Modeling Geochemical Reactions in a Typical Williston Basin Reservoir Used for CO$_2$ and Sour Gas Storage

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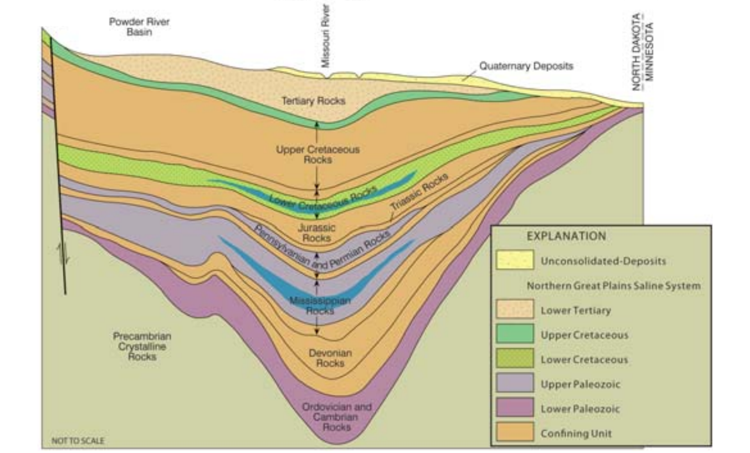
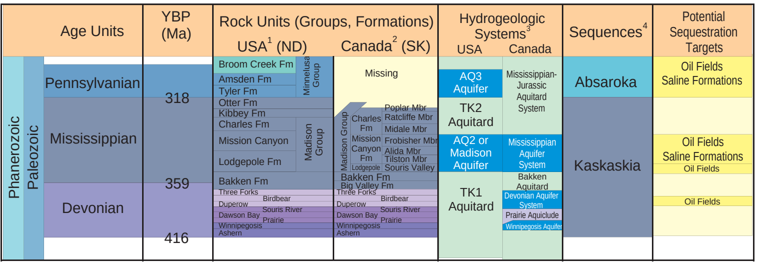


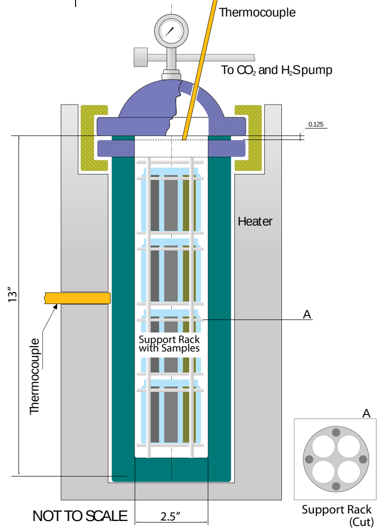


Age Units			YBP (Ma)	Rock Units (Groups, Formations) USA[1] (ND)		Rock Units (Groups, Formations) Canada[2] (SK)			Hydrogeologic Systems[3] USA	Hydrogeologic Systems[3] Canada	Sequences[4]	Potential Sequestration Targets
Phanerozoic	Paleozoic	Pennsylvanian		Broom Creek Fm Amsden Fm Tyler Fm	Minnelusa Group	Missing			AQ3 Aquifer	Mississippian-Jurassic Aquitard System	Absaroka	Oil Fields Saline Formations
		Mississippian	318	Otter Fm Kibbey Fm					TK2 Aquitard		Kaskaskia	
				Charles Fm Mission Canyon Lodgepole Fm	Madison Group	Madison Group	Charles Fm Mission Canyon Fm Lodgepole	Poplar Mbr Ratcliffe Mbr Midale Mbr Frobisher Mbr Alida Mbr Tilston Mbr Souris Valley	AQ2 or Madison Aquifer	Mississippian Aquifer System		Oil Fields Saline Formations Oil Fields
			359	Bakken Fm			Bakken Fm Big Valley Fm		TK1 Aquitard	Bakken Aquitard		
		Devonian		Three Forks Birdbear Duperow Souris River Dawson Bay Prairie Winnipegosis Ashern			Three Forks Birdbear Duperow Souris River Dawson Bay Prairie Winnipegosis Ashern			Devonian Aquifer System Prairie Aquiclude Winnipegosis Aquifer		Oil Fields
			416									

ABSTRACT

This work reports results which were obtained during a series of laboratory experiments and numerical modeling of geochemical reactions performed by the Plains CO$_2$ Reduction (PCOR) Partnership. Core samples collected from various formations of the Williston Basin (North Dakota, USA) were exposed for a period of four weeks to pure supercritical carbon dioxide and a mixture of supercritical carbon dioxide (67.3 mole %) and hydrogen sulfide (32.7 mole %) at 2250 psi (155 bar) and 158°F (70°C) in 10 wt. % NaCl synthetic brine conditions. Prior to exposure, XRD and XRF mineralogical analysis demonstrated the presence of ankerite, anhydrite, calcite, crystabolite, dolomite, halite, hematite, kaolinite, illite, pyrite, quartz, and others in the Williston Basin samples. After exposure, XRD and QEMSCAN analysis of reaction products was also performed. Some minerals displayed high reactivity with acid gas, including the conversion of dolomite to calcite. Other samples showed high reactivity while exposed to pure CO$_2$; for instance, the pyrite was completely dissolved in brine and precipitated as a siderite and hematite later in a course of the experiment; the hematite was dissolved in brine and partially re-precipitated or converted in siderite, and the dolomite partially was converted to calcite and magnesium carbonate. The results of the laboratory experiments were compared with the numerical modeling which was performed with the Geochemist's Workbench simulator and PHREEQC, where the thermodynamic database was adjusted with SUPRCRT92 code.

CO$_2$ partial pressure:	2250 psi / 155 bar
Temperature:	158 °F / 70 °C
Gas Mixture:	1) CO$_2$ – 100 mole % 2) CO$_2$ – 67.3 mole % H$_2$S – 32.7 mole %
Mass of sample:	10-15 g
Type of sample:	Core plugs
Saturation conditions:	Synthetic brine NaCl, 10% by weight
Time of exposure:	4 weeks

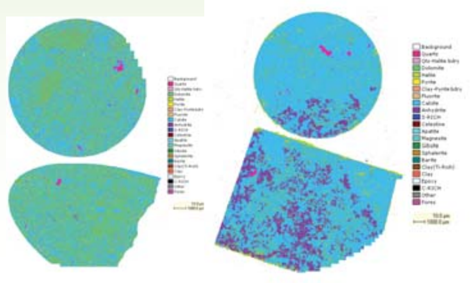


MINERALOGICAL ANALYSIS, EXPERIMENTAL RESULTS, AND MODELING

MISSISSIPPIAN-MADISON GROUP

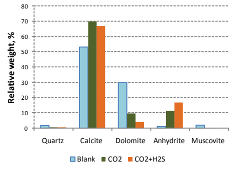
Original Sample | After exposure (CO$_2$) | After exposure (CO$_2$+H$_2$S) | After exposure (CO$_2$) | After exposure (CO$_2$+H$_2$S)

HIGH DEFINITION MINERALOGICAL ANALYSIS (QEMSCAN)

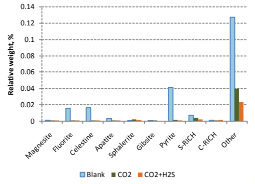


Original Sample | After exposure to CO$_2$

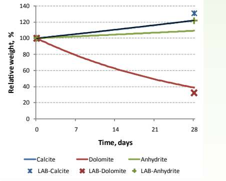
MAJOR MINERAL PHASES



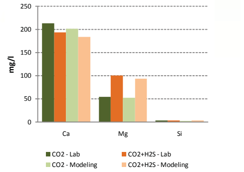
MINOR MINERAL PHASES



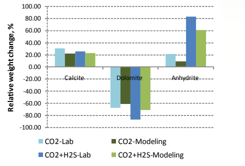
KINETICS MODELING (CO$_2$)



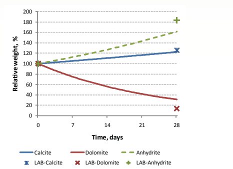
SOLUTION ANALYSIS



MINERALOGICAL CHANGES



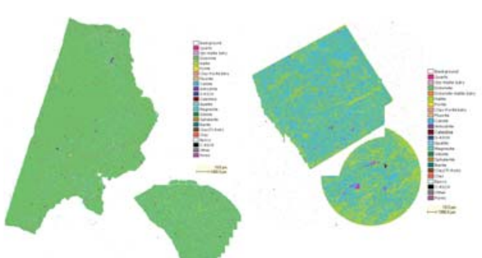
KINETICS MODELING (CO$_2$+H$_2$S)



MISSISSIPPIAN-RATCLIFFE INTERVAL

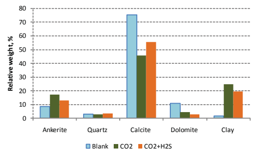
Original Sample | After exposure (CO$_2$) | After exposure (CO$_2$+H$_2$S) | After exposure (CO$_2$) | After exposure (CO$_2$+H$_2$S)

HIGH DEFINITION MINERALOGICAL ANALYSIS (QEMSCAN)

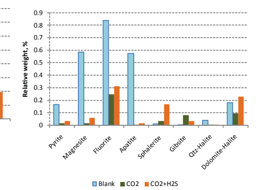


Original Sample | After exposure to CO$_2$

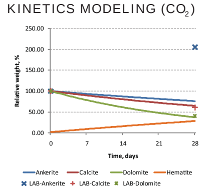
MAJOR MINERAL PHASES



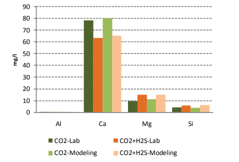
MINOR MINERAL PHASES



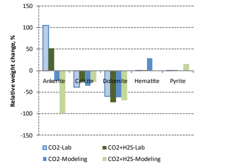
KINETICS MODELING (CO$_2$)



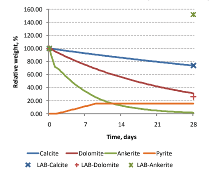
SOLUTION ANALYSIS



MINERALOGICAL CHANGES



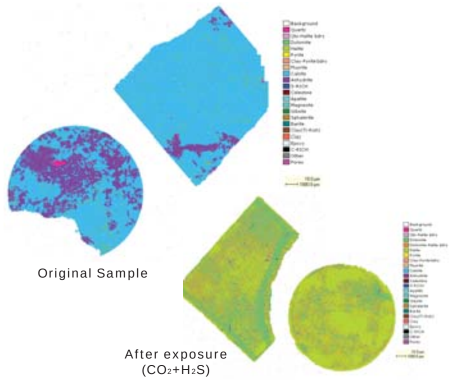
KINETICS MODELING (CO$_2$+H$_2$S)



MISSISSIPPIAN-FROBISHER-ALIDA INT.

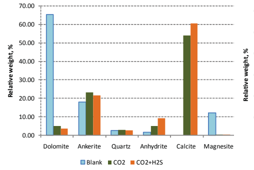
Original Sample | After exposure (CO$_2$) | After exposure (CO$_2$+H$_2$S) | After exposure (CO$_2$) | After exposure (CO$_2$+H$_2$S)

HIGH DEFINITION MINERALOGICAL ANALYSIS (QEMSCAN)

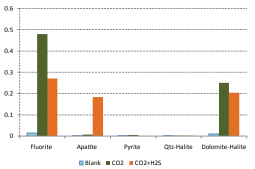


Original Sample | After exposure (CO$_2$+H$_2$S)

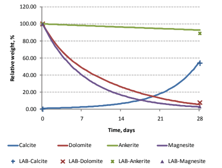
MAJOR MINERAL PHASES



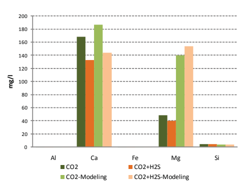
MINOR MINERAL PHASES



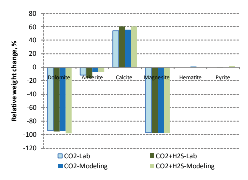
KINETICS MODELING (CO$_2$)



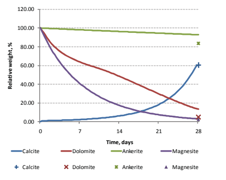
SOLUTION ANALYSIS



MINERALOGICAL CHANGES



KINETICS MODELING (CO$_2$+H$_2$S)



KINETIC RATE

$$k_M = k_{25}\exp\left[-\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{298.15}\right)\right]$$

$$rate_M = \pm k_M A_M a^n_{H^+}\left[\left(\frac{Q_M}{K_M}\right)^{\mu}-1\right]^{\nu}$$

Where,

k - the temperature dependant rate constant;
A - the reactive surface area m^2 per kg of water;
a_{H^+} - the proton activity;
Q - the ion activity product;
K - the equilibrium constant;
M - the mineral index
k_{25} - the rate constant measured at 25 °C;
R - the gas constant;
E_a - the activation energy of the reaction;
T - the absolute gas temperature;
μ & υ - correcting coefficients.

Mineral	Formula	k_{25}, moles^{-2}s^{-1}	E_a, J/mol*K	A, cm^2/g	Reference
Anhydrite	$CaSO_4$	2.5119×10^{-8}	62.76	9.8	Set to galena from Xu and Pruess (2003)
Ankerite	$Ca_2MgFe(CO_3)_4$	1.2598×10^{-9}	62.76	9.8	Zhang W. et. Al (2007)
Calcite	$CaCO_3$	6.4565×10^{-6}	62.76	9.8	Svensson and Dreybrodt (1992)
Dolomite	$CaMg(CO_3)_2$	1.2589×10^{-6}	62.76	9.8	Xu and Pruess (2003)
Hematite	Fe_2O_3	2.5120×10^{-15}	66.20	12.9	Xu, Apps, and Pruess (2004)
Magnesite	$MgCO_3$	2.5120×10^{-6}	66.20	9.8	Xu, Apps, and Pruess (2004)
Pyrite	FeS_2	2.8180×10^{-6}	56.9	12.9	Xu and Pruess (2003)
Quartz	SiO_2	1.2589×10^{-14}	87.50	9.8	Xu and Pruess (2003)
Siderite	$FeCO_3$	1.2598×10^{-9}	62.76	9.8	Zhang W. et. Al (2007)

SUMMARY

- Mineralogical changes are observed after exposure to supercritical sour gas and carbon dioxide;
- The rates of reactions in the laboratory conditions are higher than observed in the field (Northwestern McGregor EOR demonstration);
- The mineralogical analysis performed with various analytical tools (XRF, XRD, QEMSCAN) require verification with numerical modeling tools;
- Kinetic rates for numerical modeling need correlations with experimental results and field observations;
- Detailed water analysis is crucial for understanding of rock-water-sour gas interactions, accurate numerical modeling correlation, etc.
- The thermodynamic database correction with SUPRCRT92 code for pressure and temperature of interest is required for accurate numerical modeling;
- The effect of pressure on geochemical reactions is underexplored.

CONCLUSIONS

The results of these initial activities suggest that laboratory experimental results can be reasonably correlated to some aspects of geochemical modeling, thereby providing a foundation upon which to develop future laboratory and modeling work. It is anticipated that planned activities will build upon these results and lead to further insight regarding the prediction of interactions between sour gas, rocks, and formation fluids at reservoir conditions.

ABOUT PCOR PARTNERSHIP

The Plains CO$_2$ Reduction (PCOR) Partnership is a diverse group of over 80 public and private sector stakeholders working together to better understand the technical and economic feasibility of capturing and storing CO$_2$ emissions from stationary sources of CO$_2$ in the central interior of North America. The PCOR Partnership is led by the Energy & Environmental Research Center (EERC) at the University of North Dakota and is one of seven regional partnerships designated by the U.S. Department of Energy's (DOE's) Regional Carbon Sequestration Partnership (RCSP) Program. Funding comes from the RCSP program and a broad range of project sponsors.