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Effects of internally introduced sulfate on early age concrete properties: Active acoustic monitoring and molecular dynamics simulation

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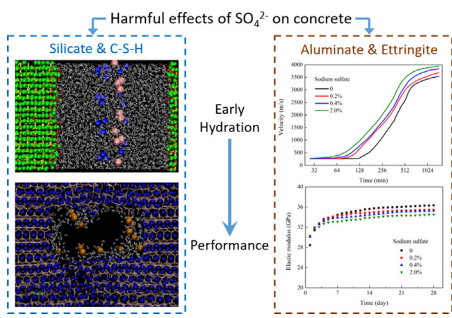
HIGHLIGHTS

- An active acoustic method can monitor the overall harmful effects of sulfate ions on concrete.
- Molecular dynamics simulations reveal the sulfate-silicates interactions.
- Existence of sulfate ions in gel pore increases the brittleness of calcium-silicate-hydrate.

GRAPHICAL ABSTRACT



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ABSTRACT

Sulfate attack of concrete is still a "confused world" that deserves further study. An active acoustic method is employed to monitor the early-age evolution of fresh concrete mixed with soluble sulfate ions. The effects of introduced sulfate salt at different dosages on the setting and hardening process of fresh concrete as well as mechanical properties of hardened concrete up to the age of 28 days are examined and analyzed. The experimental results from the active acoustic monitoring clearly reveal the acceleration effect of introduced sulfate salt on the solid skeleton formation process of fresh concrete. Introduced sulfate salt leads to higher values of mechanical property indices at early ages (e.g., 1 day), but poorer mechanical properties of hardened concrete at the age of 28 days. The corresponding mechanism has been studied in the light of molecular dynamics simulation, scanning electron microscopy and X-ray diffraction, and it is concluded that introduced sulfate ions not only damage the cement matrix due to the overexpansion of ettringite formation, but also weaken the loading resistance of the ionic-covalent bonds in the C-S-H gel.

1. Introduction

Sulfate attack is the most complicated deterioration mechanism of concrete [1]. The expansion of concrete caused by the sulfate ions present in aggregate has been reported, resulting in important structural repercussion, especially in concrete dams [2]. This expansion is due to internal sulfate attack, a physicochemical process mainly induced by the interaction between the sulfates released from aggregates and the aluminates in the cement paste binder which produces expansive secondary ettringite [3,4]. The formation of this ettringite leads to dimensional variation, increase of internal stresses and cracking of the concrete. The induced cracks in concrete matrix provide more paths for the ingress of

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other hazardous ions, which accelerates the degradation of concrete structures [5,6]. With the exploitation and utilization of resources in ocean and salt lake areas, relevant infrastructures need to be constructed in these areas. It is inevitable to use locally available raw materials (water and aggregate containing sulfate ions and other harmful ions) to make concrete due to lack of fresh water and high-quality aggregate. For example, the average concentration of sulfate ions in seawater is around 2800–3000 mg/L [7] and can be ten times higher in salt lake water, e.g. the Chaerhan Salt Lake in China (37440 mg/L) [8]. Utilization of local raw materials in these areas can subject concrete into a high risk of internal sulfate attack. Therefore, it is necessary to monitor and investigate the potential negative effects of these internally introduced soluble sulfate ions on the early-age and late-age properties of concrete.

Conventional research methods on sulfate attack to concrete are generally on the basis of the quantification of the total volumetric expansion of concrete ($\Delta V/V$) [9–11]. Nevertheless, the volumetric expansion ratio cannot directly reflect the mechanical properties of concrete, such as elastic modulus and strength. In this paper, the setting and hardening process of fresh concrete subjected to sulfate ions is monitored by means of an active acoustic method and close attention is given to the evolution of mechanical properties of concretes mixed by sulfate solution of different concentrations. The development of longitudinal wave velocity of concrete materials is monitored in the whole process from setting to hardening, which directly correlate to the mechanical indices, i.e. elastic modulus and strength. The expansion of volume and loss of modulus and strength induced by sulfate attack are normally attributed to sulfate-aluminate interaction, which is studied microscopically in this study using traditional methods, i.e., SEM and XRD. However, a question that couldn't be answered by these traditional methods is whether internally introduced sulfate ions affect C_3S and C-S-H. A first-time trial to answer this question using molecular dynamics simulation is also presented in this study.

2. Methodology

2.1. Concrete mixtures

To investigate the influence of soluble sulfate on fresh and early-age concrete, sodium sulfate (Na_2SO_4) with 0, 0.2%, 0.4% and 2.0% mass fraction of cement were utilized to prepare concrete specimens. The mix proportions of concrete materials, with or without sulfate in the mixing water, are listed in Table 1. The same ratios of water, superplasticizers, sand and coarse aggregate were kept in all mixtures, so that the influence of sulfate concentration on the mechanical properties of concrete materials could be examined. The chemical compositions of cement used in this study are given in Table 2.

For each test, raw materials were mixed in a vertical-axis planetary mixer for 10 min. The resulting fresh concrete was cast in a rectangular wood box with two embedded acoustic sensors (see Section 2.2 for details). The box was then sealed with plastic sheet to avoid water evaporation, and tests were conducted under ambient temperature. The acoustic scanning was set to be repeated every 6 min to the age of 1 day, and then the scanning interval was reset as 24 h to the age of 28 days. The longitudinal wave velocity was evaluated and recorded automatically for post-measurement analyses. Besides, compressive strength tests were carried out on 150 mm cube specimens at the age of 1 day, 3 days and 28 days, respectively, following standard test method BS EN 12390-3.

2.2. Active acoustic technique

An active acoustic monitoring system developed recently is employed in the present study [12]. The working principle of this monitoring system is to use acoustic wave to detect the setting and hardening process of fresh concrete materials. Two sensors are placed into the newly cast fresh concrete at a fixed distance. A self-developed adjustable frame is used to guarantee that the distance between these two sensors is 100 mm. One of the sensors acts as the embedded emitter for longitudinal wave generation, while the other acts as the embedded receiver to collect the transmitted signals. The adopted acoustic monitoring system has three obvious advantages over the traditional ultrasonic transmission systems used by other researchers [13–15]. Firstly, the acoustic impedance of this cement-based piezoelectric sensor utilized is quite close to that of concrete material, which ensures the minimum signal distortion and the maximum signal energy transmission efficiency between these two materials [16–18]. Secondly, the cement-based piezoelectric sensors are directly embedded in the fresh concrete mixture rather than fixed on the surface of the concrete specimen. In this way, the interface-contacting problem due to concrete shrinkage can be solved to a large extent [19,20]. Thirdly, as shown in Fig. 1, the central frequency of the acoustic signal generated is highly concentrated at around 6 kHz, which is much lower than that of traditional ultrasonic waves (higher than 20 kHz). A relatively low central frequency guarantees a high signal-to-noise ratio during monitoring, especially for fresh concrete material [21]. These three characteristics make sure that the sensor couple can produce and detect the propagation of mechanical waves with high sensitivity.

2.2.1. Longitudinal wave velocity

Longitudinal wave velocity is a fundamental factor reflecting the microstructure formation of fresh concrete during hydration process. Since the distance between the active acoustic emitter

Table 1
Mix proportions (by weight) of concrete mixtures.

No.	Cement	Na_2SO_4	Water	Superplasticizer	Sand	Aggregate
PC-0	1	–	0.38	0.05%	1.3	1.7
PC-0.2		0.2%				
PC-0.4		0.4%				
PC-2.0		2.0%				

Table 2
Chemical compositions of cementitious materials (%).

Materials	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Minors	LOI
Cement	62.60	21.35	4.67	3.31	3.08	2.25	0.54	0.21	0.78