Petrophysical and Mineralogical Research on the Influence of CO₂ Injection on Mesozoic Reservoir and Caprocks from the Polish Lowlands

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Résumé — Études pétrographique et minéralogique de l'impact de l'injection de CO₂ dans les roches réservoirs de la Basse Plaine de Pologne — Afin de mener des recherches sur l'impact CO₂ – roche – saumures, nous avons développé un modèle de simulation des conditions de gisement, pour lesquelles l'injection de dioxyde de carbone est envisagée. Des analyses ont été effectuées sur des échantillons de carotte de roche provenant des réservoirs et de la couverture, prélevés dans les forages de Pagórki (formations du Crétacé) et de Brześć Kujawski (formations du Jurassique). Ces échantillons ont été soumis, avant et après les expériences, à des analyses pétrographiques et minéralogiques classiques, afin de déterminer les variations induites par les expériences. Les études menées ont montré que les réservoirs possèdent de bonnes propriétés de stockage de CO₂, et les roches de couverture de bonnes propriétés d'étanchéité. L'expérimentation réalisée ne montre pas d'impact notable du gaz injecté sur les propriétés des roches réservoir analysées.

Abstract — Petrophysical and Mineralogical Research on the Influence of CO₂ Injection on Mesozoic Reservoir and Caprocks from the Polish Lowlands — Special equipment, simulating formation conditions, was designed to study interactions between injected CO₂, rocks and brines. The investigations were carried out on samples collected from reservoir and caprocks of the Pagórki (Cretaceous deposits) and Brześć Kujawski (Jurassic deposits) boreholes. Mineralogical and petrographic investigations were carried out on the samples before and after the experiment to determine changes occurring as a result of the processes. The investigations proved that these rocks show good quality reservoir and sealing properties. The experiment did not significantly worsen the reservoir properties of the rocks.

INTRODUCTION

Phenomena of CO₂ injection effects on rocks and reservoir fluids refer to many aspects, such as: kinetics of CO₂ dissolution in reservoir fluids, kinetics of mineral trapping, appearance of new mineral phases, migration of gas within the reservoir, evaluation of the geological storage capacity, sealing properties of caprocks, and many others. Study of these processes is very important and permits one to plan in details safe underground CO₂ storage operations.

Among many problems concerning geological storage of CO₂, the effect of the gas on rocks and reservoir fluids is highlighted. It is necessary to take into consideration during preliminary studies the usefulness of rocks and geological structures selected for underground storage.

After injection, CO₂ interacts with the rocks and reservoir liquids: it is dissolved in reservoir fluids (Muller *et al.*, 2009; Zeiduoni *et al.*, 2009), reacts with minerals of the rock matrix (Gunter *et al.*, 1993), undergoes hydrodynamic trapping (Bertier *et al.*, 2006) and, if the sealing is not perfect, can migrate outside the deposits which were selected for underground storage deposits (Gaus *et al.*, 2005). These phenomena occur during and after CO₂ injection into the reservoir. They effect the capacity of the CO₂ storage reservoir and the sealing properties of caprocks. During the CO₂SINK project, Zemke *et al.* (2009) analysed the effect of injected CO₂ on changes in petrophysical parameters of reservoir rocks under simulated conditions. In a similar way, Nightingale *et al.* (2009) examined the influence of CO₂ and brine on carbonate and siliceous rocks. Crédoz *et al.* (2009) analysed alterations in clay minerals due to reactions with CO₂ and brine. Wollenweber *et al.* (2009) conducted similar investigations on carbonate and marly rocks. Bertier *et al.* (2006, 2009a) and Wigand *et al.* (2008) analysed interactions within the systems of CO₂-sandstones-reservoir fluids and CO₂ – clay minerals – reservoir fluids (Bertier *et al.*, 2009b). Luquot *et al.* (2009) examined the influence of CO₂ and brine on chlorite- and zeolite-rich sandstones. Knowledge of the interaction processes between CO₂, rock and reservoir fluids is also

important for optimisation of the technological process of CO₂ injection into underground reservoirs and for evaluation of CO₂ storage safety. Any ignorance in these areas can result in gas leakage from the underground reservoir.

Poland has favourable geological conditions for CO₂ sequestration (Tarkowski, 2008; Tarkowski and Uliasz-Misiak, 2005, 2006; Tarkowski *et al.*, 2009). Research on various aspects of CO₂ storage (*e.g.* CO₂-brine-rocks interaction, kinetic of reactions, CO₂ fluid flow studies, etc.) is currently being considered. This paper presents the results of petrophysical and mineralogical investigations. Experimental analyses on rock samples collected from selected Mesozoic reservoir horizons were made to assess the influence of CO₂ injection on reservoir and caprocks using a special instrument constructed for the purpose of the study. Petrophysical and mineralogical investigations were carried out on rock samples before and after the experiment, performed in conditions corresponding to actual formation conditions. Physicochemical analyses of experimental brines were also carried out.

1 MATERIALS

Rock samples were derived from drill cores of the Pagórki IG 1 (samples Nos. 1-4) and Brześć Kujawski IG 2 (samples Nos. 5-8) boreholes, from reservoir horizons (representing deep saline aquifer) and caprocks selected in the Polish Lowlands for CO₂ storage (Tarkowski, 2008; Tarkowski and Uliasz-Misiak, 2005, 2006): in the lower Cretaceous horizon (samples Nos. 2-4) and Lower Jurassic horizon (samples Nos. 6-8), as well as from caprocks overlying the reservoir horizon (samples Nos. 1 and 5). The limestone and dolomite rocks were considered as caprocks because of their sealing properties (low permeability and low porosity). The rock samples come from strata of well-defined stratigraphic positions (*Tab. 1, Fig. 1, 2*). The sampled boreholes are located within the geological structures intended for underground CO₂ storage – the Gopło and Brześć Kujawski anticlines.

TABLE 1
Rock material used for investigations

No. of sample	Name of the well	Sort of material	Depth (m)	Remarks	Stratigraphy
1	Pagórki IG 1	Limestone	865-870	Caprock	Upper Cretaceous – Cenomanian
2	Pagórki IG 1	Sandstone	1 025-1 029	Reservoir rock	Lower Cretaceous – Kruszwickie member
3	Pagórki IG 1	Sandstone	1 056-1 059	Reservoir rock	Lower Cretaceous – Goplańskie member
4	Pagórki IG 1	Sandstone	1 072-1 079	Reservoir	Lower Cretaceous – Pagórczańskie member
5	Brześć Kujawski IG 2	Dolomite	1 019-1 027	Caprock	Middle Jurassic – Upper Aalenian
6	Brześć Kujawski IG 2	Sandstone	1 129-1 130	Reservoir rock	Middle Jurassic – Lower Aalenian
7	Brześć Kujawski IG 2	Sandstone	1 210-1 211	Reservoir rock	Lower Jurassic – Borucickie layers
8	Brześć Kujawski IG 3	Sandstone	1 309-1 310	Reservoir rock	Lower Jurassic – Borucickie layers

Figure 1

Location map of Gopło and Brześć Kujawski geological structures.

Figure 2

Geological cross-section of the Brześć Kujawski anticline; 1: series containing reservoir levels; 2: faults; 3: borehole on the cross-section; 4: borehole projected on the cross-section; Q + Trz: Quaternary + Tertiary; J₃: Upper Jurassic; J₂: Middle Jurassic; J₁: Lower Jurassic; T₃: Upper Triassic; T₂: Middle Triassic; T₁: Lower Triassic.

2 RESEARCH METHODS

Experimental research to assess the influence of CO₂ on reservoir and caprocks was performed in the laboratory in the presence of artificial brine. The experiment was carried out in a special instrument simulating natural formation conditions, *i.e.* elevated pressure (*P*) and temperature (*T*). (In this case

P = 10 MPa and *T* = 45°C for the Cretaceous formation and *P* = 12 MPa and *T* = 55°C for the Jurassic formation, which are the reservoir conditions established for selected structures at the considered depths – see *Tab. 1*).

The instrument is composed of a system of four stainless steel reactors. The system was also equipped with a thermostat-controlled holding oven. Inside the oven, a converter was

Figure 3

A set of reactors designed for the experiment.

measuring the pressure in the reactors. The system was connected with a CO₂-supplying medium composed of a cylinder with a helium bag, a pneumo-hydraulic booster and a screw press (Fig. 3).

To determine CO₂-induced alterations in the rocks, petrophysical, physicochemical and mineralogical investigations were performed on the rock samples in the environment corresponding to natural formation conditions, before and after CO₂ injection in the presence of brine, which was also analysed. Petrophysical parameters of the rocks, changes in the mineral and structural composition, and physicochemical alterations of brines were analysed.

These kinds of parameters were chosen because they are very important in CO₂ injection and storage actions. For example, porosity is related to injection capacity, and permeability is related to injection rate. Also, changes in mineralogical composition during the experiment are connected with changes in porosity and permeability (*e.g.* dissolution of some minerals could increase the porosity of rock) (see Gaus, 2010). In the case of caprocks they should retain good sealing properties by low permeability and low porosity (permeability below 0.1 mD – impermeable rocks, porosity below 10% – rock with reduced porosity; see Plewa and Plewa, 1992). for the inverse is true for reservoir rocks, where it is important to retain large values of these parameters (permeability above 10 mD – permeable rocks, porosity above 15 or 20% – rock with increased porosity and rock with high porosity, respectively; see Plewa and Plewa, 1992).

2.1 Petrophysical Investigations

Pore space geometry was analysed using a scanning electron microscope: JSM 6300 (SEM). The quantity of pore space, reservoir and hydraulic properties of the rocks, and the

distribution of pores within the preserved empty pore space were estimated using a mercury porosimeter (Micromeritics Pore Sizer 9320). By means of this method it is possible to measure capillary pressures by injection not-wetting liquid (Hg) into rock samples at a specific set of pressures established every time for each sample. On the basis of measurements a cumulative curve (capillary pressure curve) is obtained. This curve displays a dependence on the applied pressure-volume of injected mercury.

The maximum pressure used was 30 000 PSI, which allowed injecting mercury into the micropores with a minimum diameter to 0.006 µm. During the measurement the volume of mercury, which was pushed under an increasing pressure in the pore space in rocks, was measured. The size (diameter) of pores which mercury was forced into was calculated using the Washburn equation:

$$D = (1/p) \gamma \cos\phi$$

where D is the pore diameter, p : the pressure used (see pressure table), ϕ : the contact angle of mercury-rock and γ : the surface tension.

This equation assumes that the pore space of the rock can be depicted as a bundle of cylindrical capillaries, which may carry the reservoir fluid – the so-called pore space cylindrical model. It is also assumed that effective porosity of the real rock pore space is the same as in the space parameterised with this method.

The mercury porosimeter Pore Sizer 9320 allowed registering two cumulative curves during the analysis – for increasing and for decreasing pressure. The distance of both curves from each other, and the shape of the curve, plotted for decreasing pressure, allowed one to establish the derogation size of the assumed cylindrical shape model of the pore space from that really existing in the rock. This is called the size of the hysteresis effect, which can be calculated as the difference in saturation of the sample with mercury at the lowest pressure measured for both cumulative curves.

Analysing cumulative curves it is possible to calculate the following parameters: specific surface area (m²/g), dynamic (connected) porosity (%) and mean capillary diameter (µm). Analysing diagrams of cumulative curves the threshold diameter/threshold pressure (µm) (at this diameter a continuous flow of gas through the rock starts; this pore size ensures continuous communication of fluid in the rock – the larger the threshold diameter the better the filtration properties of the rock) was shown. Obtained from the MIP porosimeter, the digital parameters allowed drawing the histograms showing what percentage of pore spaces are engaged by pores > 1 µm (%). The framework (skeleton) density (g/cm³) and bulk density (g/cm³) were also established by this method. Permeability (mD) was determined using the EPS DGP - 100 equipment.

2.2 Physicochemical Investigations of Brines

The two brines prepared in the laboratory had a simplified composition, *i.e.* they contained only basic ions that constitute the standard brines extracted from the Strzelno 1 (for the Cretaceous deposits) and Brześć Kujawski IG 3 (for the Jurassic deposits) boreholes. The brines were analysed for the concentrations of main ions (Cl⁻, SO₄²⁻, HCO₃⁻, CO₃²⁻, Ca²⁺, Mg²⁺, Na⁺, K⁺) and selected physicochemical parameters (pH, conductivity, specific weight, dry residue).

2.3 Mineralogical Investigations

Microscopic observations in transmitted light were made on polished thin sections with a standard thickness of 0.02 mm. These examinations were carried out using the Nikon Eclipse 6000Pol polarising microscope (20 kV and 600 mA for sandstones; 14 kV and 450 mA for carbonates). Quantitative (planimetric) analysis of the rocks on the same thin sections was performed using the Jenapol polarising microscope equipped with an Eltinor platform. In total, 300 measurements were made on each sample.

XRD analyses were carried out using the PHILIPS X'Pert APD diffractometer (with the PW 1870 generator and the PW 3020 vertical goniometer). Graphite-monochromatised Cu K α 1 ($\lambda = 1.54062$ Å) radiation (using a curved monochromator) was applied. The analyses were performed within the angle range of 2-64° 2 θ with the velocity 0.02°/s, accelerating voltage 40 KV and intensity 30 mA.

Observations of the mineral composition and surfaces of rock samples before and after the experiment were made using the Hitachi S-4700 field-emission scanning electron microscope equipped with a Vantage Noran EDS micro-analytical system and a back-scattered electron detector (YAG BSE). SEM-EDS observations were also made on polished thin sections with a standard thickness of 0.02 mm.

3 EXPERIMENT DESCRIPTION

The experiment relied on placing cylinder-shaped rock samples (around 400 grams) in tightly closed reactors (capacity 1.8 dm³ each) filled with 1.5 dm³ of artificial brine. The remaining capacity of the reactors was filled with CO₂. The reactors were connected to the CO₂ injection installation and put into the holding oven. This system enables one to both simulate natural formation conditions in the laboratory and conduct the experiment on the impact of CO₂ on the rocks and reservoir fluids.

For the experiment's purpose, it was necessary to prepare brine, whose composition was determined based on the composition of brines that accompanied the formation rock materials that were taken for the experiment. Therefore, two types

of artificial brines with simplistic chemical composition were prepared (containing K⁺, Na⁺, Ca²⁺, Mg²⁺, Cl⁻, HCO₃⁻ and SO₄²⁻ ions):

- brine corresponding in composition to the Lower Cretaceous brine;
- brine corresponding in composition to the Lower Jurassic brine.

These brines were additionally analysed for the contents of main ions and physicochemical parameters, such as pH, specific conductance, specific gravity and total solids content.

The experiment proceeded in three stages:

- impact of CO₂ on brine alone (so-called blind test);
- impact of CO₂ on Cretaceous rocks in the presence of brine;
- impact of CO₂ on Jurassic rocks in the presence of brine.

The blind test was performed to check the influence of injected CO₂ on brine alone under formation conditions. This experiment was carried out in order to identify reactivity between the CO₂ and the brine in the absence of a rock sample: precipitation of secondary minerals and changes in chemical composition of the brine.

Later during the experiment, it enabled discrimination of the processes proceeding within the samples from the reactions occurring between only brines and CO₂. The experimental stand was characterised by the following reservoir conditions: $P = 12 \text{ MPa} \pm 10\%$, $T = 55^\circ\text{C} \pm 10\%$. Two reactors contained artificial Lower Cretaceous brine, and another two Lower Jurassic brine. Although two types of brines were used in the blind test, the same reservoir conditions were established for them (pressure, temperature). Setting different conditions for each reactor would be impossible, because the reactor system is connected. The blind test experiment lasted a fortnight and preceded the main experiment.

Interpretations were based on the comparison of the mineral composition of brines and petrophysical and mineralogical parameters of rock samples, determined before and after the experiment. The experiment lasted three months (see Rimmelé *et al.*, 2009 – a similar short-term experiment), both for the Cretaceous (Pagórki IG-1 borehole) and Jurassic rocks (Brześć Kujawski IG-2 and IG-3 boreholes). The short duration of the experiment was dependent on the duration of the project under which it was carried out. Therefore, the purpose of these studies was only the observation of short-term interactions between brines, CO₂ and rock samples. The formation conditions established for the Cretaceous and Jurassic rocks were as follows, respectively: $P = 10 \text{ MPa} \pm 10\%$, $T = 45^\circ\text{C} \pm 10\%$, and $P = 12 \text{ MPa} \pm 10\%$, $T = 55^\circ\text{C} \pm 10\%$. These conditions were established according to reservoir conditions occurring for those formations at the analysed depths.

TABLE 2

Physicochemical parameters of rock samples from the Pagórki IG 1, Brześć Kujawski IG 2 and Brześć Kujawski IG 3 boreholes before and after the experiment

No. of sample	Surface area		Dynamic porosity (porosimeter Hg)		Framework density		Bulk density (Hg method)		Permeability (for nitrogen)	
	Before (m ² /g)	After (m ² /g)	Before (g/cm ³)	After (g/cm ³)	Before (g/cm ³)	After (g/cm ³)	Before (g/cm ³)	After (g/cm ³)	Before (mD)	After (mD)
1	3.69	2.79	6.51	5.85	2.64	2.67	2.48	2.52	< 0.01	< 0.01
2	0.34	0.08	19.95	17.94	2.63	2.62	2.11	2.15	1196.1	358.8
3	0.14	0.06	13.06	12.68	2.63	2.62	2.28	2.29	138.8	187.4
4	0.21	0.06	21.70	21.19	2.65	2.63	2.07	2.07	557.1	251.6
5	0.16	0.23	1.23	0.73	2.79	2.78	2.75	2.76	< 0.01	< 0.01
6	0.46	0.42	16.09	19.74	2.57	2.58	2.16	2.07	325.8	121.8
7	0.28	0.11	22.97	22.18	2.62	2.61	2.03	2.03	239.7	283.8
8	0.33	0.18	22.95	22.19	2.60	2.59	2.00	2.01	121.2	326.4

4 RESULTS

4.1 Petrophysical Investigations

The sandstones under study (*Tab. 2*) are characterised by low values of specific surface area ranging from 0.14 to 0.46 m²/g. Dynamic porosity determinations revealed similar percentages of about 20% in most of the samples. Slightly lower values of this parameter were observed in samples No. 3 (13%) and No. 6 (16%). Framework density in all the sandstone samples oscillates around 2.60 g/cm³. Bulk density values vary within a wide range. Permeability of the rocks shows a considerable variability ranging from 121.2 mD (sample No. 8) to 1 196.1 mD (sample No. 2).

The sandstones show microporous pore space, as evidenced by the pore structure analysis (*Tab. 3*). The percentage of pores > 1 µm in diameter is commonly above 90%, with the exception of sample No. 6 (86%). Mean capillary diameter values are variable, ranging from 0.6 to 2.0 µm (average 1.5 µm) in samples Nos. 2, 3, 7 and 8. Threshold diameter values for Cretaceous samples are also very variable and range between 16 µm and 65 µm. For the Jurassic samples they oscillate around 23 µm. Distribution of > 1 µm pores (*Fig. 4, 5*) shows a dominant percentage of 25 µm–10 µm diameter pores, with the exception of sample No. 2.

The results of investigations of the Cretaceous and Jurassic sandstones performed before the experiment indicate that they are good quality reservoir rocks (high permeability and porosity).

The petrophysical parameters generally changed due to the effect of CO₂ and brines on the rocks (*Tab. 2, 3*). All the values of specific surface area decreased in relation to the values measured before the experiment (samples Nos. 3, 7

TABLE 3

Results of pore space structure analysis of rock samples from the Pagórki IG 1, Brześć Kujawski IG 2 and Brześć Kujawski IG 3 boreholes before and after the experiment

No. of sample	Before the experiment			After the experiment		
	Pores > 1 µm (%)	Mean capillary diameter (µm)	Threshold diameter (µm)	Pores > 1 µm (%)	Mean capillary diameter (µm)	Threshold diameter (µm)
1	4.5	0.029	0.05	*	0.033	**
2	96.0	1.109	65.00	97.0	4.076	40
3	95.5	1.652	16.00	95.5	3.923	15
4	97.5	2.031	26.00	98.5	6.990	20
5	*	0.115	**	*	0.046	**
6	86.0	0.650	23.00	91.0	0.897	24
7	95.0	1.626	25.00	95.5	3.980	25
8	93.5	1.412	20.00	96.0	2.482	20

* Analysis did not displayed a presence of pores with diameter > 1 µm.

** Because of too low a porosity of these rocks, determination of threshold diameters was impossible.

and 8 – decreased more than twofold; samples Nos. 2 and 4 – decreased fourfold; only a slight decrease in sample No. 6). The dynamic porosity did not significantly change, with the exception of sample No. 6, where it increased approximately 3%. The values of framework and bulk density remained practically unchanged. Permeability values changed variably: increased values were observed in samples Nos. 3, 7 and 8 (twice as much in sample No. 8); in the remaining samples the values decreased (over twofold less in samples Nos. 4 and 6, over three times less in sample No. 2).

Figure 4
Distribution of pore space of Cretaceous samples (1-4) before the experiment.

Figure 5
Distribution of pores in the pore spaces of Jurassic samples (6-8) before the experiment (because of very low porosity for sample No. 5, determination of pore distribution for this sample was impossible).

The experiment caused no significant changes in the percentage of pores $> 1 \mu\text{m}$ in diameter (compare Fig. 4-7). The mean capillary diameter increased in every sample (about four times greater in samples Nos. 2 and 4, over twofold greater in samples Nos. 3 and 7). In the Cretaceous samples, the values of threshold diameter decreased, whereas in the Jurassic samples they remained unchanged. The plots of pore distribution (Fig. 6, 7) measured after the experiment show that the rocks are still dominated by 25-10 μm diameter

pores, except in sample No. 2, where, like before the experiment, 45-25 μm diameter pores predominate.

The effect of CO₂ and brine on reservoir rocks changed their reservoir parameters.

Different results for petrophysical and physicochemical parameters were obtained for the caprock carbonates (limestone and dolomite) than the sandstone samples. The analyses (Tab. 2) show considerable variability in the values of specific surface area (3.69 m²/g in sample No. 1; 0.16 m²/g in

Figure 6

Distribution of pore space of Cretaceous samples (1-4) after the experiment.

Figure 7

Distribution of pore space of Jurassic samples (5-8) after the experiment.

sample No. 5). The values of dynamic porosity of the rocks are also variable, while the values of framework and bulk density remained at the same level, as in sandstones.

Analysis of the pore space structure (Tab. 3) revealed the lack of $> 1 \mu\text{m}$ pores in the dolomite sample and a very small percentage of these pores in the limestone sample (Fig. 4, 5). The values of mean capillary diameter are also very low. The threshold diameters (which are related to the capillary entry pressure) in both cases were very low (in the case of sample No. 5 it was too low to determine, which was caused by very low porosity). Both samples before the experiment also were

characterised by very low permeability (below $0.01 \mu\text{m}$). The measurements suggest good sealing properties (according to Plewa and Plewa, 1992, such lower values are obtained for impermeable rocks).

The experiment affected the petrophysical parameters. The value of specific surface area measured in the limestone sample decreased. The value measured in the dolomite sample increased. Dynamic porosity of the rocks decreased. The values of framework and bulk density remained at the same level.

Pore space structure analysis (Fig. 6, 7) after the experiment revealed the lack of $> 1 \mu\text{m}$ pores in both the samples (the

pore distribution plot shows 100% of pores < 1 µm). In the limestone sample, the value of mean capillary diameter remained unchanged; however, the value decreased by half in the dolomite sample. The determination of threshold diameter in both cases after the experiment was impossible because of very low porosity. Also, in those samples the permeability started at the same level.

The experiment did not reduce the sealing quality of the rocks; on the contrary, their sealing properties improved (decreased porosity; decreased threshold diameter in the case of sample No. 1).

4.2 Physicochemical Investigations of Brines

To determine the alterations in brines during the experiment, the initial sample was examined for the contents of chloride, sulphate, bicarbonate, carbonate, Ca, Mg, Na and K ions. The basic physicochemical parameters were also determined, such as: pH, specific conductance, specific gravity and total solids content (*Tab. 4, 5*). The same parameters were measured on brines before and after the experiment, during both the blind test (interaction between brine and CO₂ under formation conditions) and the experiment of interaction between the Cretaceous and Jurassic rocks and CO₂ under formation conditions.

The Blind test for the Cretaceous brine revealed a pH drop from 7.4 to 5.8, and an increase in bicarbonates from 292 mg/L to 329 mg/L and in sulphates from 721 mg/L to 973 mg/L. The remaining parameters did not change significantly.

The results of blind test for the Jurassic brine investigations showed no significant changes in the physicochemical parameters, except for decreases in the pH value and bicarbonate content.

No significant changes in the physicochemical parameters were observed after the experiment in brines injected into the Jurassic and Cretaceous rock samples, except as indicated below. A drop in the pH value was observed in each sample. Analysis of changes in the concentrations of individual ions in the brine solution of each sample revealed an increase in sulphate concentration in sample No. 4 (Lower Cretaceous brine), and a much greater increase in the concentration in sample No. 6 (Lower Jurassic brine). The bicarbonate concentration also greatly changed: it decreased 27 times in sample No. 6, and increased 9 times in sample No. 1. The content of Ca ions increased in most of the Lower Jurassic samples, while the content of Na ions decreased in all of the Lower Cretaceous and Lower Jurassic samples.

Physicochemical parameters, such as specific conductance, total solids content, specific gravity and post-reaction total solids content measured in brine from each reactor remained unchanged.

4.3 Mineralogical Investigations

Rock sample No. 1

The sample is represented by micritic limestone with abundant bioclasts and rare detrital quartz and mica grains. Spherical and oval accumulations of opaque minerals (pyrite, iron oxides) are locally observed. Planimetric analysis showed the presence of micrite (carbonate minerals, mainly calcite) and clay minerals (74.0%), bioclasts (25.0%) and quartz (1.0%). SEM investigations revealed the occurrence of abundant organic fragments composed of crystalline calcite. The micritic carbonate groundmass is strongly impregnated with clay minerals forming large accumulations, or with dispersed calcite crystals. XRD analysis exhibited that the mineral composition of the rock is dominated by calcite with the admixture of illite-type clay minerals. The clay fraction, separated from the rock sample, is composed mainly of illite/smectite (I/S) mixed-layer minerals and small amounts of kaolinite (K) and very fine-grained quartz grains (Q).

Some slight changes were observed in the rock sample after the experiment. Planimetric analysis showed the presence of micrite (71.0%), bioclasts (28.2%) and quartz (0.6%). SEM investigations revealed the occurrence of abundant organic fragments composed of crystalline calcite, locally replaced by pyrite. Dispersed clay minerals or their large accumulations occur between calcite grains. The XRD pattern shows the presence of subordinate quartz and clay minerals, and a small peak related to halite. The XRD pattern of clay minerals obtained after the experiment indicates the lack of any quantitative or qualitative alterations in the mineral composition.

Rock samples Nos. 2-4

The samples collected from Cretaceous deposits are represented by variously grained psammitic quartz sandstones of compact and unoriented texture. The mineral composition is dominated by quartz, commonly authigenic. There are also rare feldspars, clay minerals thinly coating quartz grains, opaque minerals (pyrite, rutile), accumulations of brownish iron compounds, muscovite and kaolinite (often authigenic). Sample No. 2 contains glauconite and rock fragments. The percentages of individual mineral components are depicted in Table 6.

The sandstones are bonded with the siliceous, regeneration and differently developed cement. Locally, it is of interstitial type. The rocks are occasionally porous. The pores in samples Nos. 2 and 3 are filled with a clay-carbonate mixture.

Mineralogical analysis of the rock samples after the experiment exhibited some changes in the grain framework, cement and pore space fill. A slight increase in quartz content in all samples and a sharp decrease in clay content (planimetric analysis) in sample No. 2 after the experiment were observed. A slightly greater amount of pyrite was detected by XRD analysis only in sample No. 4. XRD patterns of all the samples reveal small peaks related to precipitated halite.

TABLE 4

Physicochemical parameters of initial Lower Jurassic brine, the blind test and after reaction of brine with individual rock samples

Marked component	Units	Content in initial sample	Brine – blind test	Brine – the experimental sample			
				No. 1	No. 2	No. 3	No. 4
Reaction (25°C)	pH	7.4	5.8	6.6	6.3	6.0	6.3
Conductivity (20°C)	μS/cm	46 750	42 900	43 600	42 600	42 300	43 100
Specific weight	g/cm ³	1.022	1.021	1.024	1.023	1.022	1.023
Dry residue	g/L	30.948	29.572	32.136	30.74	30.044	30.928
Chlorides	mg Cl/L	17 106	17 195	17 549	17 283	17 549	17 372
Sulphates	mg SO ₄ /L	721	973	996	1 082	1 049	1 224
Bicarbonates	mg HCO ₃ /L	292	329	2 605	1 080	433	931
Carbonates	mg CO ₃ /L	0.00	0.00	0.00	0.00	0.00	0.00
Calcium	mg Ca/L	874	858	1 651	1 174	878	1 174
Magnesium	mg Mg/L	292	275	275	297	287	294
Sodium	mg Na/L	10 442	9 890	8 890	8 660	8 680	8 880
Potassium	mg K/L	122	120	125	134	140	114

TABLE 5

Physicochemical parameters of initial Lower Jurassic brine, the blind test and after reaction of brine with individual rock samples

Marked component	Units	Content in initial sample	Brine – blind test	Brine – the experimental sample			
				No. 5	No. 6	No. 7	No. 8
Reaction (25°C)	pH	7.4	6.1	6.8	6	6.2	6.5
Conductivity (20°C)	μS/cm	66 710	64 000	64 100	68 600	64 200	66 500
Specific weight	g/cm ³	1.033	1.0331	1.034	1.036	1.033	1.034
Dry residue	g/L	47.1	46.4	47.4	48.9	46.9	47.3
Chlorides	mg Cl/L	27 387	27 653	27 299	26 416	27 742	28 097
Sulphates	mg SO ₄ /L	460	477	461	2 580	533	567
Bicarbonates	mg HCO ₃ /L	589	445	1 916	21.4	519	418
Carbonates	mg CO ₃ /L	0.00	0.00	0.00	0.00	0.00	0.00
Calcium	mg Ca/L	1 094	1 082	1 319	898	1 094	1 078
Magnesium	mg Mg/L	331	336	465	396	333	340
Sodium	mg Na/L	16 322	16 900	16 200	16 000	14 600	15 900
Potassium	mg K/L	181	169	182	162	169	169

Rock sample No. 5

The sample is represented by finely crystalline strongly ferruginous dolomite. Very small dolomite grains with surfaces stained reddish by iron oxides are observed. Accumulations of clay minerals (probably kaolinite impregnated with iron oxides) are visible between the dolomite grains. The fine-grained clay-carbonate groundmass contains quartz grains, frequent pyrite accumulations and rare muscovite flakes. Quartz grains are either randomly distributed or they form

thin laminae. The rock is inhomogeneous. Iron oxides are either regularly dispersed or they form large accumulations and flasers. Planimetric analysis shows the presence of carbonates (mainly dolomite) and clay minerals (88.0%), quartz (8.7%), micas (1.0%) and pyrite (2.3%). Pyrite occurs as single grains or framboidal clusters in the finely crystalline pyrite groundmass. Dolomite grains tend to contain more iron compounds towards the grain edges, hence showing a zonal structure. The clay groundmass between the dolomite

grains is impregnated with iron oxides. XRD analysis shows that the main component of the rock is ferruginous dolomite. It probably co-occurs with ankerite (diffraction peaks of these minerals occupy the same position). In addition to dolomite, there are also quartz, kaolinite and illite-type minerals. The clay fraction, separated from the sample, contains abundant kaolinite (K), finely crystalline mica (illite-type minerals) (M) and rare vermiculite (V).

Microscopic observations after the experiment show some changes in planimetric analysis that revealed the presence of carbonates and clay minerals (91.0%), quartz (5.2%), micas (0.6%) and pyrite (3.2%). SEM investigations show no changes (neither new precipitates nor changes in mineral grains). XRD analysis exhibited the presence of ferruginous dolomite, probably mixed with ankerite, and small amounts of quartz, kaolinite, illite-type minerals and pyrite. The clay fraction contains considerable proportions of kaolinite (K) and illite-type minerals (M), and small amounts of vermiculite (V).

Rock samples Nos. 6-8

The Jurassic rock samples are represented by variously grained psammitic quartz sandstones of compact and unoriented texture. The dominant component is quartz grains coated with clay minerals. Sparse variably altered feldspars, muscovite, kaolinite, clay and opaque (pyrite and/or iron oxides) minerals are also observed. Rock samples Nos. 6 and 7 contain rock fragments, kaolinite and kaolinite-apatite aggregates and apatite and gypsum grains (sample No. 6). Organic matter accumulations occur in sample No. 8. The percentages of individual constituents are presented in Table 6.

The sandstones contain variously developed mixed, siliceous and regenerative cement. Locally, in samples Nos. 6 and 8, clay and clay-ferruginous cements are observed. The pores in sample No. 6 are filled with carbonate-clay, clay and

clay-ferruginous or kaolinite material. The pores are commonly filled with silica, locally sericite, illite and iron compounds (sample No. 7) or kaolinite (sample No. 8).

Mineralogical investigations performed after the experiment show slight changes in sandstone samples. Some differences were observed in the results of planimetric analysis (Tab. 6; similar to the case of the Cretaceous sample – some increase in quartz content after the experiment) and in the XRD diffraction pattern of sample No. 8, where a peak related to vaterite is visible. SEM and XRD analyses of every sample revealed very small percentages of halite that precipitated from brine.

Most of the changes that occurred in the determined parameters and mineralogical composition may result from not using exactly the same sample before and after the experiment. It was caused by using in some cases destructive methods to determine parameters. However, the samples were collected from the same drill core intervals, so their petrophysical parameters and mineralogical characteristics should be very similar.

DISCUSSION AND CONCLUSIONS

Petrophysical investigations proved that the experiment caused a decrease in the values of parameters such as specific surface area and dynamic porosity, confirming the results obtained by Kaszuba *et al.* (2005) and Olsen and Stentoft (2003). There were also considerable, different variations in permeability values of sandstone samples and an increase in the mean pore diameters in the case of sandstones which were observed in the results of Rimmelé *et al.* (2009). The controversial results obtained in samples No. 6 and No. 8 show little or no change in porosity before and after the

TABLE 6
Planimetric analysis of sandstones before and after the experiment (% vol.)

	Sample No. 2		Sample No. 3		Sample No. 4		Sample No. 6		Sample No. 7		Sample No. 8	
	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
Quartz	66.0	70.5	58.0	63.3	61.5	68.3	61.5	68.3	57.0	65.0	59.0	60.1
Siliceous regeneration cement (Clay-carbonate cement for sample No. 6)	12.5	16.1	27.5	27.1	28.0	20.7	21.5	17.6	28.0	17.9	23.0	24.7
Clay minerals	10.0	1.2	3.0	1.0	1.2	2.4	3.9	5.0	3.5	2.8	3.5	3.7
Feldspars	2.8	1.2	2.5	1.2	0.5	0.8	2.3	1.4	2.2	1.7	3.2	2.0
Micas	1.0	0.0	0.3	1.3	0.8	0.5	1.2	0.7	1.0	1.7	1.2	0.8
Glauconite	1.0	0.6	0.0	0.0	0.0	0.0	0.0	0.3	0.0	1.0	0.0	0.6
Pyrite	0.5	0.5	0.0	0.2	0.0	0.9	1.6	0.6	0.0	1.0	1.5	1.4
Opened pores*	7.2	9.9	8.0	5.9	8.0	6.4	8.0	7.2	8.3	7.6	8.6	8.1

* Opened pores were established on the basis of a planimetric analysis of polished thin sections, therefore this value should not correspond to the porosity denoted with mercury porosimeter use.

experiment but in one case a large decrease in permeability (No. 6) and in the other, a large increase in permeability (No. 8) were observed. This issue needs some detailed analysis because such results could be caused by some errors during analysis so those measurements should be repeated. Scanning electron microscope investigations and porosimetric measurements showed only slight, non-significant changes that should not influence on the reservoir quality parameters of the rock samples.

The experiment only slightly changed the mineralogical and petrographic composition of the samples, confirming the results of studies of Nightingale *et al.* (2009), Rimmelé *et al.* (2009), Wollenweber *et al.* (2009) and Xiao *et al.* (2009). After the experiment, almost all the samples contained halite that had crystallised from brine, partly as a result of drying out of the drill core samples saturated with the brine solution. Also, a sharp decrease in clay content (planimetric analysis) in sample No. 2 and increase in quartz content in all sandstone samples after the experiment were observed, which was a result of inhomogeneous rock samples, because the short time of reaction of the CO₂-brine-sample could not cause so large a decrease in the amount of clay minerals (see Wigand *et al.*, 2008), especially in increase in quartz content (Gaus, 2010). However, those insignificant changes in mineralogical composition (precipitation of halite and differences in amount of clay minerals in sample No. 2 before and after the experiment) did not affect the porosity of the rocks, as also mentioned by Muller *et al.* (2009) and Spycher *et al.* (2003).

Different results were obtained for one sandstone sample which, before the experiment, contained abundant carbonate cement mixed with clay minerals. After the experiment, the amount of the clay-carbonate cement significantly decreased. The decrease in the proportion of clay and carbonate materials resulted in an increase in porosity of the rocks. Similar observations were made by Bertier *et al.* (2006), Credoz *et al.* (2009), Wigand *et al.* (2008) and Wollenweber *et al.* (2009).

Additionally, it should be noted that single preparations, cut out from drill cores, are not always representative. The samples analysed before and after the experiment were not exactly the same samples, because in many examinations it was impossible to test the same rock sample as the samples were destroyed during the tests (*e.g.* XRD analysis). However, they were collected from the same drill core intervals, so their petrophysical parameters and mineralogical characteristics should be very similar. Thus, both interpretations of rock series represented by single samples and comparison of analogous samples before and after the experiment should be performed with caution, as noted by Nightingale *et al.* (2009). Particularly, these differences in obtained results (mainly petrophysical parameters) could be caused by errors during measurements. Therefore, most of the analysis should be repeated on the same sample on condition that the method used is non-destructive.

Some variability in the results of investigations can result from the lack of sufficient representativeness of the samples, whereas lack of some distinct changes can result from the minerals that react very slowly (quartz sandstones with a small amount of carbonates, sulphates and feldspars ready to react with CO₂; carbonates with a small proportion of reactive clay minerals) or from the short time of the experiment (3 months), as noted by Credoz *et al.* (2009) and Nightingale *et al.* (2009).

Part of the results can also be explained by the inhomogeneity of the rock samples. Moreover, due to single measurements of individual parameters it was often impossible to average the results or to eliminate any extreme value. Therefore, in future experiments it is recommended to use *e.g.* uncovered microscope slides in addition to drill core samples, to directly analyse the same sample fragments and to enhance the reliability of the research results.

The experiment provided new detailed results of petrophysical and mineralogical-petrographic investigations of rock samples from the Pagórki IG 1 and Brześć Kujawski IG 2 and IG 3 boreholes. The samples were taken from reservoir horizons and caprocks of the Mesozoic succession in the Polish Lowlands, selected for underground CO₂ storage. The research results proved that the sampled rocks of the reservoir horizons show good reservoir quality, whereas the caprocks are characterised by some good sealing properties (low porosity). The results of caprocks for low permeability (below 0.01 µm) and the low, indeterminable threshold diameter show that these values need detailed examinations with more precise methods, as for instance, Li *et al.* (2006) described that necessary permeability to indicate good sealing properties of rocks should range in the nD. However, comparing the porosity (which is related to permeability) obtained by Li *et al.* (2006) with the porosity in this study we could preliminarily assume that the permeabilities for the tested caprocks are sufficient to indicate their good sealing properties. The measured parameters were not affected by CO₂ injection under simulated formation conditions. The reservoir rocks of the Gopło and Brześć Kujawski structures can be taken into account in future considerations concerning CO₂ sequestration.

It should be noted that the properties of the rocks described in this article provide only preliminary and partial characterisations of reservoir and caprocks, and most of the interpretations should be acted upon with caution. Therefore, additional data should be determined. The important issue is the integrity of caprocks, through measurements of injection pressure, that depends on sealing capacity, fracture pressure and gas flow. The essential assumption for determination of CO₂ storage injection pressure is that the sealing capacity of the caprocks should be adequate to prevent the injected CO₂ from escaping through the caprock (Bachu, 2000; Voormeij and Simandl, 2000). Another criterion assumes that the injection is safe provided that the fracture pressure of the reservoir

or caprocks is not exceeded. This is dangerous when the sealing pressure of the caprocks is lower than the fracture pressure (Li *et al.*, 2006). In order to determine the integrity of the reservoir and caprocks a number of long-term modeling software programs are used, that allow one to determine mainly geochemical reaction and reaction transport modeling. Also, important data describing reservoir rocks are delivered by mechanical tests of hydraulic fracturing.

Another relevant issue is to determine a long-term permeability; therefore, predicting its evolution within the caprock environment of CO₂ storage sites requires first identifying, then quantifying its functional dependence on key system parameters and dynamic processes. The important factors influencing this evolution are conveniently subdivided into three groups: caprock properties, chemical conditions at the reservoir/caprock interface, and the influx-triggered pressure perturbation. Relevant caprock properties include geomechanical parameters, such as fracture normal stiffness and geochemical characteristics, such as bulk concentrations of carbonate-forming cations (principally Fe, Mg, Ca, Na and Al). Concentrations of these cations represent the primary control of geochemical alteration processes, while chemical conditions at the reservoir/caprock interface, which are determined by reservoir compositions and CO₂ waste-stream impurities such as CH₄, H₂S, SO_x and NO_x, exert a secondary control. The fundamental controls of geomechanical deformation processes are represented by magnitude, duration and focality of the injection-induced pressure perturbation – which depend on these same characteristics of CO₂ influx as well as on reservoir permeability, lateral continuity and compartment height (for laterally confined settings) (Johnson *et al.*, 2004).

The additional data mentioned above, and many other data necessary in CO₂ storage investigations indicate that the described research constitutes only the preliminary stage in CO₂ sequestration operations.

The investigations presented in this report, conducted in Poland for the first time, refer to a new study area selected for underground CO₂ storage. They can be used in exploration of tectonic structures suitable for geological underground CO₂ storage in Poland. Such investigations, based on analyses of reservoir and caprock samples from potential structures for CO₂ storage, should be continued using the acquired experience, obtained research results and the special and unique experimental equipment designed for this purpose.

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