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- Technical Paper -

CHEMICAL EVOLUTION OF CEMENT-BASED MATERIALS IN SODIUM AND MAGNESIUM SULFATE SOLUTIONS

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ABSTRACT

This paper presents the mineralogical distribution of three types of cement paste subjected to external sulfate attack. Specimens were immersed in water and sodium and magnesium sulfate solutions with 10 and 100 mmol/l of SO_4^{2-} concentration for a period of 9 months. Solid phases in the specimens from the exposure surface to its core were quantified by XRD/Rietveld analysis, and the mineralogical distributions results are presented. Further, the influence of the composition of cement paste on the resistance to calcium leaching in pure water and ettringite-based external sulfate attack is discussed.

Keywords: Sulfate attack; Leaching; Solid phase changes; X-ray diffraction (XRD); Cement paste

1. INTRODUCTION

Sulfate attack is an environmental issue for cement-based materials exposed to sulfate bearing groundwater or soils and threats the durability of concrete structures. The reaction between penetrating sulfate ions and cement hydrates can result in swelling, spalling and cracking of cement matrix in concrete. These processes induce a reduction of mechanical properties and a decrease of service life of an affected structure. Over the past couple of decades, an intensive work has been carried out on sulfate attack in cement-based materials [1-3]. It has been identified that the precipitation of secondary sulfate bearing phases such as ettringite, gypsum and thaumasite can cause the damage. The formation of sulfate containing phases depends upon the type and concentration of sulfate solution, the porosity of cement-based material, and the chemical composition of cement. The mechanism for the sulfate attack by $MgSO_4$ is different from Na_2SO_4 because both magnesium and sulfate ions react with cement hydrates to produce brucite and magnesium silicate hydrates (M-S-H) in addition to sulfate bearing phases. Thus, the deterioration from $MgSO_4$ is more severe than from Na_2SO_4 [1-2]. Generally, low C3A cements have been using for sulfate resistance. This type of cement reduces the formation of secondary ettringite, but it cannot reduce the gypsum formation or direct attack on calcium silicate hydrate (C-S-H) that is possible in $MgSO_4$ attack [2]. Investigating the proposed mechanism and analyzing the existing laboratory experimental results for cementitious materials in sulfate environments, makes it clear that more experimental work is necessary to clearly understand the mechanism and to provide sufficient spatial resolution as well as information about the phase assemblage in different sulfate solution for varying cement composition. In this paper, the influence of the type of sulfate solution and the concentration on the degradation of three types of hydrated cement paste was experimentally investigated. Mineralogical distribution of the pastes exposed to water and sulfate solutions are presented in here.

Table 1 Cement properties

	OPC	SRPC		OPC	SRPC
Blaine (cm^2/g)	3260	3380	Density (g/cm^3)	3.16	3.20
L.O.I	2.95	2.06			

Chemical composition (%)

	OPC	SRPC		OPC	SRPC
SiO_2	20.56	22.26	MnO	0.07	0.08
Al_2O_3	5.73	3.50	P_2O_5	0.15	0.10
Fe_2O_3	2.86	4.69	Na_2O	0.16	0.11
CaO	64.09	65.08	K_2O	0.37	0.24
MgO	0.88	0.67	Cl	0.023	0.002
SO_3	2.08	1.87			

2. EXPERIMENTAL

2.1 Materials and sample preparation

Ordinary Portland cement (OPC) and sulfate resistant Portland cement (SRPC) were used in this study. Physical properties and chemical composition of OPC and SRPC are given in Table 1. XRD/Rietveld analysis shows absence of calcite in cements. Three types of cement paste were prepared: ordinary Portland cement paste (OPCP), sulfate resistant Portland cement paste (SRPCP), and gypsum cement paste (GCP). OPCP and SRPCP contain 100 % of respective cement while GCP was made with OPC:gypsum mass ratio of 90:10. All paste specimens (Φ 5 cm * 10 cm) were prepared with a fixed water /binder ratio of 0.5. Thinkner was used as a chemical admixture to avoid

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bleeding during sample preparation. The specimens were demolded at 24 hours and sealed with aluminum foil. Afterward, the sealed samples were stored at 20℃ and 60% relative humidity (RH) for 28 days. The summary of the preparation of paste specimens is given in Table 2.

Table 2 Summary of experimental program

Test series	OPCP	SRPCP	GCP
Materials	100 % OPC	100 % SRPC	90 % OPC: 10% Gypsum
W/C	0.5		
Chemical admixture	Thickner (1% of water)		
Geometry	Φ 5 cm * 10 cm		
Curing period and condition	28 days sealed curing at 20℃ and 60 % RH		
Exposure solution	• Water • 10 mmol/l Na_2SO_4 • 100 mmol/l Na_2SO_4 • 10 mmol/l $MgSO_4$ • 100 mmol/l $MgSO_4$		
Exposure period	9 months		
Exposure solution to solid ratio	4:1		

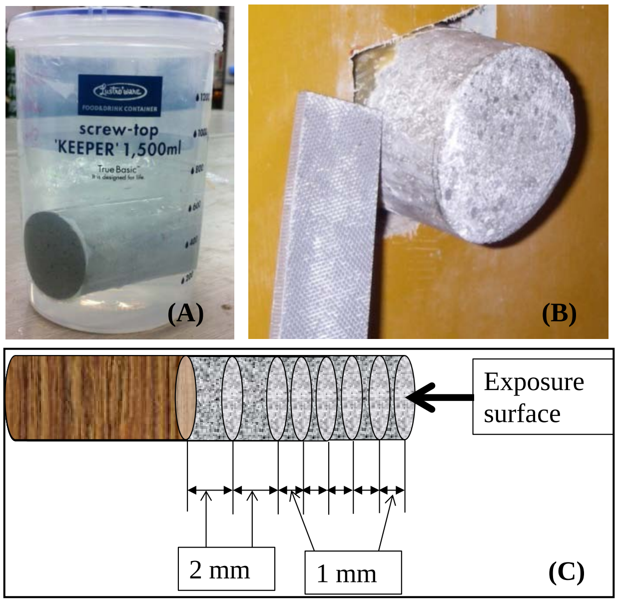

Fig. 1 Experimental setup: (A) An exposed sample to a solution; (B) Grinding of sample using file; (C) schematic representation of pitch for grinding.

2.2 Experiments

After 28 days of hydration, all the faces of cylinder sample were sealed with an epoxy resin except the bottom of circular face. They were then immersed in exposure solutions for a period of 9 months (Fig. 1 (A)). Five different exposure solutions were used: deionized water, 10 and 100 mmol/l Na_2SO_4, and 10 and 100 mmol/l $MgSO_4$. The liquid/solid volume ratio was 4 to 1. It is noteworthy that the solution was not changed during the exposure period of 9 months. After exposure test, epoxy was removed and the sample was ground, using file (Fig. 1 (B)), at different depth interval from the exposure surface to core of the specimen (Fig. 1 (C)). The collected powder samples were dried at 40℃ and 18 % RH for 24 hours before XRD measurement. The mineral composition was determined by XRD/Rietveld analysis.

3. EXPERIMENTAL RESULTS

3.1 Mineralogical distribution in OPCP

Solid phase changes in terms of weight percentage in the OPCP sample quantified by XRD/Rietveld analysis after 9 months immersion in various solutions are shown in Fig. 2 as a function of the depth. In the figure, x-axis indicates the average of the pitch from the exposed surface (Fig. 1 (C)). In addition to some un-hydrated cement, C-S-H which is quantified as amorphous, portlandite, ettringite, and monosulfate are the main products of hydrated OPCP. The amount of detected monosulfate, which is the main hydrate in the formation of ettringite as a result of sulfate ingress, is very small and the reduction of the hydrate cannot be notified in Fig. 2. As reported in ref. [4], AFm phases like monosulfate, determined by XRD are certainly underestimated owing their poor crystalline structure and lack of data concerning the structure. Further, uptake of Al by C-S-H would produce more amorphous and less monosulfate in XRD analysis. Therefore, it is difficult to provide information on the reduction of monosulfate due to sulfate ingress by XRD/ Rietveld analysis in this study.

The pictures of the exposed surface of OPCP after 9 months immersion in sulfate solutions are shown in Fig. 3. A notable expansion or damage in the sample immersed in 10 mmol/l Na_2SO_4 was not observed. The magnesium sulfate poses more serious surface deterioration than sodium sulfate, as reported previously [1-2]. Lower concentrated $MgSO_4$ solution (10 mmol/l) results less spalling at the exposed surface. The sample immersed in 100 mmol/l Na_2SO_4 or $MgSO_4$ solution show more severe damage at the exposure surface, and the identification of initial exposed surface is difficult (Fig. 3 (B) and Fig. 3 (D)). Therefore, in the XRD analysis, the most deteriorated part was brushed off and considered as depth zero.

In consistent with other studies [1-3], dissolution of portlandite is the main deterioration in cement-based materials contact with water. The dissolution of portlandite was observed up to 2 mm from the exposure surface for OPCP immersed in water (Fig. 2 (A)). Both dissolution of portlandite and precipitation of ettringite were observed when OPCP immersed in 10 and 100 mmol/l Na_2SO_4 solutions (Fig. 2 (B) and Fig. 2 (C)). These changes are agreed with other data reported in the literature [1-3]. However, gypsum formation was not observed upon ingress of Na_2SO_4. Secondary ettringite and dissolution of portlandite were observed

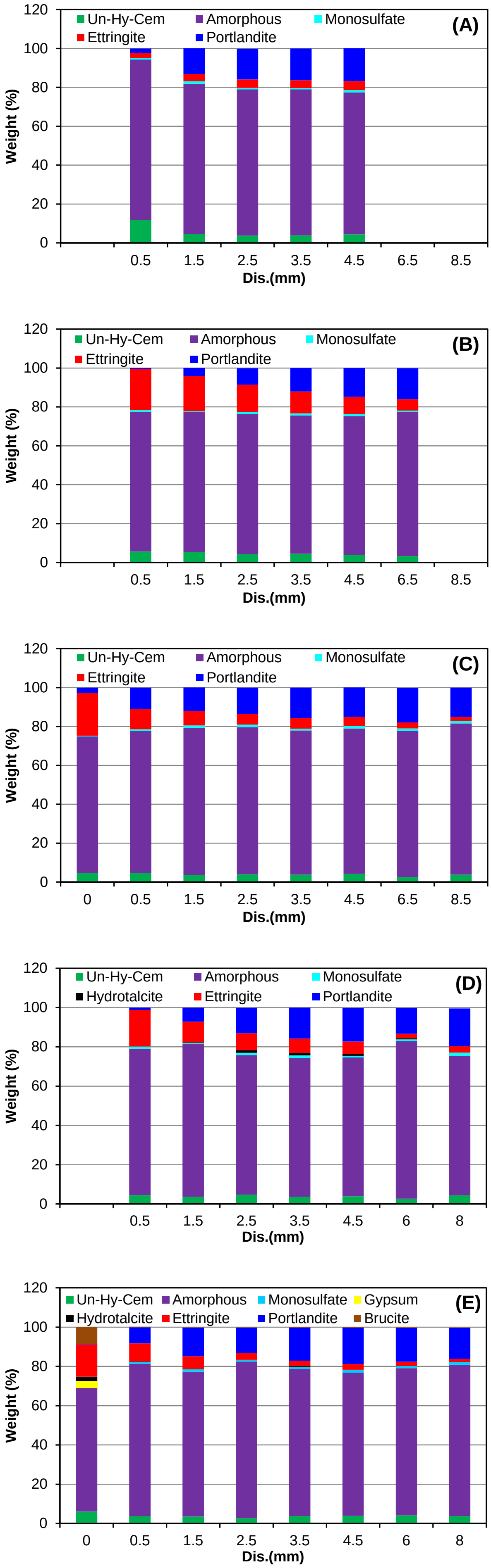

Fig. 2 Spatial distribution of solid phases deduced by XRD/Rietveld analysis in OPCP exposed to : (A) Water; (B) 10 mmol/l Na_2SO_4; (C) 100 mmol/l Na_2SO_4; (D) 10 mmol/l $MgSO_4$; (E) 100 mmol/l $MgSO_4$ for 9 months. Un-Hy-Cem: Un-hydrated cement.

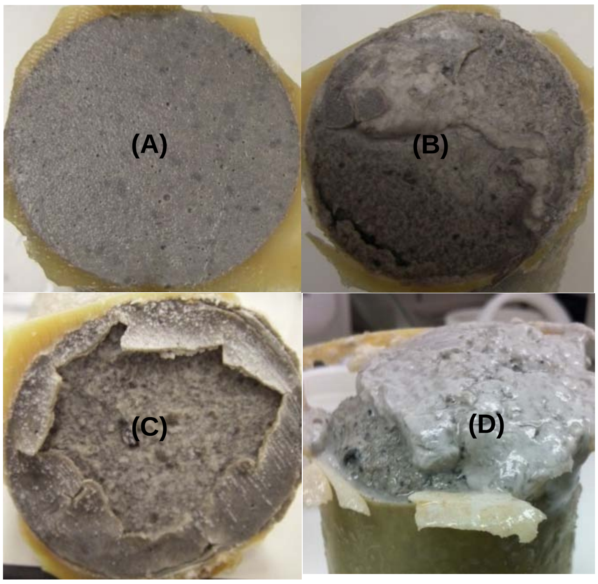

Fig. 3 Appearances of exposure surface of OPCP after 9 months in: (A) 10 mmol/l Na_2SO_4; (B) 100 mmol/l Na_2SO_4; (C) 10 mmol/l $MgSO_4$; (C) 100 mmol/l $MgSO_4$.

up to 5 mm for the sample in 10 mmol/l Na_2SO_4 solution (Fig. 2 (B)). The results indicate that the increase of ettringite and decrease of portlandite from core of the sample to the surface. In the sample immersed in 100 mmol/l Na_2SO_4 solution, the deteriorated part (depth zero which is explained in the previous paragraph) shows a large amount of secondary ettringite as well as the dissolution of portlandite and the reduction of amorphous (Fig. 2 (C)). The sample exposed to 10 mmol/l $MgSO_4$ showed the same sequence as observed in Na_2SO_4 solution except the detection of the hydrotalcite formation (Fig. 2 (D)). Comparing Fig. 2 (B) and Fig. 2 (D), ettringite formation and portlandite dissolution are higher for the sample contacted with Na_2SO_4 than that observed in $MgSO_4$. In the case of interaction with 100 mmol/l $MgSO_4$ solution, higher fraction of ettringite and brucite and a small amount of gypsum and hydrotalcite were observed in the damaged portion (depth zero). Further, the amount of amorphous is lower than that in inner layer.

3.2 Mineralogical distribution in SRPCP

The spatial distributions of solid phases for SRPCP in water and sulfate solutions are shown in Fig.4. The types of hydrated products in the unaffected core and the solid products formed as result of calcium leaching and sulfate ingress are the same as that was detected in OPCP. Fig. 4 (A) indicates that the dissolution of portlandite was observed up to 2 mm.

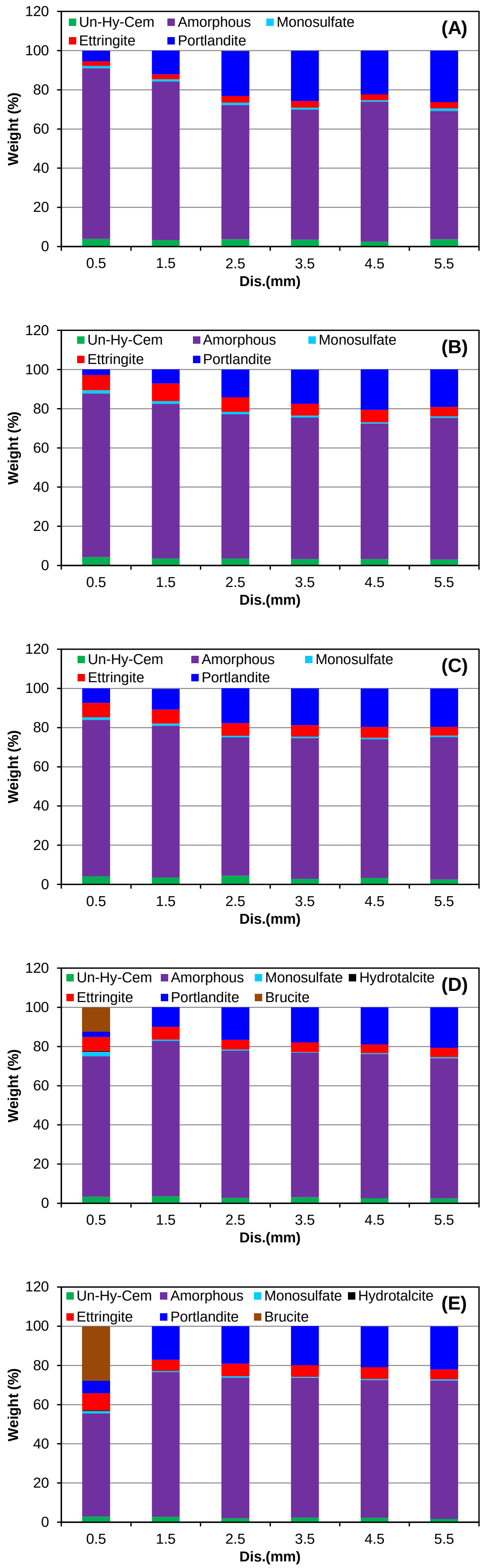

Fig. 4 Spatial distribution of solid phases deduced by XRD/Rietveld analysis in SRPCP exposed to : (A) Water; (B) 10 mmol/l Na_2SO_4; (C) 100 mmol/l Na_2SO_4; (D) 10 mmol/l $MgSO_4$; (E) 100 mmol/l $MgSO_4$ for 9 months. Un-Hy-Cem: Un-hydrated cement.

The low amount of secondary ettringite and no gypsum were obviously observed upon the ingress of Na_2SO_4 solution into SRPCP (Fig. 4 (B) and Fig. 4 (C)). For the samples exposed to both 10 and 100 mmol/l $MgSO_4$ solutions (Fig. 4 (D) and Fig. 4 (E)), the brucite precipitation was observed in addition to the other hydrated products at the outermost layer. High concentration of MgSO4 leads to form more brucite on the surface of SRPCP. As shown in Fig. 4, the associated cation in the sulfate solution does not seem to have any significant effect on the dissolution of portlandite or the precipitation of ettringite, but the reduction of amorphous was observed at the outmost layer for the samples in $MgSO_4$ solution.

3.3 Mineralogical distribution in GCP

The distributions of products for GCP in different exposure solutions as a function of depth are shown in Fig. 5. The addition of gypsum as a binder to cement changes its hydration reaction. Compared to OPCP or SRPCP, GCP produces more ettringite as a hydration product. Fig. 5 (A) shows that portlandite was completely dissolved at the outermost layer of GCP, and the portlandite dissolution was occurred up to 3 mm. A small amount of secondary ettringite was formed for the paste samples under sodium sulfate environments (Fig. 5 (B) and Fig. 5 (C)). Further, at high concentration (Fig. 5 (C)), gypsum formation was observed up to 2 mm which was not found in OPCP or SRPCP. There is no remarkable difference on the dissolution of portlandite for the paste immersed in pure water or Na_2SO_4 solution. The results show that C-S-H remains stable even after complete dissolution of portlandite at the outermost layer.

In the case of interaction with $MgSO_4$ (Fig. 5 (D) and Fig. 5 (E)), negligible level of ettringite formation was found as observed in Na_2SO_4 solution. Gypsum formation near the surface was observed for specimens exposed to both 10 and 100 mmol/l $MgSO_4$ solution. A significant distinction between two concentrations of $MgSO_4$ is the formation of brucite at the outermost layer and hydrotalcite precipitation at inner layer for the paste sample in 100 mmol/l $MgSO_4$ solution. Portlandite dissolution was not affected by the type of ions (Na_2SO_4 or $MgSO_4$) for the case of 10 mmo/l SO_4^{2-} (Fig. 5 (B) and Fig. 5 (D)). However, the paste specimens immersed in 100 mmol/l $MgSO_4$ (Fig. 5 (E)) show high dissolution of portlandite than that in 100 mmol/l Na_2SO_4 (Fig. 5 (C)) although the precipitation of brucite was found at the outermost layer of the sample in 100 mmol/l $MgSO_4$. The reduction of amorphous at the outermost layer in the sample immersed in 100 mmol/l $MgSO_4$ (Fig. 5 (E)) was observed.

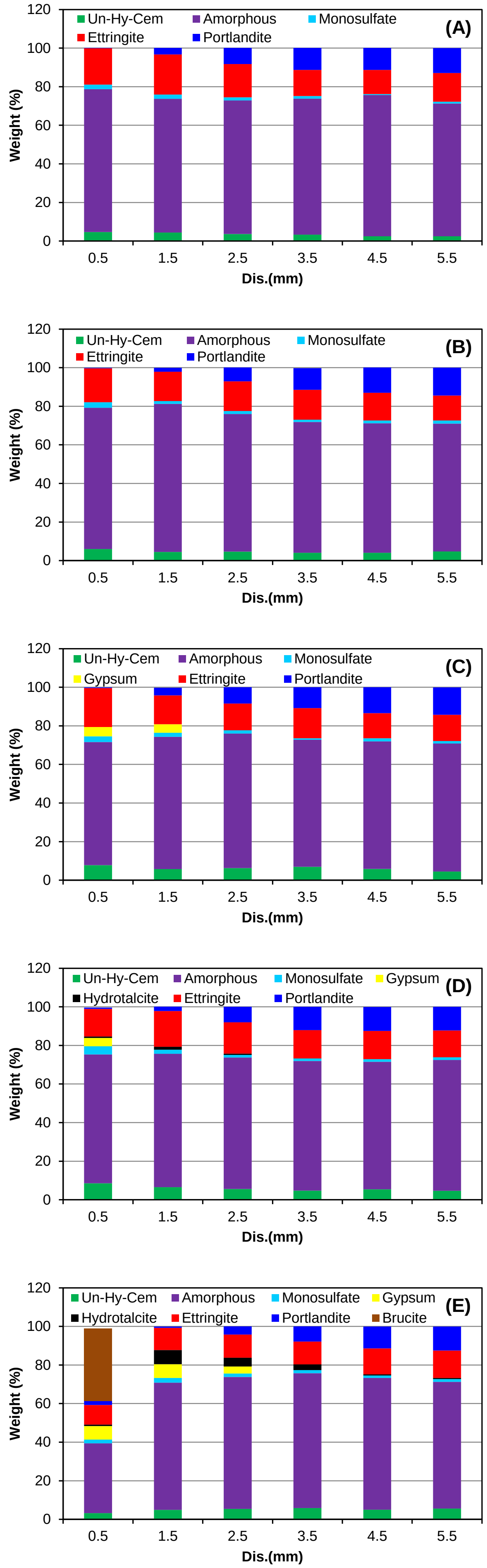

Fig. 5 Spatial distribution of solid phases deduced by XRD/Rietveld analysis in GCP exposed to : (A) Water; (B) 10 mmol/l Na_2SO_4; (C) 100 mmol/l Na_2SO_4; (D) 10 mmol/l $MgSO_4$; (E) 100 mmol/l $MgSO_4$ for 9 months. Un-Hy-Cem: Un-hydrated cement.

4. DISCUSSIONS

4.1 Influence of cement type on the resistance to calcium leaching in pure water

The reduction of amorphous in other words decalcification of C-S-H could not be observed for the specimens exposed to pure water (Fig. 2 (A), Fig. 4 (A), and Fig. 5 (A)). In the calcium leaching process, portlandite will dissolve first as its solubility is higher than other hydrates. In this study, the calcium leaching of cement paste in pure water is evaluated from the dissolution of portlandite. The percentage of total portlandite determined by XRD/Rietveld analysis as a function of depth for three types of cement paste immersed in pure water is shown in Fig. 6. Both OPCP and SRPCP show almost similar resistance to calcium leaching in water and the leaching front is up to 2 mm, whereas calcium leaching in GCP is severe. It is believed that the addition of gypsum as a binder to cement makes the cement matrix porous, thus enhances the calcium leaching.

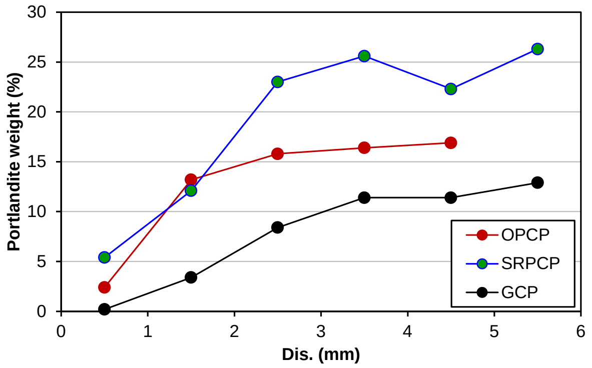

Fig. 6 Profiles of portlandite in different cement paste exposed to de-ionic water for 9 months

4.2 Influence of cement type on the resistance to sulfate attack

When sulfate ions penetrate into cement matrix, several reactions are taking place [3]. Sulfate ions react with portlandite and monosulfate to form ettringite and gypsum. The leached ions from portlandite and monosulfate have resulted to the formation of ettringite in the presence of transported sulfate ions. When portlandite is not available, C-S-H dissociates into silica gel and releases calcium ions for the formation of ettringite or gypsum. This dissolution process is controlled by the equilibrium between solid phases and pore solution. The initial ettringite resulting from hydration reaction depends on chemical composition of cement. Therefore, the secondary ettringite formed as a result of sulfate ingress is the difference between final and initial ettringite, where the initial value is average of it in the unaffected core. Fig. 7 shows weight percentage of secondary ettringite formed in the paste exposed to sulfate solutions. As expected, OPCP shows highest deterioration than SRPCP or GCP in sulfate solutions. The figure indicates that the type solution and the concentration have a significant impact on ettringite formation in OPCP. Interestingly, 10 mmol/l Na_2SO_4 solution causes more deterioration than other solutions, although the mechanism is unclear at the moment. Finally, experimental results show that GCP displays a similar or better resistance to sulfate attack than SRPCP.

5. CONCLUDING REMARKS

The effect of type of ions (Na_2SO_4 or $MgSO_4$) and the concentration (10 or 100 mmo/l) of the solution on the performance of three types of hydrated cement paste were investigated in this study. In pure water, the paste samples showed higher dissolution of portlandite near to the exposure surface, whereas C-S-H remains stable. The resistance to calcium leaching in pure water is: OPC ≈ SRPCP > GCP. The sulfate solution enhances the dissolution of portlandite. Type of associated cation with sulfate ions significantly influences deterioration of OPCP due to sulfate attack. The main sulfate attack mechanism for OPCP in Na_2SO_4 environment is the formation of ettringite, but not gypsum formation. In the lower concentrated sulfate solution (10 mmol/l), ettringite formation and portlandite dissolution are higher for OPCP immersed in Na_2SO_4 than those for the sample in $MgSO_4$. The formation of secondary ettringite is very limited in both SRPCP and GCP regardless of the type and concentration of sulfate solution. Partially replacing Portland cement with gypsum makes the cement system as highly sulfate-resistant.

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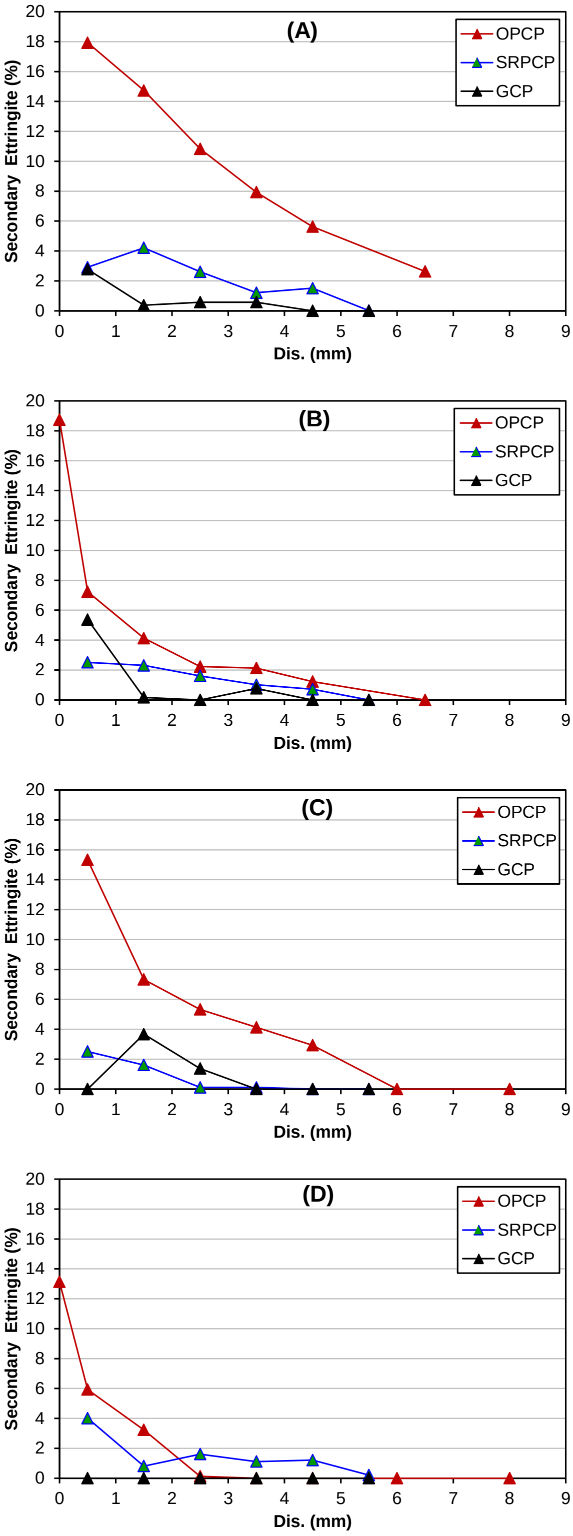

Fig.7 Profiles of secondary ettringite in different cement paste exposed to: (A) 10 mmol/l Na_2SO_4; (B) 100 mmol/l Na_2SO_4; (C) 10 mmol/l $MgSO_4$; (D) 100 mmol/l $MgSO_4$ for 9 months.