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Influences of limestone powder on the resistance of concretes to the chloride ion penetration and sulfate attack

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ABSTRACT

Influences of limestone powder on the resistance of concretes to the chloride ion penetration and sulfate attack with a constant water/binder ratio and a constant 28-day compressive strength were studied. The sensitivity of the properties of concrete to the initial moist curing time was also explored. The results indicate that, under a constant water/binder ratio condition, the resistance to sulfate attack of concrete deteriorates with the increasing of limestone powder content, and the resistance to chloride ion penetration decreases when the replacement ratio of limestone powder is 24%. As the initial moist curing time declines, the reducing magnitude of the properties of concrete containing limestone powder is larger than that of plain cement concrete. Nevertheless, lowering the water/binder ratio of concrete containing limestone powder can significantly reduce the sensitivity of the properties of the concrete to the initial moist curing time. No matter how long the initial moist curing time is, replacing cement with 8% limestone powder can improve the resistance of concrete to sulfate attack. Concrete with up to 24% limestone powder addition can still obtain a resistance to chloride ion penetration and sulfate attack similar to plain cement concrete on the premise of a constant 28-day compressive strength. Moreover, it was found that both the crystallization of sodium sulfate and the formation of ettringite collectively result in the deterioration of concrete subjected to the sulfate solution.

1. Introduction

Limestone powder, produced by grinding limestone into powder, is a by-product of the limestone quarry industry. Limestone powder has been recognized as a kind of mineral admixture in cement and concrete for many years due to its technical and economic advantages [1–3]. The main component of limestone powder is calcium carbonate ($CaCO_3$), and the content of $CaCO_3$ is typically >95% [4]. SiO_2, Fe_3O_4, MgO and Al_2O_3 are other constituents of limestone powder [5–7]. Limestone powder is used primarily as a filler material because of its small particle size in comparison to the particle size of Portland cement. Numerous studies have proved that the effect of limestone powder is neither pozzolanic nor inert since calcite has a low activity [5, 8–11]. Early in 1977, Soroka et al. [12] determined that limestone powder could act as nuclei for the formation of C-S-H gel. When limestone powder exists, a series of reactions occurs between calcium carbonate and all kinds of calcium aluminate hydrates, finally forming a stable AFm phase, i.e., calcium monocarboaluminate [9, 13, 14]. The results lead to an increase in the total solid volume and a decrease in the overall porosity [15]. Therefore, the early-age mechanical properties of concrete can be improved by the promoting effect of limestone powder on cement hydration, while the later-age strength is decreased due to the dilution effect of limestone powder, resulting from the increase of the effective water to cement ratio [16–18].

Ingress of chloride into concrete is considered one of the most dangerous mechanisms influencing the durability of the structure since chloride plays the main role in accelerating the initiation of corrosion in the reinforcing steel [19]. Good chloride resistance derives from the low ion diffusivity of concrete, resulting from hindering ion penetration. The presence of mineral admixtures is acknowledged to affect the pore structures of concrete because the mineral admixtures change the microstructures of the pastes and the interfacial transition zone (ITZ) between pastes and aggregates [20]. According to previous studies, limestone powder has significant effects on pore structure, thus affecting the durability of concrete at a later stage. Elgalhud et al. [21] found that the pore structures of cementitious mixtures remained unimpaired when the replacement ratio of limestone powder is <25%. According to Hornain et al. [22], the addition of limestone powder slightly reduces the chloride ion diffusion coefficient, which is attributed to the effect of the limestone powder filler particles on the tortuosity of the matrix. Nevertheless, Wang et al. [23] found that the long-term (up to 5 years) chloride penetration of the concrete containing limestone powder is higher than that of plain cement concrete because of the coarser pore structure and less C-S-H production, leading to the reduction of chloride binding capacity.

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Concrete structures may suffer from sulfate attack, which causes serious deterioration of the concrete and affects the service life of the structures. Sulfate ions penetrate the pores and thus form an aggressive solution, which react with certain components of hydrated cement (calcium hydroxide, hydrated calcium aluminate and AFm phases) to form ettringite (AFt) and gypsum that induce expansion [16]. As a result, the concrete begins to crack, soften and lose strength. In addition, thaumasite, another product of sulfate attack, is formed from the pore solution of the pastes in the presence of calcium silicate ions and carbonate ions (CO_3^{2-}) in damp atmosphere [24–28]. Hence, thaumasite sulfate attack (TSA) may occur in concrete containing limestone powder since it contains plenty of CO_3^{2-} [29]. This deterioration will be accelerated in cold environments (below 15 °C) [16, 30]. Proper content of limestone powder can improve the pore structure and decrease the porosity of the hardened paste because of its filling effect, thus improving the performance of concrete [31]. When limestone powder is present in cementitious materials, both the physical dilution effect that decreases the C_3A content and the chemical reaction between calcite and C_3A that forms some different AFm phases will affect the alumina-hydrated compounds. Therefore, when limestone powder replacement is <10%, the expansion is reduced and there is no impairment to the sulfate attack [32, 33]. Liu et al. [34] reported that the addition of limestone powder could improve the magnesium sulfate resistance of mortars. Torres et al. [35] found that mortars containing 5% limestone powder tended to be more tolerant to sulfate attack when compared to ordinary Portland cement mortar due to the formation of thaumasite. Nevertheless, Lee et al. [36] found that higher replacement levels of limestone powder led to more serious sulfate attack, which was also strongly associated with the formation of thaumasite.

The studies discussed above were carried out mostly under the condition of an equal w/b ratio and standard curing for 28 days. However, the 28-day compressive strength of concrete is often defined as the design strength in many engineering applications. Therefore, it is necessary to adjust the w/b ratio to obtain the design strength when limestone powder is used as a partial substitute for cement. Furthermore, the initial moist curing time affects the microstructures and thus affects the durability of concrete. A large number of concrete structures cannot be cured sufficiently at early ages, especially are built in the salty soil region that lack water and have poor construction conditions. Hence, it is necessary to investigate that the sulfate attack and chloride ion penetration of the concrete with high content of mineral admixture in the case of insufficient moist curing.

Therefore, influences of limestone powder matching with initial moisture curing time (3 days, 7 days and 28 days) on chloride ion penetration and sulfate attack of concretes were studied under different conditions including an equal w/b ratio and an equal 28-day compressive strength.

2. Experimental

2.1. Raw materials

P·I 42.5 Portland cement conforming to Chinese National Standard GB 175 and limestone powder obtained by grinding limestone into powder were used as cementitious materials. The chemical compositions determined by X-Ray Fluorescence (XRF), and particle size distributions of cement and limestone powder are presented in Table 1 and Fig. 1, respectively. Natural river sand with the maximum size of 5 mm was used as fine aggregate, while crushed limestone with a size between 5 and 25 mm was used as coarse aggregate. The polycarboxylate-based superplasticizer was used to adjust the flowability of fresh concrete.

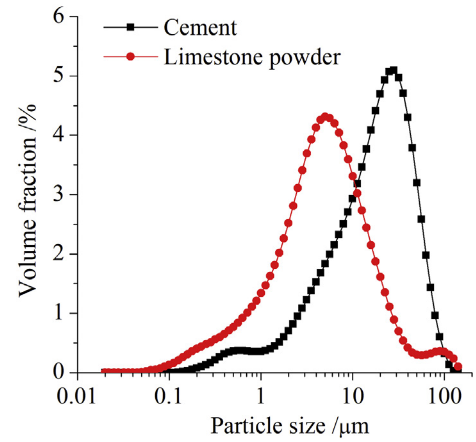

Fig. 1. Particle size distributions of cement and limestone powder.

Table 1
Chemical compositions of raw materials (%).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	$CaCO_3$
Cement	21.86	4.25	2.66	63.59	2.19	2.42	–
Limestone powder	7.25	1.88	1.18	–	2.96	0.29	84.28

2.2. Mix proportions

The mix proportions of the concretes were provided in Table 2. The concretes were divided into two groups. A plain cement concrete sample with a w/b ratio of 0.45 (Sample C-0.45) was used as the reference sample. Three replacement ratios (8, 16, and 24% by mass) of limestone powder in each group were chosen. Compared to sample C-0.45, concretes in Group I have the same w/b ratio whereas concretes in Group II have the similar 28-day compressive strength under standard curing condition (20 ± 1 °C, 95% RH). In Group II, the w/b ratio decreases with the increasing replacement ratio of limestone powder to obtain similar compressive strength at the age of 28 days, which is about 53 MPa.

2.3. Curing and testing

Concrete samples with the size of 100 mm × 100 mm × 100 mm were prepared. During the first 28 days, three kinds of early curing conditions were adopted and provided in Table 3.

After curing, the 28-day compressive strengths of the concretes were determined according to the Chinese National Standard GB/T 50081–2002. The penetration of the concrete to chloride ion was tested at the age of 28 and 90 days according to ASTM C1202 "Standard Test Method for Electrical Indication of Concretes Ability to Resist Chloride Ion Penetration".

The resistance to sulfate attack of concrete was tested using the drying-wetting cycles method. According to Thaulow et al. [37], sodium sulfate solution (5% Na_2SO_4) was selected as the corrosive solution since Na_2SO_4 is the most commonly found salt on concrete surfaces exposed to sulfate attack environments. Each cycle lasted 24 h: At the age of 28 days, the concrete was immersed in Na_2SO_4 solution for 15 h, dried

Table 2
Mix proportions of the concretes.

Samples		Mix proportions (kg/m^3)				
		Cement	Limestone powder	Fine aggregates	Coarse aggregates	Water
Reference	C-0.45	400	0	788	1044	180
Group I	L1–0.45	368	32	788	1044	180
	L2–0.45	336	64	788	1044	180
	L3–0.45	304	96	788	1044	180
Group II	L1–0.43	368	32	792	1051	172
	L2–0.39	336	64	799	1060	156
	L3–0.35	304	96	806	1069	140