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Transition metal sorption on bentonite and behaviour of the bentonite/copper/glass system

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Introduction

- In Europe, the final disposal of high-level radioactive waste is planned in deep geological repositories.
- Their long-term safety is guaranteed by natural and engineered barriers, preventing radionuclides from entering the biosphere.
- An important element of the engineered barriers is the backfill material surrounding the waste packages.
- Due to their beneficial physico-chemical properties and high cation exchange capacity, bentonites are considered as a potential backfill material in several waste storage concepts.
- Selected materials of the engineered barrier system of the deep geological repository were examined on a macro, micro and nano scale.

Objectives

- To investigate the retention of Ni(II) and Co(II) by the B75 bentonite through adsorption and desorption experiments
- To study the interactions between materials of the glass/copper/bentonite model system under repository conditions

Materials

- Bentonite/copper/glass engineered barrier system
- Waste matrix: borosilicate glass
  55%SiO_2-10%B_2O_3-25%Na_2O-5%BaO-5%ZrO_2, 2.67 g/cm^3
- Container: copper
  Cu rod (d=2mm, 99.99%), Cu tape (99.7%), Cu sliver (99.8%)
- Buffer: bentonite
  B75 bentonite (Ca,Mg-bentonite, Czechia, <100 µm fraction)

Bentonite	Mineral composition (wt.%)					
Smectite	Quartz	Kaolinite	Illite	Calcite	Siderite	Anatase
82.5	9	2	2	2	2	0.5

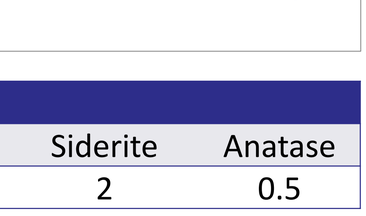
hydraulic conductivity (1.5 g/cm^3): 3.75×10^{-13} m/s
swelling pressure (1.5g/cm^3): 2.7 MPa

Porewater	Dissolved components (M)							
pH	I (M)	Na	K	Mg	Ca	Cl	CO_3/HCO_3	SO_4	Si
8.1	0.02	1.7×10^{-2}	1.8×10^{-4}	2.3×10^{-3}	3.1×10^{-3}	2.3×10^{-2}	6.1×10^{-4}	1.9×10^{-3}	-----

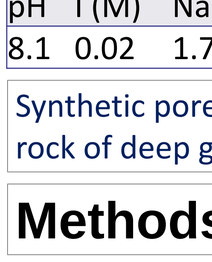
Synthetic porewater characteristic for Boda Claystone Formation, a potential host rock of deep geological repository in Hungary

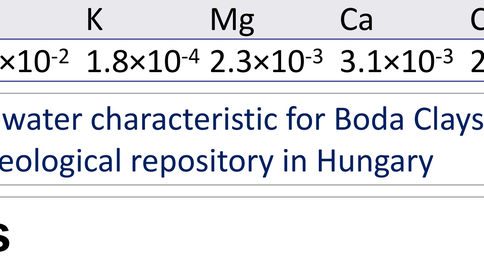
Methods

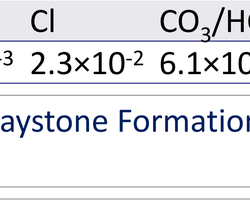
- Sorption/desorption isotherms on bentonite
  batch experiments, dispersed in porewater
  Co(II) and Ni(II) 10^{-7}–10^{-3} M ICP-OES
  Ni(II) 10^{-9}–10^{-3} M ^{63}Ni radiolabeling LSC

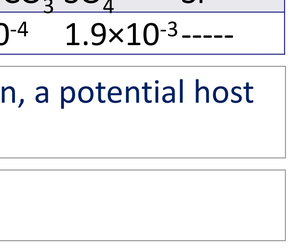


- Triplicate bentonite/copper/glass experiment
  the experimental setup was kept at 80°C
  after 3, 6, and 9 months one container opened
  the ‚system' was fully saturated using porewater





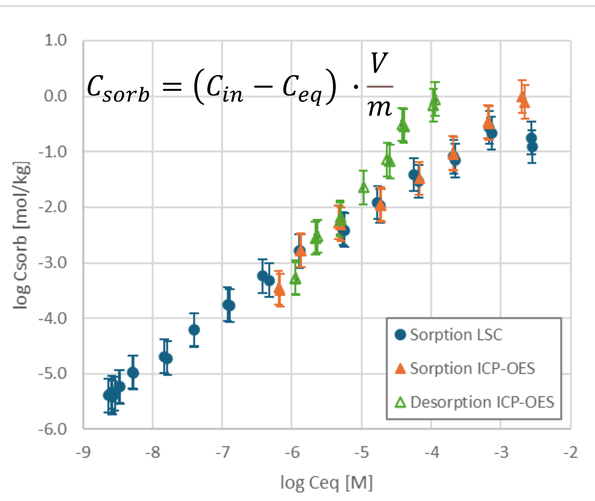


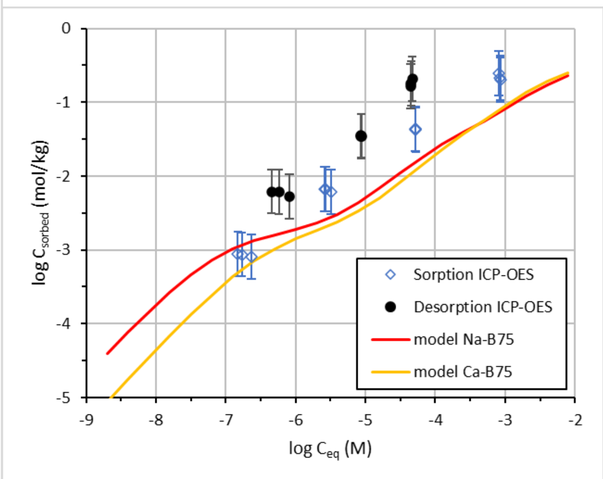


- Post-mortem analysis
  SEM/EDX
  ICP-OES
  IC
  XPS

Results

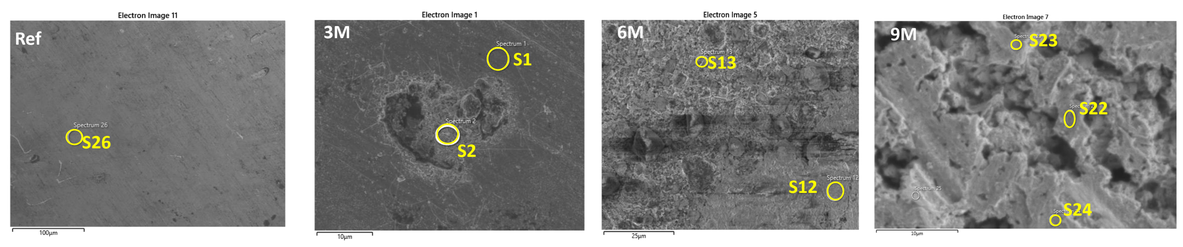
Adsorption/desorption isotherms of Ni(II) and Co(II) on B75 bentonite





Sorption and desorption isotherms indicate irreversibility of sorption for both ions at the highest concentrations.
Supported by modelling considering an 80% Ca-montmorillonite content.
Experimental isotherm underestimated for high concentrations indicating and additional uptake mechanism through formation of a new phase.

SEM/EDX results on Cu surfaces after 3, 6 and 9 months
SEM images of Cu rod surfaces



EDX elemental composition (wt.%) of different Cu surfaces

rod					tape					sliver				
C	N	O	S	Cu	C	N	O	S	Cu	C	N	O	S	Cu
4.0	-	6.3	2.4	86.4	5.2	1.4	7.7	5.4	79.8	3.3	2.9	12.4	1.0	79.6
4.1	-	11.5	-	83.0	8.1	-	42.4	1.7	46.6	3.1	-	18.4	-	74.6
6.9	4.8	28.7	-	59.7	8.6	2.3	25.6	3.7	58.9	3.1	-	17.1	2.8	77.1

It is assumed that upon saturation the canister surface will be covered by a duplex corrosion product layer comprising an inner layer of **Cu_2O** and an outer layer of basic **Cu(II) salts**, most likely malachite ($Cu_2CO_3 \cdot (OH)_2$)

In the case of tape and sliver we can infer to high quantity of $CuCO_3$ and Cu_2O, and the S concentration shows a significant increase, which contribute to the strong appearance of **Cu_2S**.

XPS surface chemical compositions (at.%) of glass surfaces
Only minor changes detected over time

Elements	Si 2p	Zr 3d	O 1s	Ba 3d5	Na 1s	Ca 2p3	K 2p	Mg KL1	B 1s
Glass Ref.	20.5	1.7	60.8	1.5	11.7	0.8	0.5	1.4	2.0
Glass 3M	17.6	7.8	69.8	0.3	2.9	1.9	0.5	0.8	0.5
Glass 6M	15.0	9.3	67.6	0.2	2.2	2.2	0.5	1.1	0.0
Glass 9M	13.8	11.3	65.7	0.1	2.0	2.0	0.6	0.0	0.0

Conclusions

- B75 bentonite binds Ni(II) and Co(II) ions to a similar extent as the Boda claystone (Hungary)
- Electron microscopy investigations revealed a slight corrosion on the copper surface, mainly Cu_2O was detected as a corrosion product
- Only minor changes were observed in the elemental composition of the borosilicate glass surface
- In the simulated geological conditions, the components of the bentonite/Cu/glass engineered barrier system do not exert a significant influence on each other, individually preserving integrity

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