Deterioration of pastes exposed to leaching, external sulfate attack and the dual actions

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HIGHLIGHTS

- Deterioration of pastes under different aggressive conditions was investigated.
- Plain and blended cement pastes were immersed in different solutions.
- Compressive strength, mass and length changes and hardness were determined.
- Damage mechanisms of pastes under different conditions were characterized.

ARTICLE INFO

ABSTRACT

This paper is aim to clarify the deterioration of concrete exposed to leaching, external sulfate attack and the dual actions. Hardened plain and blended cement pastes with different w/b ratio (water to binder ratio) and fly ash (FA) contents, respectively, were exposed to $(NH_4)_2SO_4$, NH_4Cl and Na_2SO_4 solutions. Compressive strength, linear expansion, mass variation and Vickers hardness on the cross sections were determined. SEM, EDS and XRD were used to analyze the degradation mechanism of pastes under different exposure conditions. Results showed that, the deterioration of the specimens varied between different pastes and exposure conditions. The most serious damage was observed on the specimens exposed to the $(NH_4)_2SO_4$ solution with dually corrosive actions. Deterioration of pastes was accelerated as the increase of w/b ratio. The addition of a suitable quantity of fly ash could retard the degradation rates of pastes under leaching and/or sulfate attack to some extent. The specimens under NH_4Cl condition mainly suffered from softening of matrix due to leaching. For specimens with Na_2SO_4 attack, volumetric expansion caused by the formation of gypsum and gypsum was the primary chemical attack mechanism. While in the cases of $(NH_4)_2SO_4$ attack, specimens suffered from both softening and expansion of pastes.

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1. Introduction

Chemical corrosion is one of the most significant elements which affect the durability of concrete [1–3]. Owing to the solubility and alkalinity of calcium hydrate in concrete, as well as the porosity of concrete, degradation will easily occur when concrete is exposed to aggressive solutions [4,5]. Different aggressive solutions lead to different damage in concrete. Both leaching and external sulfate attack are the most two concerned chemical attacks on concrete [6–9]. The mechanisms of both leaching and external sulfate attack can be described as a diffusion-reaction process when concrete is under environments with low pH or sulfate.

For instance, during the leaching procedure, Ca^{2+} ions dissolve in pore solution mainly from $Ca(OH)_2$ and/or C-S-H gel and diffuse outwards into aggressive solutions with low pH values [10–12]. While for sulfate attack, the primary process is SO_4^{2-} ions penetrate into concrete from aggressive solutions and react with cement hydrates to generate ettringite and gypsum [13,14]. It has often been considered that the former causes softening and the latter results in expansion, both of which lead to the deterioration of concrete at last.

Numerous investigations have been done by scientists on sole leaching or sole external sulfate attack on concrete. For example, leaching can reduce compressive strength and stiffness of concrete, however, the ductility increases as a result of pore structure variation [15–21]. The cross section of leached specimen can be constituted of different zones which are delimited by Vickers hardness profiles, different dissolutions or precipitation fronts [10,11]. For

sulfate attack, considerable efforts have been devoted to establish models that can be used to predict the deterioration process of concrete exposed to external sulfate attack [13,22–24]. The influences of Na_2SO_4 and $MgSO_4$ on the deterioration process of concrete with mineral admixtures have been investigated [25–27].

Generally, the ions considered to be aggressive to concrete can be divided into two groups, anion and cation group. The aggressive anions usually contain Cl^-, SO_4^{2-} and HCO_3^-, in which SO_4^{2-} is the cause of expansion and swelling by the formation of ettringite and gypsum in concrete. The most important aggressive cations are Mg^{2+}, Fe^{2+}, NH^+ and H^+, where NH^+ and H^+ may cause the softening of concrete due to the desorption of Ca^{2+} by the formation of volatiles or hydroxide [28,29]. When concrete constructions are exposed to solution with both SO_4^{2-} and NH^+ or H^+, more serious damage of concrete may occur than those under sole chemical corrosion. This is due to the mutual promotion of leaching and external sulfate attack accelerates the deterioration of concrete. The degradation mechanisms of concrete exposed to the couple of leaching and external sulfate can be simply considered as two stages. The first stage is the dissolution of cement hydrates, mainly portlandite, and the ingress of sulfate ions, in which softening of concrete firstly occurs. In the second stage, ettringite or/and gypsum form and cause expansion in concrete [30]. Many concrete constructions, mainly in mining industry, nuclear industry and chemical industry, are serviced in the solutions with multiple aggressive ions, which may lead to dual or multiple damage to concrete. For instance, in China, $(NH_4)_2SO_4$ is widely used in rare earth (RE) mining industry. 30% of the $(NH_4)_2SO_4$ is left in soil, which is strongly corrosive to concrete constructions [31]. Up to now, few reports have been done on the deterioration process of concrete exposed to dual actions of leaching and external sulfate attack. However, for a practical engineering, the leaching coupled with external sulfate attack often occur more commonly in concrete than any of the sole corrosion. So it is very important to clarify the degradation mechanisms of concrete under such conditions.

In this paper, a solution with $(NH_4)_2SO_4$ was chosen as an aggressive solution to investigate the deterioration of concrete exposed to dual actions of leaching and external sulfate attack. To study the difference between sole chemical corrosion and coupled chemical corrosions, NH_4Cl and Na_2SO_4 solutions were chosen as the contrastive aggressive solutions. Six groups of mixture were prepared to study the influences of w/b ratio and fly ash on deterioration of pastes exposed to the mentioned conditions. Compressive strength, linear expansion, mass variation and Vickers hardness on the cross sections of the specimens under different aggressive conditions for different exposure durations were determined. In addition, X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Energy Dispersive Spectrometer (EDS) were used to analyze the mechanisms of degradation on pastes exposed to leaching, external sulfate attack and the couple of them.

2. Experiments

2.1. Materials and mixtures

The cement used was P. II 42.5 (GB 175-2007) Portland cement, and the fly ash was Class I FA. Chemical compositions of the cement and fly ash are given in Table 1. The loss on ignition of fly ash was 4.81 wt.%. The proportions of cement paste mixtures with and without fly ash are listed in Table 2. Plain cement paste mixtures were prepared with w/b ratios of 0.35, 0.45 and 0.55, referenced PC1, PC2 and

Table 2
Proportions of paste mixtures and exposure conditions.

Ref. No.	Cement (%)	Fly ash (%)	w/b	Exposure conditions
PC1	100	0	0.35	5 wt.% $(NH_4)_2SO_4$
PC2	100	0	0.45	5 wt.% NH_4Cl, 5 wt.% Na_2SO_4, 5 wt.% $(NH_4)_2SO_4$
PC3	100	0	0.55	5 wt.% $(NH_4)_2SO_4$
FA10	90	10	0.45	5 wt.% $(NH_4)_2SO_4$
FA30	70	30	0.45	5 wt.% $(NH_4)_2SO_4$
FA50	50	50	0.45	5 wt.% $(NH_4)_2SO_4$

PC3, consulting the common ranges of concrete mix proportion in actual engineering. They were designed to study the influence of w/b ratio on degradation of concrete due to leaching coupled with external sulfate attack. The referenced mixes FA10, FA30 and FA50 were designed with a constant w/b ratio of 0.45 to investigate the influence of fly ash on deterioration of pastes under leaching and external sulfate attack. The Table 2 was designed keeping the binder weight (cement + fly ash weight) constant.

2.2. Experimental procedures

For all the paste mixtures, $\phi 50 \times 100$ mm^3 circular cylinder specimens and $2 \times 2 \times 280$ mm^3 prismatic specimens were cast and sealed cured for 24 h. After curing for 28 days in saturated limewater, the specimens were coated on the two end surfaces with epoxy resin before exposure. Then, all samples were immersed in solutions with concentration of 5 wt.% $(NH_4)_2SO_4$ (36.4 g/L SO_4^{2-} and 12.6 g/L NH_4^+). To investigate the differences between sole leaching, sole sulfate attack and the dual actions of leaching and sulfate attack, another two groups of PC2 specimens were stored in solutions with 5 wt.% NH_4Cl (9.8 g/L NH_4^+) and 5 wt.% Na_2SO_4 (33.8 g/L SO_4^{2-}). The different exposure conditions for different cement pastes were indicated in Table 2. For all the aggressive solutions, the preparation procedures were weighting the sulfate salts and water in a certain proportion, mixing them up and stirring the mixtures untill the salts are fully dissolved. The aggressive solutions were renewed every month to keep the pH value and the concentrations of NH^+ and SO_4^{2-} constant. In addition, a group of specimens were left in the limewater for comparisons.

Subsequently, at each period of time (30, 60, 90, 150, 210, 270, 360 and 540 days), three parallel samples were removed to measure the expansion, mass and the mechanical behavior. Subsamples with sizes of $\phi 50 \times 10$ mm^3 and $\phi 50 \times 50$ mm^3 were cut from the $\phi 50 \times 100$ mm^3 specimens with a cutting machine. The compressive strength was tested on $\phi 50 \times 50$ mm^3 specimens with an Electric Universal Testing Machine with a maximum capacity of 100 kN. The $\phi 50 \times 10$ mm^3 thin specimens were used to determine Vickers hardness by Micro-hardness Tester HDX-1000TC. Vickers hardness was tested every 2.5 mm from the exposed surface to the interior on the cross sections. The test force was 0.9807 N, keeping 10 s. Eight values of Vickers hardness uniformly distributed on a circle with the same depth from the exposed surface of each sample were tested. Remove the maximum and minimum values, and then take the average of the rests as the representative value of Vickers hardness with a certain depth of the sample. The final data of Vickers hardness was the average of the three parallel samples. The expansion and mass variation was determined on $2 \times 2 \times 280$ mm^3 prismatic specimens with gauge studs with length comparators and electronic balances. At the exposure time of 360 days, deteriorated material was sampled and analyzed using X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Energy Dispersive Spectrometer (EDS) in order to identify the phases present. XRD test was carried out on powder samples taken from the deteriorated portion of the immersed specimens. The samples were dried and grounded to pass a 200 μm sieve before testing. Cu-Kα radiation with a wave length of 1.54 Å was conducted at a voltage of 40 kV. The scanning speed was 2°/min at a current of 35 mA. For SEM and EDS tests, samples were prepared by cutting specimens from the deteriorated portion, dried using an oven and then coated with gold before testing.

3. Results and discussion

3.1. Visual appearance

Fig. 1 showed the visual appearances of plain cement samples immersed in different solutions for 150 days. To clarify the reasons

Table 1
Chemical compositions of cementitious materials (wt.%).

Compn.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	MnO	P_2O_5
Cement	21.74	6.32	4.32	62.62	1.02	2.18	0.41	0.97	0.13	0.11	0.08
FA	46.45	30.35	3.98	3.18	6.38	0.40	0.61	1.37	1.19	0.09	0.58