Politechnika Śląska

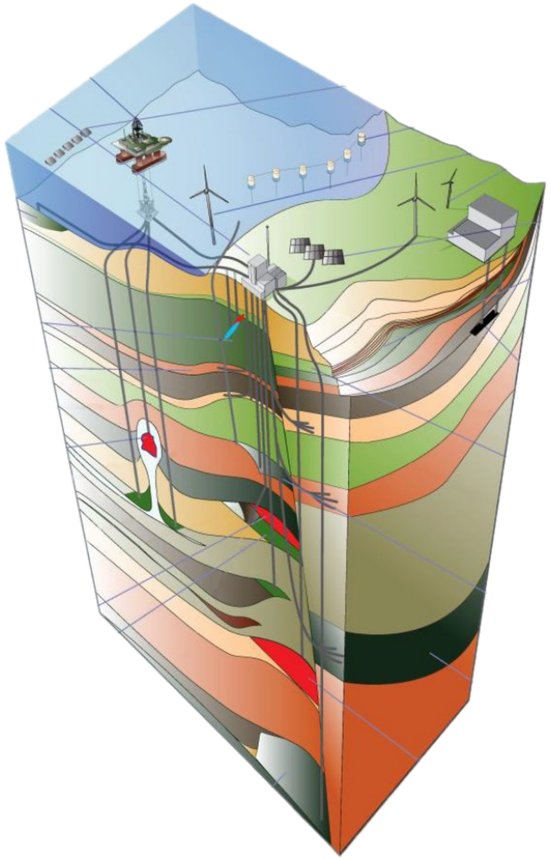
UCZELNIA BADAWCZA
INICJATYWA DOSKONAŁOŚCI

BALTIC CARBON FORUM

EXPERIMENTAL TESTS AND MODELING OF H_2S -CO_2-ROCK-BRINE SYSTEMS CASE STUDY

Krzysztof Labus – Silesian University of Technology

Contents



Motivation

Interaction of acid gases with rocks is the subject of intense research in recent decades. Interest in this topic is associated with the conviction of the necessity to reduce the greenhouse effect, and in the case of carbon dioxide - with the possibility of enhanced oil and gas recovery, as well as the hydraulic fracturing with energized fluids and foams.

Expenses of capture of CO2 from industrial emissions containing also other compounds such as H2S and other are very high. Therefore, studies on the coinjection of CO2 together with other acid gases from industrial waste streams are highly topical.

Despite extensive research on this subject there are still many questions about the hydrogeochemical results of sour gas injection into geological systems. Knowledge in this subject requires a deepening also with regard to the sedimentary basins of Central Europe.

In order to investigate these phenomena in the Upper Silesian Coal Basin (USCB) we performed experimental and modeling studies, aimed to determine the impact of CO2 and H2S, or mixtures thereof on the representative formation rocks.

Materials

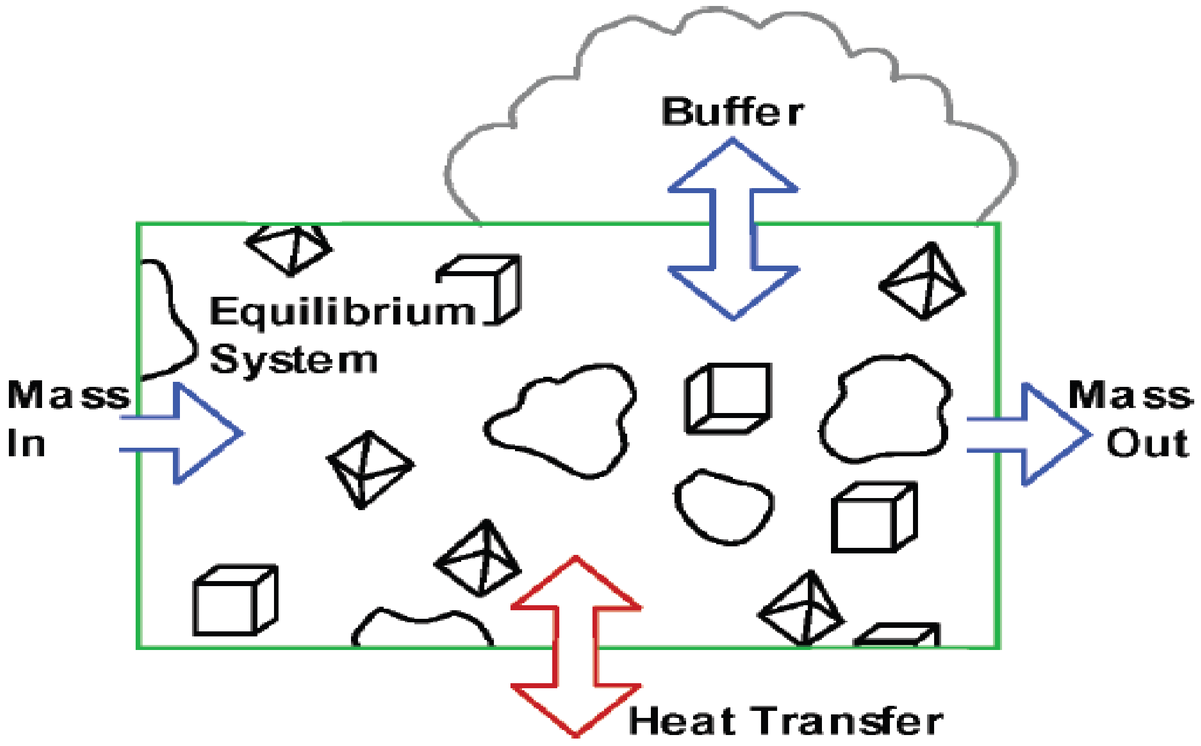
Core samples represent cap rock and aquifers typical of the Upper Silesian Coal Basin (USCB), situated on the borderland of Poland and Czechia, and the adjacent Małopolska Block.

- Paralic Series mudstones - feldspars, muscovite, chlorite, and minor siderite.
- Psephitic rocks of the Dębowiec formation - quartz muscovite, phlogopite, calcite, ankerite, feldspars and chlorites.
- Middle Devonian sandstones (psammites) - quartz, muscovite and carbonates, incl. dolomite; pyrite in minor amounts.

Methods

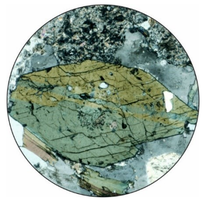
Conceptual diagram of the model

Simulation begins from calculating the system's initial equilibrium state. The program then changes the system by adding (or removing) reactants to vary the system's composition, changing the temperature, or varying the fugacity of gases in an external buffer. This process is the reaction path.

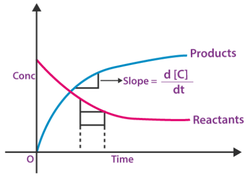


Methods

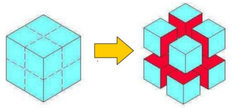
INPUT DATA



- Mineralogical composition of the aquifer, treated as a set of minerals that are reagents in kinetic reactions (data from planimetric analyzes or quantitative XRD analyses.



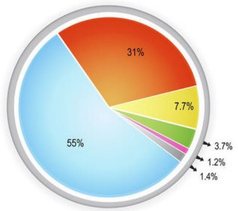
- Reaction rate and specific surface area of individual minerals. The calculations use the dissolution/crystallization kinetics equation, according to which a given mineral crystallizes when the solution is oversaturated with it (it dissolves when it is undersaturated), at a rate depending on the reaction constant and the specific surface area of the mineral.



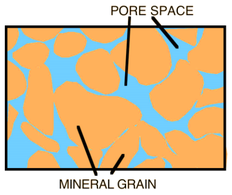
- The specific surface area of grains (SSM) can be calculated using the spherical model, for given molar volumes and molecular masses of minerals.

Methods

INPUT DATA



- The composition of pore water is best determined based on chemical analyzes of samples. In the case of experimental tests, sample 0 - corresponds to synthetic reservoir brine (before the experiment), this composition constitutes the initial data for modeling. Subsequent samples represent post-reaction liquids collected at specific intervals during the experiment and may constitute a reference to the results obtained in modeling.



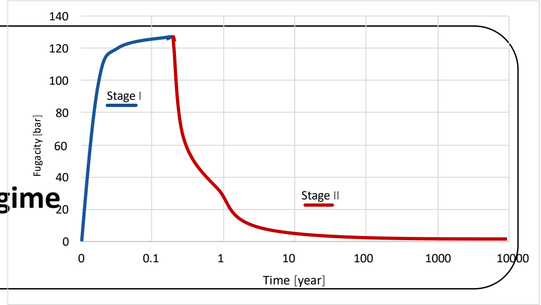
- Porosity of the aquifer - determined by mercury porosimetry.

- CO2/H2S pressure values given as gas pressure activity – fCO2, fH2S, calculated for the gas storage depth conditions.

Methods

R E S E A R C H

- planimetric analysis and XRD analysis – **quantitative assessment of mineral phases**
- mercury porosimeter - **pore space parameters**
- chromatography and ICP-MS – **chemical composition of groundwater**,
- literature data - **reaction rate, reservoir temperature, storage pressure according to the hydrostatic regime**
- SEM-EDS <u>before and after</u> autoclave experiment (**mineralogy check and morphology analysis**)



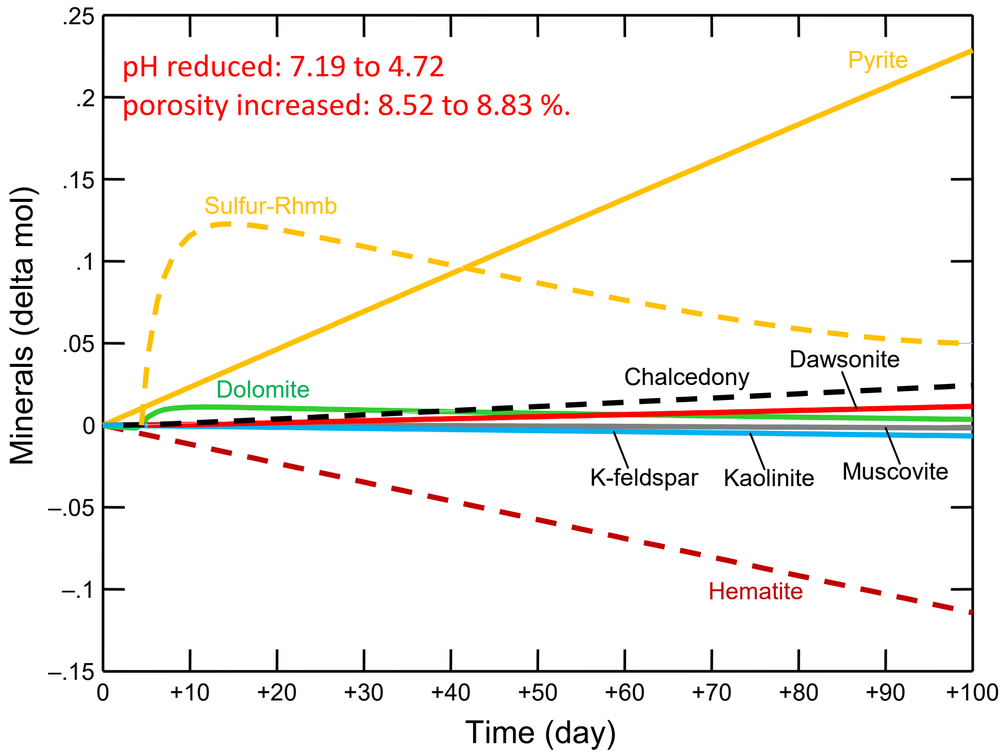
- autoclave experiment simulating reservoir PVT conditions - to **reproduce the impact of CO2 and H2S injection** on the aquifer and insulating rocks - Stage I

- geochemical simulator The GWB:
  Stage I to **reproduce the impact of CO2 and H2S injection** on the aquifer and insulating rocks
  Stage II - **long-term effects of sequestration**, including evolution of formation porosity and mineral sequestration of CO2 and S.

RESULTS

Example – 1927

Injection



Hematite dissolution leads to crystallization of pyrite and rhombic sulfur

$4\ CO_{2(g)} + 0.5\ Fe_2O_3 + 2\ H_2O + 2\ SO_4^{2-} = FeS_2 + 4\ HCO_3^- + 3.75\ O_{2(aq)}$

Confirmed by SEM analyzes after experiments

Crystallization of rhombic sulfur can also take place due to the reaction:

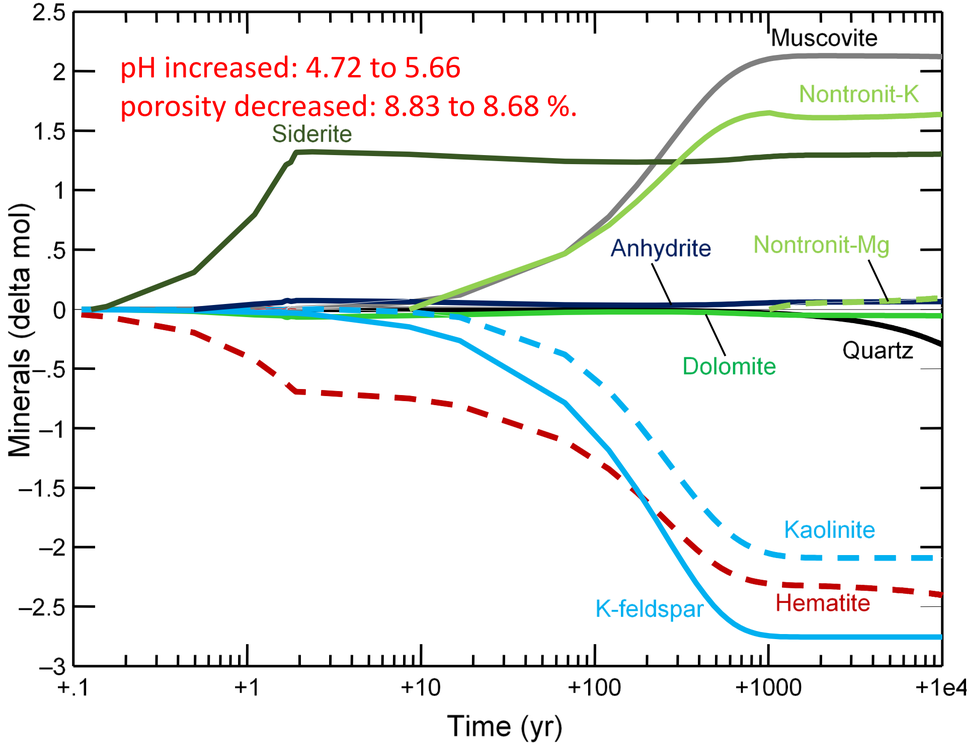
$SO_4^{2-} + 5\ H_2S_{(aq)} = 4S_{Romb} + 4H_2O + 2\ HS^-$

Kaolinite and K-feldspar decomposition, and crystallization of dawsonite and silicate minerals are less important.

Pore water pH reduced from 7.19 to 4.72, porosity increased from 8.52 to 8.83%.

f_{CO2} fugacity is 69.41 bar and f_{H2S} is 3 bar. The $CO_{2(aq)}$ conc. is 1.30 mol / kg, $H_2S_{(aq)}$ - 0.15 mol / kg, and HCO_3^- 0.054 mol / kg

Storage



In first two years storage, hematite is decompoed and siderite precipitates:

$2\ Fe_2O_3 + 3.5\ CO_{2(g)} + 0.5\ CH_{4(g)} = 4\ FeCO_3 + H_2O$

Dissolution of dolomite, K-feldspar and hematite promote crystallization of nontronite - Mg and anhydrite:

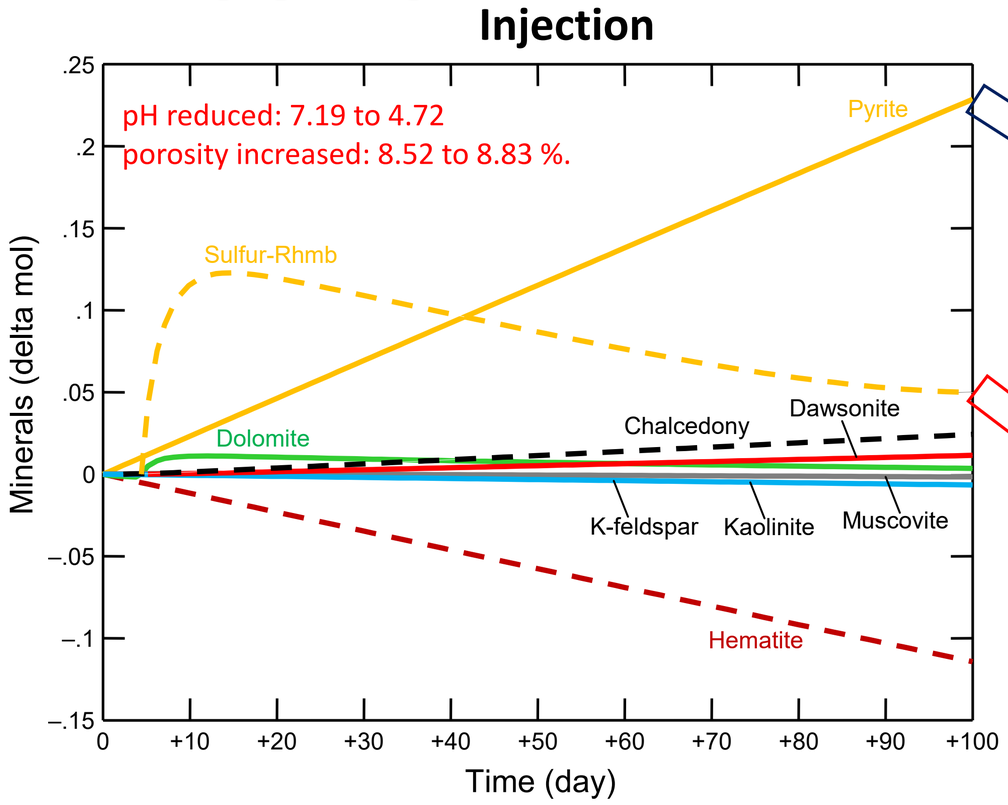
$CaMg(CO_3)_2 + 2\ CO_{2(g)} + SO_4^{2-} + 8.061\ H_2O + 16.24\ SiO_2 + 2\ KAlSi_3O_8 + 6.061\ Fe_2O_3 =$
$= CaSO_4 + 6.061\ Mg_{0.165}Fe_2Al_{0.33}Si_{3.67}O_{10}(OH)_2 + 4\ HCO_3^- + 2\ K$

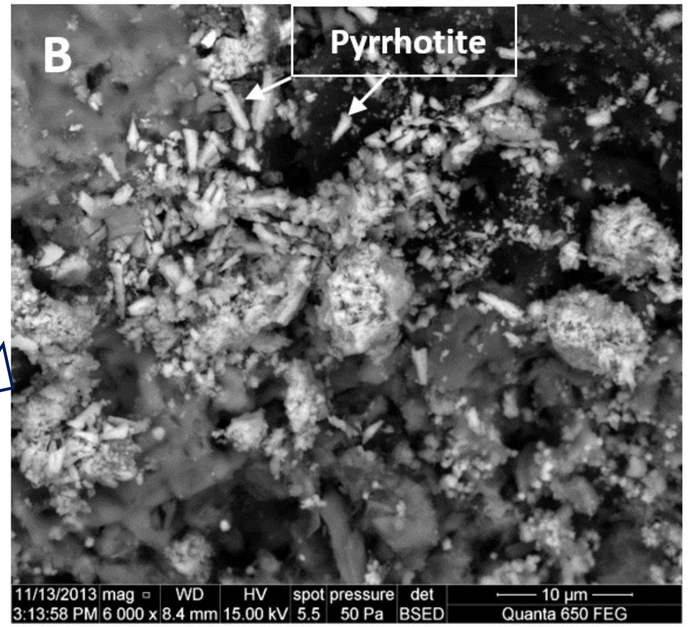
$2\ H^+ + CaMg(CO_3)_2 + SO_4^{2-} = CaSO_4 + 2\ HCO_3^- + Mg^{2+}$

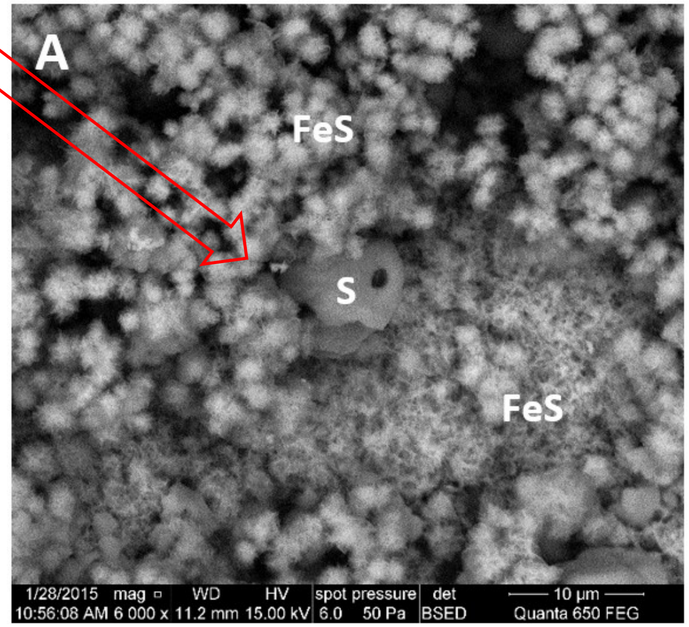
pH increases to 5.66, porosity slightly decreases to 8.68%, f_{CO2} drops to 0.63 bar, and f_{H2S} is close to zero. The $CO_{2(aq)}$ conc. decreases to 0.011 mol / kg, and HCO_3^- to 0.004 mol /kg, $H_2S_{(aq)}$ and HS^- are depleted.

RESULTS

Example – 1927







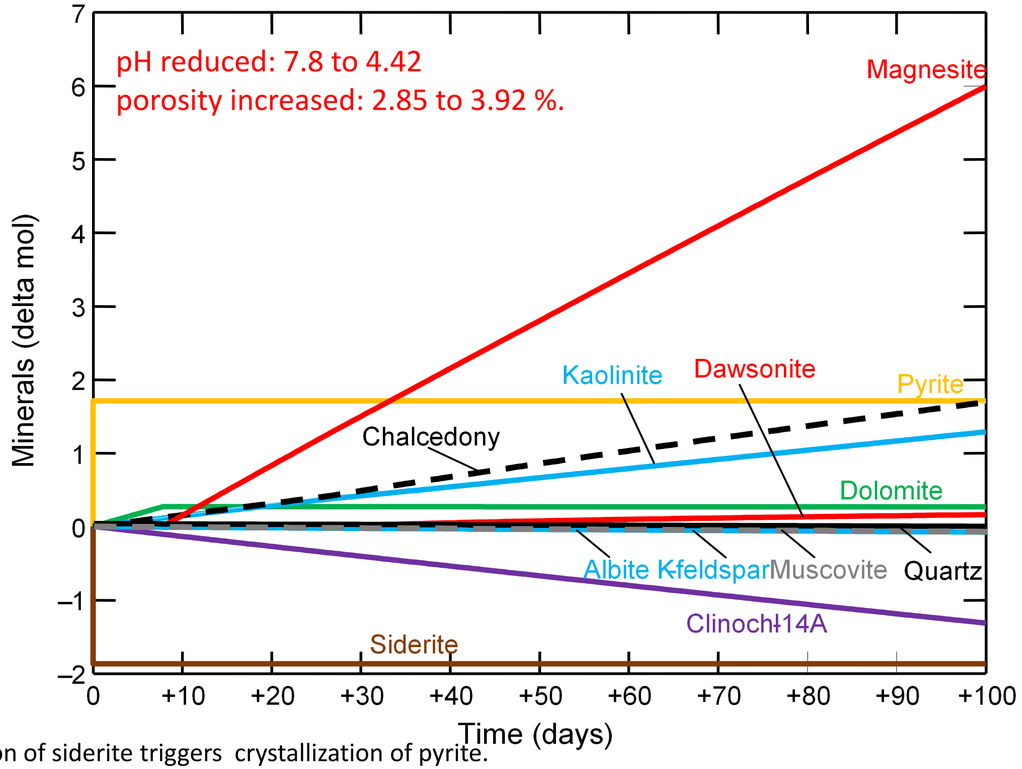
B - fine elongated pyrrhotite crystals were identified locally

A - secondary elemental sulfur in the form of irregular crystals, and radial clusters of fine iron sulphide (FeS) crystals

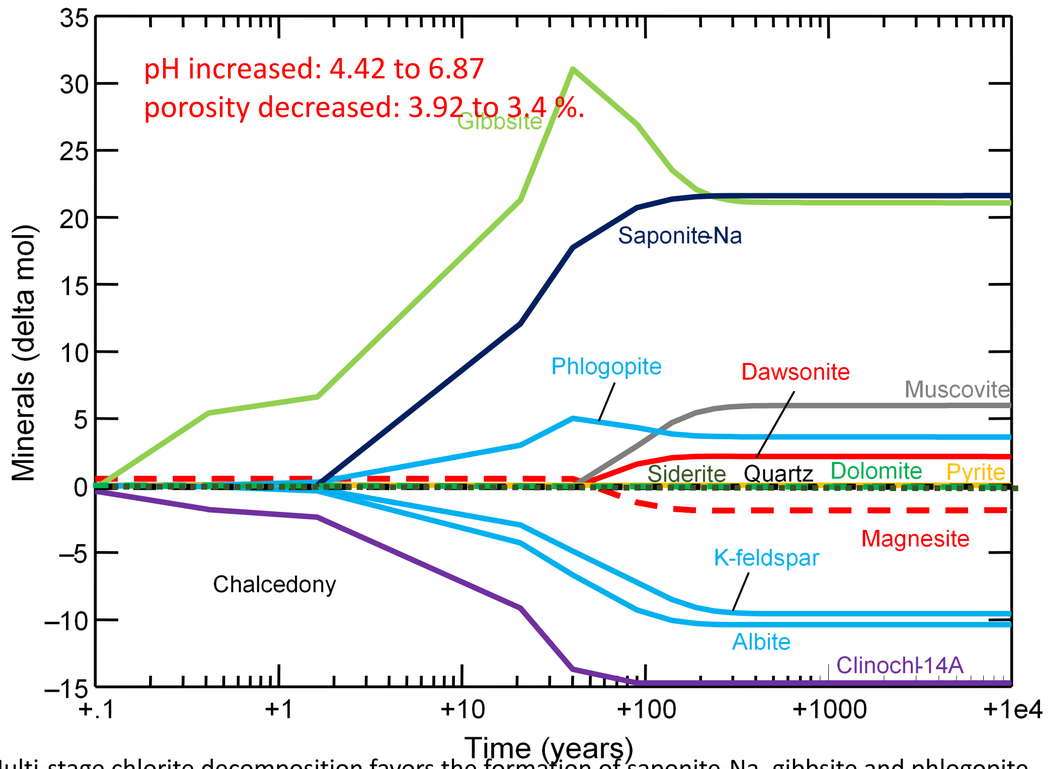
RESULTS

Example – C7

Injection



Storage



Degradation of siderite triggers crystallization of pyrite.

$4\ H_2S_{(g)} + 4\ FeCO_3 = 4\ FeS_2 + CH_{4(g)} + 6\ H_2O + 3\ CO_{2(g)}$

Decomposition of clinchlore releases Mg^{2+} ions, which can participate in the crystallization of dolomite. Magnesite crystallization begins from the eight day of modeled injection:

$Mg_5Al_2Si_3O_{10}(OH)_8 + 5\ CO_{2(g)} = 5\ MgCO_3 + Al_2Si_2O_5(OH)_4 + SiO_2 + 2\ H_2O$

Porosity increased from 2.85 to 3.92%, $CO_{2(aq)}$ conc. to 0.85 mol/kg, and HCO_3^- to 0.02 mol/kg, $H_2S_{(aq)}$ to 1.78 mol/kg, and HS^- to 0.014 mol/kg. pH dropped from 7.8 to 4.42.

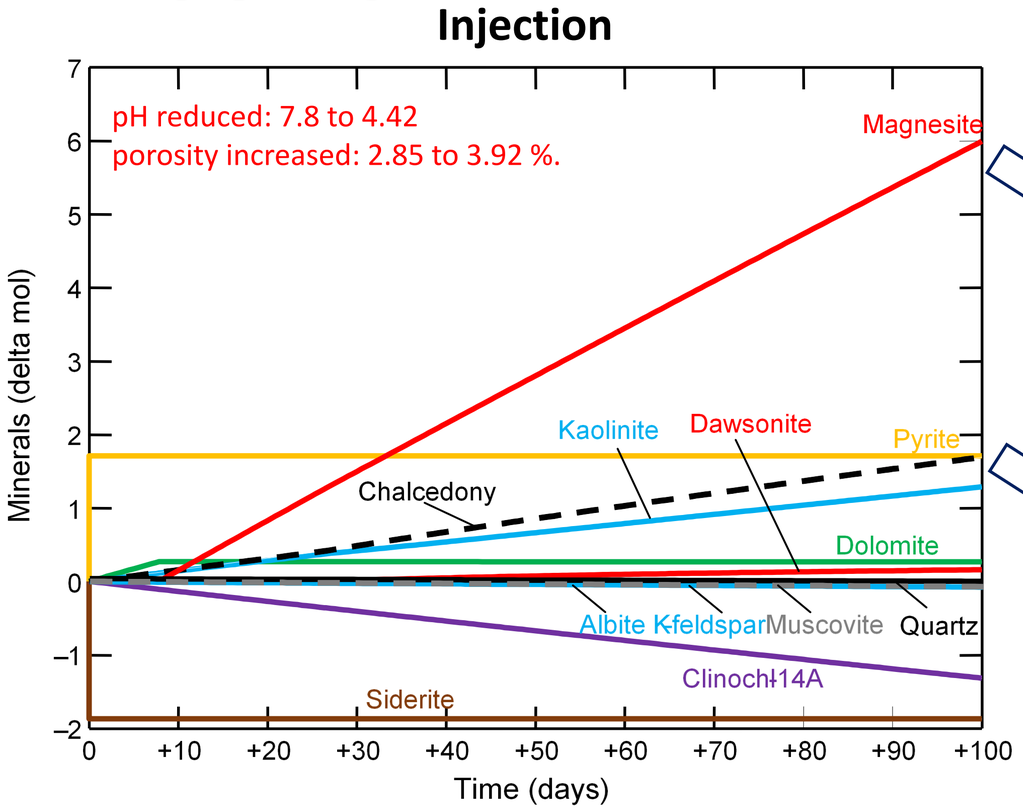
Multi-stage chlorite decomposition favors the formation of saponite-Na, gibbsite and phlogopite, which then supports muscovite crystallization:

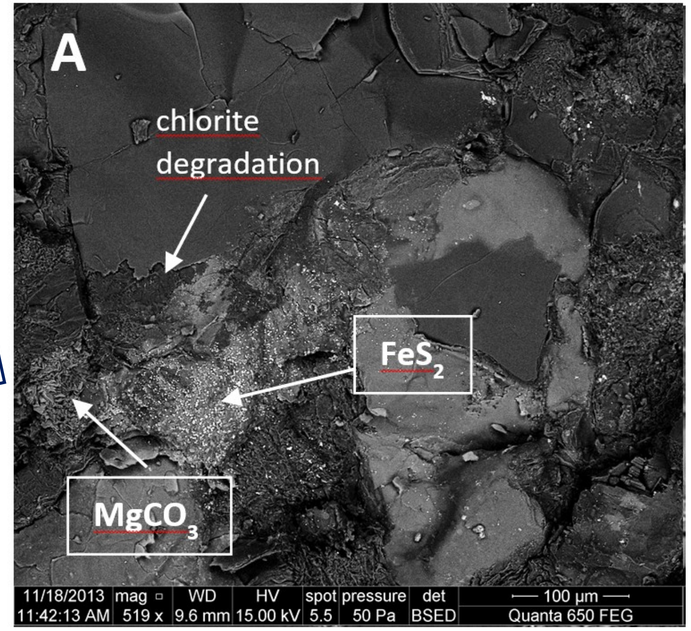
$KAlMg_3Si_3O_{10}(OH)_2 + 2\ Al(OH)_3 + 6\ CO_{2(g)} = KAl_3Si_3O_{10}(OH)_2 + 3\ Mg^{2+} + 6\ HCO_3$

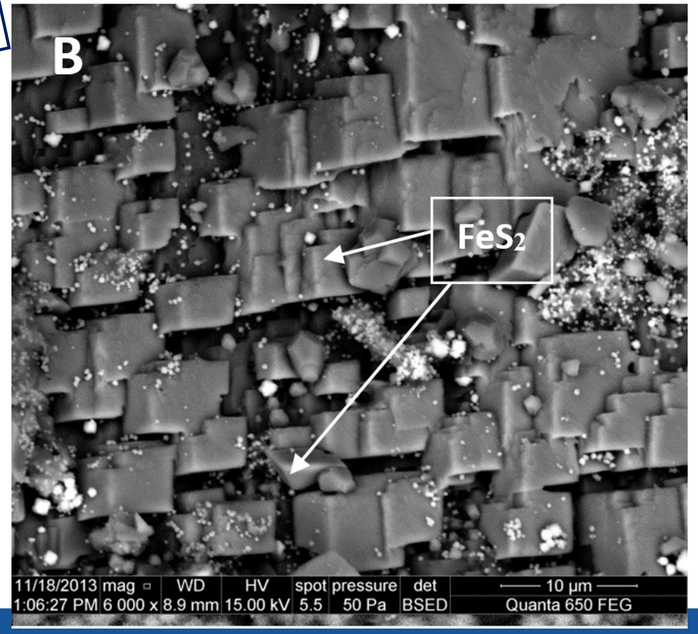
Porosity decreases by 0.52 percentage points, pH increases to 6.87. f_{CO2} decreases to 0.006 bar and f_{H2S} to 13.34 bar. Drops: $H_2S_{(aq)}$ to 0.68 mol/kg; and HS^- up to 1.44 mol/kg; HCO_3^- up to 0.001 mol / kg; $CO_{2(aq)}$ conc. is close to 0.

RESULTS

Example – C7



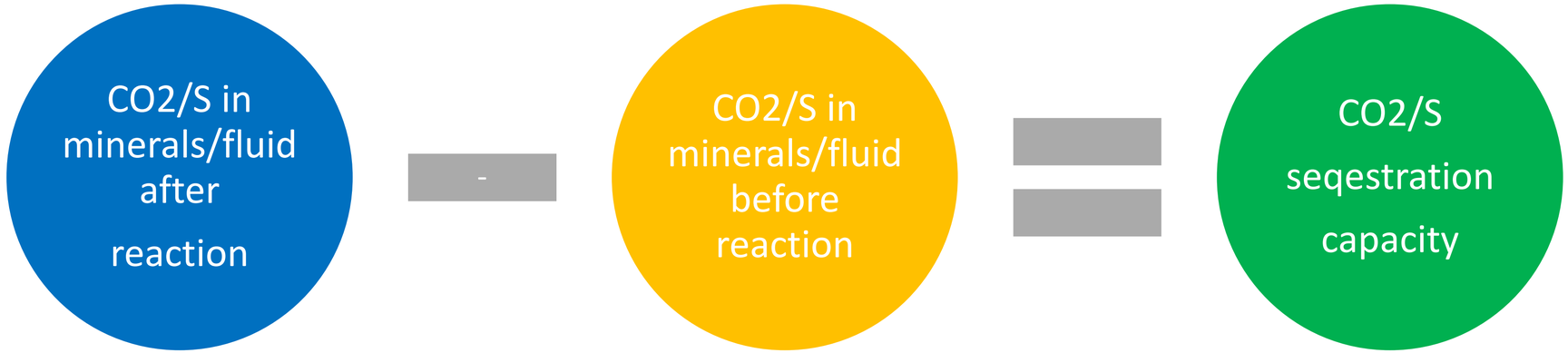




A- Degraded chlorite plate with secondary FeS_2 and $MgCO_3$

B - Initially corroded siderite rhombohedrons with secondary FeS_2 crystals

SEQUESTRATION CAPACITY



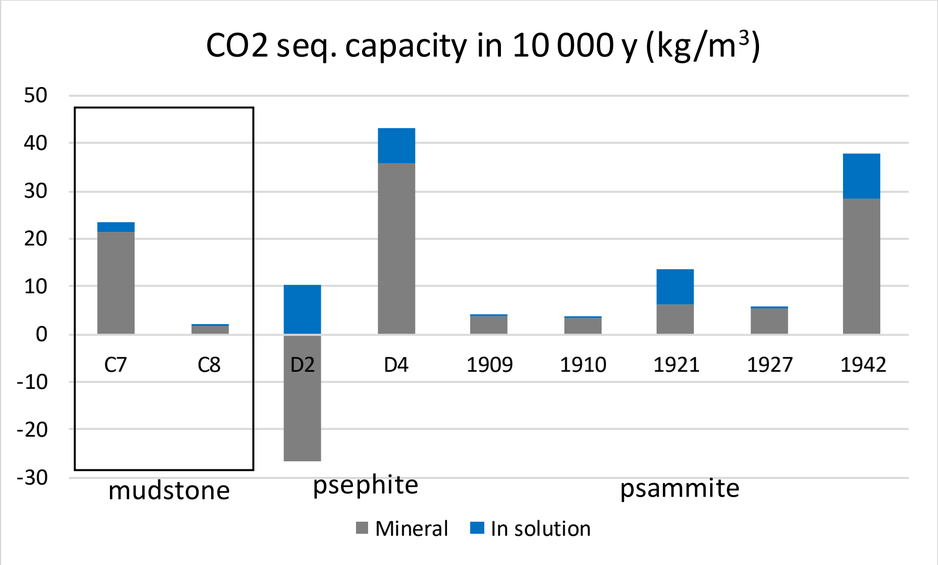
Mineral capacity - given the unitary volume of rock (UVR) of 0.01 m^3, and taking the primary porosity - n_p. we calculated the volume of the rock matrix in $1m^3$ of formation, expressed in UVR's – equal to $100(1-n_p)$. Due to the modeled reactions, per each UVR, certain quantities of carbonates or sulfides/sulfates were dissolved or precipitated, and based on their balance the amounts of immobilized CO_2 and S were calculated.

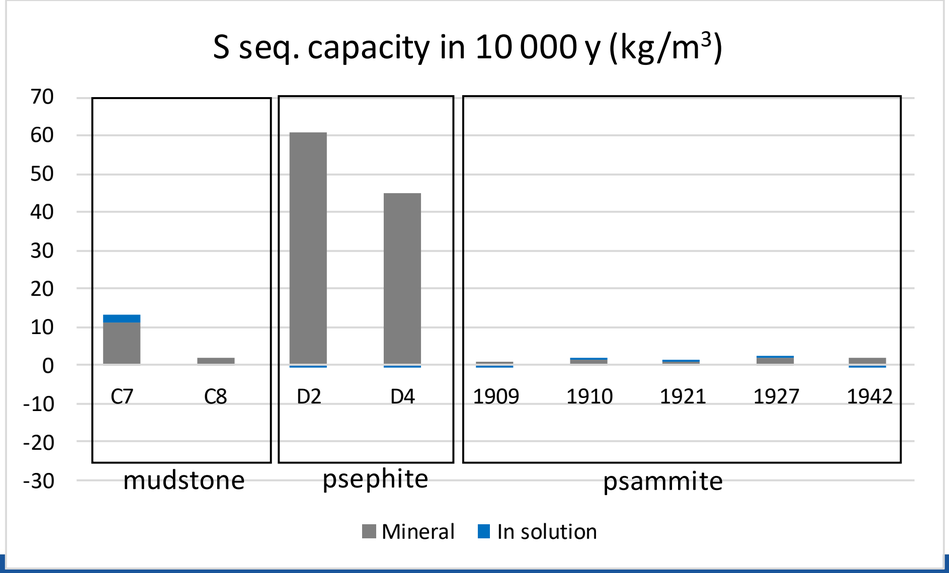
Capacity in fluid - modeled pore water chemistry enabled the assessment of the quantity of carbon dioxide and hydrogen sulfide trapped in solution. Pore space after simulated 10 ka of storage is assumed to be filled with brine of known concentrations of aqueous species (for carbon dioxide e.g.: HCO_3^-, $CO_{2(aq)}$, CO_3^{2-}, $NaHCO_3$, for hydrogen sulfide: $H_2S_{(aq)}$, HS^-). The amount of CO_2 and S trapped in solution is calculated based on the pore space volume in $1m^3$ of formation multiplied by the sum of CO_2 or S, contained in the abovementioned species

SEQUESTRATION CAPACITY

Sample	Sequestration capacity [kg/m³]	CO_2 +H_2S injected Final value at t: t = 100 d			t = 1 000 y			t = 10 000 y		
		CO_2	C	S	CO_2	C	S	CO_2	C	S
C7	1. Mineral	20.01	5.46	0.00	21.60	5.90	11.39	21.60	5.89	11.36
	2. In solution	3.41	0.93	2.12	1.95	0.53	2.13	1.95	0.53	2.13
	Sum (1+ 2)	23.42	6.39	2.12	23.55	6.43	13.52	23.55	6.42	13.49
C8	1. Mineral	0.67	0.18	0.35	1.50	0.41	2.16	1.50	0.41	2.16
	2. In solution	1.24	0.34	1.78	0.37	0.10	0.00	0.37	0.10	0.00
	Sum (1+ 2)	1.91	0.52	2.13	1.87	0.51	2.16	1.87	0.51	2.16
D2	1. Mineral	-34.26	-9.35	49.77	-26.62	-7.27	60.59	-26.66	-7.28	60.68
	2. In solution	18.29	4.99	7.90	10.37	2.83	-0.01	10.39	2.83	-0.01
	Sum (1+ 2)	-15.97	-4.36	57.67	-16.25	-4.44	60.58	-16.27	-4.45	60.67
D4	1. Mineral	-14.35	-3.92	34.02	-3.45	-0.94	33.85	35.72	9.75	44.95
	2. In solution	9.88	2.70	11.13	5.78	1.58	11.10	7.68	2.10	-0.01
	Sum (1+ 2)	-4.47	-1.22	45.15	2.33	0.64	44.95	43.40	11.85	44.94
1909	1. Mineral	9.55	2.61	0.70	0.38	0.11	1.04	3.91	1.15	0.95
	2. In solution	4.28	1.17	0.27	3.70	1.01	-0.09	0.12	0.03	-0.08
	Sum (1+ 2)	13.83	3.78	0.97	4.08	1.12	0.95	4.03	1.18	0.87
1910	1. Mineral	0.20	0.06	1.47	0.19	0.06	1.48	3.26	0.94	1.54
	2. In solution	3.14	0.86	0.20	3.17	0.86	0.20	0.03	0.01	0.12
	Sum (1+ 2)	3.34	0.92	1.67	3.36	0.92	1.68	3.29	0.95	1.66
1921	1. Mineral	0.15	0.05	1.12	0.25	0.08	1.18	6.09	1.96	1.21
	2. In solution	8.73	2.38	0.43	9.45	2.58	0.47	7.65	2.09	0.40
	Sum (1+ 2)	8.88	2.43	1.55	9.70	2.66	1.65	13.74	4.05	1.61
1927	1. Mineral	0.27	0.08	1.69	5.40	1.62	1.76	5.39	1.61	1.78
	2. In solution	5.25	1.43	0.33	0.05	0.01	0.22	0.05	0.01	0.22
	Sum (1+ 2)	5.52	1.51	2.02	5.45	1.63	1.98	5.44	1.62	2.00
1942	1. Mineral	-23.61	-7.25	38.23	28.72	8.82	2.14	28.55	8.76	2.14
	2. In solution	15.91	4.34	0.23	9.35	2.55	-0.12	9.12	2.49	-0.12
	Sum (1+ 2)	-7.70	-2.91	38.46	38.07	11.37	2.02	37.67	11.25	2.02

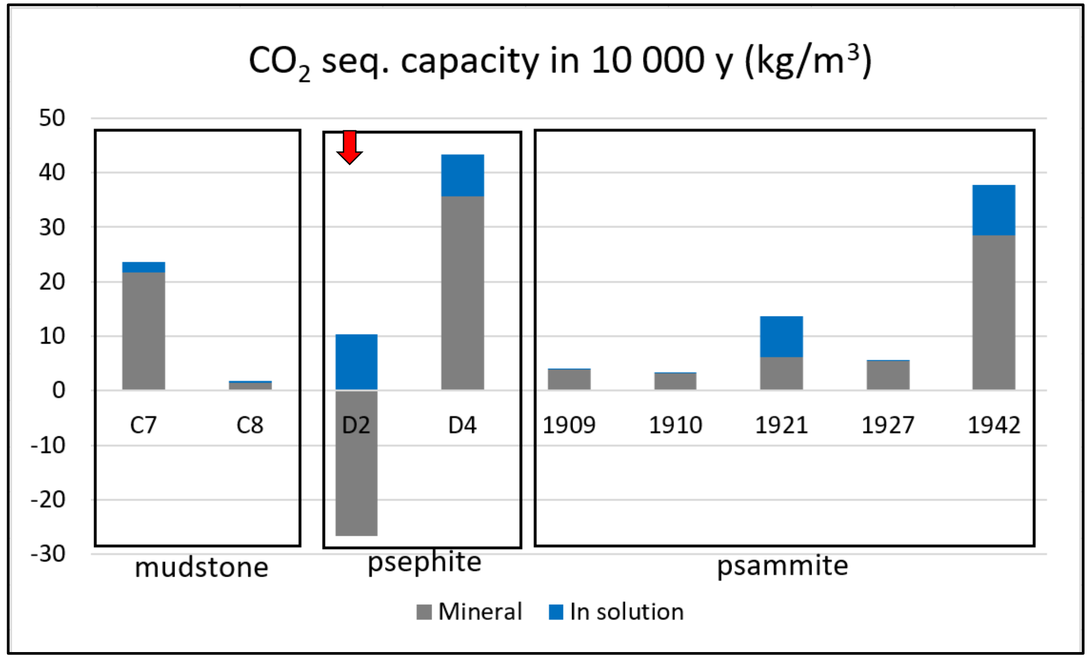
SEQUESTRATION CAPACITY

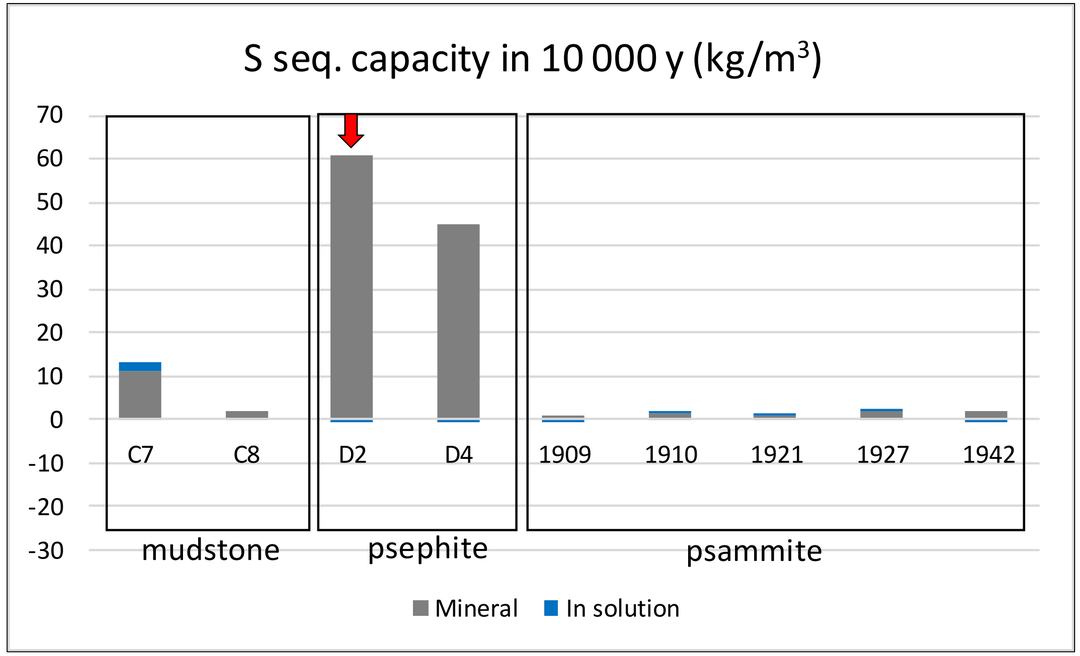




Sample	Sequestration capacity [kg/m³]	t = 10 000 y		
		CO_2	C	S
C7	1. Mineral	21.60	5.89	11.36
	2. In solution	1.95	0.53	2.13
	Sum (1+ 2)	23.55	6.42	13.49
C8	1. Mineral	1.50	0.41	2.16
	2. In solution	0.37	0.10	0.00
	Sum (1+ 2)	1.87	0.51	2.16
D2	1. Mineral	-26.66	-7.28	60.68
	2. In solution	10.39	2.83	-0.01
	Sum (1+ 2)	-16.27	-4.45	60.67
D4	1. Mineral	35.72	9.75	44.95
	2. In solution	7.68	2.10	-0.01
	Sum (1+ 2)	43.40	11.85	44.94
1909	1. Mineral	3.91	1.15	0.95
	2. In solution	0.12	0.03	-0.08
	Sum (1+ 2)	4.03	1.18	0.87
1910	1. Mineral	3.26	0.94	1.54
	2. In solution	0.03	0.01	0.12
	Sum (1+ 2)	3.29	0.95	1.66
1921	1. Mineral	6.09	1.96	1.21
	2. In solution	7.65	2.09	0.40
	Sum (1+ 2)	13.74	4.05	1.61
1927	1. Mineral	5.39	1.61	1.78
	2. In solution	0.05	0.01	0.22
	Sum (1+ 2)	5.44	1.62	2.00
1942	1. Mineral	28.55	8.76	2.14
	2. In solution	9.12	2.49	-0.12
	Sum (1+ 2)	37.67	11.25	2.02

SEQUESTRATION CAPACITY





Max. sequestration capacity, formed exclusively by mineral sequestration was for the Dębowiec Fm. Miocene, D4 rock sample - 43,4 kg CO_2/m^3 (including 7.7 kg in solution) and 44,9 kg S/m^3 (only in mineral form). D2 sample of the same formation, more rich in ankerite, is able to sequester even more sulfur – 60.7 kg S/m^3, but at the expense of release of 26,7 kg CO_2/m^3 due to decomposition of primary carbonate minerals.

$$CaMg_{0.3}Fe_{0.7}(CO_3)_2 + 0.35\ H^+ + 1.225\ H_2S + 0.175\ SO_4^{2-} = 0.7\ FeS_2 + 0.7\ CO_{2(aq)} + 0.7\ CaCO_3 + 0.3\ CaMg(CO_3)_2 + 1.4\ H_2O$$

For mudstones from the USCB Paralic series sequestration capacity equaled to 23.60 kg CO_2/m^3 (incl. 2.0 kg in solution) and 13.5 kg S/m^3 (2.1 kg in solution).

For the Małopolska Block the most promising value was 37.70 kg CO_2/m^3 (including 9.1 kg in solution) and 2.0 kg S/m^3 but only in minerals.
Such CO_2 sequestration capacities are roughly 2 - 4 times higher than in case of the Gulf Coast arenaceous sediments

CONCLUSIONS

01 Dissolution of skeletal grains, as the dominant process (the most distinct in carbonates and chlorite) was determined by means of SEM analysis in all of the samples.

02 Increase in porosity at the injection stage, depending on the mineralogy of samples was caused by the decomposition of calcite and siderite or ankerite (Dębowiec Fm.), daphnite, clinochlore, and siderite (Paralic series) and hematite, ankerite, dolomite (Małopolska Block).

03 Among the secondary minerals enabling the trapping of CO_2 and S in simulated storage we observed: dolomite and pyrite (Dębowiec Fm.), dolomite, calcite and pyrite (Paralic series) and siderite, anhydrite, pyrite (Małopolska Block).

04 Maximum calculated mineral-trapping capacity, calculated based on the results of kinetic modeling, reached 43.4 $kgCO_2/m^3$ and 44.9 kgS/m^3 for CO_2+ H_2S co-injection into the Dębowiec Fm. Miocene rock.

05 When storing CO_2+H_2S in a rock rich in carbonates, significant decomposition of e.g. dolomite should be predicted - leading to the release of CO_2 - the desequestration process.

THANK YOU

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