Microwave Curing Effect on Internal Sulphate Damage in Nano Alumina Reinforced White Cement

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Abstract. In this study, microstructural investigation was carried out to analyse the internal sulphate damage in the nano-Al₂O₃ (nAl) reinforced white cement pastes. As white cement is generally used in the production of architectural concrete, 52.5 R type white cement was preferred in the scope of the study. Nano Al₂O₃ was substituted into the cement paste at 0% and 5% ratios. Three different methods were used for microwave curing. Different microwave curing techniques were performed as 120 minutes of 100 Watt application, 75 minutes of 100 Watt-30 minutes of 150 Watt-15 minutes of 200 Watt application, and 90 minutes of 100 Watt-15 minutes of 150 Watt-15 minutes of 200 Watt. In order to accelerate the formation of DEF damage, Na₂SO₄ was added to the cement paste at 2%, and 5% ratios. Three different microwave curing methods were used to investigate the occurrence of DEF damage in nano Al₂O₃ reinforced concrete concretes. In the pastes produced for this purpose, dense ettringite structure was observed. In cement pastes without nAl, the ettringite structure had a low S / Ca ratio (<0.20). More ettringite was formed in methods 2 and 3 used as microwave curing. The heat treatment applied in the microwave curing was the same as in other thermal curing applications, and in case the inner sulphate source was present it led to the formation of ettringite. This process became more evident in the presence of NA by increasing power application.

1. Introduction
In recent years, research and development studies in the field of cement based materials are being carried out mainly to extend durability and service life [1]. In the mentioned studies, it has been determined that the durability parameters are related to the concrete air content and the bond between the aggregates and the matrix [2]. Mineral additives are known to significantly increase the durability of concrete depending on its permeability [3]. With the development of technology in recent years, the use of nano materials in cement and concrete technology has become widespread. Materials with nanoparticles have been obtained as a result of improving the particle distribution properties of materials which have conventional particle size. No changes in the chemical properties of the materials were observed during this process. The performance of cement-based materials depends largely on nano-sized calcium-silicate-hydrate particles (C-S-H) or nanoscale porosity in the interface transition zone between the cement and aggregate particles. It has been determined that nano-materials such as nano-silica, nano alumina and nano-carbon tubes affect the properties such as pressure resistance, fire resistance and pore structure in the scope of the ongoing researches. The economical production and use of cement with nanoparticles will lead to a new era for stronger and more durable concrete constructions [4]. Mohamed
Heikal et al. [1] have investigated the durability of cement pastes containing Al₂O₃ nanoparticles to physico-chemical effects and high temperature. They have reported that the addition of nano-alumina increases the compressive strength and fire resistance. SEM images reveal a much more dense microstructure formation with the addition of nano-Al₂O₃ [5]. Toklu and Şimşek have made a study on possibilities of using nano materials in repair mortars [6].

Accelerated curing methods such as steam curing and autoclave are used in the production of precast structural elements. However, in recent years, for the production of sustainable concrete, the possibility of producing concrete at the same quality with lower energy is being explored. As an alternative to autoclave and steam curing, microwave curing methods are explored for use in concrete technology. Innovative and versatile methods for heat treatment of dielectric materials are being developed. Microwave-based technologies offer a unique feature in generating heat that will overcome the limitations of traditional heating methods. Microwave processing systems are used in a wide variety of industrial applications. Microwave technology was first used in the food and rubber industry [7]. The microwave curing method used in concrete technology leads to high strength in early ages, and allows rapid progress of repair works. It has been reported that the final wet strength is reduced by about 6.75% when the microwave curing method is used. This rate is 20% in conventional thermal curing processes. Microwave curing contributes to early wet pressure resistance and long term adherence strength [8]. Various studies on microwave curing of ordinary portland cement (OPC) mortars made with different w / c ratios confirm the ability to significantly increase early age resistance of microwave curing [9]–[15].

Under certain environmental conditions, some types of concrete may be exposed to harmful chemical reactions that cause expansion and micro cracking. In relation to these harmful effects, the mechanical properties of the concrete may change and the durability of the concrete structures may be affected [16]. Sulphate attack is the most effective chemical action that damages concrete. There are two types of sulphate effects to cause damage to concrete as internal sulphate attack (ISA) and external sulphate attack (ESA). The cause of the internal sulphate damage is the sulphate ions that are present in the materials used in the concrete mix. In case of curing at high temperature or excessive increase of hydration temperature, ettringite structure is formed [17], [18]. In the external sulphate attack, sulphate, which is in the environment, permeates through the pores and propagates in the concrete along the microstructure. External sulphate damage is often seen in building elements that come into contact with sulphate-rich soils [19], [20]. Delayed ettringite formation (DEF) is known as an internal sulphate attack that causes concrete damage. Taylor et al. have simply described the chemical reactions of DEF damage. Curing at an elevated temperature above 70 °C in an early-age cement paste allows ettringite to be unstable. The sulphate ions, which are released by the dissociation of ettringite, are adsorbed loosely on the calcium silicate hydrates (C-S-H). The sulphate adsorbed onto C-S-H is gradually released when the cement paste exposed to the sphere at high temperature is stored at room temperature. Ettringite reoccurs by reacting with the mono sulphate contained in the outer product C-S-H. This reaction causes expansion and cracking of hardened concrete [21], [22]. In this study, the effect of the use of internal sulphate source and nAl on the formation of ettringite and delayed ettringite was investigated. Besides, the effect of thermal curing applied by microwave curing on the formation of ettringite was examined.

2. Materials and Method

2.1. Materials

White cement clinker and gypsum were used in the production of white cement. Chemical properties of white cement clinker and gypsum are presented in Table 1.
Table 1. Chemical properties of white cement clinker and gypsum

|            | CaO  | SiO2 | Al2O3 | Fe2O3 | MgO  | SO3  | K2O  | TiO2 | LOI* |
|------------|------|------|-------|-------|------|------|------|------|------|
| White Cement Clinker | 70.50 | 23.79 | 3.98  | 0.14  | 0.90 | 0.09 | 0.16 | 0.11 | 0.35 |
| Gypsum     | 32.39 | -    | -     | -     | -    | 45.67| -    | -    | 21.95|

Nano alumina is a chemical compound of aluminium and oxygen. Alumina is produced by Bayer process using bauxite ore. The average grain size of the nano alumina was determined to be 15 nm. The properties of the nano alumina are given in Table 2.

Table 2. Chemical and physical properties of nano alumina

|        | Al2O3 (%) | Appearance | Odor | Specific Weight | Ph | Average Grain Size (nm) |
|--------|-----------|------------|------|-----------------|----|-------------------------|
| Nano Alümina | >99       | White      | Odorless | 1.05             | 6.2 | 15                      |

Kastamonu city network water was used for the preparation of cement pastes. Sodium sulphate was used to increase the internal sulphate damage in the cement paste. The specific gravity of sodium sulphate, which is white and odorless, is 2.67 and the grain size is less than 1 mm.

2.2. Method

Experimental investigation was first started with the production of white cement. The cement was obtained after a 120-minute grinding process with a ball mill (bond type). Gypsum was used 3% ratio of the clinker weight in the cement. In the second phase, pastes were obtained with cement from clinker and gypsum. When pastes were obtained, 0% and 5% of nAl were used instead of cement. In addition, Na2SO4 was used at 5% of the amount of binding to have knowledge of the formation of ettringite. The water / binding (w / b) ratios of the cement pastes were fixed at 0.5 with constant. Mixing properties of cement pastes are given in Table 3.

Table 3. Material mixture ratios and curing process

| Mixture No | Curing Methods       | Material Ratios (%) | Material Quantities (gr) |
|------------|----------------------|---------------------|-------------------------|
|            |                      | nAl     | Na2SO4 | Cement | nAl     | Na2SO4 | Water | w/b   |
| 1          | 100W 120 min         | 0       | 0      | 50     | 0       | 0      | 25     | 0.50  |
| 2          | 5 0                  | 47.5    | 2.5    | 25     | 0.50    |
| 3          | 0 5                  | 50      | 0      | 2.5    | 25      | 0.50   |
| 4          | 5 5                  | 47.5    | 2.5    | 25     | 0.50    |
| 5          | 75 min 100W 30 min 150W 15 min 200W | 0       | 0      | 50     | 0       | 0      | 25     | 0.50  |
| 6          | 5 0                  | 47.5    | 2.5    | 25     | 0.50    |
| 7          | 0 5                  | 50      | 0      | 2.5    | 25      | 0.50   |
| 8          | 5 5                  | 47.5    | 2.5    | 25     | 0.50    |
| 9          | 90 min 100W 15 min 150W 15 min 200W | 0       | 0      | 50     | 0       | 0      | 25     | 0.50  |
| 10         | 5 0                  | 47.5    | 2.5    | 25     | 0.50    |
| 11         | 0 5                  | 50      | 0      | 2.5    | 25      | 0.50   |
| 12         | 5 5                  | 47.5    | 2.5    | 25     | 0.50    |

The resulting cement pastes were subjected to 3 different microwave curing methods after a 2-hour pre-waiting period (Table 3). In the first method the pastes were cured at 100W for 120 minutes. In the second and third methods, 3-step curing process was applied. In the second method, after applying 100W
power for 75 minutes, respectively 150W for 15 minutes and 200W power were applied for 30 minutes. In the third method, 100W power was applied for 90 minutes and then 150W and 200W powers were applied for 15 minutes. Hardened pastes were then allowed to cure for 28 days in a curing room with 80% relative humidity. After the 28th day, the pellets were taken into acetone and allowed to stand until SEM analysis was carried out.

3. Findings and Discussion
When the SEM images (in Figure 1.) of the pastes had been examined, it was seen that the ettringite structures were generally acicular. However, ball-shaped ettringite structures were observed according to the presence of nAl in some pastes. Moreover, structures such as C-S-H, CH, C-A-S-H, monosulfoaluminate were observed.

| Mixture No | SEM | EDS |
|------------|-----|-----|
| 1          | ![SEM Image](image1.png) | ![EDS Table](table1.csv) |
| 2          | ![SEM Image](image2.png) | ![EDS Table](table2.csv) |

A dense ettringite structure was found in the No. 1 paste with Na$_2$SO$_4$ and Na content of 0%. CH and low C-S-H were observed besides ettringite structure. In the EDS analyses, the presence of CH appears at regions number 1 and 2. The presence of C-S-H with the Ca / Si ratio of ~2.70 was also found in region number 3. In the region number 4, more Ca based hydration products were observed.

5% nano alumina used in no. 2 paste increases the length of the ettringite needles. The ettringite needles formed in the No. 2 paste are longer than the No. 1 paste. According to the EDS analysis, CH presence in region 1 and 2 was detected. At number 3, there is an ettringite structure with an S / Ca ratio of ~0.30. Similar structures were observed in region number 4. In region number 5, C-S-H presence was detected.
In the No. 3 paste CH, C-SH and ettringite products were observed. The ratio of nAl and Na₂SO₄ in the paste No. 3 was 0% and 5%, respectively, which resulted in less ettringite formation than pastes No. 1 and No. 2. In the EDS analysis, the presence of CH in regions number 1 and 4 was determined. In regions number 2 and 3, ettringite was observed. S / Ca ratio of ettringite in regions number 2 and 3 was found to be ~ 0.13.

In the paste No. 4 that has %5 Na₂SO₄ and nAl, ettringite structure was observed less than the other pastes. According to the EDS analysis, CH in regions number 1 and 2 and C-A-S-H in regions number 3 and 4 were observed. Although the content of Na₂SO₄ and Na is high, the CH and monosulfosaluminate structures have been observed more than ettringite. It is seen that the formed ettringite structure usually has a ball shaped structure.

|    | 1    | 2    | 3    | 4    | General |
|----|------|------|------|------|---------|
| Ca | 58.82| 41.72| 36.02| 42.90| 53.27   |
| Si | 0.36 | 2.25 | 4.71 | 0.34 | 1.62    |
| Al | 0.34 | 3.82 | 3.88 | 0.95 | 1.93    |
| S  | 0.63 | 5.66 | 4.70 | 0.52 | 3.07    |
| O  | 36.96| 37.68| 40.18| 52.88| 35.64   |

|    | 1    | 2    | 3    | 4    | General |
|----|------|------|------|------|---------|
| Ca | 56.10| 94.66| 34.49| 35.85| 42.42   |
| Si | 0.46 | 1.23 | 7.49 | 12.06| 5.38    |
| Al | 0.37 | 0.72 | 5.22 | 3.83 | 2.90    |
| S  | 0.35 | 0.02 | 2.63 | 0.79 | 1.97    |
| O  | 40.11| -    | 41.79| 42.54| 40.26   |

|    | 1    | 2    | 3    | 4    | General |
|----|------|------|------|------|---------|
| Ca | 75.32| 30.78| 27.39| 71.29| 48.47   |
| Si | 0.36 | 4.90 | 0.34 | 0.27 | 1.35    |
| Al | 1.71 | 4.73 | 5.95 | 0.39 | 1.16    |
| S  | 1.25 | 6.11 | 8.72 | 0.20 | 2.92    |
| O  | 18.43| 44.09| 48.52| 25.30| 41.20   |
It is seen that the ettringite structure is intense in the paste No. 5. According to the EDS analysis, CH presence in regions number 1 and 4 was observed. In regions number 2 and 3, ettringite structures were seen. The S / Ca ratios of the ettringite structures vary between 0.20 and 0.30. Although the contents of Na$_2$SO$_4$ and nAl are 0%, the ettringite structure was detected by SEM analysis. The presence of C-S-H jellies was also observed.

In the No. 6 paste, 5% nAl was used and dense ettringite structure was observed. SEM analysis also revealed the presence of C-S-H. Aluminum based hydration products have been formed depending on the use of nAl. In the EDS analysis, an ettringite structure with an S / Ca ratio of 0.20 was observed at region number 1. C-A-S-H structure was obtained in region number 2. In the general EDS scan, S presence was detected at 4.47%.

The ettringite structure was observed in paste No. 7 in which 5% Na$_2$SO$_4$ was used. However, it seems that the ettringite structure is not very dense. Similar properties were observed in the No. 3 paste. There is less ettringite presence in the pastes which have 5% Na$_2$SO$_4$ but not nAl.
In the paste No. 8, the most dense ettringite structure was found. The ratio of nAl and Na₂SO₄ is 5%, which makes the ettringite structure very dense. Although the ratio of Na and Na₂SO₄ in the paste No. 4 was 5%, the presence of ettringite was found to be low. The increase in the level of power applied to the paste No. 8 caused intense ettringite formation. According to the general EDS analysis, the S / Ca ratio was found to be 0.30.

A dense ettringite structure was observed in the paste No. 9 with nAl and Na₂SO₄ ratio of 0%. In the EDS analysis, the ettringite structure with an S / Ca ratio of ~ 0.20 was observed in region number 1. In addition, CH presence was detected in area 2. SEM analysis also revealed the presence of C-S-H.
5% NaAl was used in the paste No. 10. In this paste, the density of ettringite was observed less than pastes No. 2 and No. 6. The presence of C-S-H jellies were determined by SEM analysis. Also the CH structure is seen in some regions. According to the EDS analysis, the presence of ettringite in region number 1 was observed and the S / Ca ratio was determined to be ~ 0.25. C-S-H structure was observed in region number 2.

| 1   | 2      | 3      | 4 | General |
|-----|--------|--------|---|---------|
| Ca  | 94.66  | 83.26  | 60.28 |
| Si  | 0.17   | 1.40   | 0.65 |
| Al  | 1.12   | 2.16   | 3.89 |
| S   | 0.36   | 8.61   | 6.26 |
| O   | -      | -      | 23.21 |

In the paste No. 11, CH, C-S-H and ettringite structures were observed. In the paste No. 11, 5% Na2SO4 was used and it was observed that the ettringite formations were ball shaped. According to the EDS analysis, a Ca-based non-hydrated component was obtained in region number 1. In region number 2, ettringite structure with S / Ca ratio of 0.10 was observed.

| 1   | 2      | 3      | 4 | General |
|-----|--------|--------|---|---------|
| Ca  | 66.63  | 72.28  | 67.13 |
| Si  | 0.53   | 1.67   | 0.37 |
| Al  | 4.47   | 5.67   | 6.55 |
| S   | 17.18  | 13.85  | 17.00 |
| O   | 5.02   | -      | -   |

Similar to paste No. 8, a rather dense ettringite layer was obtained in the paste No.12. The application of high power with the use of 5% Na2SO4 and nAl increased the intensity of ettringite. According to the EDS analysis, an ettringite structure with an S / Ca ratio of 0.25 was observed at region number 1. In region number 2, the ettringite structure with an S / Ca ratio of 0.20 was obtained. Ettringite structures were usually observed in the acicular structure.

| 1   | 2      | 3      | 4 | General |
|-----|--------|--------|---|---------|
| Ca  | 66.63  | 72.28  | 67.13 |
| Si  | 0.53   | 1.67   | 0.37 |
| Al  | 4.47   | 5.67   | 6.55 |
| S   | 17.18  | 13.85  | 17.00 |
| O   | 5.02   | -      | -   |

**Figure 1.** Images of SEM and EDS
4. Conclusions
Even though Na$_2$SO$_4$ was not used, the ettringite structure was observed in cement pastes produced. The SO$_3$ source required for ettringite originates from the gypsum used during grinding. Therefore, gypsum used in cement-based composites, to which thermal curing applied, can cause ettringite formation. This effect is also valid for microwave curing.

The nAl substitution material used in the white cement increases the formation of ettringite even if there is not Na$_2$SO$_4$. The use of Na in microwave-cured mortar mixtures causes the formation of ettringite due to the presence of gypsum.

The increase in the power level applied in the microwave curing increases the intensity of the ettringite. The intensity of ettringite is low in pastes with a power of 100 watts for 120 minutes and a content of 5% Na and Na$_2$SO$_4$. When the power level is 150-200 watts, the intensity of ettringite increases.

The use of high Al content substitutes in mortar mixtures to which microwave curing will be applied can increase the presence of ettringite. Because gypsum acts as an internal sulphate source and it is effective in the presence of ettringite.

In the application of microwave curing (such as steam cure and autoclave), a delayed presence of ettringite is observed. Internal sulphate sources, such as gypsum, cause ettringite formation in the future in the presence of moisture. Adding Al-based materials such as nAl to this process increases the presence of ettringite. For the mixtures to be microwave cured, the formation of delayed ettringite should be investigated in more detail considering the dimensional stability and mechanical strengths. Furthermore, microwave curing and gypsum optimization for cement should be done.

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