

DETERMINATION OF CO₂ AND H₂S INFLUENCE ON MINERALOGICAL COMPOSITION AND PETROPHYSICAL PARAMETERS OF AQUIFER AND CAP ROCKS

Krzysztof Labus¹⁾, Grzegorz Leśniak²⁾, Renata Cicha-Szot²⁾

¹⁾Silesian University of Technology, 44-100 Gliwice, Poland;

²⁾Oil and Gas Institute-NRI, Lubicz 25A, 31-503 Kraków, Poland

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ABSTRACT

We designed and performed a comprehensive study, enabling the hydrochemical models, calibrated on the basis of experiments, considering the impact of acid gases: CO₂ and H₂S on deep hydrochemical systems. Representative core samples of aquifers and cap rocks were selected, and the composition of mineral assemblages determined by means of microscopy and XRD analysis. Porosity of the rock samples was examined by Mercury Intrusion Porosimetry, prior to the experimental tests. Samples were placed in the autoclave filled with brine, and acid gas, to reproduce water-rock-gas interactions at the PVT regime of possible storage site. The experiments were carried on for 75 days in order to simulate the initial period of storage. Reacted samples were examined by means of scanning electron microscope with an EDX detector. Analysis of reacted samples revealed significant changes in mineral constitution and structure – mineral dissolution and new minerals formation during autoclave experiments. It was also observed, that pressure of approx 150 bar, exerted on clay min. sheets, forces water to be expelled, and this, further enables oxidation of pyrite, and precipitation of secondary minerals. Geochemical modeling, based on the experimental results, allowed for calculation the amounts of acid gas trapped in mineral phases, in 20 000 years of storage.

INTRODUCTION

Acid gas (mainly CO₂ and, H₂S) interactions with rocks became of interest during the last decades due to greenhouse effect abatement (e.g. Holloway, 2005), and in the case of carbon dioxide - enhanced oil and gas recovery and energized fluid fracturing (Sinal, Lancaster, 1987). Although a considerable research and published work on this subject, there are still uncertainties about the behaviour of rocks under the influence of gases, in such artificial geochemical systems. In order to investigate these phenomena in selected aquifers and low permeability rock formations of Central Europe, we designed and performed a comprehensive study, enabling the hydrochemical models, calibrated on the basis of experiments, considering the impact of acid gases: CO₂ and H₂S.

MATERIALS AND METHODS

Core samples were selected to represent Upper Carboniferous sandstones and mudstones of the Upper Silesian Coal Basin, and additionally Jurassic marls the Mikulov Formation of the Vienna Basin, and gas shales of Lower Paleozoic of the East European Craton.

Composition of mineral assemblages was determined by means of petrographic and planimetric analysis of thin sections, conducted using Axioscope Zeiss Microscope. Additionally XRD analysis was performed on Bruker-AXS D8 X-ray diffractometer, with the use of CoK α lamp in the following conditions: voltage 40kV, intensity 40mA, angle range 2 Θ : 6 - 80°, step 0.014°. The semi quantitative interpretation of results was aided by the Bruker Topas 4.1. software, and PDF-2, v. 2011 (International Centre for Diffraction Data) helped in qualitative determination of phases.

Scanning electron microscope FEI Quanta-650 FEG (15kV, 8–10 nA, 50 Pa vacuum), with EDX analyzer was used in examination of mineral phases in the bare samples before and after autoclave experiments.

For determining the porosimetric properties of the examined rocks the Mercury Intrusion Porosimetry was used - Autopore 9220 Micrometrics. Cylindrical samples of about 10 g were cut from the rock. Prior to testing the material was dried at 110°C to constant mass.

Experiments

Samples were placed in the autoclave (Hastelloy EZE Seal 1000 ml - Autoclave Engineers), optionally filled with brine, CO₂ and/or H₂S were injected to the desired pressure 60 – 180 bar, and the temperature was set at required level 40 - 80°C (\pm 0.2°C). Experiment was carried on for 40-75 days in order to simulate the initial period of storage (after the termination of injection). The reacted samples were dried in a vacuum dryer and examined by means of SEM - EDX and XRD analysis.

Numerical modeling

Chemical composition of the pore waters for the purpose of the simulation was obtained by equilibration of the relevant formation water with the minerals assemblage typical for the modeled environment. The pore waters, of Cl-Na type, were characterized by TDS ranging from 34,3 to 128,1 g/l and pH between 6,18 and 7,37.

Formation pressures according to hydrostatic regime were assumed in modeling; temperatures were estimated basing on the direct measurements and archival data. The kinetic dissolution/precipitation rate equation, simplified after Lasaga (1984) was used in the calculations. The kinetic rate constants for minerals involved in modeled reactions were taken from literature (eg. Palandri, Kharaka, 2004) and recalculated for the formation temperature.

Modeling of water-rock-gas interactions was performed in two stages. The first one was aimed at simulating the immediate changes in the aquifer and insulating rocks impacted by the beginning of CO₂ and/or H₂S injection, the second – enabled assessment of long-term effects of sequestration. Simulations were performed with use of the Geochemist's Workbench (GWB) software (Bethke, 2008). The GWB package was used for equilibrium, and kinetic modeling of water-rock-gas system. The reactions quality and

progress were monitored and their effects on formation porosity and mineral sequestration capacity (C and/or S trapping) were calculated.

RESULTS AND DISCUSSION

Experimental results

Examination of the reacted material by means of SEM analysis verified the process of skeletal grains dissolution (the most intense in carbonates – Figure 1), observed in all of the samples. Apparent cavities, developed parallel to cleavage planes in microcline, were formed due to selective etching of the potassic lamellae relative to the sodic ones – as it was also reported by Kaszuba et al., 2003.

Amongst the secondary components of the rock also the framboidal pyrite crystals are found. On the surface of quartz grains small pits are being developed, initiating the process of the crystals destruction – Figure 2. On the other hand secondary minerals formation leads to partial occlusion of the pore space. Dawsonite crystals, observed only in the samples after the experiments; were found to be formed in the pore space between framework grains and within clay mineral blades.

In case of the high pressure experiment in gas-rock systems (air dry sample, no brine in autoclave) the effect seems to be dependent on the physical action of injected gas and temperature. For the Mikulov marl sample, the pressure of 150 bar, exerted at T 80°C on clay mineral sheets, forced water to be expelled. This, further enabled some oxidation of pyrite. In such an environment created, the desorbed cations may form secondary minerals – e.g. gypsum, celestite (identified by EDX analysis) – Figure 3. At lower pressure experiment (80 bar, 80°C) however, there were no apparent effects of pure CO₂ interaction with the gas shale from Polish Paleozoic province. Lower pressure did not allow for water migration out of clay sheets and prevented mineralogical transitions of the mineral assemblage. Hence we suppose that this is the abnormal pressure to trigger the phenomena as, in the analyzed case, precipitation of secondary minerals.

SEM/EDX analysis of mudstones reacted in brine with H₂S-CO₂ mixture injected (partial pressures: 12 and 108 bar respectively, 50°C), revealed elemental sulfur, surrounded by midget FeS₂ crystals – Figure 4; no other secondary minerals were observed.

Numerical modeling - Gas-rock-water reactions

- Equilibrium modeling was applied to reproduce the composition of pore water. The model required the thermodynamic data for the reacting minerals, their abundance in the assemblages within the host- and the cap rock, relative fraction of pore water and information on its physic-chemical parameters.
- Kinetic modeling allowed for evaluation of changes in the formation, due to the injection and storage of gas. This enabled assessment of volume and amount of mineral phase precipitating or dissolved during simulated reactions, and their influence on porosity, and amounts of gases sequestered.

At the first stage, the injection of CO₂, lasting for 100 days, causes the increase of gas fugacity. In effect a significant elevation of CO₂ (aq) concentrations, and a drop of pore waters reaction are observed. In such environments the increase of porosity – Figure 5, is controlled mainly by the dissolution carbonates and much less of kaolinite. Minerals

precipitating in CO₂ experiment are chalcedony and dawsonite - NaAlCO₃(OH)₂, while iron sulfides and elemental sulfur are secondary minerals in H₂S-CO₂ sequestration experiment. During the 20 000 years of storage the total porosity decreases in the sandstones by several percent points – Figure 5, mainly due to precipitation of calcite, dolomite and dawsonite in CO₂ experiment, in favor of the rock insulating properties. The evaluation of long-term impact of acid gas sequestration on the aquifer rocks is still under research.

Sequestration capacity

Results of core analyses and geochemical modeling allowed for the assessment of sequestration capacity of the formations analyzed. Assuming the unitary volume of modeled rock - UVR - equal to 0.01 m³ and taking the primary porosity (measured on cores) - n_p, we calculated the volume of the rock matrix in 1m³ of formation, measured in UVR units – equal to 100(1-n_p).

Modeled reactions led to dissolution or precipitation of certain quantities of carbonates, sulfides or sulfates per each UVR. On this basis the balance of CO₂ and/or H₂S was calculated. Amounts of carbon dioxide and /or hydrogen sulfide trapped in solution were calculated based on modeled chemical constitution of pore water, assuming that after simulated storage time the final pore space (calculated on the balance of modeled volumes of primary and secondary minerals) is filled with pore fluid of known (modeled) concentrations of CO₂ and/or H₂S aqueous species: eg. HCO₃⁻, CO_{2(aq)}, SO₄²⁻, HS⁻, etc.

For example: the calculated mineral-trapping capacity, for most of the sandstone aquifers varies between 1.2 and nearly 1.9 kgCO₂/m³, and for cap rocks is between 0.89 and 1.42 kgCO₂/m³ (Labus, Bujok, 2011), which is 2-3 times lower than for the Gulf Coast arenaceous sediments (Xu et al., 2003) considered as perspective CO₂ repositories. Solubility trapping capacity is the highest for the aquifers of high final porosities, and reaches over 4.0 kgCO₂/m³.

CONCLUSION

Two aims of the study were achieved: determination of the influence of acid gases on the mineralogical composition and porosity of aquifers and cap rocks, and evaluation of trapping capacity of acid gas.

Dissolution of skeletal grains, as the dominant process (the most distinct in carbonates) was determined by means of SEM analysis in all of the samples, in gas-rock-water systems. In high pressure experiment, in gas-rock system, the higher pressure probably expelled water from clay mineral sheets, and in such an environment the desorbed cations formed secondary sulphate minerals.

Modeling study resulted in the observation, that at the stage of CO₂ injection, the increase of porosity, is controlled mainly by the dissolution carbonates, which exceed the volume of secondary minerals. After 20 000 years of simulated storage, the total porosity decreased in the sandstones by several percent points, mainly due to precipitation of carbonates in CO₂ experiment, and pyrite and elemental sulfur in CO₂-H₂S experiment, in favor of the rock insulating properties

Calculations based on the results of core analyses and modeling, revealed the average mineral trapping capacity values, up to 1.9 kgCO₂/m³ for the sandstones and 1.42 kgCO₂/m³ for the cap rocks. Solubility trapping capacity is directly proportional to the final porosity of the reacted rocks.

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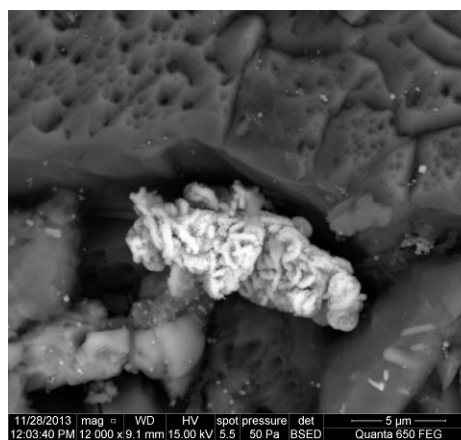
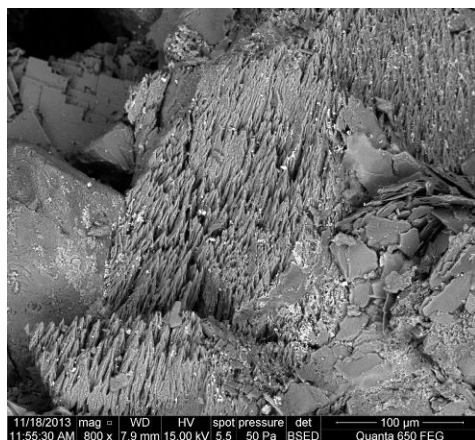


Fig. 1. Deeply corroded calcite grain covered with tiny crystals of iron sulfides. H₂S/CO₂ experiment.

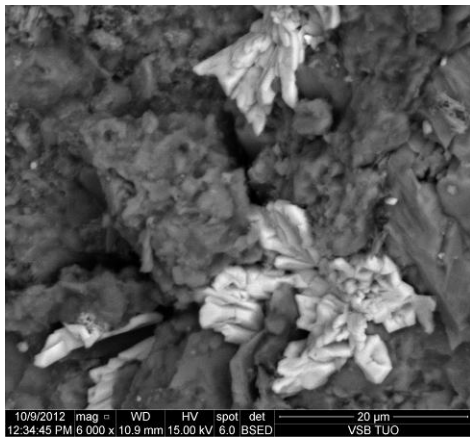


Fig. 2. FeS aggregate and initially corroded quartz grain. H₂S experiment.

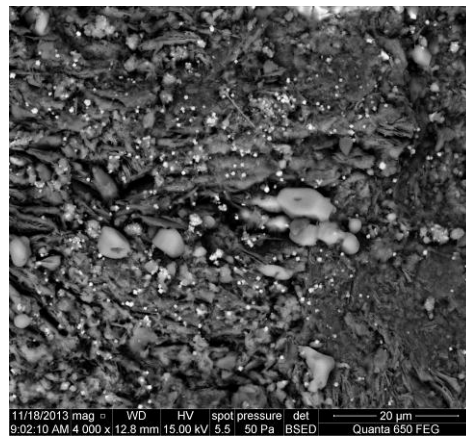


Fig. 3. Secondary rosettes of celestite in Mikulov Marl sample. Pure CO₂ experiment.

Fig. 4 . Elemental sulfur (centre of image), surrounded by midget FeS₂ crystals. H₂S/CO₂ experiment.

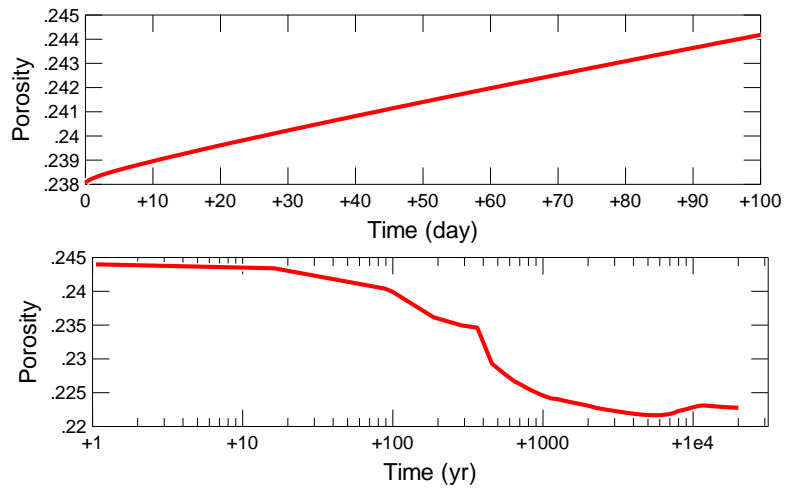


Fig. 5. Example changes in porosity on the stage of CO₂ injection (100 days), and storage (20 ka) - a sandstone sample