Physical and chemical effects of natural zeolite additives on the cementitious stabilization of cesium and barium isotopes in boric acid liquid waste

Gabriel Iklaga[1]*, Nándo Kaposy[2], Istvan Tolnai[2], Viktória Gável[5], Margit Fábian[2], Csaba Szabó[1,3], Péter Völgyesi[2] and Zsuzsanna Szabó-Krausz[1,4]
[1]Lithosphere Fluid Research Lab, Eötvös Loránd University, Doctoral School of Environmental Science, Budapest, Hungary, (*giklaga@gmail.com)
[2]HUN-REN Centre for Energy Research, Konkoly-Thege Miklós út. 29-33, 1121Budapest
[3]Institute of Earth Physics and Space Science, 9400, Sopron, Hungary
[4]Centre of Environmental Sciences, Eötvös Loránd University, Pázmány P. s. 1/A, 1117, Budapest, Hungary
[5]CEMKUT Research and Development Ltd., Becsi út 122 - 124, 1034, Budapest, Hungary

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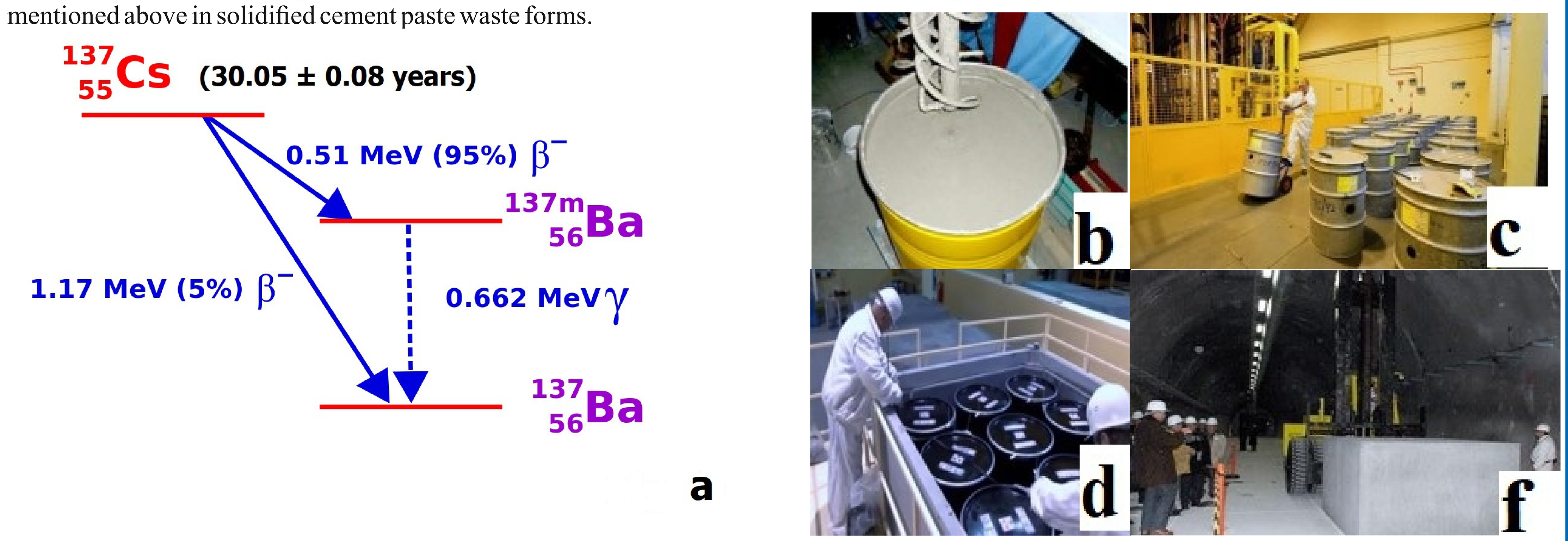
1. Introduction

Boric acid is used in pressurized water reactor (PWR) systems as an efficient neutron absorber for activity control which aids in the maintenance of steady state operating temperature control. Boric acid liquid waste is one of the main waste-streams during the operation of PWR (2000 m^3/year). The boric acid liquid waste produced from the system might contain low concentrations of nuclear fission produced radioisotopes such as ^{137}Cs and its metastable decay product ^{137m}Ba (Fig. 1a). Adequate repository storage of this high-volume liquid waste has become environmentally important for study, as these radioisotopes can become bio-available in the natural systems if not effectively immobilized.

Cementitious matrices can attain physical and chemical stabilities as certain hydrated cement mineral phases can immobilize borates as practised in several repositories around Europe such as the underground disposal facility at Bátaapáti, Hungary (Figs. 1b - f). The aim of our research is to assess the geochemical effects of two natural zeolite (i.e., clinoptilolite and mordenite) additives in sulfoaluminate cement (SAC) and ordinary Portland cement (OPC) blends for optimizing chemical and mechanical stability for immobilizing boric acid liquid waste and contained fission isotopes, mentioned above in solidified cement paste waste forms.



Figs. 1 (a) illustration of ^{137}Cs decay scheme. **(b)** at nuclear waste disposal repository: showing the mixing of liquid waste with cement. **(c)** storage in drums **(d)** packaging in metallic moulds. **(e)** filling the metallic moulds with secondary cement paste layer. **(f)** disposal in underground facility (www.rhk.hu/en) Bátaapáti, Hungary.

2. Geological Background (Natural zeolite-rich samples collection)

Tokaj Mountains, were formed about 11-13 million years ago as a product of volcanism created by a deep structural fault line on the border of the Carpathians and the Great Hungarian Plain. Tokaj - Hegyalja section of the mountain is known to have zeolite-rich rhyolite-tuff (Zajzon, et. al., 2021). For our research, we collected rhyolite-tuff samples from two quarry sites in the region i.e. Rátka quarry site mined by JOSAB Hungary Ltd. geo-position (decimal) 48.21186,21.23374 (where we collected sample ZC Fig. 2) and from Bodrogkeresztúr mined by COLAS Hungary Ltd. geo-position (decimal) 48.17386323878016, 21.33974075317383 (where we collected sample ZM Fig. 2).

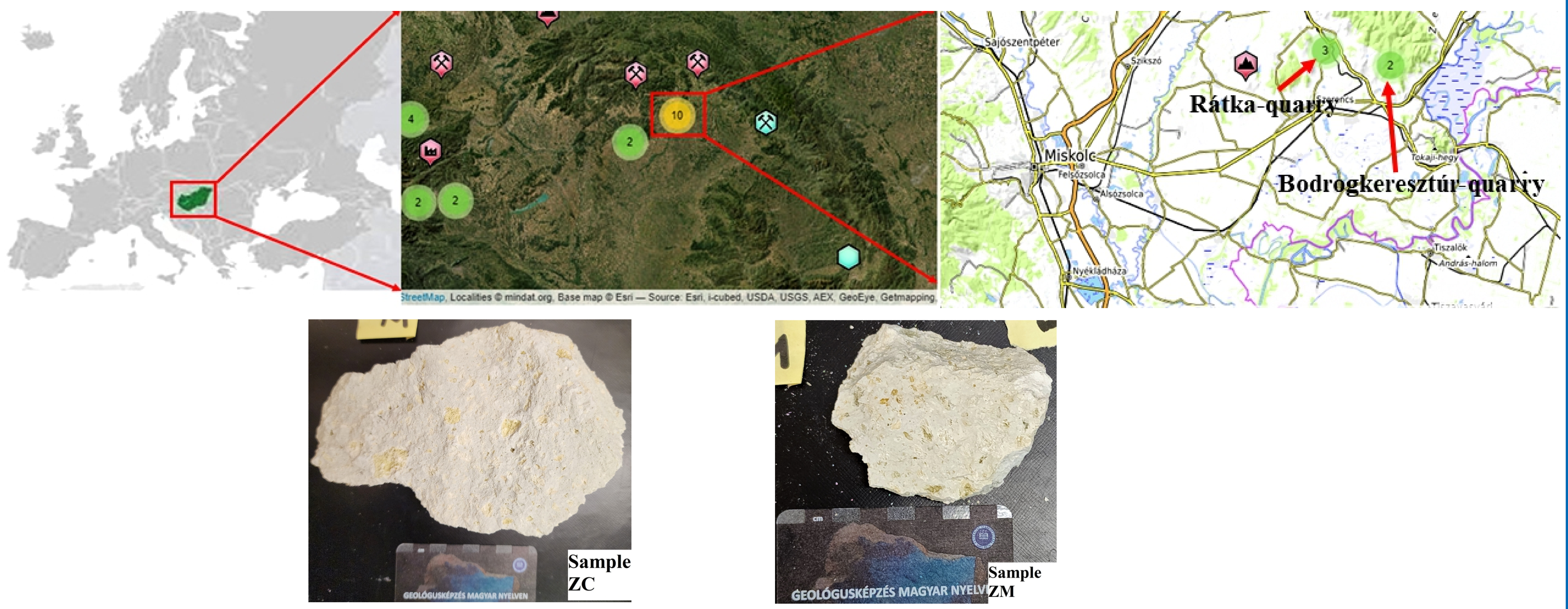


Fig. 2 Showing the sample collection sites (i.e. sample ZC collected from Rátka quarry and sample ZM collected from Bodrogkeresztúr quarry).

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3. Samples ZC and ZM characterization

SEM - SE

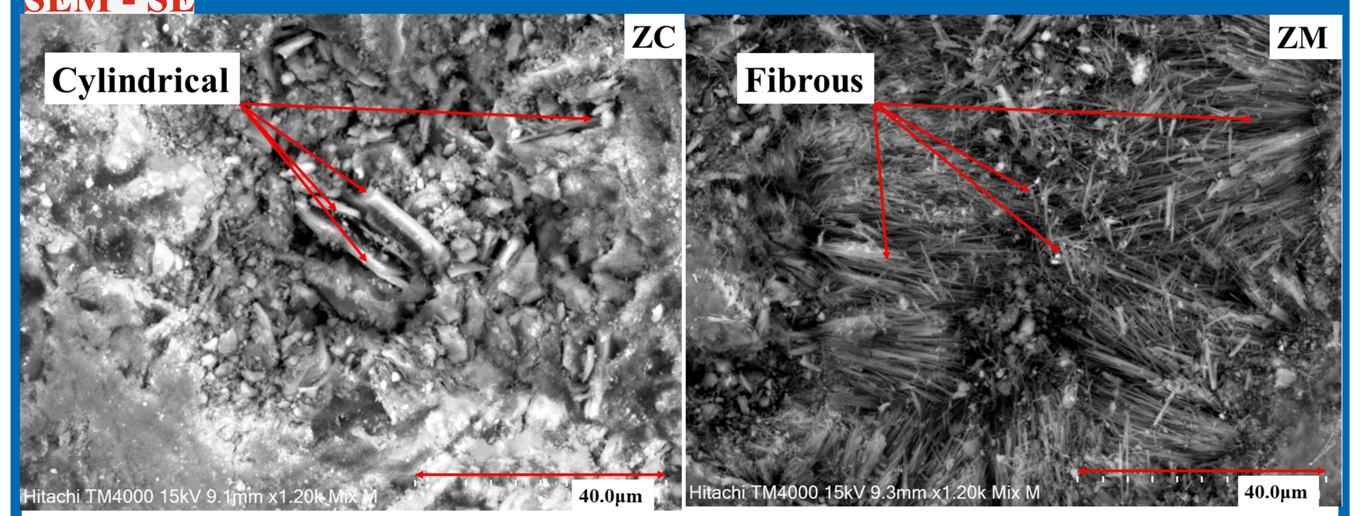


Fig. 3 Scanning electron microscopy (secondary electron) images showing the morphologies of samples ZC and ZM.

ZC: presence of **cylindrical and flake-like shaped** grains
ZM: presence of **fibre-shaped** grains

XRD

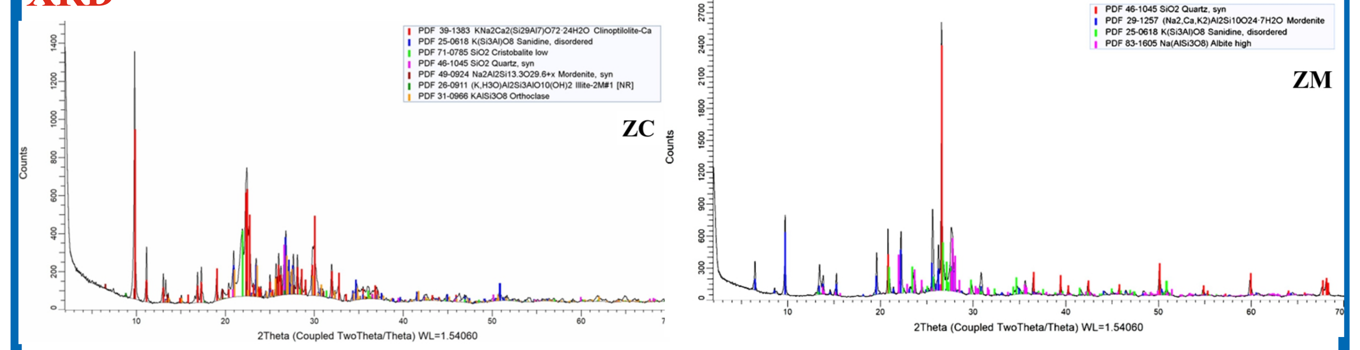


Fig. 4 X-ray diffractograms showing the mineral phases identified in samples ZC and ZM.

ZC: presence of **clinoptilolite $Ca_{3-6}(Si_{30}Al_6)O_{72}\cdot 20H_2O$ (54 m/m %)**
ZM: presence of **mordenite $(Na_2,Ca,K_2)_4(Al_8Si_{40})O_{96}\cdot 28H_2O$ (49 m/m %)**

ICP-MS

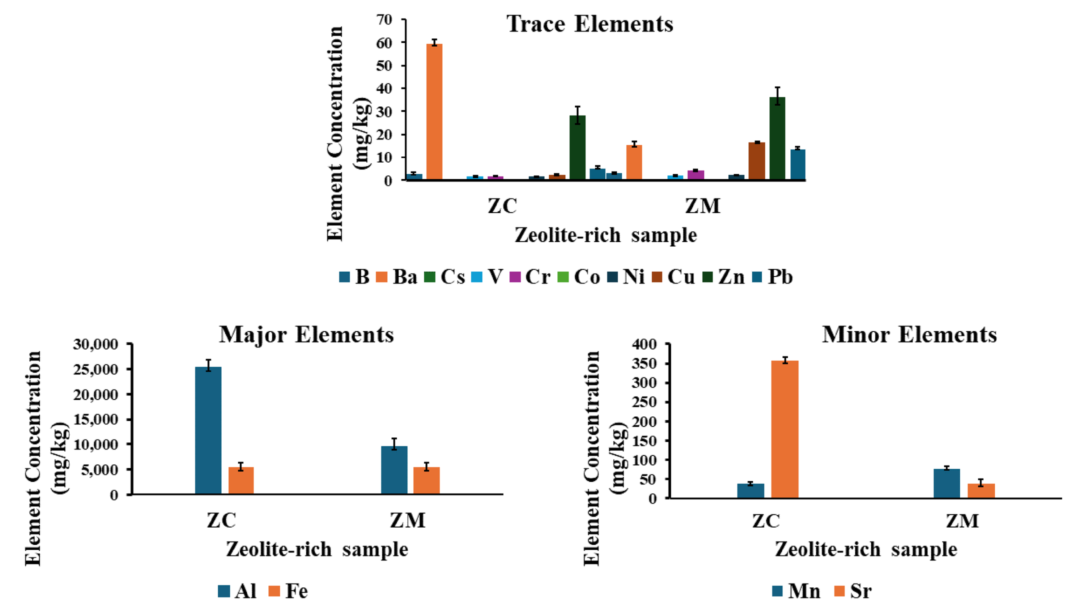


Fig. 5 ICP-MS results of elemental concentrations (mg/kg) measured in samples ZC and ZM.

ZC: significant concentrations of Al, Fe, Sr, Zn and **Ba (59.5±1.7 mg/kg)** with trace amounts of **B (2.85±0.32 mg/kg)** and **Cs (0.631±0.052 mg/kg)**
ZM: significant concentrations of Al, Fe, Mn, Zn and Cu with trace amounts of **Ba (15.2±0.7 mg/kg), B (3.18±0.53 mg/kg)** and **Cs (0.465±0.064 mg/kg)**

4. Cs^+ and Ba^{2+} adsorption test

- A batch adsorption experiment was carried out to assess the possibility of Cs^+ and Ba^{2+} ions adsorption in boric acid liquid waste by the zeolite-rich samples ZC and ZM.
- Furthermore, samples ZC and ZM were **treated with potassium copper(II) hexacyanoferrate (KCuHFC, $CuSO_4$ + $K_4Fe(CN)_6$)** to test its selectivity towards Cs^+ (Kazemian, et al., 2005; Banerjee, et al., 2017; Voronina, et al., 2017; Wang & Zhuang, 2019; Ri, et al., 2023)
- The experiment was carried out at the nuclear chemistry laboratory of the HUN-REN centre for Energy Research, Budapest Hungary. During the experiment, the laboratory was in sterile condition with room temperature regulated at 20 ºC.

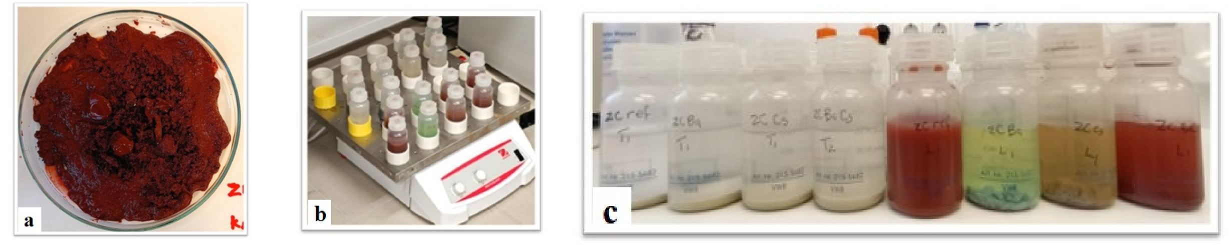
5. Adsorption test materials and methods

Materials

- **Samples ZC and ZM:** were crushed and sieved to 200 - 400 µm range.
- **Orthoboric acid powder (H_3BO_3):** used to prepare the solution that simulates boric acid radioactive waste.
- **Sodium hydroxide (NaOH):** added to the liquid waste to increase boric acid solubility forming borate solution.
- **Cesium nitrate ($CsNO_3$):** added to the borate solution to simulate ^{137}Cs in the liquid waste.
- **Barium nitrate ($Ba(NO_3)_2$):** added to the borate solution to simulate ^{137m}Ba in the liquid waste.
- **Demineralized (DM) water:** used as mixing solvent for the liquid waste solution.
- **Hydrochloric acid (HCl)**: used to treat samples ZC and ZM.
- **Copper (II) sulfate ($CuSO_4$):** loaded into pores of ZC and ZM to optimize ion-exchange capacity.
- **Potassium hexacyanoferrate (II) trihydrate ($K_4Fe(CN)_6$):** loaded in ZC and ZM to optimize ion-exchange capacity.

Methods

- **Simulated liquid waste preparation:** solid H_3BO_3, NaOH, $CsNO_3$ and $Ba(NO_3)_2$ were mixed in DM water to simulate boric acid liquid waste containing 40000 ppm boron and 300 ppm cesium and barium trace concentrations.
- **ZC and ZM treatment:** the crushed samples were immersed in 0.5 M HCl solution for 24 hr, vacuum-filtered and dried to eliminate carbonate mineral phases. The samples were then immersed in 0.5 M CuSO4 solution for 3 hr while been magnet-mixed at 530 rpm at 80 ºC, then vacuum-filtered and dried. Finally, the samples were immersed in 0.5 M $K_4Fe(CN)_6$ solution and magnet-mixed at 530 rpm at room temperature for 24 hr, then vacuum-filtered and dried to produce a coffee-brown substrate (Fig. 6a).
- **Adsorption test procedure:** each set of treated and untreated crushed zeolite-rich sample (ZC and ZM) were immersed in the prepared simulated liquid waste and table stirred at 150 rpm for 3 hr (Fig. 6b) until equilibrium concentration between the liquid and solid phase was attained (Fig. 6c). The liquid phase was decantated from the solid phase for analytical measurement.



(**Fig. 6 (a)** potassium copper hexacyanoferrate-treated ZC and ZM samples appear brownish. **(b)** samples ZC and ZM stirred to attain adsorption equilibrium concentration. **(c)**solid and liquid phases produced after the adsorption test.

6. Result: ICP-OES

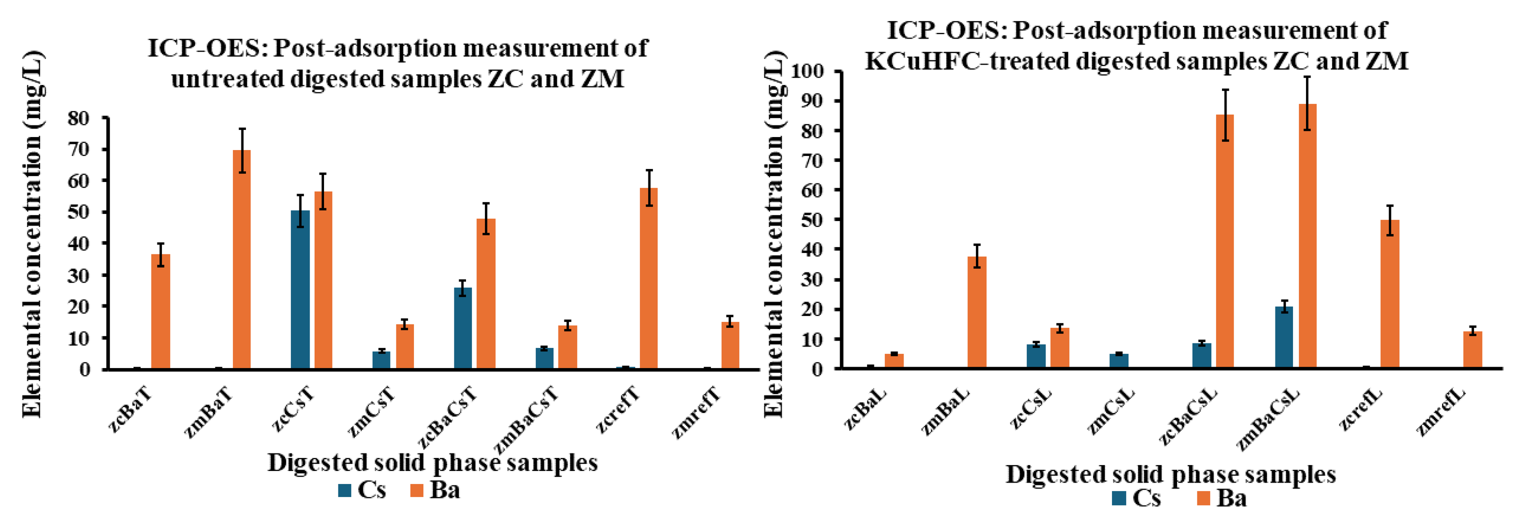


Fig. 7 Measured Showing the post-adsorption test ICP-OES elemental concentration of Cs and Ba in the digested solid phase samples that had been immersed in the simulated boric acid solution with pre-adsorption concentrations of **B** = 40000 ppm; **Cs** = 300 ppm and **Ba** = 300 ppm.

Note: zc = sample rich in clinoptilolite; **zm** = sample rich in mordenite; **T** = untreated samples; **L**= samples treated with potassium copper hexacynoferrate; **Ba** = sample immersed in boric acid liquid waste + barium nitrate; **Cs** = solid sample immersed in boric acid liquid waste + cesium nitrate; **BaCs** = solid samples immersed in boric acid liquid waste + barium nitrate + cesium nitrate; **ref** = solid samples immersed in DM water.

7. Summary

- Characterization analyses of the samples collected from Tokaj Mountain, Hungary indicated that sample ZC is rich in clinoptilolite (54 m/m %) and sample ZM is rich in mordenite (49 m/m %)
- A batch adsorption test was carried out on untreated and KCuHCF-treated ZC and ZM samples immersed in simulated boric acid liquid waste with trace concentrations of Cs and Ba.
- ICP-OES results indicate that untreated sample ZC showed the most significant Cs adsorptivity with about 7 order of magnitude more than sample ZM. However, the KCuHCF-treated samples showed no sign of improving the Cs adsorptivity of the natural zeolite-rich samples.

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