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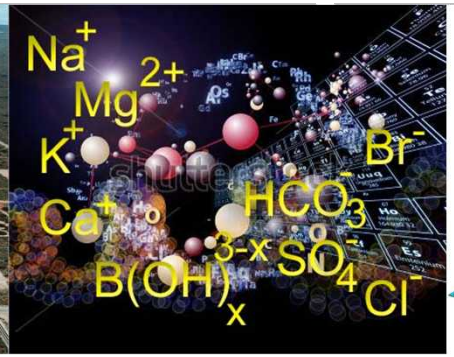

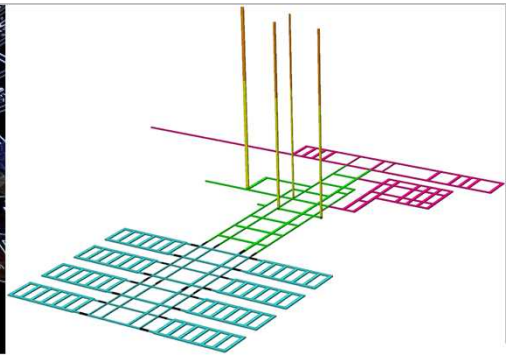

Experiments and Thermodynamic Modeling of Chukanovite ($Fe_2(OH)_2CO_3$) to High Ionic Strengths

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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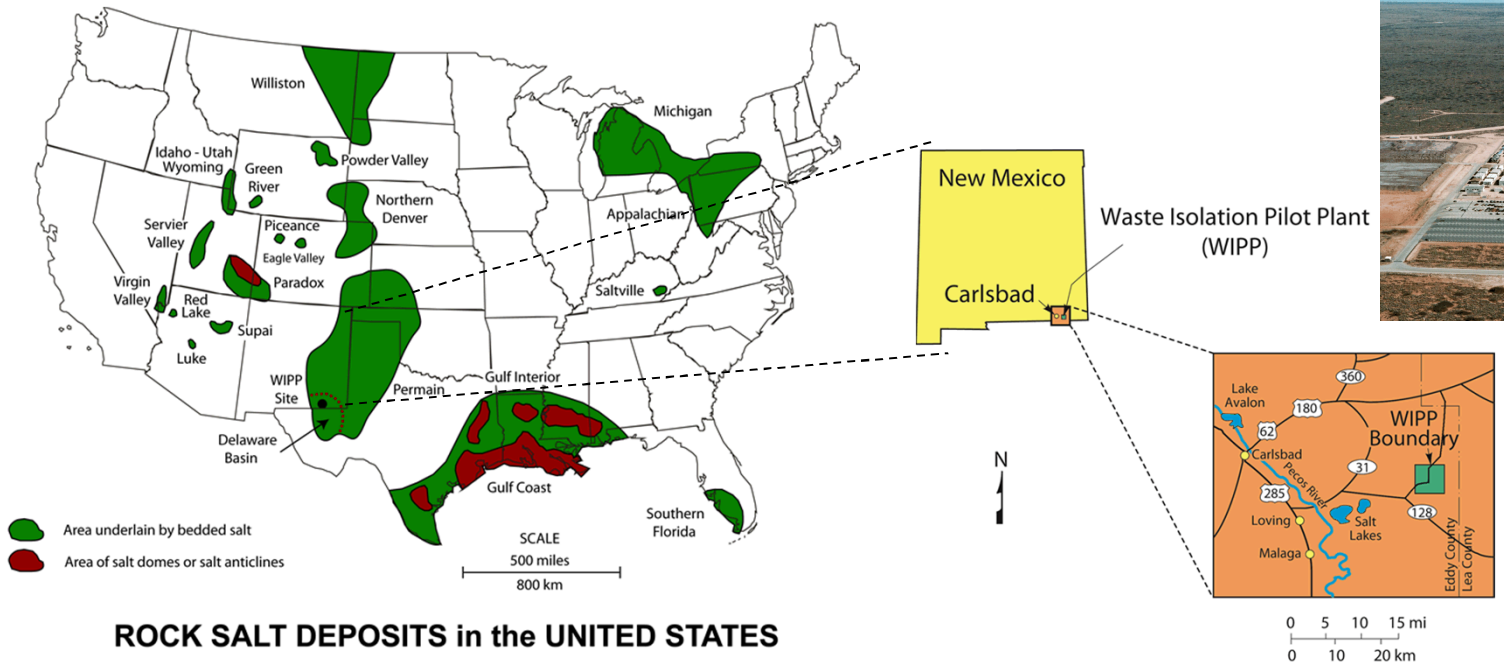
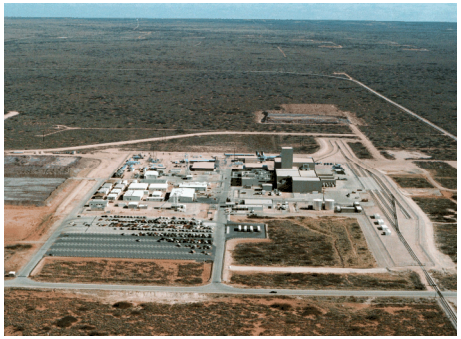
Waste Isolation Pilot Plant (WIPP)

- The Waste Isolation Pilot Plant (WIPP), located in southeastern New Mexico, has been developed by the U.S. Department of Energy (DOE) for the deep geologic disposal of transuranic (TRU) waste.

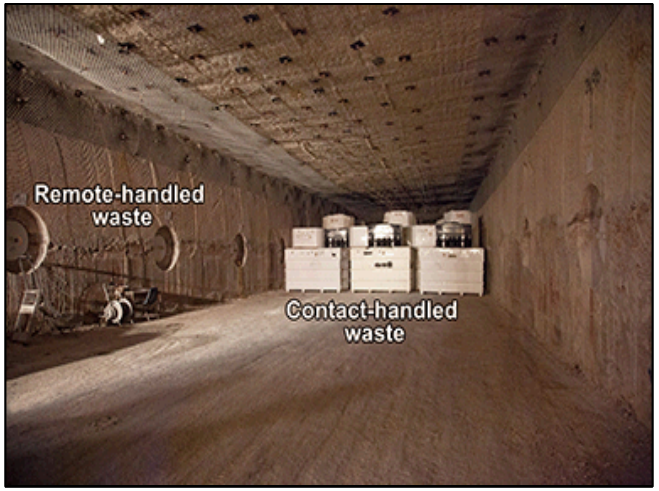


ROCK SALT DEPOSITS in the UNITED STATES



WIPP

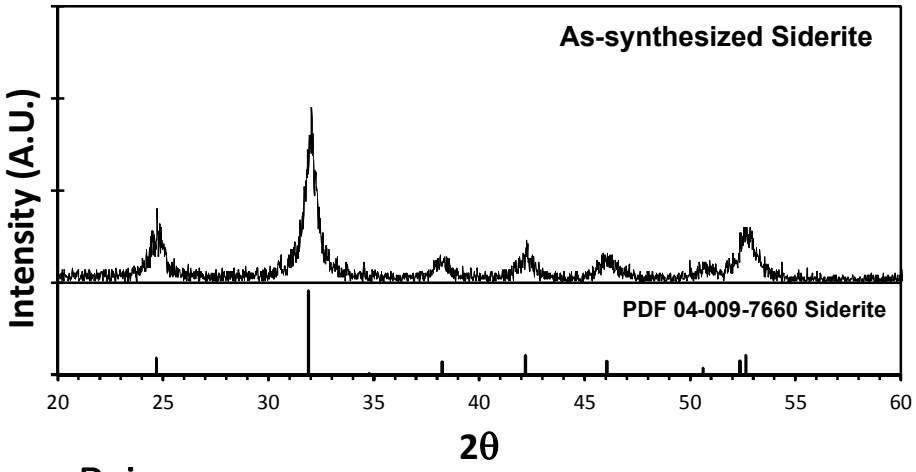
- WIPP Performance Assessment calculations estimate the probability and consequence of potential mobile (dissolved and colloids) radionuclide releases from the repository to the accessible environment for a regulatory period of 10,000 years after facility closure.
- Steel (Fe) in waste containers and Lead (Pb) in shielded containers
- Anions – sulfide (S^{2-}), carbonate (CO_3^{2-}), etc.
- Organic ligands – citrate ($C_6H_8O_7$), EDTA ($C_{10}H_{16}N_2O_8$), oxalate ($C_2O_4^{2-}$), etc.



- Updating WIPP thermodynamic database – Pitzer model

Experimental

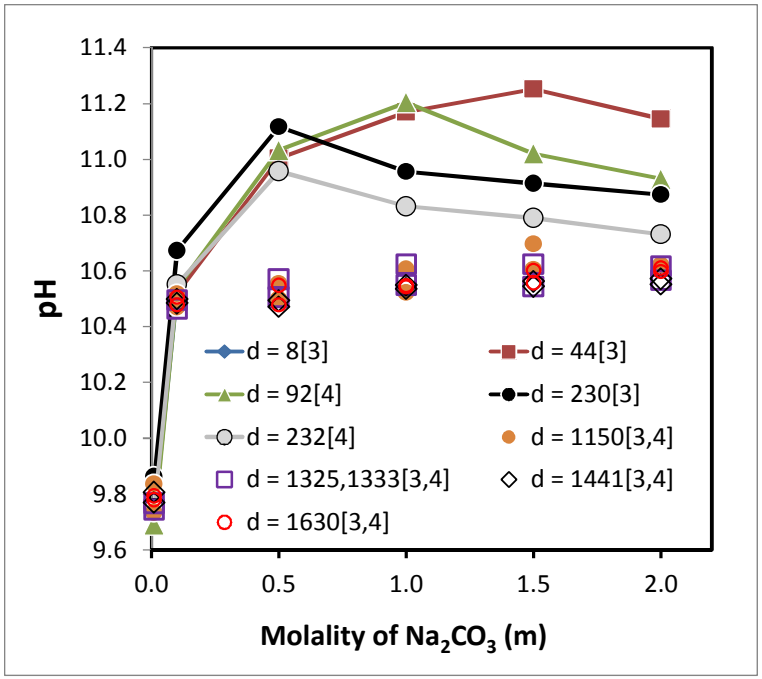
- Inside a glovebox (< 2 ppm O_2)
- Siderite (FeCO3) Synthesis
  - $FeCl_2 \cdot 4H_2O + NaHCO_3 \Rightarrow FeCO_3 + Na^+ + 2Cl^- + H^+ + 4H_2O$

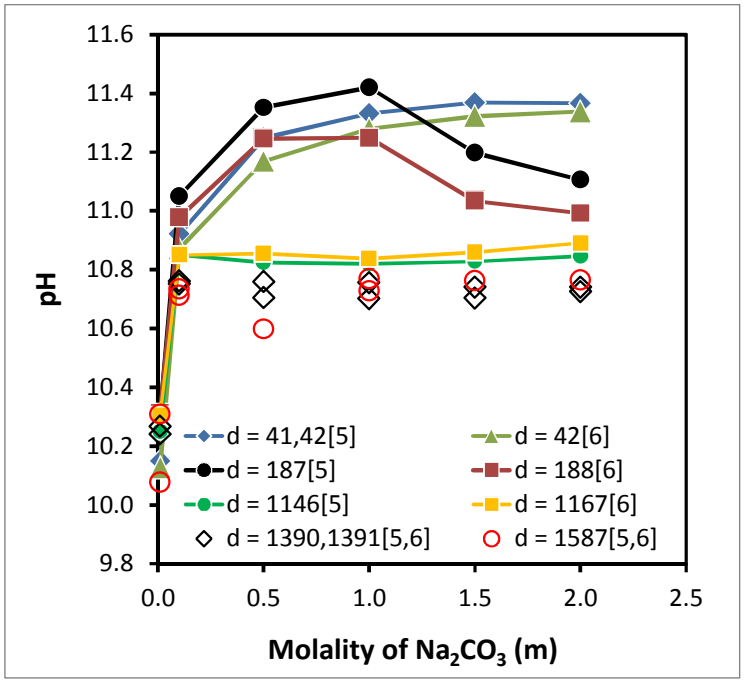


- Brines:
  - Y*m* NaCl + X*m* Na_2CO_3
  - Y = 0.15, 1.5
  - X = 0.01, 0.1, 0.5, 1.0, 1.5, 2.0
- Siderite (~0.5g) added to Brines

Brine Id	NaCl (*m*)	Na_2CO_3 (*m*)	$FeCO_3$ (g)
1.5*m* NaCl + 0.01*m* Na_2CO_3	1.50	0.01	0.47,0.53
1.5*m* NaCl + 0.1*m* Na_2CO_3	1.50	0.10	0.49,0.52
1.5*m* NaCl + 0.5*m* Na_2CO_3	1.50	0.50	0.50,0.49
1.5*m* NaCl + 1.0*m* Na_2CO_3	1.50	1.00	0.46,0.48
1.5*m* NaCl + 1.5*m* Na_2CO_3	1.50	1.50	0.48,0.49
1.5*m* NaCl + 2.0*m* Na_2CO_3	1.50	2.00	0.50,0.46
0.15*m* NaCl + 0.01*m* Na_2CO_3	0.15	0.01	0.52,0.50
0.15*m* NaCl + 0.1*m* Na_2CO_3	0.15	0.10	0.47,0.48
0.15*m* NaCl + 0.5*m* Na_2CO_3	0.15	0.50	0.51,0.48
0.15*m* NaCl + 1.0*m* Na_2CO_3	0.15	1.00	0.48,0.47
0.15*m* NaCl + 1.5*m* Na_2CO_3	0.15	1.50	0.49,0.48
0.15*m* NaCl + 2.0*m* Na_2CO_3	0.15	2.00	0.53,0.51

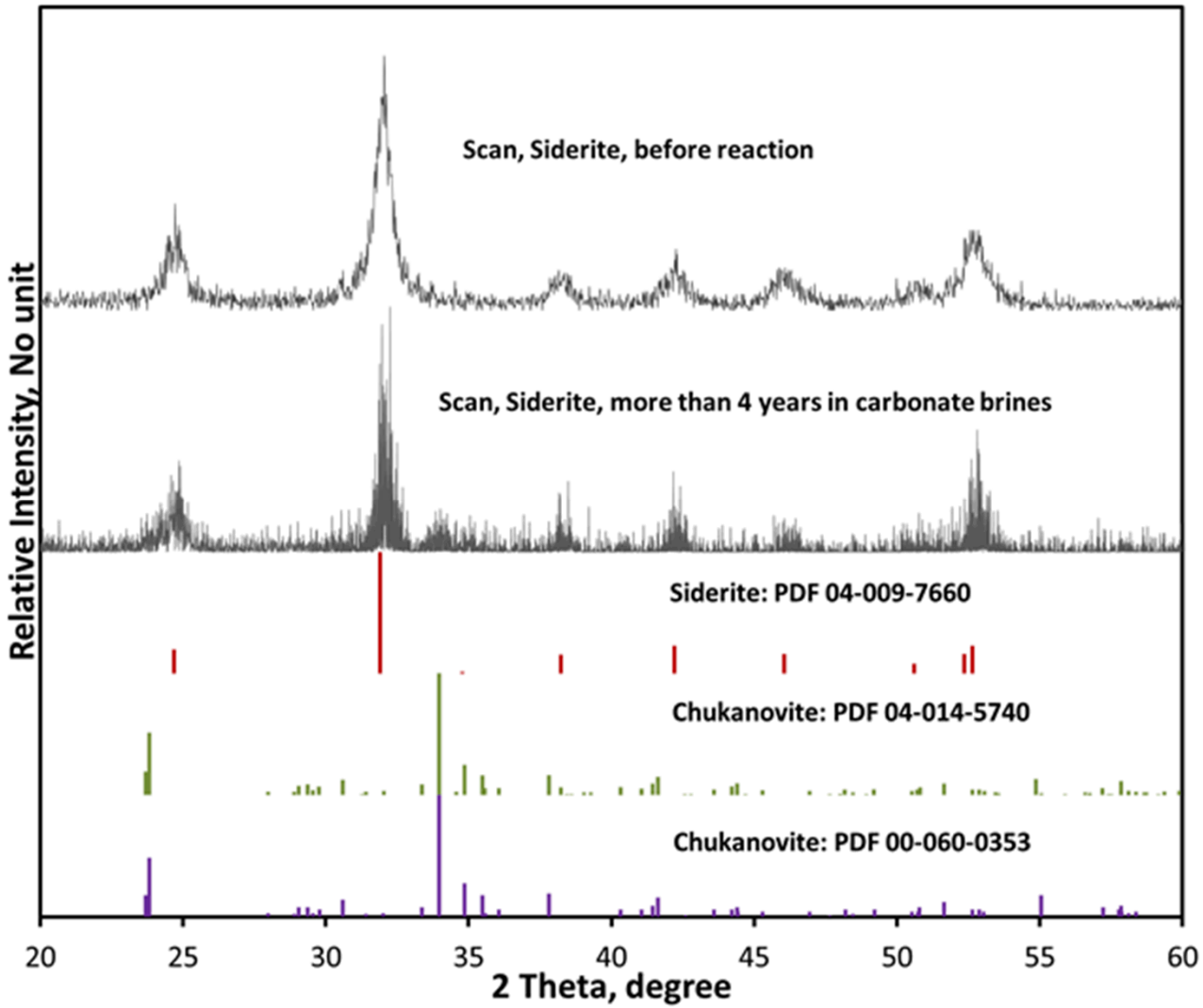
pH changes





- With increasing aging time, the pH of the solution progressively decreased.
  - Signaling potential precipitation of a hydroxyl-bearing phase such as chukanovite ($Fe_2(OH)_2CO_3$)
- > 4 year-aged solutions, the pH was stabilized.
  - Chemical equilibrium between the hydroxyl-bearing phase and ion species
  - Sluggish phase transition kinetics to the hydroxyl-bearing phase
- In the literature[1-4], chukanovite is stable at pH values between 7.8-11.0.
- XRD analysis of > 4 year-aged solid precipitates

1. Nishimura et al., Journal of Power and Energy Systems 3[1], 23-30 (2009); 2. Lee et al., Journal of Contaminant Hydrology 116, 47-57 (2010); 3. Azoulay et al., Corrosion Science 58, 229-236 (2012); 4.Chen et al., Environmental Technology 37[21], 2786-2792 (2016)



- Possible identification of chukanovite peak

Thermodynamic Modeling (Pitzer Model)

Reactions	logK	Source
Aqueous reactions		
(1) $H^+ + OH^- = H_2O$	13.9967	data0.fm2
(2) $CO_3^{2-} + H^+ = HCO_3^-$	10.3392	data0.fm2
(3) $CO_2(aq) + H_2O = H^+ + HCO_3^-$	-6.3374	data0.fm2
(4) $FeOH^+ + H^+ = Fe^{2+} + H_2O$	9.3148	data0.ymp.R2
(5) $Fe(OH)_3^- + 3H^+ = Fe^{2+} + 3H_2O$	31.0	data0.ymp.R2
(6) $Fe(OH)_2(aq) + 2H^+ = Fe^{2+} + 2H_2O$	20.8214	Jang and Kim, 2016
Dissolution		
(7) $NaCl(s) = Na^+ + Cl^-$	1.5704	data0.fm2
(8) $NaHCO_3(s) = Na^+ + HCO_3^-$	-0.4030	data0.fm2
(9) $Na_2CO_3{\cdot}10H_2O(s) + H^+ = 2Na^+ + HCO_3^- + 10H_2O$	9.5145	data0.fm2
(10) $Na_2CO_3{\cdot}7H_2O(s) + H^+ = 2Na^+ + HCO_3^- + 7H_2O$	9.8791	data0.fm2
(11) $Na_2CO_3{\cdot}H_2O(s) + H^+ = 2Na^+ + HCO_3^- + H_2O$	10.8211	data0.fm2
(12) $Na_3H(CO_3)_2{\cdot}2H_2O(s) + H^+ = 3Na^+ + 2HCO_3^- + 2H_2O$	9.2948	data0.fm2
(13) $FeCO_3(s) + H^+ = Fe^{2+} + HCO_3^-$	-0.192	data0.ymp.R2
(14) $Fe_2(OH)_2CO_3(s) + 3H^+ = 2Fe^{2+} + HCO_3^- + 2H_2O$	16.216	Present study

- Thermodynamic model for dissolution of chukanovite was included

data0.fm2, WIPP thermodynamic database, ERMS-565730, Sandia National Laboratories (2016)
data0.ymp.R2, Yucca Mountain Project thermodynamic database coming with EQ3/6
Jang and Kim, Analysis Report Rev2, ERMS-567283, Sandia National Laboratories (2016)

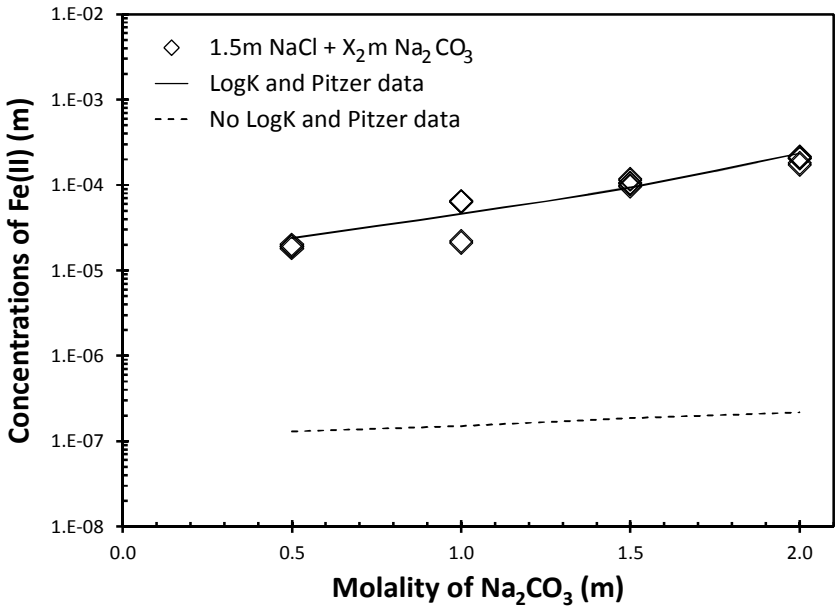
i	*j*		β^0	β^1	β^2	C^φ	Source
Na^+	Cl^-		0.0765	0.2664		0.00127	data0.fm2
Na^+	OH^-		0.0864	0.253		0.0044	data0.fm2
Na^+	HCO_3^-		0.0277	0.0411			data0.fm2
Na^+	CO_3^{2-}		0.0399	1.389		0.0044	data0.fm2
H^+	Cl^-		0.1775	0.2945		0.0008	data0.fm2
Fe^{2+}	Cl^-		0.37324	1.13499		-0.02152	Moog et al., 2004
Fe^{2+}	CO_3^{2-}		-1.335	3.27	-45.74	0.0	Present study
$FeOH^+$	CO_3^{2-}		-0.4128	1.74	0.0	0.0	Present study
i	*j*		$\theta_{cc'}$ or $\theta_{aa'}$	Source			
Na^+	H^+		0.036	data0.fm2			
Na^+	Fe^{2+}		0.10945	Moog et al., 2004			
Na^+	$FeOH^+$		-0.0974	Jang and Kim, 2016			
Cl^-	OH^-		-0.05	data0.fm2			
Cl^-	HCO_3^-		0.03	data0.fm2			
Cl^-	CO_3^{2-}		-0.02	data0.fm2			
OH^-	CO_3^{2-}		0.1	data0.fm2			
HCO_3^-	CO_3^{2-}		-0.04	data0.fm2			
i	*j*	*k*	$\psi_{cc'a}$ or $\psi_{aa'c}$	Source			
Na^+	H^+	Cl^-	-0.004	data0.fm2			
Na^+	Fe^{2+}	Cl^-	-0.01605	Moog et al., 2004			
Cl^-	OH^-	Na^+	-0.006	data0.fm2			
Cl^-	HCO_3^-	Na^+	-0.015	data0.fm2			
Cl^-	CO_3^{2-}	Na^+	0.0085	data0.fm2			
OH^-	CO_3^{2-}	Na^+	-0.017	data0.fm2			
HCO_3^-	CO_3^{2-}	Na^+	0.002	data0.fm2			
i	*j*		λ_{nc} or λ_{na}	Source			
CO_2 (aq)	H+		0.0	data0.fm2			
CO_2 (aq)	Na^+		0.1	data0.fm2			
CO_2 (aq)	Cl^-		-0.005	data0.fm2			

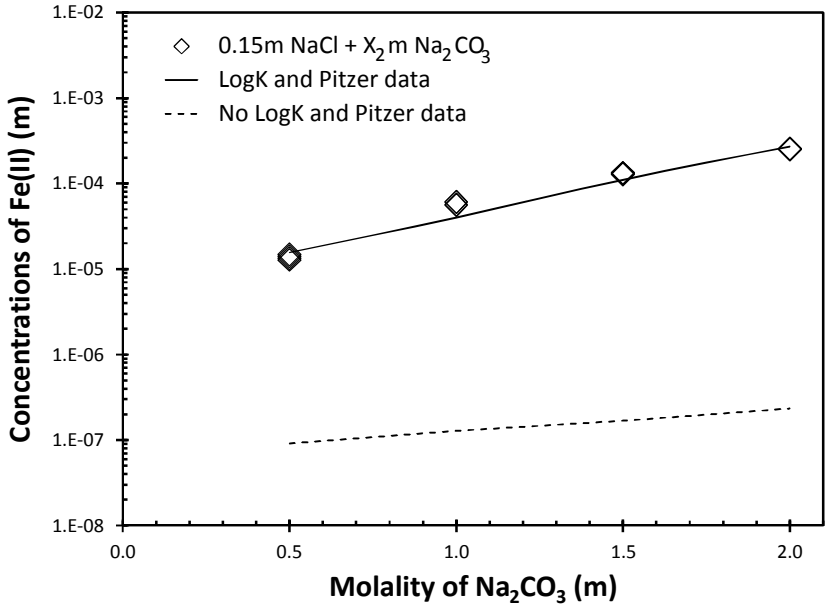
Moog et al., International Journal of Research in Physical Chemistry & Chemical Physics 218[9], 1063-1087 (2004)

Total Fe(II) solubility

- Thermodynamic model fitting to experimentally analyzed Fe(II) solubility data
- The derived Pitzer interaction parameters and equilibrium constant for dissolution of chuakanovite

Parameters	Fit parameter values
Fe^{2+}/CO_3^{2-}	$\beta^{(0)} = -1.335$, $\beta^{(1)} = 3.27^*$, $\beta^{(2)} = -45.74^*$, $C^\phi = 0.0^*$
$FeOH^+/CO_3^{2-}$	$\beta^{(0)} = -0.4128$, $\beta^{(1)} = 1.74^*$, $\beta^{(2)} = 0.0^*$, $C^\phi = 0.0^*$
Log K (chukanovite)	16.216





Standard Formation Energy

- Dissolution of Chukanovite:
  - $Fe_2(OH)_2CO_3(s) + 3H^+ = 2Fe^{2+} + HCO_3^- + 2H_2O$
- From LogK=16.216, the standard formation energy of chukanovite was estimated at -1149.8 kJ/mol.
- The standard formation energies of chukanovite in the literature were used to compute LogK for its dissolution, and compared with the present study.

pH	ΔG_f^o (kJ/mol)	Source	Log K at 25 °C
~8.3	-1169.3	Nishimura et al., 2009	12.795
8.2 – 9.1	-1174.4	Lee et al., 2010	11.902
10.26 – 10.91	-1171.5	Azoulay et al., 2012	12.410
7.87 – 10.34	-1151.1	Chen et al., 2016	15.983
10.4 – 10.9	-1149.8	Present study	16.216

Nishimura et al., Journal of Power and Energy Systems 3[1], 23-30 (2009)
Lee et al., Journal of Contaminant Hydrology 116, 47-57 (2010)
Azoulay et al., Corrosion Science 58, 229-236 (2012)
Chen et al., Environmental Technology 37[21], 2786-2792 (2016)

Summary

- Siderite solubility experiments in high pH and ionic strength solutions indicate the presence of a second, more stable phase, which is tentatively identified as chukanovite.
- The aqueous thermodynamic modeling to total Fe(II) solubility data provided:
  - Pitzer interaction parameters for Fe^{2+}/CO_3^{2-} and $FeOH^{+}/CO_3^{2-}$ pairs
  - Equilibrium constant for the dissolution reaction of chukanovite
- Chukanovite formed slowly in brines with nominal carbonate concentrations $\geq 0.5m$ and in the pH range of 7.8 – 10.9.
- Chukanovite appears to be more stable than siderite at higher carbonate concentrations.
- Further works:
  - Identification of chukanovite from more XRD study
  - Influence to Fe(II) solubility and the related mobility of radionuclides in WIPP brines containing dissolved carbonate.