EVOLUTION OF MINERALOGY AND RADIONUCLIDE DIFFUSION ON PORTLAND-TYPE CEMENTITIOUS MATERIALS DUE GEOCHEMICAL AND THERMAL EFFECTS

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INTRODUCTION

The determination of changes in mineralogy and HTO diffusivities of hardened cement paste (based on Portland cement) after interaction with underground water (GW Josef) and bentonite, belongs to the goals of Czech laboratory program within CEBAMA project. The interaction experiments are designed for two different temperatures: 10 °C corresponds to the in-situ conditions in Josef Underground Laboratory and 95 °C, as an extreme temperature, represents a tool for accelerating geochemical reactions in three curing periods (9, 18 and 27 months) that were planned, of which the third one has not been finished yet [1, 2].

MATERIALS & EXPERIMENTAL SETUP

GROUNDWATER FROM UNDERGROUND LABORATORY JOSEF (GW): see Table 1

HARDENED CEMENT PASTE (HCP): CEM II A-S 42.5R (Lafarge Cement, a.s.), w.c = 0.45

- major phases: portlandite, ettringite, calcite
- minor phases: CO2/Cl-hydrocalumite

BENTONITE SUSPENSION (B75): CZ Bentonite 75 (Keramos, a.s.) mixed with GW (s:l = 1:5)

INTERACTION STUDIES lasted 9 and 18 months in series (see Figure 1):

- HCP+GW: 10 °C or 95 °C
- HCP+B75: 10 °C or 95 °C

ANALYSES OF LIQUID PHASES: pH, AAS, HPLC, titration

MINERALOGY: XRD

HTO THROUGH DIFFUSION EXPERIMENTS at 25°C:

- evolved samples (d = 50 mm; L = 8 mm) from all series – after termination of interaction studies, precipitated carbonates on the surface were peeled off
- in solution: evolved water from series "HCP+GW: 10°C; 9 or 18 months"
- decreasing volume activity in the inlet reservoir
- monitoring HTO volume activity in both working reservoirs; liquid scintillation counter
- concentration profile in the sample using abrasive technique after the termination of diffusion experiments (using artificial corundum sand mixed with cooling water), activity of supernatant was measured
- evaluation: GoldSim software; \( D_e = 2.44 \times 10^{-9} \text{ m}^2 \text{s}^{-1} \) fitting porosity and geometrical factor

RESULTS

HTO THROUGH DIFFUSION EXPERIMENTS: see Figures 2 – 4

EVOLUTION OF LIQUID PHASE: see Table 2

EVOLUTION OF SOLID PHASE: see Figure 5

CONCLUSIONS

The high temperature accelerated the dissolution / transformation of ettringite, which resulted in increase of sulfate concentration in the solution. In the heated samples it was observed newly contained formed hydrothermal mineral katoite and the phases with stability under lower temperatures (CO3/Cl-hydrocalumite) with lower bulk density were missing. The oversaturation of calcium in series with bentonite suspension is linked to large carbonates pool in bentonite and calcium originating from HCP. HTO through-diffusion experiments on samples from both sampling campaigns (after 9 and 18 months) showed that the high temperature treatment raised value of effective diffusion coefficient \( D_e \) even in order of magnitude, which could be related to the dissolution of material under higher temperature (forming minerals with higher density \( \rightarrow \) higher porosity) but also to decreasing of elasticity (formation of microcracks). The geochemical effect (bentonite vs. Groundwater Josef) is less significant in comparison to the thermal effect but the clogging of voids by carbonates from bentonite can not be excluded.

REFERENCES


ACKNOWLEDGEMENT

The research leading to these results has received funding partly from the European Union’s Horizon 2020 Research and Training Programme of the European Atomic Energy Community (EURATOM) (H2020-NFRP-2014/2015) under grant agreement n° 662147 (CEBAMA) and partially from the Grant Agency of the CTU in Prague, grant n° SGS16/250/OHK4/37/11.

Figure 1: a) experimental scheme, b-d) preparation of HCP samples and bentonite suspension, e) in-situ conditions, f) sampling campaign (18 months), g) diffusion cell, h) abrasive technique

Figure 2: Relative volume activity in both reservoirs for series "HCP+GW: 10 °C; 9 or 18 months"

Figure 3: Relative volume activity in both reservoirs for series "HCP+GW: 95 °C; 9 or 18 months"

Figure 4: Mean HTO effective diffusion coefficient \( D_e \), geochemical and thermal effects

Figure 5: Evolution of HCPs mineralogy in sampling campaigns

Table 1: Composition of GW Josef

<table>
<thead>
<tr>
<th>cation</th>
<th>Na+</th>
<th>K+</th>
<th>Ca2+</th>
<th>Mg2+</th>
<th>Cl−</th>
<th>F−</th>
<th>SO42−</th>
<th>OH−</th>
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<tr>
<td>ppm</td>
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<td>ppm</td>
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<td>&lt;1</td>
<td>20</td>
<td>1</td>
<td>245</td>
</tr>
</tbody>
</table>

Table 2: Composition of evolved water from series "HCP+GW: 10 or 95 °C; 9 or 18 months"

<table>
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<tr>
<th>series</th>
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