2Ca(SO_4)_2{\bullet}H_2O$(syngenite) ↔ $K^+ + Ca^{2+} + 2SO_4^{2-} + H_2O$	$Ca(OH)_2$ (portlandite) $+ 2H^+$ ↔ $Ca^{2+} + 2H_2O$
$KHCO_3$(kalicinite) ↔ $K^+ + HCO_3^-$	$CaSO_4$(anhydrite) ↔ $Ca^{2+} + SO_4^{2-}$
$K_2CO_3{\bullet}1.5H_2O(s) + H^+$ ↔ $2K^+ + HCO_3^- + 1.5H_2O$	$CaSO_4{\bullet}2H_2O$(gypsum) ↔ $Ca^{2+} + SO_4^{2-} + 2H_2O$

Appendix GEOCHEM: CRA 2019

Repository Chemistry: Solubility & Complexation

Dissolution Reactions for MgO Solids Implemented in the WIPP Chemical Conditions Conceptual Model

$Mg(OH)_2$(brucite) + $2H^+ \leftrightarrow Mg^{2+} + 2H_2O$
$MgCl_2 \bullet 6H_2O$(bischofite) $\leftrightarrow Mg^{2+} + 2Cl^- + 6H_2O$
$Mg_2Cl(OH)_3 \bullet 4H_2O$(phase 3) + $3H^+ \leftrightarrow 2Mg^{2+} + Cl^- + 7H_2O$
$Mg_3Cl(OH)_5 \bullet 4H_2O$(phase 5) + $5H^+ \leftrightarrow 3Mg^{2+} + Cl^- + 9H_2O$
$Mg_2CaCl_6 \bullet 12H_2O$(tachyhydrite) $\leftrightarrow 2Mg^{2+} + Ca^{2+} + 6Cl^- + 12H_2O$
$KMgCl_3 \bullet 6H_2O$(carnallite) $\leftrightarrow K^+ + Mg^{2+} + 3Cl^- + 6H_2O$
$CaMg(CO_3)_2$ (dolomite) $\leftrightarrow Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$
$MgCO_3$(magnesite) + $H^+ \leftrightarrow Mg^{2+} + HCO_3^-$
$MgCO_3 \bullet 3H_2O$(nesquehonite) + $H^+ \leftrightarrow Mg^{2+} + HCO_3^- + 3H_2O$
$Mg_4(CO_3)_3(OH)_2 \bullet 3H_2O$(hydromagnesite4323) + $5H^+ \leftrightarrow 4Mg^{2+} + 3HCO_3^- + 5H_2O$
$Mg_5(CO_3)_4(OH)_2 \bullet 4H_2O$(hydromagnesite5424) + $6H^+ \leftrightarrow 5Mg^{2+} + 4HCO_3^- + 6H_2O$
$K_2Mg(SO_4)_2 \bullet 4H_2O$(leonite) $\leftrightarrow 2K^+ + Mg^{2+} + 2SO_4^{2-} + 4H_2O$
$Na_2Mg(SO_4)_2 \bullet 4H_2O$(bloedite) $\leftrightarrow 2Na^+ + Mg^{2+} + 2SO_4^{2-} + 2H_2O$
$MgSO_4 \bullet 7H_2O$(epsomite) $\leftrightarrow Mg^{2+} + SO_4^{2-} + 7H_2O$
$MgSO_4 \bullet 6H_2O$(hexahydrite) $\leftrightarrow Mg^{2+} + SO_4^{2-} + 6H_2O$
$MgSO_4 \bullet H_2O$(kieserite) $\leftrightarrow Mg^{2+} + SO_4^{2-} + H_2O$
$KMgClSO_4 \bullet 3H_2O$(kainite) $\leftrightarrow K^+ + Mg^{2+} + Cl^- + SO_4^{2-} + 3H_2O$

Appendix GEOCHEM: CRA 2019

Repository Chemistry: Solubility & Complexation

Reactions with Organic Ligands Implemented in the WIPP Chemical Conditions Conceptual Model

$Ca_2EDTA \bullet 7H_2O(s) \leftrightarrow 2Ca^{2+} + EDTA^{4-} + 7H_2O$
$Ca_3(Citrate)_2 \bullet 4H_2O$ (earlandite) $\leftrightarrow 3Ca^{2+} + 2Citrate^{3-} + 4H_2O$
$NaHOxalate \bullet H_2O(s) \leftrightarrow Na^+ + H^+ + Oxalate^{2-} + H_2O$
$Na_2Oxalate(s) \leftrightarrow 2Na^+ + Oxalate^{2-}$
$CaOxalate \bullet H_2O(s)$ (whewellite) $\leftrightarrow Ca^{2+} + Oxalate^{2-} + H_2O$
$H_2Oxalate \bullet 2H_2O(s) \leftrightarrow Oxalate^{2-} + 2H^+ + 2H_2O$
$MgOxalate \bullet 2H_2O(s)$ (glushinskite) $\leftrightarrow Mg^{2+} + Oxalate^{2-} + 2H_2O$

Reactions with Borate Implemented in the WIPP Chemical Conditions Conceptual Model

$Na_2B_4O_7 \bullet 10H_2O$(borax) $\leftrightarrow 2Na^+ + 4B(OH)_4^- + 2H^+ + H_2O$
$B(OH)_3(s) + H_2O \leftrightarrow B(OH)_4^- + H^+$
$KB_5O_8 \bullet 4H_2O$(K-pentaborate) (s)$+ 8H_2O \leftrightarrow K^+ + 5B(OH)_4^- + 4H^+$
$K_2B_4O_7 \bullet 4H_2O$(K-tetraborate) (s) $+ 5H_2O \leftrightarrow 2K^+ + 4B(OH)_4^- + 2H^+$
$NaBO_2 \bullet 4H_2O$(Na-metaborate) (s)$\leftrightarrow Na^+ + B(OH)_4^- + 2H_2O$
$NaB_5O_8 \bullet 5H_2O$(Na-pentaborate) (s) $+ 7H_2O \leftrightarrow Na^+ + 5B(OH)_4^- + 4H^+$
$NaBO_2 \bullet NaCl \bullet 2H_2O$(teepleite) (s)$\leftrightarrow 2Na^+ + B(OH)_4^- + Cl^-$

Appendix GEOCHEM: CRA 2019

Repository Chemistry: Solubility & Complexation

Reactions with Lead Implemented in the WIPP Chemical Conditions Conceptual Model

α-PbO(litharge) + $2H^+ \leftrightarrow Pb^{2+} + H_2O$
$PbCO_3$(cerussite) + $H^+ \leftrightarrow Pb^{2+} + HCO_3^-$
$Pb_2CO_3Cl_2 + H^+ \leftrightarrow 2Pb^{2+} + HCO_3^- + 2Cl^-$
$PbSO_4(s) + H^+ \leftrightarrow Pb^{2+} + HSO_4^-$

Reactions with Iron Implemented in the WIPP Chemical Conditions Conceptual Model

$Fe(OH)_2(s) + 2H^+$ (ferrous hydroxide) $\leftrightarrow Fe^{2+} + 2H_2O$
$Fe_2Cl(OH)_3(s) + 3H^+$ (hibbingite) $\leftrightarrow 2Fe^{2+} + Cl^- + 3H_2O$
$FeCO_3(s) + H^+$ (siderite) $\leftrightarrow Fe^{2+} + HCO_3^-$
$Fe_2CO_3(OH)_2(s) + 3H^+$ (chukanovite) $\leftrightarrow 2Fe^{2+} + HCO_3^- + 2H_2O$

Appendix GEOCHEM: CRA 2019

Future Directions to Geochemistry at SNL

Corrosion & Products

Reducing

Eh

Eh

Oxidizing

Half-Reaction				Reduction E° (V)
Fe^{3+}	+ e	⟶	Fe^{2+}	0.77
$2H^{+}$	+ 2e	⟶	H_2 (g)	0
Pb^{2+}	+ 2e	⟶	Pb (s)	- 0.13
Fe^{2+}	+ 2e	⟶	Fe (s)	- 0.45
Al^{3+}	+ 3e	⟶	Al (s)	- 1.66

Compound	Δ G KJ/mol
H_2S (g)	-33.4
H_2O (g)	-237.2
FeS (s)	-100.4
PbO (s)	-187.9
FeO (s)	-255.0
Fe_2O_3(Hematite)	-742.2
Fe_3O_4(Magnetite)	-1015.4
Al_2O_3 (corundum)	-1582.0

Oxidizing Potential

Al >> Fe > Pb

Relative Reactivity

Al_2O_3 > Fe_3O_4 > Fe_2O_3

Amphoteric and stable at pH ~ 4 - ~8

Stable phase

Standard Reduction Potentials in Aqueous Solutions at 25 °C

Oxidizing Agent				Reducing Agent	Reduction Potential (V)
F_2	+	$2e^-$	→	$2F^-$	2.87
H_2O_2	+	$2H^+ + 2e^-$	→	$2H_2O$	1.78
MnO_4^-	+	$8H^+ + 5e^-$	→	$Mn^{2+} + 4H_2O$	1.51
Au^{3+}	+	$3e^-$	→	Au	1.50
Cl_2	+	$2e^-$	→	$2Cl^-$	1.36
O_2	+	$4H^+ + 4e^-$	→	$2H_2O$	1.23
$Cr_2O_7^{2-}$	+	$14H^+ + 6e^-$	→	$2Cr^{3+} + 7H_2O$	1.23
Br_2	+	$2e^-$	→	$2Br^-$	1.07
NO_3^-	+	$4H^+ + 3e^-$	→	$NO + 2H_2O$	0.96
Ag^+	+	e^-	→	Ag	0.80
I_2	+	$2e^-$	→	$2I^-$	0.54
Cu^+	+	e^-	→	Cu	0.52
O_2	+	$2H_2O + 4e^-$	→	$4OH^-$	0.40
Cu^{2+}	+	$2e^-$	→	Cu	0.34
$2H_3O^+$	+	$2e^-$	→	$H_2 + 2H_2O$	0.00
Pb^{2+}	+	$2e^-$	→	Pb	–0.13
Sn^{2+}	+	$2e^-$	→	Sn	–0.14
Ni^{2+}	+	$2e^-$	→	Ni	–0.26
Fe^{2+}	+	$2e^-$	→	Fe	–0.45
Cr^{3+}	+	$3e^-$	→	Cr	–0.74
Zn^{2+}	+	$2e^-$	→	Zn	–0.76
$2H_2O$	+	$2e^-$	→	$H_2 + 2OH^-$	–0.83
Mn^{2+}	+	$2e^-$	→	Mn	–1.19
Al^{3+}	+	$3e^-$	→	Al	–1.66
Mg^{2+}	+	$2e^-$	→	Mg	–2.37
Na^+	+	e^-	→	Na	–2.71
Ca^{2+}	+	$2e^-$	→	Ca	–2.87
Ba^{2+}	+	$2e^-$	→	Ba	–2.91
K^+	+	e^-	→	K	–2.93
Li^+	+	e^-	→	Li	–3.04

Increasing Strength of Oxidizing Agent

Increasing Strength of Reducing Agent

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Future Directions of Geochemistry at SNL: Metal Corrosion

- Oxidation and sulfidation rates of Fe, Pb, Al under controlled conditions
- Relative oxidation and sulfidation rates of Fe, Pb, Al under controlled redox conditions
- Corrosion rates at differential pressure
- Evaluate passivation of Fe, Pb, Al under mechanical stress
- Corrosion products in brine systems
- Stability of corrosion products
- Corrosion retardation effects such as sacrificial metal effect

Future Directions of Geochemistry at SNL:
MgO Hydration/Carbonation

Current Approach

MgO in Brines Inundated Experiments

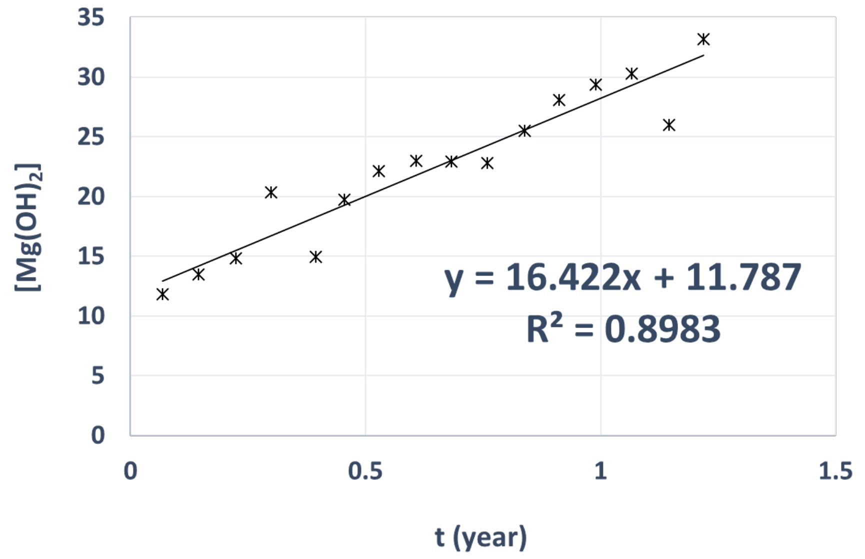
↓ f(Time)

Filtered Cake

↓

Loss of Ignition(LOI)
XRD

Amount of brucite was calculated from the mass loss



$Mg(OH)_2 .X\ H_2O \xrightarrow{150\ °C} Mg(OH)_2 \xrightarrow{800\ °C} MgO$

Assumption: Dominant mineral phase is Brucite

Future Approach

MgO in DI Water Inundated Experiments

↓ f(Time)

Filtered Cake

↓

XRD
TGA

MgO in DI Water Humid Experiments

↓

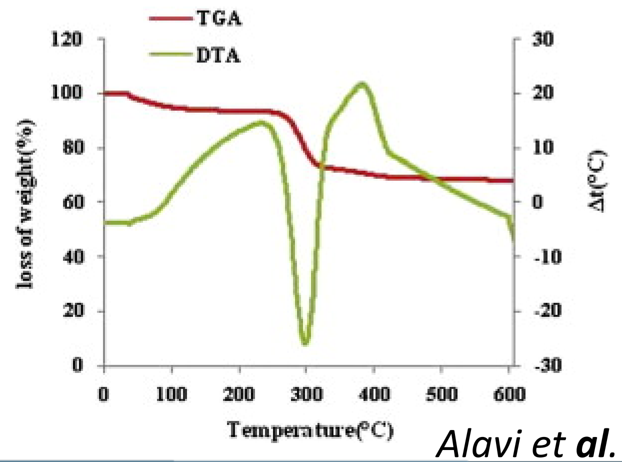
XRD
TGA

- ***Evaluate effect of brine due to vapor pressure variation on hydration***
- ***Introduce CO_2 to evaluate carbonation under dry condition***
- ***Evaluate simultaneous carbonation/hydration***

$Mg(OH)_2 .X\ H_2O \longrightarrow Mg(OH)_2 \longrightarrow MgO$

Identify water removal by heat absorption

Increase the complexity of the experiment by adding one variable at a time

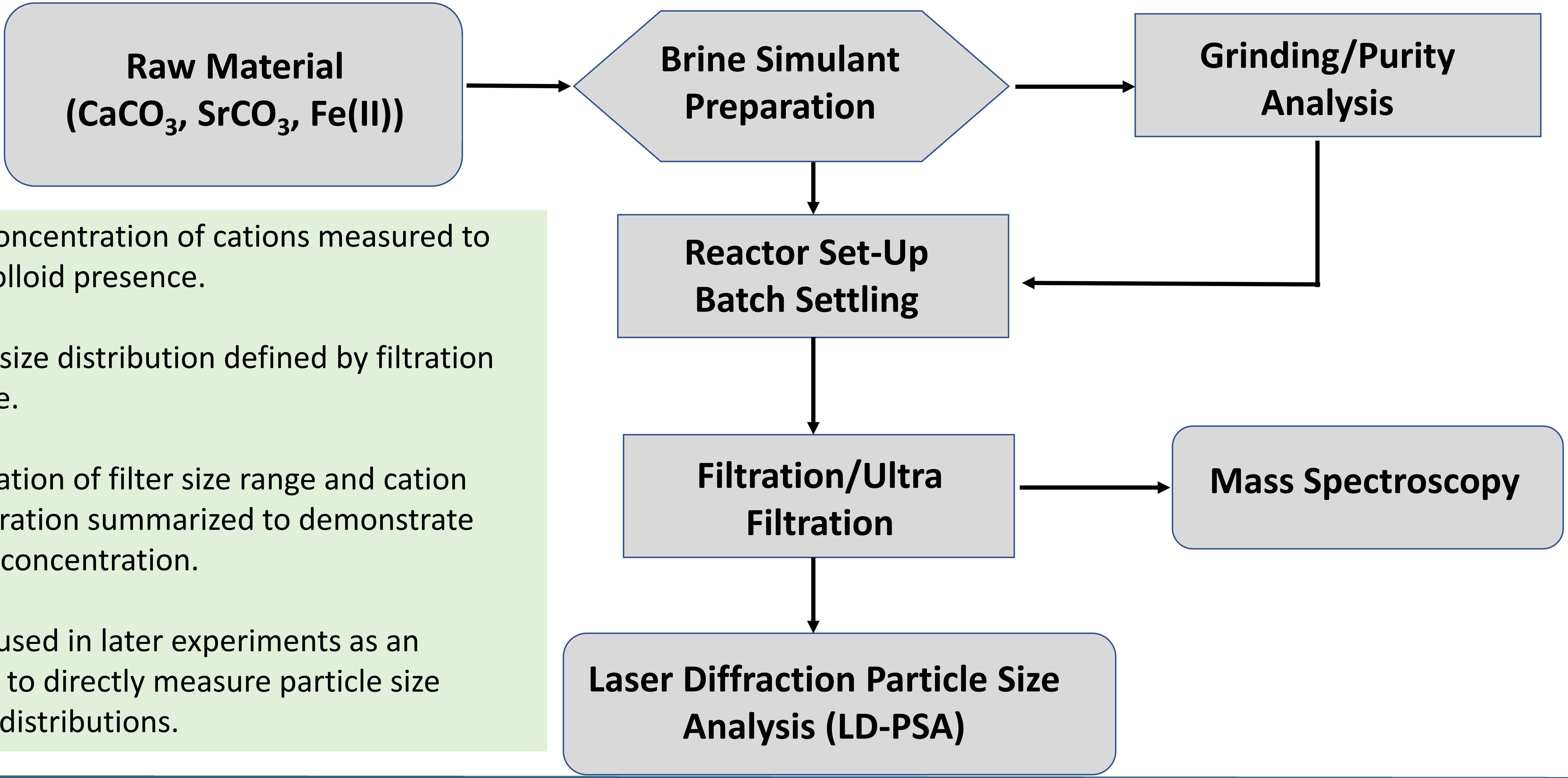


*Alavi et **al**. 2020*

Future Directions of Geochemistry at SNL:

Mineral Fragment Colloids

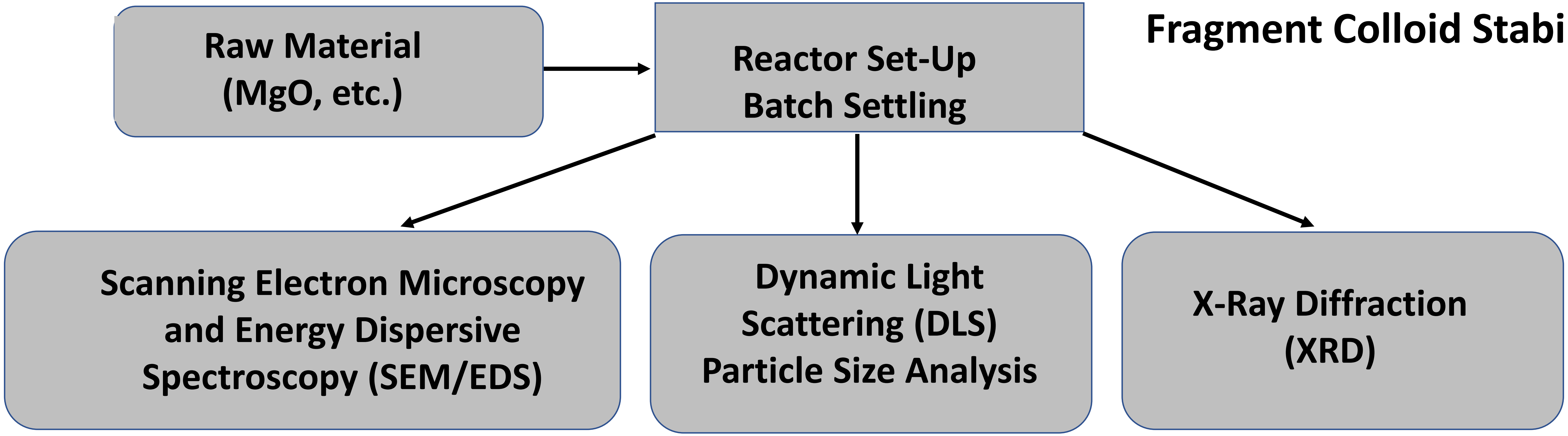
Current Approach - Mineral Fragment Colloid Stability



- Molar concentration of cations measured to prove colloid presence.
- Particle size distribution defined by filtration pore size.
- Combination of filter size range and cation concentration summarized to demonstrate particle concentration.
- LD-PSA used in later experiments as an attempt to directly measure particle size volume distributions.

Future Directions of Geochemistry at SNL:
Mineral Fragment Colloids

Proposed Approach: Mineral Fragment Colloid Stability



- Simplification of experimental design – *colloid suspension allowed to stabilize (e.g., no grinding) to eliminate the need and bias of filtration.*
- Particle size distribution defined by DLS – *demonstrates higher accuracy and precision with lower (particle diameter) detection limits than laser diffraction.*
- Assisted drying and SEM analysis on ultra- smooth surface wafers for qualitative size ranging and crystal habit analysis/Mineral identification of DLS sample aliquots.
- XRD for final mineral phase identification of bulk settled solids.

Future Directions of Geochemistry at SNL:
Solubility & Complexation

Definition of Solubility and Complexation

$$mM^{n+}{}_{(aq)} + xX^{y-}{}_{(aq)} \rightleftharpoons M_mX_y\,(s)$$

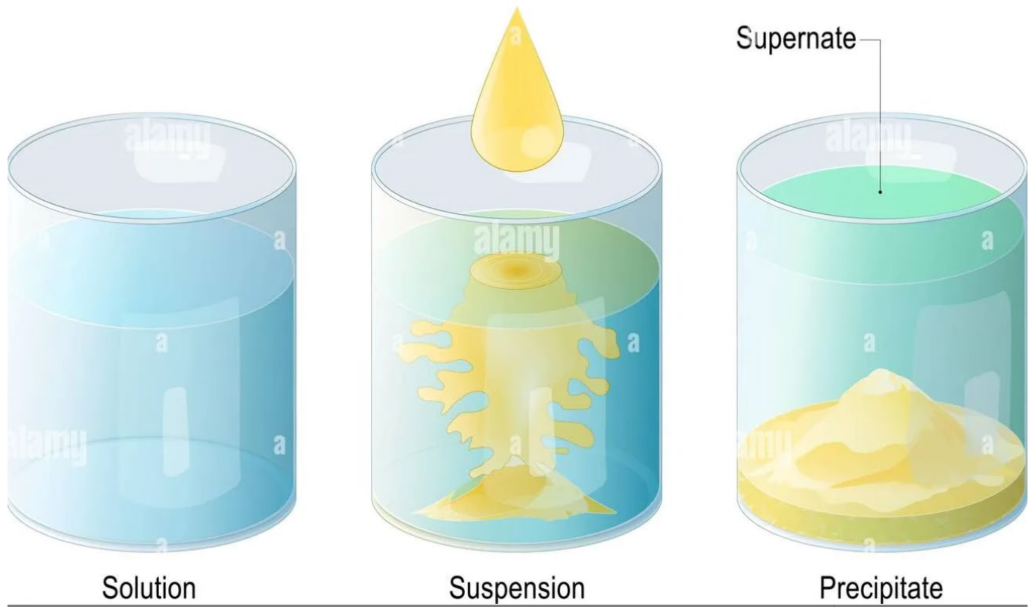
$$\text{IP (Ion Product)} = [M^{n+}]^m[X^{y-}]^x$$

If **IP < Ksp** under saturated

If **IP = Ksp** saturated and equilibrium exist

If **IP > Ksp** over saturated

Ksp = Solubility Product



https://menloservice.sandia.gov/https://www.alamy.com/stock-photo/solubility.html

M = Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{2+}, Pb^{2+}, Na^{+}, K^{+}, Th^{4+}, Am^{3+}

X = SO_4^{2-}, S^{2-}, OH-, CO_3^{2-}, Cl^{-}, PO_4^{3-}, silica, borate

Future Directions of Geochemistry at SNL:
Solubility & Complexation

Complexity of Solubility and Complexation

M = Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{2+}, Pb^{2+}, Na^{+}, K^{+}, Th^{4+}, Am^{3+}

X = SO_4^{2-}, S^{2-}, OH-, CO_3^{2-}, Cl^{-}, PO_4^{3-}, Silica, Borate

Organic Ligands = carboxylates, amines, sulfides, carbenes, oxalate

Complexation => f (electron affinity, ion concentrations, molecular orbital symmetry)

Complexation results molecular clusters (complex bonding structures)

Complexation => Thermodynamic stability and reaction kinetics

Metal – anion inorganic complexation – decrease probability of solubility

Metal - anions – organic complexation – increase probability of solubility

Future Directions of Geochemistry at SNL:

Solubility & Complexation

Analytical Methods for Solubility

1. Isopiestic Methods: Vapor Pressure, Osmosis (Well studied – sensitivity for less soluble solid phases in question)
2. Boiling point elevation (sensitivity limitations)
3. Freezing point depression (sensitivity limitations)
4. Ion analysis: solubility evaluation (ICP-MS, IC, TOC, UV-VIS)

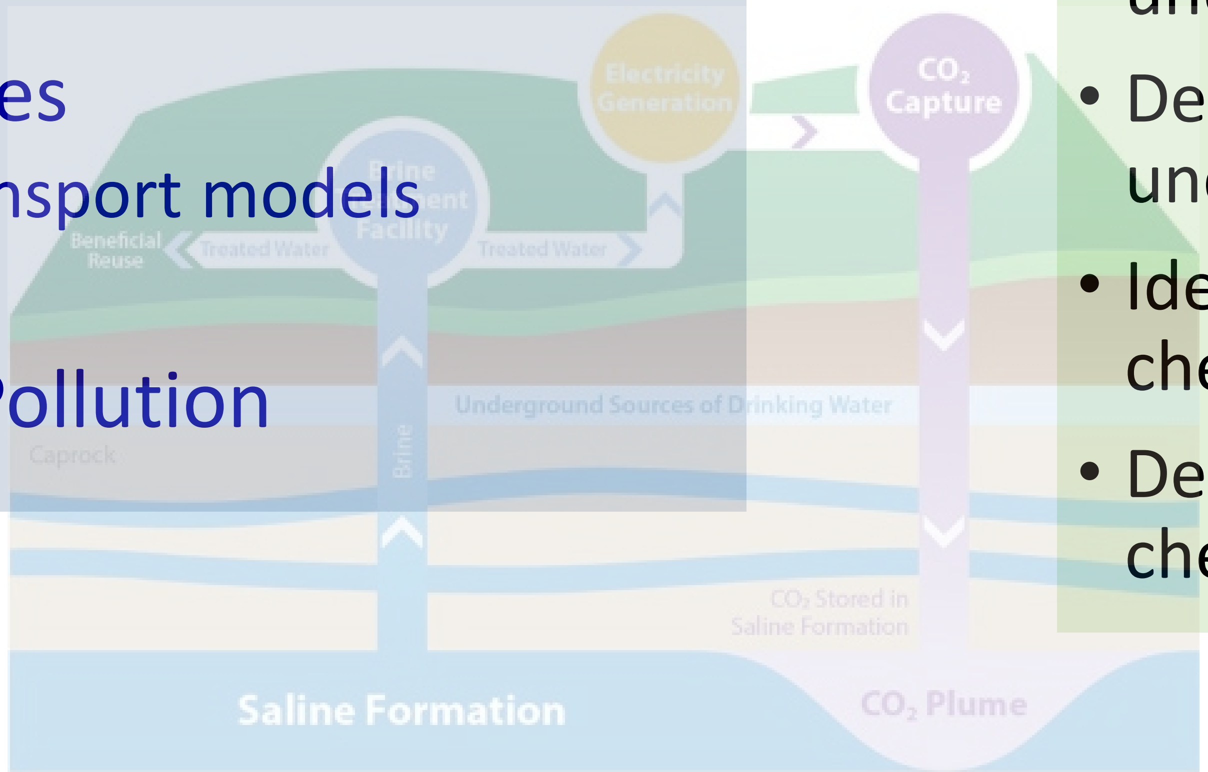
Solid Analysis

1. XRD, XRF
2. Raman, FT-IR
3. Mössbauer Spectroscopy
4. SEM

Future Directions of Geochemistry at SNL: Thermodynamic Database Development for Repositories and other geological research

Research Areas need Geochemistry Models and Database Developments

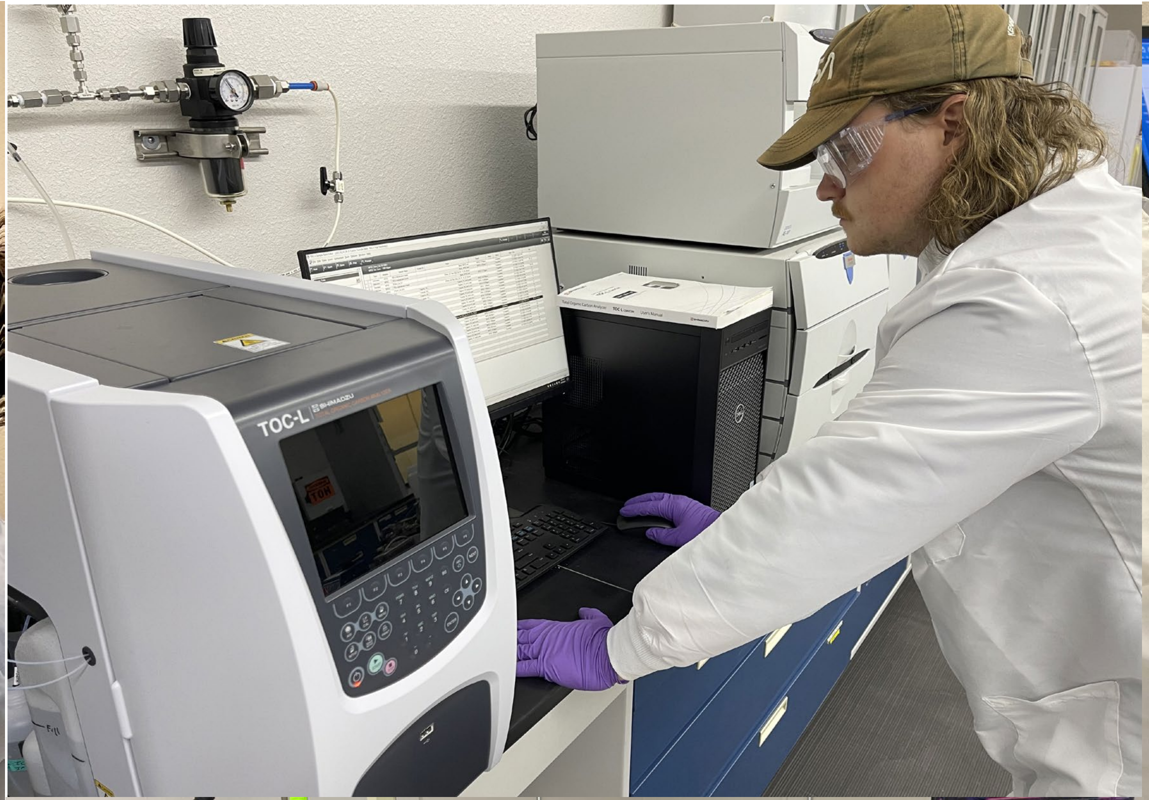
- Petroleum Engineering
  - Low salinity water flooding
  - Shale EOR using smart water
  - Hydrogen storage
  - Carbon sequestration
- Restoration of Mangroves
  - To develop chemical transport models
- Minimize Heavy metal Pollution

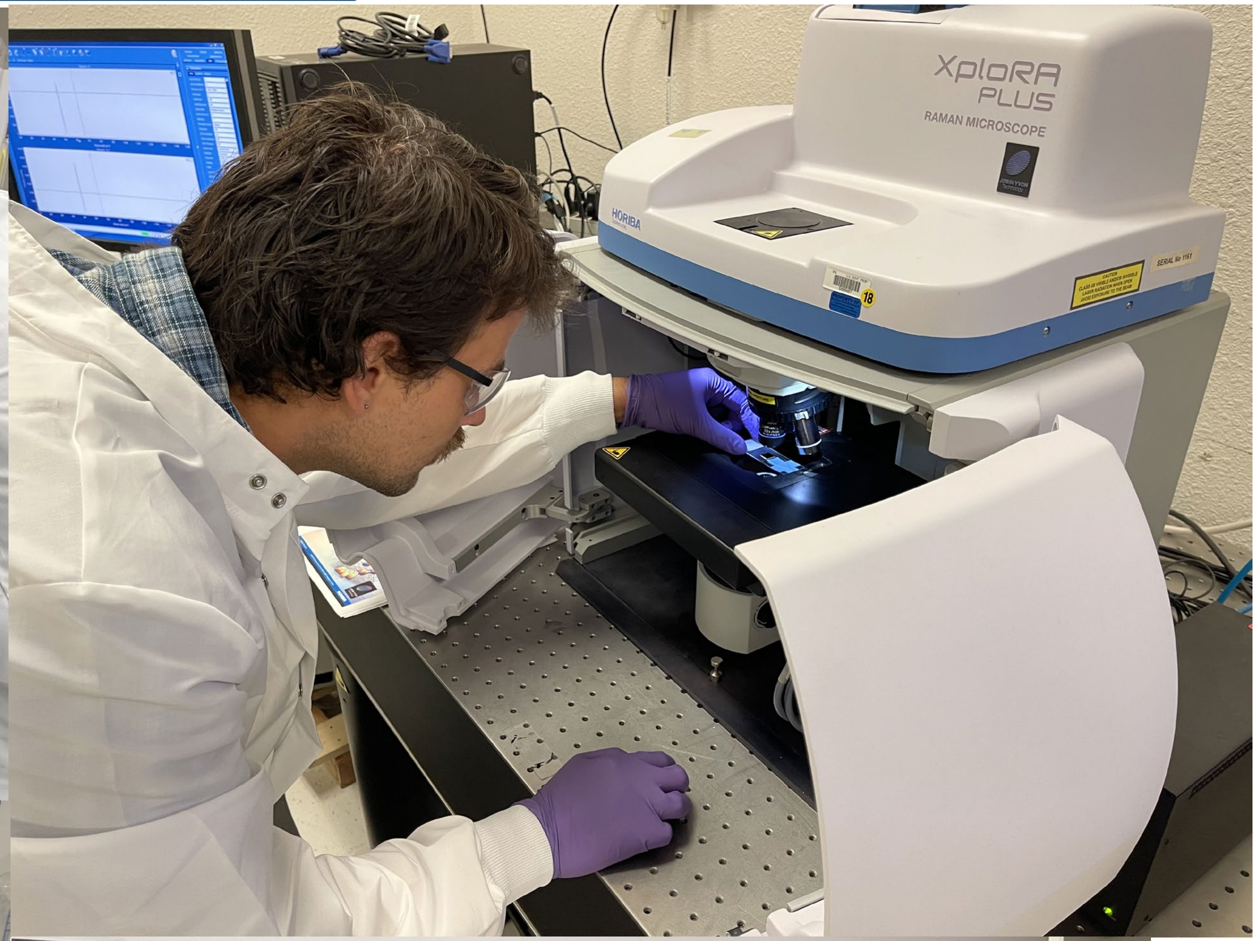


Research Focus

- Synthesis of mineral phases under controlled conditions. *Hills, et al. "Mineralization technology for carbon capture, utilization, and storage.", 2020*
- Predict mineral phases using molecular modeling. *Wu, et al. "Analysis and molecular modeling of the formation, structure, and activity of the phosphatidylserine-calcium-phosphate complex associated with biomineralization.", 2008.*
- Develop analytical methods for solid characterization under anoxic conditions.
- Develop analytical methods for ion characterization under anoxic conditions.
- Identify role of B, Si, P, Zn, and Al in complexation chemistry.
- Develop techniques to conduct redox solubility chemistry.

SNL Geochemistry Lab





Thank You

Discussion – Q & A