CHAPTER 16

CHARACTERIZATION OF EARLY POZZOLANIC REACTION OF CALCIUM HYDROXIDE AND CALCIUM SILICATE HYDRATE FOR NANOSILICA MODIFIED CEMENT PASTE

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ABSTRACT

This study intends to investigate the early pozzolanic reaction of Nanosilica (nS) modified cement paste (NMCP) by the characterization technique of Calcium Hydroxide (CH) and Calcium Silicate Hydrate (C-S-H) using Fourier Transform Infrared Spectroscopy (FT-IR). NMCP samples were prepared with water-binder ratio of 0.50. nS of 5-15nm particle size were used as 1%, 3% ,5% ,7% and 10% replacement of cement by weight. All samples were cured in the concrete laboratory at daily room temperature (T) and relative humidity (RH) in the range of 18-28ºC and 65-90%, respectively. Powdered samples were prepared and tested at day 1,7,21 and 28. It was found that characterization technique used were able to give satisfactory qualitative indication of pozzolanic reactivity of NMCP by the presence and absence of C-S-H and C-H that can indicate which replacement has higher pozzolanicity. NMCP exhibited a higher pozzolanic reactivity compare to conventional cement paste by which cement performance was enhanced.

Keywords: Nanosilica, CH, C-S-H, FT-IR, Cement Paste

INTRODUCTION

Concrete is the most widely used material in construction industry and consumes almost the total 90% cement production in the world. The consumption of large quantity of cement causes greenhouse effects to environment producing global warming issues. This is due to the emission of significant amount of carbon dioxide, CO_2 as by-product from the combustion of fuel fossil and calcination of limestone during its production. As much as 1.25 tonnes of CO_2 is emitted to produce every ton of cement and the CO_2 emission from cement industry is responsible 5% for the total global gas emissions of CO_2 [1]. One of the alternatives to reduce the amount of CO_2 emitted is reducing the amount of cement used in cement based material by partial replaced it with supplementary cementitious materials such as fly ash, ground granulated blast furnace slag, silica fume and natural pozzolans.

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Introduction of nanotechnology in cement industry has the potential to reduce the amount of CO_2 emissions by partial replacement of cement in cement based material with nanoparticles. Previous research found that remarkable improvements in the mechanical and chemical properties of cementitious materials can be observed with incorporation of nanomaterial such as SiO_2, ZnO_2, Al_2O_3, TiO_2, carbon nanotubes, nanoclays, carbon nanofibers and other nanomaterial. In the recent development, the addition of nanosilica (nS) has attracted increasing interest because of its filling effect which improve the particle size distribution thus reduced the porosity and permeability of cement based materials in effect increase durability and sustainability [2]. The aspect that makes nS an excellent cement replacement material is due to its high pozzolanicity resulted in enhanced durability of cement based material. It has proven to be an excellent admixture for cement to improve strength and durability and decrease permeability [2]. Besides that, nS is also typically a highly effective pozzolanic material and addition of nS into cement paste will improved the microstructure of the paste and reduced calcium leaching as nS reacts with CH and form additional C-S-H gel [3]. Highly pozzolanicity of nS particles is due to its size which is typically 5 - 100 nanometers (nm) with specific surface area (SSA) in the 25 - 50 m^2/g range and its fine vitreous particles approximately 1000 times smaller than the average cement particles.

According to ASTM C125 pozzolan is a siliceous and aluminous material which itself possesses little or no cementitious value but which will in finely divided form in the presence of moisture, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties [4]. Pozzolanic reaction in cement system is the reaction of silica with Calcium Hydroxide (CH) formed during the hydration of the OPC. It produces additional Calcium Silicate Hydrate (C-S-H) which is the main constituent for the strength and density in the harden binder paste. The pozzolanic activity includes two parameters; the maximum amount of lime (CaOH2) that pozzolan can react to and the rate of reaction. The rate of the pozzolanic activity is related to the surface area of pozzolan particles where higher surface area of pozzolan particle gives higher pozzolanic reactivity. Larsen investigated and analyzed pozzolanic reaction by monitoring the production of CH based on changing cement and admixture [5]. Through his findings in 1961, it was determined that the concentration of CH, commonly known as Portlandite, can be used to quantify the C-S-H formed in the same specimen. There should be a decrease in the amount of Portlandite in a given specimen based on addition of silica and maximum nominal size of the graded silica due the pozzolanic reaction [5].The objective of this study is to investigate the early pozzolanicity of nS modified cement paste (NMCP) by monitoring the presence of crystalline form CH and its subsequent reduction in abundance with time as the pozzolanic proceeds to form more amorphous C-S-H gel.

MATERIALS AND METHOD

MATERIALS AND SAMPLE PREPARATION

Nanosilica (nS) used in this study was Silicon Dioxide Nanopowder (CAS 14808-60-7) of 5-15nm particle size (BET) with 99.5% silica purchased from Sigma-Aldrich, Germany. Cement used was Ordinary Portland Cement (OPC) (ASTM Type 1 recognized by ASTM C150) manufactured by Cahaya Mata Sarawak Cement Sdn. Bhd (CMS).The chemical and mineralogical characteristics of the OPC are given in Figure 1. NMCP samples were prepared with water-to-cement ratio (w/c) of 0.5 and 1%, 3%, 5%, 7% and 10% cement replacements by weight. Universal Containers 30ml (28 mm diameter , 85mm height) were used as moulds. All samples were cured in the concrete laboratory at daily room temperature (T) and relative humidity (RH) in the range of 18-28°C and 65-90%, respectively. Powdered samples were prepared from small samples collected from the demoulded samples.

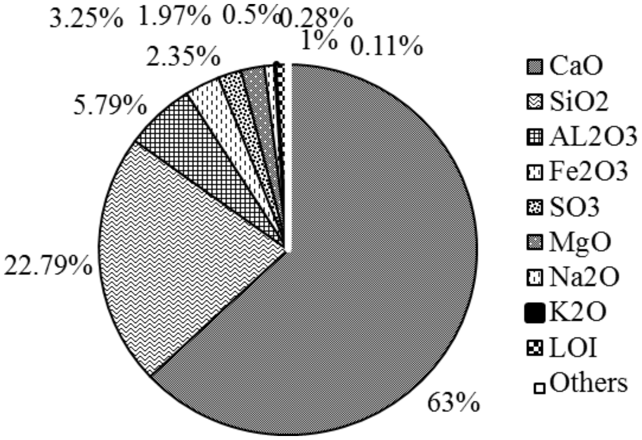

Figure 1: Chemical Composition of OPC

METHOD

Early pozzolanic reaction of Nanosilica Modified Cement Paste (NMCP) samples was analysed using characterization technique namely Fourier Transform Infrared Spectroscopy (FT-IR) at day 28. Test was performed on all samples with a Shimadzu Fourier Transform Infrared Spectroscopy (FT-IR) 81001 Spectrophotometer. The spectrum measurement method applied in this FT-IR study is Attenuated Total Reflection (ATR) method. Transmission infrared spectrum of each sample was recorded using a Fourier Transform Infrared Spectrophotometer (IRAffinity-1) in the region of 400 to 4000 cm^{-1} with 2.0 cm^{-1} resolution.

RESULTS AND DISCUSSION

Cement contains several chemical components with various functional groups, such as SiO_2, SO_4, H_2O, OH, and CO_3, which are infrared active. The absorbed infrared wavelengths of the functional groups are dependent on the chemical surroundings of the group. Hence, there will be shifts of the absorption bands of the functional groups [6]. The main products of hydration, calcium hydroxysilicate of the C_2SH_2 and CSH (β) types can be detected in the IR spectra from the v3 (Si-O) absorption band at 965–975 cm^{-1} and calcium hydroxide (CH) from the v (OH) absorption band at 3640 cm^{-1} [7].

ANALYSIS SAMPLE WITHIN THE SAME PERCENTAGES OF NS REPLACEMENT WITH AGE DEVELOPMENT

Figure 2.1 to 2.5 showed the FT-IR spectrum for different percentages of nS replacement from day 1 to 28. When the hydration progresses from day 1 to 28, the CH band around 3630 cm^{-1} for 1%, 3%, and 5% NMCP shown a decrease in intensity (as shown in Figure 2.1B, 2.2B and 2.3B) which indicated that the CH contents were reduced with the age development. The trend of CH development is opposite if compared with control set.

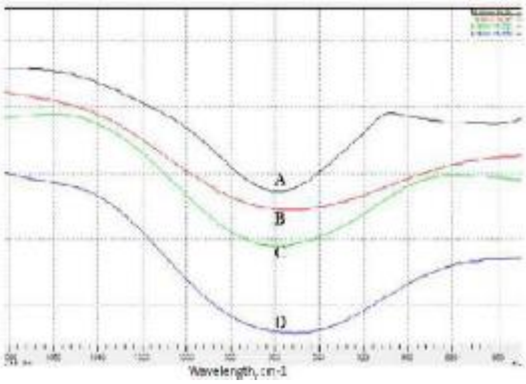

Figure 2.1A: C-S-H band of cement paste sample with 1% NMCP at (A) 1 day (B) 7 days (C) 21 days and (D) 28 days

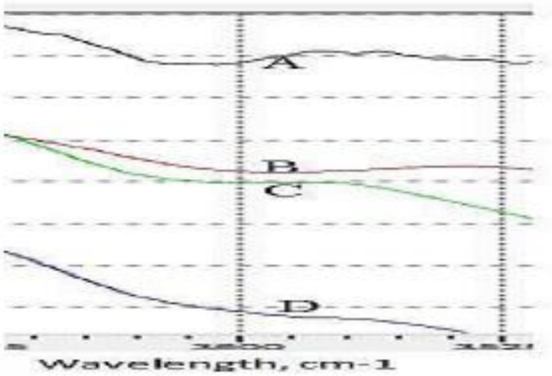

Figure 2.1B: CH band of cement paste sample with 1% NMCP at (A) 1 day (B) 7 days (C) 21 days and (D) 28 days

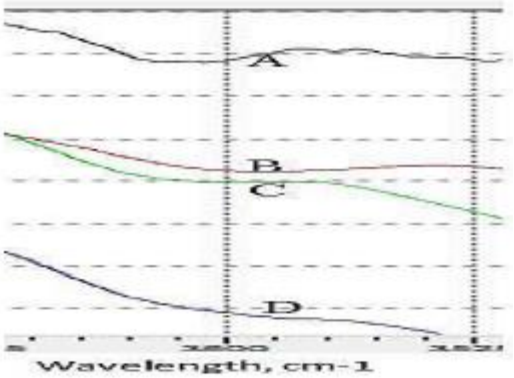

Figure 2.2A: C-S-H band of cement paste sample with 3% NMCP at (A) 1 day (B) 7 days (C) 21 days and (D) 28 days

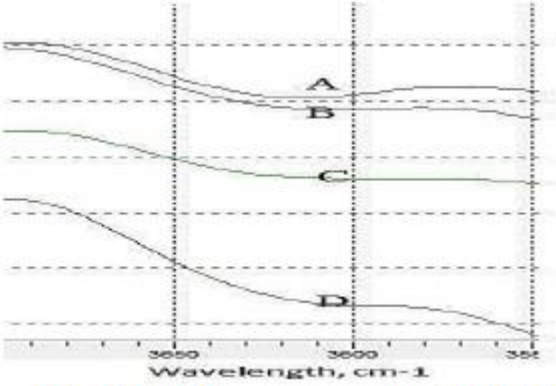

Figure 2.2B: CH band of cement paste sample with 3% NMCP at (A) 1 day (B) 7 days (C) 21 days and (D) 28 days

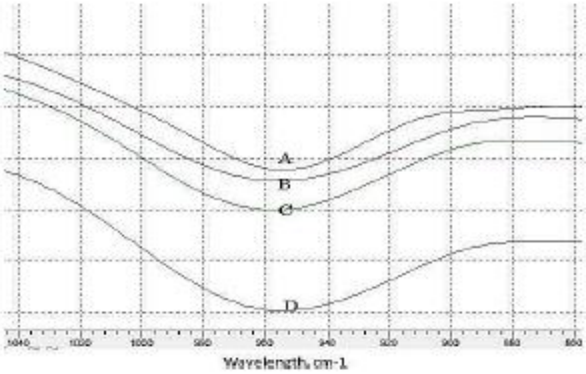

Figure 2.3A: C-S-H band of cement paste sample with 5% NMCP at (A) 1 day (B) 7 days (C) 21 days and (D) 28 days

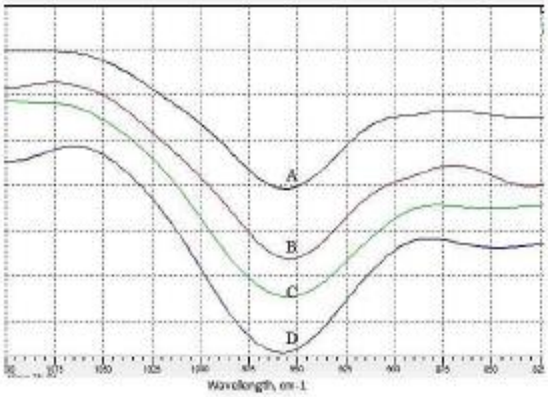

Figure 2.3B: CH band of cement paste sample with 5% NMCP at (A) 1 day (B) 7 days (C) 21 days and (D) 28 days

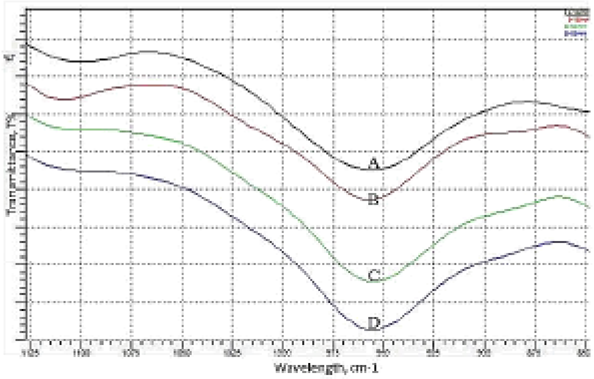

Figure 2.4A: C-S-H band of cement paste sample with 7% NMCP at (A) 1 day (B) 7 days (C) 21 days and (D) 28 days

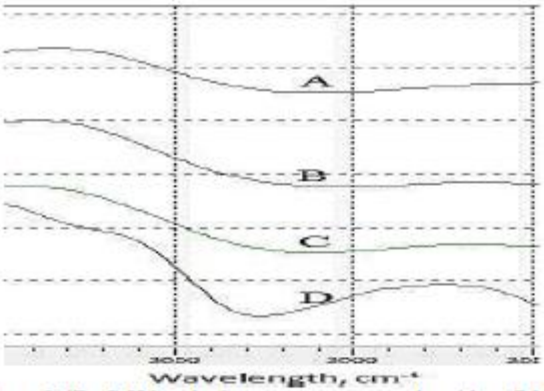

Figure 2.4B: CH band of cement paste sample with 7% NMCP at (A) 1 day (B) 7 days (C) 21 days and (D) 28 days

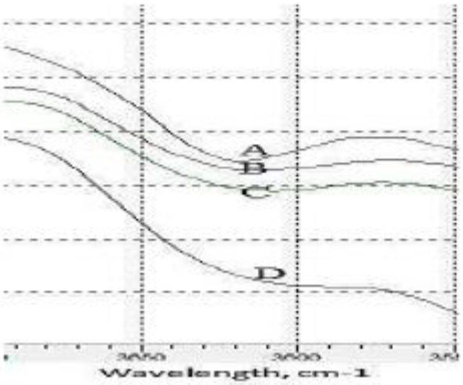

Figure 2.5A: C-S-H band of cement paste sample with 10% NMCP at (A) 1 day (B) 7 days (C) 21 days and (D) 28 days

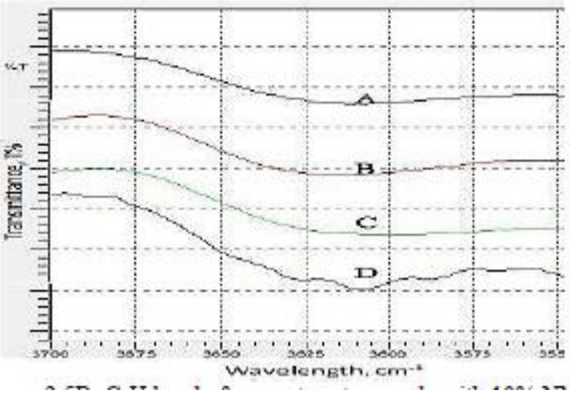

Figure 2.5B: CH band of cement paste sample with 10% NMCP at (A) 1 day (B) 7 days (C) 21 days and (D) 28 days

This phenomenon is due to the pozzolanic reaction of nS where nS reacts with CH to produce additional C-S-H. The CH band for 7% and 10% NMCP samples have shown an increasing intensity (as shown in Figure 2.4B and 2.5B). The increasing intensity of the CH band indicated that there was no reduction of the CH content in the sample. Therefore, pozzolanic reactivity did not occur for 7% and 10% NCMP. This may be due to the agglomeration of nS that prevented its participation in hydration reaction. The intensity of the C-S-H band increased as hydration progresses for all samples (as shown in figure 2.1A-2.5A). The C-S-H content for sample with 1%, 3% and 5% NMCP were more than 7% and 10% NMCP. This was due to the pozzolanic reactivity that produced an additional C-S-H that was purely from the cement hydration. As a summary, 1%, 3% and 5% NMCP showed pozzolanic reactivity and produced additional C-S-H to the cement sample. Meanwhile 7% and 10% NMCP did not show pozzolanic reactivity due to the agglomeration of nS.

COMPARISON BETWEEN SAMPLES WITH DIFFERENT PERCENTAGES OF NS REPLACEMENT AT DAY 28.

Figure 2.6 A and B showed comparison between samples with different percentages of nS replacement at day 28. The C-S- H band peak around 970 cm^{-1} for 1%, 3% and 5% NMCP samples (as shown in Figure 2.6A) have higher intensity compare to the control sample. The increasing trend of the C-S-H band indicated that there were more C-S-H produced in NMCP samples due to the pozzolanic reactivity of nS. The C-S-H band had shown the strongest intensity for the cement paste sample in 3% NMCP since it menifested the deepest and steepest downward peak for the C-S-H band as shown in Figure 2.6A. The 7% and 10% NMCP samples had low intensity in C-S-H band compare to the control sample. These indicated that there was lesser C-S-H produced in 7% and 10% NMCP sample. It can be concluded that, 3% was the optimum dosage for 5-15nm NMCP.

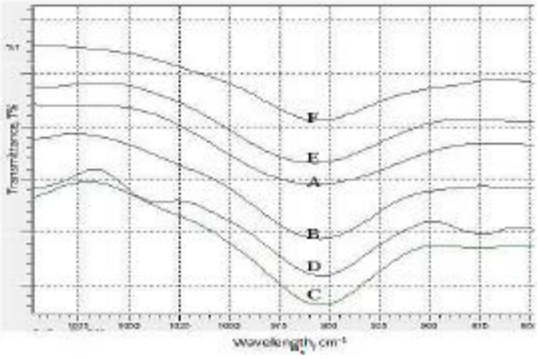

Figure 2.6A: C-S-H band around 970 cm-1 for (A) Control (B) 1% (C) 3% (D) 5% (E) 7% and (F) 10% NMCP sample at 28 day

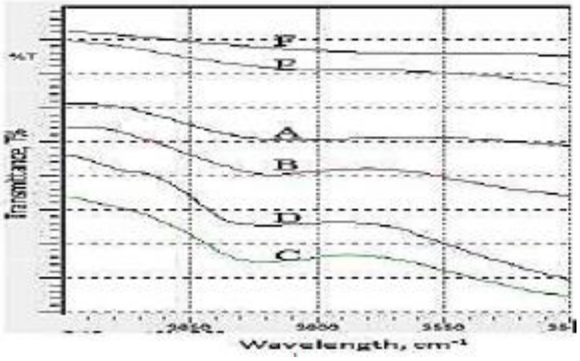

Figure 2.6B: CH band around 970 cm-1 for (A) Control (B) 1% (C) 3% (D) 5% (E) 7% and (F) 10% NMCP sample at 28 day

CONCLUSION

In conclusion, 1%, 3% and 5% NMCP samples have shown pozzolanic reactivity. The CH content in 1%, 3% and 5% NMCP samples decreased as the hydration progressed from day 1 day to day 28. The reduction of the CH is due to the pozzolanic reaction between nS and CH content in hydrated cement paste that produced additional C-S-H gel. Meanhile 7% and 10% NMCP samples did not show pozzolanic reactivity due to agglomeration of nS that did not permit the nS to join the hydration process. Analysis done between samples with different percentages of nS replacement had found that the optimum dosage of nS by comparing the C-S-H content was 3%. Therefore, 3% NMCP was the optimum and the most effective percentage replacement that produced pozzolanic reactivity that can improve the microstructure of the cement system.

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