

UNRAVELING COUPLED SALT TRANSPORT AND DAMAGE MECHANISMS IN POROUS LIMESTONE USING 4D X-RAY TOMOGRAPHY AND ADVANCED IMAGE ANALYSIS

Syrine Ben Elhadj Hamida^{1,2,*} , Marijn A. Boone³ , Veerle Cnudde^{3,4} ,
Peter Moonen^{1,2} , Hannelore Derluyn^{1,2,*} 

¹Universite de Pau et des Pays de l'Adour, CNRS, LFCR, Pau, France; ²Universite de Pau et des Pays de l'Adour, CNRS, DMEX, Pau, France; ³Ghent University, PProGress-UGCT, Krijgslaan 281/S8, 9000 Ghent, Belgium;

⁴Utrecht University, Environmental Hydrogeology, Princetonlaan 8a, 3584 CB Utrecht, The Netherlands

1. PHREEQC SIMULATION OF CALCITE STABILITY

A PHREEQC simulation was performed to assess the stability of calcite in the 6 molal NaCl solution used in the experiment. The simulation input and main output results are presented in the following pages. The results show that calcite rapidly reaches equilibrium with the solution ($SI_{\text{calcite}} = 0.00$), with only negligible calcite dissolution ($\Delta_{\text{calcite}} \approx 4.94 \times 10^{-4}$ mol/kgw). These results support the assumption that calcite dissolution did not significantly affect the observed image changes during the experiment.



PHREEQC Simulation of Calcite Stability

Input file: C:\Users\sbehamida\Desktop\PHREEQC simulation.pqi
Output file: C:\Users\sbehamida\Desktop\PHREEQC simulation.pgo
Database file: C:\Program Files (x86)\USGS\Phreeqc Interactive 3.7.3-15968\database\phreeqc.dat

Reading data base.

■SOLUTION_MASTER_SPECIES
■SOLUTION_SPECIES
■PHASES
■EXCHANGE_MASTER_SPECIES
■EXCHANGE_SPECIES
■SURFACE_MASTER_SPECIES
■SURFACE_SPECIES
■RATES
■END

Reading input data for simulation 1.

■DATABASE C:\Program Files (x86)\USGS\Phreeqc Interactive 3.7.3-15968\database\phreeqc.dat
■TITLE Calcite stability in 6 molal NaCl solution - Savonnières limestone
■SOLUTION 1 6 molal NaCl solution
■ temp 26
■ units mol/kgw
■ pH 7 charge
■ pe 4
■ Na 6
■ Cl 6
■ water 1
■EQUILIBRIUM_PHASES 1
■ Calcite 0 10
■SELECTED_OUTPUT 1
■ file calcite_stability_output.txt
■ reset false
■ ph true
■ si Calcite
■ totals Ca C Na Cl
■ equilibrium_phases Calcite
■END

TITLE

Calcite stability in 6 molal NaCl solution - Savonnières limestone

Beginning of initial solution calculations.

Initial solution 1. ■6 molal NaCl solution

-----Solution composition-----

■Elements	Molality	Moles
■Cl	6.000e+00	6.000e+00
■Na	6.000e+00	6.000e+00

-----Description of solution-----

pH	=	6.942	Charge balance
pe	=	4.000	
Specific Conductance (S/cm, 26C)	=	278281	
Density (g/cm)	=	1.19362	
Volume (L)	=	1.13156	
Activity of water	=	0.796	
Ionic strength (mol/kgw)	=	6.000e+00	
Mass of water (kg)	=	1.000e+00	
Total alkalinity (eq/kg)	=	4.562e-16	
Temperature (C)	=	26.00	
Electrical balance (eq)	=	6.983e-13	
Percent error, 100*(Cat- An)/(Cat+ An)	=	0.00	
Iterations	=	5	
Total H	=	1.110124e+02	
Total O	=	5.550622e+01	

-----Distribution of species-----

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma	mole V cm/mol
OH-	1.619e-07	7.613e-08	-6.791	-7.118	-0.328	4.77
H+	1.619e-07	1.142e-07	-6.791	-6.942	-0.152	0.00
H2O	5.551e+01	7.960e-01	1.744	-0.099	0.000	18.07
Cl	6.000e+00					
Cl-	6.000e+00	3.640e+00	0.778	0.561	-0.217	20.12
H(0)	4.591e-26					
H2	2.295e-26	9.138e-26	-25.639	-25.039	0.600	28.60
Na	6.000e+00					
Na+	6.000e+00	9.507e+00	0.778	0.978	0.200	1.27
NaOH	1.818e-17	7.238e-17	-16.740	-16.140	0.600	(0)
O(0)	0.000e+00					
O2	0.000e+00	0.000e+00	-42.778	-42.178	0.600	30.48

-----Saturation indices-----

Phase	SI**	log IAP	log K(299 K, 1 atm)	
H2(g)	-21.94	-25.04	-3.10	H2
H2O(g)	-1.58	-0.10	1.48	H2O
Halite	-0.03	1.54	1.57	NaCl
O2(g)	-39.28	-42.18	-2.90	O2

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
For ideal gases, phi = 1.

Beginning of batch-reaction calculations.

Reaction step 1.

Using solution 1. 6 molal NaCl solution

Using pure phase assemblage 1.

-----Phase assemblage-----

Phase	SI	log IAP	log K(T, P)	Initial	Final	Delta
Calcite	0.00	-8.49	-8.49	1.000e+01	1.000e+01	-4.944e-04

-----Solution composition-----

Elements	Molality	Moles
C	4.944e-04	4.944e-04
Ca	4.944e-04	4.944e-04
Cl	6.000e+00	6.000e+00
Na	6.000e+00	6.000e+00

-----Description of solution-----

pH = 9.682 Charge balance
pe = -4.263 Adjusted to redox equilibrium
Specific Conductance (S/cm, 26C) = 278284
Density (g/cm) = 1.19366
Volume (L) = 1.13157
Activity of water = 0.796
Ionic strength (mol/kgw) = 6.001e+00
Mass of water (kg) = 1.000e+00
Total alkalinity (eq/kg) = 9.888e-04
Total CO2 (mol/kg) = 4.944e-04
Temperature (C) = 26.00
Electrical balance (eq) = 1.094e-12
Percent error, 100*(Cat-|An|)/(Cat+|An|) = 0.00
Iterations = 20
Total H = 1.110124e+02
Total O = 5.550770e+01

-----Distribution of species-----

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma	mole V cm/mol
OH-	8.899e-05	4.183e-05	-4.051	-4.379	-0.328	4.77
H+	2.947e-10	2.078e-10	-9.531	-9.682	-0.152	0.00

H2O	5.551e+01	7.960e-01	1.744	-0.099	0.000	18.07
C(-4)	5.320e-28					
CH4	5.320e-28	2.118e-27	-27.274	-26.674	0.600	35.54
C(4)	4.944e-04					
NaCO3-	3.461e-04	1.248e-03	-3.461	-2.904	0.557	29.71
CO3-2	5.786e-05	6.702e-06	-4.238	-5.174	-0.936	6.53
HCO3-	4.990e-05	2.911e-05	-4.302	-4.536	-0.234	40.72
NaHCO3	3.887e-05	1.548e-04	-4.410	-3.810	0.600	1.80
CaCO3	1.402e-06	5.583e-06	-5.853	-5.253	0.600	-14.60
CaHCO3+	3.002e-07	1.831e-07	-6.523	-6.737	-0.215	10.12
CO2	4.239e-09	1.688e-08	-8.373	-7.773	0.600	34.48
(CO2)2	1.357e-18	5.404e-18	-17.867	-17.267	0.600	68.96
Ca	4.944e-04					
Ca+2	4.926e-04	4.859e-04	-3.308	-3.313	-0.006	-14.22
CaCO3	1.402e-06	5.583e-06	-5.853	-5.253	0.600	-14.60
CaHCO3+	3.002e-07	1.831e-07	-6.523	-6.737	-0.215	10.12
CaOH+	8.567e-08	3.089e-07	-7.067	-6.510	0.557	(0)
Cl	6.000e+00					
Cl-	6.000e+00	3.640e+00	0.778	0.561	-0.217	20.12
H(0)	5.106e-15					
H2	2.553e-15	1.017e-14	-14.593	-13.993	0.600	28.60
Na	6.000e+00					
Na+	6.000e+00	9.509e+00	0.778	0.978	0.200	1.27
NaCO3-	3.461e-04	1.248e-03	-3.461	-2.904	0.557	29.71
NaHCO3	3.887e-05	1.548e-04	-4.410	-3.810	0.600	1.80
NaOH	9.989e-15	3.978e-14	-14.000	-13.400	0.600	(0)
O(0)	0.000e+00					
O2	0.000e+00	0.000e+00	-64.871	-64.271	0.600	30.48

-----Saturation indices-----

Phase	SI**	log IAP	log K(299 K,	1 atm)
Aragonite	-0.14	-8.49	-8.34	CaCO3
Calcite	0.00	-8.49	-8.49	CaCO3
CH4(g)	-23.86	-26.67	-2.81	CH4
CO2(g)	-6.29	-7.77	-1.48	CO2
H2(g)	-10.89	-13.99	-3.10	H2
H2O(g)	-1.58	-0.10	1.48	H2O
Halite	-0.03	1.54	1.57	NaCl
O2(g)	-61.37	-64.27	-2.90	O2

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
For ideal gases, phi = 1.

End of simulation.

Reading input data for simulation 2.

End of Run after 0.56 Seconds.
