Characterization of simulated liquid radioactive waste in a new type of cement mixtures

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Abstract

There is still a safety challenge for the long-term stabilization of nuclear wastes. Thanks to its affordable price and easy manufacturing, cement is one of the most promising materials to immobilize large volume of low- and intermediate-level radioactive liquid wastes. To investigate the effect of borate on the cementation of radioactive evaporator concentrates, and to provide more data for solidification formula optimization, simulated liquid wastes in various concentrations were prepared. Different borate concentrations were solidified in the ordinary Portland cement (OPC), and in two new cement compositions with water-resistance and boron binding additives. The chemical and mechanical properties were investigated for nine cementitious samples, altogether with three compositions in three concentrations. The leaching rate of the boron is lower in case of high strength cement mixture. The compressive strengths of the solidified waste correlate with the leaching rates of the boron. The leaching rates of the Ca were changed with the cement composition and even with the boron concentrations, firstly: were less in the initial OPC in case of same boron concentration (50 g/l), secondly; were less at higher boron concentration (250 g/l) for the OXY-B composition. The simulated liquid waste with higher boron concentrations solidified with newly developed cement composition (OXY-B) shows a homogeneous boron distribution in the volume of the cement cylinder both before and after leaching. The formulas of OXY and OXY-B developed to this application were effective for cementation of the simulated borate evaporator concentrates.

1. Introduction

Cements, due to their chemical, physical and thermal stability, are widely accepted for immobilization of low- and intermediate level liquid radioactive wastes (LLW and ILW, respectively). Basic and applied research is conducted world-wide to study the solidification methods, to find the best cement-mixtures, to understand their structure, to determine solubility limits and to investigate chemical durability of the host materials. During operation of Nuclear Power Plants (NPPs) with WWER (water, water, energy, reactor - refers to Soviet design water cooled, water moderated, electricity generating reactors) Pressurized Water Reactors (PWR)-type reactor large amounts of liquid LLW/ILW containing inorganic boron compounds are produced and accumulated.[1] Cement is useful for solidifying wastes such as boric acid and borate salts, but, unfortunately, borates tend to inhibit or retard the hydration of the cement powder. Boric acid, which is the precursor of the borates, is used as a moderator in PWRs, and the borates which it forms are contained in both ion exchange resins and evaporation concentrates. The boric acid wastes are generally solidified with cement matrix and these solidified radioactive wastes are packed into containers that are isolated from human environment by safe disposal.[2] This study was carried out on the immobilization of evaporator concentrates containing borates in a new cement matrix and evaluation of its long-term stability.[3,4,5]

Borate waste concentrates vary in their content, ratios, and amounts of their salts according to conditions of operation, pretreatment, and coolant constituents (exp. ^{137}Cs, ^{60}Co). A simulated concentrated borate waste solution was used in the present study to evaluate the chemical characterization of the solidified borate-containing cement. Based on the literature, boric acid waste could contain ^{90}Sr, ^{137}Cs, ^{51}Cr, ^{60}Co and other radionuclides.[4,6]

To ensure the radiological safety after the waste disposal, these solidified radioactive wastes are required to have some properties such as adequate mechanical strength, low leachability, beneficial effects during water immersion, and good durability. Our study takes into account the main guidance document the Waste Acceptance Criteria (WAC)[7,8] of the National Radioactive Waste Repository. Leaching is generally considered as the basic criterion to evaluate the safety, acceptability, and chemical behavior of the final waste forms in the disposal sites. A key property of any waste form is its leaching resistance, which determines how well the radionuclides of concern are retained within the waste form in a wet environment. Estimating the rate of leaching from a matrix during disposal is a key consideration in assessing an immobilization method. Low matrix solubility means reduced likelihood of radionuclide release. The neutron scattering provides information on the nature of the phase transitions and structure of condensed systems, gives information on the local environment and short-range structure. In this paper we report neutron diffraction measurements of the bulk dried cements, with the aim to characterize the structure of cement compounds. Using neutron imaging it is possible to assess the homogeneity of the boron content of the samples. Moreover, applying the prompt-gamma activation imaging (PGAI) method localized elemental information can be gathered, which can support the findings from imaging tests.

The article aims at studying the solidification properties of the three different types of cement compositions, applying inactive 'simulated' liquid borate in different concentrations. With focus on the changes in mechanical and chemical properties, we would like to find the best association regarding the compositions and borate concentrations for the future way of stabilizing liquid radioactive wastes.

2. Sample preparation

2.1 Materials used for the experiments

This study was aimed to understand the chemical stability of borates in cementitious structures, as the most common hosting matrix for LLW/ILW. For the study, three types of cement mixtures were used. The basis of all three types was ordinary Portland cement, and its variously doped versions. The basic compositions were a Portland 42.5 N cement (hereafter referred as OPC). Additives (Sika Fume 10w%, Glenium 51 1w%, Sika DM 2 1w%)[9,10,11] was added to OPC that changed the macro/micropore ratio of initial concrete from 70/30 to 3/97, increasing chemical stability and ensuring water resistance, the composition was named to Oxydtron (hereafter referred as OXY). In the Oxydtron composition 2w% of the Sika Fume was replaced with Sika ViscoCrete obtained the Oxydtron-B composition (hereafter referred as OXY-B). The OXY-B has a double improved composition with explicit purposes to make the cement as watertight as possible to further reduce leachability and to prevent the release of bound boron from the system in aggressive conditions. The raw materials we used are dried powder mixtures, of which compositions were measured with X-ray diffraction analysis, and the results can be seen in Table 1.

Table 1. Phase composition (in wt%) of cements used.

	OPC	OXY	OXY-B
Quartz (SiO_2)	29	38	40
Calcite ($CaCO_3$)	15	17	10
Dolomite ($CaMg(CO_3)_2$)	12	15	6
Alite (Ca_3SiO_5)	39	25	39
Brownmillerite ($Ca_2(Al,Fe)_2O_5$)	2	2	3
Gypsum ($CaSO_4 \cdot 2H_2O$)	2	2	1
Ettringite	1	-	-

$(Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O)$			
Portlandite $(Ca(OH)_2)$	-	1	1

2.2 Cementation technology in laboratory conditions

Cements are used to immobilize both liquid and solid radioactive wastes. Here we focus on the solidification of liquid waste mixtures. Composition of the evaporator concentrates may vary, but the most significant components are NO_3^- (5-72 g/dm^3), H_3BO_3 (110-203 g/dm^3) and $NaOH/H_3BO_3$ (0.95-1.21 molar ratio).[12] Inactive model solutions, simulated liquid boric acid wastes with 50 g/l, 150 g/l, and 250 g/l boric acid concentrations were prepared. During the experiments, the mixtures were designed to have a water/cement ratio (w/c) of 0.214, which is unusually low, but not unprecedented.[13,14] The addition of Glenium 51 allows for a high strength and low permeability final product even with such extremely low water/cement ratio. Our nine prepared and studied samples are indicated in the Table 2.

Table 2. Samples and their notations, used in this study.

	OPC	OXY	OXY-B
50 g/l H_3BO_3	50 OPC	50 OXY	50 OXY-B
150 g/l H_3BO_3	150 OPC	150 OXY	150 OXY-B
250 g/l H_3BO_3	250 OPC	250 OXY	250 OXY-B

This ratio differs from the traditional cement full hydration ratio (0.42) but showed good paste workability during the mixing and the molds filling steps.[15] The boron concentration covered a range around 40 g/l which is the average boron concentration of residues in NPPs' evaporated sludge.[16,17] Ortho-boric acid powder (VWR Chemicals; CAS-No. 10043-35-3) was used, and was mixed with demineralized water (DMW) (conductivity=1.1 µS/cm, pH=7.5 at 23 °C). For increasing the boric acid solubility in DMW, having completely homogeneous mixtures, and to overcome the cement retarding effect of boric acid, granular sodium hydroxide (NaOH; VWR Chemicals; CAS-No. 1310-73-2) with 1 to 1 $NaOH/H_3BO_3$ molar ratio was added to the solution.[18,19] The cement powder was first poured into a mixer (HAUSER DM-601) and then the simulated liquid was added to the cement step by step. The mixtures were stirred mechanically (90 rpm for 12 min) at room temperature and humidity to obtain a completely homogeneous paste.[20] The wet paste was filled into 2.5 cm diameter and 5 cm height Polyethylene cylindrical molds.[21] The molds were then shaken for 5 minutes to remove air bubbles from the paste. Then, the molds were put in an incubator (VWR-INCU Line 68R) with fixed temperature of 20 ºC.[21] The specimens were cured for 28 days then they were demolded by a manual-hydraulic press (SPECAC 25T).[22]

3. Characterization of solidified cement mixtures

3.1 Leaching test

The measurement method for calculating the diffusion coefficient was performed according to the ASTM C1308-21 standard.[21] According to this standard, the cylindrical solid samples with 49.09 cm^2 contact surface were immersed in 500 ml DMW (leachant) and the resulting solutions (leachates) were changed at time intervals of 2, 5, 17 and 24 hours, and then daily for the next 10 days. After the leachate's extraction, their pH values were measured by calibrated electronic pH meter (XS pH 50+ DHS), where the changes of pH can be a sign of different phases releasing into the leachates.[23,24] All the leachates

were then filtered through a cellulose acetate membrane (FILTER-BIO; pore diameter of 0.45 μm) and acidified by 1 m/m% nitric acid (HNO$_3$ 65%; Sigma-Aldrich; CAS-No. 7697-37-2). The treated samples were analysed by an inductively coupled plasma - optical emission spectrometer (ICP-OES; Perkin Elmer Avio 200[25]).

3.2 Compressive strength tests of hardened cement

The compressive strength of hardened cement is one of the most important properties. After the curing time (28 days) 12 cylindrical specimens of 3 samples (50 OXY-B, 150 OXY-B, 250 OXY-B) were tested, designated 'before leaching'. After the leaching test[21], 11 specimens of 3 samples (50 OXY-B, 150 OXY-B, 250 OXY-B) were tested, designated 'after leaching'. The age of this cements was 39 days (28 days curing period and 11 days leaching period). We used compressive strength testing machine, calibrated press (Producer: Toni Technik Baustoffprüfsysteme GmbH) with geometry measuring tool: a calibrated digital caliper. Mass measuring device: a calibrated digital laboratory scale. Each device used meets the requirements of the European Standard EN 196-1:2016.[26]

3.3 Neutron diffraction measurements

Neutron diffraction (ND) experiments were performed at room temperature by using monochromatic neutrons (λ_0=1.069 Å) at the 2-axis PSD diffractometer of Budapest Neutron Centre in the momentum transfer range Q=0.45-9.8 Å^{-1}.[27] The cylinders - from OPC and OXY-B cements - with 2.5 cm diameter were placed in the neutron beam and measured cc. 24 hours/each. Data were corrected for detector efficiency, background scattering and absorption effects. The total structure factor, $S(Q)$ was calculated by local software packages.

3.4 Neutron imaging

The neutron imaging measurements were carried out at the radiography/tomography (RAD) station of the Budapest Neutron Centre (BNC).[28] Neutrons as electrically neutral particles usually easily penetrate a sample (see Figure 1), and the interactions that take place there cause the attenuation of the incoming neutron beam.[29] The attenuated beam provides a shadow image on a detector screen, which can digitally be sampled by an optical system to match the attenuation values to the grayscale values (grv) pixelwise. Beam hardening (BH) means that lower energy neutrons in the beam tend to be absorbed more likely than higher energy ones, biasing so the reconstructed 3D tomographic slices with an imaging artifact called cupping.[30] Since the linear attenuation coefficient of boron for thermal energy neutrons is rather high (102 1/cm), the BH effect is considerable for the white neutron beam of the RAD station. We used a beam hardening correction (BHC) method to provide unbiased 3D images. It was applied for the objects prepared from OXY-B with 250 g/l boric acid content so that the neutron attenuation values for several cement cylinders with known thicknesses were measured to calculate a calibration curve. This curve, which is valid only in the beam of the RAD station was used in the 3D reconstruction process to provide beam-hardening-free images, which can then be used to assess the homogeneity of the boron content of the samples.

Figure 1. A cut from the cement cylinder (250 OXY-B) and its sample support used to gather localized boron profile from the PGAI measurements. The scan was accomplished along the vertical diameter of the sample. Photograph courtesy of Zoltan Kis.

3.5 Prompt-gamma activation imaging

The neutron elemental analysis measurements were carried out at the Neutron-Induced Prompt Gamma-ray Spectroscopy-Neutron Optics and Radiography for Materials Analysis (NIPS-NORMA) station of the Budapest Neutron Centre (BNC).[31] Prompt-gamma activation analysis (PGAA) is a neutron-based element analysis method[32] for non-destructive quantification of major and minor components and several trace elements in the irradiated volume. PGAA relies on the radiative neutron capture process, which emits gamma-rays with well-defined energies. The detected gamma-rays can be assigned to the emitting elements while from the intensities of these gamma-peaks, quantitative analysis can be done. Prompt-gamma activation imaging (PGAI) is an extension of PGAA, where localized elemental information is gathered.[33] Both by limiting the impinging beam and positioning the sample in the beam we can choose the probing areas of interest. Boron is an ideal element for PGAI because its neutron absorption cross section is exceptionally high (767 barn) compared to that for most of the other elements. In this case, we applied PGAI for an 8 mm high disk, which was cut out from the 250 OXY-B cement cylinder after the leaching process. We limited the beam size to 3×3 mm^2 and scanned along the vertical diameter of the disk in eight successive steps (see Figure 1). In the resulting spectra the boron to calcium ratio was calculated to be able to provide a localized profile of boron.

4. Results and discussion

4.1 Consistency test results

The consistency of the fresh cement paste was measured according to the Suttard method.[34] A 2.5 cm internal diameter and 5.0 cm height Polyethylene cylinder was placed on a horizontal, smooth, and scaled base plate. The cylinder was filled to the top with fresh cement paste. Then the mold was lifted and let the cement paste flow and spread on the base plate for 30 seconds, then we measured the maximum of the cement paste spread in the two directions, presented in Table 3. The diameter of the spreading paste is calculated from the average of these two measurements.

Table 3. Consistency measurements.

Sample	x+ (cm)	x- (cm)	y+ (cm)	y- (cm)
50 OPC	2.0	2.1	2.1	1.9
50 OXY	1.9	2.2	1.8	1.8
50 OXY-B	1.5	1.4	1.6	1.6

150 OPC	2.0	1.5	1.5	1.9
150 OXY	1.8	2.0	1.7	2.0
150 OXY-B	1.7	1.6	1.7	1.9
250 OPC	1.9	1.9	1.9	2.0
250 OXY	1.8	1.8	1.7	1.9
250 OXY-B	1.8	2.0	1.7	2.0

One of the WAC requirements is associated with the consistency of the cement pastes which allows the free cavity volume to be filled inside the solidified waste in the containers. The Suttard consistency must be in the range of 1.5 to 2.0 cm. It can be seen from the Table 3 that the consistency parameters were not significantly affected by the cement compositions or borate concentrations, even the numbers are in the range of WAC. The numbers show a random consistency without any trends.

4.2 Leaching test results

The pH diagram for the three-cement series is presented in Figure 2. Based on the figures, changes for all three cements can be observed in the first period of the leaching. There is an active decreasing/increasing change, up to the Day-2, and, after that time, the pH shows a balanced downward trend. Comparing the three cement compositions (OPC, OXY, OXY-B) the characteristics of pH are similar to each other.
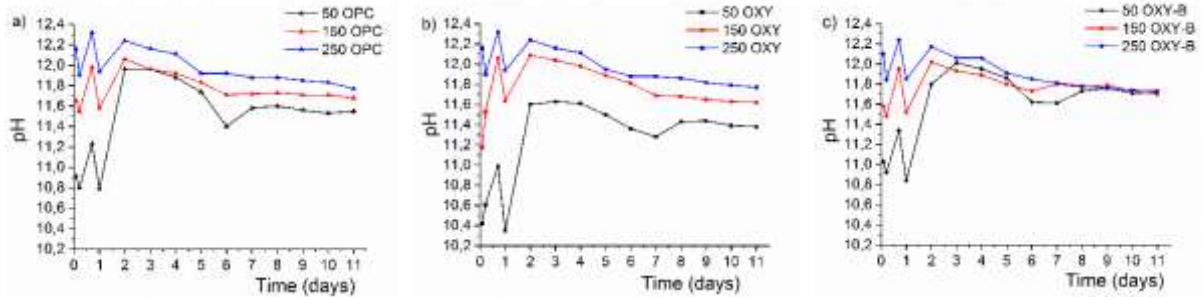
Figure 2. The pH diagrams of the OPC (a), OXY (b) and OXY-B (c) leacheats, after sampling according to the ASTM C1308-08 protocol.

Based on the standard procedure[21], the unitless incremental fraction of leached boron (IFL), which is the indexed parameter for sustainability comparison, during test interval n is calculated by:

$$IFL_n = a_n^B / A_0^B \qquad (1)$$

Where a_n^B is the quantity of boron measured in the leachate from the nth test interval, and A_0^B is the quantity of boron in the solid specimen at the beginning of the test.

The cumulative fraction of leached boron until j^{th} interval (CFL$_j$) is calculated by:

$$CFL_j = \sum_{n=1}^{j} a_n^B / A_0^B = \sum_{n=1}^{j} IFL_n \qquad (2)$$

Plotting the *CFL* values versus the cumulative time can provide a straightforward graphical comparison of leaching data from the various solidified cementitious samples.

The results of leaching tests in DMW for OPC, OXY and OXY-B cements are summarized in the panels of Figure 3. The panels show the cumulative leached fractions of B as a function of time for the three types of concentrations. The boron leachability is one of the most important parameters in the waste-form durability calculations. For all cement samples and for all the boric acid concentrations, the

boron dissolution shows dynamic activity between 0 and 24 h, followed by a slow rise, perhaps approaching a plateau. In case of the 50 g/l simulated liquid wastes (as 50 OPC, 50 OXY, 50 OXY-B) the leached fraction of B shows similar rates for all three cement compositions (Figure 3a). Figure 3b and c indicate an increasing trend as the initial concentration of boron increases to 150 g/l and to 250 g/l in the simulated liquid wastes. For all cement samples, the 150 g/l boric acid concentration shows the highest leached rate. A relatively higher jump was observed in case 150 OXY sample, below this the leached fraction of B are in the same range for the OPC and OXY-B samples. Figure 3c shows the B leachability in case of the 250 g/l simulated liquid wastes, where a slight increase was obtained in the case of the OXY-B sample, but the leached fractions from OPC and OXY samples are similar. According to the B leachability results there is almost no significant difference between cement specimens used for solidification of borates. In contrast, the different initial simulated liquid waste concentrations play a vital role to the leachability.
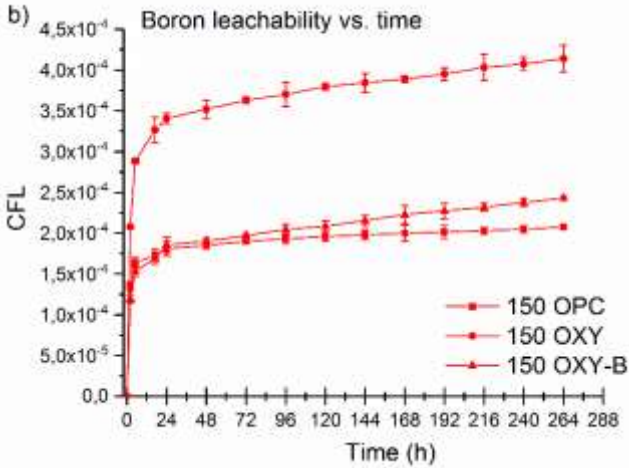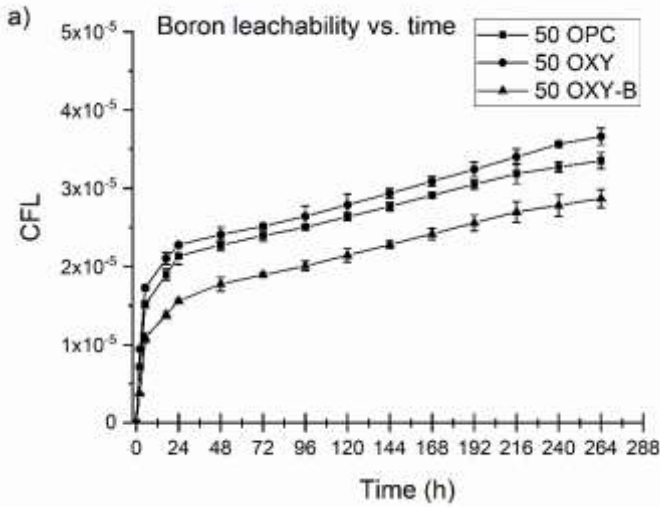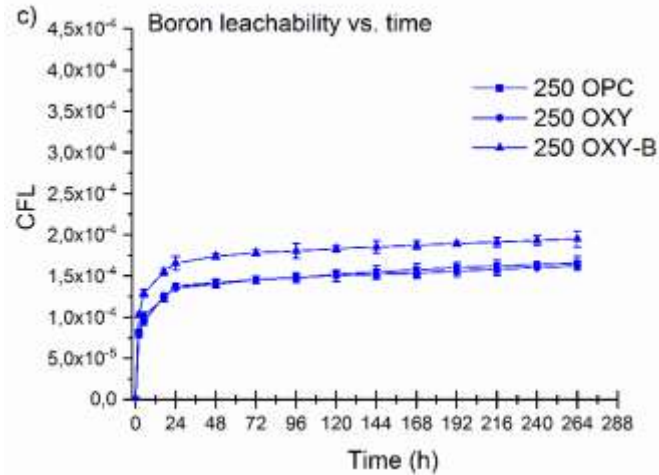
Figure 3. Cumulative leach fraction of B from the different cementitious waste form in different simulated liquid wastes concentrations, 50 g/l H_3BO_3 (a), 150 g/l H_3BO_3 (b) and 250 g/l H_3BO_3 (c).

Based on the results obtained from the CFL calculations, it could be concluded that from the viewpoint of leached B, the most suitable cement composition is the OPC cement with low, 50 g/l simulated liquid wastes concentration (Figure 3a).

The cumulative leaching fraction values of the Ca and Al elements within the leached samples, as obtained from ICP-OES, are presented in Figure 4. Ca is the major cement component; the Al is secondary element in the cement mixture. In Figure 54 we present the Ca and Al leached fractions in the same simulated liquid waste concentration (50 g/l H_3BO_3) with different compositions and in function of time. Calcium should show the highest elemental leaching ranking in cementitious waste form.[35] Significant increase in leached fraction of Ca was obtained for the 50 OXY-B samples (Figure 4a), while for the 50 OXY and 50 OPC samples the leached fraction was closer to each other. The cumulative leached fraction obtained for Al (Figure 4b) were much lower than for Ca, the trends between the compositions were similar, even in case of 50 OPC and 50 OXY samples at the last part of the leaching experiments the dissolution were much more intense than in case of 50 OXY-B sample.
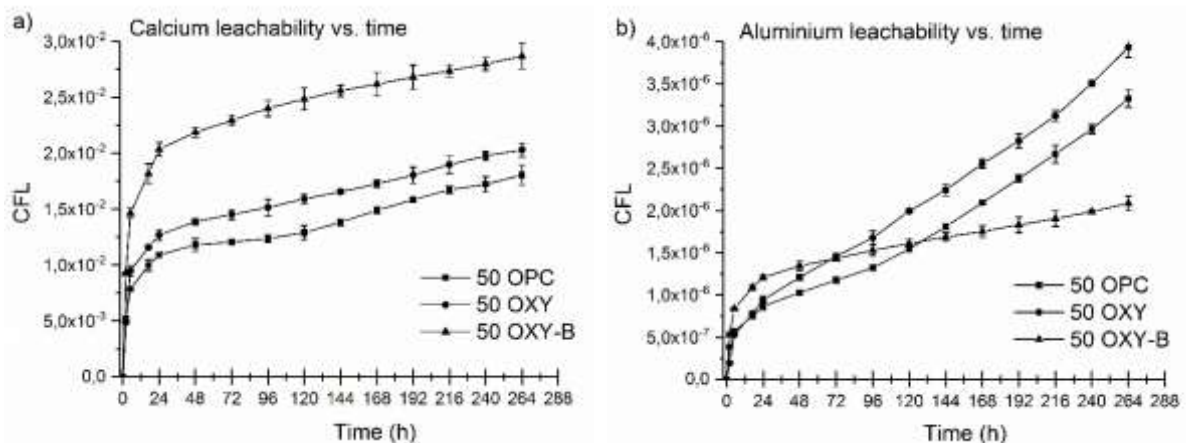

Figure 4. Cumulative leach fractions of Ca (a) and Al (b) from the different cementitious waste form es with the same simulated liquid wastes (50 g/l H_3BO_3) concentrations.

The cumulative leached fraction values for the Ca, Al and Mg were compared for different simulated liquid waste concentrations but with the same cement composition, OXY-B (Figure 5). The leached fraction of Ca element shows a decrease with increasing of H_3BO_3 concentrations; 50g/l>150g/l>250g/l

(Figure 5a). This high leaching expectation of calcium is seen in the result of the leaching test on the Figures 4a and 5a. However, the comparison results of the *CFL* for calcium leachability for OXY-B composition (Figure 5a) show that the cementitious specimens containing lower initial H_3BO_3 concentration (50 OXY-B) have 2-3 times higher calcium leaching than the higher initial H_3BO_3 concentration samples (150 OXY-B and 250 OXY-B). The general higher calcium leaching is due to retarding effects of boron on the cement hydration and the effect of boron leaching on the porosity of cementitious matrix.[36,37]

The release of Al element was not influenced by the concentrations, the cumulative leached fractions were almost similar (Figure 5b). Based on the results of this study, aluminum shows the low leachability, which is in agreement with the previous similar studies.[35] However, the low amount of aluminum release can mostly take place to compensate the non-equilibrium charge induced by boron replacement in the cementitious matrix.[38] In all the studied cementitious specimens, magnesium shows the lowest leachability (Figures 5c). Low leachability was observed for the Mg, but a slightly higher leached fraction for the sample 250 OXY-B was measured.
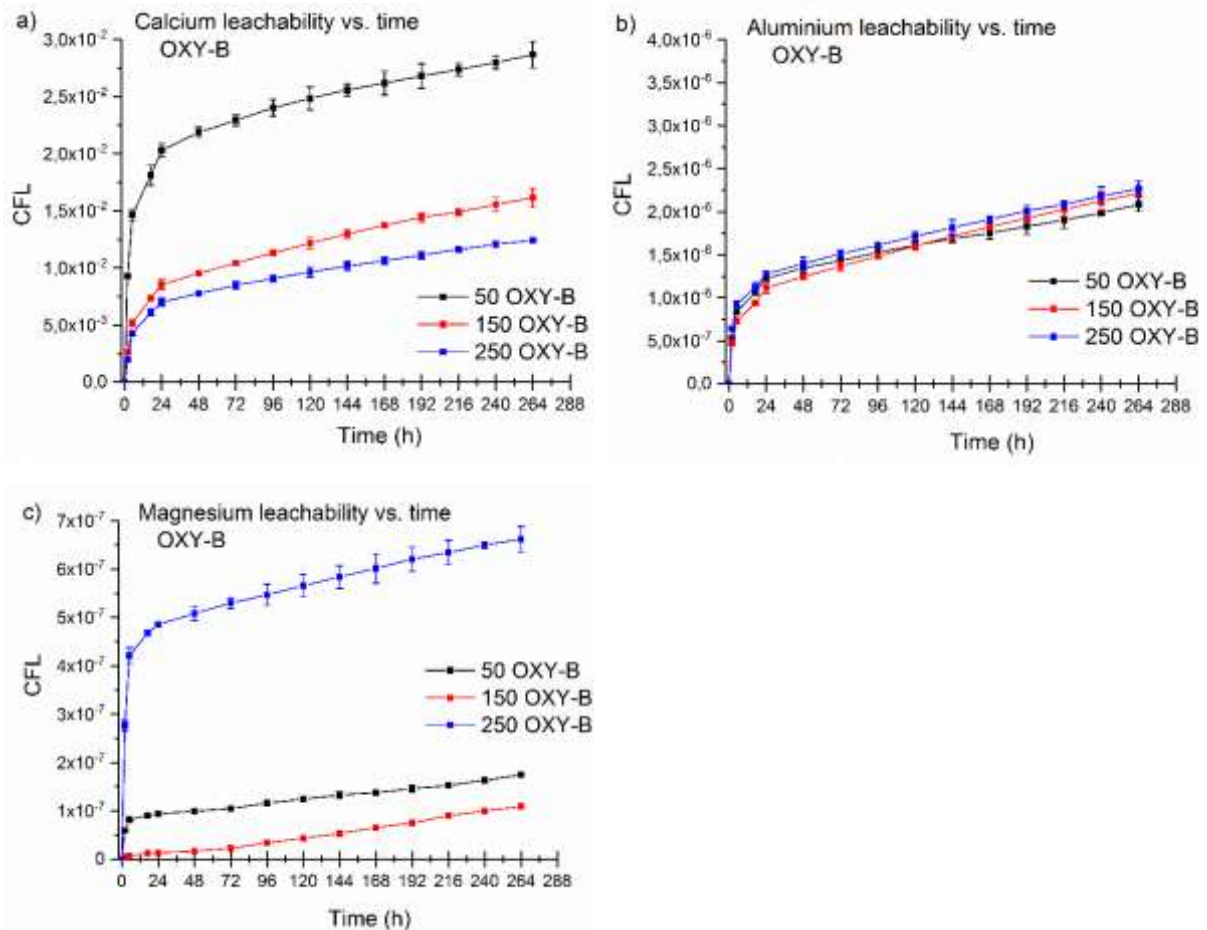

Figure 5. Cumulative leach fractions of Ca (a), Al (b) and Mg (c) from the OXY-B cement composition with different initial concentrations (50 g/l H_3BO_3 (black), 150 g/l H_3BO_3 (red), 250 g/l H_3BO_3 (blue)).

Leachability of the Ca is a key factor, due to the main composition of the cements. Low cumulative leaching fractions were found for the OPC cement in the case of the same initial H_3BO_3 concentration (50 OPC, Figure 4a) and for highest initial H_3BO_3 concentration in case of the same cement composition (250 OXY-B, Figure 5a).

4.3 Compressive strength tests results

Most of the additives affects the compressive strength, therefore the most improved composition, OXY-B samples were investigated from this viewpoint. The compressive strength measurements were obtained for the OXY-B series before and after the leaching test, after 28 days and after 39 days, respectively. Increasing boric acid content in OXY-B cement waste forms decreased the compressive strength values (Figure 6), according to the order 50 OXY-B>250 OXY-B>150 OXY-B. There are quite big differences between the concentrations, but the parallel results of the same sample before and after the leaching are very similar. It means that the leaching conditions do not significantly affect the strengths of the samples, which in terms of application, is a significant result. After the leaching test, the strengths of the 250 OXY-B samples decrease with 5%, and the strengths of the 50 OXY-B and 150 OXY-B samples increase with 1.5 % and 5%, respectively.
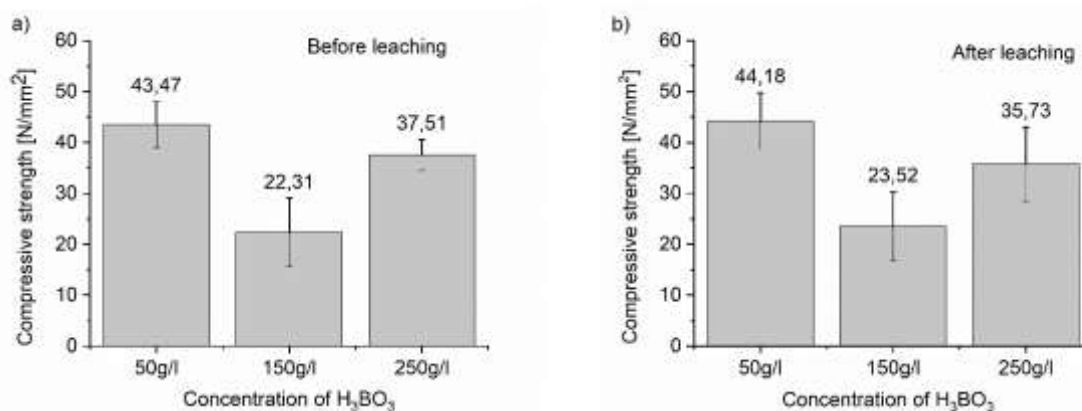

Figure 6. Compressive strength data for OXY-B cement, before (a) and after (b) the leaching experiments.

Several studies discussed that with reaction of the boric acid and calcium hydroxide (produced during the cementations) calcium borate were produced, which is insoluble, it acts as a barrier, retards the diffusion of elements.[39] In case of B, the lower leached fraction was associated with highest compressive strengths in case of 50 OXY-B. However, the leachability of B correlates with the obtained mechanical data. The WAC requirement for the compressive strength is min. 10 N/mm^2, each sample surpasses the expected value.

4.4 Neutron structure factors of the cements

The cement samples at the end of the curing period (28 days) were put in the oven at 100°C for 2 days. The OPC and OXY-B cement samples used in neutron diffraction measurements were made from cement powder mixed with H_2O (DMW). The incoherent scattering from the hydrogen in the samples prepared with H_2O covered up the pattern from coherent scattering in the spectra and only approximate results could be obtained on these samples. Figure 7 shows neutron structure factors[40] of the OPC and OXY-B samples.
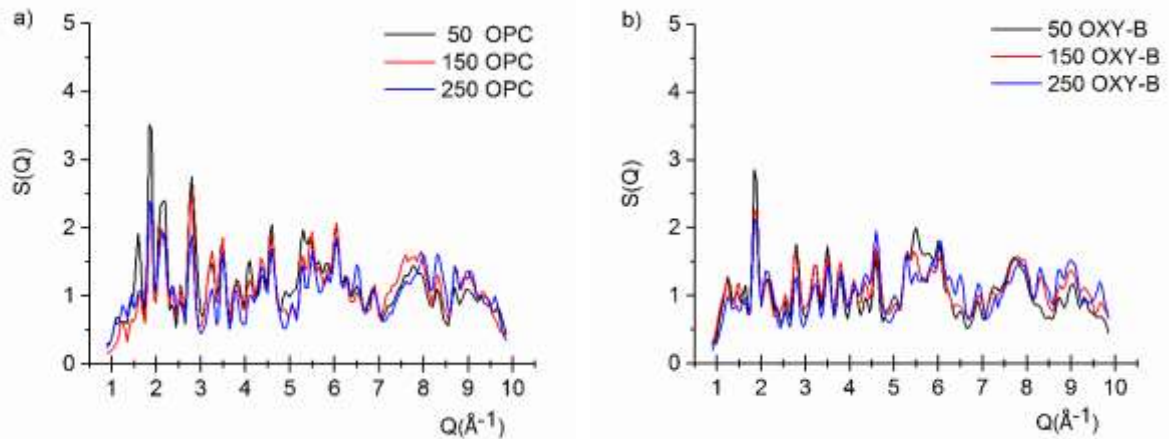
Figure 7. Total structure factors for OPC (a) and OXY-B (b) samples, for all three boric-acid concentrations.

Differences can be observed in low Q-range between the two series, but within a series the character of the spectra is similar. From neutron diffraction we obtained mixed phases, amorphous phases can be identified as indicated by the broad distributions, and crystalline phases are also present. The broad amorphous component is attributed to the calcium-silicate-hydrate (C-S-H) gel[41] with typical Ca/Si molar ratio of 1.7 ± 0.1[42] and may also contain a contribution due to strongly bound water on the gel surface. The sharp peaks could be attributed to the unreacted crystallites of the cement components. Due to the resolution limitation of our instrument, we don't have the possibility to separate these various components of the scattering. Several diffraction peaks are present in both samples' series, varying only in intensities. In the case of OPC series, some of the peak intensities have been enhanced due to the contribution of H_2O. However, the peaks are present with almost the same intensity indicating that the basic structure of the crystalline component has not changed significantly.

4.5 Neutron imaging results

We provide boron homogeneity results showing beam hardening corrected 3D neutron tomographic images for a cement cylinder prepared from OXY-B with a 250 g/l H_3BO_3 solution. The same BHC calibration curve was used for the sample before and after leaching. One can see the dark spots in Figure 8, where there are grains/particles or pores in the volume, while the brighter areas show where the boron is located. Based on the 3D cuts and the plot profiles we can state that the spatial distribution of the boron is rather homogeneous in the volume of the cement cylinder both before and after leaching. It strengthens the idea of the very low mobility of boron in this matrix.
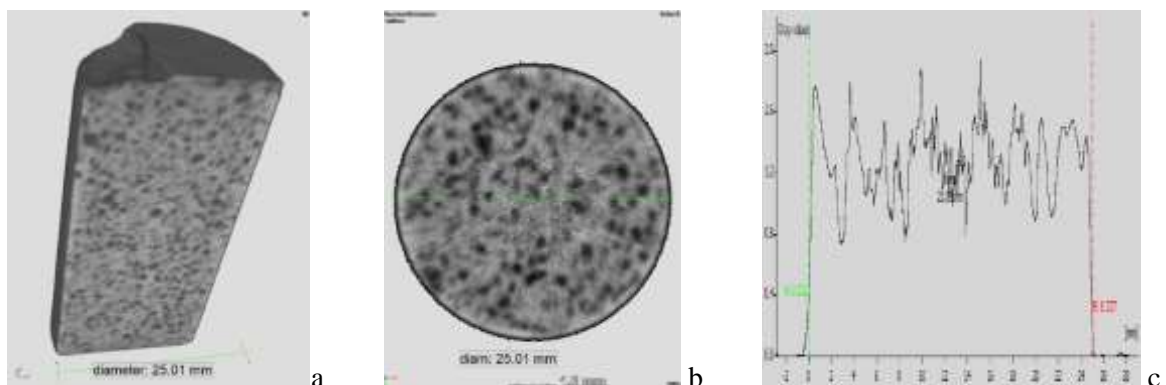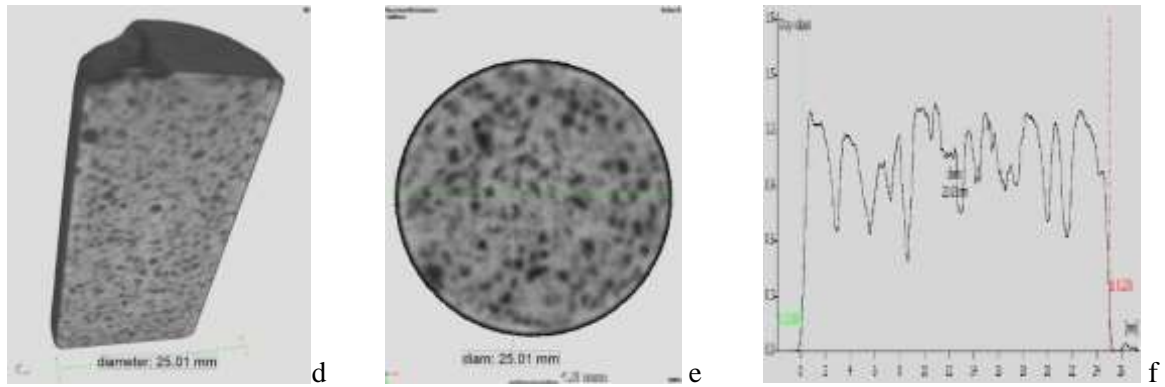
Figure 8. Neutron tomography results for spatial distribution of boron in 250 OXY-B cylinder (a) 3D cut before leaching, (b) xy-cut before leaching, (c) a grayscale value profile along the diameter in the xy-cut before leaching, (d) 3D cut after leaching, (e) xy-cut after leaching, (f) a grayscale value profile along the diameter in the xy-cut after leaching.

4.6 Prompt-gamma activation imaging (PGAI)

The results from PGAI scan supported the findings from the neutron tomography. In Figure 9 the B/Ca atomic and mass ratio show a rather constant profile along the diameter of the cylinder. The slight changes could be attributed to the non-homogeneous structure of the matrix because boron is not absorbed by particles/grains, which can bias the ratio between B and Ca.
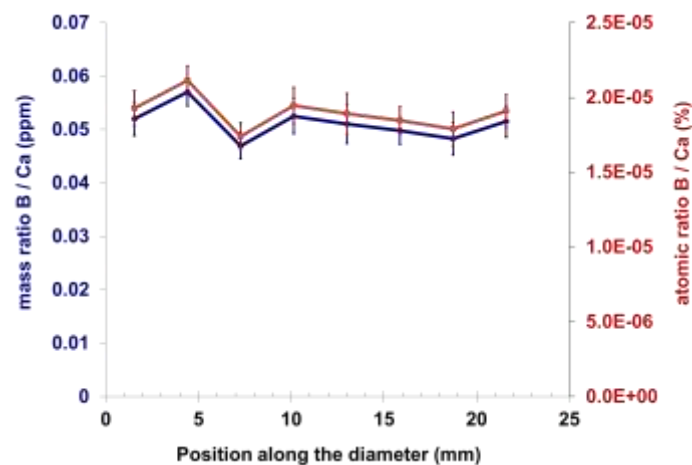

Figure 9. The B/Ca atomic and mass ratio profiles from a PGAI scan along the diameter of a disk in eight successive steps. The disk was cut out from the cement cylinder (250 OXY-B) after the leaching process and the beam size was limited to 3×3 mm^2. Error bars are for 2σ confidence interval.

5. Conclusions

In this study we focused on the investigations of nine inactive cementitious samples, to find the best cement composition which can solidify as much borate as possible from simulated liquid waste. Based on Portland 42.5 cement, two cement compositions were developed for this application. The technological compliance was assessed by compressive strength tests and consistency measurements. We proved that all our samples meet the consistency requirements. Considering different borate concentrations within the same OXY-B composition, each cement specimens meet the strength criteria.

The chemical characterization of solidified mixtures relied on leaching data and neutron-based investigations. The leached fraction of boron showed an increasing trend in all cements up to 24 hours, after that a barely noticeable growth was detected. The highest cumulative leached fraction for boron was obtained for the 150 g/l initial concentration and the lowest for the 50 g/l H_3BO_3 initial concentration. No significant differences were observed between the cement compositions, only one significant change was measured in case of 150 OPC. Both the neutron imaging and elemental analysis results showed a homogeneous boron distribution in 250 OXY-B sample, which is the most extreme combination due to the high H_3BO_3 concentration associated with a newly developed OXY-B cement composition (presumably there is a homogeneous boron distribution in the other samples with lower concentrations, too). The homogeneous boron distribution was not affected by the 11 days of leaching. The presence of the calcium-silicate-hydrate gel was proved by neutron diffraction measurements. We worked with inactive, simulated liquid wastes therefore the chemical requirements of the WAC were not fulfilled.

Competing interests

The authors declare no competing interest.

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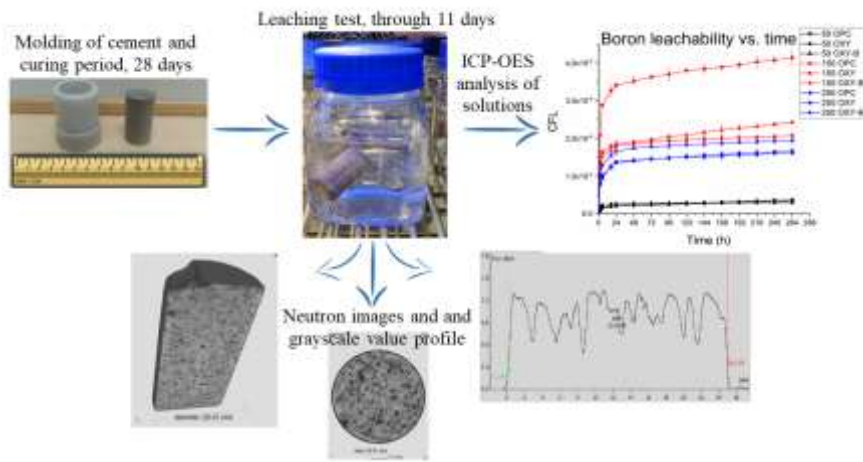
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