

Mineralogical, Physical and Chemical Characterization of Cementitious Materials Subjected to Accelerated Decalcification by an Electro-Chemical Method



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ABSTRACT

To facilitate the service life predictions regarding durability of nuclear waste repositories acceleration methods enhancing the decalcification process are needed. In this study an electro-chemical migration method to accelerate leaching of calcium from cementitious specimens of sizes 50×100Ø and 75×50Ø mm is presented. The mineralogical, physical and chemical properties of degraded samples are characterized. The results demonstrate that up to 70% decrease in strength, 50 % decrease in E-modulus, 90 % increase in gas permeability, at least 70% increase in chloride diffusion coefficient and 70 % increase in pore volume could be expected due to leaching of portlandite from concrete.

Key words: Acceleration method, Calcium leaching, Service life, Mineralogical properties, Diffusion, Adsorption, Mechanical Properties, Permeability

1 INTRODUCTION

Exchange of ions between cementitious materials and the surrounding environment due to concentration differences will result in dissolution or precipitation of minerals, and

consequently alteration in the microstructure and composition of the cementitious materials. One of the important factors in this process is the long-term contact between the concrete barrier and the surrounding groundwater [1, 2]. In concrete calcium hydrates are the major portion of hydrated cementitious material whilst the repositories are surrounded with low calcium content groundwater. As calcium leaching is a dissolution/diffusion governed transport process, decalcification will proceed, due to the calcium concentration gradients [3].

In repositories of nuclear waste where concrete is used in the engineered barriers to prevent the release of radio nuclides, detailed understanding of how the properties of the material are developed over the entire operational life of the repository is required. Of particular importance are the mechanical, physical and diffusion/adsorption properties of the degraded materials.

To account for the long term effect of degradation on properties of cementitious materials used in nuclear waste repositories several studies are reported in the literature regarding leaching of calcium from cementitious materials based on immersion of the solid cementitious specimens in water or enhancement of the decalcification process with acceleration methods [4-15]. However, although several conclusions can be drawn from these studies regarding the properties of aged cementitious materials these types of experiments are either very time consuming due to the slow kinetics of the decalcification process or small sample sizes should be implemented which limits further examination of the mechanical properties of the samples or their diffusivity. In addition it should be noted that there are not many studies reported in the literature with implication of concrete samples [16-19] of proper size rather paste specimens or powder samples have been used [4-7, 9, 10, 12-15, 20-22].

Moreover, although the common feature for both natural and accelerated leaching scenarios will be a total dissolution of portlandite and a significant decalcification of the CSH phases, other effects of the aging processes may differ considerably between specimens aged by different acceleration methods and comparably natural leaching methods. This emphasizes on the importance of reproducing accelerating tests and characterizing the aged samples to account for the comparability of the ageing function of different methods in order to produce databases with low variability and less uncertainties demonstrating properties of degraded cementitious materials.

It should be noted that in any acceleration method some involved processes may not be present in the natural situation. Characterization of the material after application of the accelerated method is of high importance in order to show the comparability as well as to build up a better base for further investigations.

Furthermore, as the rate of diffusion through concrete not only depends on molecular diffusion in pore solution, but also on the porosity and sorption properties of the cementitious materials, within assessments of diffusion properties of degraded cementitious specimens the changes in pore structure and adsorption properties should also be considered. As presented by Ochs et al. [23] an increase in sorption properties of degraded cementitious materials is expected after degradation, specifically for Cs ions. However, in general the available information in the literature regarding the sorption properties of cementitious materials exhibit a large variation and uncertainty due to considerable differences in the composition of the cementitious specimens which emphasizes on the importance of adsorption tests in parallel with investigations regarding diffusion properties. In addition, although combined effect of porosity, adsorption and molecular diffusion is of high importance, but available literature data on

adsorption have mostly been obtained from studies on powdered hydrated cement paste excluding the effect of changes in porosity and molecular diffusion.

All these implies that effective acceleration methods with comprehensible kinetic, simulating the calcium leaching process for specimens with a size suitable for further mechanical or physical tests are required. In this study a newly developed acceleration method simulating the leaching of calcium from cementitious materials is presented. The gradual changes of the physical, chemical and mineralogical properties of the samples are followed with the progress of the leaching process. Further, the diffusion properties of solid specimens of cement paste are investigated and the physical properties such as porosity, pore size distribution and specific surface area of decalcified samples are studied and compared with the untreated reference material. Moreover, the diffusive characteristics of Cs^+ , Na^+ and Li^+ ions are accounted for by means of a diffusion cell test and the adsorption characteristics for Cs^+ ions, as exhibiting no solubility limitation and only weak retention by fresh hydrated cement paste [23], is considered for both fresh and aged cementitious materials. Finally, the changes in mechanical and physical properties of solid concrete specimens are presented and the following properties have been studied: tensile strength, elastic modulus, permeability and water adsorption. In addition, the chloride diffusion coefficient of concrete samples has been studied in order to give an indication of the transport properties of the specimens.

2 MATERIAL AND METHODS

2.1 Specimen Preparation

In this study, all solid specimens were manufactured from pure cement paste and water in order to facilitate chemical and mineralogical analysis of the specimens. The paste specimens were casted from a mixture of Swedish structural Portland cement for civil engineering (CEM I 42.5N BV/SR/LA) and deionised water at a water-cement ratio of 0.5. The chemical composition of the cement is listed in Table 1. Fresh cement paste was cast in acrylic cylinders with an internal diameter of 50 mm and a length of 250 mm. The cylinder's ends were sealed with silicone rubber stops. The cylinders containing fresh paste were rotated longitudinally at a rate of 12-14 rpm for the first 18-24 hours of hydration to homogenize the paste, after which the rubber stops were removed and the ends of the cylinders were sealed with plastic tape in order to produce specimens with a homogeneous composition and structure. The specimens were stored for over 6 months in a moist plastic box and then cut to cylinders with the size of $\text{Ø}50 \times 75$ mm for use as specimens in the experiments. In order to prevent carbonation, saturated lime water was used at the bottom of the plastic box. The initial calcium and silica contents in the cement paste specimens presented in Table 2 were calculated with the assumption that the composition of CSH corresponded to $\text{C}_3\text{S}_2\text{H}_3$.

Table 1. Chemical characteristics of Swedish CEM I 42.5N BV/SR/LA

Chemical formulation	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	SO ₃	Cl
Weight Percentage	64	22.2	3.6	4.4	0.94	0.07	0.72	2.2	0.01

Table 2. Initial calcium and silica contents in a cement paste specimen (Considering $C_3S_2H_3$ as the composition of CSH)

Total	Component	mole/gr paste	mole/specimen*
Calcium content	CSH	0.0044	1.02
	CH	0.003	0.68
	Other hydrates	0.0018	0.41
	Total	0.0092	2.11
Silica content	CSH	0.003	0.68

*Approximately 230 g paste/specimen

The Concrete specimens used in this study were cast using Swedish structural Portland cement for civil engineering (CEM I 42.5N BV/SR/LA) and crushed aggregates with maximum size of 16 mm. The specimens were casted in cylinders in two different sizes of Ø100×200 mm and Ø50×250 mm with two different water cement ratios. The ratios are decided according to the properties of the concrete used in The Final Repository for Short-lived Radioactive Waste, SFR, in Sweden [24, 25], Table 3. It should be noted that SFR consists of several parts with respect to the radioactivity level of the waste, the Silo (intermediate waste), BMA (intermediate waste), 1BTF and 2BTF (dewatered ion exchange resins) and BLA (low level waste) are the included parts. The observations from the slump test prior to casting was 25 mm slump for the concrete with W/C=0.48 and 35 mm for W/C=0.62. The specimens were cured in saturated lime water for more than 3 months after which they were stored for over 3 months in a moist plastic box and then cut to cylinders with the size of Ø50×75 and Ø100×50 mm to be used in electrochemical migration method.

Table 3. Properties of concrete used in SFR repository located in Forsmark

Properties	Silo ¹⁾	BMA ²⁾
Cement type	Swedish structural cement	Swedish structural cement
W/C	0.48	0.62
Cement content kg/m ³	350	300

1) Based on Emborg et al. 2007 [26] but with symmetrical deviation of 48 ± 5 MPa in compressive strength instead of 43-58 MPa with mean 48 Mpa.

2) Estimated based on the previous Swedish concrete class K30.

2.2 Materials and Methods

The experimental set-up of the electrochemical migration method is inspired by the rapid chloride migration test developed by Tang, Figure 1 [27]. In this method, the specimen was placed between two electrolyte solutions providing a porous medium for ion migration. Specimens of size Ø50×75 and Ø100×50 were used. The curved surface of the specimen was

sealed using an asphalt tape which was extruded up to 2-3 times longer than specimen's height providing an empty volume of about 200 ml as the anolyte container. A plastic box with the capacity of 30 liters was used as the catholyte container. The anode was made of a titanium mesh which was equipped with a plastic support preventing direct contact with the specimen. The cathode was made of stainless steel which was mounted on a plastic support in a similar way as described in NT BUILD 492 [28]. The cells were connected to an external potential supplier with adjustable current and potential. In order to avoid a temperature-induced mechanical destruction of the specimen due to the Joule effect the current applied to the specimen was controlled. The choice of electrical current was based on the findings by Babaahmadi et al [29] showing that a constant current of 250 mA was suitable for a paste specimen of size $\text{Ø}50 \times 75$ mm and also taking into consideration that the paste fraction of the concrete specimens used in this study and in which the leaching takes place was 30 percent of the total volume, Table 3.

Ammonium nitrate solution was used as catholyte solution in order to dissolve the calcium hydroxides and Lithium hydroxide solution was selected as anolyte solution. This was motivated by the fact that the Li^+ ions do not exist in the pore solution. Moreover, Li^+ ions with a crystallographic radius of 0.07 nm, have a high surface charge density and therefore they are strongly hydrated in water and acquire a large size [30]. The thick water layer around Li^+ in a solution will reduce the tendency for diffusion or migration and consequently will also reduce any competing potential in migration with calcium ions. Furthermore, with application of a hydroxide salt of lithium, the produced H^+ ions at the anode were neutralized and localized acidic characteristics in the anolyte solution with corrosive effects on the specimen were prevented.

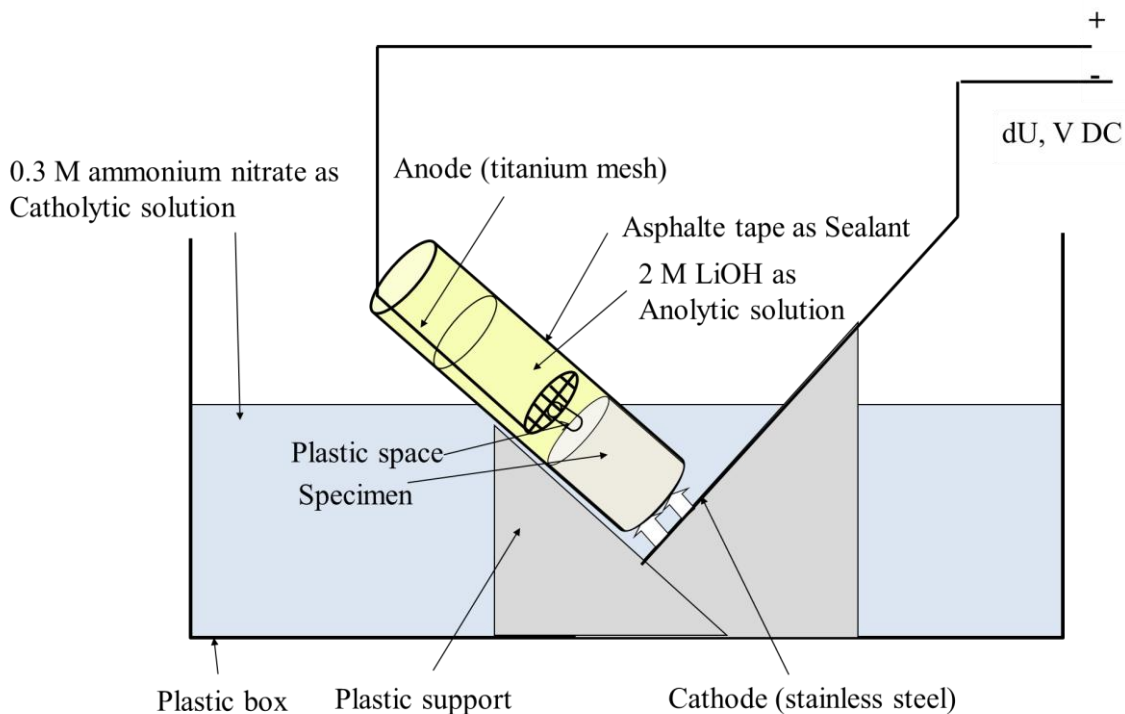


Figure 1. Setup design of electrochemical migration test

In order to maintain the pH level in the catholyte and anolyte solutions as well as to compensate for the consumed ions (OH^- ions in the anolyte solution and H^+ ions in the catholyte solution),

the solutions were frequently recharged. The quantities of the salts required for recharging were calculated according to the Faraday's rule of electrolysis as given in Equation (1).

$$I \cdot t = F \cdot z \cdot \left(\frac{m}{M}\right) \quad (1)$$

where, I : Current (A), t : time (seconds), F : Faraday number = 96485 C/mol, M : Molecular mass of substance (g/mol), m : mass of substance (g) and z : the valance number of ions.

With the application of a current of 250 mA, approximately 20 grams of ammonium nitrate and 6 grams of lithium hydroxide per specimen were needed to recharge the catholyte and anolyte solutions, respectively, for every 24 hours. When the current was set to 80 mA the catholyte solution was instead recharged with same amount of chemicals every 3rd day. The experimental time was set to approximately 6 weeks in order to reach to complete leaching of portlandite content as concluded by Babaahmadi et al. [29]. It should be noted that for the specimens with W/C=0.62 the experiment was terminated faster than for the specimens with W/C=0.48 as the portlandite content differs.

2.3 Instrumental analysis

To quantify the content of charged substances in the catholyte solution, Ion Chromatography (IC) was utilized. An IONEX (ICS 900) Ion Chromatograph was used in this study. Using this instrument the ions of interest were detected typically by conductivity or UV/visible light absorbance. The samples were injected in to the instrument with an auto-sampler. Moreover, the gradual change in the calcium concentration in the catholyte solution was analyzed by potentiometric titration on Metrohm Titrator 702 SM Titrino, using a calcium selective electrode and 0.1 N EDTA-solution as titrant.

Characterization of the crystalline phases in the solid samples was performed with X-Ray Diffraction (XRD) analysis. A Siemens D5000 ($\text{CuK}\alpha = 1.5418 \text{ \AA}$) X-Ray diffractometer, equipped with Gobel mirror was used. The measurements were carried out by using 0.050° per step and at a time step of 2 s. The powder sample was prepared by crushing and grinding the solid sample in a mortar while immersed in ethanol and vacuum drying after grinding. For each analysis 0.5 grams of the powder placed on a thin-walled glass sample holder was used. The results were calibrated using 0.05% mass of Si powder as standard.

Line scans quantifying the longitudinal changes in Ca/Si ratios of solid samples were performed by Laser Ablation- Inductive Coupled Plasma- Mass Spectrometry (LA-ICP-MS). Laser Ablation analysis was performed using a New Wave NWR213 laser ablation system coupled to an Agilent 7500a quadrupole ICP-MS (upgraded with shield torch and a second rotary vacuum pump). A 30 micron laser spot size, beam energy density of ca. 6 J/cm² and repetition rate of 10 Hz was used in line scan mode (scan speed 100 $\mu\text{m}/\text{sec}$).

The surface topography and elemental composition of the solid samples were analyzed with Scanning Electron Microscopy (SEM). A FEI Quanta ESEM 200 equipped with field emission gun and Oxford Inca EDX system was used to perform the analysis. Thin cubes of the solid sample of about 20×10 mm, thickness of 10 mm were used. The samples were vacuum dried prior to analysis. It should be noted that in order to prevent the samples from carbonation they were neither polished nor coated which may cause charging effects in the results as well as uncertainties due to uneven surface of the sample. The analyses were performed in high vacuum

mode and in 9-12 mm working distance. The reference sample and aged samples with different degrees of leaching were selected for the analysis.

The pore size distribution was studied with Mercury Intrusion analysis, using Micrometrics, Auto pore 9500 with a 5 ml penetrometer. Also the Brunauer-Emmett-Teller (BET) specific surface area was measured by N_2 adsorption with a Micrometrics, TriStar 3000.

2.4 Diffusion/Adsorption tests

The diffusion properties of the reference and the aged specimens were investigated for 0.5 M and 0.05 M solutions of LiCl, NaCl and CsCl respectively.

Conventionally, diffusivity of ions in a porous material is measured using a natural diffusion cell test at a certain concentration gradient [31]. Typically, two solution containers (cells) are separated by a slice of the specimen. The cell filled with a solution containing the ions of interest is called the upstream cell and the other cell, which is usually filled with deionized water, is called the downstream cell. Due to the concentration gradient between the cells, diffusion of ions through the specimen is always from the upstream cell to the downstream cell.

As shown in Figure 2, a paste specimen of $\varnothing 50 \times 15$ mm was assembled in the central part of the silicone rubber tube and kept in position with a clamp of stainless steel. Cells made of Plexiglas tube were attached to the ends of the silicone rubber tube using a clamp of stainless steel on each ends of the tube. The upstream cell was filled with 250 ml of a selected solution and the downstream cell was filled with 250 ml of deionised water. A rubber stop was used to close the cells in order to prevent evaporation and carbonation. 10 ml of sample was taken from the downstream solution approximately every 10 days (replaced with deionised water) and chemically analyzed with Ion Chromatography in order to account for accumulated ionic content (Q_{ion}), diffused through the specimen, against time ($Q_{ion}-t$ curve). The experiment was terminated when a linear relationship observed from the $Q_{ion}-t$ curve, which was an indication of the steady state flow.

Moreover, in order to analyze the adsorption properties, reference and calcium leached paste specimens prepared according to the methods described in sections 2.1 and 2.2 respectively were hand crushed and powdered in a mortar. 3 grams of the powder was mixed with 30 ml of CsCl solutions with approximate concentrations of 0.3, and 5 ppm respectively in separate plastic tubes in a glove box filled with nitrogen gas in order to prevent any carbonation. The solutions were mixed by placing the tubes in a rotating chamber. The Cs concentration in the solutions was determined after 2 and 6 weeks with ion chromatography.

2.5 Mechanical tests

Splitting test

The tensile strength of the leached and reference materials was measured using a Toni-Technik compression testing machine with a maximum capacity of 100 KN. The concrete sample of size $\varnothing 100 \times 50$ mm was loaded across its vertical diameter. Plywood strips were inserted between the concrete cylinders and the top and bottom plates of the equipment to ensure homogeneous loading. 2 specimens representative for each W/C-ratio and each degradation state were tested to ensure reproducibility of the results.

Elastic Modulus

Elastic modulus of the specimens was obtained as the slope of stress-strain curves recorded by means of an ALPHA compression testing machine, Figure 3. The load cell had a maximum capacity of 50 KN and was loaded with a mechanical press at a constant rate of 0.01 KN/millisecond. The vertical stress was measured utilizing a calibrated LVDT (Linear Variable Differential Transformers) sensor. The end surfaces of the specimens, perpendicular to the longitudinal axis of specimen, were cut with a diamond saw and polished in order to have a smooth surface. The concrete specimens of the size $\text{Ø}50 \times 75$ mm were placed between two platens and positioned under the load cells. 4 LVDT sensors were used to measure the displacement of the bottom platen and 3 more sensors were employed to measure the displacement of the upper platen. The sensors were connected to a data-log system to record the gradient of strain as a function of stress. The calcium depleted samples were kept in 100% RH until being tested in order to avoid any internal cracks.

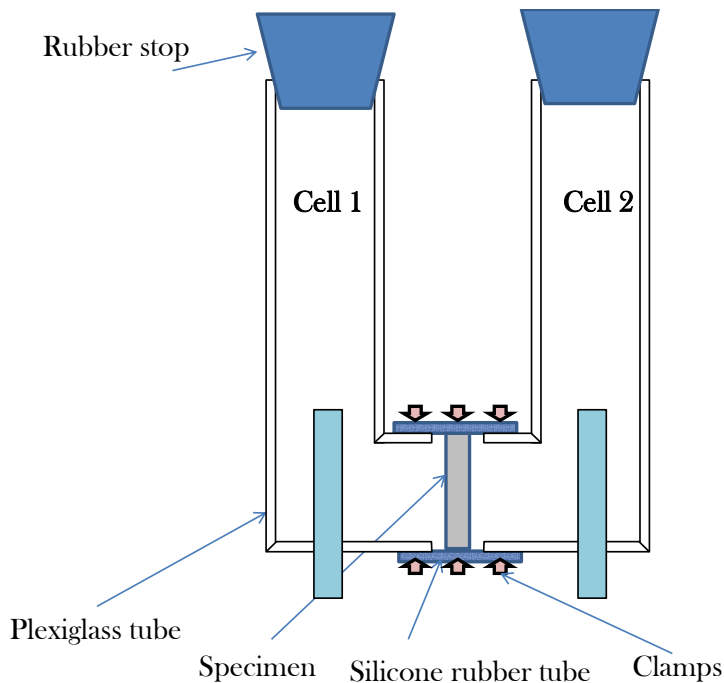


Figure 2. Diffusion cell test setup

2.6 Gas permeability and capillary water adsorption

The gas permeability and capillary water adsorption tests were performed according to state of the art report of Rilem technical committee 189-NEC [32] and the recommendations by Kollek (1989)[33]. The measurements were performed on concrete specimen of the size $\text{Ø}50 \times 75$ mm. The specimens were preconditioned for 2 weeks according to recommended procedures stated in Rilem technical committee 189-NEC [32] and the recommendations by Kollek (1989) [33] prior to the measurements. 2 specimens representative for each W/C-ratio and each degradation state were tested to ensure reproducibility of the results.

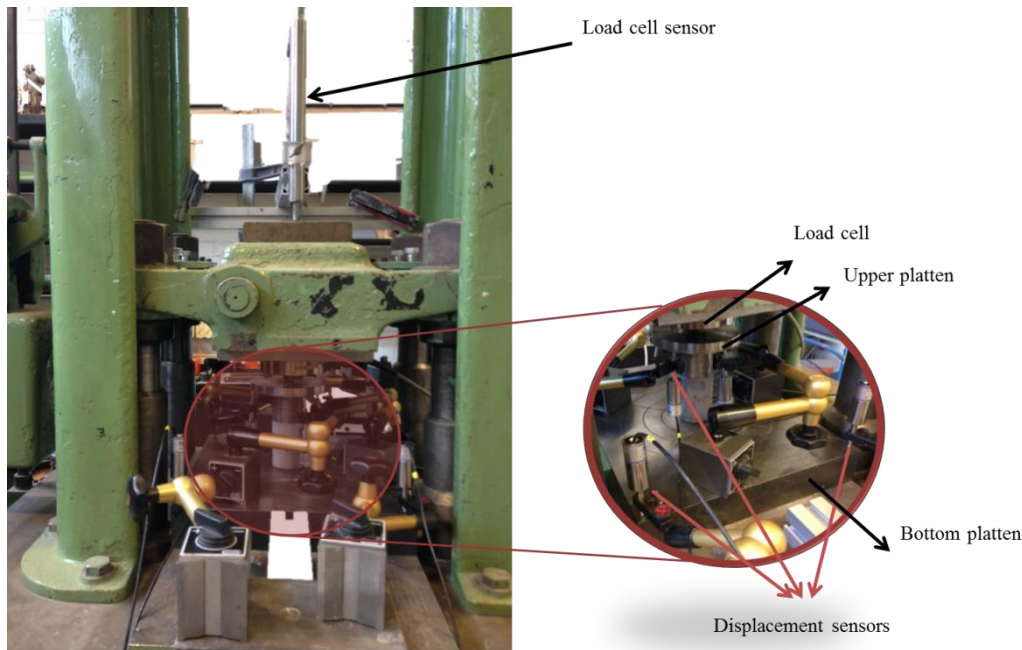


Figure 3. Instrumental setup concerning producing stress-strain curves

2.7 Rapid chloride migration test

The chloride diffusion coefficient of the pristine and leached specimens was studied by means of the rapid chloride migration test according to NT BUILD 492 and as described by Tang [27, 28]. It should be noted that in the case of the calcium depleted specimens owing to a reduced ionic concentration in pore solution compared to normal concrete specimens, adjusted shorter experimental duration was applied to these specimens. Moreover, due to a considerable increase in porosity of the calcium depleted concrete it is not easy to predict the proper test duration. In this study the test duration was set to 15 hours instead of 24 hours. However, chloride ions penetrated through the whole thickness of the specimens in this time duration. As a result the minimum chloride diffusion coefficient was calculated for the calcium depleted concrete specimens.

3 RESULTS AND DISCUSSIONS

3.1 Characterization of degraded specimens

In Figure 4, the Ca:Si ratio is plotted as a function of axial and radial position in the specimen and the number of days of leaching. In this figure it can be seen that leaching starts from the cathodic side of the specimen and propagates towards the anodic side. Considering the gradual changes in Ca:Si profile, the leaching develops towards a homogenized leaching level throughout the specimen (leached portlandite content).

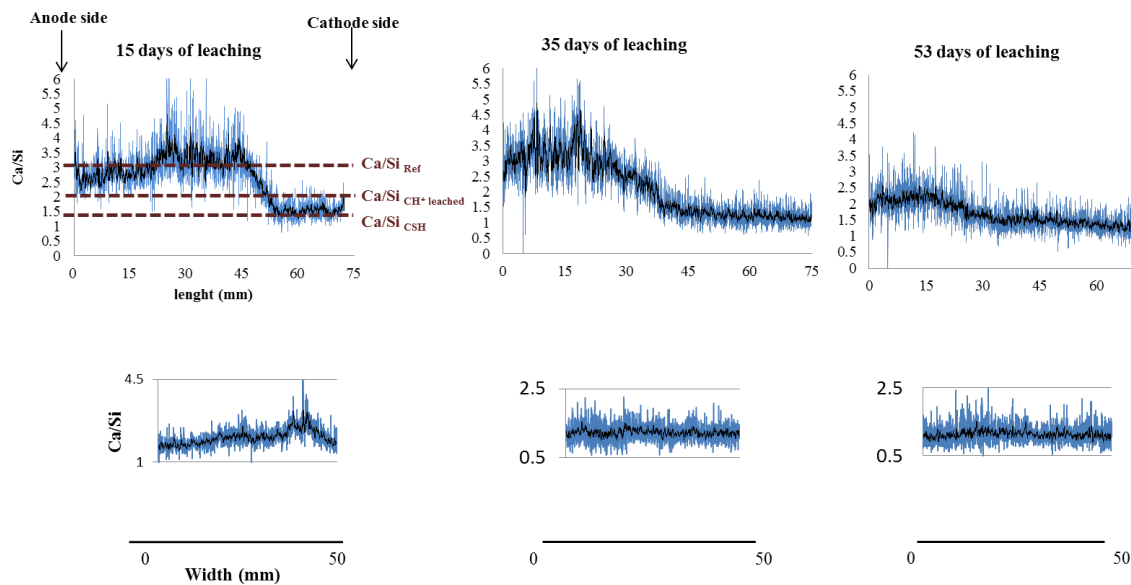
The hypothesis regarding the preferential leaching of portlandite is investigated with XRD analysis. As shown in Figure 5. It is clearly shown that the portlandite peaks are dramatically reduced as compared to the pristine material. It should be noted that the ettringite peaks remain present in treated samples which, as discussed in part 2.2, should be due to low solubility of SO_3^{2-} ions as well as higher mobility of NO_3^- ions.

Figure 6 show SEM images of the pristine material and the leached specimens, respectively. As illustrated the aged samples show a higher porosity compared to the reference one. Moreover the detectable crystalline phases like portlandite, which are present in the reference sample, cannot be seen in the aged samples. The elemental composition of samples was analyzed and compared with the reference sample utilizing EDX method. The results are presented in Table 4, indicating a considerable lower Ca/Si in the aged sample compared to the reference sample. This is in good agreement with the LA-ICP-MS results.

Mercury Intrusion analysis results are presented in Figure 7. As shown the total porosity (cumulative pore volume) increased considerably for the degraded samples. As shown total pore volume of pores with sizes between 100-1000 nm increased whereas the total pore volume of pores with sizes between 1-100 nm decreased after leaching. The decrease in pore volume for smaller pores should be due to recrystallizations taking place during the leaching which might further dissolve after longer leaching time.

The changes in specific surface area of the aged samples as a function of pore distribution were studied by means of BET measurements. The results show that the pore area of the samples changes from 80 cm²/g to 160 cm²/g after degradation. As illustrated in Figure 8, the aged samples present a considerable higher N₂-adsorption and consequently a higher surface area than the reference samples. These results are in very good agreement with the results from mercury intrusion analysis presented in Figure 7.

Comparing the leaching depths in the specimens leached for 53 days (size Ø 50×75 mm) as shown in Figure 5, with the values reported in literature for natural leaching rates [4, 34-37] (leaching depth equal to 5-10 mm can be expected after up to 100 years and in 1000 years it is expected to be up to 8-20 mm), a considerable acceleration rate is demonstrated for presented method in this study. Moreover, The results are in good agreement with the pore distribution data from naturally leached samples as reported by Haga et al. [6] or reported results by Adondet and Buil [4] stating that total dissolution of portlandite content followed by progressive decalcification of CSH gel is expected in natural leaching process which was demonstrated to be similar for degraded samples in this study.



*CH: Portlandite content

Figure 4. LA-ICP-MS analysis results

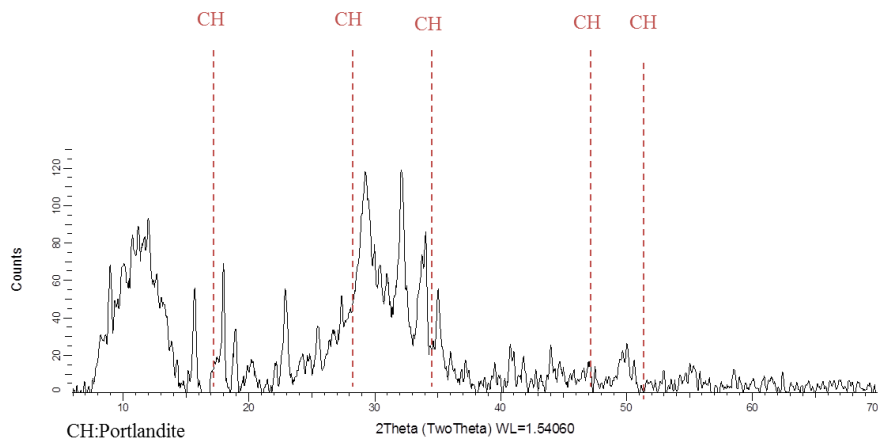


Figure 5. XRD analysis for degraded paste sample

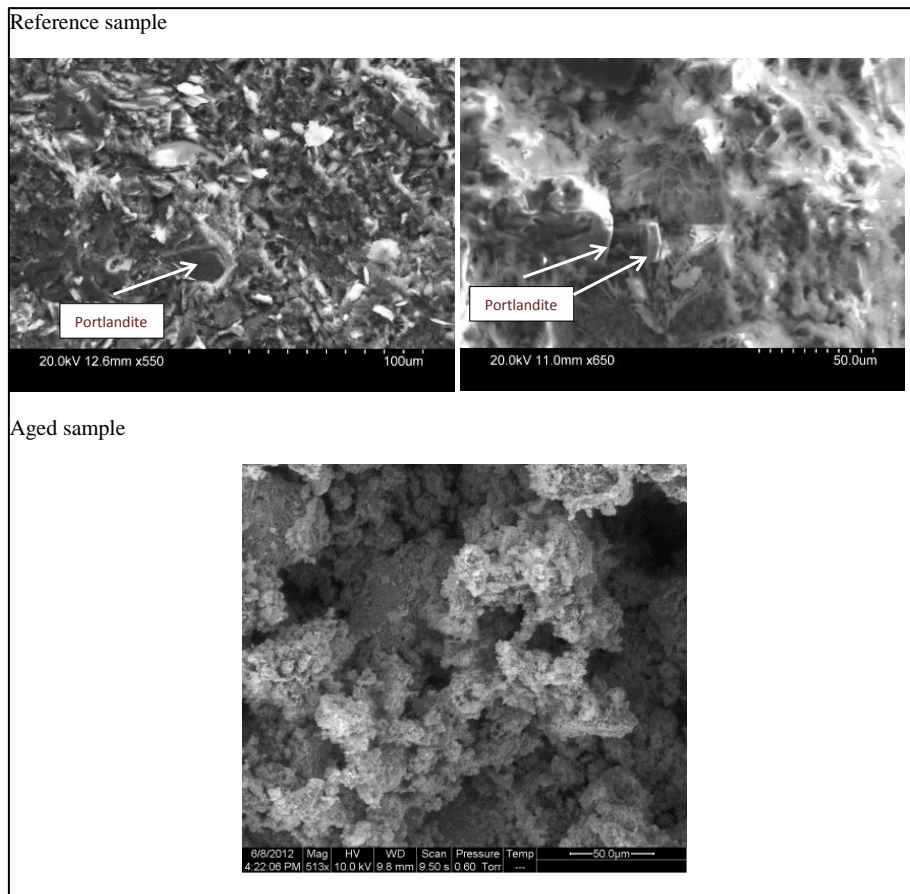


Figure 6. SEM analysis results

Table 4. EDX analysis results

Spectrum (% Atomic)		Al	Si	Ca	Fe
Reference	Mean	1.62	11.09	30.32	1.02
	Std. deviation	0.17	1.73	2.51	0.22
	Max.	1.8	13.14	33.08	1.37
	Min.	1.35	0.51	27.44	0.8
		Ca/Si : 2.73			
Aged	Mean	2.34	15.03	22.97	1.74
	Std. deviation	0.22	0.52	0.58	0.42
	Max.	2.97	15.91	24.28	2.91
	Min.	2.08	13.4	21.55	1
		Ca/Si : 1.52			

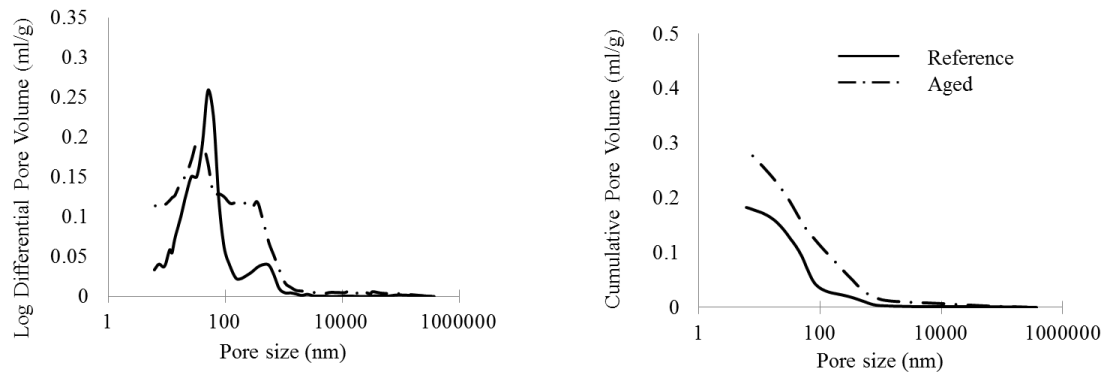


Figure 7. Mercury intrusion analysis results

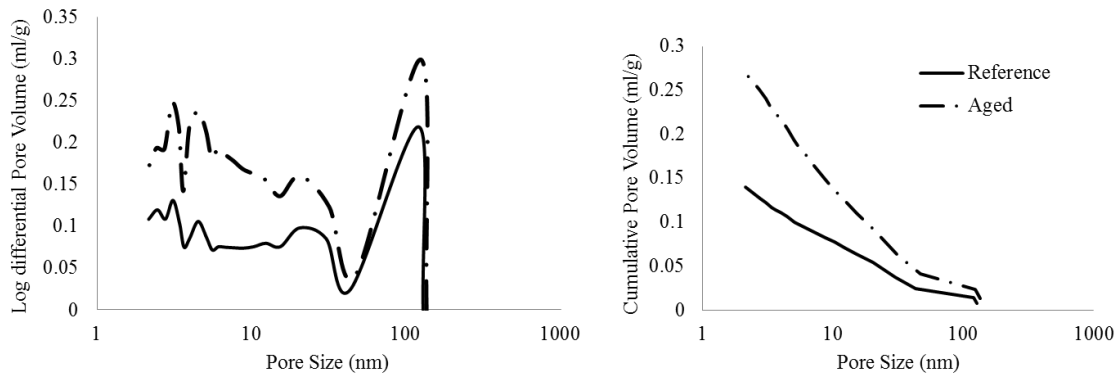


Figure 8. BET analysis results

3.2 Diffusion/Adsorption properties

As shown in Figure 9, the cement and CsCl mixtures reached equilibrium latest after 2 weeks. It is apparent from the figure that the free concentrations of cesium ions in the mixtures containing leached cement paste are considerably lower than the mixtures containing reference samples i.e., unleached specimens. This indicates a higher binding potential of aged cementitious materials, which has previously been reported by Ochs et.al [23].

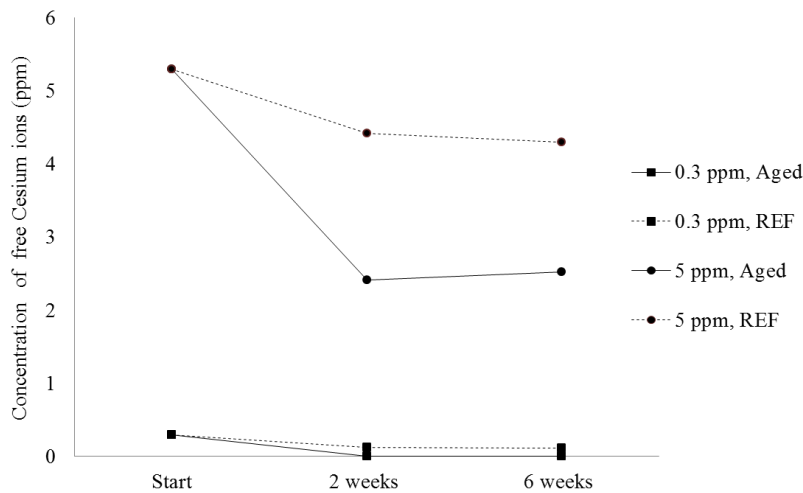


Figure 9. Adsorption test results

Figure 10, illustrates accumulated concentration of diffused ions in diffusion cell test as a function of time. As shown the diffusion rate is higher for all elements in the case of aged samples compared to the reference. Considering that decalcification changes the bulk density and the pore structure of the degraded cementitious materials, higher porosity in aged specimens reasonably causes a higher diffusion rate in these specimens.

Further, comparing plot (a) and (b) in Figure 10, it can be seen that the diffusion rate of Cs ions in the case of the aged sample is very close to diffusion rate of Na ions in plot (a), while it is considerably higher in plot (b). Considering higher mobility of Cs compared to Na ions, this can be due to adsorption/binding effect in the case of plot (a). However, a higher concentration gradient in the case of plot (b) overcomes this effect.

3.3 Mechanical properties

The results from the mechanical tests are presented in Table 5. As shown the average tensile strength (2 specimens for each W/C) for the specimens with a W/C ratio of 0.48 is reduced approximately up to 70 % due to calcium depletion whereas the reduction in tensile strength for the specimen with a W/C ratio of 0.62 is about 55%. Interestingly the residual tensile strength of the samples after degradation is similar in both water cement ratios, which indicates that although the different initial portlandite content in specimens would cause differences in strength properties, but similar residual strength can be predicted in specimens with different W/c ratios if leaching is propagated only up to leaching of portlandite content for all specimens. Moreover, the change in elastic modulus is also presented showing that the elastic modulus is reduced by 40% after leaching for both types of specimens.

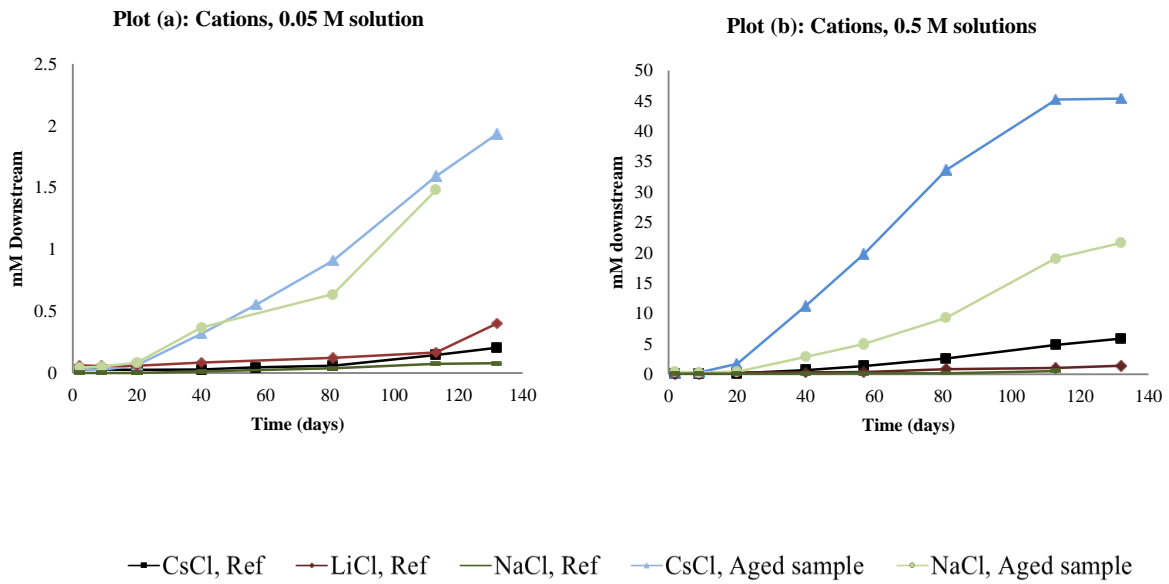


Figure 10. Diffusion cell test results

Table 5. Mechanical test results

	Tensile strength (MPa)			E-Modulus (GPa)		
	Ref	Aged	% Decrease	Ref	Aged	%Decrease
W/C=0.48	10	3	70	~ 50	~ 30	40
W/C=0.62	5.5	2.5	55			

3.4 Physical properties

Figure 11, illustrates the adsorbed water content as a function of time. As it can be seen up to 3-4 times of higher water adsorption rate for the calcium leached specimens is shown compared to pristine materials. The result indicate that a higher pore volume in calcium depleted samples which results mainly from dissolution of portlandite content has a detrimental influence on strength properties of cementitious materials [6, 8, 22].

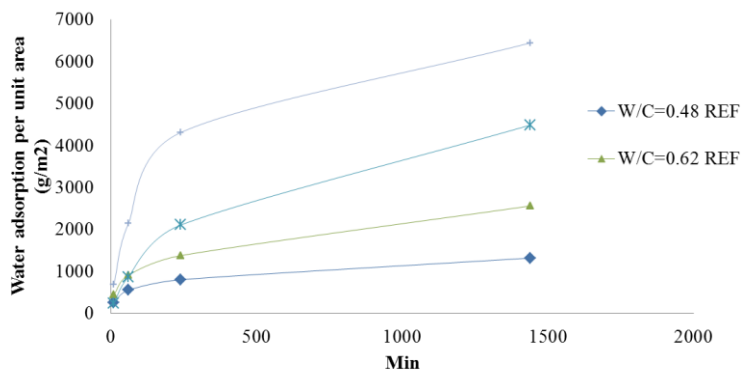


Figure 11. Capillary adsorption of water

Furthermore, the changes in gas permeability coefficient of the concrete due to degradation are presented in Figure 12, indicating up to 15 times of increase in gas permeability as a result of depletion in calcium.

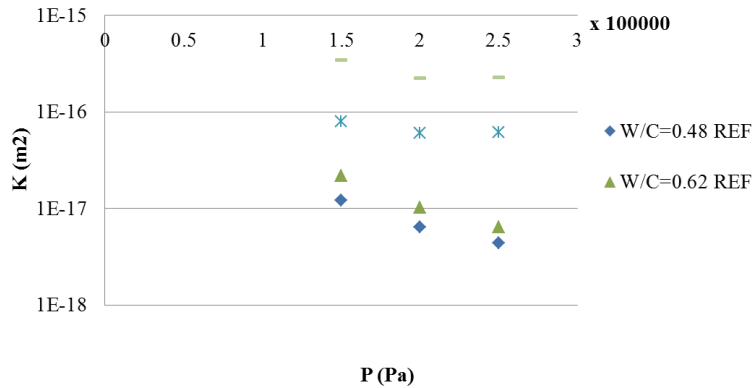


Figure 12. Gas permeability test results

Finally, the changes in chloride diffusion coefficient of the concrete samples due to degradation are presented in Figure 12. As it can be seen up to at least 70% increase in chloride diffusion coefficient is expected after calcium depletion. It should be noted that the presented results regarding the calcium depleted specimens are the minimum chloride diffusion coefficient owing to the full penetration through the specimen thickness as it was pointed out previously. The results are in good agreement with the presented results by Choi et al. (2013) [16].

Table 6. Rapid Chloride Migration test results

	Average Chloride diffusion coefficient ($\times 10^{-12}$)	
	Ref	Aged
W/C=0.48	~28	>110
W/C=0.62	~51	>132

4 CONCLUSIONS

A newly developed acceleration method with the flexibility of producing decalcified cementitious specimens with different sizes suitable for further testing methods was presented. Electro-chemical migration method enhances ageing of cementitious materials with a rate far higher than natural leaching. The ageing function can be controlled and the sample size is flexible. Any acceleration method may involve some processes which may not be present in the natural situation. However, considering the changes in mineralogical, physical, chemical and mechanical properties of aged material is of high importance in order to show the comparability as well as to build up a better base for further numerical situations. One of the direct applications of this study is to provide experimental approaches to be able to supply databases in order to validate the risk assessment analyses regarding the functionality of engineered cementitious barriers. Based on the results presented in this study the following conclusions can be drawn:

- Leaching of portlandite from concrete followed by gradual degradation in CSH gel can be demonstrated by utilizing electrochemical migration method.

- The aged samples exhibit a higher binding potential for Cs ions. It was found that the specific surface area of aged samples was increased by up to 50%, which might be the reason to the enhanced adsorption of Cs⁺ ions compared with the pristine material.
- The pore volume was increased by up to 40-50% after decalcification, which cause considerable increase in ionic diffusion rate of aged samples compared with pristine materials.
- Calcium depletion for sample with W/C=0.48 will lead to Up to 70% of increase in capillary water adsorption whilst 55% of increase is predicted for the case of W/C=0.62.
- Decalcification decreases the tensile strength and this reduction is proportional to the change in pore volume: 70% for W/C=0.48 and 55% for W/C=0.62.
- Up to at least 35% of decrease in E modulus is concluded whilst compressive strength at failure is shown to be reduced up to 50%.
- The gas permeability is shown to be increased up to 90% and at least up to 10 times higher water permeability is expected.
- The chloride diffusion coefficient is shown to increase at least up to 70%.

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