Geochemical modelling of processes in near-wellbore zone under CO₂ injection conditions

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Abstract. In the conditions of sequestration of acid gases to the rock formation between rocks, reservoir fluids, injected gases, wellbore cement and the casing, the complex geochemical changes occur. Although these processes have been the subject of some research in recent decades, their mechanisms are still not sufficiently recognized, and especially the impact of these processes on the preservation of leak-tightness of boreholes, which is a key element for the success of the sequestration process.

The computer simulation accurately reflects the direction of changes taking place during real experiments, additionally providing detailed information on the mineral phases involved in the mineral transformation process within rock and wellbore cement. In the acidic environment created in the analyzed system, the dissolution of portlandite and C-S-H phases, as well as the crystallization of calcite, vaterite and silica, takes place. During the time taken into account in the simulation, the volume of minerals crystallizing in the cement is greater than the volume of dissolved components, but on the other hand, micro-voids may appear in the contact zone. In the case of penetration of pore waters, coming from rocks into the cement, the most intense transformations occur in the cement to a depth of 3 cm from the contact zone with the rock.

1. Introduction
During acid gases sequestration multiple complex geochemical processes occur between host rock, brine, injected gases, wellbore cement and well casing. These processes have been under research for last decades, but still their mechanism is not fully recognized. The most interesting aspect of this problem is an impact of these processes on the preservation of leak tightness, which is a key element for the success of the sequestration process. In order to investigate the reactions occurring at the contact of wellbore cement and reservoir rocks the geochemical modelling was carried out, as a complement to the previously conducted experimental studies.

2. Methodology
Geochemical modelling of reactions in the wellbore cement - rock - brine system under CO₂ sequestration conditions was carried out with the use of Geochemist's WorkBench (GWB) software version 8.0 [1]. The following GWB software modules: React and X1t, were used for equilibrium, reaction path and kinetic modelling. In the simulation, when using the X1t package, the mineralogical composition of the rock matrix and the chemical composition of the pore solution should be determined. The simulation assumes that the model domain determined in a linear, radial or spherical coordinate...
system is fed by a solution of a given composition, which, when moving, reacts with the other components of the system [2].

The thermodynamic data base Thermoddem [3] was used for calculations, taking activity coefficients, calculated according to the extended Debye-Hückel equation. For the purpose of this work, the database has been supplemented with thermodynamic data of the SiO$_2$(aq) phase.

5 rocks representing reservoir rocks and cap rocks of perspective formations in the aspect of CO$_2$ storage in Poland were selected for the research. These were: 5-S (Rotliegend) sandstone, 7-S sample (Pennsylvanian quartz arenite), 8-SH (Ordovician shale) sample, 12-L (Jurassic limestone) sample and an 18-A sample (Permian anhydrite).

To perform the model tests, it was necessary to collect the following initial data: the composition of drilling cement and cement pore water, the composition of particular rocks and the composition of their pore waters, porosity of rocks and cement, specific surface of grain in rocks, CO$_2$ pressure activity and reaction kinetics parameters.

Mineral composition of rocks and cement was determined by XRD method with use of Bruker-AXS D8 Advance spectrometer. Porosimetric parameters of rocks were obtained from MIP porosimetry with use of Micromeritics Autopore 9220 porometer. Porosity of wellbore cement was obtained from gas adsorption method in Micromeritics TriStar II apparatus.

3. Data used for modelling

3.1. Determination of the cement pore water composition

In order to determine the chemistry of cement pore water, an equilibrium modelling was performed. The composition of pore water was obtained as a solution of 1.88 mol NaCl/kg (approx. 105 g NaCl/dm$^3$), in equilibrium with cement constituents (table 1). The assumed composition of the solution was imposed by the conditions of the experiment, which was carried out in an autoclave for real rock samples and brine. The cement composition by volume percent (% vol.) was calculated basing on the results of the XRD analysis of the wellbore cement before the reaction, weight by weight (% w/w). The results of modelling of the pore water composition in cement are presented in table 2.

| Component   | By volume percent of the components | By volume percent of the components taking into account pore area |
|-------------|------------------------------------|---------------------------------------------------------------|
| C-S-H 1,6   | 43.2                               | 24.9                                                          |
| Portlandite | 24.2                               | 14.0                                                          |
| Ettringite  | 15.2                               | 8.8                                                           |
| Katoite     | 7.0                                | 4.0                                                           |
| C$_3$FH$_6$ | 4.4                                | 2.5                                                           |
| Hydrotalcite| 2.5                                | 1.4                                                           |
| Calcite     | 3.5                                | 2.0                                                           |
| Porosity    | -                                  | 42.3                                                          |
| TOTAL       | 100.0                              | 100.0                                                         |
Table 2. Results of modelling of the pore water composition in cement (mg/kg).

| Component       | Pore water in equilibrium with cement | Pore water after 200 days of reaction $f_{CO2} = 63.29$ bar |
|-----------------|--------------------------------------|----------------------------------------------------------|
| pH              | 11.761                               | 4.895                                                    |
| $Al^{+++}$      | 1.740                                | 7·10^{-4}                                               |
| $Ca^{++}$       | 1140.000                             | 1900.000                                                |
| $Cl^{-}$        | 66.590                               | 66.590                                                   |
| $Fe^{++}$       | 0.014                                | 5·10^{-5}                                               |
| $H_2SiO_3(aq)$  | 0.438                                | 27.500                                                  |
| $HCO_3^{-}$     | 2.540                                | 71600.000                                               |
| $Mg^{++}$       | 3.82·10^{-4}                         | 119.000                                                 |
| $Na^{+}$        | 43.220                               | 43.220                                                   |
| $O_2(aq)$       | 0.100                                | 0.060                                                   |
| $SO_4^{2-}$     | 275.000                              | 186.000                                                 |

3.2. Determination of rock pore water composition

The composition of pore waters for examined rocks was determined in similar way to the composition of wellbore cement pore water, based on equilibrium modelling. It was assumed that the pore water is a solution with a concentration of 1.88 mol/kg NaCl, which is in equilibrium with rock components. Similarly to the case of cement, the composition of selected rocks was calculated from the weight percent (wt%) obtained from the XRD analysis to volume percent (table 3). The results of modelling of the pore water composition of the rocks are presented in table 4.

Table 3. Mineral composition (% vol) of examined rocks: column a – not taking pores into account, column b – taking into account pore volume.

| Sample          | 5-S  | 7-S  | 8-SH | 12-L | 18-A |
|-----------------|------|------|------|------|------|
|                 | a    | b    | a    | b    | a    | b    | a    | b    | a    | b    | a    | b    | a    | b    | a    | b    |
| Porosity        | 11.0 | 4.0  | 43.8 | 10.5 | 0.6  |
| Quartz          | 84.6 | 75.4 | 93.0 | 89.3 | 39.2 | 22.1 | 0.6  | 0.5  |
| Muskovite 2M1   | 3.5  | 3.5  | 3.3  | 23.7 | 13.3 |
| Albite          | 8.7  | 7.5  | 5.0  | 8.7  | 4.9  |
| Chlorite IIb    | 10.5 | 2.5  | 10.5 | 5.9  |
| Orhtoklas       | 3.8  | 3.8  | 2.2  | 3.8  | 2.1  |
| Calcite         | 5.6  | 3.1  | 5.6  | 3.1  | 89.8 | 80.4 |
| Dolomite        | 7.1  | 4.0  | 7.1  | 4.0  | 9.6  | 8.6  |
| Kaolinite       | 1.3  | 3.4  | 3.5  | 3.4  | 1.3  | 0.8  |
| Piritre         |      |      |      |      |      |      |      |      |
| Magnesite       |      |      |      |      |      |      |      |      |
| Anhydrite       |      |      |      |      |      |      |      |      |

Table 4. Mineral composition (% vol) of examined rocks: column a – not taking pores into account, column b – taking into account pore volume.
The next stages of model ing work required determining the CO₂ fugacity for the required injection depths. They were adopted assuming hydrostatic conditions and the corresponding value of CO₂ fugacity was calculated using the on-line calculator: http://models.kl-edi.ac.cn/models/co2/}, based on the gas equation, according to Duan et al. [7] (table 5).

**Table 5.** CO₂ fugacity for given temperatures and injection depths.

| Depth (m) | Temperature (°C) |
|-----------|------------------|
|           | 50          | 60          | 80          |
| 1000      | 0.6329     | 0.6732     | 0.7067     |
| 1200      | 0.5634     | 0.6134     | 0.6542     |

The fugacity of the system—fCO₂—is calculated according to the following equation:

\[ f_{CO_2} = \alpha P_{CO_2} \]  

where: \( P_{CO_2} \) is the CO₂ injection pressure, or the partial pressure of the gas prevailing in the original system, \( \alpha \) is the activity coefficient, depending on pressure and temperature.
3.5. Parameters of reaction kinetics

The calculations taking into account the interaction between elements of cement-water-rock-CO$_2$ systems were performed based on the Lasaga dissolution/crystallization kinetic equation (1984 vide [1]). According to this equation a given mineral crystallises in a situation, when the solution is supersaturated (it dissolves when it is undersaturated), at a rate depending on the reaction rate constant and the specific surface area of the mineral:

$$ r_k = A_k k_T \left(1 - \frac{Q}{K}\right) $$

(3)

where:

- $r_k$ – reaction rate ($[\text{mol} \cdot \text{s}^{-1}]$; dissolution $r_k > 0$, precipitation $r_k < 0$),
- $A_k$ – mineral’s surface area $[\text{cm}^2]$,
- $k_T$ – reaction rate constant $[\text{mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}]$,
- $Q$ – activity product,
- $K$ – equilibrium reaction for dissolution.

The kinetic parameters were taken from the literature [8] and recalculated according to the temperature of the modelled geological environment. The dependence of the reaction rate constant on the temperature results from the Arrhenius law and can be calculated on the basis of the following formula, taking into account: neutral, acidic or alkaline mechanism:

$$ k_T = k_{N25} \exp \left[ -\frac{E_N}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right] + k_{H25} \exp \left[ -\frac{E_H}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right] a_{H}^{n_H} + k_{OH25} \exp \left[ -\frac{E_{OH}}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right] a_{OH}^{n_{OH}} $$

(4)

where:

- $k_{25}$ – rate constant at 25°C ($[\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}]$),
- $E$ – activation energy ($[\text{J} / \text{mol}]$),
- $R$ – gas constant ($8.3143 \text{ J} / \text{K} \cdot \text{mol}$),
- $T$ – temperature of the reaction (K),
- $a$ – ion activity;
- index: $N$, $H$, $OH$ – neutral, acidic or alkaline mechanism,
- $n$ – constant.

4. Results

4.1. Modelling of CO$_2$ reaction with wellbore cement

In order to determine the effect of injected CO$_2$ on cement constituents, the kinetics of the reaction were modelled, assuming the composition given in table 1, a chemical composition of cement pore water from table 2, and the following reservoir conditions: temperature 50°C and pressure 100 bar. The gas fugacity $f_{CO2}$ under these conditions equals 63.29 bar. Gas fugacity at the assumed depth (1000 m) is reached gradually after 200 days of CO$_2$ injection into the rock formation. Simulations were conducted for a unit volume of cement (including pore volume), amounting to 10 000 cm$^3$.

It has been assumed that the drilling cement is most exposed to the impact of supercritical CO$_2$ in the roof zone of the permeable layer to which carbon dioxide is injected.
Figure 1. Changes in the amount and volume of cement constituents under the influence of CO$_2$ injection.

The conducted simulation proved that for the formation of the cement composition under the influence of CO$_2$ injection mainly the processes of decomposition of portlandite and C-S-H 1.6 phase, and crystallization of calcium carbonate and silica (in diagrams presented as quartz) are of importance. The processes can be described by the following equations:

$$
\text{C-S-H 1.6} + 3.2 \text{CO}_2(\text{aq}) \rightarrow 3.2 \text{Calcite} + 2 \text{SiO}_2(\text{beta}) + 3.413 \text{H}_2\text{O}
$$

$$
\text{Portlandite} + \text{CO}_2(\text{aq}) \rightarrow \text{Vaterite} + \text{H}_2\text{O}
$$

$$
\text{Portlandite} + \text{CO}_2(\text{aq}) \rightarrow \text{Calcite} + \text{H}_2\text{O}
$$

It is worth noting here, that during the initial several days of simulation there is clearly visible the crystallisation the unstable CaCO$_3$ phase - vaterite, which is later transformed in calcite) - figure 1.

4.2. One-dimensional transport model

A one-dimensional transport and reaction model was made to determine the interaction and geochemical changes, which potentially run along the flow path of pore solutions between the rock saturated with CO$_2$ due to its injection and cement with the original composition of pore waters. The model presents simplified migration of pore water from rock to cement.

It was assumed that under the influence of gas injection into the reservoir rock, within the period of 200 days, the expected pressure is reached. Gas injection causes disruption of the current hydrochemical balance in the rock-water system. After starting the interaction between pore water (in which CO$_2$ was dissolved) and rocks, these waters gain a new composition. Also, thanks to the pressure gradients generated during the gas injection, they can move both within the rock, migrate to open spaces between rock and cement, and to some extent migrate from the rock directly to the interior of the cemented zone.

Noticeable changes in the parameters of cement and its pore waters, under the influence of fluids migrating from rocks to cement during 200 days, are visible to a depth of about 3 cm from the contact with the rock. The changes involved lowering the pH of pore water to a minimal level of about 9 pH, what is a result of displacement of cement pore water by water coming from the rock. Simultaneously, in this zone phase distribution of C-S-H 1.6 and portlandite, as well as crystallization of calcite are observed, which confirms the results obtained during experimental research [9].

Figure 2 shows a simulation of the course of changes in mineral composition of cement during 200 days of reaction at a distance of 1 cm from the entrance zone of the model for samples 7-S, 8-SH, 12-L and 18-A. On the basis of one-dimensional transport and reaction modelling it should be stated that only small differences between the effects of pore water coming from different formation rocks are
noticeable. This is due to the relatively small differences in the composition of these waters. For the formation of their chemical composition the contact with the carbon dioxide injected into the formation is dominant, and consequently, the dissociation of the resulting carbonic acid. Other pore water components (except Cl$^-$ and Na$^+$) occur in such low concentrations that in the modelled reaction time of 200 days the effects differentiating the composition of the analyzed cement samples are not achieved.

The attention is drawn to the fact, that the sum of mineral phases in cement increases by about 4% (table 6). It is associated with a positive balance of the volume of secondary minerals relative to the primary decomposing the cement components.

As a result of the intensive decomposition of C-S-H 1.6 phase there can be produced calcite and girolite in significant quantities:

\[
\text{C-S-H 1.6} + 1.867 \text{H}^+ + 1.867 \text{HCO}_3^- \rightarrow 3.613 \text{H}_2\text{O} + 0.6667 \text{Girolite} + 1.867 \text{Calcite}
\]

On the other hand, decomposition of portlandite contributes mostly to calcite crystallisation.

Formation of silica minerals; such as girolite, ksonotlite or tobermorite, as a result of the reactions, contributes to the increase of cement tightness and strength. Also recrystallizing calcite, filling the gaps that arise, strengthens the structure of drilling cement, as was also shown in the paper of Brandl et al. [10].

**Table 6.** Simulated mineral composition of cement before the experiment, and after 200 days of contact with pore fluids migrating from formation rocks (% vol) at a depth of 1 cm from the contact zone.

| Cement composition       | Initial   | After 200 days contact with rocks’ pore water |
|--------------------------|-----------|-----------------------------------------------|
|                          | 5-S       | 7-S   | 8-SH | 12-L | 18-A |
| C-S-H 1.6                | 24.9      | 4     | 4.4  | 6.7  | 4.1  | 4.0  |
| Portlandite              | 14.0      | 9.9   | 10.2 | 11.9 | 10.0 | 9.9  |
| Calcite                  | 2.0       | 19.1  | 17.8 | 19.2 | 19.1 | 18.3 |
| Katoit                  | 4.0       | 3.8   | 3.8  | 3.8  | 3.8  | 3.8  |
| Ettringite               | 8.8       | 8.8   | 8.8  | 8.8  | 8.8  | 8.8  |
| Hydrotalcite Mg$_6$Al$_2$(OH)$_{12}$(CO$_3$)$_2$ · 2H$_2$O | 1.4 | 0     | 0    | 0    | 0    | 0    |
| Gyrolite Ca$_2$Si$_3$O$_7$(OH) · 2H$_2$O | 0 | 10.9  | 10.8 | 2.5  | 10.7 | 10.7 |
| Edenite Na(Ca$_2$Mg$_5$)(AlSi$_7$)O$_{22}$(OH)$_2$ | 0 | 1.5   | 1.3  | 1.4  | 1.5  | 1.9  |
| Phillipsite (Na) NaAlSi$_3$O$_8$ · 3H$_2$O | 0 | 1.5   | 1.6  | 1.4  | 1.5  | 1.2  |
| SiO$_2$                 | 0         | 0     | 0    | 3.3  | 0    | 0    |
| All minerals (total)     | 55.1      | 59.5  | 58.7 | 59   | 59.5 | 58.6 |
Figure 2. Changes of mineral composition within wellbore cement after 200-days reaction with pore waters migrating from rocks: a – sandstone 7-S, b – shale 8-SH, c – limestone 12-L, d – anhydrite 18-A.

5. Conclusions
1. As a result of the dissolution of the wellbore cement components, the pore solution is enriched with $\text{Ca}^{2+}$ ions, which in the static conditions of the experiment diffuse into the rocks’ pore waters, as evidenced by the crystallization of secondary calcite observed in rocks (irrespective of their lithology).

2. The general balance of soluble components of primary and crystallizing secondary minerals determines the porosity of the tested materials, what in the deposit conditions affects the tightness of the reservoir. The research results show that even if initially a good bonding of rocks and cement was obtained, in the case of the dominance of dissolution processes in the aggressive environment of $\text{CO}_2$ saturated brine, micro-voids may appear in the contact zone. Their further development leads to the loss of the bonding of rock and cement, and threatens the security of the sequestration process.

3. The carried out geochemical modelling proved that due to the contact of the pore waters of the cement with the brine saturated with $\text{CO}_2$, the pH drops rapidly and the environment changes from alkaline to acidic. The simulation also confirms that the main processes occurring in such an environment is the dissolution of C-S-H phases and portlandite, with the simultaneous crystallization of calcite, vaterite and silica. During the time taken into account in the simulation (200 days), the volume of crystals crystallizing in the cement is greater than the volume of dissolved components.

4. Model tests show that in the case of penetration of pore waters from rocks into cement, the most intense transformations occur in cement to a depth of 3 cm from the contact zone with the rock. In this area there is a drop in pH, dissolution of C-S-H phases and portlandite, as well as crystallization
of calcite and other secondary minerals. If the pore water of the cement is not displaced by the pore waters of the rocks, but liquids are mixed, a few percent admixtures of rock water is enough for the pH drop to about 6, and calcite crystallization, and - with further mixing of water - its dissolution.

5. Model tests show that carbon dioxide affects the properties of wellbore cement and rocks, and also changes the geochemical balance in the system. It seems, however, that changes caused by its presence are much stronger in cement. This confirms that in order to guarantee the tightness of underground carbon dioxide traps for many years, it is necessary to ensure proper cementation of the well, using a properly prepared cement paste.

6. References

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Acknowledgments

The research leading to these results has received funding from the Polish-Norwegian Research Programme operated by the National Centre for Research and Development under the Norwegian Financial Mechanism 2009-2014 in the frame of Project Contract No Pol-Nor/207125/66/2013.