Experimental assessment of chemical stability of waste-forms containing OPC and SAC cement and a novel radioactive waste, ^{10}B enriched boric acid

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Abstract
Due to the technical capabilities of enriched boric acid (EBA) compared to normal/natural boric acid (NBA), some pioneer nuclear power plants have started to apply EBA instead of NBA, as a novel neutron absorber. The volume of EBA-radwastes is increasing while there is no available data about the conditioning of EBA waste streams. The significant mass difference between the stable isotopes of boron (^{10}B/^{11}B) and also the pH dependence of borate molecules' geometries are expected to cause varied behaviors of NBA and EBA in cementitious matrices which can influence the chemical stability and durability of their final waste-forms. This is the first study to prove this phenomenon by providing XRD, SEM, ICP-OES, and ICP-MS data about leaching tests on OPC and SAC cement pastes containing NBA/EBA. The results showed that the cement pastes prepared with EBA have different mineralogy and varied boron-leachabilities compared to the specimens prepared with NBA.

Keywords: novel neutron absorber; radioactive waste immobilization; boron leaching; molecular geometry; stable isotope fractionation

Introduction
Boric acid waste streams are the most significant radioactive waste residues during the operation of nuclear power plants, which are commonly solidified by different formulations of cementitious materials before their long-term disposal. Lately, and with the aim to optimize the reactor moderators, some countries have replaced the natural boric acid (NBA, 20% ^{10}B and 80% ^{11}B) with a novel borate absorber, ^{10}B enriched boric acid (EBA, up to 90% ^{10}B) [1]. However, even though there are many studies about the technical and even economic advantages of EBA compared to NBA, there is no available data about the conditioning of EBA containing radioactive wastes. Nevertheless, due to several factors including a) high relative mass difference between the dominant boron isotopes of NBA and EBA (^{11}B and ^{10}B), b) pH dependence of the borate molecules' geometries [2], and c) borate geometries' tendency to incorporate different boron isotopes [3], the geochemical behaviors of NBA and EBA are expected to be different in cementitious matrices. If this theory is confirmed, it means the compatibilities of NBA and EBA and consequently, the long-term stability and durability of the cementitious final waste-forms containing these two neutron absorbers are different, which should be considered in the long-term disposal design.

In this study, both isotopic and elemental boron leachabilities from simulated waste-forms made with ordinary Portland cement (OPC) and also sulfoaluminate cement (SAC) were selected as indices and used to compare the chemical stability of cementitious waste-forms containing EBA and NBA.

Experimental
Preparation of the materials
For reaching the aims of this study, three main stages were followed: 1) preparation and mineralogical assessment of simulated final waste-forms before leaching test, 2) running leaching tests and evaluation of the amount and rate of released boron, and 3) mineralogical analysis of the cementitious specimens after leaching test.

Accordingly, cementitious final waste-forms were prepared via mixing simulated liquid boric acid wastes (Table 1) and appropriate mass of cement powder with W/C=0.4. Cement powders contained pure OPC, pure SAC, and a 50-50 % mix of these two cement types. To overcome the boron retarding effects and increase the boric acid solubility, NaOH powder was added to the liquid waste with a Na/B ratio of 1.25. The cement pastes were poured into molds and were let to cure for 28 days at adjusted temperature and humidity. Then the solidified specimens were immersed in demineralized water (as leachant) and the leaching test was started according to the procedure introduced in ASTM C1308-08 (2017) standard. The extracted leachate solutions were analyzed elementally and isotopically by ICP-OES and ICP-MS for getting to know the amounts and the rates of boron leaching as well as the ratios of $^{10}B/^{11}B$. The cementitious specimens were analyzed before and after the leaching test by using XRD and SEM-EDX techniques.

Table 1. Specifications of simulated boric acid wastes

Sample ID	Boron elemental concentration (g/l)	^{10}B enrichment (%)
L0	0	-
LE2	20	95
LN2	20	19.8
LE4	40	95
LN4	40	19.8
LE6	60	95
LN6	60	19.8

Results and discussion

The results of mineralogical analyses on the solidified samples before running the leaching tests showed that for all the cementitious samples, the mineralogy of the specimens changes significantly with increasing the boron concentration. These changes are mostly related to the retarding effects of boron on the cementitious matrices and also to the shortage of necessary pore water for cement hydration. This incomplete hydration can cause several adverse physical effects on the stability and durability of the cementitious matrices. The results of the mineralogical tests on the solidified samples after the leaching test showed a limited depth of water diffusion into the OPC samples (less than 300 µm) where almost all of the boron-containing phases disappeared (dissolved) from the NBA specimens but just some of these phases dissolved from the EBA specimens during the leaching process. The mineralogical comparisons of the pure SAC and the OPC-SAC samples are ongoing. The results of ICP-OES and ICP-MS for the OPC waste-forms showed that both the amount and the rate of boron leaching from the cementitious matrices increase when the initial boron concentration increases (Fig. 1). This phenomenon is related to the higher availability of boron-containing phases and the subsequent higher possibility of their release from the solidified matrix. Furthermore, in each fixed concentration, the OPC solid samples made by EBA showed lower boron leachability in both the amount (29%) and the rate (46%) than the samples made by NBA (Fig. 1). This phenomenon is related to the existence of different molecular geometries of boron and the isotopic composition of the EBA and NBA solutions. Borates exist in two main geometries, trigonal and tetrahedral forms where trigonal prefers the heavier isotopes (^{11}B) and tetrahedral prefers the lighter isotope (^{10}B) [3]. Therefore, the different liquid solutions can provide varied interactions with cement and subsequently different mineralogies occur in their final waste-forms where varied values of chemical stabilities and consequently different long-term durabilities can be expected. The assessments of the samples with pure SAC and SAC-OPC will be presented at the conference.

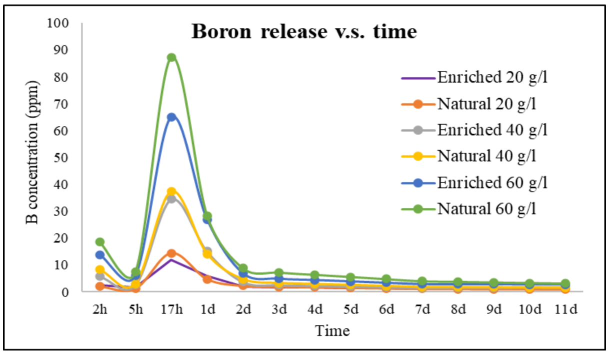

Figure 1. Boron leachability v.s. time of OPC samples

Conclusions

This is the first study to compare the chemical stability of cementitious radioactive wastes-forms containing EBA with OPC and SAC. The results showed that the mineralogy of cementitious waste-forms made by EBA and NBA are different. Also, the OPC waste-forms made by EBA showed a lower both amount and rate of boron leaching than the samples made by NBA. These refer to different stability and long-term durability of waste-forms containing EBA or NBA.

Acknowledgments

The authors express their thanks to Levente Illés at the Institute of Technical Physics and Materials Science at the Centre for Energy Research, Viktória Gável at CEMKUT Research & Development Ltd., and László Előd Aradi and others at Eötvös Loránd University for their support during this study. This work was supported by the Stipendium Hungaricum Scholarship to Mojtaba Rostamiparsa; the Premium Postdoctorate Research grant to Zsuzsanna Szabó-Krausz provided by the Hungarian Academy of Sciences; and the ELTE Institutional Excellence Program to Zsuzsanna Szabó-Krausz and Csaba Szabó funded by the Hungarian Ministry of Human Capacities.

References

[1] J. Xu, W. Zhang, The application of 10B enriched boric acid in nuclear power industry, Int. Conf. Nucl. Eng. Proceedings, ICONE. 3 (2010) 1–5.

[2] S. Böhlke, C. Schuster, A. Hurtado, About the volatility of boron in aqueous solutions of borates with vapor in relevance to BWR-reactors, in: Int. Conf. Phys. React. " Nucl. Power A Sustain. Resour., Interlaken, Switzerland, 2008: pp. 3089–3096.

[3] H. Marschall, G. Foster, Advances in Isotope Geochemistry- Boron isotopes, Springer, Switzerland, 2018.