# INTERACTION OF CEMENT SAMPLES WITH SUPERCRITICAL $CO_2$

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## Introduction

Safety of any waste storage is based on safety functions of storage system components. $CO_2$ storage multibarrier system comprises of injection borehole casing, cement, used for infill and pluging, and host rock. Their performance and behaviour in both short term and long term periods has to be studied in order to evaluate changes of the materials under $CO_2$ and underground condition influence. The anthropogenic material changes are the most important parameters for injection borehole integrity and potential $CO_2$ leakage.

The main goal of the activities presented in this paper is the study of sp$CO_2$ interaction with cement samples that could be present as an infill around $CO_2$ injection borehole. Two types of concrets were used

**1) Archive Portland type**, used for borehole infill and plugging in Czech Republic untill late 90ties (sample 1, **simulation of old boreholes plugging**)

**2) Mixed Portland type CEM II.**, used for borehole infill and plugging in Czech Republic untill 2011 (sample 2, **simulation of recent pluggings**).

The programme consisted of material selection, laboratory experiments and measurements and result evaluation.

## Experimental measurement

The experimental activities were based on long term interaction of sp$CO_2$ with material samples – static batch experiment - under conditions that would represent storage conditions. The materials used for experiments were **cement paste sample** (see above).

All the samples were carefully characterised using XRD analyses before and after the static experiment. Measurements were carried out on Bruker-AXS D8 Advance device, using LynxEye (radiation CuKλ, voltage 40 kV, current 40 mA). Difraction database PDF-2, 2011 (International Centre for Diffraction Data, Pensylvania, USA) was used for data quantitative evaluation.

The solution used for the experiment was a **synthetic brine** (Tab. 1), prepared on the basis of GCH evaluation of GW composition from potential horizon for $CO_2$ injection in the Permian-Carboniferous basin in NW Bohemia.

The samples were inserted into the glass vials and the synthetic brine was added [V/m = 5:1 in the case sample 1); 2:1 in the case sample 2)]. All the vials were inserted into the high pressure steel chamber (Fig. 1). In the case of experiment 2) two chambers were connected in order to examine more samples (Fig. 2). Blank sample with the brine solution only, was also added. The chamber was closed and filled with sp$CO_2$ (p = 7.5 MPa, T = 35 °C). The samples were kept under selected conditions for at least 100 days. After the experiment the vials were carefully taken out of the chamber and the pH and the conductivity were measured in each vial.

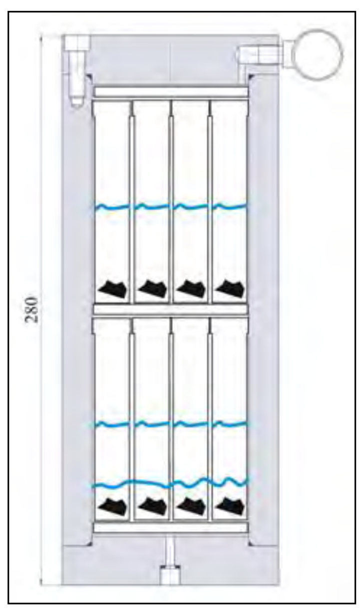

Fig. 1: Pressure steel chamber for long-term static experiment with vial layout and samples.

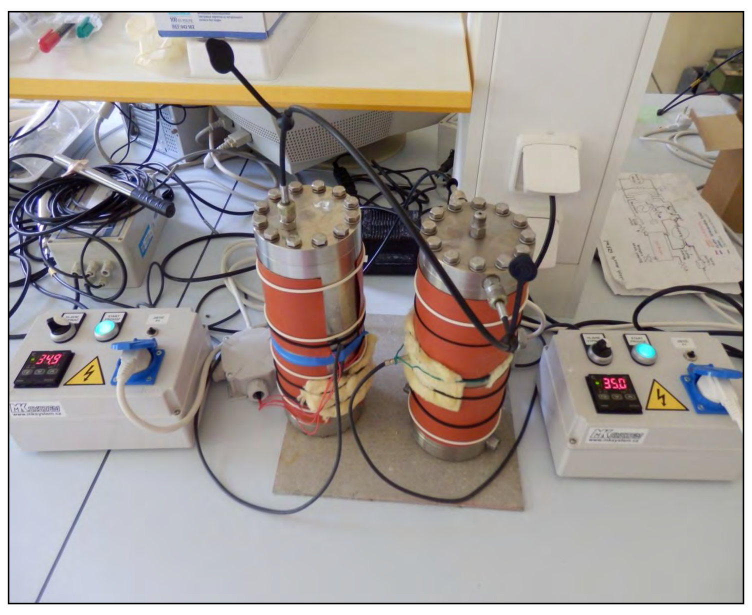

Fig. 2: Photo of double chamber apparatus for long-term static experiment.

## Results

The presented results are focused on cement exposure to sp$CO_2$. The measurement results are showed on the figures and in the tables. The composition of the brine before the static experiment is shown in the Tab. 1. The XRD results were compared before and after static experiment. Results are shown in the Tab. 2, 3 and Fig. 3 - 6.

Tab. 1: The composition of the brine before the static experiment.

| Synthetic brine C (Dn-2/1) | |
|---|---|
| TDS (g/l) | 68 |
| $Ca^{2+}$ (mg/l) | 12,1 |
| $Mg^{2+}$ (mg/l) | 1850,9 |
| $Na^{+}$ (mg/l) | 19298,4 |
| $K^{+}$ (mg/l) | 960,1 |
| $Li^{+}$ (mg/l) | 50,0 |
| $Cl^{-}$ (mg/l) | 34572,0 |
| ($HCO^{3-}$) (mg/l) | 3094,7 |
| $SO_4^{2-}$ (mg/l) | 120,5 |
| $NH_4^{+}$ (mg/l) | 77,0 |
| pH | 7,65 |
| T (°C) | 19,2 |

Tab. 2: The composition of the **archive Portland cement paste (old borehole filling) prior** and after the static experiment (XRD analyses).

| (%) | Cement before $CO_2$ exposure | Cement after static experiment 1 | Cement after static experiment 2 |
|---|---|---|---|
| Portlandite | 41,9 | 0 | 0 |
| Ettringite | 21,37 | 8,46 | 3,9 |
| Brownmillerite (Si,Mg) | 18,21 | 11,01 | 9,48 |
| Calcite | 16,24 | 45,28 | 50,52 |
| Gypsum | 1,27 | 0 | 0 |
| Dolomite | 0 | 1,85 | 6,62 |
| Hydrocalumite | 0 | 15,78 | 11,53 |
| Vaterite | 0 | 16,57 | 16,85 |
| C12A7 Mayenite | 0 | 1,05 | 1,1 |

Tab. 3: The composition of the **mixed cement CEM III. (recent borehole filling)** before and after the static experiment (XRD analyses).

| (%) | Cement before $CO_2$ exposure | Cement after static experiment 1 | Cement after static experiment 2 | Cement after static experiment 3 |
|---|---|---|---|---|
| Portlandite | 29,15 | 11,36 | 7,2 | 14,8 |
| Ettringite | 24,89 | 17,8 | 15.18 | 18,67 |
| | | | | |
| Calcite | 42,95 | 46,06 | 57,23 | 42,34 |
| Gypsum | 1,33 | 0 | | |
| Dolomite | 0 | | | |
| Hydrocalumite | 0 | 24,78 | 18,93 | 22,72 |
| Quartz | 1,69 | 0 | 1,46 | 1,47 |
| | | | | |

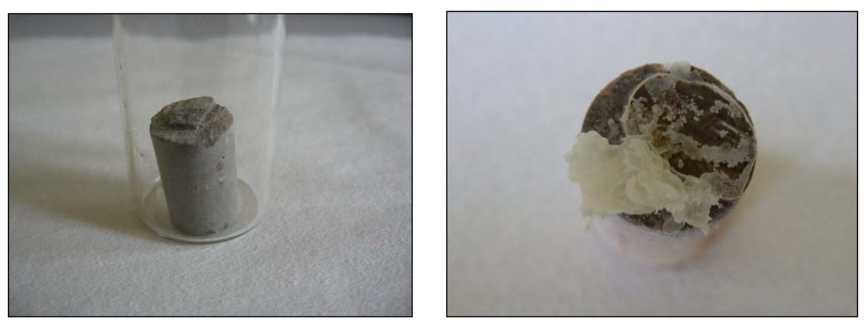

Fig. 3: Photos of **archive Portland cement paste (old borehole filling)** before and after sp$CO_2$ exposure.

Fig. 4: Photos of **mixed cement paste CEM II. (recent borehole filling)** before and after sp$CO_2$ exposure.

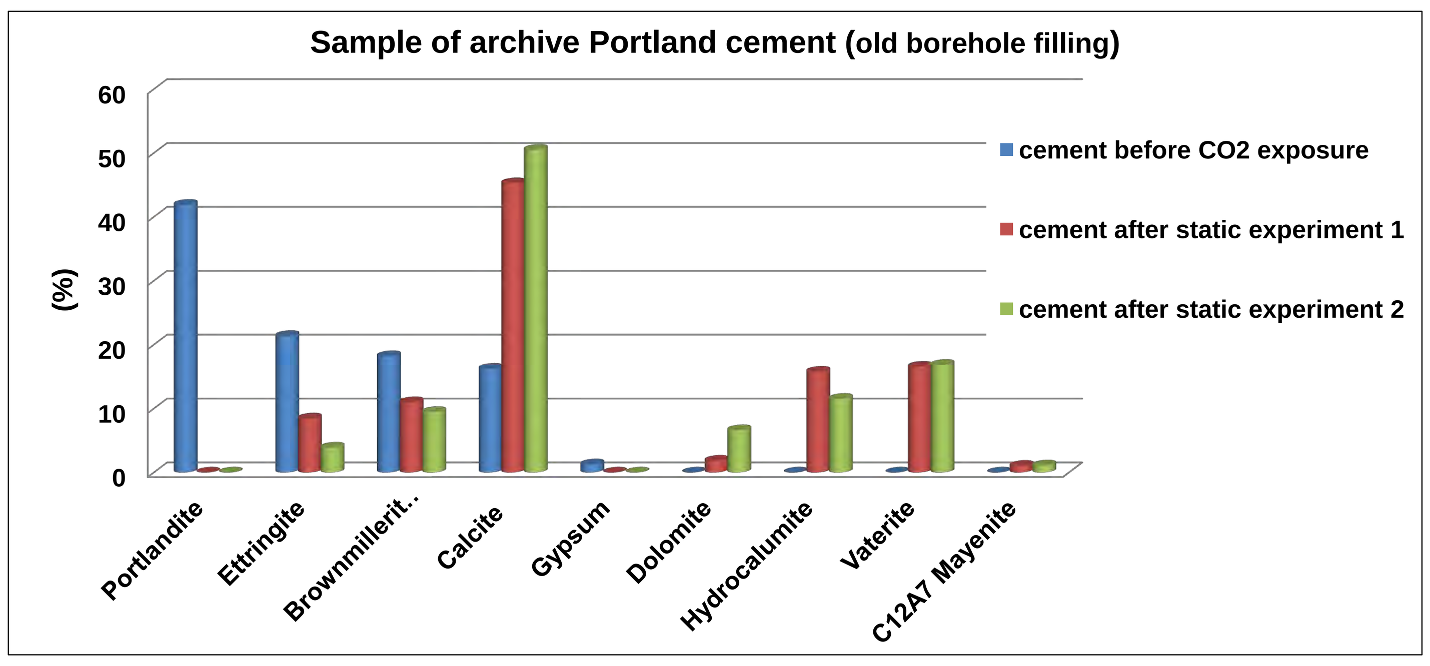


Fig. 5 Comparison of mineralogical composition (wt%) before and after sp$CO_2$ exposure.

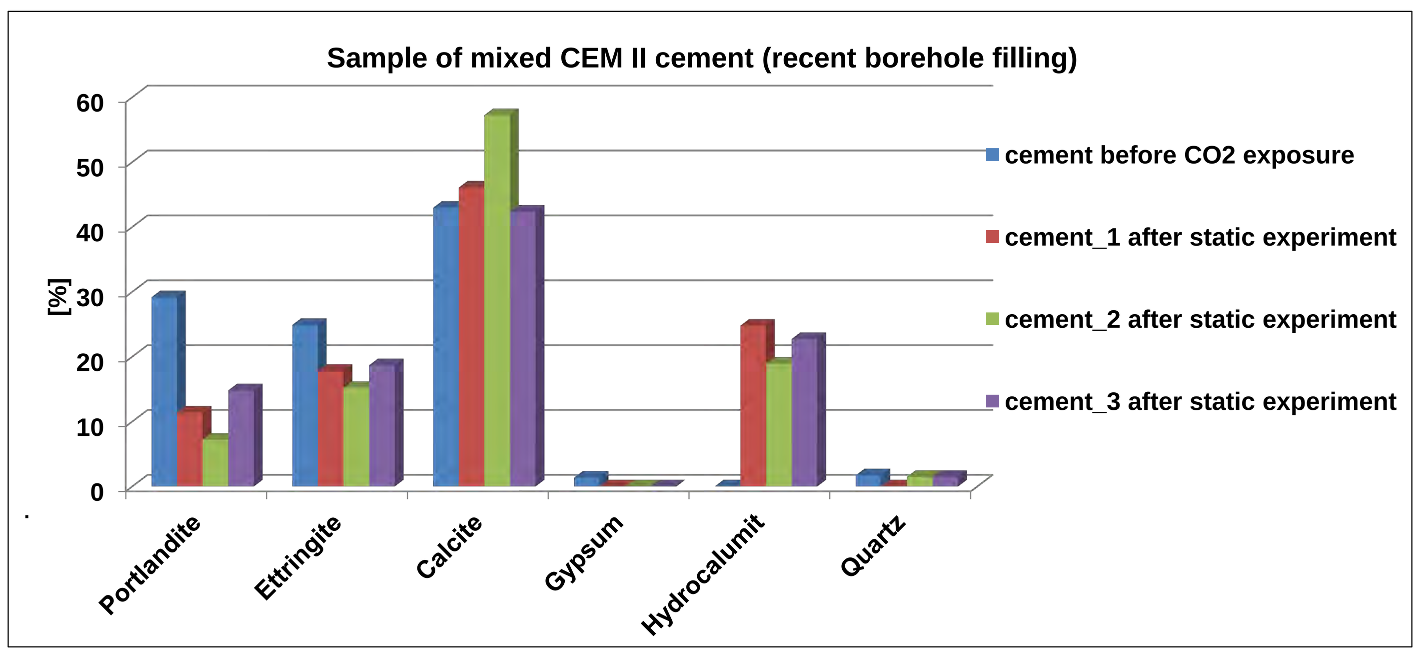


Fig. 6 Comparison of mineralogical composition (wt%) before and after sp$CO_2$ exposure.

## Conclusions

The static experiment was conducted for 100 days. Two types of cement were used: archive Portland cement (sample 1, old borehole infill with higher portlandite content) and mixed cement CEM II. (sample 2; recent borehole filling; higher content of calcite). XRD analyses were carried out before and after exposure $CO_2$. Both cement composition changed after exposure with spCO2. Portlandite phase was dissolved, accompanied by decrease of ettringite and brownmillerite (sample 1). The content of calcite increase drastically for archive Portland cement (sample 1), not so intesively for sample 2. Moreover, content of hydrocalumite incresed in both cement types, and, so as vaterite content in archive Portland cement (sample 1).

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