Internal relation between hydration kinetic and endogenous shrinkage in an ettringite-based compound

Ngoc-Lam Nguyen
Faculty of Building Material - National University of Civil Engineering
55 Giai Phong Road - Hai Ba Trung District - Hanoi - Vietnam

Abstract. Ettringite based compound is a new materials used in construction because of high early-age strength, good chemical resistance, low CO₂ emission…etc. However, research on not only the microstructure characteristics but also macrostructural properties and their internal relation is very limited. The aim of this study is to evaluate the relation between the microstructure characteristics such as chemical shrinkage and ettringite development by the infrared spectroscopy method with endogenous volumetric shrinkage in case of an ettringite based compound without setting regulators. The results indicated the evolution of the ettringite measured continuously by the infrared spectroscopy method corresponds to the development curves of the endogenous and chemical shrinkage. The swelling phenomenon expressed by volumetric shrinkage measurement related to the ettringite formation is verified by infrared spectroscopy and DRX technic. The greater the amount of ettringite formation, the more swelling of the compound increases.

1. Introduction

An ettringite-based binder is a new binder promised with very low CO₂ emissions when comparing with conventional OPC-based composites [1]. The hydration and hardening process are mainly based on the reaction between a calcium aluminate cement (CAC) and a calcium sulfate (CaSO₄), which lead to the formation of ettringite (C₆A₅H₃₂), aluminum hydroxide (AH₃). The ettringite-based compound exhibit advantages compared to ordinary Portland cement (OPC) due to their high early-age strength [2], good chemical resistance [3], and their ability to stabilize heavy metals within their structure [4-5]. Therefore, the binder can potentially partially replace OPC in order to achieve environmental and economic benefits while attaining high mechanical performance.

The hydration process in ettringite-based binders usually happens quickly. As reported in the literature ettringite-based binders' rapid setting (i.e., initial setting time of roughly 10 min) is due to the associated increased rate of hydration reaction [6-9]. Besides, as the microstructure evolves and causes the change of the macrostructure, the material passes from the liquid state to the solid state and leads to the setting and increasing mechanical strength [10, 11]. It depends on the mineral composition (or chemical) of binder, the water/binder ratio, the temperature and the nature of the adjuvant … The beginning of the structuration of ettringite based binder can begin at early-age, within a few minutes to a few hours. This period may be associated with rapid hydration process after the contact between the binder with water and lead to the development of the microstructure relating to structuration and macroscopic properties evolution. Therefore, understanding and in-depth study of this phase transition is necessary; however, research on this process is very limited [12]. In this part, the structuration of ettringite based compound is studied from the monitoring of the evolution of physical parameters.
more related to the hydration of the material such as chemical shrinkage, amount of ettringite formation and endogenous shrinkage of ettringite based compound. The aim of this study is to evaluate the internal relation between hydration kinetic and endogenous shrinkage in a compound based on ettringite binder without setting regulator. A superplasticizer was used to prolong the setting time to be able to research the change of microstructure.

2. Materials and Experimental Method

2.1. Materials

The main components of the binder used to make ettringite based compound include calcium alumina cement (CAC), Portland cement CEM I and hemihydrate C$H_{0.5}$. The skeleton of this compound consists of ground granulated furnace slag, quartz sand and carbonate powder. Adjuvants used in this paper were superplasticizer (SP), viscosity modified agent (VMA) and shrinkage resistance agent (SRA). The chemical composition of this binder is shown in Table 1:

| Binder      | Al$_2$O$_3$ | CaO | SiO$_2$ | Fe$_2$O$_3$ | MgO | TiO$_2$ | K$_2$O | Na$_2$O | SO$_3$ | MnO | L.O.I |
|-------------|-------------|-----|---------|-------------|-----|---------|--------|--------|-------|-----|------|
| CAC         | 69.68       | 29.78 | 0.26       | 0.16          | 0.15 | 0.04   | -      | 0.23   | 0.27  | 0.01 | -    |
| Hemihydrate | -           | 38.70 | 0.27       | 0.03          | 0.1  | 0.003  | -      | -      | 52.40 | -   | 8.4  |
| Cement      | 5.30        | 67.28 | 20.22      | 0.20          | 1.02 | 0.18   | 0.26   | 0.20   | 2.63  | 0.06 | -    |

The ettringite based compound without setting regulators is presented in the table 2 below:

|                | CAC | C$H_{0.5}$ | CEM I – 42.5 | Superplasticizer, Viscosity Modified Agent and Shrinkage resistance agent | Quartz sand, Carbonate powder and Slag | Water | Total |
|----------------|-----|------------|--------------|--------------------------------------------------------------------------|----------------------------------------|-------|-------|
| Content by weight, % | 24.33 | 8.11       | 3.98         | 5.48                                                                      | 33.51                                  | 24.58 | 100   |

Normally, the hydration and the structuration of the ettringite based compound using setting adjuvant systems take place quickly, the hydration kinetics indicators are difficult to analyze. Therefore, to properly observe the chemical and physical processes in ettringite based compounds, setting regulators (accelerator and retarder) were not used in this compound. The goal is to extend the setting time. The hydration process will thus be slowed down to encourage a clearer observation of the structure and the relationship between the change in microstructure and the deformation.

2.2. Experimental methods

2.2.1. Chemical shrinkage

In this research, the gravimetric measurement method was used to determine the chemical shrinkage as a function of time. This method is described in the literature [13]. The fresh ettringite based compound was placed in a cylindrical plastic box (70 mm in diameter and 10 mm in height). The amount of sample used for this measurement is around 45 g. The samples were initially subjected to vibrations to eliminate all the bubbles in the mixture [13-14]. The box then was placed in a steel basket always immersed in water at 20°C and suspended on an electric balance recording the data automatically as a function of time. The weight of the sample is recorded every minute. The chemical shrinkage is expressed in (mm$^3$/g of binder) of water per gram of anhydrous binder. Knowing the initial weight of the sample as well as its composition, the chemical shrinkage can be calculated such as:
2.2.2. Endogenous volumetric shrinkage

The volumetric shrinkage of the ettringite-based compound was measured as described in detail in [15-16]. A rubber membrane containing the mixture was submerged in water. The change of volume of the mixture was measured by the amount of water displaced by the immersed sample, typically by measuring its weight change. After filling with fresh ettringite-based compound, a plastic membrane (or rubber) bag is sealed and immersed into water bath immediately. Autogenous shrinkage is assessed by recording the weight change of the plastic membrane over time.

![Figure 1. Measurement of autogenous shrinkage by using rubber bag [16].](image)

### 2.2.3. Infrared spectroscopy FTIR

Infrared spectroscopy (IR) is based on the absorption phenomenon that occurs when infrared radiation passes through a material. This method was carried out on a Nicolet iS50 FT-IR spectrometer (ThermoScientific). In order to study the structuring of the ettringite-based compound, the spectra are then recorded every minute for 24 hours. This monitoring during the hydration phase of the mixture makes it possible to identify chemical bonds such as the sulfate bonds associated with ettringite thanks to the variations in absorbance of the bands at 1110 cm\(^{-1}\) [17-18]. This method permits to highlight variations in the kinetics of a sample by monitoring the evolution as a function of time of the absorbance of the band of ettringite.

### 2.2.4. Microstructure analysis by XRD

The mineralogical composition of the hydrated ettringite-based compound was performed by an X-ray diffractometer (XRD) Bruker D8 Advance controlled by a computer coupled with Diffrac Plus EVA software (Bruker Software), which allows the exploitation of the results. This paper focused only on the main peak of the ettringite (at 2θ = 9.11º) and gypsum (at 2θ = 11.65º).

### 3. Results and discussion

#### 3.1. Endogenous volumetric shrinkage

Results of the endogenous volumetric shrinkage with time of the ettringite-based compound is shown in Figure 2:
After mixing and starting experiments, the shrinkage of the ettringite based compound took place relatively large, can reach 7mm$^3$/g. However, from 1 - 6h after mixing, the ettringite based compound has almost no change in volume. This may be due to the competition between chemical shrinkage and expansion of the compound thanks to ettringite formation. After the first 6 hours, the compound begins to set, gradually changes from a liquid state to a solid state and hardens. This proves that the ettringite content is large enough to make the sample start to be swelling. The interesting in the figure 2 above is the appearance of two shrinkage peaks at 1.2 h and 5.5 h; each peak was accompanied by the volume expansion process of the sample.

3.2. Development of ettringite formation by infrared spectroscopy method

The growth of ettringite phase was recorded by the infrared spectrophotometer at pic 1100cm$^{-1}$ and presented in the Figure 3:

**Figure 2.** Endogenous volumetric shrinkage of compound

**Figure 3.** Intensity of ettringite phase in compound with time
The higher the ettringite content, the greater the intensity of this peak. The results in Figure 3 show that when ettringite mineral content increases over time. During the first 6 hours, the content of ettringite phase increased sharply then began to slow down but still developed relatively steadily over time. The question here is whether the phenomenon of ettringite formation and other properties are related to each other? That is the question this research wants to answer.

3.3. Chemical shrinkage

The chemical shrinkage of ettringite-based compound is shown in Figure 4:

![Figure 4. Chemical shrinkage of compound with time](image)

Experimental results also show the chemical shrinkage of ettringite-based compound with time is in good agreement with the volumetric shrinkage. After the first 1-1.5 hours, the rate of chemical shrinkage increased rapidly, then from 1.5 to 6 hours later, the reaction rate did not increase faster but remained at 9.5 cm³/g of binder. After the first 6 hours, the rate of chemical shrinkage is relatively large and can reach 80mm³ after 20 hours of experiment. This result is quite similar to the development of ettringite phase when determined by infrared spectroscopic method.

3.4 Internal relation between hydration kinetic and endogenous shrinkage in an ettringite based compound

It is known that the volumetric shrinkage of the binder is the result of chemical shrinkage. Meanwhile chemical shrinkage is involved in the formation of ettringite in compound. Therefore, these 3 factors must have relation to each other? The indicators monitored are the evolution expressed by differential with time of endogenous deformation (endogenous volume shrinkage), chemical shrinkage and the intensity of the IR signal. The results are shown in Figure 5 - Figure 7:
Figure 5. Differential of autogenous volumetric shrinkage of compound

Figure 6. Differential of chemical shrinkage of compound
Figure 7. Differential of ettringite formation of compound

Thanks to the results of Figure 5-7, a clearer vision on the relation of ettringite formation with endogenous deformation and chemical shrinkage was observed. In each figure, every characteristic has its own peak, which reflects the change in the evolving microstructure over time. These peaks occur at the same time and are closely related to each other. In fact, there is a small lag between the peaks because the experimental environment such as temperature and humidity is not the same. In Figure 5, it is found that the curves have two main peaks: a peak before 2 hours and a peak at about 5.5h. These two peaks well coincide with the peaks of IR. The reason of these 2 peaks may be due to the rapid solubility of the hemihydrate to form gypsum during the first 2 hours and a large peak occurring after 5.5 - 6 hours related to the formation of ettringite. This explanation was confirmed by the XRD results on the Figure 8. There is still gypsum (at $2\theta = 11.60^\circ$) in the mixture after 2h of hydration; it means that the first peaks in figure 5 and figure 7 are related to gypsum formation. At this moment, the ettringite was already formed but the content is still not very much.
Figure 8. XRD diffraction of the composition without accelerator and retarder (the peak of ettringite (E) at 2θ = 9.10° and the peak of gypsum (G) at 2θ = 11.60°)

a) XRD at 1h of hydration  
b) XRD at 2h of hydration

The results indicate that the compound has the main peak identified by the chemical shrinkage that occurs simultaneously (approximately 10 to 12 h) but they exhibit quite different endogenous deformations. Therefore, the results of the chemical shrinkage cannot help explain the deformation (contraction or expansion) mechanism of the sample. However, the infrared spectroscopy signal peaks occur at the same time as the chemical and endogenous shrinkage peaks, so the chemical shrinkage has been used as a useful tool to study the hydration kinetics of ettringite compounds.

4. Conclusion

Some key points based on the experimental results are drawn as follows:

- In ettringite-based compound, the swelling phenomenon is due to the ettringite formation, which is verified by infrared spectroscopy and DRX technic. The greater the amount of ettringite formation, the more swelling of the compound increases.

- Internal relation between hydration kinetic and endogenous shrinkage in an ettringite-based compound is clarified. The evolution of the ettringite measured continuously by the infrared spectroscopy method corresponds to the development curves of the endogenous and chemical shrinkage.

- By differential method, the peaks determined of the shrinkage measurement well coincide with the peaks of infrared spectroscopy technic.

References

[1] Nguyen H, Staudacher M, Kinnunen P, Carvelli V and Illikainen M (2019) Multi-fiber reinforced ettringite-based composites from industrial side streams J. Clean. Prod. (211): 1065-1077.

[2] Kim J M, Choi S M and Han D (2016) Improving the mechanical properties of rapid air cooled ladle furnace slag powder by gypsum Constr. Build. Mater. (127): 93-101.

[3] Quillin K (2001) Performance of belite–sulfoaluminate cements Cem. Concr. Res. (31): 1341-1349.
[4] Peysson S, Péra J and Chabannet M (2005) Immobilization of heavy metals by calcium sulfoaluminate cement Cem. Concr. Res. (35): 2261-2270.

[5] Nguyen H, Adesanya E, Ohenoja K, Kriskova L, Pontikes Y, Kinnunen P and Illikainen M (2019) Byproduct-based ettringite binder – a synergy between ladle slag and gypsum Constr. Build. Mater. (197): 143-151.

[6] Ma B, Ma M, Shen X, Li X and Wu X (2014) Compatibility between a polycarboxylate superplasticizer and the belite-rich sulfoaluminate cement Constr. Build. Mater. (51): 47-54.

[7] Iacobescu R I, Pontikes Y, Koumpouri D and Angelopoulos G N (2013) Synthesis, characterization and properties of calcium ferroaluminate belite cements produced with electric arc furnace steel slag as raw material Cem. Concr. Compos. (44): 1-8.

[8] Rungchet A, Chindaprasirt P, Wansom S, Pimraksa K (2016) Hydrothermal synthesis of calcium sulfoaluminate–belite cement from industrial waste materials J. Clean. Prod. (115): 273-283.

[9] Ricardo M R and Escalante-Garcia J I (2014) Anhydrite/hemihydrate-blast furnace slag cementitious composites: Strength development and reactivity composites: strength development and reactivity Constr. Build. Mater. (65): 20-28.

[10] Tazawa E I, Miyazawa S and Kasai T (1995) Chemical shrinkage and autogenous shrinkage of hydrating cement paste Cem. Concr. Res. (25): 288-292.

[11] Barcelo L, Boivin S, Rigaud S, Acker P and Clauvaud B (1998) Linear vs. volumetric autogenous shrinkage measurements: material behaviour or experimental artefact. In: Persson B, Fagerlund G, editors. Proceedings of the Second International Research Seminar on Self-desiccation and Its importance in Concrete technology.

[12] Boivin S, Acker P, Rigaud S and Clauvaud B (1999) Experimental assessment of chemical shrinkage of hydrating cement paste. In: Tazawa E, editor. Autoshrink’98 Proceedings of the International Workshop on Autogenous Shrinkage of Concrete; pp. 77–88.

[13] Tongsheng Z, Peng G, Ruifeng L, Yiqun G, Jiangxiong W and Qijun Y (2013) Measurement of chemical shrinkage of cement paste: Comparison study of ASTM C 1608 and an improved method Cons. & Build. M. (48): 662-669.

[14] Justness H, Sellevold E J, Reyneiere B, Vanloo D, Gemert AV and Verboven F (2000) Chemical shrinkage of cement pastes with plasticizing admixtures”, Nordic Concrete Research (24):39-54.

[15] Bensted J and Varma S P (1971) Studies of ettringite and its derivatives Cement Technology (3): 73–76.

[16] Frost R L, Kloprogge J, Russell S C and Szetu J L (1999) Dehydroxylation and structure of alumina gels prepared from trisecbutoxyaluminium Thermochimica Acta 329(1): 47–56.

[17] Perkins R B and Palmer C D (1999) Solubility of ettringite Ca₆[Al(OH)₆][SO₄]₃·26H₂O at 5–75°C Geochimica et Cosmochimica Acta (63): 1969–1980.