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Effect of Limestone Powder and Fly Ash on Magnesium Sulfate Resistance of Mortar

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Abstract: The effect of limestone powder and fly ash on magnesium sulfate resistance of mortar was studied by testing on the strength, expansion and hydration products of the specimens stored in $MgSO_4$ solution at certain periods. The experimental results show that the strength of mortar stored in $MgSO_4$ solution increases a little before 28 d, but decreases fast subsequently. The more the contents of limestone powder and fly ash, the less the strength losses. Mortar swells in the $MgSO_4$ solution with the soaking time. And the more the contents of limestone powder and fly ash, the less the expansion rate is. The expansion or strength loss of mortars results from the expansion of gypsum, as well as the loss of $Ca(OH)_2$ and other hydration products of cement. The magnesium sulfate resistance of the mortars containing limestone powder and fly ash is high.

Key words: limestone powder; fly ash; mortar; magnesium sulfate resistance

1 Introduction

High-performance concrete (HPC) mixtures contain a large volume of cement and low w/cm ratio; in addition, high workability can be achieved by using superplasticizer. In these mixtures, there is not available space to locate the hydration compounds and, as a result, a large volume of cement remains unhydrated, causing an irrational use of resources and energy in concrete production[1].

Modern cements often incorporate several mineral admixtures, one of which is limestone powder[2]. Cement plants are being built on or close to the limestone quarries, so the practice of limestone grinding with clinker is obviously cheap. Limestone dust, which is produced in quarrying operations, possesses disposal and environmental problems[3]. There is current interest, however, in the use of limestone powder as an addition to Portland cement.

The use of portland cement containing limestone powder is a common practice in Europe. European standard EN 197 identifies two types of Portland limestone cements (PLC): Type Ⅱ/A-L containing 6%-20% and Type Ⅱ/B-L containing 21%-35% [4]. The use of limestone powder can improve properties of concrete, decrease the costs and reduce the CO_2 and NO_x emissions during cement manufacture [5-7].

Considerable researches have been carried out within the last 20 years on the use of limestone powder in ordinary concrete, however, many problems still remain, especially the durability of the concrete containing limestone powder. Some researchers concluded that limestone powder could increase the sulfate resistance of cement, but there are still other researchers hold the opposite views[8-15]. It can be pointed out that the courses of sulfate attack are quite different depending on whether magnesium solution or sodium solution is used. In this paper, the magnesium sulfate attacks on mortars containing limestone powder and fly ash were studied.

2 Experimental

2.1 Raw materials

The mixtures used were prepared with ordinary portland cement PO 42.5 (the Chinese standard GB175-2007). Limestone powder, produced from carboniferous limestone with a very high purity (95% of $CaCO_3$ content), was added as filler, and its chemical composition is shown in Table 1. The shape of the limestone powder particles is shown in Fig.1, which indicates that the limestone powder particles are fine and the

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Table 1 Chemical compositions of limestone powder/%

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	SO_3	K_2O	Na_2O	L.I
2.50	0.60	0.36	54.03	0.54	0.05	0.01	0.10	0.08	41.59

dominant particle size of which is below 5 μm. The particle size distributions of portland cement, limestone powder and fly ash measured by laser diffraction are shown in Fig.2. Obviously, the particle size of limestone powder is smaller than those of portland cement and fly ash.

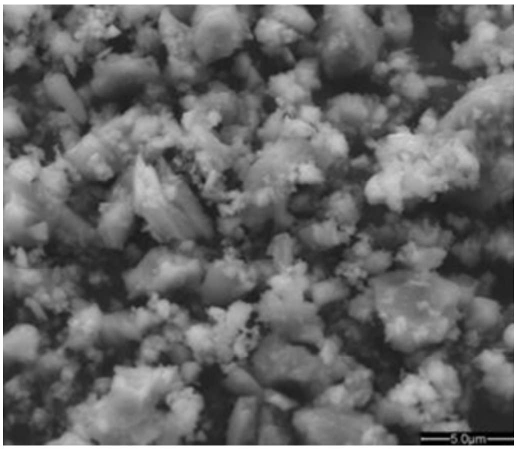


Fig.1 Shape of limestone powder particles

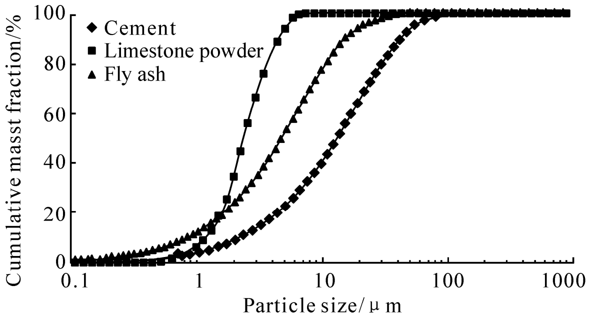


Fig.2 Particle size distributions of cement, limestone powder and fly ash

2.2 Mix Proportions

Mortar specimens (40 mm×40 mm×160 mm) were cast according to the Chinese standard GB/T 17671-1999. The mix proportions and properties of five kinds of mortars containing limestone powder or fly ash are shown in Table 2. After 24 h in a moist cabinet, they were removed from the mold and cured in water till 28 d. And then the mortars were stored in plastic tank containing $MgSO_4$ solution, in which the mass concentration was 2% in the next 90 d. The strength development, expansion change, XRD analysis and the mechanism of magnesium sulfate resistance on mortar containing limestone powder were studied, respectively.

Table 2 Mix proportions and properties of mortar

Mixture	LP-0	LP-30	LP-50	LF-30	LF-0
Cement/g	450	315	225	225	225
Limestone powder/g	0	135	225	135	0
Fly ash/g	0	0	0	90	225
Sand/g	1350	1350	1350	1350	1350
Water/g	225	225	225	225	225
Fluidity/mm	161	183	193	186	173
Compressive strength(28 d)/MPa	53.6	40.4	21.0	27.0	23.9
Flexural strength (28 d)/MPa	8.65	7.58	5.58	6.13	5.95

3 Results and Discussion

3.1 Strength

Many white dissolving-out substances can be found at the surface of the specimens stored in $MgSO_4$ solution at 90d, which means that the specimens are deteriorated by magnesium sulfate attack. The compressive strength and flexural strength of the samples stored in $MgSO_4$ solution at 7 d, 28 d, 56 d and 90 d are shown in Table 3, which indicates that the compressive strength and flexural strength of the specimens increase a little before 28 d, but decrease fast subsequently.

3.2 Expansion

The expansion rates of the samples stored in $MgSO_4$ solution until 13 weeks are shown in Fig.3. The samples swell in the $MgSO_4$ solution with the development of soaking time. The expansion rate of LP-O sample is the maximum and that of LP-50 sample is the minimum, which shows that the mortars containing limestone powder and fly ash have higher magnesium sulfate resistance.

Table 3 Influence of magnesium sulfate attack on strength of mortars

Specimen	Compressive strength/MPa					Flexural strength/MPa				
	0 d	7 d	28 d	56 d	90 d	0 d	7 d	28 d	56 d	90 d
LP-0	53.6	55.0	55.9	49.7	44.5	8.65	8.19	8.86	8.32	8.01
LP-30	40.4	41.6	42.1	40.8	38.9	7.58	7.93	7.34	7.18	6.55
LP-50	21.0	20.6	23.2	21.2	19.8	5.58	6.07	5.35	5.49	5.23
LF-30	27.0	28.8	29.1	28.0	27.4	6.13	6.76	6.16	5.74	5.51
LF-0	23.9	25.3	24.8	22.9	20.8	5.95	6.42	6.22	5.27	4.98

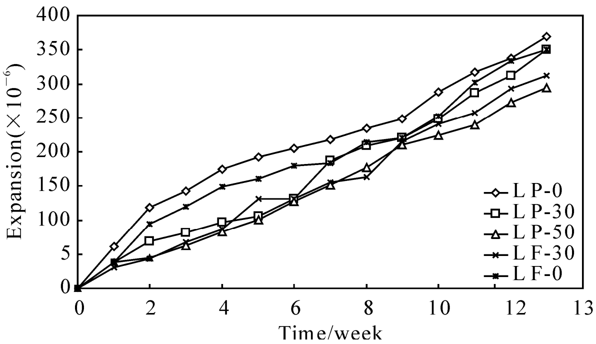


Fig.3 Influence of magnesium sulfate attack on expansion rate of mortars

3.3 XRD analysis

XRD measurements were implemented on a Philips X'Pert diffractometer equipped with a graphite monochromator using Cu K α radiation and operating at 40 kV and 20 mA. Step scanning was performed with a scan speed of 2°/min and sampling interval of 0.02°/2 θ. XRD was used to identify the hydrates in the cement paste containing limestone powder. The mixture proportions of the three paste specimens are shown in Table 4. The specimens (10 mm×10 mm×10 mm) were cured in water before 28 d and then stored in plastic tank containing $MgSO_4$ solution with 2% of mass concentration in the next 90 d. XRD analysis was carried out at 28 d and 90 d.

Table 4 Mix proportions of paste

Mixture	LP-0	LP-50	LF-0
Cement/g	200	100	100
Limestone powder/g	0	100	0
Fly ash/g	0	0	100
Water/g	80	80	80

Fig.4 shows the results of XRD analysis of hydration products of pastes stored in $MgSO_4$ solution at 28 d and 90 d. Figs.4a, 4b, 4c show the hydrates of LP-O, LP-50 and LF-0 respectively, which indicates that $Ca(OH)_2$ is the main hydration product. And there is a gypsum peak, which is caused by sulfate attack.

3.4 Mechanism analysis

It is known that the degradation of concrete, which is a result of the chemical reactions between hydrated portland cement and sulfate ions from the outside, exists two forms that are different from each other distinctly. Which one of the deterioration processes is predominant in a given case depends on the concentration and source of sulfate ions (*i e*, the associated cation) in the contact water and the composition of the cement paste in concrete.

Sulfate attack can manifest in the form of expansion of concrete. When concrete cracks, its permeability increases and the aggressive water penetrates more easily into the interior, thus accelerating the process of deterioration. Sometimes, the expansion of concrete causes serious structural problems such as the displacement of building walls due to horizontal thrust by an expanding slab. Sulfate attack can also take the form of progressive loss of strength and mass due to deterioration in the cohesiveness of the cement hydration products.

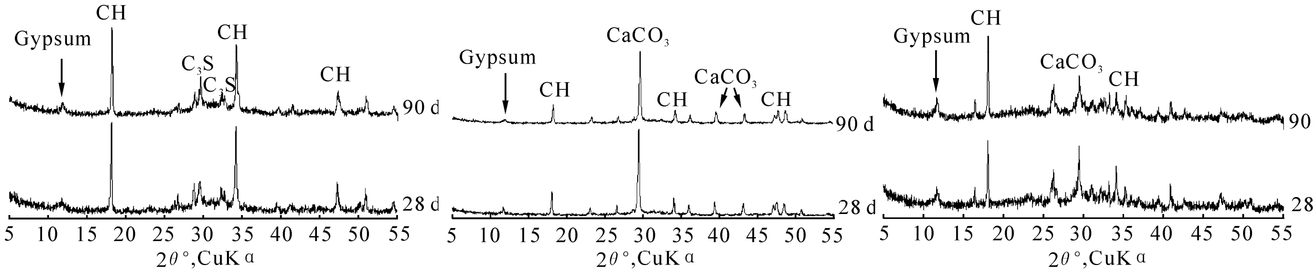
Gypsum formation as a result of cation-exchange reactions is also capable of causing expansion. However, it has been observed that the deterioration of hardened Portland cement paste is caused by gypsum formation, and ,the reduction of stiffness and strength is occurred in the formation process, meanwhile, the expansion and cracking are occurred, and the eventual transformation of the material is mushy or noncohesive mass.

Depending on the cation type presented in the sulfate solution (*i e*, Na^+ or Mg^{2+}), both calcium hydroxide and the C-S-H of portland cement paste may be converted to gypsum by sulfate attack: when it is magnesium sulfate attack, the conversion of calcium hydroxide to gypsum is accompanied by formation of the relatively insoluble and poorly alkaline magnesium hydroxide; thus the stability of the C-S-H in the system is reduced and it is also attacked by the sulfate solution. The magnesium sulfate attack is, therefore, more severe on concrete.

$$MgSO_4+Ca(OH)_2+2H_2O \rightarrow CaSO_4 \cdot 2H_2O+Mg(OH)_2 \quad (1)$$

$$3MgSO_4+3CaO \cdot 2SiO_2 \cdot 3H_2O+8H_2O \rightarrow 3(CaSO_4 \cdot 2H_2O)+3Mg(OH)_2+2SiO_2 \cdot H_2O \quad (2)$$

The hydrated portland cement reacts with magnesium sulfate and forms gypsum and $Mg(OH)_2$, which leads to the expansion of the specimens, and as shown in Fig.4, the specimens expand with soaking time in $MgSO_4$ solution. At the early age (before 28 d), the expansion products fill the voids in the mortars and increase the



(a) LP-0 (b) LP-50 (c) LF-0

Fig.4 XRD analysis about hydration products of pastes stored in $MgSO_4$ solution at 28 d and 90 d mortar strength; at the later age (after 28 d), the expansion of mortar destroys the microstructure and causes a progressive loss of strength and mass, as shown in Table 2. Gypsum is found in three figures of Fig.4, which is the expansion source. The $Ca(OH)_2$ peaks at 28 d are lower than those at 90 d, which indicates that the amount of $Ca(OH)_2$ decreases and $Ca(OH)_2$ lapses from the pastes into $MgSO_4$ solution. The expansion of gypsum and the loss of $Ca(OH)_2$, as well as the formation of other products of cement, will lead to expansion and decrease of the mortar's strength. The more the content of limestone powder is, the less the expansion and the strength loss is. When limestone powder replaces some cement, the hydration products, i.e. gypsum and $Ca(OH)_2$, decrease, and then the expansion of gypsum and the loss of $Ca(OH)_2$ and other hydration products of cement decrease subsequently. Therefore, the expansion and the strength lose decrease, and the magnesium sulfate resistance of the mortar improves.

4 Conclusions

a) The compressive strength and flexural strength of mortar stored in $MgSO_4$ solution increase a little before 28 d, but decrease fast subsequently. The more the content of limestone powder and fly ash is, the less the strength loss is.

b) Mortar swells in the $MgSO_4$ solution with the development of soaking time. The more the content of limestone powder and fly ash is, the less the expansion rate is.

c) Mechanism analysis shows that the expansion or strength loss of mortars results from expansion of gypsum, as well as the loss of $Ca(OH)_2$ and other products of cement. The magnesium sulfate resistance of the mortars containing limestone powder and fly ash is high.

References

[1] RAO Meijuan, LIU Shuhua, FANG Kunhe. Influence of Admixtures on Strength of Ultra-high Performance Cement-based Composites[J]. *Architecture Technology,* 2009, 40(7): 633-635

[2] LIU Shuhua, YAN Peiyu. Summarization of Utilization and Researches on Stone Powder Used as Mineral Admixtures in Roller Compacted Concrete[J]. *Waterpower*, 2007, 33(1): 69-71

[3] RAO Meijuan, LIU Shuhua, FANG Kunhe. Review of Applied Research on Limestone Powder in Hydraulic Concrete[J]. *Yangtze River*, 2009, 40(20): 41-43

[4] IRASSAR E F, BONAVETTI V L and GONZALEZ M. Microstructural Study of Sulfate Attack on Ordinary and Limestone Portland Cements at Ambient Temperature[J]. *Cem. Concr. Res.*, 2003, 33(1): 31-41

[5] SCHMIDT M. Cement with Interground Materials– capabilities and Environmental Relief, Part 1[J]. *Zement-Kalk-Gips*, 1992, 45(4): 87-92

[6] BARON J, DOURVE C. Technical and Economical Aspects of the Use of Limestone Filler Additions in Cement[J]. *World Cem.*, 1987, 18(4): 100-104

[7] BONAVETTIET V. Limestone Filler Cement in Low *w/c* Concrete: A Rational Use of Energy[J]. *Cem. Concr. Res.*, 2003, 33(5): 865-871

[8] TORRES S M, SHARP J H, SWAMY R N, *et al.* Long Term Durability of Portland- limestone Cement Mortars Exposed to Magnesium Sulfate Attack[J]. *Cem. Concr. Res.,* 2006, 36(7): 865-871

[9] TORRES S M, LYNSDALE C J, SHARP J H, *et al.* Microstrucure of 5-year-old Mortars Containing Limestone Filler Damaged by Thaumasite[J]. *Cem. Concr. Res.*, 2006, 36(3): 384-394

[10] LIU Shuhua, FANG Kunhe. Influence of Limestone Powder and Fly Ash on the Properties of Mortar under Dry Condition[J]. *Water Power,* 2009, 35(6): 41-43

[11] SOROKA I, STEM N. The Effect of Fillers on Strength of Cement Mortars[J]. *Cem. Concr. Res.,* 1977, 7(4): 449-456

[12] GUO Y X, GONG J X, LI J. Influence of Mass Fractions of Limestone Powder on Mechanical Property and Durability of Concrete[J]. *Journal of Building Materials*, 2009, 12(3): 266-271

[13] HEIRMAN G, VANDEWALLE L, GEMERT D V, *et al.* Time-dependent Deformations of Limestone Powder Type Self-compacting Concrete[J]. *Engineering Structures*, 2008, 30(10): 2945-2956

[14] SPRUNG S, SIEBEL E. Assessment of the Suitability of Limestone for Producing Portland Limestone Cement (PKZ)[J]. *Zem. Kalk Gips*, 1991, 44(1): 1-11

[15] LIU Shuhua. *Influence of Limestone Powder on Hydration Characteristics of Complex Binder*[R]. Tsinghua University, Beijing, 2007