

# The Effect of Nano-sized CaCO<sub>3</sub> Addition on the Hydration of Cement Paste Containing High Volumes of Fly Ash

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## Abstract

The use of high volumes of supplementary cementing materials in cement systems is considered strategic with respect to sustainable development issues. The decreased rate of hydration, however, continues to be a disadvantage. The accelerating effect of the nano-sized CaCO<sub>3</sub> addition to cement paste containing high volumes of fly ash was investigated by conduction calorimetry and determinations of microhardness and modulus of elasticity. The results indicate that the hydration of cement paste containing high volumes of fly ash is significantly accelerated by the nano-sized CaCO<sub>3</sub> addition. The times of occurrence of the main calorimetry peaks are significantly decreased and the rate of heat development increases depending on the amounts of addition. It is apparent from the conduction calorimetry results and the engineering properties studied that the nano-sized CaCO<sub>3</sub> addition to cement paste containing high volumes of fly ash fully compensates for the delayed hydration process.

## 1. Introduction

It is unquestionable that more clean water, infrastructure, landfills and most importantly more sources of energy will be required worldwide to comply with a growing population. It is accordingly recognized that all the industries are responsible for implementing policies for sustainable development. The cement industry, one of the most energy-intensive and resource-consuming industries, is no exception. The amount of CO<sub>2</sub> emitted in the course of cement manufacture accounts for about 7% of the total CO<sub>2</sub> emissions in the world [1].

Use of supplementary cementing materials (SCMs) as a partial replacement of ordinary Portland cement (OPC) in a concrete system is widely known and a very practical contribution to sustainable development in the cement industry. Use of higher volumes of fly ash, one of the most

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common SCMs, serves to reduce more CO<sub>2</sub> emissions and save more energy and natural resources. One of the major disadvantages of concrete containing high volumes of SCMs however is the delayed initial setting and slower early strength development. This is critical especially for a tight construction schedule in a competitive industry.

Use of ground limestone (CaCO<sub>3</sub>) to replace a certain portion of OPC in the concrete system has been intensively studied in order to save the energy and natural resources. The Canadian Standards Association (CSA) and the American Society for Testing and Materials (ASTM) allow a maximum of 5% addition of limestone to Portland cement. In Europe, the British / European Standard, BS EN 197-1 specifies "Portland limestone cement" which contains 6% to 35% of the ground limestone. The use of CaCO<sub>3</sub> was first initiated as a simple replacement of a more valuable material (OPC) by a less valuable material (CaCO<sub>3</sub>). The results from a number of studies, however, have indicated positive effects of the CaCO<sub>3</sub> addition on the hydration of cement paste and strength development of hardened concrete, especially its accelerating effect on the rate of hydration. A study on the accelerating effect of the finely ground CaCO<sub>3</sub> addition on the hydration of C<sub>3</sub>S was conducted [2]. It was concluded that the hydration of C<sub>3</sub>S was accelerated effectively and the higher the CaCO<sub>3</sub> addition, the greater was the accelerating effect. The accelerating effect of the finely ground limestone addition on the hydration of OPC was also observed [3].

Nanotechnology has made it possible to synthesize a nano-sized CaCO<sub>3</sub> within a relatively reasonable cost to be practically used in the construction industry. The accelerating effect of the nano-sized CaCO<sub>3</sub> addition, as opposed to the reagent grade micro-sized CaCO<sub>3</sub> addition, on the delayed hydration of cement paste containing high volumes of fly ash was investigated in this study.

## 2. Experimental

### 2.1 Materials

Type GU CSA cement was supplied by the Lafarge North America, Herndon, Virginia, USA. Class "F" fly ash was supplied by the Shaw Resources, Milford, Nova Scotia, Canada. Its chemical composition is shown in Table 1. Reagent grade micro-sized CaCO<sub>3</sub> and nano-sized CaCO<sub>3</sub> respectively were supplied by the Anachemia Canada Inc., Montreal, Quebec, Canada and the READE, Riverside, Rhode Island, USA. The scanning electron microscope (SEM) images of each CaCO<sub>3</sub> type are shown in Figures 1 (a) and (b), of magnifications of ×5,000 and ×50,000, respectively. The average particle size, observed by the SEM, of

the micro-sized  $\text{CaCO}_3$  is approximately 5 to 20  $\mu\text{m}$ , whereas that of nano-sized  $\text{CaCO}_3$  is about 50 to 120 nm. The nitrogen BET surface area results for the micro-sized and nano-sized  $\text{CaCO}_3$  are 0.35 and 20.50  $\text{m}^2/\text{g}$ , respectively.

Table 1: Chemical composition of type F fly ash (wt, %)

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{SO}_3$
38.22	17.29	29.66	7.58	1.22	1.55

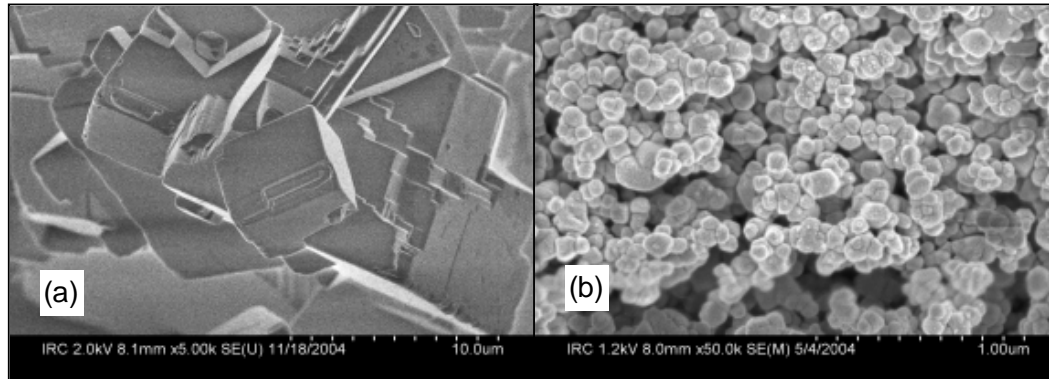


Figure 1: SEM images of (a) micro-sized  $\text{CaCO}_3$  and (b) nano-sized  $\text{CaCO}_3$

## 2.2 Experimental Techniques

The nitrogen BET surface area determination was conducted using the Quantachrome Corporation, Quantasorb Sorption System. The SEM analysis was conducted using the Hitachi S-4800 Field Emission Scanning Electron Microscope, with the accelerating voltage and the emission current at 2.0 kV and 10 mA, respectively. The Thermometric TAM Air Isothermal Calorimeter, 3114/3236 was used for the conduction calorimetry. The conduction calorimetry was performed for two series of specimens. They are summarized in Table 2. The  $\text{CaCO}_3$  content percentages for Series 1 are based on the mass of OPC excluding that of  $\text{CaCO}_3$ . The OPC with or without  $\text{CaCO}_3$  was mixed with deaerated water for a w/c ratio of 0.5 based on the mass of OPC. The rate of heat development was calculated in calories per mass of OPC (excluding that of  $\text{CaCO}_3$ ) per hour. The fly ash content percentages for Series 2 are based on the total mass of OPC and fly ash excluding that of  $\text{CaCO}_3$ . The w/c ratio was 0.5 based on the mass of OPC and fly ash. The rate of heat development was calculated in calories per mass of OPC and fly ash (excluding that of  $\text{CaCO}_3$ ) per hour. Thermogravimetric analysis (TGA) was conducted, using a TA Instruments, Q600, to calculate the amount of  $\text{CaCO}_3$  in a specimen at various hydration periods. The temperature was

ramped from room temperature to 1050°C at 10°C/min with a 100 ml/min nitrogen gas flow. TGA was conducted for the same series of specimens indicated in Table 2. The specimens were mixed with deaerated water, demoulded the day following the casting and cured at 23°C in a 100% relative humidity environment for a desired hydration period. The specimen was immersed in isopropyl alcohol for 1 day and dried under vacuum for another day in order to stop hydration at a specific hydration period prior to TGA. The amount of CaCO<sub>3</sub> in the specimen was calculated based on the total mass of OPC and CaCO<sub>3</sub>.

Table 2: Specimen Descriptions

Series 1	<ul style="list-style-type: none"> <li>• OPC</li> <li>• OPC + Micro-sized CaCO<sub>3</sub> [10%]</li> <li>• OPC + Nano-sized CaCO<sub>3</sub> [10%]</li> <li>• OPC + Micro-sized CaCO<sub>3</sub> [20%]</li> <li>• OPC + Nano-sized CaCO<sub>3</sub> [20%]</li> </ul>
Series 2	<ul style="list-style-type: none"> <li>• OPC</li> <li>• OPC + Fly Ash [50%]</li> <li>• OPC + Fly Ash [50%] + Micro-sized CaCO<sub>3</sub> [10%]</li> <li>• OPC + Fly Ash [50%] + Nano-sized CaCO<sub>3</sub> [10%]</li> <li>• OPC + Fly Ash [50%] + Micro-sized CaCO<sub>3</sub> [20%]</li> <li>• OPC + Fly Ash [50%] + Nano-sized CaCO<sub>3</sub> [20%]</li> </ul>

The microhardness determination was performed using the DURIMET, Small-hardness Tester. A hydrated specimen was sliced into a circular plate, about 31.5 mm in diameter and 1.0 mm in thickness. The modulus of elasticity was determined using an instrument designed and fabricated at the Institute for Research in Construction, National Research Council Canada. A circular plate specimen with approximately 31.5 mm in diameter and 1.0 mm in thickness supported at 3 points was tested with centre point loading. The deflection at the centre point was recorded. The helium pycnometry method was used to determine the porosity of a specimen using the Quantachrome Corporation, Stereopycnometer. A circular plate specimen was prepared in the same manner as for the TGA. The specimen was immersed in isopropyl alcohol for 1 day and dried under vacuum for 1 day. It was then weighed and its dimensions were determined before the testing in order to calculate the bulk volume of the specimen.

### 3. Results and Discussion

The following section consists of two parts. In the first part of this section, the effect of each addition of micro- and nano-sized CaCO<sub>3</sub> on the

hydration of the control OPC is discussed (Series 1 in Table 2). No fly ash was therefore added. In the second part of this section, the effect of each addition of micro- and nano-sized  $\text{CaCO}_3$  on the hydration of OPC containing high volumes of fly ash is discussed (Series 2 in Table 2). The efficacy of the addition of the nano-sized  $\text{CaCO}_3$  to compensate for the delayed initial setting and slower early strength development caused by the presence of high volumes of fly ash was investigated. The behaviour up to 28 days hydration was also studied to examine the effect of the accelerated early hydration on the long-term strength development.

### 3.1 The effect of the micro- and nano-sized $\text{CaCO}_3$ additions on the hydration of OPC

The conduction calorimetry curves for the control OPC and OPC with 10% and 20% additions of micro-sized  $\text{CaCO}_3$  and nano-sized  $\text{CaCO}_3$  for w/c 0.50 are shown in Figure 2. The curve of the control OPC is almost identical to those of the OPC with the additions of both 10% and 20% micro-sized  $\text{CaCO}_3$ , indicating that the additions of micro-sized  $\text{CaCO}_3$  have little or almost no effect on the hydration of OPC in terms of the rate of heat development. It is evident, however, that the additions of both 10% and 20% nano-sized  $\text{CaCO}_3$  significantly accelerate the early hydration of OPC. The first main peak of the control OPC occurs at approximately 9.5 hours whereas those of the OPC with the additions of 10% and 20% nano-sized  $\text{CaCO}_3$  occur at 5.8 and 4.8 hours, respectively. This implies that the higher the amount of nano-sized  $\text{CaCO}_3$  addition, the greater is the accelerating effect.

The TGA was conducted for the same series of specimens in order to determine the amount of  $\text{CaCO}_3$  in the specimens hydrated for 10 hours, 1 day and 3 days. The results are shown in Figure 3. There is about 2% of  $\text{CaCO}_3$  in the control OPC constantly observed throughout the hydration up to 3 days, indicating that the anhydrous OPC powder might have been carbonated during the storage period. It is important to note that the amount of  $\text{CaCO}_3$  in each specimen is lower than the amount added to the specimen and decreases as the hydration takes place. The OPC with the addition of 10% micro-sized  $\text{CaCO}_3$  has about 10.5%  $\text{CaCO}_3$  at 10 hours hydration. Considering that the control OPC has about 2.1%  $\text{CaCO}_3$  at 10 hours hydration, the OPC with the addition of 10% micro-sized  $\text{CaCO}_3$  has lost about 1.6%  $\text{CaCO}_3$  at 10 hours hydration. The OPC with the addition of 20% micro-sized  $\text{CaCO}_3$  has lost about 4.6%  $\text{CaCO}_3$  at 10 hours hydration. These phenomena become more noticeable with the additions of nano-sized  $\text{CaCO}_3$ . The OPC with the additions of 10% and 20% nano-sized  $\text{CaCO}_3$  lost about 4.2% and 8.6%, respectively at 10 hours hydration. It is suggested that some portion of  $\text{CaCO}_3$  added to the specimen might be chemically reacted in the hydration process.

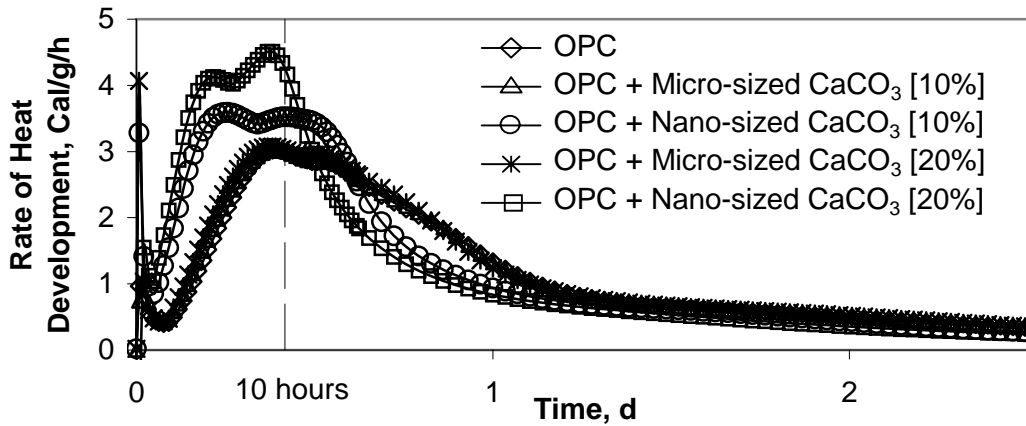


Figure 2: Conduction calorimetry curves for OPC and OPC with the additions of micro- and nano-sized  $\text{CaCO}_3$  for w/c 0.50

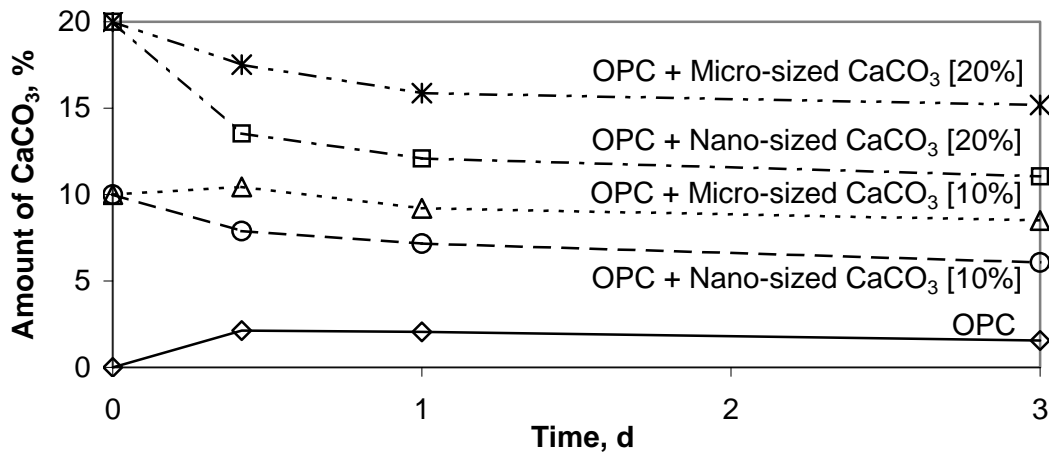


Figure 3: The amounts of  $\text{CaCO}_3$ , determined by TGA, for OPC and OPC with the additions of micro- and nano-sized  $\text{CaCO}_3$  for w/c 0.50 hydrated for 10 hours, 1 day and 3 days

It has been previously shown that the  $\text{CaCO}_3$  chemically reacts with tricalcium aluminate,  $\text{C}_3\text{A}$  to form calcium carboaluminate hydrates [4, 5]. The chemical reaction of  $\text{C}_3\text{A}$  with  $\text{CaCO}_3$  produces both high- and low-carbonate forms of calcium aluminate hydrate, respectively,  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaCO}_3\cdot 32\text{H}_2\text{O}$  and  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$ . This chemical reaction is very similar to that of  $\text{C}_3\text{A}$  with  $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$  (gypsum) that produces both high- and low-sulphate forms of calcium aluminate hydrate. The high carbonate form of calcium aluminate hydrate,  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaCO}_3\cdot 32\text{H}_2\text{O}$  has a needle-like structure, which is very similar to ettringite [6]. It is often observed that the conduction calorimetry curve of control OPC has a small shoulder right after the main peak of hydration as shown in Figure 4. It has been suggested that this shoulder is related to the formation of ettringite [7]. When the 20% nano-sized  $\text{CaCO}_3$

is added, this shoulder is not only significantly enhanced but also significantly accelerated as shown in the figure. The SEM images shown in Figures 5 (a) and (b) are respectively the control OPC and the OPC with the 20% nano-sized  $\text{CaCO}_3$  addition hydrated for 10 hours. No needle-like structure of ettringite can be observed in the control OPC. In the OPC with the 20% nano-sized  $\text{CaCO}_3$  addition, however, the needle-like structure can be observed where the enhanced and accelerated small shoulder observed in Figure 4 has occurred before 10 hours due to the addition of the nano-sized  $\text{CaCO}_3$ . This needle-like structure may be a mixture of ettringite and  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaCO}_3\cdot 32\text{H}_2\text{O}$ . The formation of ettringite could be accelerated by the addition of nano-sized  $\text{CaCO}_3$  and/or there could be a reaction of  $\text{C}_3\text{A}$  with the added nano-sized  $\text{CaCO}_3$  itself. Nevertheless, the formation of  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaCO}_3\cdot 32\text{H}_2\text{O}$  was minimum. The study previously mentioned concludes that some portion of the added  $\text{CaCO}_3$  was consumed during the hydration of  $\text{C}_3\text{S}$  [2]. This indicates that the added  $\text{CaCO}_3$  might also be consumed in the hydration of  $\text{C}_3\text{S}$  and the amount of the added  $\text{CaCO}_3$  that may react with  $\text{C}_3\text{A}$  can be very small.

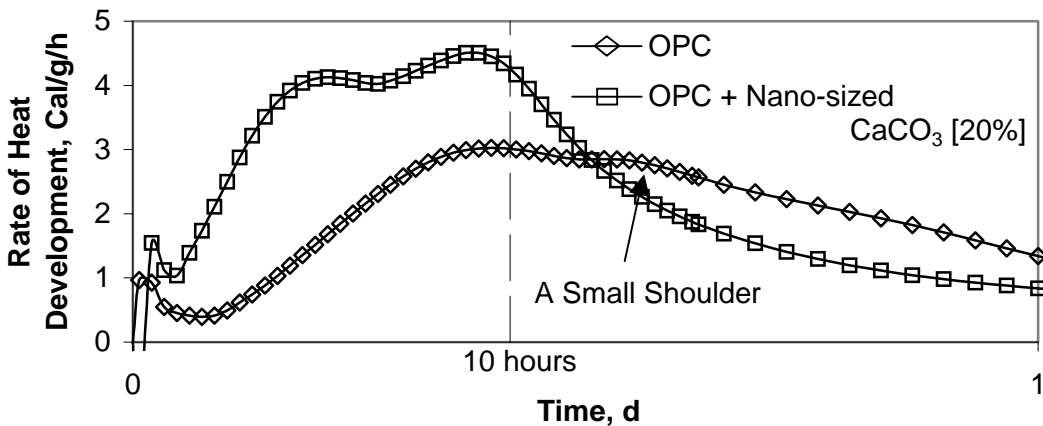


Figure 4: Conduction calorimetry curves for OPC and OPC with the additions of 20% nano-sized  $\text{CaCO}_3$  for w/c 0.50

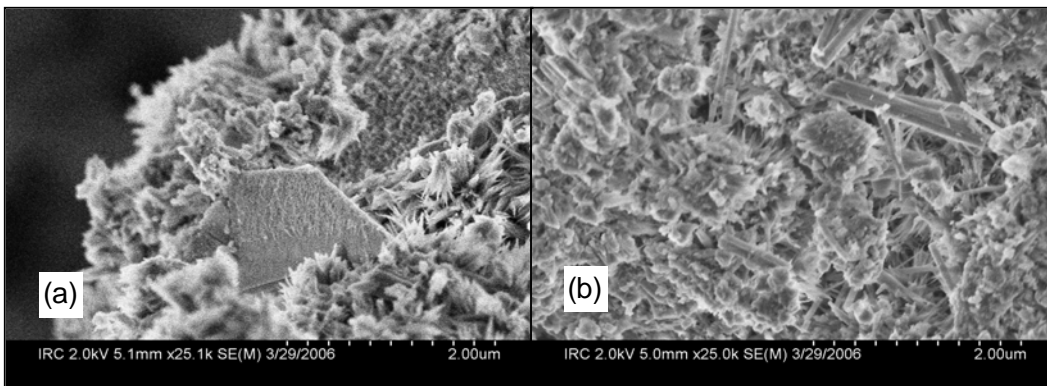


Figure 5: SEM images of (a) control OPC and (b) OPC with the 20% nano-sized  $\text{CaCO}_3$  addition hydrated for 10 hours

### 3.2 The effect of the micro- and nano-sized $\text{CaCO}_3$ additions on the hydration of OPC containing high volumes of fly ash

It is widely known that the use of high volumes of SCMs delays the initial setting and early strength development of OPC. The conduction calorimetry curves for the control OPC and OPC containing 50% fly ash and OPC containing 50% fly ash with the additions of 10% and 20% micro- and nano-sized  $\text{CaCO}_3$  for w/c 0.50 are shown in Figure 6. The hydration of OPC containing 50% fly ash is significantly delayed compared to that of OPC itself, owing mainly to the delayed hydration of  $\text{C}_3\text{S}$  in OPC in the presence of fly ash. The curve of the OPC containing 50% fly ash is almost identical to those of the OPC containing 50% fly ash with the additions of 10% and 20% micro-sized  $\text{CaCO}_3$ . It is clearly evident, however, that the additions of nano-sized  $\text{CaCO}_3$  accelerate and compensate for the delayed early hydration of OPC containing 50% fly ash. The 10% nano-sized  $\text{CaCO}_3$  addition significantly accelerates the delayed hydration caused by high volumes of fly ash. Furthermore, the OPC containing 50% fly ash with the 20% nano-sized  $\text{CaCO}_3$  addition hydrates almost as fast as the control OPC. A considerable improvement on the engineering properties may be expected.

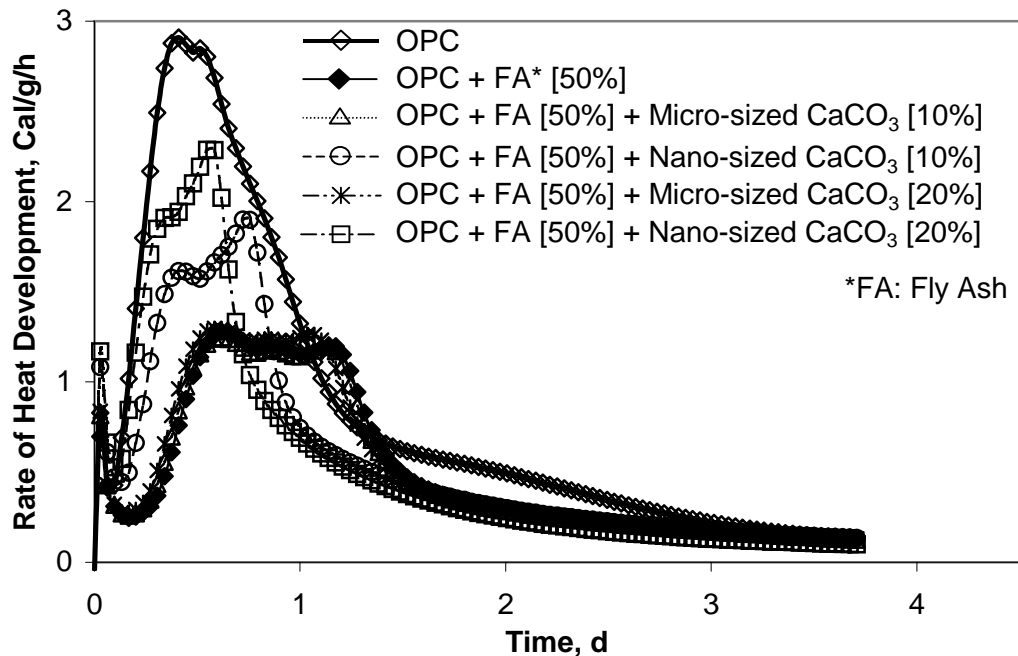


Figure 6: Conduction calorimetry curves for OPC, OPC containing 50% fly ash and OPC containing 50% fly ash with the additions of micro- and nano-sized  $\text{CaCO}_3$  for w/c 0.50



Microhardness determinations were performed to investigate the effect of the  $\text{CaCO}_3$  addition on the engineering property of the OPC containing high volumes of fly ash. It has been reported that the microhardness data for the control OPC correlate well with compressive strength data [8]. The microhardness values of OPC, OPC containing 50% fly ash and OPC containing 50% fly ash with the additions of micro- and nano-sized  $\text{CaCO}_3$  hydrated up to 3 days and 28 days are shown in Figures 7 (a) and (b). In Figure 7 (a), it is evidently illustrated that the early strength development of the OPC containing 50% fly ash is significantly delayed. The microhardness value at 3 days hydration for the control OPC and that containing 50% fly ash are 102.4 MPa and 28.0 MPa, respectively. However the microhardness value becomes 53.4 MPa when the 20% nano-sized  $\text{CaCO}_3$  was added.

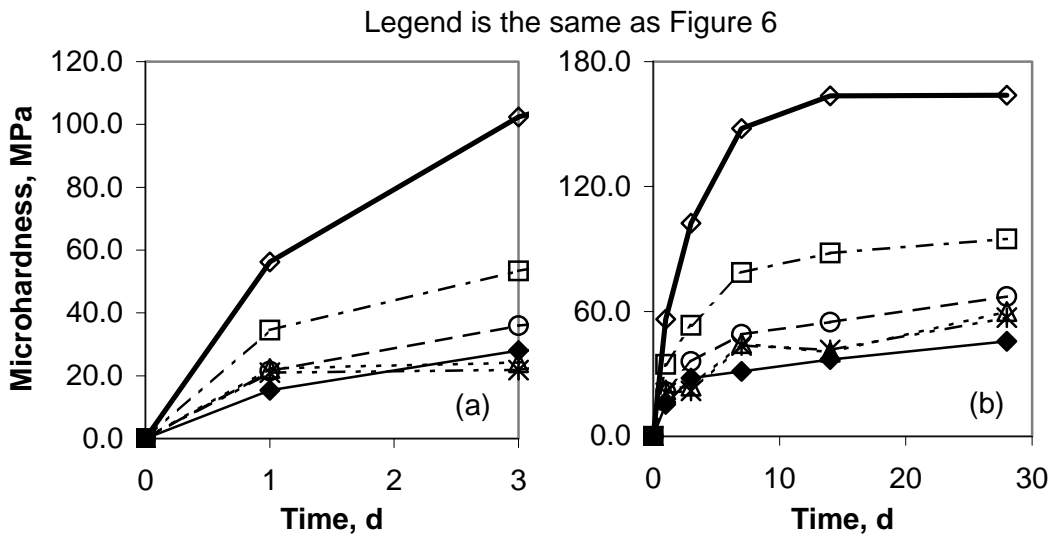


Figure 7: Microhardness values of OPC, OPC containing 50% fly ash and OPC containing 50% fly ash with the additions of micro- and nano-sized  $\text{CaCO}_3$  for the hydration period up to (a) 3 days and (b) 28 days

It was previously indicated that some portion of the added  $\text{CaCO}_3$  was chemically reacting in the hydration process to form calcium carboaluminate hydrates. A formation of calcium carboaluminate hydrates, however, might not be relevant to the improvement of strength development owing to the following reasons. The high carbonate form of calcium aluminate hydrates,  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaCO}_3\cdot 32\text{H}_2\text{O}$ , detected by the conduction calorimetry in Figure 4 and the SEM analysis in Figure 5 (b) respectively, might not contribute remarkably to the strength development. Assuming its mechanical characteristics are analogous to those of ettringite, it would appear that it may have a small direct influence on the strength development. Further, not only the small shoulder of the calorimetry curve enhanced and accelerated by the addition of nano-sized  $\text{CaCO}_3$ , but also the whole main peak of the calorimetry curve is enhanced

and accelerated by the additions of nano-sized  $\text{CaCO}_3$ , as shown in Figure 4. This main peak is primarily attributed to the hydration of  $\text{C}_3\text{S}$ . This is central to strength development and it is clear that the significant strength development shown in Figure 7 was a result of the accelerated hydration of  $\text{C}_3\text{S}$ . The study on the effect of the finely ground limestone addition on the hydration of  $\text{C}_3\text{S}$  mentioned in the previous section noted that the reaction products formed between the hydrating  $\text{C}_3\text{S}$  and the added  $\text{CaCO}_3$  could not be identified, as they were present in only small amounts [2]. This indicates that there is likely something else responsible for accelerating the  $\text{C}_3\text{S}$  hydration and the significant strength development. One suggestion is that the nano-sized  $\text{CaCO}_3$  particles serve as nucleation sites to accelerate the hydration process. The nucleation of C-S-H was accelerated by the presence of the well-crystalline nano-sized  $\text{CaCO}_3$  particles in the hydration process. The effect of two calcareous fillers, ground limestone and reagent grade  $\text{CaCO}_3$  on the compressive strength of OPC was studied and it was argued that the calcareous fillers acted as nucleation sites responsible for the acceleration effect on the early strength development [9]. The lower efficacy of the micro-sized  $\text{CaCO}_3$  addition, as opposed to the nano-sized  $\text{CaCO}_3$  addition, on the strength development can be explained by its larger particle size that would not function as nucleation sites as effectively as the nano-sized  $\text{CaCO}_3$ .

The modulus of elasticity was also determined. The results were very similar to that of microhardness. The early development of modulus of elasticity in the presence of 50% fly ash is significantly improved by the addition of nano-sized  $\text{CaCO}_3$  addition.

The effect of accelerated early hydration on the longer-term hydration can be observed in Figure 7 (b). It is commonly known that the strength development after a long-term hydration would be similar with or without an accelerating admixture, even if the early hydration was accelerated by the admixture. This is not the case with the addition of nano-sized  $\text{CaCO}_3$ . The strength development in the early stages of hydration accelerated by the addition of  $\text{CaCO}_3$  continues to be improved up to 28 days hydration. The strength development of the OPC containing high volumes of fly ash is much lower than that of the control OPC. The additions of nano-sized  $\text{CaCO}_3$  however significantly improve the strength development.

In addition to the determinations of microhardness and modulus of elasticity, the porosity determinations were performed by the helium pycnometer. The mechanical properties of the materials as a function of porosity in lieu of hydration in time were obtained. The logarithms of microhardness values versus porosity for OPC, OPC containing 50% fly ash and OPC containing 50% fly ash with the additions of micro and nano-sized  $\text{CaCO}_3$  are shown in Figure 8. The figure indicates that the OPC has the highest values of microhardness and OPC containing 50% fly ash the lowest. The microhardness values between those two specimens are in the following order, OPC containing 50% fly ash with 20% nano-sized

$\text{CaCO}_3 > 10\%$  nano-sized  $\text{CaCO}_3 > 10\%$  micro-sized  $\text{CaCO}_3$  and 20% micro-sized  $\text{CaCO}_3$ . It is also clearly illustrated in the figure that the lower the porosity, the higher is the microhardness for each specimen.

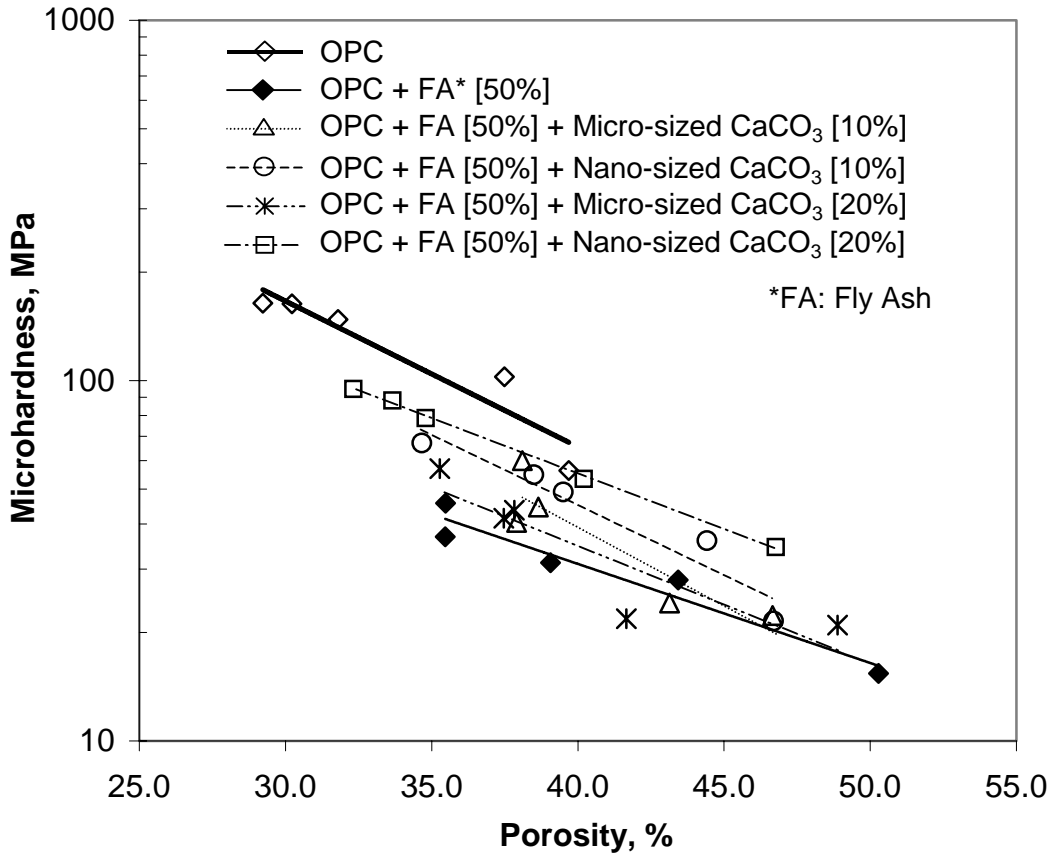


Figure 8: The logarithms of microhardness values versus porosity for OPC, OPC containing 50% fly ash and OPC containing 50% fly ash with the additions of micro- and nano-sized  $\text{CaCO}_3$

#### 4. Conclusions

- The early hydration of the control OPC is significantly accelerated by the additions of 10% and 20% nano-sized  $\text{CaCO}_3$ . The higher the amount of  $\text{CaCO}_3$  addition, the greater is the accelerating effect.
- The amounts of  $\text{CaCO}_3$  added to the specimen decrease as the hydration takes place, indicating some portion of added  $\text{CaCO}_3$  is chemically reacting during the hydration process.
- The needle-like characteristics of ettringite and carboaluminate phases are observed by the SEM analysis in the OPC with the addition of 20% nano-sized  $\text{CaCO}_3$ .

- The significantly delayed early hydration, observed by the conduction calorimetry, of the OPC containing 50% fly ash is counteracted by the additions of nano-sized  $\text{CaCO}_3$ .
- Engineering properties, microhardness and modulus of elasticity, in the early stage of the hydration are remarkably improved by the addition of nano-sized  $\text{CaCO}_3$ .
- It is suggested that the added nano-sized  $\text{CaCO}_3$  particles serve as nucleation sites to accelerate the hydration process. This process results in the enhanced strength development.
- The additions of nano-sized  $\text{CaCO}_3$  are effective not only for the early hydration, but also for the longer-term hydration. The strength development at 28 days hydration was significantly improved by the addition of nano-sized  $\text{CaCO}_3$ .

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