

## Evolution of interfacial water speciation during the initial leaching stage of alkali- borosilicate-glasses

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**Abstract:** Alkali-borosilicate glasses (ABS) are used as host immobilization matrices for different radioactive waste streams and are characterized by their ability to incorporate a wide variety of metal oxides with respectively high waste loadings. The vitreous wasteform is also characterized by very good physical and chemical durability. The durability of three ABS compositions were analyzed by investigating their leaching behavior using the MCC1 test protocol and these data were used to investigate the waste components retention in the altered layer and the evolution of the interfacial water composition during the test. The results indicated that the Mg species evolution is exceptional with respect to other alkaline elements and dependent on glass matrix composition and leaching progress, while transition elements speciation is fairly constant throughout leaching process and independent on glass compositions. Si and B species are changing during leaching process and are affected by waste composition. For modified wasteform sample, evolution of Mg, Si and B species is respectively constant, whereas at highest waste loading, these elements have fairly constant speciation evolution within the first 2 weeks of leaching.

**Keywords:** Vitreous wasteforms, Alkali borosilicate glass, Leaching, Retention factors, Speciation.

### INTRODUCTION:

The long-term safety of nuclear/radioactive waste disposal sites depends on the integrated performance of passive engineered barriers and natural barriers to control

radionuclides releases from the disposal facility [1, 2]. To assess the long-term performance of the disposal practice, the features, events, and processes (FEP) that may occur and affect the safety of the practice are used to build reference and alternative scenarios [1, 2]. The developed scenarios are used to model the evolution of the disposal performance [3]. Natural evolution scenario is usually considered as the reference scenario for geological disposal, it describes the projected state of the natural and engineered barriers due to the presence of most probable features, events and process [4-6]. In natural evolution scenario, the performance of the waste package could be compromised due to different chemical, thermal, mechanical, hydraulic, biological, and radiological processes that take place over thousands of years, leading to radio-contaminant and chemical elements releases from the waste package [7,8]. For example, the reference scenario for Forsmark site assumed waste package failure due to hydraulic process and to lesser extent to mechanical process after one million year [4]. The released radio-contaminants and chemical will be available for transport through or retention in different engineered and natural barriers via water, gas, or/and solid media. The chemical speciation and solubility of the released elements largely affect their migration or retention in different media.

The hydraulic failure process is initiated due to the presence of water in the natural barriers in the form of interstitial water and/or flowing water at very low flow rate [9]. The presence of water can lead to waste package failure and wastefrom corrosion and facilitate radionuclides and chemical element transport. The processes that lead to wastefrom corrosion include ion-exchange, dissolution, and diffusion, whereas the main processes that affects the fate of the released chemical elements and radio-contaminants through different engineered and natural barriers includes advection, dispersion, molecular diffusion, dissolution, precipitation, and mineralization, speciation and solubility, complexation, colloidal transport, and sorption [7]. Subsequently, the performance of any barrier is assessed by investigating the release, retention, and transport of the radio-contaminant in the barrier within specified timeframe.

Generally, leaching tests are conducted to determine the leach rate from the wastefrom and used to understand contaminant binding and leaching mechanisms, design and optimize the wastefrom composition, support the disposal long-term safety assessment and as a quality control tool to assess compliance with regulatory or operational criteria [8, 10-14]. Standard leaching tests are designed to simulate contaminant and structure elements releases into the interfacial water under a specific set of experimental conditions that reflects the adopted safety strategy [8]. The investigations of leaching characteristics of glass based wastefrom was carried out using dynamic and static leaching tests by varying the waste and leachant compositions under different leaching conditions [15-23]. The analysis of the glass leaching results led to the identification of the main corrosion processes, the basic corrosion stages, the nature of the altered glass layers and the factors that affect them. The investigation of the evolution of the leachant compositions during the leaching test was used to calculate the normalized release rate and determine the altered glass fraction and thickness [15, 16, 23-26].

Speciation of different elements in the altered and unaltered glass layers and in the leachant were carried out to quantify the coordination nature of these elements and determine the progress of the corrosion process and the secondary alteration phases [27, 28]. This work is a continuation of our previous research, where the initial leaching characteristics of alkali-borosilicate, modified borosilicate-waste glass, and borosilicate-waste glasses of two waste loading ratios were evaluated [15, 16]. The immobilization of Ruthenium and Chromium in modified alkali borosilicate waste matrix was evaluated and the role of the ion exchange process in the leaching was quantified [15]. The leaching process were identified for alkali-borosilicate nuclear wastes and the main process were identified for the structural element, modifier and waste components and the role of each element in the determining the matrix instability was quantified [16]. In this work, the

evolution of the leachant chemical compositions as a simulation for interfacial water will be evaluated during the initial leaching stage for three vitreous nuclear wasteforms.

## MATERIALS AND METHODS

Alkali-borosilicate-waste (ABS) glass samples that represent different Magnox loadings in unmodified and modified matrices, i.e. ABS-waste(17)(ABS-17% Magnox), MABS-Waste (20) (Modified ABS-20% Magnox), and ABS-Waste (25) (ABS-25% Mixed oxide) were prepared as described in Farid et.al. [15,16]. The chemical compositions of the studied samples are listed in Table 1, where Magnox waste composed of alkali (Cs<sub>2</sub>O), Alkaline (BaO, MgO, SrO), post transition and metalloid (Al<sub>2</sub>O<sub>3</sub>, TeO<sub>2</sub>), transition (Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub>, RuO<sub>2</sub>, ZrO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>), and rare earth (CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>) Oxides. Glass leaching experiments were carried in triplicates according to MCC1 (ASTM C1220-10) static leaching test [17]. The evolution of the leachant chemical composition during the progress of the leaching process was detected by using inductively coupled plasma optical emission spectroscopy (ICP-OES). The experimental data (average of triplicates) were used to study the evolution of the different element species in the leachant and calculate the retention factors (RF) in the altered layer, where RF is given by [9, 29]:

$$RF(i) = 1 - \frac{NL_i}{NL_B} \quad (1)$$

Table 1 Chemical composition of studied glasses

Waste components	Glass forming oxides				Modifier oxides		Magnox waste oxides
	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	Li <sub>2</sub> O	CaO	ZnO	
ABS-Waste (17*)	50.2	15.4	8.8	8.7	--	--	16.9
MABS- Waste (20*)	44.26	17.95	9.01	2.11	1.39	4.43	20.85
ABS-Waste (25*)	46.28	16.43	8.33	3.98	--	--	24.98

\*approximately

The speciation studies were performed using hydra-medusa and Visual Minteq [3], where the temporal concentration of the glass elements, modifiers, and waste components were used to trace the evolution of the species fraction for all the studied elements by fixing the temperature at 90°C and the pH was calculated from the mass and charge balance.

## RESULTS AND DISCUSSION

### Waste components retention in the altered layer

The retention factors of all components of waste matrices in the altered layer after 21 day of leaching are illustrated in Fig. 1. The retention of the alkaline earth, transition, and rare earth elements is the lowest in the sample ABS-Waste 17 except for magnesium and cerium. The relative mobility of alkaline and rare earth elements was further investigated by plotting Mg and Ce concentrations versus (Ba and Sr), and (Nd and La) concentration in the leachant, respectively (Fig 2 (a-d)). Mg relative mobility is much higher than that of Sr and Ba for all studied times independent on the glass matrix

compositions(Fig 2(a, b)), where the relative mobility of Nd is similar to that of Ce from sample ABS-Waste (17) and decreases by increasing the leaching duration for modified sample and the sample with the highest waste loading ( Fig 2.c).The relative mobility for La is much smaller than that of Ce (fig.2.d). The relative mobility of Mg could be explained by its high hydration free energy and high loading in the magnox waste [16].

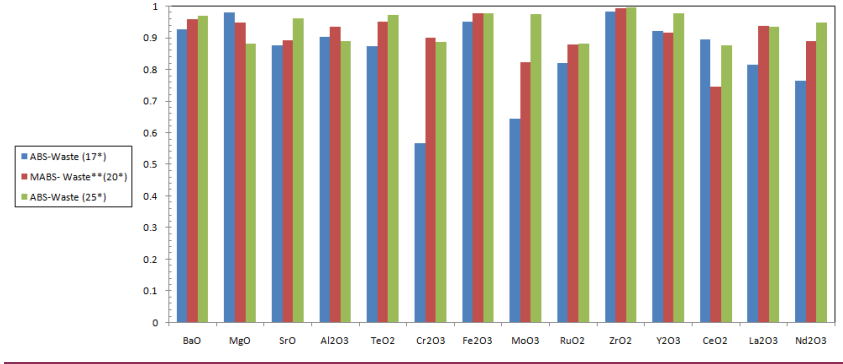


Fig. 1 Retention factor for waste components at 21 days

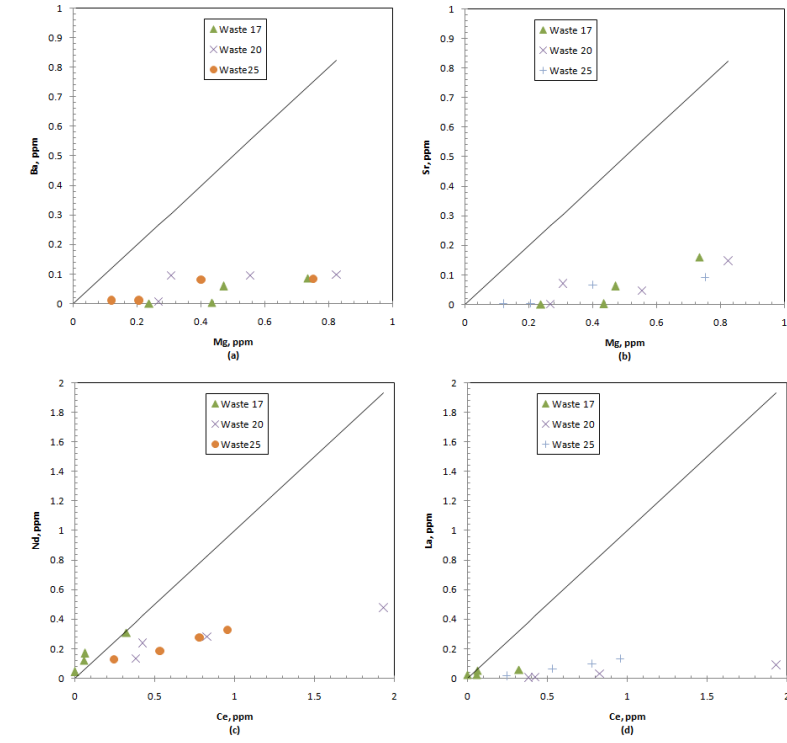
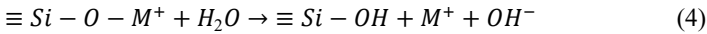
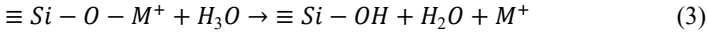
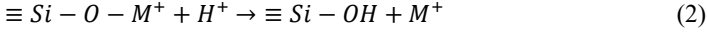


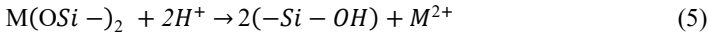
Fig.2 Relative mobility of (a) alkaline elements, (b) rare elements in the leachant of the studied glasses

## Leachant speciation for ABS-Waste 17

The calculated pH was found to increase with increasing the leaching time which is typical for glass leaching. The released alkali elements is mainly found in free ion state, i.e.  $\text{Na}^+$ ,  $\text{Li}^+$ , and  $\text{Cs}^+$  (fraction >99.9%) minor amount of hydroxide (OH) and borate ( $\text{H}_2\text{BO}_3$ ) of Na and Li are formed and increase slightly by the progress of the leaching process (Fig.3). The release of free ions from the glass matrices could be attributed to the following reactions [15, 30-32]:



The speciation of the alkaline elements is nearly constant for barium and strontium with free ion species (%) >98.5 and 98.25, respectively. Minor hydroxide and borate species exist and their contribution increases with increasing the leaching time (Figure omitted). The release of free divalent ions that are incorporated in the vitreous matrix could be described by the following reaction [33]:



An exception for this behaviour is the Mg speciation, which is largely affected by the progress of leaching, where  $\text{MgOH}^+$  starts to build up at the onset of the leaching process to reach steady state after a week and then slightly reduced to allow the release of minor borate and molybdate species (Fig 3.). The presence of  $\text{MgOH}^+$  ions can be due to the  $\text{Mg}^{2+}$  hydrolysis or release of hydrolysed cation.

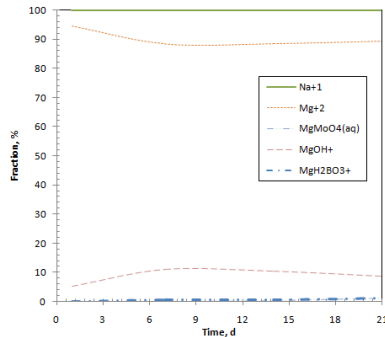
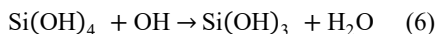


Fig.3. Speciation of Na and Mg released from ABS-Waste 17

The evolution of Si and B species with the progress of the leaching process is illustrated in Fig.4,  $\text{H}_4\text{SiO}_4$  and  $\text{H}_3\text{BO}_3$  are the major species of Si and B at the onset of the leaching process, whereas by increasing the leaching duration,  $\text{H}_3\text{SiO}_4^-$  and  $\text{H}_2\text{BO}_3^-$  start to build-up (Fig .4 a) as a result of hydrolysis reaction as shown below [34]:



Al and transition elements are found as hydroxide in III, VI and IV states, the species are not sensitive for the progress of the leaching process. Table 2 lists major species of transition elements released from the three studied glasses.

Table 2 Major species of transition elements in the leachant of the three studied samples

Species	Cr(OH) <sub>3</sub>	Fe(OH) <sub>4</sub> <sup>-</sup>	MoO <sub>4</sub> <sup>-2</sup>	Zr(OH) <sub>4</sub>	YOH <sup>+2</sup>	RuO <sub>4</sub> <sup>-2</sup>
ABS-Waste (17 <sup>*</sup> )	98.98	99.91	97.56	93.84	98.76	100
MABS- Waste(20 <sup>*</sup> )	97.84	99.7	95.74	98.21	97.41	100
ABS-Waste (25 <sup>*</sup> )	99.38	99.98	98.06	91.337	99.68	100

Rare earth elements speciation results indicated that these elements are in III state in the form of hydroxides, and their speciation is slightly affected by the progress of the leaching process (Fig. 4 b). It should be noted that Ce and Nd have nearly similar specie distribution with a majority of hydroxides throughout the leaching that is fairly constant throughout the leaching process. For lanthanum, hydroxyl specie is the main one and a small amount of free lanthanum ions exist that is slightly reduced within two weeks, and then slightly increased.

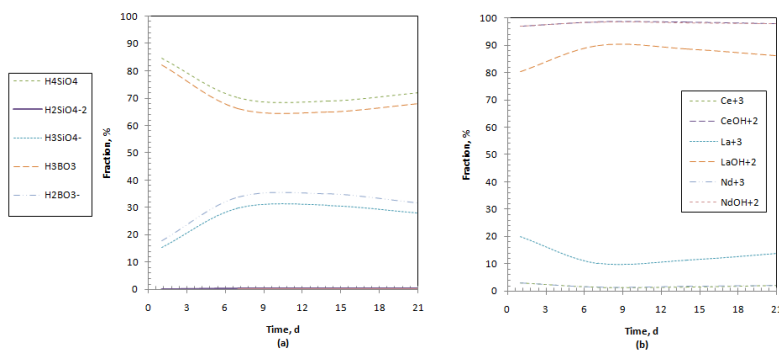


Fig 4 Evolution of the (a) Si and B and (b) rare earth elements species with the progress of the leaching process of ABS-Waste 17

### Leachant speciation for MABS-Waste 20

The calculated pH increase with the progress of the leaching process and the evolution of the alkali and alkaline elements speciation during the leaching process is similar to that found in the leachant of ABS-Waste 17. Mg species evolution is different from that form sample ABS-Waste 17, where the formation of MgOH<sup>+</sup> was hindered by two or three orders of magnitude and the available major specie was Mg<sup>2+</sup>(Fig 5.a).This indicates that the presence of modifiers acts as stabilizing for Mg species evolution throughout the leaching process. The speciation of the modifiers indicated that Ca shows typical behaviour to that of the alkaline element except at the end of the studied leaching time, where borate species build-up to nearly 1.5%. Zn species evolution is illustrated in Figure 5.b, where major zinc specie is in the hydroxide form.

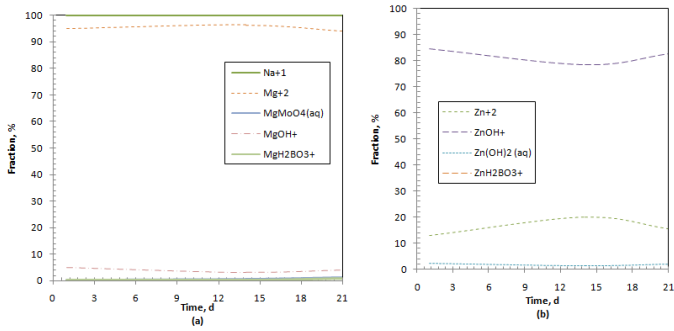


Fig.5. Evolution of the mobile element species (a) Na and Mg, (b) Zn from glass MABS-Waste 20

$H_4SiO_4$  and  $H_3BO_3$  are the major species of Si and B released from sample ABS-Waste 17, where the content of species released from MABS-Waste 20 is fairly constant and larger (Fig 6.a). This indicates that the presence of modifiers acts as stabilizing speciation of these structural elements. The released rare earth elements have similar species to that released from ABS-Waste 17 with a considerable increase in the La free ions (Fig 6.b).

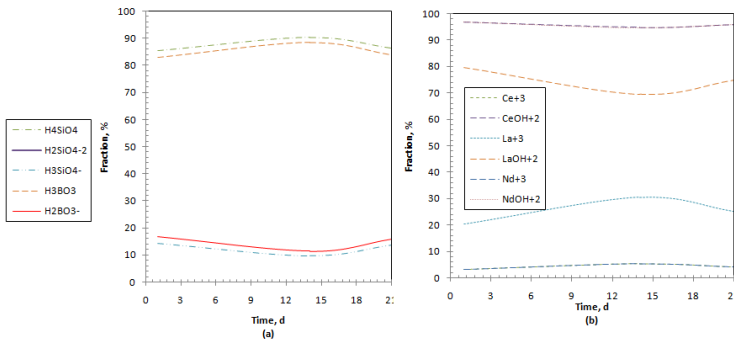


Fig 6 Evolution of the (a) Si and B and (b) rare earth elements species with the progress of the leaching process of MABS-Waste 20

### Leachant speciation for ABS-Waste 25

The evolution of the speciation of alkali and alkaline elements is similar to that of the other glass samples. Mg species looks different within the first two weeks, where free ions dominate the species released (95%), then hydroxide species start to build-up to represent nearly the quarter of the available species in the leachant (Figure omitted). This change is also noted for the release of other structural elements and rare earth elements as shown in Figure 7, where increasing the waste loading led to enhanced hydrolysis for the released structural elements after two weeks.

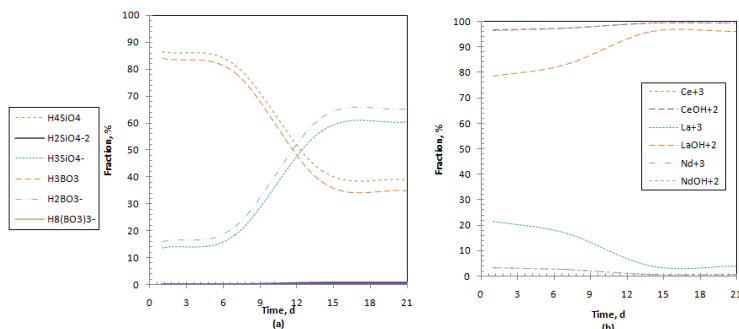


Fig 7 Evolution of (a) Si and B and (b) rare earth elements species with the progress of the leaching process of ABS -Waste 25

## CONCLUSION

This paper addresses the evolution of the interfacial water species with progress of the leaching process. Three glass waste matrices were subjected to MCC1 leach test and the experimental data were analyzed to calculate the retention factors of the structural elements, modifiers, and waste components. Then the leachant speciation was modelled to have insights into the evolution of the distribution of the structural elements and the waste components species. The following tentative conclusions can be drawn:

- The evolution of transition, post transition, and metalloids species is independent on the waste composition and progress of leaching process,
- Mg speciation has an exceptional evolutionary behaviour that is dependent on the glass matrix composition and the leaching progress,
- Glass structural elements, i.e. Si and B, species evolution is dependent on the glass composition and leaching progress,
- The presence of modifiers led to the stabilization of Mg, Si and B species throughout the leaching process.
- Increasing waste loading led to stabilization of Mg Si and B species within the first two weeks then enhanced hydrolysis occurred.

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