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Author(s)	Nguyen, Thi Hai Yen
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**VERIFICATION OF PRACTICAL EFFECTIVENESS
OF VARIOUS APPLICATIONS OF
ELECTROCHEMICAL CHLORIDE EXTRACTION
FOR CEMENT CONCRETE**

種々の条件下でセメントコンクリートに適用した
電気化学的脱塩の有効性評価に関する研究

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of
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by

Nguyen Hai Yen Thi



Laboratory of Lifetime Engineering

Division of Engineering and Policy for Sustainable Environment

Graduate School of Engineering

Hokkaido University, Japan

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Abstract

Maintaining and prolonging the service life of existing reinforced concrete structures are crucial contributions of civil engineer to solve the sustainability issues. Electrochemical chloride extraction (ECE) is one of the maintenance and repair methods to prevent further deterioration of a reinforced concrete structure that is exposed to chloride environments. It arose to answer the question that when the source of corrosion, chloride ions, is extracted or eliminated out the zone around steel reinforcement, it is not clear if the corrosion of reinforcement stops, the passive layer is re-passivated or the deterioration progress could be slowdown. Theoretically, the principle of ECE is similar to cathodic protection since a direct current is applied on reinforced concrete structure in which reinforcing steel is used as cathode and a temporary anode is set up on the surface of concrete. However, the application of the high current or the large quantity of cumulated-applied charge number by using ECE can result the adversities on binding capacity of hydrated cement products or the diffusibility of concrete matrix. Consequently, these adversities would affect the future durability of reinforced concrete structure. Furthermore, while there have been many structures using fly ash and granulated blast furnace slag as mineral admixtures to improve durability of reinforced concrete structure, there are very few studies of ECE on concrete or cement pastes containing them. How to reduce the charge number applied with preserving the efficiency of ECE needs to investigate. Therefore, this research included two objectives.

Firstly, the effects of electrical current application thanks to the conduct of ECE on hydrated cement products of cement pastes, especially on C-S-H phase, were investigated. A pair of modified migration cells were used with the applied current density of 4.5 A/m^2 and synthesized pore solutions as electrolytes for 8 weeks. Three types of cement pastes with the size of 40 mm by 40 mm by 160 mm were prepared with the water-to-binder ratio of 0.4 including ordinary Portland cement (OPC), fly ash cement (FC) and ground granulated blast furnace slag cement (SC) pastes. After casting, these paste specimens were cured in saturated calcium hydroxide for three months before stopping the hydration process by immersing them into acetone. These pastes were sliced into the size of 40 mm by 40 mm by 5 mm before applying the extraction. Chloride source was supplied by adding 1.5% sodium chloride with respect to mass of binder during mixing cement pastes. After extraction, the acid-soluble and water-soluble chloride contents significantly reduced. Portlandite content increased proportionally with the time of extraction in OPC and FC pastes. Some unsteady gel phases were obtained after a short time the extraction was stopped. Furthermore, the alteration and decomposition of C-S-H were inevitable with different rates depending on the type of cement. The breakage of the chain of calcium silicate hydrate was obtained and the rates of breakage seemed proportionally to the period of ECE application, especially the dimer-silicate chain. Therefore, how to lessen the time of the electrical current application or in another term how to reduce the amount of applied charge number, but

still preserving the chloride removal efficiency is necessary to study. Sequentially, intermittent application of ECE needs to be taken into account.

Secondly, based on the necessity of carrying on more study on intermittent application of ECE in order to remediate the adversities of ECE by using large amounts of cumulated-applied charge number, the experimental research program was conducted. It focused on investigation of the capacity of intermittent application of ECE on extracting chloride compared to continuous application and finding out the adequate period for current-off and current-on intervals in order to uphold or preserve the chloride extraction efficiency. Two modes of intermittent applications and a continuous application of electrochemical chloride extraction (ECE) were conducted on reinforced concrete blocks with the size of 20 cm by 20 cm by 10 cm. These concrete blocks were contaminated chloride by exposing the NaCl solution containing 3.5% percent of chloride ions Cl^- with wet and dry cycles. In each cycle, the concrete blocks were immersed in salt solution for 6 hours and then dried for 66 hours. After 60 cycles of immersing, since the chloride content in concrete at the zone beside the steel reinforcements was approximately $1.4\text{--}1.6 \text{ kg/m}^3$, the extraction was applied with the electrical current density of 1 A/m^2 with respect to concrete surface. The result indicated that intermittent applications expressed much greater charge-efficiency than continuous application in removing chloride, though the quantity of chloride extracted in three modes were approximate. Since the cumulated applied charge number exceed $800\text{--}900 \text{ A}\cdot\text{hour/m}^2$, concrete matrix tended to be unstable and the decomposition of C-S-H phase may take place. Furthermore, sodium ions inclined to agglomerate with hydroxide, a product of cathodic reaction, to form NaOH in concrete at the zone beside steel reinforcement.

The less adverse effects of ECE on C-S-H phase was obtained by using the intermittent application. Conclusively, intermittent application is the potential means to apply ECE in order to remediate the adverse side effects of continuous application of ECE on concrete properties.

Furthermore, this research figured out that intermittent applications would be conducted with sophisticated applications, which comprise of several different periods of current-off and current-on. At the first stage of extraction process, the time for current-on could be lasted for couple days before interrupting it for approximately 2-3 days. However, after that first stage, the time for current-on should be lessened, approximately 1.5-2 days, and the break of the electric current should be iterated more often during conducting ECE.

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1.1. Background of study

Today, degradation of reinforced concrete structures has been a problematic issue. The corrosion of steel reinforcement in reinforced concrete structure due to the abundant contamination of chloride ions is one of the main reasons to account for the degradation of reinforced concrete structure, as shown in Figure 1.1. It declines the performance of the structure and shortens the structure's service life [1-5]. Constructing a new structure to replace the degraded one is one of the best choices to guarantee human safety; instead, it evokes many other issues such as a budget problem, carbon dioxide emission as well as earth's resource consumption, which have currently been running out quickly. Besides, carbon dioxide emission and earth's resource are the essential risks of sustainability issues. Therefore, prolonging the service life of existing structures has become one of the main priorities to mitigate the further degradation of structure and contribute to solve these issues [6-10].

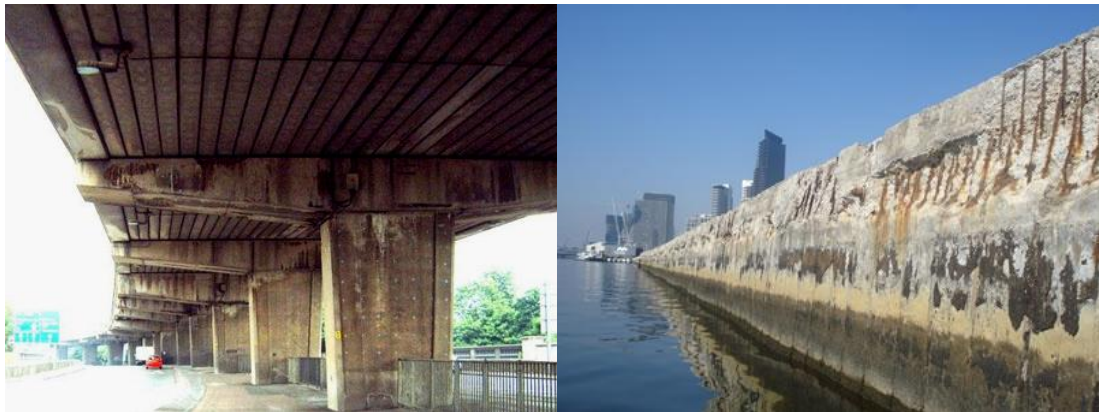


Figure 1.1 Corrosion of steel in reinforced concrete bridge (left) and breakwater (right).

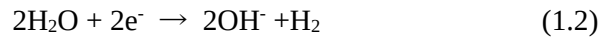
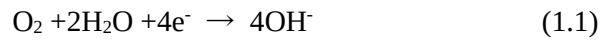
Cathodic protection and cathodic prevention are the popular options to prevent steel corrosion. However, these methods need to be maintained until the end of structure's service life from the moment it is installed. Therefore, it is demanded a method which not only can mitigate the corrosion of steel reinforcement, but also can be applied in such shorter time. Electrochemical chloride extraction (ECE) had emerged as a content option. There are many studies and applications done in some last decades to investigate its capability on mitigating the further deterioration of reinforced concrete structures, which underwent the performance's decline by chloride contamination [11-16]. Although the efficiency of chloride extraction varies widely and depends on many criteria, most of the research lead to the conclusion that ECE can extract approximately 20-80 % chloride content [12-21] and be able to re-passivate the corroded steel reinforcing bars.

In contrast to the relatively consistent results of ECE, which express the feasibility of ECE on re-passivating the steel reinforcements and mitigating the corrosion progress of the reinforced concrete structures [22-26], the impacts of ECE in concrete matrix as well as the bond strength between concrete and steel bars emerged some critical controversies which primarily relates to the later durability of the structures.

While the significant reduction of bond strength between concrete and reinforcement which measured immediately after extraction were indicated [27-28] there were negligible diminution of flexural strength obtained [29]. The accumulation of alkali ions at the cathode after extraction is assumed to be the prospect of alkali silica reaction. Nevertheless, that assumption currently is still uncertain since the conflicting results came up. Some authors [21, 30-31] expressed a potential of alkali silica reaction, even with no or little reactive aggregate. However, Swamy et al [29] indicated that alkali silica reaction took place only in reactive aggregate but not in unreactive aggregate.

The severe reduction of bond strength has been presumed to increase proportionally with the current density and the application time of ECE [11-15, 27-28]. Likely, it increases with the cumulated charge number (A.hour/m²) applied [11, 32]. Therefore, lessening the applied charge number may accordingly alleviate the main drawback of ECE.

The generation of hydroxide ions thanks to cathodic processes, which are expressed in Equations (1.1) and (1.2), as well as the reduction of free chloride concentration during extraction process undoubtedly diminish the supply of chloride ions into the ionic fluid for current transference. Consequently, it leads to the reduction of chloride removal efficiency quickly [23, 33].



The evolution of hydrogen is perhaps another critical cause, which can ruin the well contact between steel and concrete. Therefore, reducing the generation of hydroxide ions and the evolution of hydrogen not only can improve the removal efficiency of chloride ions, but also able to cease one of the main side effects of ECE due to the utilization of a large quantity of applied charge number.

In order to lessen the quantity of applied charge, but somehow uphold or at least preserve the efficiency of removal chloride, intermittent application of ECE has been considered. It is assumed that during the period in which the current is switched off, a new equilibrium condition between bound and free chloride is established and it can then release a new quantity of free chloride [12-16]. Therefore, in the next period where the current is turned on, free chloride

may take more part in the ionic fluid than before turning it off.

However, the lack of previous studies of ECE with intermittent application causes difficulties not only in confirming these suggestions, but also in selecting the satisfactory intervals for the current-off and current-on periods. While Fajardo et al [25] figured that there are no significant differences between continuous application and intermittent application, the others [33-34] indicated a significant advantage of the current-off period during operating ECE. Nevertheless, it is hard to get the complete comparison of chloride removal efficiency between intermittent and continuous applications since there was no continuous application in these research [33-34]. Therefore, it is necessary to conduct more studies of ECE with the intermittent applications in order to reach a more consistent conclusion and suggest a conduct which can uphold the efficiency of chloride removal but suppress the drawbacks caused by using a large quantity of charge number.

It should be noticed that the source of chloride ions in most of previous studies was internal chloride ions, which was added during mixing concrete [26-32, 34]. There are very few studies on concrete contaminated chloride by external sources [25, 33]. Obviously, the internal source of chloride is unable to fully represent the distribution of chloride in different depths of concrete cover. In addition, it is unable to display the correlation and the proportion between free chloride and bound chloride in concrete matrix which chloride contaminated by exposing to chloride environments. Furthermore, while the qualities of concrete using in reinforced concrete structures which exposes to chloride environments have been specified and guided clearly, these previous studies applied on concrete with low or medium quality, where water to cement ratio was usually larger than 0.5 [19-34]. Consequently, a study on concrete which qualifies the specific properties of reinforced concrete structures using in chloride environment is necessary in order to evaluate the prospect of ECE method to rehabilitate the reinforced concrete structure in the current facility.

Notably, most of the previous studies focus only on the efficiency of chloride removal from concrete and the corrosion state of reinforcement [23, 25, 29, 33]. There are very few studies on the impacts of ECE to the cement hydrated products. Meanwhile, the cement hydrated products, especially C-S-H phases, are the main properties affecting not only the bearing capacity but also the durability of a reinforced concrete structure. Therefore, research that focuses on the alteration of C-S-H phases due to the effects of ECE is necessary to evaluate the performance, capability of ECE on preventing the further deterioration progress and durability of a reinforced concrete structure after terminating the extraction.

Moreover, substitution materials in concrete have been applied widely for the last decades, but there are also very few studies in the influences of ECE on blended cement [35-36].

Besides, the studies on cement hydrated products and the morphology of the matrix phase in concrete are usually undertaken with the interferences of the preparation process and these interferences may then cause some inaccuracy.

1.2. Objectives

From these points of view, the aims of this research are to evaluate:

1.2.1. Effect of ECE to hydration products of cement

One of the main objectives of this research is to investigate the impacts of the application of electrical current on chemical properties and morphology of various types of cement pastes. Three types of cement pastes were studied which include ordinary Portland cement (OPC), fly ash cement (FC) and ground granulated blast furnace slag cement (SC).

1.2.2. Efficiency of intermittent applications of ECE on reinforced concrete

The other main aim of this research is to compare the efficiency of various intermittent applications and a continuous application of ECE on reinforced concrete specimens. Furthermore, the effect of ECE on concrete matrix additionally is investigated to obtain the proper number of charge applied which not only can adequately withdraw chloride out of concrete, but also be able to mitigate the severe effects of ECE by using ECE with abundant quantities of charge number.

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CHAPTER II **RESEARCH METHODOLOGY AND EXPERIMENTAL PROCEDURES**

In this chapter, the methodology and the experimental procedures in each individual objectives of the research are described.

2.1. Effect of ECE to hydration products of cement

2.1.1. Research methodology

As mentioned in Chapter 1, most of the previous studies focused only on the efficiency of chloride removal from concrete and the corrosion state of reinforcement [1-5]. Very few studies aimed to examine the impacts of ECE to the cement hydrated products [6]. Meanwhile, the cement hydrated products, especially C-S-H phase, are the main factor affecting not only the bearing capacity but also the durability of a reinforced concrete structure. Therefore, the research that focuses on the alteration of C-S-H phases due to the effects of ECE is necessary to indirectly evaluate the performance, capability of ECE on preventing the further deterioration progress and durability of a reinforced concrete structure after terminating the extraction. Furthermore, substitution materials in concrete have been applied widely for the last decades, but there are also very few studies on the influences of ECE on blended cement [7-8]. Besides, studies on cement hydrated products and morphology of concrete matrix are usually undertaken with the interferences of the preparation process and these interferences may then cause some inaccuracy.

For these reasons, in this part of the research the impacts of ECE on chemical properties and morphology of cement pastes are studied by using a modified migration cell. A newly invented migration cell allows to conduct the migration test on a thin disk sample. The achievement is to investigate the alteration in minute region of the cement paste morphology by using SEM-EDS on samples without any interference in the preparation procedure. The alteration of C-S-H phases, the main component that decides the binding capacity and durability of cement-based materials, is mainly focused. The study was done with various types of cement including ordinary Portland cement (OPC), fly ash cement (FC) and ground granulated blast furnace slag cement (SC) to follow widely using of substitution materials in the concrete industry.

2.1.2. Experimental procedures

The experimental procedure consisted of three steps: casting the cement pastes and preparing the disk specimens for migration test, running the migration test, and examining the variation of chemical properties and microstructure of cement pastes.

2.1.2.1. Casting the cement pastes and preparing the disk specimens for migration test

The paste specimens were casted with the size of 40 mm by 40 mm by 160 mm in stainless steel mold and with the water-to-binder ratio of 0.4. Three types of binder were used, ordinary Portland cement (OPC), fly ash cement (FC) with 20% fly ash replacement and ground granulated blast furnace slag cement (SC) with 40% slag replacement by weight of binder. The source of chloride ions in the pastes was supplied by adding 1.5% NaCl into mixing water during casting. The proportions of cement pastes are summarized in Table 2.1. Their compositions and physical properties are listed in Tables 2.2 and 2.3, respectively. To prevent the unexpected segregation of solid particles in the mix, the paste was kept mixing for five minutes during two hours and a half at 15-minute intervals before pouring into the molds. These molds were then wrapped by polyethylene film for 24 hours before the paste specimens were removed from the mold and immersed in saturated calcium hydroxide solution to prevent leaching of Portlandite.

Table 2.1 Proportion of cement paste with water-to-binder ratio of 0.4 (%. wt of binder).

	Cement	Fly ash	Ground granulate blast furnace slag	NaCl
OPC paste	100	0	0	1.5
FC paste	80	20	0	1.5
SC paste	60	0	40	1.5

Table 2.2 Chemical compositions of OPC cement, fly ash, and ground granulated blast furnace slag (%. wt of powder).

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	MnO	I.L
OPC	21.9	5.2	3.1	64.4	1.4	1.7	0.2	0.4	0.3	0.3	2.26
Fly ash	66.42	18.88	3.63	0.90	0.54	0.15	0.04	1.23	0.82	0.03	1.12
Slag	34.3	15.2	0.5	42.8	5.9	0.1	0.2	0.3	0.5	0.5	0.3

Table 2.3 Physical properties of OPC, fly ash, and ground granulated blast furnace slag powder.

	Density (g/cm ³)	Blaine fineness(cm ² /g)	Strength (MPa)			Activity index (%)		
			3d	7d	28d	7d	28d	91d
OPC	3.16	3340	30.3	45.1	61.6	-	-	-
Fly ash	2.16	3610		-		-	87	99
Slag	2.91	4030		-		73	97	113

After curing for three months submerged in saturated calcium hydroxide solution, the paste specimens were cut into disks with the size of 40 mm by 40 mm by 5 mm as shown in Figure

2.1. These disks were soaked in acetone for one day and then dried in desiccator for two days. Two disks of them were crushed and pulverized to gain the powder for the initial powder sample. One disk was crushed into small pieces with the size ranged from 2-5 mm. After that, these disk samples, powdered samples and crushed samples were preserved in a vacuum chamber before conducting the test in order to avoid the effect of carbonation.



Figure 2.1 Cement paste specimen and paste disks using in migration cell.

2.1.2.2. Running the migration test

To set up the extraction, the disk specimen was assembled with a pair of rubber cases and then held in an acrylic holder of the migration cell as shown in Figure 2.2. Similar to the others, the modified migration cell using in this study involves two transparent compartments with the acrylic holder at the middle to hold the disk and two electrodes to connect to the power supplier as shown in Figure 2.3a. However, some modifications on the acrylic holder were made, as presented in Figure 2.3b, so as to allow conducting the experiment on much thinner specimens in comparison with the other migration cells. Therefore, the effect of the electrical current on the chemical and morphological properties of cement paste can be investigated in more detail with less interference of the preparation procedure.

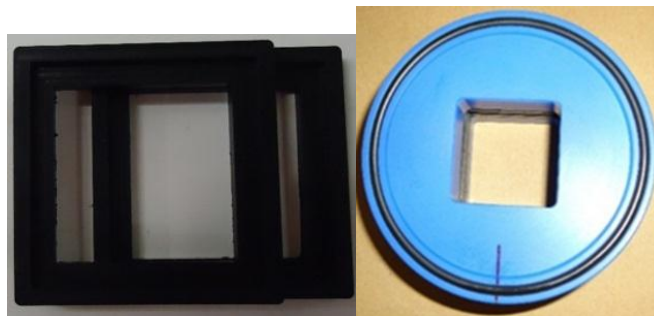


Figure 2.2 Rubber case and acrylic holder.

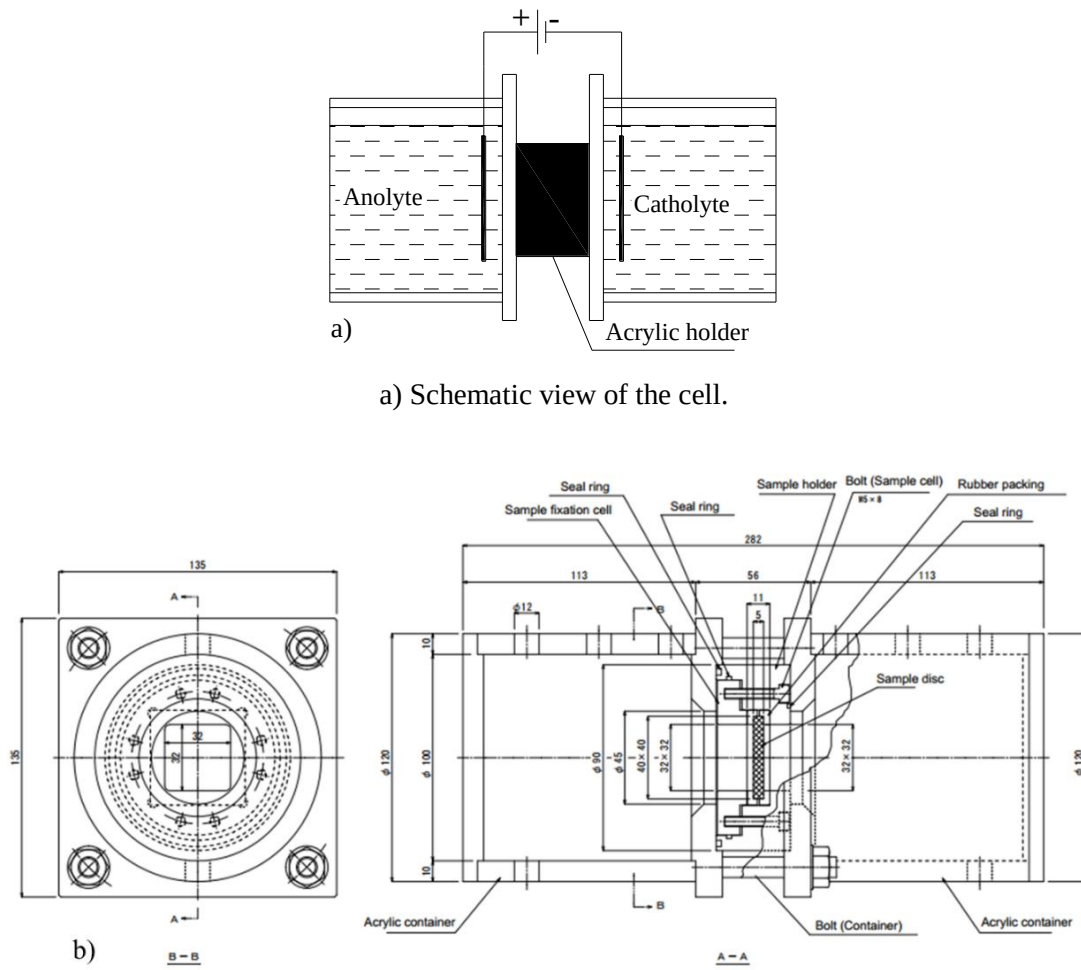


Figure 2.3 Modified migration cell.

To simulate the extraction process in a reinforced concrete structure, synthesized pore solution with appropriate concentration of chloride ions, solution 1, was used as catholyte for first four weeks of the extraction process; and then the catholyte was replaced by the other synthesized pore solution that contains no chloride ions, solution 2. Solution 2 was also used as anolyte throughout the extraction process. The existence of ions and their concentration in pore solution of cement-based materials varies widely and depends on many criteria such as the composition of cement, type of admixtures, water-to-binder ratio, environmental exposure conditions, and associated ions. There are many studies about the relationship between the ionic concentration in pore solution and these fore-mentioned criteria in cement-based materials, especially chloride ions. The concentration of chloride ions in pore solution is also studied widely while cement based materials are added or contaminated with different quantities of chloride ions [9-17]. Nowadays, the relationship between free chloride and bound chloride can generally be represented by the Fleundlich isotherm equation at high free chloride concentrations and the Langmuir isotherm

equation at low free chloride concentration [18-19]. The effects of other criteria are described by adsorption constants which varied widely. According to the research of Delagrave et al. [19] in which the authors studied the chloride binding capacity of various types of cement paste with the water-to-binder ratio of 0.25 to 0.45, the free chloride concentration varies about 0.2-0.3 mol/L since the bound chloride content is in the range of 0.25-0.5%, which is approximate to the binding chloride in this research. On the other study, Tritthart [14], who investigated the change of chloride ions in pore solution and total chloride content at different depths of cement paste plates under different storage condition, showed that at the quantity of approximately 0.85-1.1% of total chloride content, which equal to 1.3-1.65 % NaCl, the chloride concentration in pore solution is about 0.226-0.240 mol/L. Tang et al. [18] and Delagrave et al. [19] indicated that the bound and free chloride relationship is mainly depended on the total quantity of hydration products. Therefore, in this study the chloride concentration in solution 2, which is used to simulate the pore solution in cement paste that contain 1.5% NaCl, which associates to 0.91% Cl^- , is assumed 0.227mol/L. The concentration of the other ions and solution 1 are determined based on consulted Bertoliti [9]. The details of solution 1 and solution 2 are given in Table 2.4.

Table 2.4 Composition of electrolytes (mol/L).

Solution	KCl	KOH	NaCl	NaOH	Ca(OH)_2	pH
1	0.11	0.10	0.117	0.15	Oversaturated	13.39
2	0.00	0.20	0.00	0.10	Oversaturated	13.47

Eight migration cell tests were conducted for each type of binder. The electrical current density of 4.5 A/m^2 with respect to the surface area of paste specimen was employed for eight weeks by using a constant direct power supplier. The detailed current and voltage applied for each type of cement pastes are presented in Table 2.5. The value of current employed here is 3-5 times higher than that usually applied in a reinforced concrete structure. However, as Ismail [7] and Tritthart [15] demonstrated it is reasonable to assume that the paste disks in this test endured an appropriate amount of charge in comparison to a reinforced concrete structure which is applied a current about 1 A/m^2 if the relationship between cement and concrete is considered.

Table 2.5 Applied current and voltage for each type of cement paste.

	Current (mA)	Voltage (V)
OPC paste	4.61	~ 2.0
FC paste	4.61	~ 7.0
SC paste	4.61	~ 3.9

After every two-week interval of extraction, two of those eight migration cells were

terminated current application.

2.1.2.3. Examining the variation of chemical properties and microstructure of cement pastes

These extracted disks were immersed in acetone for 24 hours before cutting off the edge that was held by the rubber case during extraction as shown in Figure 2.4. Ethanol was used as a lubricant during cutting. Three-quarters of the remaining were crushed and pulverized to gain the powdered samples. A half of the remaining quarter was crushed into small pieces with the size in the range from 2-5 mm. Those powdered samples, crushed samples and the remaining were dried in a desiccator in which the air was withdrawn by operating an aspirator at less than 6 KPa for three days. Then they were preserved in a vacuum chamber with pressure less than 80 MPa to counteract the effect of carbonation.

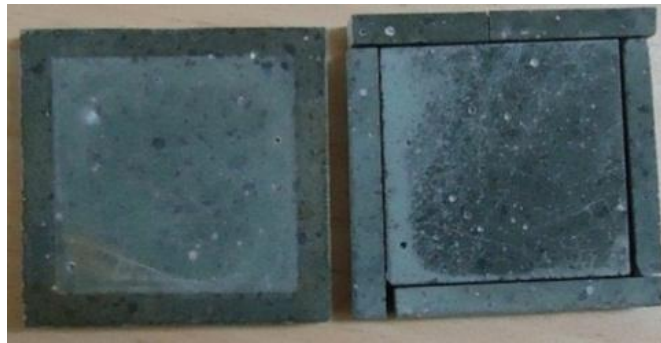


Figure 2.4 Disk specimen after ECE application and cutting-off the edge

These extracted powdered samples and the initial powdered sample were used to determine the remaining of acid-soluble and water-soluble chloride contents according to ASTM C1152/C1152M [20] and ASTM C1218/C1218M [21], respectively. Moreover, in order to investigate the effect of ECE on Friedel's salt as the main chemical binding chloride, X-ray diffraction (XRD) was conducted on those powdered samples with voltage of 50 kV and current of 250 mA in the scan range from 5° to 70° at the step of 0.02° and scan speed of 2°/min on those powdered samples.

To evaluate the general variation of Portlandite contents in the pastes during the extraction process, thermal analysis was carried out on the initial powdered sample and the extracted powdered samples after preserving in a vacuum chamber for 6 weeks. To conduct the analysis, the powdered samples with the size of approximately 0.04 mm were employed on TG/DTA apparatus with the temperature covering from 20-900 °C at the constant rate of 10 °C/min under nitrogen atmosphere.

Moreover, to investigate the alteration and decomposition of hydration products in the pastes, especially C-S-H gel phase, scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) analyses [22-27] were conducted on the initial crushed samples and the crushed samples that had been extracted for 8 weeks but preserved in the vacuum chamber with two certain times: 6 weeks and 3 months. SEM/EDS semi-quantitative analysis was applied with an accelerating voltage of 15kV and measuring distance of 10 mm. The area of EDS analysis was approximately 400 nm [28]. For each type of sample, the EDS analysis was performed on approximately 150 to 250 spots or areas in order to eliminate the random results.

In order to confirm the transformation of unstable phases occurring in cement pastes after stopping the current application, the cement paste samples which have been applied electrochemical chloride extraction for 8 weeks were taken SEM and EDS again after 9 months preserving in a vacuum chamber. TG-DTA was also carried out again to examine the effect of carbonation to samples when they were preserved in the vacuum chamber.

^{29}Si Magic angle spinning nuclear magnetic resonance (^{29}Si MAS NMR) was measured by using Bruker MSL 400 spectrometer with spinning rate of 4kHz and a single pulse of width 5ms followed by a pulse delay 3s. For FC pastes, they were collected after 2400 scans; nevertheless, for OPC and SC pastes they were recorded after 1200 scans.

2.2. Efficiency of intermittent applications of ECE on reinforced concrete

2.2.1. Methodology

As mentioned in previous chapter, the longer time ECE applied the more chloride ions can be extracted. However, it can additionally cause more severe effect on C-S-H phase, the most important phase in cementitious materials. Afterwards, the further drastic effects can be resulted on the later durability of the structure. Lessening the actual time of the current application, or the quantity of applied charge number, is one of the modified technique has been studied to alleviate the drawbacks of ECE.

In order to reduce the quantity of charge numbers to be applied, but somehow uphold or at least preserve the efficiency of removal chloride, the intermittent application of ECE has been considered. It is assumed that during the period in which the current is switched off, a new equilibrium condition between bound and free chloride is established and then a new quantity of free chloride can be released. Therefore, in the next period where the current is turned on, free chloride may take more part in the ionic fluid than before turning it off [4-5]. However, the lack of previous studies of ECE with the intermittent application [2, 4-5] causes difficulties not only in confirming these suggestions, but also in selecting the satisfactory intervals for the current-on period and the current-off period on intermittent process. Therefore, it is necessary to conduct more studies of ECE with the intermittent applications in order to reach a more consistent

conclusion and suggest a proper manner to conduct ECE which not only can preserve the efficiency of chloride removal but also can suppress the drawbacks caused by using large quantity of applied charge number.

From these points of view, the aim of this research is to obtain the experimental data which would allow to:

- 1) Compare the efficiencies of chloride removal between intermittent applications and continuous application of ECE on concrete contaminated external chloride.
- 2) Find out the proper number of applied charge and proper interval period of current-off and current-on, which are adequate to withdraw chloride out of concrete matrix, in addition, be able to suppress the severe effects of ECE by using ECE with abundant quantity of the charge number.

In order to attain that, ECE including a continuous application (Mode 1) and two modes of intermittent application (Modes 2 and 3) were employed for 10 weeks on concrete blocks which contaminated chloride by exposing to NaCl solution with 3.5% Cl⁻. The wet and dry cycle of chloride exposure was applied to accelerate the sorption of chloride into concrete.

2.2.2. Experimental procedures

2.2.2.1. Concrete preparation and process of accelerating chloride sorption

Thirty three reinforced concrete blocks having a rectangular cross section as shown in Figure 2.5 were cast. Each reinforcing bar was connected to a copper wire in order to conduct the electrochemical chloride extraction later. The mix proportion of concrete with the water to cement ratio of 0.4 is presented in Table 2.6 in which Ordinary Portland cement was used. The chemical composition and mineral components of ordinary Portland cement are expressed in Table 2.7. After casting, these concrete blocks were covered with wet burlap, and then, a PE tarpaulin. One day later, these blocks were removed out from the molds and then covered with wet burlap and tarpaulin again. The burlap was sprayed with water 1 time at 3-day intervals during one month to reserve wet condition.

After curing for one month, the surfaces of these concrete blocks were dried by placing them in room condition at approximately 20 °C and relative humidity of 60-75% in one week. In order to reach the necessary quality of concrete structure which exposes to chloride environments, the thickness of concrete cover should be higher than 5 cm. Therefore, the surfaces of concrete blocks were coated with approximately 2 mm of epoxy on five surfaces except the bottom surface, as presented in Figure 2.6.

One week after coating epoxy, the uncoated surface of these blocks was turned over and put in a PVC container with the size 59 x 39 x 20.5 cm, which placed in the curing room at 20 °C and 95% relative humidity. Each PVC container contained two blocks. Then, the NaCl solution

with 3.5% chloride ions was poured into the container until the solution level was higher than uncoated surface approximately 10 cm. These blocks were submerged in this solution with the cycle of 6-hour wet followed by 66-hour drying. After 10 cycles, they were moved to another room, which was at 20°C but with 60-70% relative humidity, where these blocks were again submerged in salt solution with the same wet and dry cycle as the fore-mentioned.

The acid-soluble chloride content in concrete was examined after each 10 cycles of wetting and drying by drilling the block at five determined depths from the uncoated surface: 0-1 cm, 1-2 cm, 2-3 cm, 3-4 cm, and 4-5 cm. After 60 cycles, since the acid-soluble chloride content at the depth 4-5 cm, which was beside the steel bars, reached to approximately 1.4-1.6 kg/m³, the acceleration process for chloride contamination was stopped.

Table 2.6 Concrete mix proportions (kg/m³).

W/C	Water	Cement	Sand	Coarse Aggregate
0.4	165	412	790	1020

Table 2.7 Chemical compositions and mineral component of cement (% wt of powder).

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	MnO	TiO ₂	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
21.9	5.2	3.1	64.4	1.4	1.7	0.2	0.4	0.3	0.3	56	18	9	9

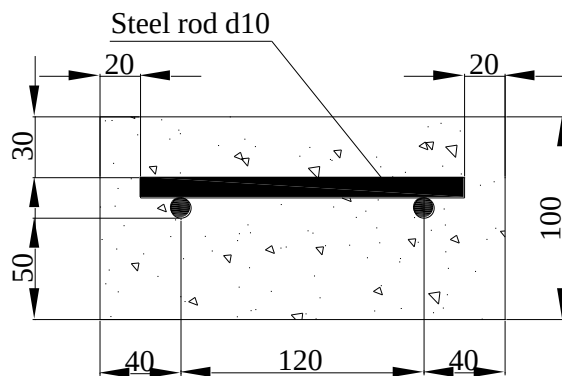


Figure 2.5 Cross section of reinforced concrete block.

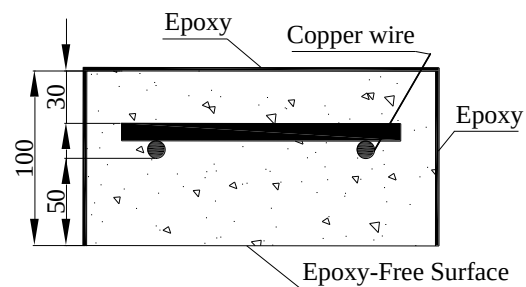


Figure 2.6 Epoxy-coating before immersing in salt solution.

2.2.2.2. Electrochemical chloride extraction applications

After 60 cycles of immersion, since the chloride content in the concrete region beside the steel bars reached approximately 1.4-1.6 kg/m³, ECE was set up. The current density of 1A/m² with respect to uncoated concrete surface was employed for 10 weeks while saturated calcium hydroxide was used as electrolyte. Titanium weave mesh with the opening of approximately 6.9 mm was cut into a small segment with the size of 250 mm x 250 mm to utilize as auxiliary anode.

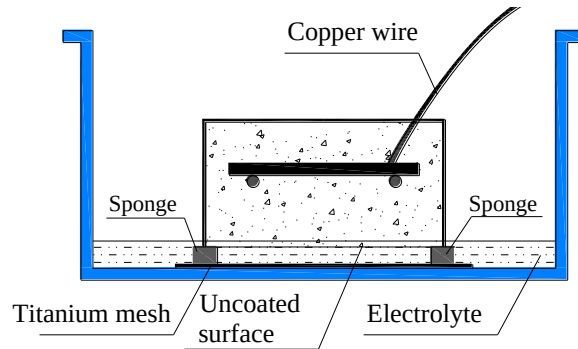


Figure 2.7 Cross section of ECE set-up.

Table 2.8 Timetable of extraction process for three modes of ECE application.

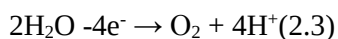
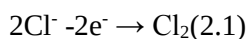
Time	Mode 1	Mode 2	Mode 3
First week	The current was applied continuously throughout 10 weeks	The current was turned on 5 days then followed by 2 days off	The current was turned on 5 days then followed by 2 days off
Second week			
Third week		For the rest 8 weeks: the current was turned for 4 days and then turned off 3 days within each week	The current was turned on 4 days then followed by 3 days off
Fourth week			
Fifth week			
Sixth week			
Seventh week			
Eighth week			
Ninth week			
Tenth week			

Table 2.9 Cumulative applied charge number (A.hour/m²) at a certain period of different applications.

Time of application (weeks)	2	4	6	8	10
Mode 1	336	672	1008	1344	1680
Mode 2	204	432	624	816	1008
Mode 3	204	432	624	768	960

To set up the extraction process, each specimen was treated individually in different PVC containers as shown in Figure 2.7. Titanium mesh was adhered firmly at the bottom of the PVC container by using two pieces of hard sponge with the size of 2.0 x 2.0 x 30 cm. These sponges were placed 20 cm away another in order to support the concrete block. The concrete block was

put into the container where the uncoated surface faces to titanium mesh. The saturated calcium hydroxide solution was poured into the PVC container until the level of solution fully immersed the sponges and 5mm higher than the level bottom surface. In order to prevent the acidification due to anodic processes as shown in Equations 2.1 to 2.3, approximately 20 g of calcium hydroxide was sprinkled into that container to assure the basic condition of electrolyte. During the extraction process, the depth level of electrolyte was always checked and add solution if necessary to prevent the disruption of electrical current while about 15 g of calcium hydroxide was added in after each two-week period of extraction.



Three modes of application were carried out which consisted of one continuous mode, referred as Mode 1, and two intermittent modes, referred as Mode 2 and Mode 3. For each mode, ten blocks were used. The timetable of current applications in each mode is given in Table 2.8. After each two week interval, the application was stopped on two specimens of each mode. Table 2.9 presents the cumulate charge numbers (A.hour/m²) which were applied to the blocks before they were cut off the electrical current.

2.2.2.3. Measurements

After stopping the electric current, the surface of reinforced concrete blocks was rinsed with tap water in order to remove the accumulation of calcium hydroxide which had added into electrolyte during extraction. Then, they were submerged in tap water for 2 months before drying the uncoated surface in atmospheric condition for approximately 1 week. The powder of concrete at different depths from 0-1 cm, 1-2 cm, 2-3 cm, 3-4 cm, and 4-5 cm were collected by drilling the concrete blocks. These powder samples were then ground by using laboratory ball mill pulverizer with the speed of 450 min⁻¹ within 6 minutes in which acetone was used as a lubricant. After that, these samples were dried in a desiccator approximately a week with aspirator at 6 kPa before preserving in a vacuum chamber at 80 kPa.

As mentioned, the first fundamental aim of this study is to investigate and compare the efficiencies of chloride extraction in continuous and intermittent applications. Therefore, after approximately 1 month preserving in a vacuum chamber, the acid-soluble and water-soluble chloride contents were determined on these powder samples. These experiments were carried out in accordance with ASTM C1152/C1152M and ASTM C1218/C1218M, respectively.

DTA-TG was taken on concrete powder with the temperature covering from 20-900 °C

at the constant rate of 10 °C/min under nitrogen atmosphere to investigate the variation of Portlandite content in concrete.

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CHAPTER III EFFECTS OF ELECTROCHEMICAL CHLORIDE EXTRACTION ON HYDRATION PRODUCTS OF VARIOUS TYPES OF CEMENT PASTE SYSTEMS

As mentioned in previous chapters, one main aim of this research is to investigate the effects of electrochemical chloride extraction on hydration products of various types of cement paste. In this chapter, the results of experimental test are presented and discussed.

3.1. Chloride removal and XRD results

The acid-soluble chloride content profiles or total chloride content in cement paste versus the time of extraction are shown in Figure 3.1. As expected, when the synthesized pore solution with chloride ions, solution 1 as addresses in chapter 2, was still used as catholyte during the first four weeks, which simulates the condition that chloride ions in pore solution around the cathode migrate towards the anode under the impact of the electrical field, the chloride content in the pastes generally increased. However, after the catholyte was changed to solution 2, the chloride content in the pastes significantly reduced, especially in ordinary Portland cement and fly ash cement pastes. Based on the acid-soluble chloride content profiles, as shown in Figure 3.1, approximately 53% and 48% of the initial acid-soluble chloride were released from the OPC and FC pastes after the current applied for 8 weeks. The reduction of acid-soluble chloride in the BFS paste was lower, only approximately 30%.

Figure 3.2a shows the variation in the water-soluble chloride contents during the extraction process. These results are corresponding to the acid-soluble chloride content profile as shown in Figure 3.1. When solution 2 was used as catholyte in the first four weeks, water-soluble chloride content increased. It followed by the significant reduction after the catholyte was replaced by solution 2. At the end of the extraction process, 67% and 52% of the initial water-soluble chloride in initial specimens were removed from the OPC and the FC pastes, while it was only approximate 35% from the SC paste. For the OPC and SC pastes, the reduction of bound chloride contents during the extraction was insignificant, it was about 10-20% of the initial bound chloride content at the end of the current application; on the contrary, in the case of the FC paste the reduction of bound chloride was much higher than that in OPC and SC pastes, it reached to 35-45% of the initial bound chloride content, as shown in Figure 3.2b.

However, the area of the specific peak of Friedel's salt at the angle (2θ) of 11.3° from the X-ray diffraction results employed in the initial paste powders (OPC paste - 00, FC paste - 00 and SC paste - 00) and the specimens had been applied the current for 8 weeks (OPC paste - 08, FC paste - 08 and SC paste - 08) generally present greater reduction in OPC and SC pastes than

that in FC paste as shown in Figure 3.3. There is no significant difference on the area at that specific peak in the FC paste after extraction in comparison with the other types of binder. It seems that the reduction of bound chloride in the FC paste during extraction process primarily contribute from the chloride that adsorbed on the surface of C-S-H.

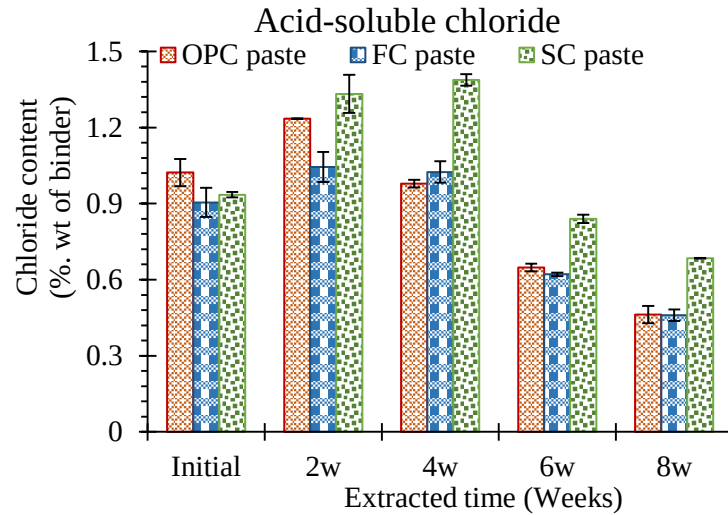
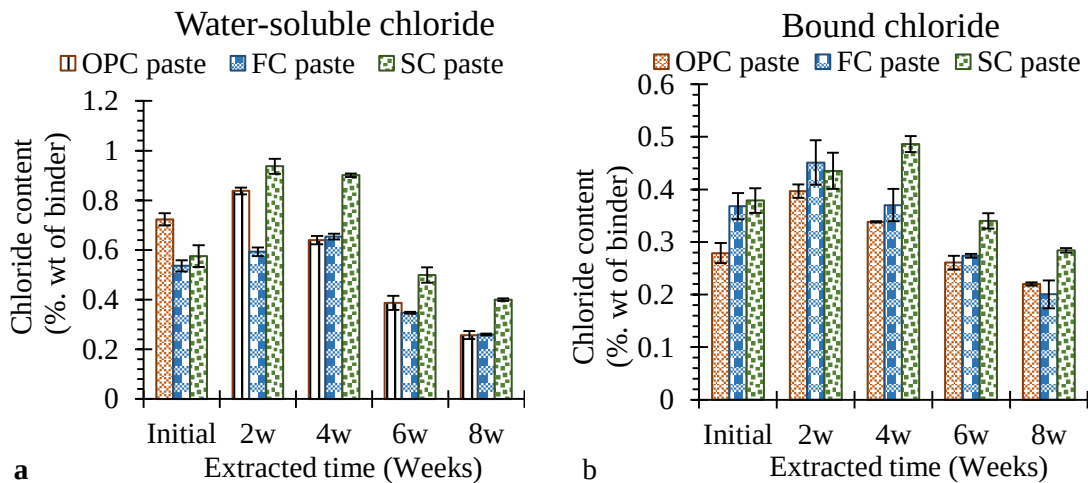


Figure 3.1 Acid-soluble chloride content in cement pastes versus time of extraction.



a) Water-soluble chloride content in cement pastes versus time of extraction.

b) Bound chloride content in cement pastes versus time of extraction

Figure 3.2 Remaining chloride content.

It is interesting here that, in this study, the aluminum oxide contents in SC and FC are almost the same; that is 9.67% and 9.9%, which are considerably higher than that in OPC. However, the efficiency of extraction process on releasing chloride in the OPC paste and in the FC paste was almost the same; and their efficiency was much greater than that in the SC paste. Moreover, with

nearly the same content of aluminum oxide, the removal of bound chloride in the FC cement paste was remarkably higher than that in the SC paste. This occurrence may relate to the difference on hydration mechanisms of slag cement and fly ash cement where fly ash with rather low content of calcium oxide performs as a pozzolanic admixture, while ground granulated blast furnace slag acts as a cementitious material. Therefore, theoretically they affect the surrounding environment such as pH, ion concentration in pore solution that could, in turn, influence to the durability and solubility of Friedel's salt. Moreover, Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is always found in fly ash, component of which contains a certain amount of aluminum oxide that is inert in the hydration of cement.

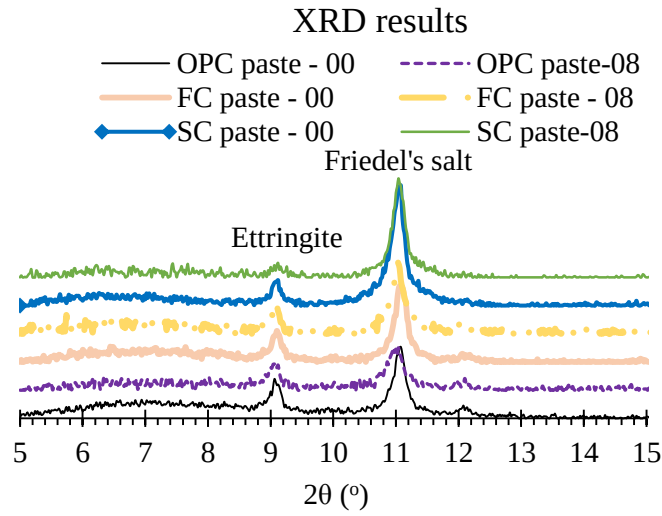
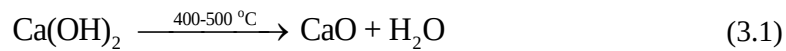


Figure 3.3 X-ray diffraction results on cement pastes before and after 8-week extraction.

3.2. Variation of Portlandite content

Based on the weight loss in TGA plot at the endothermic peak at temperature of 450 oC in the DTA result, the relative dehydrated water content can be computed. From that dehydrated water content and the relationship between dehydrated water and calcium hydroxide as shown in Equation (3.1), the Portlandite content in the paste can be calculated easily by Equation (3.2)



$$m_{\text{Ca(OH)}_2} = m_{\text{mass loss}} * \frac{M_{\text{Ca(OH)}_2}}{M_{\text{H}_2\text{O}}} \quad (3.2)$$

The variation of Portlandite content versus the application time of the electrical current is shown in Figure 3.4.

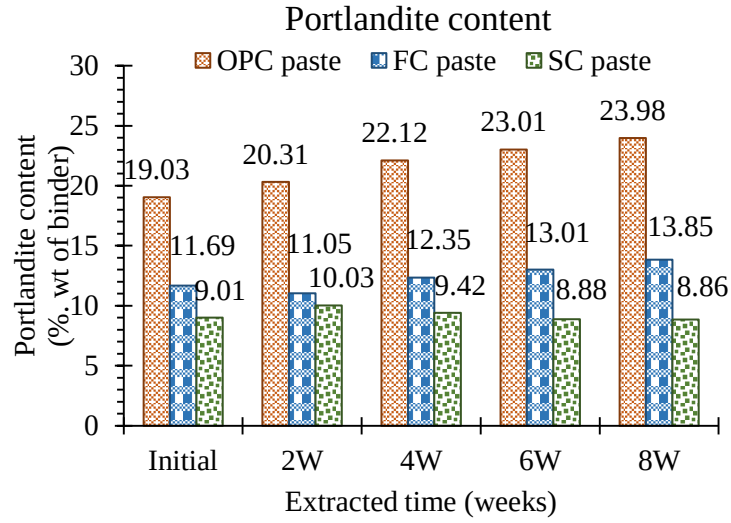
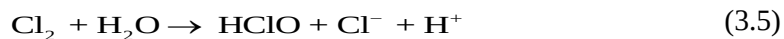


Figure 3.4 Portlandite content in paste specimens versus time of extraction.

For OPC paste, during the application of current, the Portlandite content gradually increased. A similar trend was observed in the FC pastes, except the first week of application. Nevertheless, in the SC paste the Portlandite content increased in the first week of extraction process, followed by the slight reduction although the electrolytes using in two compartments of migration cell were always oversaturated with $\text{Ca}(\text{OH})_2$.

The difference in tendencies of Portlandite variation on the OPC and the FC pastes with the SC paste may concern to the alteration of their hydrated products during the application of current and the vulnerability of their hydrated products under the change of surrounding environment.

Besides, the negligible reduction of Portlandite content after extraction in the case of SC paste where the surrounding environment was always oversaturated with $\text{Ca}(\text{OH})_2$ indicates that the contribution of Ca^{2+} to transferring the charge during the application of direct current is insignificant. The use of saturated calcium hydroxide solution as electrolyte on existing reinforced concrete structures is rather to neutralize hydrogen ions (H^+) generating from anode due to anodic reactions as shown in Equations (3.3) to (3.6) compared to transfer the electrical current; moreover, the erosion of concrete surface and the emission of chlorine gas in acidic solution can be avoided.



3.3. Alteration of morphology in cement pastes

Obviously, the application of a direct current strongly affects the microstructure of cement phases, including C-S-H phases that are the main phases responsible for the binding capacity of cement-based materials. They, in turn, impact to the diffusivity and stability of structure against the surrounding environment and finally, to the lifetime of reinforced concrete structures. Therefore, in this study scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) were employed to investigate the alteration of morphology of cement pastes due to the application of electrical direct current, especially on C-S-H phases.

In addition, it should be noted that recently many research have pointed out that the morphology of C-S-H gels strongly depends on the humidity, drying conditions and drying rate of sample [1]. Therefore, the preparation process in this study was done similar for all the specimens as mentioned above to eliminate the inconsistency. Moreover, the gel was analyzed and distinguished mainly based on its chemical components from EDS results rather than its own morphology only from SEM.

Firstly, morphology of the initial sample before extraction and the sample that had been extracted for 8 weeks and preserved in vacuum chamber 6 weeks of three types of cement pastes were analyzed and compared.

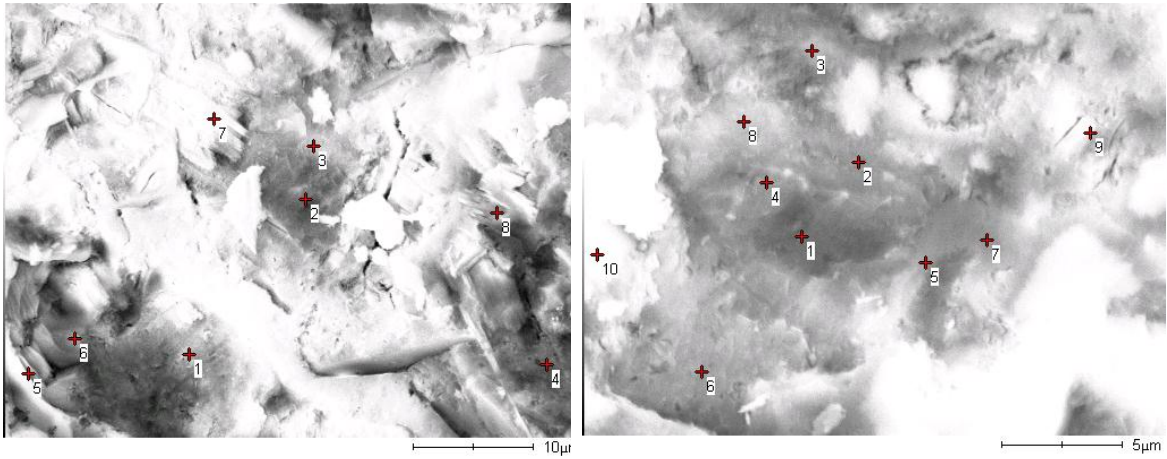
3.3.1. Alteration of morphology in OPC paste

For the OPC paste, bulk phase of Portlandite was easily captured in both cases, before and after the application of electrical current, as shown in Figures 3.5a (points +5, +6, +7 and +8), 3.5b (points +9 and +10), 3.6a (point +1) and 3.6b (points +1 and +2).

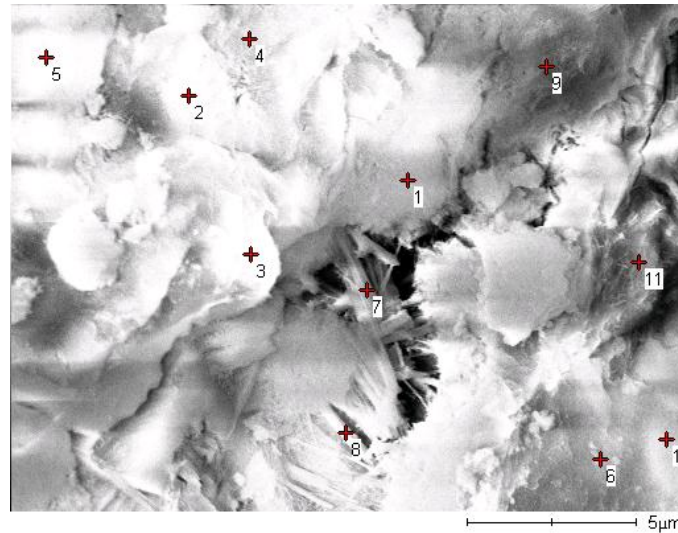
Moreover, ettringite was also observed in the pores of these matrices although it seems that ettringite needle before extraction was generally greater in its diameter than that of the 8-week extracted sample, as shown in Figures 3.5c (points +7, +8 and surrounding) and 3.6c (point +14 and around), respectively.

Certainly, the existence of gel phases was observed in both cases, before and after extraction. Although there were no significant differences on the morphology of gel phases before and after extraction, the CaO/SiO_2 (C/S) ratio in the gel given from the EDS results was very distinctive.

Before extraction, the C/S ratio of C-S-H phases in the OPC paste varied quite consistently, mostly from 1.75 to 2.2; their mean value was about 1.9, as shown in Figure 3.5. There were very few occasions that the C/S ratio was out of this range



a) Bulk phase of Portlandite (+5, +6, +7 and +8) and C-S-H gel phase (+1: C/S=2.28, +2: C/S=1.84, +3: C/S=1.75 and +4: C/S=1.76).
b) Typical C-S-H gel phase (+1: C/S=2.26, +2: C/S=1.72, +3: C/S=1.77, +4: C/S=1.93, +5: C/S=1.93, +6: C/S=1.97, +7: C/S=2.04 and +8: C/S=1.85).

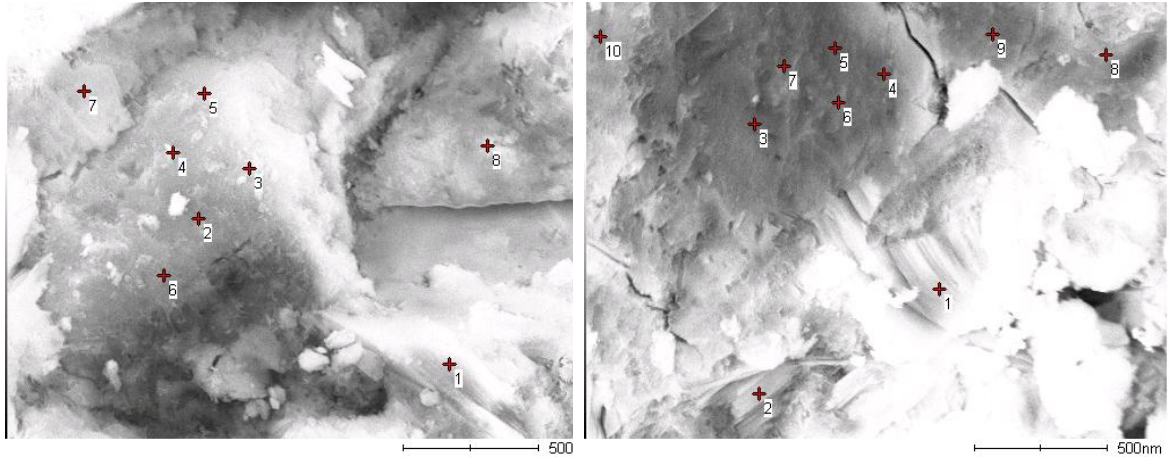


c) Ettringite (+7, +8 and +11) and C-S-H gel phase (+1: C/S=1.41, +2: C/S=1.50, +3: C/S=1.92 and +4: C/S=2.14, +5: C/S=2.08, +6: C/S=2.12, +9: C/S=1.70, +10: C/S=2.5).

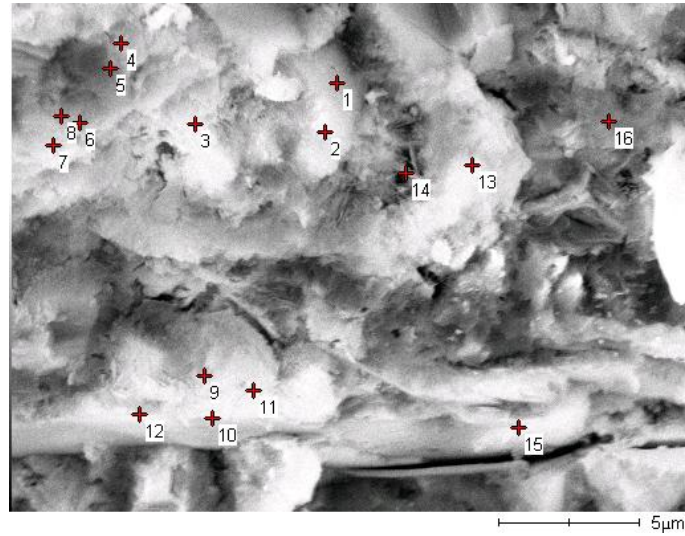
Figure 3.5 Morphology OPC paste before extraction.

Meanwhile, after eight weeks of extraction the C/S ratio of gel phases is distinctly divergent. On some few occasions, the C/S ratio in the gel phases from 1.3 to 1.7 was observed, as indicated in Figure 3.6a; it is lower than that before extraction. On the other occasions, it was very easy to capture the gel that its morphology from SEM is closely analogue to C-S-H but C/S ratio unusually high; the C/S ratio in these gels varied quite widely, from 4 to 20 as shown in Figures 3.6b and 3.6c; however, most of the cases C/S ratios were about 7-13. The C/S ratios of C-S-H phases, the phases resembled to C-S-H before and after 8-week extraction are summarized in

Table 3.1. Moreover, the number of EDS analysis for each type of amorphous phases was also mentioned in Table 3.1.



a) Bulk phase of Portlandite (+1) and typical gel phases with low C/S ratio (+2: C/S=1.97, +3: C/S=1.73, +4: C/S=1.51, +5: C/S=1.57, +6: C/S=12.44, +7: C/S=1.48, +8: C/S=1.72 and +9: C/S=1.76).
b) Portlandite (+1 and +2) and gel phases with unusually high C/S ratio (+3: C/S=9.31, +4: C/S=11.32, +5: C/S=5.73, +6: C/S=9.92 and +10: C/S=5.89).



c) Ettringite (+14 and surrounding) and gel phase with high C/S ratio (+1: C/S=12.53, +2: C/S=16.10, +3: C/S=9.20, +4: C/S=4.00, +5: C/S=6.39, +6: C/S=14.50, +7: C/S=13.76, +8: C/S=9.86, +9: C/S=12.30, +10: C/S=20.22, +11: C/S=13.53, +12: C/S=7.32, +13: C/S=3.80, +15: C/S=10.72 and +16: C/S=9.15).

Figure 3.6 Morphology of OPC paste after 8-week extraction and 6-week preserving in vacuum chamber.

It is remarkable here that no occurrence of silicon species or gel with high SiO_2/CaO (S/C) ratio in the OPC paste after extraction that corresponded proportionally to the high C/S ratio gels was detected. The existence of high C/S ratio gels that resembled to C-S-H gels is in agreement with the result of the study of Marcotte *et al* [2] in concrete using ordinary Portland cement at the zone surrounding steel rebar after extraction.

Table 3.1 C/S and S/C ratios in C-S-H and resembled C-S-H phases before and after extraction.

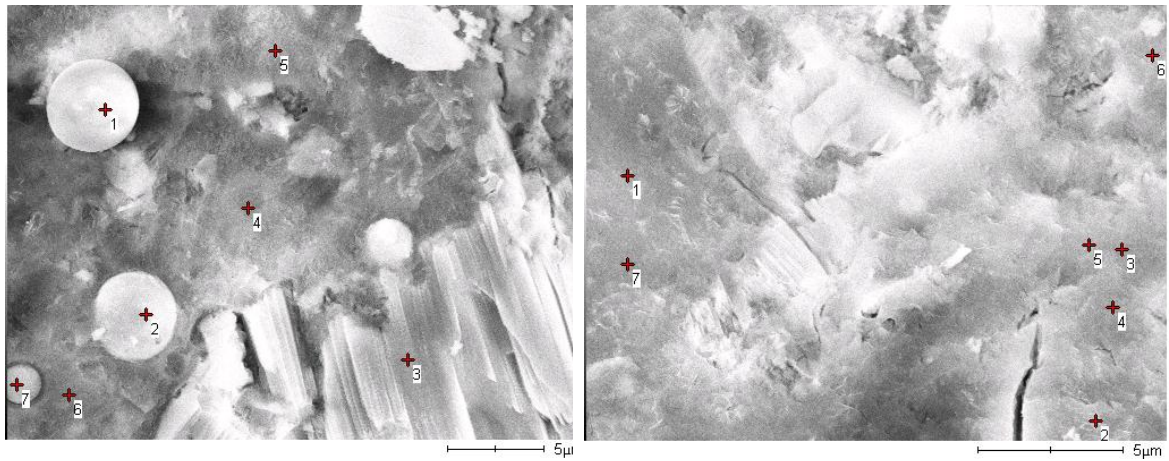
Type of cement paste	Before extraction	6 weeks after stopping the extraction						
		C/S of C-S-H phase	C/S of phase	C-S-H	Resembled with unusually high C/S	C-S-H	Gel phase with remarkably high S/C	with high
		C/S	Number of analysis	C/S	Number of analysis	S/C	Number of analysis	
OPC paste	1.75-2.2	1.3-1.7	39	4-20	201	-	-	
FC paste	1.5-1.9	1.0-1.6	124	3-13	82	2.7-3.5	19	
SC paste	1.0-1.5	1.0-1.5	156	20-40	11	-	-	

3.3.2. Alteration of morphology in FC pastes

For the FC paste, in both cases before and after the application of direct current, the remained particles of fly ash were obviously obtained, as shown in Figures 3.7a (points +1, +2 and +7), 3.8a (points +1, +2 and +3) and 3.8e (round particles). Furthermore, the bulk phase of Portlandite can also be observed as presented in Figures 3.7a (point +3) and 3.8c (points +1, +2 and +3).

The smaller needle of Ettringite after extraction than that before extraction was also captured as shown in Figures 3.7c and 3.8b (in the hollow near point +3), respectively.

The similar trend in the alteration of C-S-H gel phases as OPC paste was also observed in the FC paste. Before extraction, the C/S ratio in the FC paste was in the range of 1.5 to 1.9, as presented in Figures 3.7a and 3.7b. This ratio reduced on some occasions after 8-week extraction where the amorphous phases with the C/S ratio of about 1.0 to 1.6 was easily observed, as indicated in Figures 3.8a, 3.8b and 3.8e; however, on the other occasions gel phases with unusually high C/S ratio was also captured, as shown in Figures 3.8b (points +7 and +13), 3.8c and 3.8d; its ratio varied widely but mostly in the range of 3 to 13, slightly lower than that corresponding phases in the OPC paste.



a) Bulk phase of Portlandite (+3), remained fly ash particles (+1, +2, +7) and C-S-H gel phases (+4: C/S=1.08, +5 C/S=1.34, +6: C/S=1.54).
b) Typical C-S-H gel phases (+1: C/S=1.66, +2: C/S=1.30, +3: C/S=1.57, +4: C/S=2.05, +5: C/S=1.76, +6: C/S=1.60 and +7: C/S=1.57).



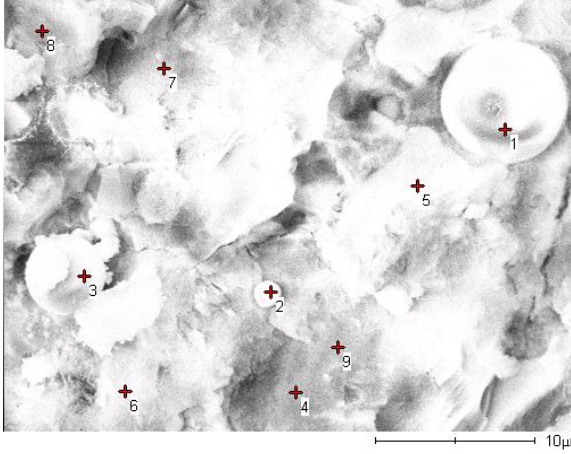
c) Ettringite (needles such as +3, +4 and +5) and Friedel's salt (hexagonal plates +1 and +2).

Figure 3.7 Morphology of FC paste before extraction.

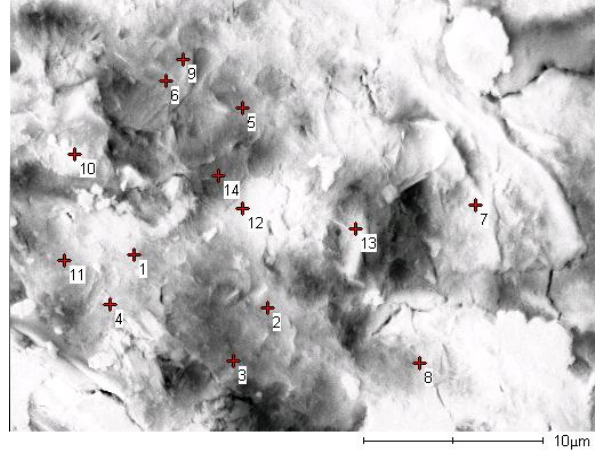
It should be emphasized that, unlikely to the OPC paste, where the probability to capture the amorphous phases with the low C/S ratio after 8-week extraction was significantly poor, in the FC paste the chance to catch the gel phases with low C/S ratio after 8-week extraction was as high as the chance to capture the resembled C-S-H gel phases with the unusually high C/S ratio.

Moreover, it is very interesting that, where no occurrence of silicon species was obtained that corresponded proportionally to the high C/S ratio gel phases in the OPC paste, some gels with remarkably high S/C ratio were captured after 8-week extraction in the FC paste, as shown in Figure 3.8e (point +1: $S/C=2.9$ and point +4: $S/C=2.71$). However, the probability to meet the gel

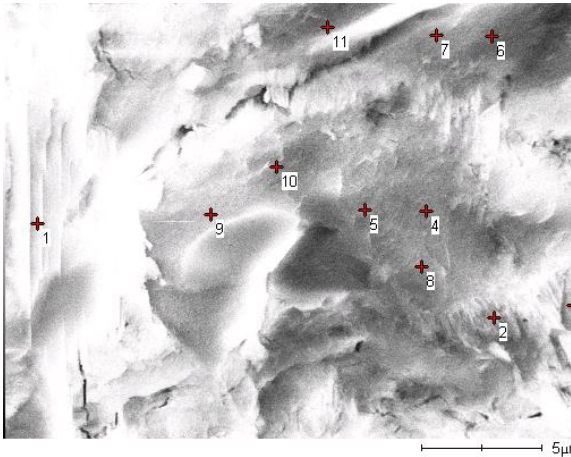
phases with remarkably high S/C ratio was rather low in comparison to the chance to meet the gel phases with high C/S ratio; simultaneously, that S/C ratio was nonlinearly proportional to the gel phases with high C/S ratio. The C/S ratios and S/C ratios in the C-S-H phases as well as the resembled C-S-H phases before and after 8-week extraction are presented in Table 3.1.



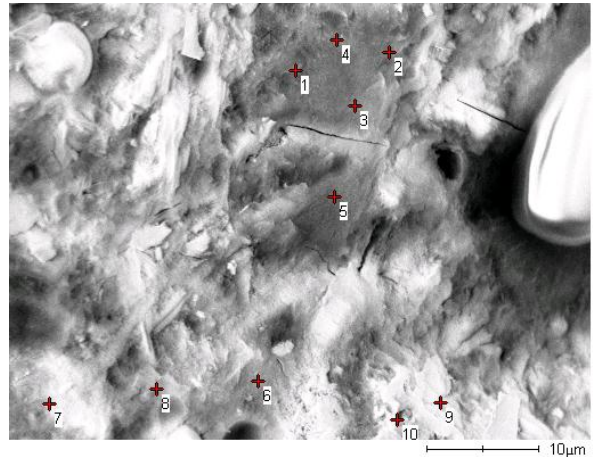
a) Remained fly ash particles (+1, +2 and +3), gel phases with low C/S ratio (+4: C/S=1.08, +5: C/S=18.02, +6: C/S=1.17, +7: C/S=1.54, +8: C/S=5.05 and +9: C/S=1.43).



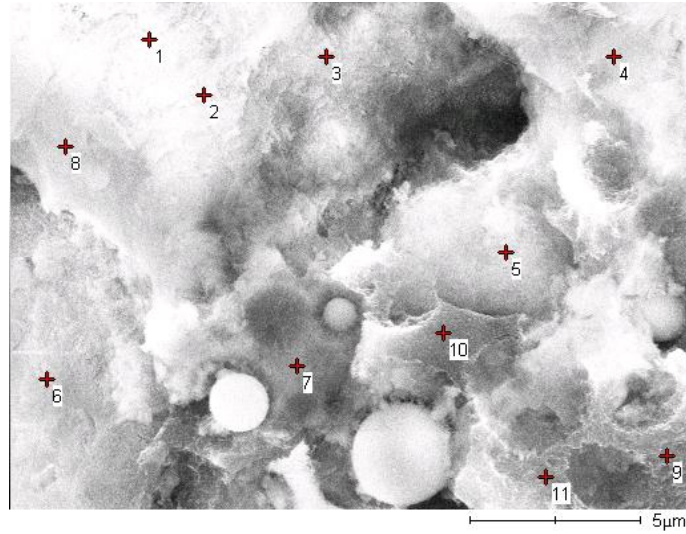
b) Typically gel phases with low C/S ratio (+1: C/S=1.43, +2: C/S=1.80, +3: C/S=1.57, +4: C/S=1.71, +5: C/S= 1.99, +6: C/S=1.55, +7: C/S=11.49, +8: C/S=1.51, +9: C/S=0.92, +10: C/S= 2.12, +11: C/S=1.00, +12: C/S=1.22, +13: C/S=4.26 and +14: C/S=2.02).



c) Portlandite (+1, +2 and +3) and gel phases with extremely high C/S ratio (+4: C/S=14.53, +5: C/S=20.93, +6: C/S=20.01, +7: C/S=7.32, +8: C/S=13.85, +9: C/S=7.61, +10: C/S=22.0, +11: C/S=12.63).



d) Typically gel phases with high C/S ratio (+1: C/S=5.49, +2: C/S=4.64, +3: C/S=7.27, +4: C/S=4.00, +5: C/S= 4.11, +6: C/S=9.53, +7: C/S=2.84, +8: C/S=2.86, +9: C/S=2.56 and +10: C/S=7.09).



e) Morphology of gel phases with high S/C ratio (+1: S/C=2.90, +2: C/S=1.20, +3: C/S=8.32, +4: S/C=2.71, +5: C/S=0.88, +6: C/S=1.52, +7: C/S=1.53, +8: C/S=2.07, +9: C/S=1.01, +10: C/S=0.83 and +11: C/S=1.00).

Figure 3.8 Morphology of FC paste after 8-week extraction and 6-week preserving in vacuum chamber.

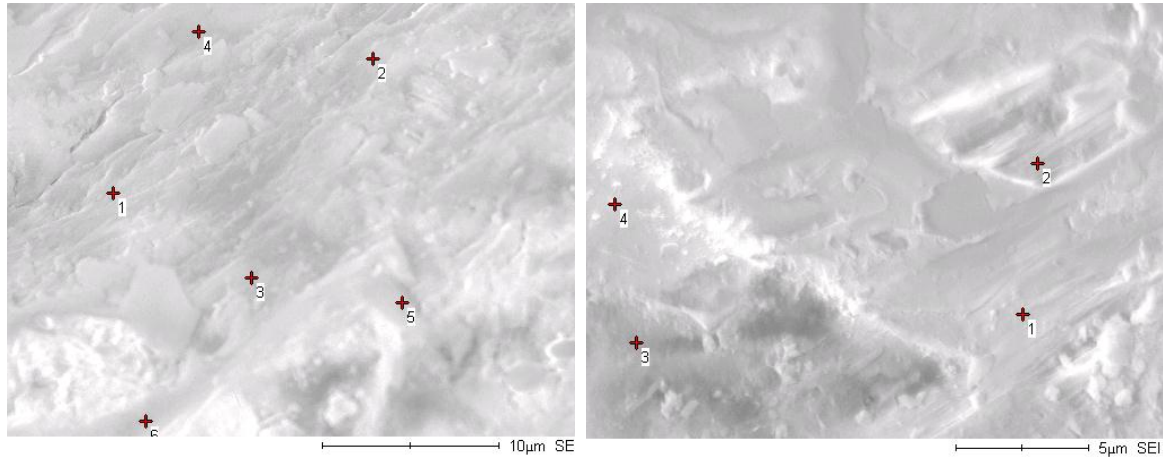
3.3.3. Alteration of morphology in SC pastes

In comparison to the OPC and the FC pastes, the C-S-H gel phases in the SC paste is rather consistent in both cases, before extraction and after the direct current was conducted for 8 weeks.

Before extraction, the C/S ratios of C-S-H gel phase mostly varied from 1.0 to 1.5, as shown in Figure 3.9a. After 8-week extraction, the morphology of C-S-H gels in the SC paste is mostly unchanged, the C/S ratio of the gel phases was also mainly in the range of 1.0 to 1.5, as shown in Figures 3.10a, 3.10b and 3.10c. However, it is likely as in the other types of cement pastes, there were few cases that the new phases with the extremely high C/S ratio was detected as shown in Figure 3.10d.

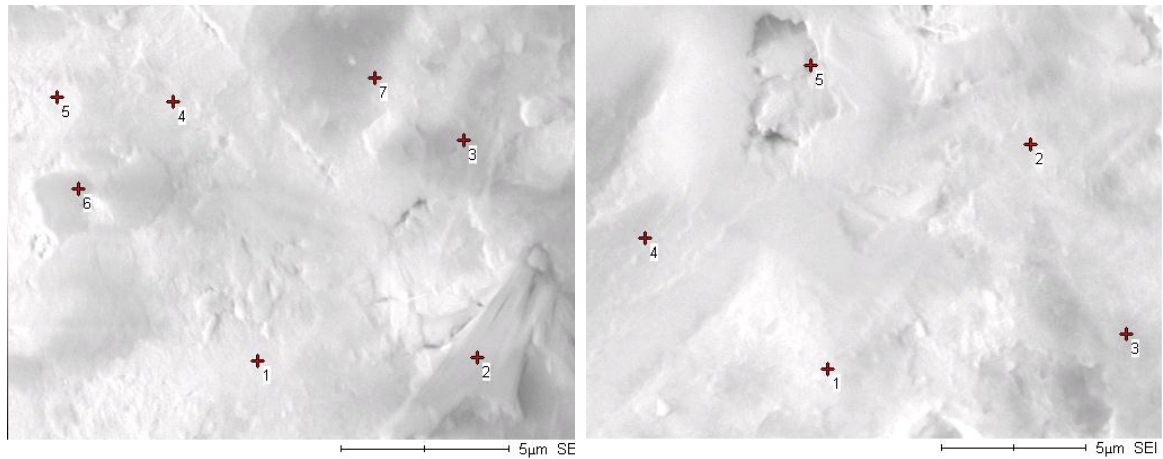
It is worth pointing out here that the probability to meet that abnormal C-S-H phases after extraction was remarkably rare in the SC paste; and, the C/S ratio in this abnormal phases was rather consistent and significantly greater than the corresponding phases in the FC paste and the OPC paste; it was mostly in the range of 20 to 40. Moreover, likely to the OPC paste, no existence of the gel phases with the high S/C ratio after 8-week extraction was attained as in the FC paste. The C/S ratios of these phases are presented in Table 3.1.

The bulk phase of Portlandite was observed easily in both cases, before and after 8-week extraction, as shown in Figures 3.9b (points +1 and +2) and 3.10a (point +2), respectively. The existence of Ettringite and Friedel's salt after 8-week extraction were still captured as shown in Figure 3.10c.

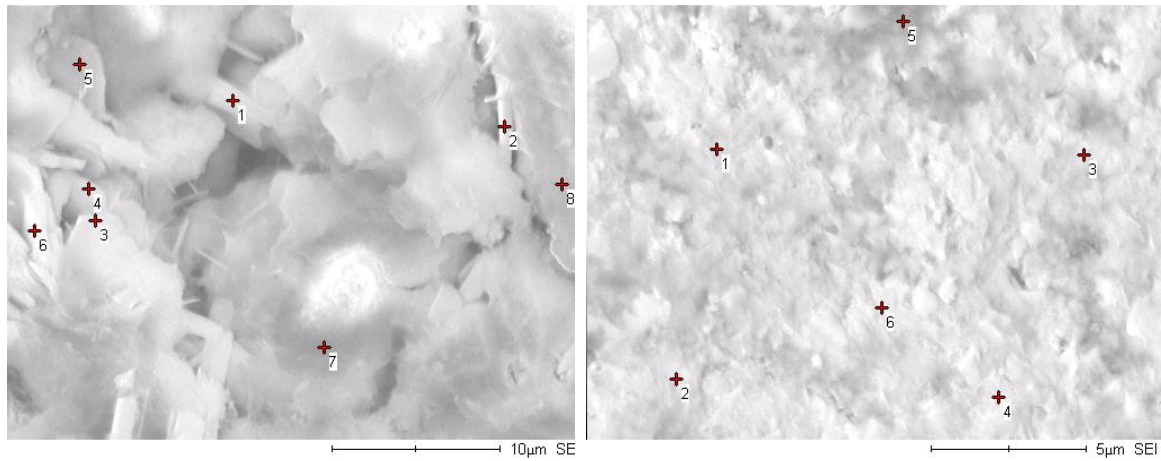


a) Morphology of typical C-S-H gel in SC paste b) Portlandite (+1 and +2) and C-S-H gel (+3: (+1: C/S=1.25, +2: C/S=1.10, +3: C/S=1.18, C/S=0.80, +4: C/S=0.83). +4: C/S=1.18, +5: C/S=1.26, and +6: C/S=1.11).

Figure 3.9 Morphology of SC cement paste before extraction.



a) Portlandite (+2) and gel phase with low C/S ratio (+1: C/S= 1.26, +3: C/S= 1.15, +4: C/S=1.12, +5: C/S=1.65, +6: C/S= 2.26 and +7: C/S=1.60). b) Typically gel phase with low C/S ratio (+1: C/S= 1.26, +2: C/S= 1.13, +3: C/S=1.09, +4: C/S=0.94 and +5: C/S= 1.16).



c) Ettringite (+1 and needles), Friedel salt (+3, +4, +5, +6), gel phase with low C/S ratio (+7: C/S=1.1, +8: C/S=1.09).
 d) New gel phase (+1: C/S=21.97, +2: C/S=9.96, +3: C/S=46.49, +4: C/S=30.54, +5: C/S=8.11, +6: C/S=20.9).

Figure 3.10 Morphology of SC cement paste after 8-week extraction and 6-week preserving in vacuum chamber.

After extraction, the resembled C-S-H gel phases with the extremely high C/S ratio and the absence of silicon element in the matrix in the three types of cement pastes occur which imply that not only the alteration but also the decomposition of C-S-H gels happened during the application of electrical current.

Moreover, the random presence of the gel which happened to have abundant silicon contain in the case of the FC paste and the lack of silicon species in the OPC paste or the SC paste make also sense to postulate that the decomposition of C-S-H gel during extraction process can fragment silicate chain into small species; and, these small silicon species might migrate towards the positive chamber due to the effect of electrical field, particularly in the case of OPC paste.

It cannot be ignored that the rate of these alteration and decomposition strongly depends on the type of cement paste. The C-S-H phases in the OPC paste with relative higher C/S ratio had shown a more severe decomposition during the application of current than that in the others; while C-S-H in the SC paste usually with lower C/S ratio was nearly unchanged. Then, it is reasonable to conclude that the C-S-H phases in the FC paste and the SC paste is more stable than that in the OPC paste after 8-week extraction with applied current density 4.5 A/m^2 .

Many previous studies have indicated that the morphology of C-S-H phases in outer product regions of cement paste that is mainly impacted by exposure environment, is affected significantly since they involves substitution materials such as fly ash, ground granulated blast furnace slag, silicafume or metakaolin [3-5]. In OPC paste, the microstructure of C-S-H phases

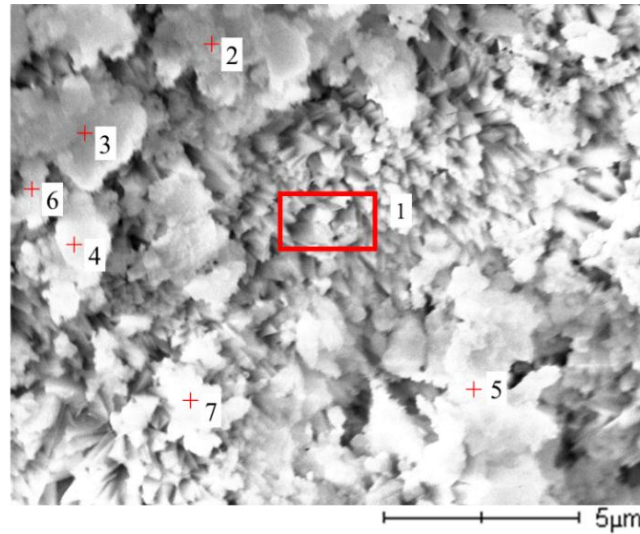
in outer product regions is strongly linear directional, it appears as fibril in transition electron microscopy (TEM) [6-10]. However, in cement paste involving reactive substitution materials, the linear dimensional characteristic or fibrillar nature of C-S-H in outer product regions is gradually replaced by crumpled-like or foil-like characteristic since the fraction of substitution increases [6, 8, 11-13]. The crumpled-like or foil-like morphology appears with pore spaces between fibrils are filled. Therefore, the gel pores in C-S-H in outer product regions in cement paste involving substitution materials are finer and much less interconnected, which leads to the less intrusion of exposure phase into C-S-H phases as well as the diminution of diffusion rate or migration rate of C-S-H phases. Subsequently, it results in the much less interaction between C-S-H phases and exposure phase during diffusion process or migration process than that in the paste without substitutions. Therefore, the impacts of electrical current to C-S-H phases in SC paste and FC paste is probably less than its effect to C-S-H in OPC paste. Moreover, the mean chain length of the C-S-H in FC paste and SC paste is much longer than that in OPC paste. In OPC paste, the C-S-H phases is dominant with dimetric silicate chain [5, 14]; although the mean chain length increases with the hydration time, that increase is very slowly and it only reaches to approximately 5 after 20 year-old hydration [13-14]. On the contrary, the C-S-H phases in SC paste and the FC paste is dominate with pentametric and longer silicate units; and the replacement ratio of Al^{3+} with Si^{4+} on C-S-H phases in the SC paste and the FC paste is much higher than that in the OPC paste. Therefore, under the impact of the same electrical current C-S-H phases in the SC paste and the FC paste may not be fragmented or depolymerized easily into SiO_4^{4-} ions which can migrate toward anodic chamber as that in the case of OPC paste.

3.3.4. Alteration of morphology in the extracted paste samples after preserving 3 months and 9 months in vacuum chamber

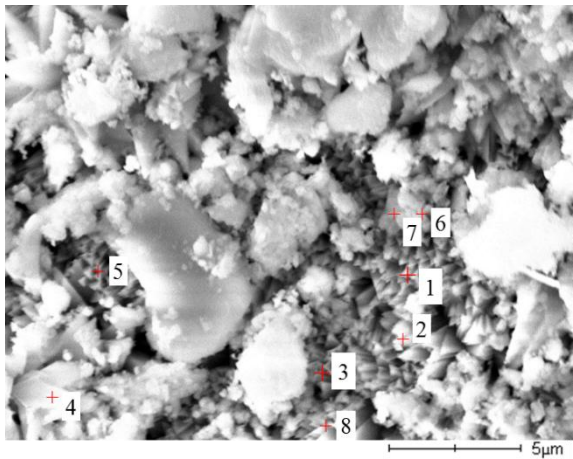
Intentionally, the 8-week extracted samples were received SEM and EDS again after preserving 3 months in the vacuum chamber. The similar attainments as discussed earlier were obtained.

Besides, it is very interesting that there was the blossom of the new phase in the OPC paste, FC paste, and SC paste as shown in Figures 3.11a (zone 1), 3.11b (points +1 to +8), 3.11c (points +8 to +10), 3.12a, 2.16b (surrounding points +2, +3 and +6), and 3.13 (surrounding points +1 to +4 and +7). The EDS was carried out carefully in each fore-mentioned points and zones. The EDS results at each point and zone in Figures 3.11a, 3.11b, 3.12b, and 3.13 are presented in Tables 3.2 to 3.5, respectively. These results were shown in term of atomic ratio indicated that the main elements in that new occurred phase are calcium and oxygen, there is insignificant contamination of the other elements such as sodium, potassium, silicon, iron, aluminum, and

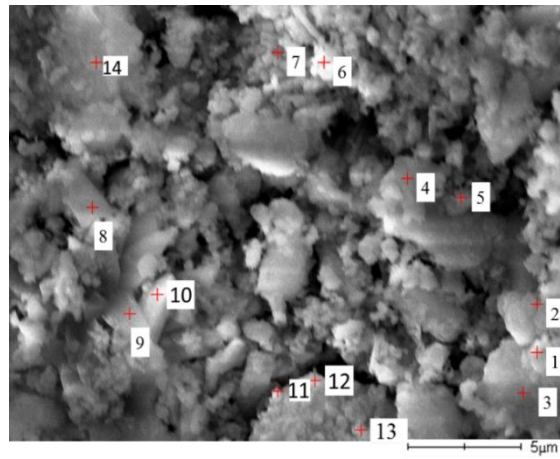
magnesium. Moreover, carbon was not detected in these phases. Therefore, it is reasonable to believe that the new blossomed phase could be Portlandite.



a) New blossomed phase (zone 1) and gel phase (+2: C/S= 5.13, +3: C/S=8.50, +4: C/S=6.02, +5: C/S=1.93; +6: C/S=2.01, +7: C/S=2.93).



b) Blossom of new phase (points +1, +2, +3, +4, +5, +6, +7, +8)



c) New blossomed phase (points +8, +9 and +10) and gel phase (+1: C/S=1.78, +2: C/S=1.90, +3: C/S=3.37, +4: C/S=8.21, +5: C/S=2.95, +6: C/S=2.69, +7: C/S=2.37, +11: C/S=2.52, +12: C/S=2.38, +13: C/S=2.34, +14 C/S=6.26).

Figure 3.11 Morphology OPC paste after 8-week extraction and 3-month preserving in a vacuum chamber.

Simultaneously, it cannot be neglected the occurrence of some gels, which resemble to the C-S-

H gel phases that exists surrounding the new blossomed phases, as shown in Figures 3.11a (points +2 to +7), 3.11c (points +1 to +7 and points +11 to +14), 3.12b (points +1, +4 and +5) and 3.13 (points +5 and +6).

However, the existence of these gels can be categorized in two groups. One is the big spherulite zone of gels such as points +2, +3 and +4 in Figure 3.11a or points +3, +4 and +14 in Figure 3.11c where the C/S ratios of amorphous phases are rather high, in the range of 4 to 10. The other is some small pieces of gels or at the edge of the big pieces where the C/S ratios are relatively lower and more consistent, as shown in points +5 to +7 in Figure 3.11a or points +1, +2, +5 to +7 and +11 to +13 in Figure 3.11c; the C/S ratios in these amorphous phases were mostly in the range of 1.7 to 2.9. The similar phenomenon was also observed in the FC paste and the SC paste as indicated in Figures 3.12 and 3.13.

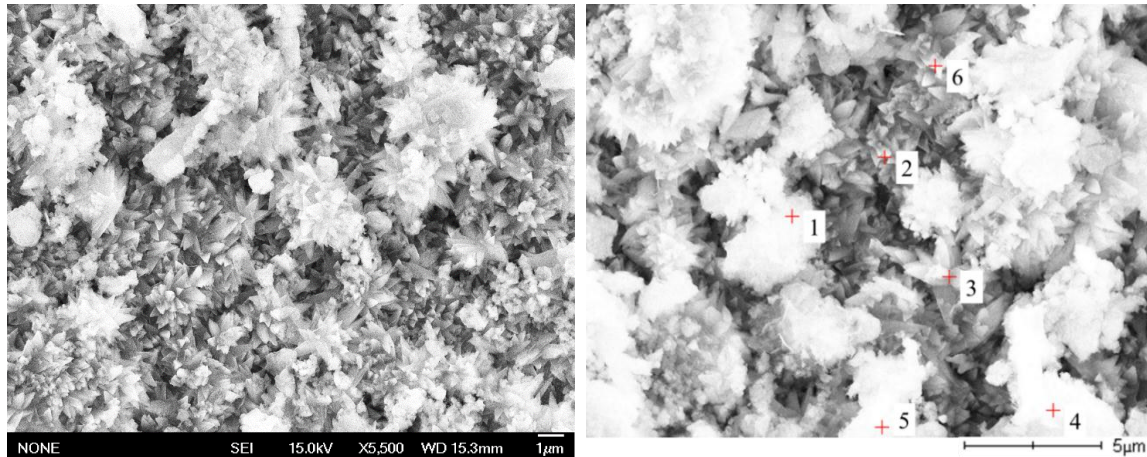
Table 3.2 EDS results in 8-week extracted sample of OPC paste after 3-month preserving as shown in Figure 3.11a (atomic %).

Point/Zone	1	2	3	Point 4	Point 5	Point 6	Point 7
CK	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OK	41.19	31.66	28.08	37.06	39.69	31.10	34.62
NaK	0.78	0.00	0.48	0.70	1.40	1.10	1.80
AlK	0.00	1.11	0.95	0.78	1.43	1.41	1.03
SiK	1.98	10.78	7.13	8.23	19.01	21.51	15.54
SK	0.00	0.00	0.00	0.39	0.20	0.43	0.12
ClK	0.00	0.62	0.00	0.43	0.08	0.31	0.04
KK	0.60	0.53	2.76	2.87	1.50	0.90	0.79
CaK	55.45	55.30	60.60	49.54	36.69	43.24	45.53
FeL	0.00	0.00	0.00	0.00	0.00	0.00	0.53

Table 3.3 EDS results in 8-week extracted sample of OPC paste after 3-month preserving as shown in Figure 3.11b (atomic %).

Point	1	2	3	4	5	6	7	8
CK	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OK	39.08	45.79	44.16	43.38	38.41	47.01	40.18	41.80
NaK	0.00	0.00	0.15	0.53	0.00	0.36	0.71	0.48
AlK	0.07	0.08	0.68	2.36	0.00	0.49	0.00	0.00
SiK	1.57	1.10	3.18	6.61	2.40	1.30	2.23	1.33
SK	0.00	0.00	0.64	0.38	0.09	0.00	0.26	0.52
ClK	0.23	0.00	0.00	0.00	0.00	0.15	0.21	0.64

KK	0.76	0.69	1.00	1.42	0.65	0.04	0.16	0.82
CaK	56.87	52.34	46.58	45.32	58.45	50.65	56.25	52.83
FeL	1.42	0.00	3.61	0.00	0.00	0.00	0.00	1.58



a) Blossom of new phase.

b) New blossomed phase (point +2, +3 and +6) and Gel phases with variety C/S ratio (+1: C/S=2.45, +4: C/S=4.24, +5: C/S=4.72).

Figure 3.12 Morphology of FC paste after 8-week extraction and 3-month preserving in vacuum chamber.

Table 3.4 EDS results in 8-week extracted sample of FC paste after 3-month preserving as shown in Figure 3.12b (atomic %).

Point	1	2	3	4	5	6
CK	0.00	0.00	0.00	0.00	0.00	0.00
OK	40.84	39.01	40.61	26.80	50.65	38.95
NaK	1.63	0.00	0.00	0.53	0.00	1.65
MgK	0.55	0.81	0.00	0.28	2.76	0.77
AlK	2.51	0.70	0.00	1.01	1.04	0.00
SiK	14.68	1.24	2.74	13.31	7.37	1.61
SK	1.04	0.84	0.00	0.46	0.00	0.04
ClK	0.16	0.38	0.43	0.00	0.00	0.00
KK	0.95	3.68	0.00	0.59	1.75	1.62
CaK	35.94	51.00	53.56	56.43	34.85	55.36
FeL	1.70	2.34	2.66	0.59	1.58	0.00

Table 3.5 EDS results in 8-week extracted sample of SC paste after 3-month preserving as shown in Figure 3.13 (atomic %).

Point	1	2	3	4	5	6	7
CK	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OK	38.29	40.27	41.62	39.68	25.29	40.57	37.96
NaK	0.93	0.49	0.27	0.56	0.54	0.77	0.00
MgK	0.00	0.00	1.04	0.00	0.64	1.32	0.23
AlK	0.00	0.01	0.27	0.19	2.76	2.72	0.62
SiK	0.57	0.38	1.30	0.48	13.12	15.43	1.30
SK	0.00	0.17	0.14	0.38	0.70	0.13	0.32
ClK	0.00	0.04	0.11	0.00	0.81	0.06	0.05
KK	0.45	0.57	0.71	0.18	0.39	1.80	0.00
CaK	59.76	58.04	54.54	57.87	55.24	36.14	58.69
FeL	0.00	0.03	0.00	0.66	0.51	1.06	0.83

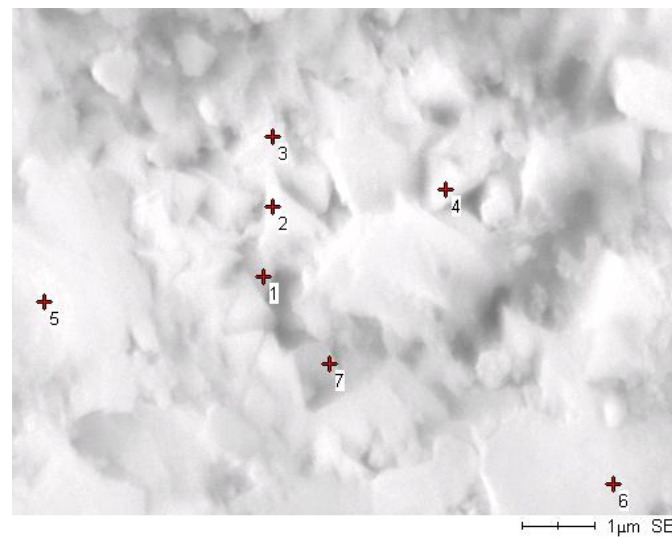


Figure 3.13 Morphology of SC cement paste after 8-week extraction and 3-month preserving in vacuum chamber with new blossomed phase (point +1, +2, +3, +4 and +7) and gel phases (+5: $C/S=4.21$, +6: $C/S=2.30$).

The occurrence of the small gel pieces with usual C/S ratios (in the range of 1.7 to 2.9) between the bigger gel pieces with remarkably high C/S ratios (in the range of 4 to 10) and the blossom of new phase imply that the extremely high C/S ratio gel phases that exists in these cement pastes after stopping the current application a short time is the unsteady phases. Therefore, the transformation of these unsteady phases to the other steadier phases is spontaneous to reach a more stable equilibrium condition of all phases in the paste matrix. Further studies on the

transformation of these phases under the effects of atmosphere or humidity conditions are necessary.

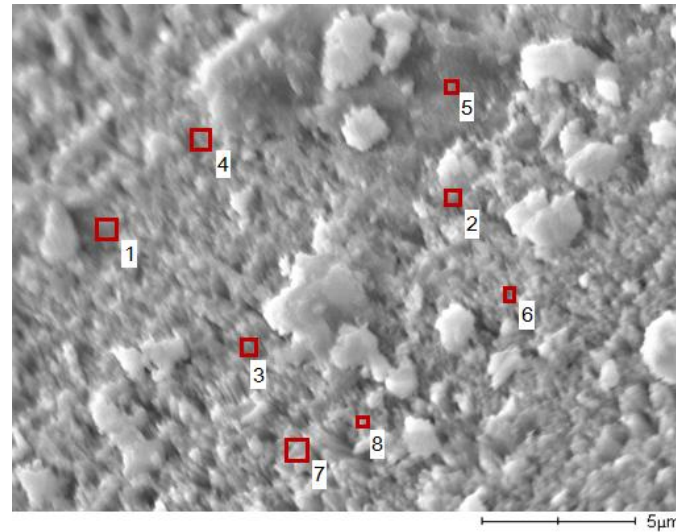


Figure 3.14 New phase in OPC paste after 8-week extraction and 9-month preserving in vacuum chamber.

Table 3.6 EDS results in 8-week extracted sample of OPC paste after 9-month preserving as shown in Figure 3.14 (atomic %).

Zone	1	2	3	4	5	6	7	8
CK	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OK	61.73	62.95	57.13	63.20	58.36	59.48	60.63	51.97
NaK	0.28	0.40	0.81	0.00	0.04	0.00	1.11	0.00
MgK	0.17	0.56	0.04	0.49	0.09	0.31	0.00	0.55
AlK	0.00	0.54	0.51	0.15	0.01	0.04	0.12	0.00
SiK	2.54	2.46	2.25	0.46	4.60	2.88	2.06	1.54
SK	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ClK	0.00	0.00	0.00	0.00	0.06	0.05	0.00	0.19
KK	0.25	0.00	0.27	0.07	0.95	0.62	0.56	1.01
CaK	33.20	33.09	31.30	33.42	32.80	36.62	35.52	37.79
FeL	1.83	0.00	7.69	2.21	3.09	0.00	0.00	6.95

After preserving 9 months in a vacuum chamber, these 8-week extracted samples were taken SEM and EDS again to examine that transformation. Similar to the results obtained after 3-month preserving in the vacuum chamber, the existence of that blossomed phase can be observed easily in extracted ordinary Portland cement paste and fly ash cement paste as presented in Figures 3.14

and 3.15 (points +1 to +9), respectively. In slag cement paste, as the consequence of rare amorphous phases with the unusually high C/S ratio measured in extracted sample after 6-week preserving the vacuum chamber, the new blossomed phase was harder to be found than that in ordinary Portland cement paste and fly ash cement paste; however, the existence of it was also observed, as shown in Figure 3.16. The EDS results in these three types of cement pastes were shown in Tables 3.6 to 3.8, respectively, which indicated there is no carbon detected in that new blossomed phase.

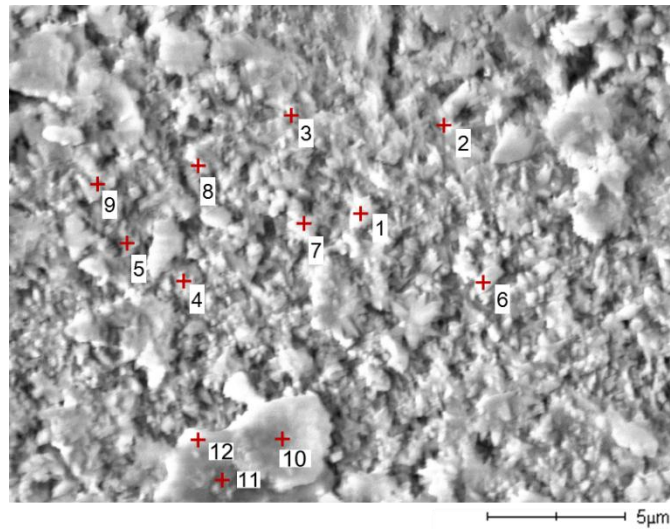


Figure 3.15 Morphology FC paste after 8-week extraction and 9-month preserving in vacuum chamber with new blossomed phase.

Table 3.7 EDS results of 8-week extracted sample of FC paste after 9-month preserving as shown in Figure 3.15 (atomic %).

Point	2	3	4	5	6	7	8	9	10	11
CK	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OK	59.98	54.86	45.71	38.41	56.93	29.00	38.36	51.19	16.91	13.37
NaK	0.26	0.00	0.68	0.01	0.71	0.46	0.78	0.86	1.24	0.00
MgK	0.06	1.00	0.00	0.15	0.00	0.27	0.08	0.45	0.00	0.44
AlK	0.05	0.71	0.07	0.67	0.57	0.16	2.22	0.76	1.39	0.23
SiK	5.75	5.47	5.42	4.81	6.35	3.68	8.83	4.89	7.05	5.65
ClK	0.01	0.00	0.62	0.00	0.00	0.01	0.01	0.00	0.00	0.00
KK	0.19	0.84	1.16	0.00	0.22	0.67	0.70	0.96	1.25	1.33
CaK	33.70	37.12	46.34	55.40	34.49	65.75	48.96	40.48	72.16	77.50
FeL	0.00	0.00	0.00	0.55	0.73	0.00	0.06	0.41	0.00	1.48

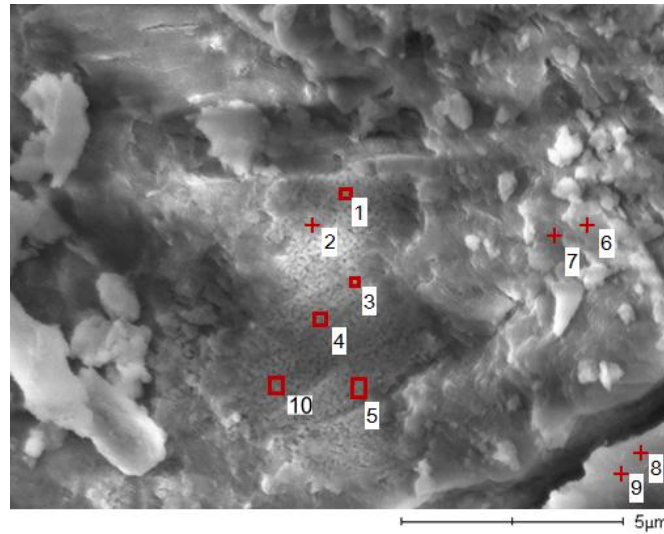


Figure 3.16 Morphology SC paste after 8-week extraction and 9-month preserving in vacuum chamber with new phase.

Table 3.8 EDS results of 8-week extracted sample of SC paste after 9-month preserving as shown in Figure 3.16 (atomic %).

Point/Zone	1	2	3	4	5	6	7	8	9	10
CK	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OK	54.66	39.84	51.83	47.66	45.82	39.34	31.70	36.05	37.17	34.69
NaK	0.31	0.23	1.05	1.42	0.00	1.51	0.21	0.62	0.48	0.00
MgK	0.00	0.45	0.13	0.44	0.33	3.55	5.94	4.91	3.27	0.45
AlK	0.95	1.63	0.88	0.64	1.48	4.82	6.68	5.93	5.26	0.79
SiK	1.55	3.85	2.65	1.88	3.05	29.31	31.07	28.05	26.96	3.72
ClK	0.15	0.03	0.00	0.00	0.04	0.00	0.00	0.00	0.01	0.32
KK	0.61	0.99	0.98	1.62	1.03	1.61	1.84	3.24	2.90	1.16
CaK	41.78	48.32	42.48	46.34	48.26	19.86	22.57	21.19	20.07	58.87
FeL	0.00	4.65	0.00	0.00	0.00	0.00	0.00	0.00	3.88	0.01

Moreover, TG-DTA in these 8-week extracted samples were conducted to determine the carbonation of samples after 9-month preserving in the vacuum chamber. Ordinary Portland cement, fly ash powder, and ground blast-furnace slag powder were also analyzed to examine the initial calcium carbonate in the source materials. These results are shown in Figures 3.17 to 3.22.

Figures 3.17 shows that, there is occurrence of calcium carbonate in ordinary Portland cement powder, which is indicated by the peak at 560 °C-700 °C in Figure 3.17. The weight loss in that position is 1.8 % by weight of cement. The calcium carbonate in fly ash powder and ground

blast-furnace slag powder is negligible as presented in Figures 3.18 and 3.19. As the consequence, the existence of calcium carbonate in the pastes is inevitable.

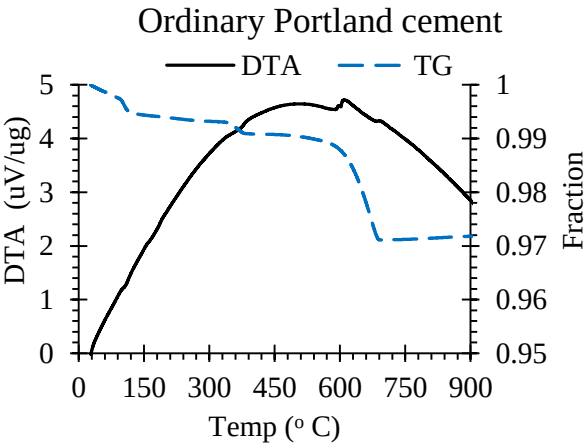


Figure 3.17 DTA-TG curves of ordinary Portland cement.

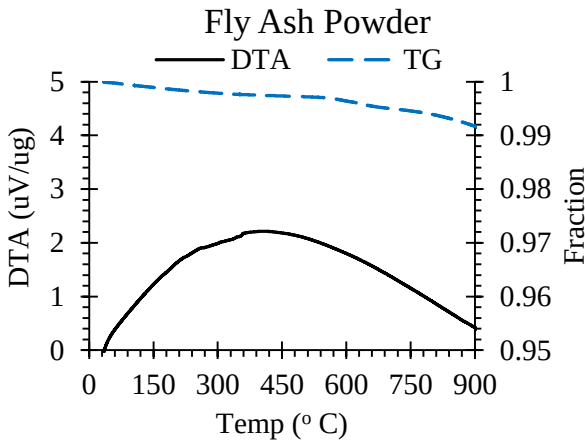


Figure 3.18 DTA-TG curves of fly ash powder.

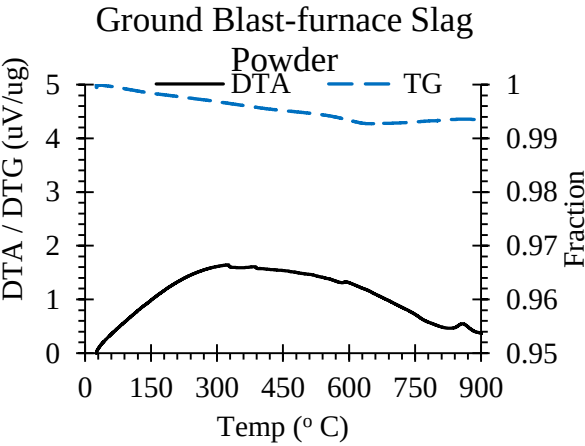


Figure 3.19 DTA-TG curves of ground blast-furnace slag powder.

The TG-DTA results of these 8-week extracted samples after preserving in vacuum chamber are present in Figures 3.20 to 3.22. They indicate that, there is no significant difference in weight loss at 560-700 °C compared to ordinary Portland cement powder. Their weight loss is approximately 1.6-2.0% by weight of paste powder. It is corresponding to 2.2-2.4% by weight of binder. And it was the highest in slag cement paste, approximately 2.4% by weight of binder. However, it should be noticed that, there is a complete dehydration of Friedel's salt at the temperature about 600-670 °C [15-16]. Then, these weight loss results are the accumulation of both calcium carbonate and the dehydration of Friedel's salt, which is still remained after extraction as shown in Figure 3.3.

Therefore, it is reasonable to conclude that, the carbonation during preserving process in vacuum chamber is negligible. And the new phase occurred as fore-discussed is not calcium carbonate.

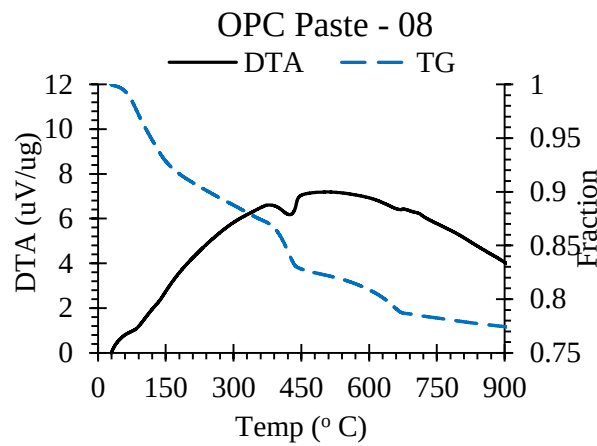


Figure 3.20 DTA-TG curves of 8-week extracted OPC paste after preserving in vacuum chamber 9 months.

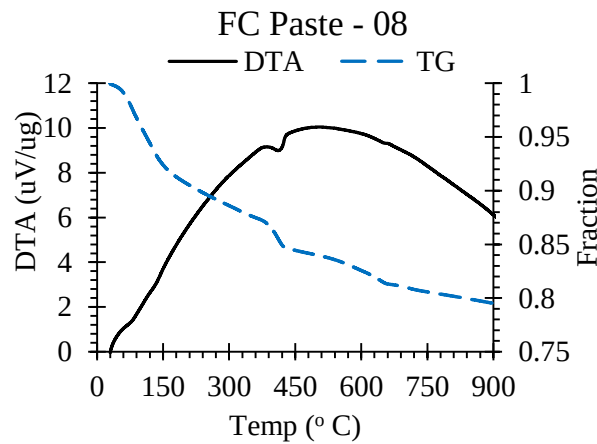


Figure 3.21 DTA-TG curves of 8-week extracted FC paste after preserving in vacuum chamber 9 months.

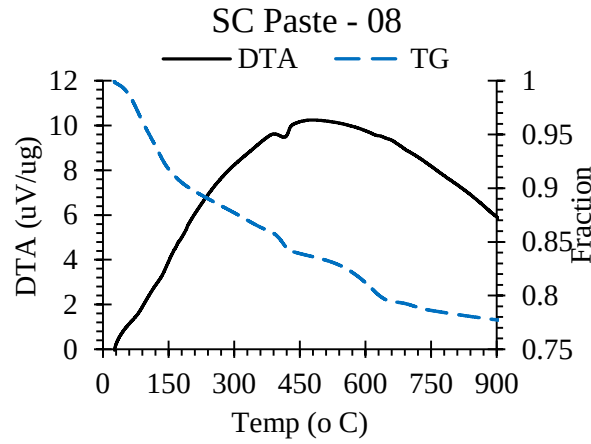


Figure 3.22 DTA-TG curves of 8-week extracted SC paste after preserving in vacuum chamber 9 months.

3.4. ^{29}Si Magic angle spinning nuclear magnetic resonance (^{29}Si MAS NMR)

It has been proven that the structure of calcium silicate hydrates in cementitious materials closely resembles to tobermorite or jennite and comprises of a disorder of dreierkette species.

Solid state nuclear magnetic resonance ^{29}Si MAS NMR has been used widely to study the hydration rate of cement, chain length of calcium silicate hydrates as well as the replacement of Al(IV) in C-S-H chain [10-14, 17-22]. In this study, the ^{29}Si MAS NMR was conducted in these three types of paste which experienced different periods of electrical current application in order to assess the variation of C-S-H chain length under the effect of ECE.

For all samples, ^{29}Si MAS NMR was measured by using Bruker MSL 400 spectrometer with spinning rate of 4kHz and a single pulse of width 5ms followed by a pulse delay 3s. For FC pastes, they were collected after 2400 scans, nevertheless, for OPC and SC pastes they were recorded after 1200 scans.

The red bold lines in Figures 3.23 to 3.31 present the experimental ^{29}Si MAS NMR spectrum of ordinary Portland cement paste, fly ash cement paste, and slag cement paste before extraction (OPC Paste - 0W, FC Paste - 0W, and SC Paste - 0W) and after 4 and 8 week extraction, respectively (OPC Paste - 4W, FC Paste - 4W, SC Paste - 4W, OPC Paste - 8W, FC Paste - 8W, and SC Paste - 8W).

It can be seen in these red bold lines that they include four main peaks representing for Q^0 , Q^1 , $\text{Q}^2(1\text{Al})$, and $\text{Q}^2(0\text{Al})$ Si sites which located at chemical shift in the range of -68 to -72 ppm, -76 to -80 ppm, -80 to -82 ppm, and -82 to -86 ppm, respectively. Besides, in the case of fly

ash cement pastes there occur two more minor peaks at -95 to -104 ppm and -106 to -112 ppm assigned for the existence of Q^3 silicon site and Q^4 silicon site of glassy phase in fly ash relics, respectively, as shown in Figures 3.26 to 3.28.

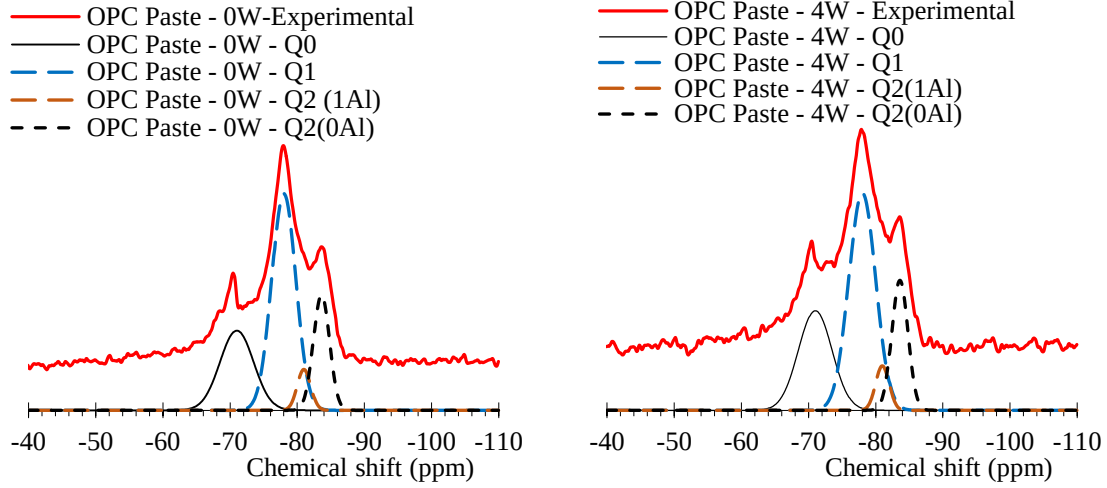


Figure 3.23 ^{29}Si MAS NMR spectra deconvolution of ordinary Portland cement paste before extraction. Figure 3.24 ^{29}Si MAS NMR spectra deconvolution of ordinary Portland cement paste after 4-week extraction.

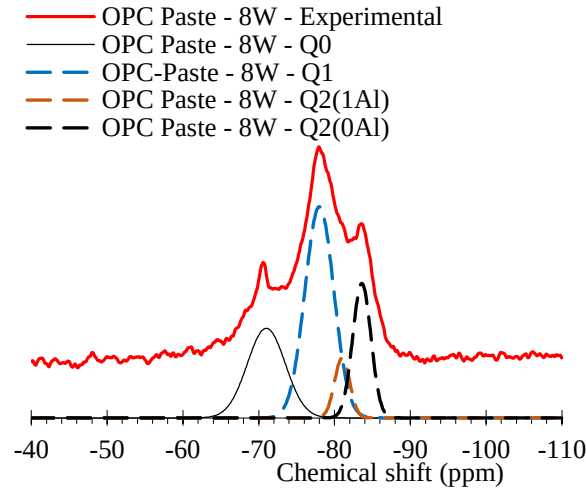


Figure 3.25 ^{29}Si MAS NMR spectra deconvolution of ordinary Portland cement paste after 8-week extraction.

The deconvolution results of these spectra which comprise of Q^0 , Q^1 , $Q^2(1\text{Al})$, and $Q^2(0\text{Al})$ spectrum are additionally presented in Figures 3.23 to 3.31. Based on the relative deconvolution proportion of Q^1 , Q^2 silicate sites, the chain length of C-S-H gel in each type of samples were calculated by Equation 3.7 [19-22] and presented in Table 3.9.

As seen in Table 3.9, it is surprising since in both three types of cement pastes the chain length of C-S-H phase increased slightly along to the application time. These results seem totally opposite to the SEM/EDS results which have mentioned previously.

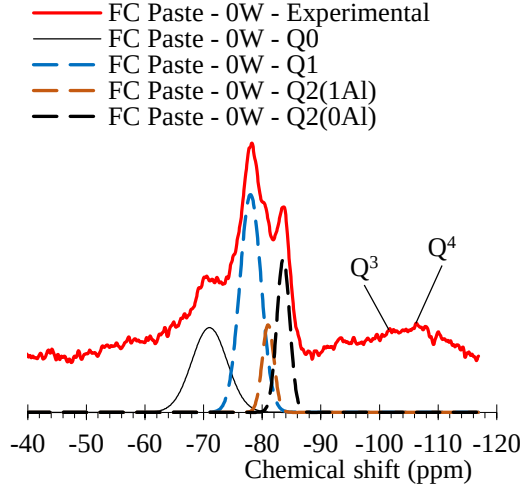


Figure 3.26 ^{29}Si MAS NMR spectra deconvolution of fly ash cement paste before extraction.

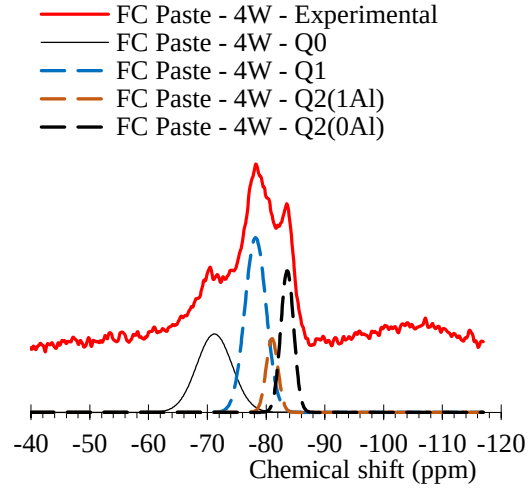


Figure 3.27 ^{29}Si MAS NMR spectra deconvolution of fly ash cement paste after 4-week extraction.

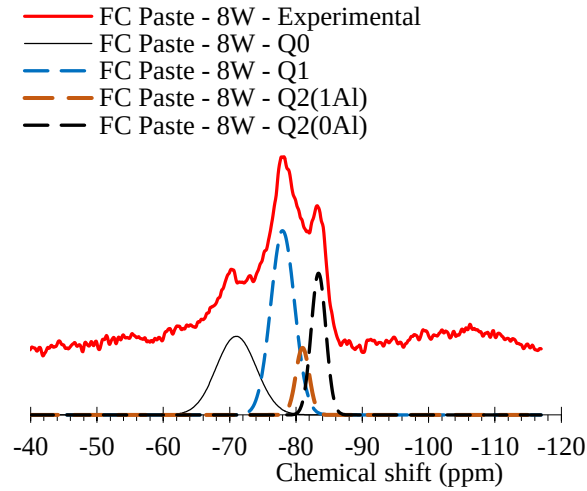


Figure 3.28 ^{29}Si MAS NMR spectra deconvolution of fly ash cement paste after 8-week extraction.

Naturally, thanks to the polymerization process of natural curing cement paste sample, the dimer silicate site can conjoin together by a monomer silicate site or tetrahedron monomer aluminate site to result longer chain of C-S-H. Additional, the content of the monomer silicate site should reduce proportionally to curing time as the results of hydration process. Therefore, in natural curing samples the reduction of both monomer silicate site and dimer silicate site co-occur. Accordingly, the enlargement of Q^2 site can be resulted.

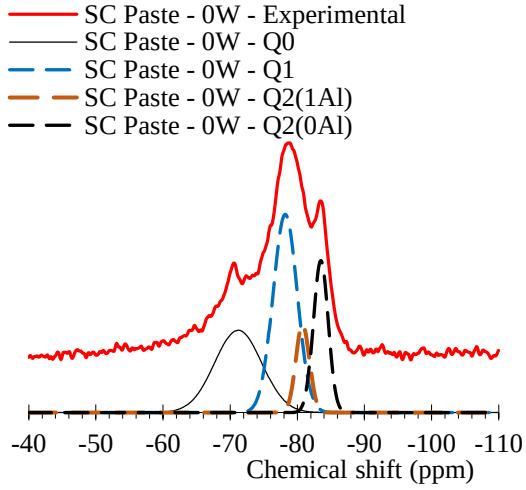


Figure 3.29 ^{29}Si MAS NMR spectra deconvolution of slag cement paste before extraction.

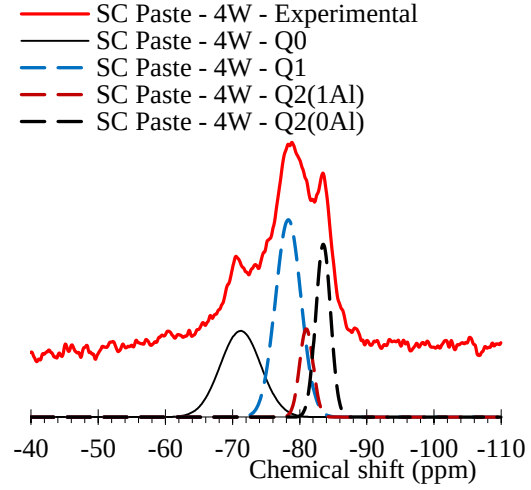


Figure 3.30 ^{29}Si MAS NMR spectra deconvolution of slag cement paste after 4-week extraction.

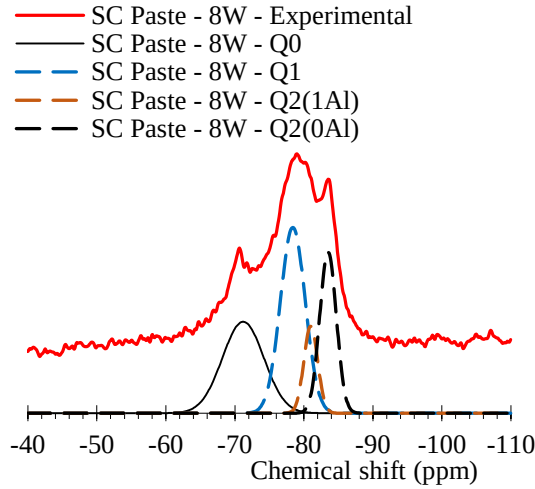


Figure 3.31 ^{29}Si MAS NMR spectra deconvolution of slag cement paste after 8 week extraction.

$$\text{CL} = \frac{2}{\left(\frac{Q^1}{Q^1 + Q^2(0\text{Al}) + (3/2)Q^2(1\text{Al})} \right)} \quad (3.7)$$

Unlike to previous discussion, the ^{29}Si MAS NMR spectrum of cement pastes which experienced the current application indicate an slight enlargement of the relative proportion of monomer silicate site Q^0 while the relative proportion content of Q^1 silicate site decrease. Though the relative proportion of $Q^2(0\text{Al})$ and $Q^2(1\text{Al})$ increased slightly in the first four weeks of extraction process, and then reduced in the later 4 week extraction, as shown in Table 3.9, they are hardly to offer much information.

Table 3.9 Proportion (%) of Q^0 , Q^1 , $Q^2(1Al)$, and $Q^2(0Al)$ of cement paste samples.

	Q^0 (%)	Q^1 (%)	$Q^2(1Al)$ (%)	$Q^2(0Al)$	Chain length of C-S-H
OPC Paste-0W	25.9	50.7	5.3	18.0	3.02
OPC Paste-4W	29.6	46.6	5.3	18.6	3.19
OPC Paste-8W	42.7	36.2	4.8	18.9	3.32
FC Paste-0W	28.6	44.2	9.9	17.3	3.45
FC Paste-4W	29.3	41.2	8.3	21.1	3.63
FC Paste-8W	30.1	40.3	9.5	20.0	3.69
SC Paste-0W	31.3	40.9	9.6	18.2	3.59
SC Paste-4W	29.0	39.8	9.9	21.3	3.81
SC Paste -8W	31.4	38.3	10.0	20.3	3.84

Nevertheless, since the experimental results of each type of cement pastes are presented on the same scale, as shown in Figures 3.32 to 3.34, it is obvious that in both three types of cement paste the absolute value of Q^1 peak diminished significantly after the electric current operated for 4 weeks. In the later four weeks of extraction process, the slight reduction of Q^1 content was also obtained. In contrast to the slight increase of the relative proportion of $Q^2(1Al)$ and $Q^2(0Al)$ as shown in Table 3.9, Figures 3.32 to 3.34 indicate a consistent reduction of absolute value of Q^2 site on OPC and FC pastes along the application time of ECE.

Obviously, the reduction of Q^2 is significantly less than Q^1 site, especially in OPC and FC paste. There is no meaningful decrease of the Q^2 site in SC paste. Moreover, the slight decrease of Q^0 was obtained while there was no notable reduction of it in FC and SC pastes.

The reduction of Q^2 in FC and OPC pastes which happened along to the decrease of the Q^1 silicate site figures out that there is hardly polymerization of calcium silicate hydrates in these samples. Therefore, it is reasonable to suggest that, during extraction process dimer silicate chain was fragmented to monomer silicate SiO_4^{4-} which was attached toward anode easily. The fragment of long chain of C-S-H positively existed but not as easy as dimer silicate chain. Accordingly, the chain length of C-S-H can increase. However, the content of gel phase in cement pastes could undoubtedly reduce.

As mentioned previously, the reduction of the Q^2 silicate site in SC paste was less than that in OPC and FC pastes, as presented in Figures 3.32 to 3.34. Table 3.9 additional presents that the chain length of C-S-H phase in SC paste before extraction is longer than that in FC or OPC pastes. Therefore, these results seem to positively suggest that C-(A)-S-H phase in SC paste is perhaps more stable than in OPC and FC pastes. On the other hand, they may imply that the long chain of calcium silicate hydrates phase in SC paste may be dominated by octamer silicate

chain. However, this hypothesis seems hardly to be possible since the average chain length of C-S-H in SC paste is quite short, approximately 3.59.

Nevertheless, except there is a slight reduction of Q^0 silicate site in OPC paste as shown in Figure 3.32, no notable difference of it in FC and SC pastes were obtained as presented in Figures 3.33 and 3.34. It seemed that the fragmented monomer silicate SiO_4^{4-} which is a product of C-S-H decomposition during current application can be easily extracted by electrical field.

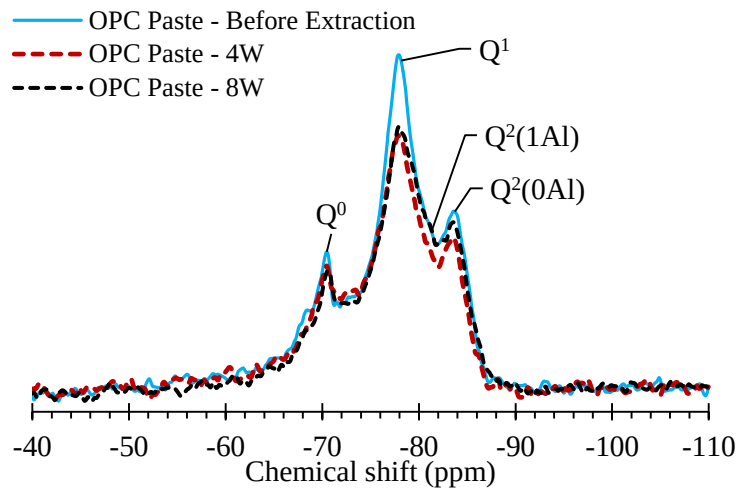


Figure 3.32 ^{29}Si magic angle spinning nuclear magnetic resonance of ordinary Portland cement paste.

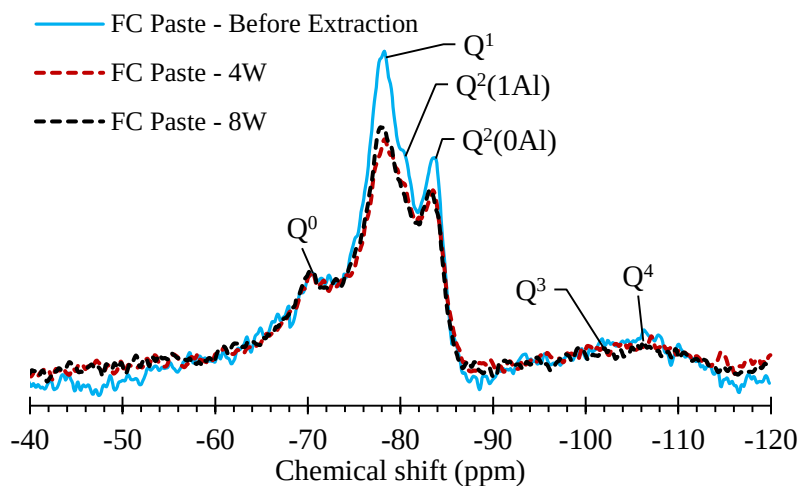


Figure 3.33 ^{29}Si magic angle spinning nuclear magnetic resonance of fly ash cement paste.

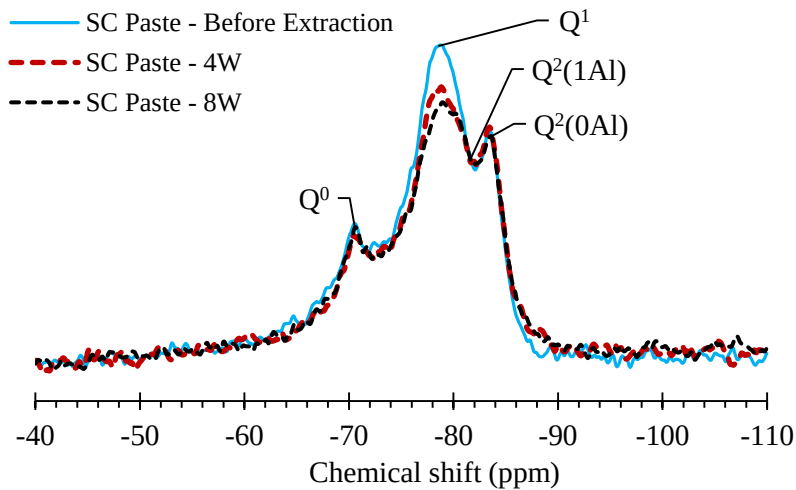


Figure 3.34 ^{29}Si magic angle spinning nuclear magnetic resonance of slag cement paste.

3.5. Summaries

Electrochemical chloride extraction is an efficient method to remove chloride ions from the cement pastes. It can remove approximately 50% of acid-soluble chloride ions in the OPC paste and the FC paste. Moreover, there are insignificant differences in efficiency of reducing acid-soluble chloride contents in the OPC paste and the FC paste, 53% and 48%, respectively. However, the reduction of acid-soluble chloride in the SC paste is lower; that is approximately 30%.

The removal of binding chloride ions depends on the types of cement. While approximately 35% of binding chloride in the FC paste is extracted, the only approximately 7% of binding chloride ions can be extracted in the OPC and the SC pastes.

Portlandite content in the OPC and FC pastes gradually increases during extraction. Nevertheless, in the SC paste it is insignificantly reduced after slight increase in the first week of extraction.

From the XRD results, it seemed the contents of Friedel's salt and ettringite were lower after 8-week extraction. They can be still detected by SEM although the diameter of ettringite needle seemed smaller.

The alteration and decomposition of C-S-H gel phases are inevitable in the three types of cement pastes. However, the rate of decomposition depends strongly on the types of binder. The decomposition of C-S-H is highly remarkable in the OPC paste but lower in the FC paste. The C-S-H phases in the SC paste is much more stable than those in the other two types of cement paste under the impact of the same electrical current.

Shortly after the extraction is stopped, the unsteady gel phase is obtained with the unusually high C/S ratio. However, it is spontaneously transformed to steadier phases.

The decomposition of calcium silicate hydrates phase in cement pastes thanks to the application of electric current seemed inevitably. It existed not only on dimer silicate chain but also on the longer chain of C-S-H. ^{29}Si MAS NMR spectrum indicated that the dimer silicate chain was affected severely. Nevertheless, its effect to longer chain of C-S-H was less than that.

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CHAPTER IV EFFICIENCY OF ELECTROCHEMICAL CHLORIDE EXTRACTION ON REINFORCED CONCRETE WITH VARIOUS TECHNIQUES OF APPLICATION

The efficiencies of continuous application and various intermittent applications of electrochemical chloride extraction are presented and discussed.

4.1. Chloride extraction

4.1.1. Removal of acid-soluble chloride ions

Based on the results of the remaining of acid-soluble chloride in concrete at different depths, the efficiencies of ECE on concrete cover can be categorized into three main regions which are presented in Figure 4.1 to 4.3. One is the concrete regions right beside electrodes, anode and cathode, which were in the depths of 0-1 cm and 4-5 cm from the surface of the block, respectively. The other is the regions next to previous mentioned zones, which includes the concrete zones at the depths of 1-2 cm and 3-4 cm from the surface of the block. And the last region is the middle zone of concrete cover which is at the depth of 2-3 cm.

Figure 4.1 presents the remaining acid-soluble chloride ions at the regions right beside electrodes, which are in the depths of 0-1 cm and 4-5 cm, respectively. Within the first two weeks of the extraction process, approximate 50 to 55% of the initial quantity of acid-soluble chloride were removed. Mode 1 resulted a slightly higher efficiency than that in Mode 2 and Mode 3 in this first period of the extraction process. After that first two-week period, their efficiencies dropped quickly, however, the declining rate depends slightly on the concrete zone and on the mode applied.

In the period from 2 to 4 weeks of extraction process, approximately 10% of chloride in concrete at the depth of 0-1 cm was extracted by using in Mode 1, as shown in Figure 4.1a. In Mode 2 or Mode 3, it was approximately 8%, slightly lower than that in Mode 1. They were even lower in the period from 4 to 6 weeks, approximately 4-6%. In the periods from 6 to 10 weeks, the removal of chloride by using Mode 1 was negligible, just only 1-2 % of chloride were removed in each two-week period while the removal in Mode 2 and Mode 3 was approximately 4-5%, higher than that in Mode 1. After 10 weeks of extraction, in this concrete region, Mode 1 can extract more chloride than that in Mode 2 and Mode 3, they were approximately 77%, 72% and 70%, respectively.

It was similar since in concrete at the depth of 4-5 cm, which was right next to the cathode, since the efficiencies of chloride removal declined abruptly after first two weeks of extraction, as presented in Figure 4.1b. However, unlikely to the concrete beside anode where

Mode 1 showed higher efficiencies, in this region Mode 2 and Mode 3 presented a higher capacity for removing acid-soluble chloride ions at the later periods from 2 to 10 weeks of the extraction process. Furthermore, the declining rate of removal efficiency in Mode 1 was clearly steeper than in Mode 2 and Mode 3. In Mode 1 while about 7% of acid-soluble chloride ions were removed in the period from 2 to 4 weeks, only a half of that was removed in the period from 4 to 6 weeks, approximately 3-4%. In the period from 6 to 10 weeks of extraction, the removal of chloride ions in Mode 1 was negligible since only approximately 2% of chloride were removed in each two-week period. Nevertheless, in Mode 2 and Mode 3, approximately 10% of acid-soluble chloride ions were removed in the period from 2 to 4 weeks; in the later periods, approximately 5-7% of acid-soluble chloride ions were removed in each two-week period. Therefore, in contrast to concrete at the depth of 0-1 cm, after the 10 weeks of extraction process Mode 2 and Mode 3 removed slightly more chloride out of this zone than that in Mode 1. They were 70%, 72% and 74% in Modes 1, 2, and 3, respectively.

The remaining of acid-soluble chloride in concrete at the depths of 1-2 cm and 3-4 cm are presented in Figure 4.2. It can be seen that in the first two weeks of extraction process the removal efficiencies of chloride in these regions were quite diverse but strongly dependent on the mode applied.

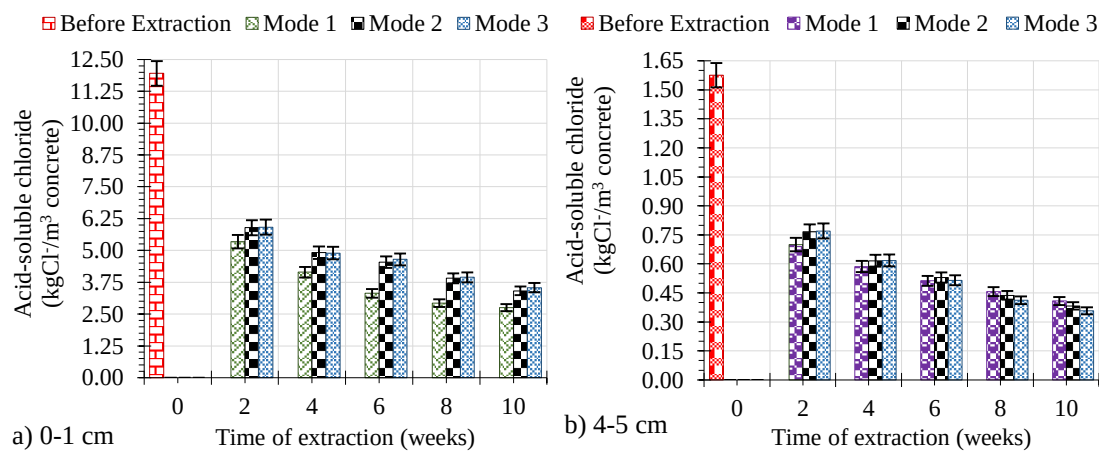


Figure 4.1 Remaining of acid-soluble chloride in concrete regions beside electrode sites a) beside anode, at the depth of 0-1 cm and b) beside cathode, at the depth of 4-5 cm.

In concrete at the depth of 1-2 cm, which is presented in Figure 4.2a, Mode 1 showed a similar trend as the removal of chloride in the concrete regions beside electrode since approximately 50% of acid-soluble chloride ions were removed within first two weeks of the extraction process. After that, the efficiencies of this mode dropped quickly. Nevertheless, during that first period only half of that in Mode 1, approximately 25% of chloride, were removed by using Mode 2 or Mode 3. However, in the later periods of extraction process, since the efficiency of Mode 1 declined

harshly, in Mode 2 and Mode 3 the reduction was much less steep as that in Mode 1. Approximately 23% of acid-soluble chloride were removed in the period from 2 to 4 weeks by using Mode 2 or Mode 3 while it was only 10% in Mode 1. At the end of the extraction process, similar to concrete at the depth of 0-1 cm Mode 1 removed more chloride than that in Mode 2 or Mode 3. After 10 weeks of extraction, approximately 76% of acid-soluble chloride in concrete at the depth of 1-2 cm were removed by applying Mode 1, while it was 74%, and 70% in Mode 2 and Mode 3, respectively.

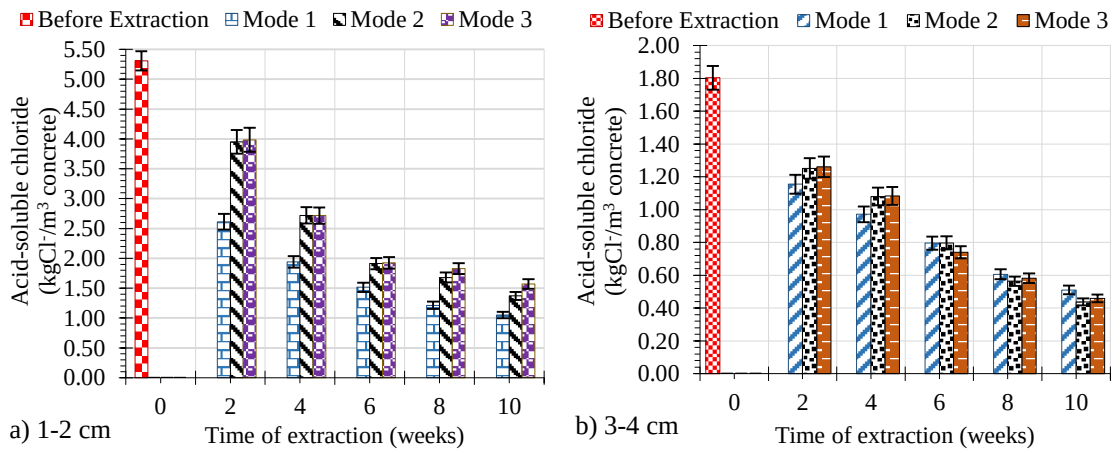


Figure 4.2 Remaining of acid-soluble chloride in concrete regions at the depths of a) 1-2 cm and b) 3-4 cm.

Figure 4.2b displays the remaining of acid-soluble chloride in concrete at the depth of 3-4 cm from the surface of the block. Regardless of application modes, approximately 30-35% of acid-soluble chloride ions in this region were removed within first two weeks of extraction. At the following periods, in contrast to the removal of chloride in Mode 1, where the efficiency consistently decreased, the tendency of chloride removal rate in Mode 2 and Mode 3 was quite uneven. In Mode 1, about 10% of acid-soluble chloride were removed within the period from 2 to 4 weeks; after that, it declined slowly along extraction process. At two last weeks of extraction process, from 8 to 10 weeks, about 5% of chloride were extracted. Nevertheless, in Mode 2 and Mode 3 although there was a decline of chloride removal efficiencies in the period from 2 to 4 weeks where approximately 10% of chloride were removed, the extraction efficiencies increased surprisingly in the later period from 4 to 6 weeks in which approximately 15% and 19% of chloride were removed, respectively. After that, they consistently decreased but not as harsh as in the concrete regions at the depths of 0-1 cm or 4-5 cm. At the end of the extraction process, similar to concrete at the depth of 4-5 cm, Mode 2 and Mode 3 showed a slightly higher efficiencies than that in Mode 1. Approximately 75% of chloride were extracted by Mode 2 or Mode 3 while it was 71% in Mode 1.

The remaining of acid-soluble chloride in the middle region of concrete cover, which was at the depth of 2-3 cm from the surface, is presented in Figure 4.3. It is apparent that the removal of chloride in this depth is different to the other regions not only in the tendency of chloride removal, but also in the final efficiencies at the end of extraction process. During first two weeks of extraction process, only 12% of acid-soluble chloride in this zone were removed by using Mode 1, it was even lower than that in Mode 2 and Mode 3, only approximately 4%. Obviously, they are substantially lower than that in the other regions, as previously mentioned. In the immediate following period of extraction process, from 2 to 4 weeks, their efficiencies did not present significant improvement, only 6-8% of acid-soluble chloride were removed. However, from 4 to 10 weeks of extraction process the removal efficiencies were higher than that in the previous periods unanticipatedly. Moreover, insignificant decline of efficiency was obtained with respect to time of extraction. By using Mode 1, approximately 14-16% of chloride ions were removed in each two-week period from 4 to 10 weeks of extraction. In Mode 2 and Mode 3, about 20% chloride were removed in the period from 4 to 6 weeks. After that, their efficiencies reduced in the following period from 6 to 8 weeks, where 10-13% of chloride were removed. However, in the last period of extraction process, from 8 to 10 weeks approximately 20-25% of acid-soluble chloride were extracted by using Mode 2 or Mode 3.

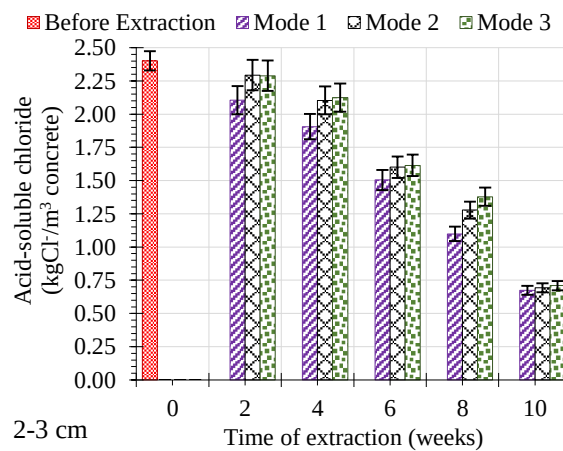


Figure 4.3 Remaining of acid-soluble chloride in the middle region of concrete, at the depth of 2-3 cm.

It is remarkable that while in the other regions of concrete most of chloride were mainly removed in some first weeks of the extraction process and after that reduced abruptly, the removal of chloride ions in the middle zone at the depth of 2-3 cm were quite stable and tended to increase in the later periods of extraction process, especially in Mode 2 and Mode 3. After 8 weeks of extraction process, only 47% and 42% of acid-soluble chloride in concrete at the depth of 2-3 cm were removed in mode 2 and 3, respectively, while mode 1 resulted a higher, about 54%. However, the two-week prolongation of extraction process can significantly increase the efficiencies to

reach to approximately 65-70%.

4.1.2. Removal of water-soluble chloride ions

In corresponding to the removal of acid-soluble chloride, the tendency of water-soluble chloride extraction happened similarly, as shown in Figures 4.4 to 4.6.

In the concrete regions which were right beside the cathodic and anodic sites at the depths of 0-1 cm and 4-5 cm, respectively, approximately 52-59% of water-soluble chloride were removed within first two weeks of extraction process, as presented in Figure 4.4. There were slightly higher efficiencies in Mode 1 than that in Mode 2 and Mode 3 during this first two-week period. After that, the efficiencies in these regions decreased quickly.

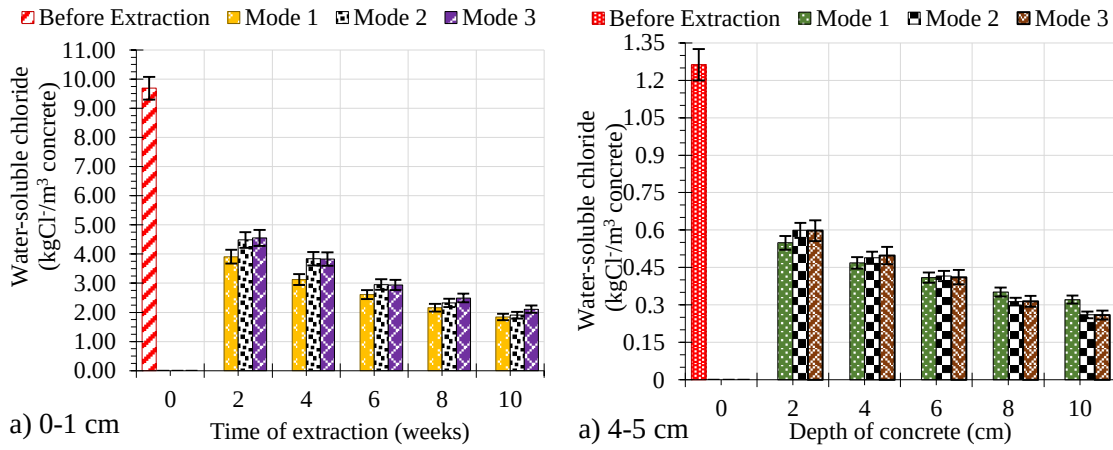


Figure 4.4 Remaining of water-soluble chloride in concrete regions beside electrode sites a) beside anode, at the depth of 0-1 cm and b) beside cathode, at the depth of 4-5 cm.

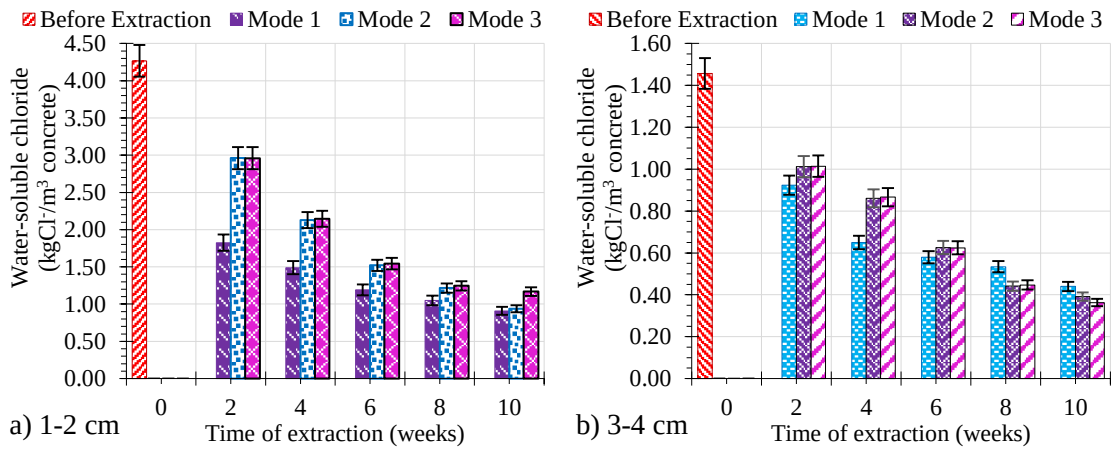


Figure 4.5 Remaining of water-soluble chloride ions in concrete regions at the depths of a) 1-2 cm and b) 3-4 cm.

At the end of extraction process, approximately 81% of water-soluble chloride in concrete at the depth of 0-1 cm were removed by using Mode 1; in Mode 2 and Mode 3, the efficiencies were slightly lower than that in Mode 1 where approximately 77-79% of water-soluble chloride were removed, as shown in Figure 4.4a.

Nevertheless, in concrete at the depth of 4-5 cm from the block surface, after 10 weeks of extraction process Mode 2 and Mode 3 displayed higher efficiencies than that in Mode 1, as shown in Figure 4.4b. Furthermore, the decline of chloride removal efficiency during extraction process from 2 to 10 weeks in Mode 2 and Mode 3 were less steep than that in Mode 1. Therefore, at the end of extraction process, while approximately 79% of water-soluble chloride were removed by applying Modes 2 and 3, it was about 74% in Mode 1.

The remaining of water-soluble chloride in the concrete regions which were in the depths of 1-2 cm and 3-4 cm are presented in Figure 4.5a and Figure 4.5b, respectively. Apparently, the efficiencies of water-soluble chloride removal in these regions were significant lower than that in the electrode site regions as previous mentioned. Moreover, the removal of chloride in these regions are strongly dependent on the modes applied as shown in Figure 4.5a and Figure 4.5b.

In concrete at the depth of 1-2 cm, approximately 57% of water-soluble chloride were extracted within first two weeks of the extraction period by using Mode 1, as presented in Figure 3.8a. Much lower efficiencies were obtained by using Mode 2 or Mode 3 in this first period where only 30% of water-soluble chloride were removed. In the immediately following two-week period, from 2 to 4 weeks of extraction process Mode 1 showed a significant decline of efficiency while there was a gradual reduction of chloride removal in Mode 2 or Mode 3. Only 7% of water-soluble chloride were removed by applying Mode 1 in this period, in contrary, approximately 20% of water-soluble chloride were extracted by using Mode 2 or Mode 3. At last two weeks of extraction process, from 8 to 10 weeks, regardless of application modes, there was only about 1-3% of chloride extracted. After 10 weeks extraction, Mode 1 and Mode 2 showed slightly higher efficiencies than that in Mode 3 where in Mode 1 and Mode 2, approximately 78% of chloride were removed while in Mode 3 it was 72%.

Unlikely to concrete at the depth of 1-2 cm where within first two weeks of extraction process, there were significant difference of efficiencies among these application modes, in concrete at the depth of 3-4 cm there was no significant difference of removal efficiencies among Mode 1, Mode 2, and Mode 3 in this first two weeks of extraction process. As shown in Figure 3.8b, 35% of water-soluble chloride were removed by using Mode while in Modes 2 or 3, they were approximately 30%. Moreover, since the removal efficiencies at the regions beside electrodes dropped abruptly after two week extraction, in this concrete region which was at the

depth of 3-4, the efficiencies of extraction gradually decrease with respect to time of extraction. At the end of extraction process, Mode 3 offered a slightly higher efficiency than that in Mode 1 and Mode 2 where 75% of water-soluble chloride were extracted. In Mode 1 and Mode 2, they were 69% and 73%, respectively.

Figure 4.6 exhibits the remaining of water-soluble chloride in the middle zone of concrete, where its depth was 2-3 cm from the surface of the block, versus the time of extraction. As corresponding to the removal of acid-soluble chloride as shown in Figure 4.3 in first four weeks of extraction process, there was no significant removal of chloride ions in this concrete region. By employing Mode 1, only 8% of water-soluble chloride was removed; in the following period from 2 to 4 weeks, its efficiency was even lower than that while only 3% were extracted. It is interesting since in Mode 2 and Mode 3, after first two weeks of extraction the water-soluble chloride content in this region were even higher than that before extraction. In the period from 2 to 4 weeks of extraction process by using Mode 2 or Mode 3, only approximately 5% of water-soluble chloride were extracted. However, in the periods from 4 to 10 weeks their efficiencies became substantially higher. After 10 weeks extraction, approximately 63% of water-soluble chloride were extracted by using Mode 3. Mode 1 and Mode 2 showed a higher efficiencies than that, approximately 70%.

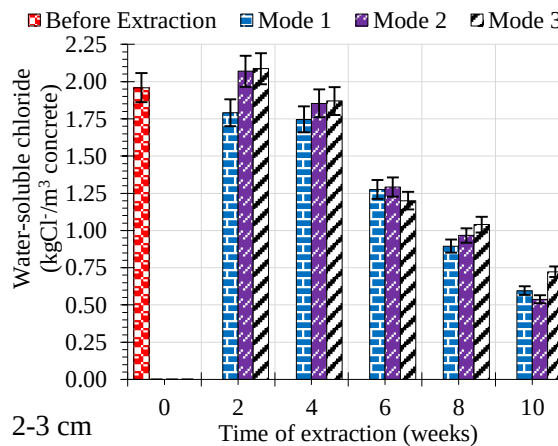


Figure 4.6 Remaining of water-soluble chloride in the middle region of concrete, at the depth of 2-3 cm.

Figure 4.7 presents the diminution of remaining water-soluble and acid-soluble chloride in concrete at the depth of 4-5 cm, which surrounds the reinforcements, with respect to the number of charge applied during ECE in different modes applied. After 10 weeks of extraction, Mode 2 and Mode 3 can withdraw more chloride content than that in Mode 1. It is important to emphasize here that while the efficiencies in Mode 2 and Mode 3 were slightly higher than that in Mode 1, the charge number applied in Mode 2 or Mode 3 were significantly much lower than that in Mode

1.

As seen in Figure 4.7, in concrete at the depth of 4-5 cm Mode 1 experienced the most intense dropping of chloride removal efficiency than Mode 2 or Mode 3.

In Mode 1, the removal of chloride ions was most efficiency before the applied charge number reached to 336 A.hour/m² which corresponded to 2 weeks of continuous application. Within this 2 weeks of extraction, approximately 55% of chloride were extracted. The removal of chloride was still noticeable since the applied charge number increased from 336 A.hour/m² to approximately 800-900 A.hour/m², in which approximately 10-13% of chloride were removed. After that, although a further massive charge number were continuously applied, approximately 800-900 A.hour/m², which corresponded to 4-6 weeks of extraction process, the quantity of chloride ions removed were insignificant, only about 2-5%.

Nevertheless, in despite of the reduction of chloride removal efficiencies in Mode 2 and Mode 3 since the applied charge number reached to 204 A.hour/m², which corresponded to 2 week application, the declining rate of chloride removal after that was not as substantial as in Mode 1. The remaining of chloride gradually decrease since the applied charge numbers increased from about 204 to the end of extraction process, where the charge number reached to approximately 1000 A.hour/m². Therefore, after 10 weeks of application Mode 2 or Mode 3 can remove more chloride than Mode 1.

Therefore, it is evidentially reasonable to assume that the interrupting time during applying ECE was greatly important to improve the electrical applied charge-effectiveness on removing chloride ions. Furthermore, there perhaps exists a threshold quantity of the applied charge number in which since the charge numbers reach to that value, the chloride removal efficiency of the further application approach to negligible.

Besides, Figure 4.7 reveals the correlation between the acid-soluble and water-soluble chloride in concrete since the current application was stopped for approximately 4 months. Before extraction, approximately 83-87% of chloride in concrete existed as water-soluble form. However, the fraction of water-soluble form in total content of chloride after extraction was lower than that although these samples were preserved 4 months which included 2 months wet-preserving of concrete blocks after extraction and 2 months for sample preparation and testing. Furthermore, the fraction of water-soluble chloride in total content after extraction in Mode 2 or Mode 3 seemed lower than that in Mode 1. After 10 weeks extraction and preserving for about 4 months, in Mode 1 approximately 75% of acid-soluble chloride existed as water-soluble form, while they were approximately 68% in Mode 2 and Mode 3.

It is important to mention that before extraction the content of water-soluble chloride in

concrete at the depth of 4-5 cm were approximately 83-87% of acid-soluble chloride. However, after the ECE was applied 10 weeks, these modes can extract only approximately 70-74 % of total chloride, as previous mentioned. Obviously, water-soluble chloride is supposed to be the main form of chloride can be released thanks to the impact of electrical current. Furthermore, ECE is unable to extract completely water-soluble chloride, although intermittent applications were applied.

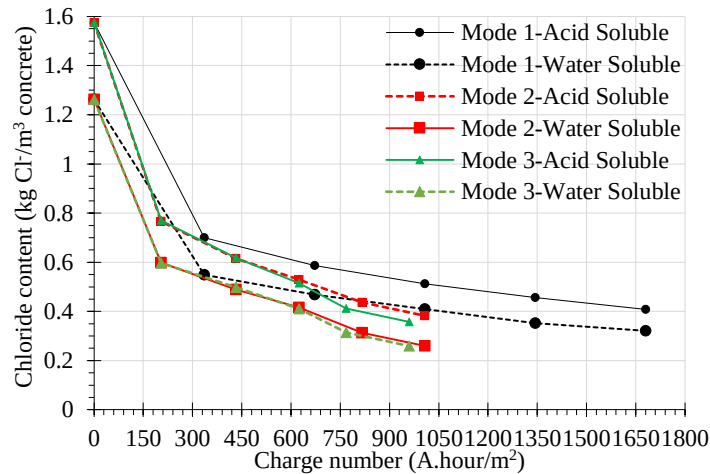


Figure 4.7 Remaining chloride at the depth of 4-5 cm versus cumulative applied charge number.

According to Equations 4.1 and 4.2, which are different forms of electric conservation equations [1-2], they express clearly that the contribution of each ionic species in the fluid to transfer the electrical charge during current application depend not only on its concentration in ionic fluid but also its own mobility and charge. Before extraction, hydroxide ions and free chloride ions are supposed to be abundant in pore solution. Therefore, they would be the main ions in ionic fluid which transfers the charge from cathode to anode during current application. However, the diminution of chloride concentration in pore solution thanks to extraction would obviously lessen the contribution of chloride in ionic fluid. Furthermore, the rise of hydroxide concentration thanks to cathodic processes as presented in Equations (1.1) and (1.2) and the significantly high mobility of hydroxide ions than the other ions, which is expressed in Table 4.1, would importantly result the significant dropping of extraction efficiencies in the later time of extraction process, especially chloride in concrete at the regions at the depth of 4-5 which were beside cathode and where hydroxide ions were generated directly. The more charge number were applied, the more hydroxide ions was generated in pore solution of concrete and accordingly, the less contribution of chloride in ionic fluid. Therefore, it can be understood that at first two weeks of extraction, in concrete at the depth of 4-5 cm, when the concentration of chloride ions was still high, it would be one of the main species in ionic fluid, beside hydroxide ions chloride, carried the charge during

current application. However, since the generation of hydroxide took place, its concentration increased and dominated in the ionic fluid, chloride ions which concentration continuously reduced showed less effect on the current transference. Consequently, the efficiency of chloride removal dropped quickly.

After every certain time of extraction process, the cumulated charge numbers applied in Mode 1, continuous mode, were much higher than that in Mode 2 and Mode 3, the intermittent modes, as showed in Table 2.9. Therefore, in concrete at the depth of 4-5 cm, Mode 1 can obviously generated much more hydroxide ions than that in Mode 2 or Mode 3 and accordingly hydroxide ions easily resulted the domination of it in the ionic fluid. Consequently, the efficiency of chloride extraction by using Mode 1 was easily to approach to a threshold value where in the later extraction period, its efficiency was negligible although the applied charge number kept increasing significantly. Nevertheless, the charge number applied in Mode 2 or Mode 3 were much lower than that in Mode 1. Then, it could generate lower content of hydroxide ions. Moreover, the interrupting time could be the time for the phases in concrete rebalanced. In this interrupting time, free chloride ions which can contribute into ionic fluid to transfer the current can be replenished by bound chloride ions, perhaps physical bound chloride which is easy to dissolve in water and apart of water-soluble chloride. Consequently, the dropping level of the chloride removal efficiencies in Mode 2 and Mode 3 were not as harsh as that in Mode 1. Consequently, the removal efficiencies of Mode 2 and Mode 3 were slightly lower than that in Mode 1 at some first periods of extraction process, but were higher at the end after 10 week extraction [3].

Obviously, the impact of the electrical field to the ions in pore solution of concrete at the middle region of concrete cover would be much less than that in the regions which were near electrodes. Therefore, chloride ions here is difficult to be attract towards anode. Furthermore, the rapid repulsion of chloride ions from cathode in some first weeks of extraction process can lead to the congestion of chloride ions in this middle zone. After that first periods, since concentration of chloride in ionic fluid flowed from cathode was significant lower, that congestion could be resolved and chloride ions accumulated there easily removed.

In concrete at the depths of 0-1 cm and 1-2 cm, which were near anode, the chloride content before extraction were significantly high as well as there was no significantly rise of hydroxide during current application as in concrete at the cathodic region. Therefore, it seemed reasonable since the removal of chloride ions proportionally increased to the charge number applied. Consequently, in these zones Mode 1 expressed higher efficiencies of chloride extraction than that in Mode 2 and Mode 3.

As expressed in Figure 4.7, at the end of extraction process Mode 3 offered slightly higher efficiency on removing chloride than that in Mode 2. There was still no crucial evidence

to optimize the suitable time for current off and current on for intermittent applications, which would be not only enough for the rebalance among chloride forms, but also would lessen the time of ECE application. Nevertheless, the slightly higher of chloride removal in Mode 3 than that in Mode 2 is essential result implying that it would be more productive for the efficiency of chloride removal in term of applied charge number if the intermittent applications would conduct with sophisticated applications.

$$I_{\text{Current}} = I_{\text{Ionic Transference}} = \sum C_i U_i |Z_i| \quad (4.1)$$

$$t_{\text{Cl}^-} = \frac{I_{\text{Cl}^-}}{I_{\text{Current}}} = \frac{C_{\text{Cl}^-} U_{\text{Cl}^-} |Z_{\text{Cl}^-}|}{\sum C_i U_i |Z_i|} \quad (4.2)$$

Where

- t_{Cl^-} : the chloride transference number I_{Cl^-} : amount of current carried by chloride ion
- I_{Current} : electrical impressed current C_{Cl^-} : concentration of chloride ion in pore solution
- Z_i : charge of ion i U_{Cl^-} : mobility of chloride in pore solution
- U_i : mobility of ion i in pore solution Z_{Cl^-} : charge of chloride ion, $Z_{\text{Cl}^-} = 1$
- C_i : concentration of ion i in pore solution

Table 4.1 Mobility of some ions dissolved.

Ion	Ionic mobility x 10 ⁻⁴ (cm ² .V ⁻¹ .s ⁻¹)
Cl ⁻	7.91
SO ₄ ²⁻	8.27
OH ⁻	20.64
Na ⁺	5.19
Ca ²⁺	6.17
K ⁺	7.62

The intermittent application should be comprised of several different periods of current off and current on. Within approximately 2-3 first weeks of extraction process, the time for current on could be lasted for couple days before interrupting it for approximately 2-3 days. However, after that first periods, since the remaining of free chloride ions is getting poor, it would be more productive if the interruption which would last for couple days is iterated more often and the time for current on is shorter, perhaps about 1.5 to 2 days.

4.2. Variation of Portlandite and C-S-H phase content

The movement of ions during current application as well as the generation of hydroxide ions at cathode obviously affect to the properties of concrete matrix, and then impact to later durability of structure after applying ECE. The variation of Portlandite in different depths of concrete cover were investigated as an indirect criteria to evaluate the influence of the current application to concrete matrix. TG/DTA were conducted in concrete powder which collected at the depths of 0-1 cm, 4-5 cm, and 2-3 cm with the temperature covering from 20-900 °C at the constant rate of 10 °C/min under nitrogen atmosphere.

The change of Portlandite in concrete at the depth of 0-1 cm, which was beside the anode and exposed directly to saturated calcium hydroxide solution during extraction process, is presented in Figure 4.8a. It can be seen in Mode 1, after a significant increasing of Portlandite content within first two weeks of extraction process, approximately 15%, Portlandite content in concrete at this depth raised gradually from 2 to 6 weeks where approximately 4% of Portlandite was increase within each two-week period. However, there was an abrupt increasing in the period from 6 to 8 weeks of extraction process since within that two weeks, approximately 15% of Portlandite was added in this zone. The augmentation in the period from 8 to 10 weeks of extraction process seemed slightly lower than that previous two-week period, 9%. In Mode 2 or Mode 3, the increasing tendency of Portlandite was similar to Mode 1. However, since in Mode 1 the abrupt augmentation of Portlandite happened during period from 6 to 8 weeks of extraction process, in Mode 2 it took place at period from 8 to 10 weeks, the end of extraction process while about 12% of Portlandite was increased in this period. Nevertheless, in Mode 3 that abrupt increasing seemed unclear. The rise of Portlandite by using Mode 1 was consistently higher than that in Mode 2 and Mode 3 through whole extraction process, especially at last four weeks of extraction process, from 6 to 10 weeks. At the end of extraction process, the quantity of Portlandite in Mode 1 augmented 45%. It was 39% and 32% in Mode 2 and Mode 3, respectively. The migration of calcium ions from electrolyte, saturated calcium hydroxide solution, due to the repulsion of anodic site may lead to more precipitation of the Portlandite in this concrete region. However, the abrupt increasing of Portlandite in the period from 6 to 10 weeks in Mode 1 and from 8 to 10 weeks in Mode 2 is hardly to elucidate due to the effect of electrical field only.

Figure 4.8b presents the variation of Portlandite content in concrete at the depth of 4-5 cm, which region was beside cathode, with the same scale as Figure 4.8a. It expresses apparently that through whole extraction process the augmentation of Portlandite in this region was lower than that in concrete at the depth of 0-1 cm, which was presented in Figure 4.8a. Furthermore, unlike to concrete at the depth of 0-1 cm while Mode 1 constantly displayed higher increasing of Portlandite than that in Mode 2 or Mode 3 through extraction process, in this region Mode 1

presented higher increasing only within first four weeks of extraction process. After that, Mode 2 or Mode 3 expressed higher augmenting until the end of extraction. After 10 weeks of extraction, the Portlandite content increased 35% in Mode 3; it was 31% and 21% in Mode 2 and Mode 1, respectively. It seems there was unexpected increasing of Portlandite during the last two-week period of extraction process, from 8 to 10 weeks, in all three modes of application. The attraction of electrical field from cathode certainly resulted the concentration of calcium ions beside cathode where it can easily be agglomerated with hydroxide ions, which is in abundance thanks to cathodic processes and form Portlandite. As presented in Table 3.5, hydroxide ions possess high ionic mobility. It is probably one of the most important species in ionic fluid in transferring the charge during current application. According to Equation 3.4, the lower quantity of it in ionic fluid obviously uphold the role of other ions, including calcium ions. Hypothetically, the less generation of hydroxide ions by using Mode 2 and Mode 3 may result the less contribution of it in the ionic fluid. Consequently, the additional contribution of calcium ions in ionic fluid can be taken into accounted for the conservation of electrical current. Therefore, the more accumulation of Portlandite in Mode 2 and Mode 3 than that in Mode 1 can be resulted. However, the abrupt augmentation of Portlandite within last two weeks of extraction process is hardly to be comprehended since at the end of extraction process, the concentration of hydroxide ions in ionic fluid would be abundant.

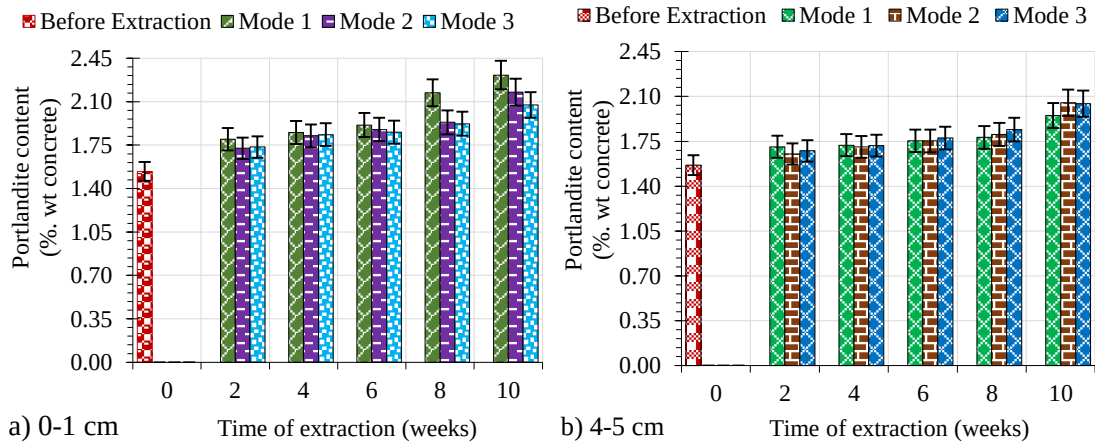


Figure 4.8 Portlandite content in concrete at the depth of a) 0-1 cm b) 4-5 cm.

The variation of Portlandite in concrete at the depth of 2-3 cm is presented in Figure 4.9. It is remarkable here since the variation of Portlandite in concrete at this depth is completely contrary to the previous mentioned regions. In general, in this region Portlandite content declined gradually with respect to time of application. In Mode 1, the quantity of Portlandite tended to diminish steadily until 8 weeks of extraction process before reversing its tendency surprisingly in last two weeks. Nevertheless, in Mode 2 and Mode 3 the decrease of Portlandite in concrete at this depth

endured consistently until the end of extraction process although the decline within the last two weeks was quite fierce.

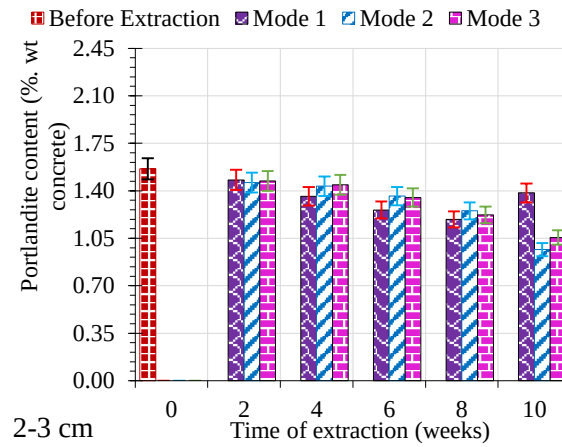


Figure 4.9 Portlandite content in concrete at the depth of 2-3 cm.

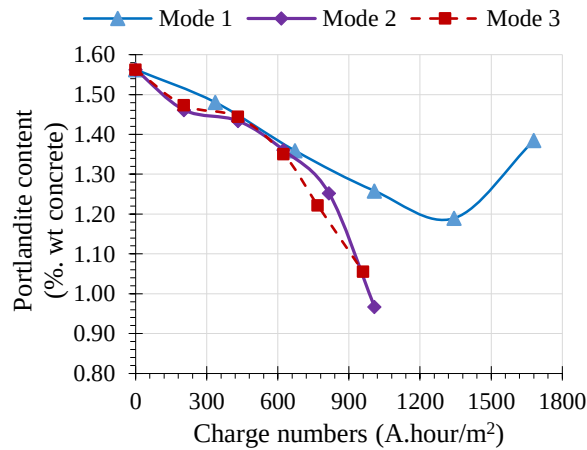


Figure 4.10 Portlandite content in concrete at the depth of 2-3 cm versus applied charge number.

Taking the increase of charge number applied during extraction process into account for the alteration of Portlandite content, as shown in Figure 4.10, it supports the hypothesis that there may exist a critical charge numbers for the stability of concrete matrix during employing ECE. Since the charge number applied reach to that critical numbers, it would cause a severe effect to stability of concrete matrix. Consequently, a significant change in cement hydration products of concrete may take place, such as the decomposition of C-S-H, which contains an abundant quantity of calcium. In consideration of the variation of Portlandite in concrete at different depths as mentioned, the critical charge number is perhaps approximately 800-900 A.hour/m² with respect to concrete surface. Furthermore, the critical number in Mode 1 seem slightly higher than that in Mode 2 and Mode 3. However, it is unable to distinguish the exact value of critical charge

number in each mode of applications here.

Figure 4.11 presents the DTA, DTA, and TG profiles of concrete at the depth of 4-5 cm before extraction and after applying extraction 10 weeks on three modes. The first peak of DTG curves displaying in Figure 4.11a is attributed essentially to the dehydration of C-S-H gel phase [4-7], which correspond to the mass loss on TG profiles up to approximately 150 °C. The mass loss in that stage of TG profiles, which are presented in Figure 4.11b, is mainly ascribed to the loss of weakly binding water in C-S-H phase. Before extraction the weight loss of concrete within this stage was approximately 3% of concrete powder. It is needed to emphasize here that thought the weight loss seems quite minute, it magnifies significantly, approximate 17.04% if considering it with respect to cement content which owned approximately 17.3% of concrete powder. After 10 weeks applying ECE, the quantity of water evaporated reduced significantly. The reduction rate seems proportionally to charge numbers applied. As presented in Figure 3.14b, in Mode 1 where the largest quantity of charge numbers were used, the mass loss within this stage was approximately 2.2% of concrete mass, corresponding to 12.5 % by cement weight. This mass loss reduced approximately 27% compared to the weight loss of non-extracted concrete. In Mode 2 or Mode 3, the reduction seem less severe than that in Mode 1 since the weight losses were approximately 2.5% and 2.7%, respectively, which is equivalent to 14.20% and 15.34% by weight of cement, respectively. Correspondingly, they were 17% and 10% less than the weight loss in non-extracted concrete, respectively.

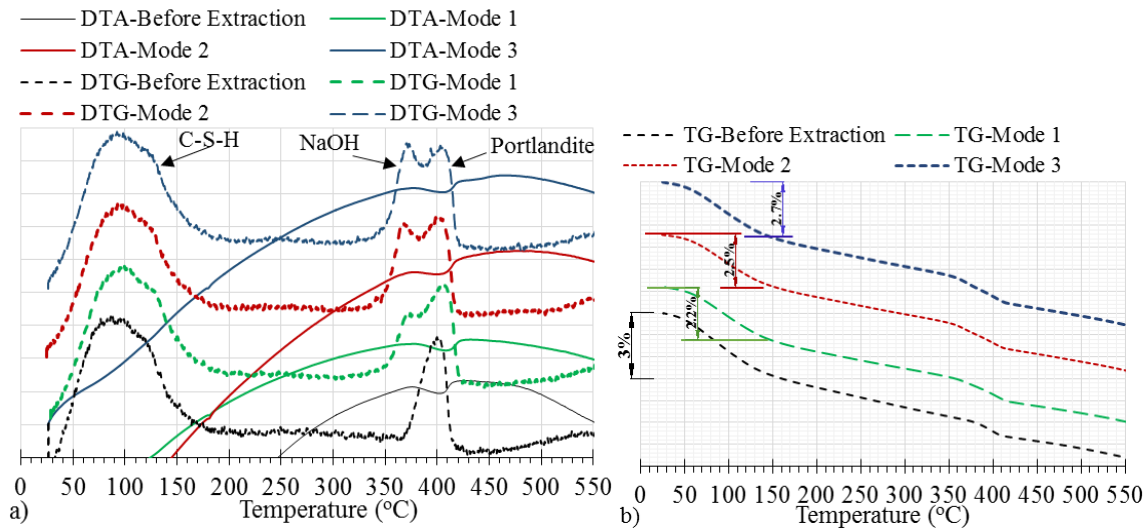


Figure 4.11 Thermal analysis of concrete at the depth of 4-5 cm before and after 10-week extraction a) DTG-DTA profiles b) TG profiles.

The reduction of these weight losses evidently imply the reduction of C-S-H gel quantity in concrete after extraction. Additionally, it also infers that during extraction a fraction of C-S-H gel

phase may decompose. This suggestion could elucidate the abrupt increasing of Portlandite content in concrete after a certain time ECE was applied.

Furthermore, while DTA profiles as shown in Figure 4.11a do not display visible difference between non-extracted concrete and extracted concrete in the range of temperature from 350 °C to 450 °C, the DTG profiles present an impressive distinction. In DTG profiles of 10-week extracted concrete, there occurred a peak at 370 °C which did not exist in DTG curve of non-extracted concrete. This peak is supposed to be the dehydration of NaOH [8-9] which agglomerates beside cathodic site where there were abundance of sodium ions thanks to its accumulation at cathode and plenty of hydroxide ions due to cathodic processes. Theoretically, there is no dehydration readily of pure sodium hydroxide which owns strong ionic bonding. Instead of dehydration, pure sodium hydroxide melts at temperature above 300 °C. However, it was proved that since less than 10 mol % of sodium hydroxide mix with calcium hydroxide it can dehydrate completely [8-9].

Notably, most of previous studies assumed the existence of abundant sodium at the zone beside cathode interfered the C-S-H gel and finally formed a new gel phase which contained significantly high content of calcium and sodium [10-11]. Some others obtained an occurrence of sodium-rich phase [10-12]. Based on these DTG profile which mentioned previous, it evidently proved the agglomeration of sodium hydroxide and the accumulation of more Portlandite after extraction would be preferred rather than its interference into C-S-H phase or other phases.

4.3. Summary

The efficiency and effect of electrochemical chloride extraction with various intermittent applications and continuous application were studied in this research. The results confirmed a great significance of the interrupting period during applying ECE in intermittent applications on improving the electrical applied charge-efficiency of chloride removal. The utilization of intermittent applications can extract approximate quantity of chloride ions as in continuous application however with nearly half applied charge number. There is no notable difference of the chloride quantity removed among intermittent applications and continuous application after 10 week extraction. At the end of extraction process, approximately 70-75% of acid-soluble chloride in concrete at the regions near electrode sites were extracted while 65-70% of acid-soluble chloride in concrete at the middle region were removed.

Regardless of using large quantity of charge number in continuous application or using intermittent applications with interrupting periods, they were unable to remove all water-soluble chloride although the main chloride removed was water-soluble chloride. After 10 week extraction, approximately 80% of water-soluble chloride in concrete at the zones electrode sites

was extracted while it was approximately 70-75% in concrete at the middle zone of concrete cover. The removal of bound chloride seemed very limited.

The rebalance to establish equivalent condition on all phases in concrete matrix after stopping ECE was certainly spontaneous. However, after stopping the extraction 4 months, the ratio of water-soluble to acid-soluble chloride in concrete were still lower than that before extraction. In 10-week-extracted concrete, approximately 60-75% of acid-soluble chloride were water-soluble while it was approximately 83-87% in non-extracted concrete. Notably, the remaining of chloride ions in concrete near the surface were still significant. The diffusion of free chloride towards further depth concrete regions is apparently. Therefore, it is crucial if after extraction the concrete surface is covered with epoxy or waterproof products in order to hinder the further sorption of chloride ions from outside environment.

The charge number applied during ECE should not be exceeded 800-900 A.hour/m². Since it gets transcended that critical quantity, it can cause adverse effects on concrete matrix.

The content of Portlandite increased at the zones beside electrodes but declined at the middle zone. Sodium ions accumulated at cathode would agglomerate with hydroxide which generated from cathodic processes to form NaOH rather than interfering into C-S-H phase or any unknown phases. However, the concentration of sodium hydroxide at cathodic regions is perhaps a threat for the provocation of alkali silica reaction, especially in concrete contain reactive aggregate.

Intermittent applications is the potential means to applied ECE in order to remediate the adverse side effects of continuous application of ECE on concrete properties.

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CHAPTER V CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn from the experimental results.

5.1. Conclusions

ECE is an efficient method to remove chloride ions from concrete and cement pastes. The efficiency of it depends strongly not only on the type of cements or concrete regions, but also on the application technique.

The application of electric current apparently causes some adversities to microstructure of hydration products. Furthermore, these adversities are in proportion to cumulative charge number during ECE applications. The transportation of ions in pore solution under the effect of electrical field can alternate the cement hydration products and break the calcium silicate hydrates (C-S-H) chain into smaller species, especially dimersilicate. Consequently, it affects later load carrying capacity and durability of structure. The diminution of dimersilicate and the reduction of monosilicate thanks to electrical attraction hinder the polymerization process to recreate the longer silicate chain afterwards.

In concrete region besides steel reinforcement, within first 2-4 weeks of the extraction process the continuous application of ECE can result a slightly higher efficiencies of chloride extraction than that in intermittent applications. However, in the later periods of extraction process intermittent applications led to a higher efficiencies. After 10 week application, there are insignificant differences in their efficiencies though the intermittent applications presented a slightly higher efficiencies than that in the continuous application.

It should be marked that intermittent application greatly improves the charge-efficiencies in extracting chloride. Less adverse effects of ECE on C-S-H phase are obtained by using the intermittent application. It indicated a potential to remediate the adverse side effects of continuous application of ECE on concrete properties.

The content of Portlandite increases at the zone beside electrodes but declined at the middle zone. Sodium hydroxide (NaOH) is detected in concrete region besides steel reinforcement.

5.2. Recommendations

The cumulative charge number applied in ECE should not be exceeded 800-900 A.hour/m². Since it gets transcended that critical quantity, it can cause adverse effects on C-S-H phase.

In order to extract chloride, intermittent applications should be conducted. The application of intermittent technique should be employed with sophisticated processes which comprise of several different periods of current off and current on. At the first stage of extraction process, the time for current on should be lasted for a couple of days before interrupting it for approximately 2-3 days. However, after that first stage, about a couple of weeks, the time for current-on should be shortened, approximately 1.5-2 days, and the interruption should be iterated more often.

The concentration of sodium hydroxide at the region near steel reinforcement is perhaps a threat for provoking the alkali silica reaction, especially in concrete contained reactive aggregate. Therefore, more research should be conducted in order to investigate the feasibility of this threat. The alternative of electrolyte which contains cation with high mobility and is able to hinder the provocation of alkali silica reaction is needed.

The chloride near concrete surface still remains high after stopping extraction. Therefore, preventing the later sorption of chloride ions after extraction is necessary. It is recommended to cover the surface exposing to chloride environment with epoxy or water-resistance products.

The severe effect of electric current on C-S-H by using the intermittent application is much less than that in the continuous application. Therefore, it is prospective to repeat conducting ECE with the intermittent technique 3-4 times due to the resorption of chloride after extraction.