

EXPERIMENTAL AND MODELLING INVESTIGATIONS ON CEMENT PASTE EXPOSED TO LEACHING AND EXTERNAL SULFATE ATTACK

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1. INTRODUCTION

Extensive dissolution of cement hydrates increases porosity and transport characteristics and eventually loss of mechanical properties of the concrete structures. Degradation of cementitious materials due to dissolution plays an important role in the service-life of concrete structures. On the other hand, sulfate attack is an environmental issue for cement-based materials exposed to sulfate bearing groundwater or soils and threatens the durability of concrete structures. 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. Over the past couple of decades, an intensive work has been carried out on leaching and sulfate attack in cement-based materials [Scrivener & Skalny, 2004]. However, there are several uncertainties still exist regarding the mechanism for the damage of concrete in the environments. Therefore, more experimental and modelling works are necessary to understand the concrete damage in leaching and sulfate environments. In this study, a combined experimental and modeling work has been carried out to investigate the chemical degradation of cementitious materials in deionized water and various sulfate solutions.

2. MATERIALS AND METHODS

Ordinary Portland cement (OPC) and sulfate resistant Portland cement (SRPC) were used in this study. 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. The summary of the preparation of paste specimens is given in Table 1.

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, and the exposure solution was not changed during the exposure period. After exposure test, epoxy was removed and the sample was ground at different depth interval from the exposure surface to core of the specimen. The collected powder samples were dried at 40°C and 18 % RH for 24 hours before XRD measurement. The mineral composition was determined by XRD/Rietveld analysis.

A coupled model, developed by authors in a previous work, was used to investigate the leaching and external sulfate attack in cement paste (Elakneswaran & Ishida, 2012). To simulate the experiments, one-dimensional numerical analysis was performed and the necessary input parameters such as clinker composition, mix proportion and boundary conditions were the same as those adopted in experiments. As for multi-ionic transport, the main ions such as Na^+ , K^+ , SO_4^{2-} , Ca^{2+} , OH^- , Mg^{2+} , Al^{3+} , and $\text{H}_2\text{SiO}_4^{2-}$ were taken into account. To reproduce the conditions of exposure test in the simulation, analytical elements representing the exposure solution was considered (Figure 1). The elements of exposure solution were considered as dummy during the curing period of 28 days. The initial ($t=0$) concentration of ionic species in the sample is set to zero because they are automatically calculated during the analysis. The concentration of exposure solution was assigned as the initial concentration of ionic species in the solution elements at 28 days. Multispecies diffusion in both pore water and exposure solution was taken into account in this approach

Table 1 Summary of experimental program

Test series	OPCP	SRPCP	GCP
Materials	100 % OPC	100 % SRPC	90 % OPC: 10% Gypsum
W/C	0.5		
Chemical admixture	Thinkner (1% of water)		
Geometry	Φ 5 cm * 10 cm		
Curing period and condition	28 days sealed curing at 20°C and 60 % RH		
Exposure solution	<ul style="list-style-type: none"> • 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		

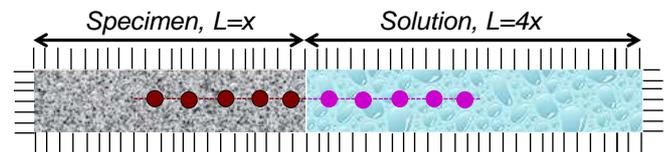


Figure 1 Schematic representation of mesh for analysis

Keywords: Sulfate attack, Leaching, X-ray diffraction (XRD), Solid phase changes, DuCOM, PHREEQC

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3. RESULTS AND DISCUSSIONS

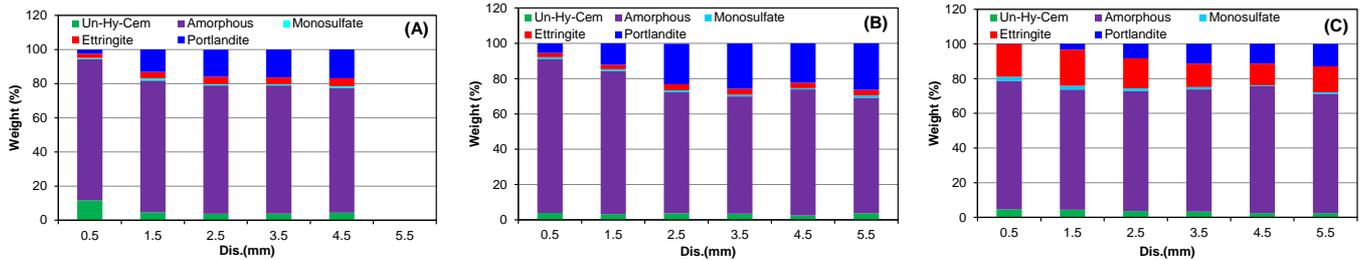


Figure 2 Spatial distribution of solid phases in: (A) OPCP; (B) SRPCP; (C) GCP, exposed to deionized water

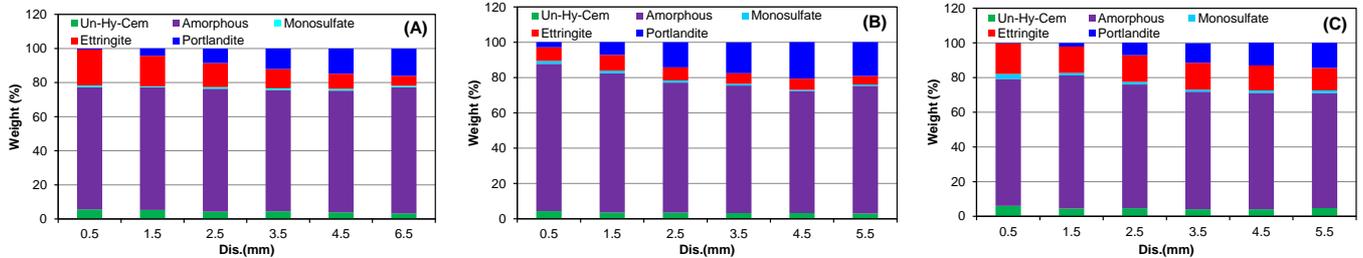


Figure 3 Spatial distribution of solid phases in: (A) OPCP; (B) SRPCP; (C) GCP, exposed to 10 mmol/l Na_2SO_4

Solid phase changes in terms of weight percentage for three types of paste in deionized water are shown in Figure 2 as a function of the depth. In the figure, x-axis indicates the average of the pitch from the exposed surface. The reduction of amorphous in other words decalcification of C-S-H could not be observed for the specimens exposed to deionized water. Thus, in consistent with other studies [1], dissolution of portlandite is the main deterioration in the paste contact with deionized water. Both OPCP and SRPCP show almost similar resistance to calcium leaching in deionized 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.

The distribution of products for the pastes in 10 mmol/l Na_2SO_4 solution is shown in Figure 3. Dissolution of portlandite and formation of ettringite were observed upon ingress of sulfate ions, but there is no gypsum formation. Sulfate solutions cause more dissolution of portlandite than deionized water for three types of paste. As expected, OPCP shows highest deterioration due to ettringite formation than SRPCP or GCP in sulfate solutions.

In this study, the OPCP specimens exposed to deionized water and sulfate solution were simulated by DuCOM-PHREEQC model. The simulation results in terms of volume percentage are shown in Figure 4. The dissolution of portlandite, as observed in experiment (Figure 2 (A)), is responsible for the deterioration of OPCP in deionized water, and the model qualitatively predicts the dissolution in the sample. Upon ingress of sulfate, the destabilization of portlandite and monosulfate and the precipitation of ettringite are predicted close to the sample surface (Figure 4 (B)). These changes are agreed with experimental determination (Figure 3 (A)). The simulation result shows a stronger leaching of portlandite near the sample surface for the paste interacting with sulfate solution than that observed in deionized water which agreed again with experimental observation.

4. CONCLUSIONS

The resistance to calcium leaching in deionized water is: $\text{OPC} \approx \text{SRPCP} > \text{GCP}$. The sulfate solution enhances the dissolution of portlandite. The main sulfate attack mechanism for OPCP in Na_2SO_4 environment is the formation of ettringite, but not gypsum formation. The formation of secondary ettringite is very limited in both SRPCP and GCP and thus, addition of gypsum as a binder increases the resistance of Portland cement systems to sulfate attack. Finally, the experimental observations and simulation results on mineralogical distribution of phases in OPCP were compared.

REFERENCES

- Elakneswaran Y & Ishida T. 2012. Coupled physical and geochemical model for external sulfate attack in concrete. JCI proceedings 34: 754-759.
- Scrivener, K & Skalny, J. 2004. International RILEM work-shop on internal sulfate attack and delayed ettringite formation. Proceedings pro035, RILEM publications.

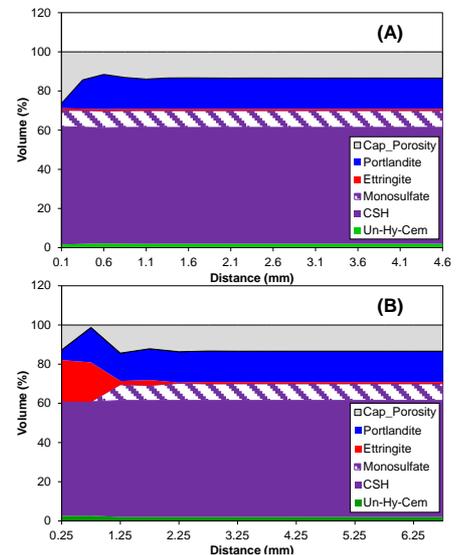


Figure 4 Predicted mineralogical distributions in terms of volume percentage for OPCP in: (A) deionized water; (B) 10 mmol/l Na_2SO_4