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 curring 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: CO_2/Cl-hydrocalumite
- **BENTONITE SUSPENSION (B75):** CZ Bentonite 75 (Keramost, 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
- **ANALYZES OF LIQUID PHASES:** pH, AAS, HPLC, titration
- **MINERALOGY:** XRD
- **HTO THROUGH DIFFUSION EXPERIMENTS at 25°C:**
  - evolved samples ($d \approx 50$ mm; $L \approx 8$ mm) from all series – after termination of interaction studies, precipitated carbonates on the surface were peeled of
  - 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; $D_w = 2.44 \cdot 10^{-9}$ $m^2 \cdot s^{-1}$ fitting porosity and geometrical factor

Table 1: Composition of GW Josef

pH	mg·L^{-1}			
	Na^+	K^+	Ca^{2+}	Mg^{2+}
	18	2	87	18
7.6	Cl^-	F^-	SO_4^{2-}	HCO_3^-
	15	1	106	206

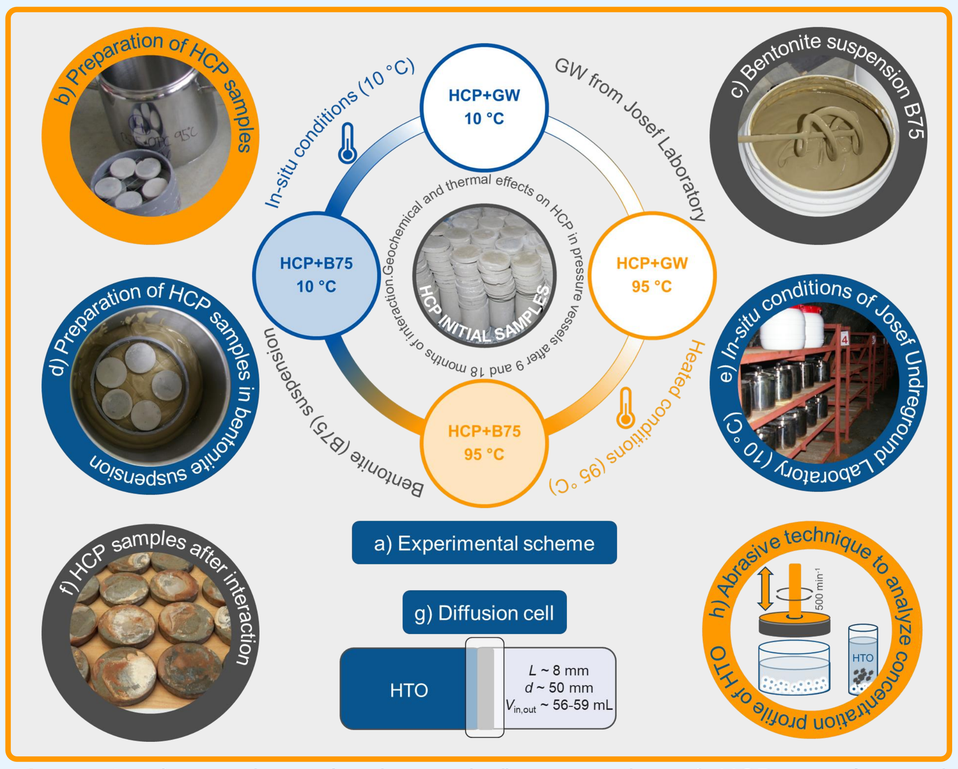

Figure 1: a) experimental scheme, b-d) preparation of HCP samples and bentonite suspension, e) *in-situ* conditions, f) sampling campaign (18 months), g) diffusion cell, h) abrasive technique

RESULTS

- **HTO THROUGH DIFFUSION EXPERIMENTS:** see Figures 2 – 4
- **EVOLUTION OF LIQUID PHASE:** see Table 2
- **EVOLUTION OF SOLID PHASE:** see Figure 5

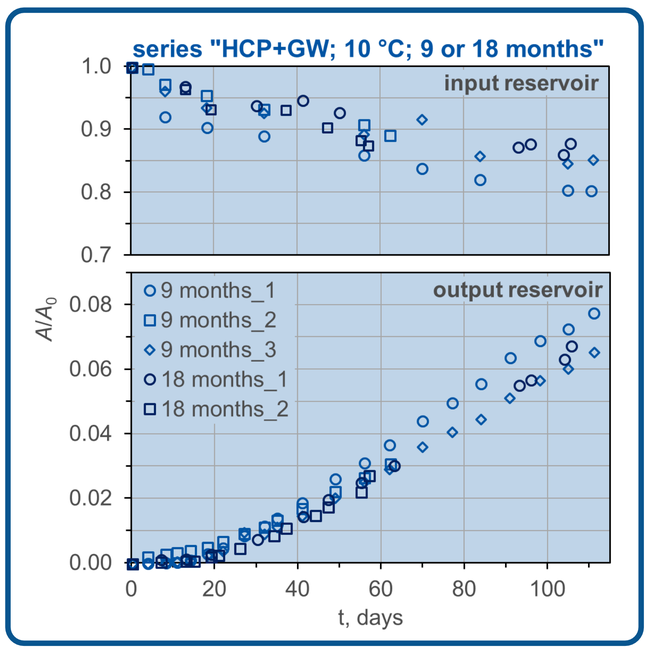

Figure 2: Relative volume activity in both reservoirs for series "HCP+GW; 10 °C; 9 or 18 months"

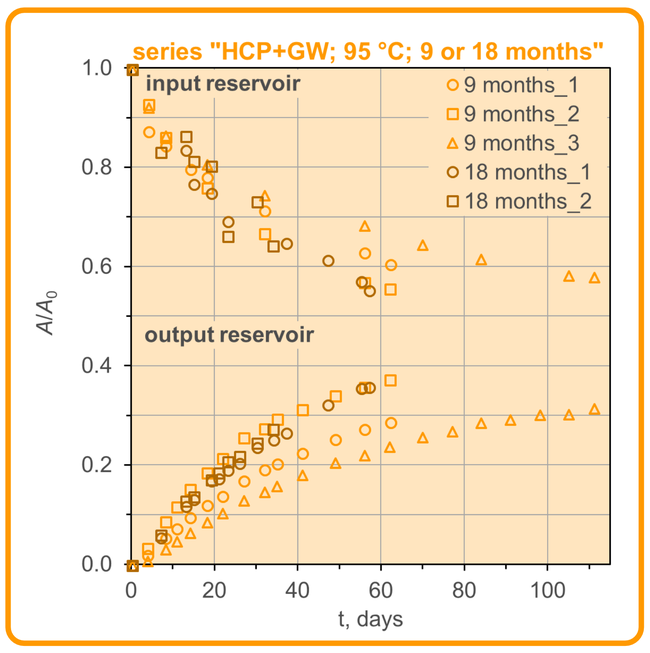

Figure 3: Relative volume activity in both reservoirs for series "HCP+GW; 95 °C; 9 or 18 months"

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

series	pH	mg·L^{-1}							
		Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	F^-	SO_4^{2-}	OH^-
HCP+GW; 10 °C; 9 months	12.5	77	493	15	<1	7	2	36	295
HCP+GW; 10 °C; 18 months	12.3	69	421	2	<1	5	<1	16	227
HCP+GW; 95 °C; 9 months	12.4	85	475	214	<1	19	1	268	380
HCP+GW; 95 °C; 18 months	12.4	79	461	142	<1	20	1	245	262

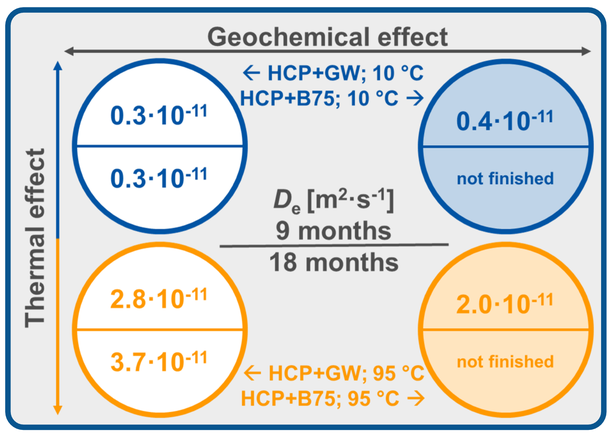

Figure 4: Mean HTO effective diffusion coefficient D_e: geochemical and thermal effects

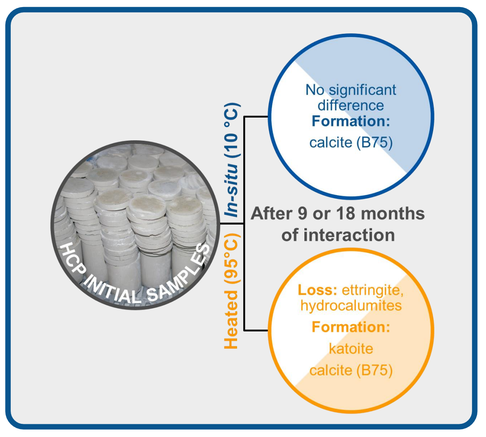

Figure 5: Evolution of HCP's mineralogy in sampling campaigns

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 (CO_2/Cl-hydrocalumite) with lower bulk density were missing. The oversaturation of calcite 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 → 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

[1] Altmaier M. et al. (Edits.) Proceedings of the First Annual Workshop of the HORIZON 2020 CEBAMA Project, KIT Scientific Reports 7734, 77-85.

[2] Altmaier M. et al. (Edits.) Proceedings of the Second Annual Workshop of the HORIZON 2020 CEBAMA Project, draft (available on www.cebama.eu).

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