



Stability and decomposition mechanism of ettringite in presence of ammonium sulfate solution [☆]



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HIGHLIGHTS

- Decomposition of ettringite can be occurred when the concentration of $(\text{NH}_4)_2\text{SO}_4$ reached to a certain extent.
- Main products of decomposition of ettringite were gypsum and $\text{Al}(\text{OH})_3$.

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ABSTRACT

The formation and transformation characteristics of ettringite play an extremely important effect on the accelerated hardening and expansion of concrete as well as its long term durability. In alkaline condition, ettringite can be existed stably; but when the alkalinity exceeds a certain value, ettringite can be decomposed into calcium monosulfaluminate (AFm). In this paper, the stability and its decomposition mechanism of ettringite in alkaline $(\text{NH}_4)_2\text{SO}_4$ solution were then investigated. The results show that in alkaline environment, decomposition of ettringite can be occurred and main products were gypsum and $\text{Al}(\text{OH})_3$ as long as the concentration of $(\text{NH}_4)_2\text{SO}_4$ reached to a certain extent. Based on experiment data, a kind of NH_4^+ involved decomposition mechanism of ettringite had been proposed by method of quantum mechanics combined with frontier molecular orbital theory and thermodynamic theory.

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1. Introduction

Ettringite always exists in cement based materials, it begins to form during cement hydration process [1]. Ettringite is also applied to the shrinkage compensation and hardening accelerating and set accelerating of concrete [2]. However, formation of excess ettringite has negative effect on durability of cement based materials. Moreover, the negative effect in front of sulfate attack can become still much more negative because it is more aggressive and faster if the Portland cement is replaced partially by metakaolin due to its large reactive alumina content [3–6]. Therefore, to clarify the stability and transformation of ettringites in a variety of environment conditions plays an important guiding significance for

understanding mechanical properties and sulfate attack of cement based materials.

Ettringite is not only originated from the hydration of cement, but also from sulfate attack of cement based materials [7]. This originated ettringite may face many hostile environments and its stability is maybe changed. Factors affecting the stability of ettringite mainly include temperature, pH and others. J. Skalný [8] found that ettringite was instable and decomposed when temperature was exceeded 60–70 °C. If temperature was reached 80 °C, ettringite was converted into metaettringite by losing part of water [9]; K. Ogawa [10] claimed that ettringite was decomposed at 130–150 °C yielding monosulfate hydrate as the main decomposition product, hemihydrate and anhydrite were also formed. At 260 °C ettringite was completely dehydrated which was investigated by Sytle M. Antao [11]. Gruszczinski [12] and R.A. Livingston [13] found that morphology of ettringite was also changed at elevated temperature. But different surrounding would also affect the critical temperature of decomposition of ettringite. H.F.W. Taylor [14] considered supersaturated OH^- and SO_4^{2-} in pore solution can increase the stability of ettringite which still was existed even at 90 °C; stability of ettringite also was changed in the solutions

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with different pH. J. Havlica et al. [15] claimed that ettringite was decomposed at pH below 10.7; J Hill et al. [16] and Z Chang [17] studied combined sulfate and acid attack of concrete with different SCM and found that content of ettringite was less. However, ettringite was also not stable even in condition of high alkaline. C.J. Warren et al. [18] found ettringite can be converted into monosulfate with pH above 13.

$(\text{NH}_4)_2\text{SO}_4$ existing in sewage facilities and industrial areas [19] always reduce the service performance of cement based materials. Anti-freezing admixtures such as urea and melamine superplasticizer sometimes can also generate ammonia and NH_4^+ ions. Therefore, cement based materials in service time may be threatened by ammonium. NH_4^+ can react with OH^- so that it can reduce the pH of system, therefore, many reference always classify ammoniate salt as acid attack on concrete and the main purpose of NH_4^+ is to decrease the pH [20–22] and following induce the instability of many hydration products such as C-S-H and ettringite. Raoul Jauberthie [23] had investigated that corrosion product was gypsum when cement mortar were immersed in 0.25 mol/l ammonium solutions for a period of 2 years, and pH of surrounding solution was changed from 6 to 8 by leaching of alkali. Michel Mbessa [24] found gypsum was existed on the surface of high-strength concrete when concrete was immersed in 20% ammonium solutions. M.T. Bassuoni [19] considered that ammonium sulfate caused a combined acid and sulfate attack characterized by decomposition/softening associated with expansion, cracking and spalling. U. Schneider et al. [25] claimed that disadvantage of ammonia in cement concrete mainly due to the change of alkaline environment of the presence of ettringite. However, due to unshared pair of electrons, NH_3 has strong coordination ability and may react with ettringite especially in high pH value. When the pH > 9.25 $\text{NH}_3(\text{aq})$ was the dominant species in the NH_4^+ solution [23], so NH_3 may be involved into decomposition of ettringite. In this paper, (i) In terms of the pH distribution over depth, stability of ettringite was investigated to achieve the critical NH_4^+ concentration of decomposition of ettringite; (ii) To investigate the impact of NH_4^+ and avoid the impact of acid, products changes of decomposition of ettringite in high alkaline was studied; (iii) Decomposition mechanism of ettringite was thus proposed.

2. Experimental

2.1. Raw materials

- (1) Cement: Commercial P.II 52.5 Portland cement, its physical properties and chemical compositions were listed in Tables 1 and 2.
- (2) Sand: China ISO standard sand.
- (3) Chemical reagents: Analytical reagent CaO , $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, CaSO_4 , $(\text{NH}_4)_2\text{SO}_4$, Na_2SO_4 .

2.2. Experimental process

2.2.1. Synthesis of ettringite

Ettringite was synthesized by the method of Struble et al. [26]. 13.40 g CaO was weighed and dissolved in 890 ml distilled water; 26.55 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ was also weighed and dissolved in 40 ml

Table 2

Oxide compositions of cement/wt.%.

CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	K ₂ O	TiO ₂	LOI	Total
64.68	18.36	4.33	2.95	0.79	2.60	0.73	0.19	3.70	98.33

distilled water; two solutions were mixed and stirred 2 h, stood after one week and pumping filtered, synthesized ettringite was then dried at 60 °C and stored in a closed container.

2.2.2. Mortar specimen preparation

Cement mortars were prepared according to ASTM C305-99 (Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency), the sand/binder mass ratio was maintained equal to 3, water/cement ratio being 0.5, and mortar specimen size being in 40 mm × 40 mm × 160 mm. Mortar specimens were then cured under the condition of ambient temperature 20 ± 2 °C and RH not less than 90% in molds for 24 h, then demoulded and cured in water at 20 ± 1 °C for 28 days.

2.2.3. Sulfate corrosion conditions

Mortar specimens curing after 28 days were immersed in 5% Na_2SO_4 (0.35 mol/L) and 5% $(\text{NH}_4)_2\text{SO}_4$ (0.38 mol/L) respectively. After 180 days mortars were removed from different sulfate solutions and then the surface water was dried by cloth, and following dried for 24 h at 60 °C. Mortar specimens were then layered sampled every 0.5 mm from exposed surface by precision lathe, powder samples cutting down were collected respectively, then immersed in ethyl alcohol for 4 h and vacuum dried 24 h at 60 °C and stored in a closed container until analysis.

Ettringite was accurately weighed and added in 100 ml 5% (0.380 mol/L) $(\text{NH}_4)_2\text{SO}_4$ solution, and different dosages of NaOH solution (pH = 13) according to the test program was dropped into this solution to adjust the pH. After reaching of equilibrium state of system, the correlatively analysis was started.

2.2.4. Methods of physical-chemical properties

X-ray diffraction analysis was carried out on ARL X' TRA X-ray diffract-meter. Experimental parameters: 2.2 kW Cu target; stepping being 0.02°, scanning speed being 10°/min; TG-DSC analysis was carried out on STA449C thermal gravimetric instrument equipped with DSC 204 differential thermal analyser. Experiment parameters: temperature ranged from 40 °C to 900 °C; weight sensitivity being 0.1 µg; heating rate being 10 °C/min; nitrogen atmosphere. SEM-EDS was carried on JSM-5900 scanning electron microscope equipped with NORAN VANTAGE DSI energy dispersive spectrometer. Experiment parameters: accelerating voltage being 15 kV; resolution being 3 nm; magnification being $-18 \times -300,000\times$; FTIR was carried out on Nexus 670 Fourier transform infrared spectrometer. Experiment parameters: resolution being 0.1 cm^{-1} ; signal to noise being 33,400:1 (peak to peak in one minute).

Table 1

Physical properties of cement.

Specific surface area/ m^2kg^{-1}	Standard consistency water consumption/%	Setting time/min		Flexural strength/MPa		Compressive strength/MPa	
		Initial	Final	3d	28d	3d	28d
397	27.6	139	187	5.9	8.6	33.1	57.2

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