

Effect of Limestone Powder on Acid Attack Characteristics of Cement Pastes

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crossref <http://dx.doi.org/10.5755/j01.ms.20.4.6231>

Received 17 January 2014; accepted 10 September 2014

The acid resistance of cement pastes containing limestone powder with two different water-binder (w/b) ratios exposed to acetic (pH = 4) and sulfuric acid (pH = 2) solutions respectively were investigated in this paper. Limestone powder, fly ash and silica fume were also added to the cement paste mixture at different proportions. Static and flowing aqueous environments were set in this experiment. Strength and microstructure of the pastes after acid attack were investigated by using strength test, X-ray diffractometer (XRD) and scanning electron microscopy (SEM). The experimental results show that the erosion degree depends not only on pH value of the solution and w/b ratio of the pastes, but also on the content of limestone powder. Acetic acid reacts with calcium hydroxide and carbonate thus dissolving the pastes, while sulfuric acid consumed calcium hydroxide, and generated gypsum and ettringite. The consumption of calcium hydroxide in the flowing solution group is higher than that in the static solution because the flowing sulfuric acid solution has negative effect upon the gypsum crystallization. Fly ash and silica fume are beneficial to limestone cement paste because of the less calcium hydroxide formation, which is among the hydrates vulnerable to acid erosion.

Keywords: cement paste; acid attack; limestone powder; strength; microstructure.

1. INTRODUCTION

Concrete, as the most widely used building material, plays a significant role in civil engineering, especially in developing countries. Its deterioration is a key issue regarding to concrete members' durability and service life due to high cost for maintenance [1]. The acidic materials falling with rain in the developed industrial districts, the chemical waste flowing in the sewage systems, and the complicate solutes in the marine environment are all the sources of acidic deterioration for civil buildings, bridge decks and piers, and concrete sewage pipes [2]. Portland cement concrete is vulnerable to acid erosion because of its high content of alkaline hydrates. In recent years, Portland cement concrete often incorporates supplementary cementing materials (SCMs) due to various benefits. Fly ash, slag and silica fume could exhibit filling effect, nucleation effect and pozzolanic effect [3]. Dense microstructure and reduced $\text{Ca}(\text{OH})_2$ are the main reasons accounted for the durability improvement. The use of fly ash and silica fume will contribute to a better chemical resistance of concrete than other SCMs.

Limestone powder as another SCM was massively produced and used in European and Latin-American for the past decades [4]. Portland limestone cements containing up to 35 % limestone powder is identified in European standard EN 197 [5]. Besides, application of Portland limestone cement in China is becoming wide [6] and Chinese standard GB 175-2007 permits certain amounts of limestone powder as inert mineral mixture in Portland cement [7]. Limestone powder can improve properties of concrete, decrease cost and reduce carbonous

gas emissions during cement and concrete preparation [8]. Limestone powder has filling effect, active effect and accelerating effect during hydration process of complex binder. It has little pozzolanic activity, but the filling effect can improve the pore structure of paste and increase the compactness and strength [9, 10]. The improvement in strength is essentially the same for all non-pozzolanic filler increasing with its fineness. Limestone powder also delays the transformation of ettringite to monosulfate, while forms calcium aluminate monocarbonate hydrates at early age [11, 12]. Nowadays, more focus has been concentrated on sulfate attack on concrete containing limestone powder. Limestone powder can improve sulfate resistance of mortars [13] while the limestone cement paste behaves worse than pure Portland cement paste [14]. The different effects depend on the replacement ratio, the clinker structure and the sulfate solutions [15]. Compared to sulfate resistance of limestone cement pastes studies, less attention has been paid to its acid attack resistance. Different with fly ash and silica fume, whose chemical compositions are mainly SiO_2 and Al_2O_3 , the main composition of limestone powder is calcium carbonate, CaCO_3 , which is easily to be suffered from acid attack.

In this paper, Portland limestone cement pastes with different mix proportions were prepared, and immersed in acetic acid solution and sulfuric acid solution (pH = 2) respectively. Besides the normal static acid solution, a rotated device was set to create a similarly flowing aqueous environment. Strength and microstructure of pastes after different attack periods were investigated by strength test, XRD and SEM analysis.

2. EXPERIMENTAL

The raw materials consist of ordinary Portland cement P.O.42.5 (GB175-2007), limestone powder, fly ash and

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Table 1. Chemical compositions of SCMs (mass, %)

Materials	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	SO ₃	R ₂ O	K ₂ O	Na ₂ O	TiO ₂	MnO	P ₂ O ₅	Loss
Limestone powder	1.79	0.56	54.69	0.35	0.4	0.03	0.06	–	–	–	–	–	41.93
Fly ash	61.30	24.10	2.20	3.79	1.43	1.39	–	3.00	0.42	0.87	0.05	0.15	3.60
Silica fume	93.42	0.41	0.47	0.56	0.48	0.40	–	–	–	–	–	–	3.60

silica fume. Limestone powder with CaCO₃ content of 95 % was produced from carboniferous limerock. Its density, specific surface area and water demand are 2.69 g·cm⁻³, 457.9 m²·kg⁻¹ and 98 % respectively. And the chemical compositions of SCMs are listed in Table 1.

Laser particle analyzer was adopted to measure the particle size distribution of Portland cement, limestone powder and fly ash (Fig. 1). Apparently, compared with cement and fly ash, the particle size of limestone powder is much smaller and its dominant particle size is below 5 μm.

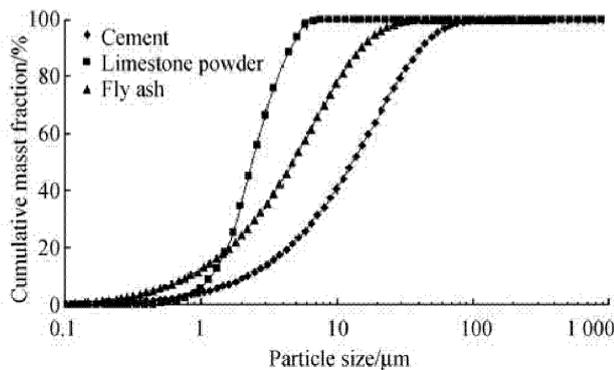


Fig. 1. Particle size distributions of cement, limestone powder and fly ash

Ten different mix proportions were designed to study the effect of limestone powder on acid attack resistance of pastes including two water-binder ratio, i.e., 0.3 and 0.5, (Table 2).

Table 2. Mix proportion of the cement pastes

sample	water	cement	limestone powder	fly ash	silica fume
L-1	0.3	1.0	0	0	0
L-2	0.3	0.7	0.3	0	0
L-3	0.3	0.5	0.5	0	0
L-4	0.3	0.5	0.25	0.25	0
L-5	0.3	0.5	0.4	0	0.1
H-1	0.5	1.0	0	0	0
H-2	0.5	0.7	0.3	0	0
H-3	0.5	0.5	0.5	0	0
H-4	0.5	0.5	0.25	0.25	0
H-5	0.5	0.5	0.4	0	0.1

Cubic specimens (2×2×2 cm³) were cast. After molding for 24 hours, the pastes were removed from the molds and then placed for standard curing till 28 days when their strength was tested as reference. All procedures were conducted according to test code GB/T17671-1999. Thereafter they were immersed in acetic acid solution (pH = 4) and sulfuric acid solution (pH = 2). Compressive strength of the specimens was measured at 1, 3, 7, 14 and

28 days. In order to investigate the degradation mechanism, broken pieces of the specimens were examined by SEM and XRD to analyze their microstructure development.

3. RESULTS AND DISCUSSION

3.1. Strength

The compressive strength of the pastes soaked in static and dynamic acid solutions for different time are shown in Figs. 2–5 and Figs. 6–9, respectively. It decreases with the increase of w/b ratio and the content of limestone powder correspondingly. But incorporation of fly ash and silica fume mitigates the decline. The pozzolanic effect of these SCMs reduces the presence of calcium hydroxide and permeability of pastes. Thus the acid attack resistance improves. Figs. 2–3 show the strength decreases at the beginning because calcium hydroxide and calcium carbonate reacted with the acetic acid and the product, calcium acetate, leaches out. Then unhydrated cement particles continue their hydration and leads to a slight recovery of strength.

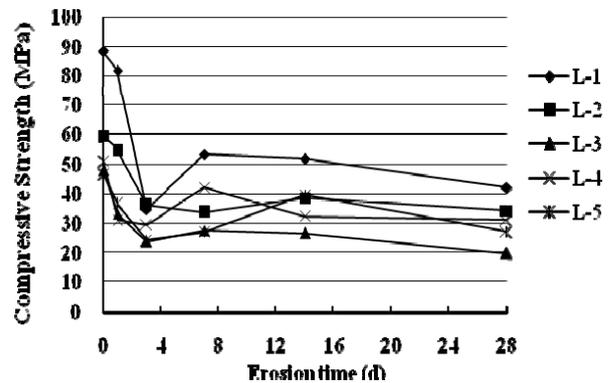


Fig. 2. Paste strength under static acetic acid attack condition

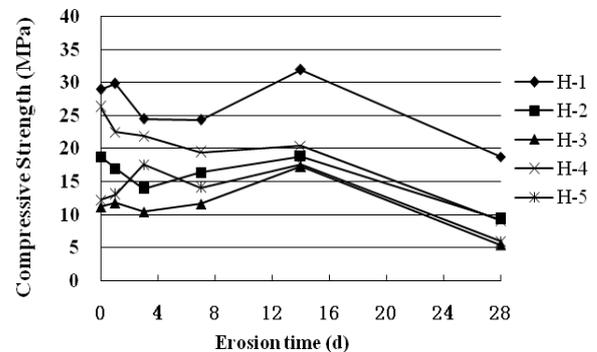


Fig. 3. Paste strength under static acetic acid solution condition

With further attack into the interior, more calcium hydroxide and calcium carbonate are consumed. Hydration products decompose owe to the destruction of the requisite alkaline environment, hence the strength descends again.

In Figs. 4–5 during early stage the strength decreases because calcium hydroxide and calcium carbonate react with the sulfuric acid. Analogous with the acetic acid attack, the hydrates leache out and the microstructure is damaged. Then unhydrated cement particles' proceeding hydration and the expansive formation of gypsum contribute to the slight strength recovery. This conclusion can be drawn from Figs. 4 and 8. Except these two figures, strength of pastes containing the highest limestone powder content (L-3, H-3) is the lowest. While in Figs. 4 and 8, strength recovery is so strong that it surpasses L-4 and L-5 groups. It is not only owing to continuing hydration but also the expansive formation of generated gypsum. As the limestone powder content in L-3 and H-3 is the highest, the generated gypsum from reaction between CaCO_3 and sulfuric acid is most. This can be found from comparisons of Figs. 2 vs. 4, Figs. 6 vs. 8. In acetic acid solutions, only continuing hydration is insufficient to recover the strength. But in sulfuric acid solutions, gypsum plays an important role of strength recovery. Nevertheless, for the high w/b ratio group in sulfuric acid solutions (Figs. 5 and 9), strength recovery is not as strong as the low w/b group (Figs. 4 and 8). This is possibly due to the more open pore structures of paste where attack under strong acid (sulfuric acid, $\text{pH}=2$) is more intense, which contradicts the expansive effect of gypsum formation.

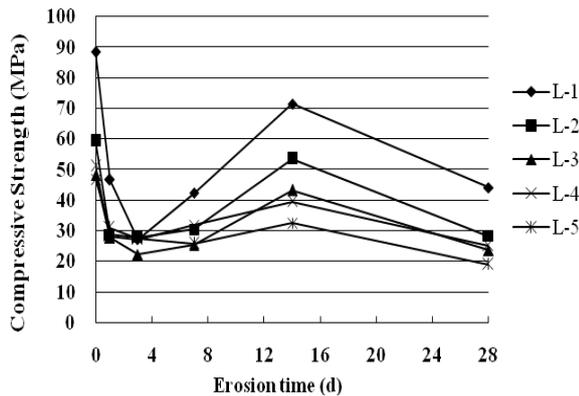


Fig. 4. Paste strength under static sulfuric acid attack condition

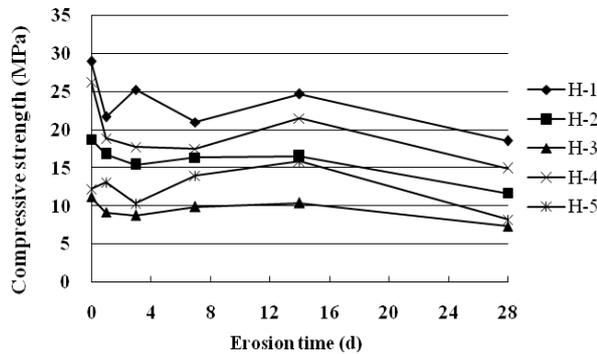


Fig. 5. Paste strength under static sulfuric acid attack condition

In comparison with the static acetic acid attack (Figs. 2 and 3), compressive strength of pastes ($w/b = 0.3$) exposed to the dynamic acetic acid solution (Figs. 6 and 8) apparently recovers more because the flowing liquid promotes the continued hydration. Besides, it can be found from the contrasts of Figs. 3 vs. 7, Figs. 5 vs. 9 that for high

w/b ratio ($w/b = 0.5$) groups, the time points when the highest strength recovery occurs are brought in advance for about a week. This may be attributed to more open pore structure which provides path for the water in the solution to enter into the paste for faster continuing hydration than the low w/b ratio group (Figs. 2 vs. 6, Figs. 4 vs. 8). Comparing Figs. 4 and 8 with Figs. 2 and 6, unlike the acetic acid attack, the difference of strength developments between static and dynamic sulfuric acid solution isn't obvious. As is explained previously, generated gypsum should account for the strength recovery. So the dynamic solutions environment may have a inhibiting effect upon the gypsum crystallization. Besides, in general, strength recovery is more obvious in low w/b ratio groups than the high ones where there is already more water for cement hydration before the pastes are put into the acid solutions. So the strength developments of high w/b ratio groups don't differ much.

Limestone powder is usually incorporated into the cementing materials as fillers because of its low reactivity. The advantages it brings to the concrete mixtures are its excellent filling effect and reduction of water demand. As mentioned above, the amount of limestone powder put into the concrete is normally restricted. But from the compressive strength developments displayed in the above figures, it is clear that limestone powder doesn't exacerbate the deteriorations under the acid attacks. For pastes ($w/b = 0.3$) in the acetic acid solutions (Fig. 2 and Fig. 6), the severest strength loss, about 50 MPa, both comes from the control groups (L-1, H-1), while that of the limestone pastes is no more than 30 MPa. For pastes ($w/b = 0.5$) in the acetic acid solutions (Fig. 3 and Fig. 7), strength loss of control group is about 10 MPa and the severest loss, about 15 MPa, happens on group H-4 (Fig. 3). Strength losses of the remaining groups range from 5 MPa to 10 MPa. The strength loss situation is similar for the pastes in the sulfuric acid solutions. Take the highest limestone powder content group (H-3) for example: although the compressive strength is the lowest, the pastes never experience the greatest strength loss. Besides, the calcium carbonate, the main composition of limestone powder, still exists under the acid attacks and the acid is more readily to react with calcium hydroxide first, which will be seen in the below calcium carbonate peaks of XRD results. In this way, although providing no strength contribution, limestone powder plays the role of filling in the paste mixture to improve the microstructure to prevent from great damage in the acid solutions.

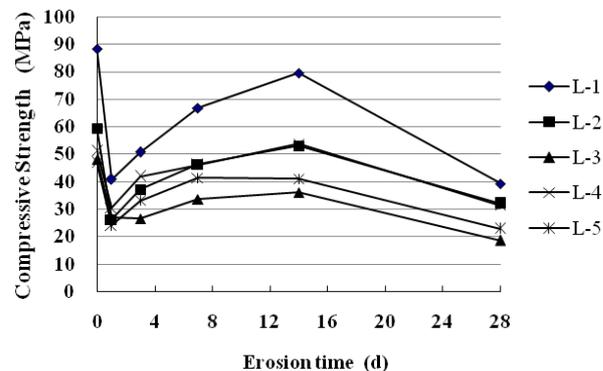


Fig. 6. Paste strength under flowing acetic acid attack condition

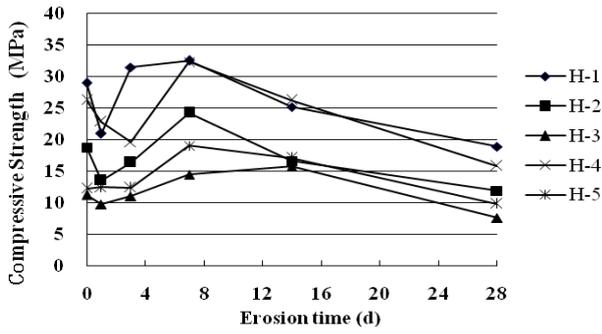


Fig. 7. Paste strength under flowing acetic acid attack condition

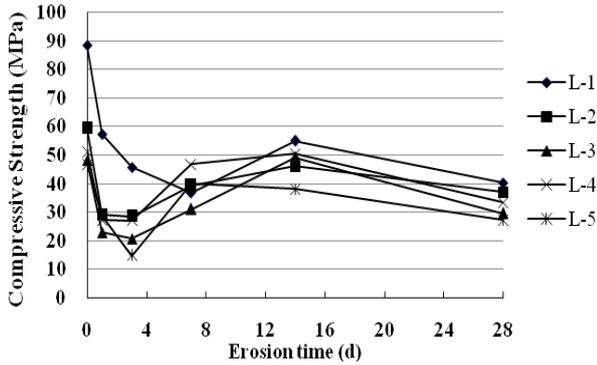


Fig. 8. Paste strength under flowing sulfuric acid attack condition

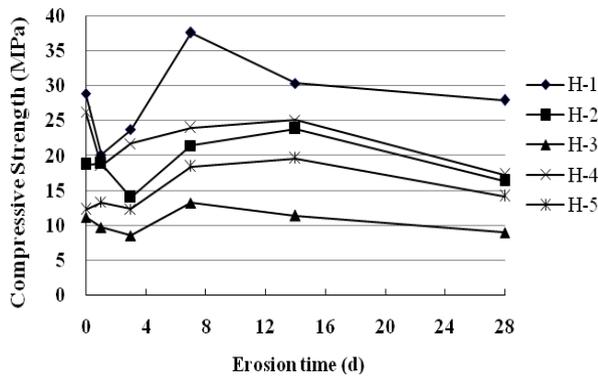


Fig. 9. Paste strength under flowing sulfuric acid attack condition

3.2. XRD analysis

The XRD patterns of specimens ($w/b = 0.5$) soaked in acetic ($pH = 4$) and sulfuric ($pH = 2$) acid solutions at 28 days are depicted in Figs. 10–13. From Figs. 10 and 12, it can be seen that the XRD patterns of hydrates of pastes exposed to static and dynamic acetic acid solutions are nearly the same. There are mainly two peaks: calcium carbonate and calcium hydroxide. The higher the content of limestone powder, the higher the calcium carbonate peak. Calcium carbonate peak is much higher than calcium hydroxide peak because calcium hydroxide is consumed by acetic acid while calcium carbonate is not consumed by acetic acid entirely. It can be seen the acid is more likely to react with calcium hydroxide first. So the destruction of alkaline is the main reason for the deterioration. Figs. 11 and 13 depict the results in sulfuric acid solutions. Calcium hydroxide peak is very low in both figures because it is consumed by sulfuric acid. Comparing the two figures, calcium carbonate peak is far lower in static sulfuric acid

solutions than that in dynamic solutions, on the contrary, the gypsum peak is on the other way round. This indicates in static solutions, sulfuric acid reacts with calcium carbonate and forms much gypsum. While in dynamic solutions, the flowing sulfuric acid doesn't consume calcium carbonate but only reacts with calcium hydroxide. However, the conclusion that gypsum is formed only from the reaction between carbonate and sulfuric acid is not right. As shown in Fig. 11, gypsum peak also appears in the control group where there is no limestone powder in the paste. From this perspective, the dynamic aqueous environment not only inhibits the reactions between sulfuric acid and calcium carbonate, but also exerts an inhibiting effect on gypsum crystallization. It demonstrates the corresponding explanation at the strength analysis. In addition, the calcium hydroxide peak in the flowing acetic acid solutions (Fig. 12) is higher than that in the static acetic acid solutions (Fig. 10). This difference also appears in the sulfuric solutions (Figs. 11 and 13). It reveals the dynamic aqueous acid attack is not as intense as static aqueous. Maybe reactions between the flowing acid solutions and pastes are not as sufficient as the static solutions for the attacking ions are not readily to penetrate inside the pastes. The different calcium carbonate peaks in Figs. 11 and 13 is another relevant phenomenon.

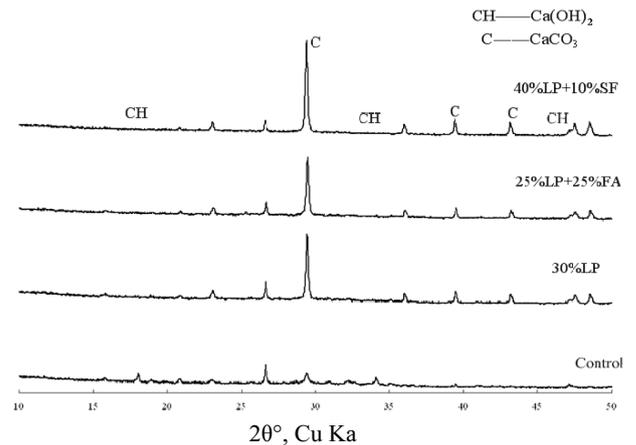


Fig. 10. XRD patterns of cement pastes under static acetic acid attack condition

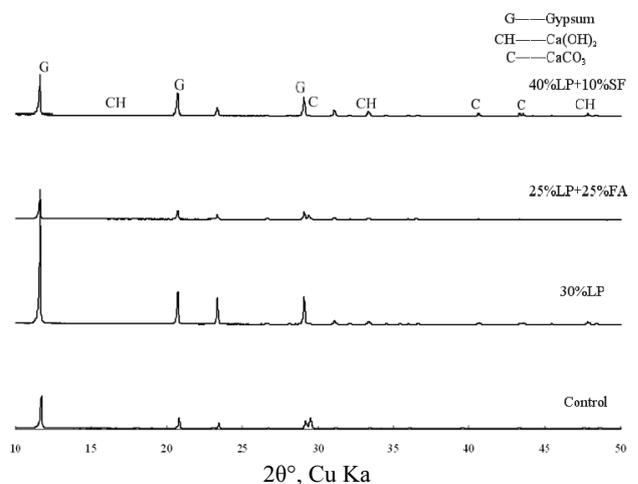


Fig. 11. XRD patterns of cement pastes under static sulfuric acid attack condition

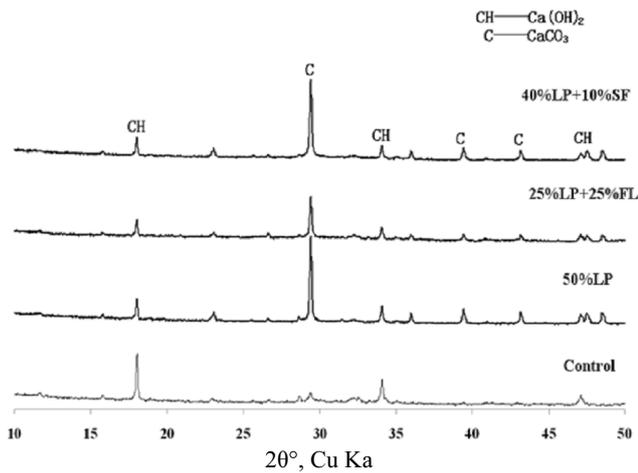


Fig. 12. XRD patterns of cement pastes under flowing acetic acid attack condition

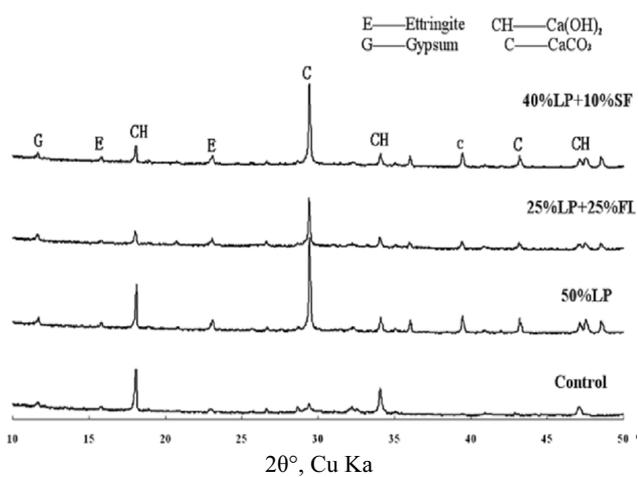


Fig. 13. XRD patterns of cement pastes under flowing sulfuric acid attack condition

3.3. SEM analysis

Fragments of specimens broken off and washed by acetone were examined by SEM. The grey and dark districts in all pictures reveal the loose microstructure of the acidic eroded pastes. Fibrous shape calcium silicate hydrates (Figs. 14 and 15) and granular shape calcium silicate hydrates (Figs. 16 and 17) are the main hydration product. In Fig. 14, the characteristic spherical calcium carbonate particles with eroded surface can be found. This is consistent with the obvious calcium carbonate peak in the XRD test result (Fig. 10). In the static aqueous solutions (Fig. 14 and 15) no calcium hydroxide is photographed while in the dynamic aqueous solutions (Fig. 16) calcium hydroxide layers are found adhered to the other hydrates. This difference under two acid attack environments, which indicates calcium hydroxide is consumed more in static acid solutions than in dynamic acid solutions, is also displayed in the XRD calcium hydroxide peaks. As for the pastes in static sulfuric acid solutions, much granulous quadrangular gypsum crystals, product of the reaction of sulfuric acid and calcium hydroxide, are found amid the hydrates. This is in conformity with the apparent gypsum peak shown in XRD result (Fig. 11). Moreover, for pastes in the dynamic sulfuric acid solutions, layered gypsum crystals are found

to be piled together in Fig. 17 with their characteristic length of several microns. Though the attack isn't sufficient in the dynamic sulfuric acid solutions, gypsum crystals presence discovered in SEM pictures agrees well with the relatively low gypsum peak in the XRD result (Fig. 14).

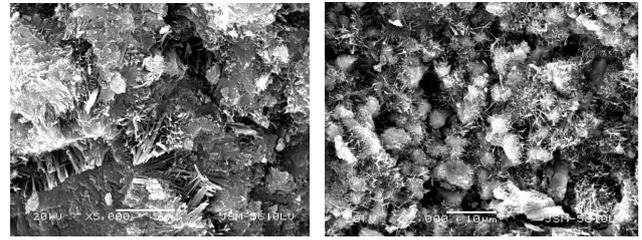


Fig. 14. SEM pictures of sample H-3 immersed in static acetic acid solution at 28 days

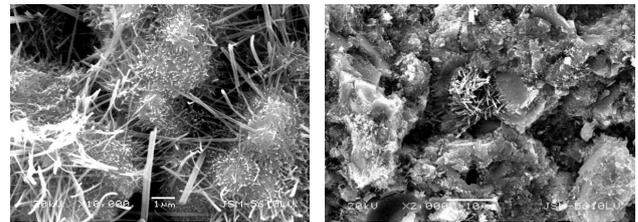


Fig. 15. SEM pictures of sample H-3 immersed in static sulfuric acid solution at 28 days

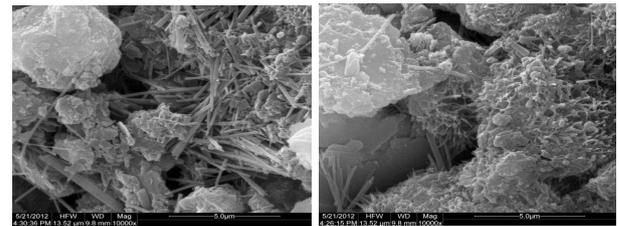


Fig. 16. SEM pictures of sample H-3 immersed in flowing acetic acid solution at 28 days

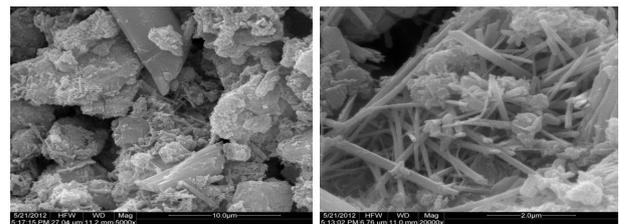


Fig. 17. SEM pictures of sample H-3 immersed in flowing sulfuric acid solution at 28 days

4. CONCLUSIONS

1. The compressive strength of the pastes would firstly decrease then increase slightly and finally decrease again under acid attack. Strengths of pastes mixed with fly ash or silica fume decreases more slowly than those only containing limestone powder because of reduced calcium hydroxide and paste permeability.

2. Limestone powder as an excellent inert filler doesn't exacerbate the pastes deterioration as expected. The acid is more readily to react with calcium hydroxide. Acid attack from strong sulfuric acid solutions is more intense than acetic acid solution.

3. Strength recovery of pastes with high w/b ratio is less than that with low w/b ratio. Anhydrate cement particles' continuing hydration should account for the strength recovery of all pastes soaked in the solutions. Apart from this, expansive formation of gypsum generated from the reaction between sulfuric acid and calcium hydroxide is another main reason for the pastes soaked in the sulfuric acid solutions.

4. Acid attacks in static solutions are more intense than in dynamic solutions. The amount of gypsum in dynamic sulfuric acid solutions is less than in static sulfuric acid solutions.

Acknowledgments

This project is funded by Opening Funds of State Key Laboratory of Silicate Building Materials (SYSJJ2012-11).

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