CONCRETE RESEARCH LETTERS

www.crl.issres.net Vol. 5 (2) – June 2014

Characterization of Calcium Hydroxide (CH) crystals in Nano Modified Binder (NMB)

Norsuzailina Mohamed Sutan[1,*], Ibrahim Yakub [2], Sinin Hamdan[3]andChuo Sin Kiong[1]

[1]*Departmentof Civil Engineering, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia*
[2]*Department of Chemical Engineering and Sustainability, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia*
[3]*Department of Mechanical and Manufacturing Engineering , Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia*

Abstract

With the advent of nanotechnology, such nano scale materials have been developed for the application in binding material namely cement.A new synthetic material, namely Nano-SiO_2(nS), has been produced and available in the market. It is based on silica particles of 5-50 nm which is much smaller than those of silica fume (microsilica) with particles of 0.1-1 μm. Previous studies have shown that due to the very high specific surface area (80-1000 m^2/g) and the spherical shape of silica particles, it can potentially enhance the performance of cement mainly due to its reaction with calcium hydroxide (CH) to develop more of the strength-carrying compound in cement structure namely calcium silica hydrate (C-S-H). This reaction namely pozzolanic reaction is crucial in the mitigation of efflorescence by its relation to C-H leaching. The early hydration behaviour of a Nano Modified Binder (NMB) that hypothetically affects efflorescence has been investigated through physicochemical characterization namely Puddle Test (PT), Standard Chemical Method (SCM), Compressive Strength Test (CS), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). NMB mortar samples were prepared with water-to-cement ratio (w/c) of 0.50. nS of 10-20 nm particle size was used as 2%, 3% and 5% replacement of cement by weight. Samples were cured at room temperature (32^o C) and average relative humidity (90%). Powdered and polished samples were prepared and tested at 28 days of binder hydration. Results from CS, XRD analysis and SEM images show that in comparison to conventional binder, NMB exhibited a lesser efflorescence where validation from CS, XRD analysis and SEM images show the evidence of the pozzolanic reaction.

Keywords: Nano-SiO_2 ; Efflorescence ;pozzolanic; XRD ;SEM

1. Introduction

Cement plays an important role in the construction industry worldwide. As the fourth largest consumer amongst the Southeast Asia countries, Malaysia consumed 17 million tons of cement by the end of 2011[1]. Cement based material are strongly influence by their micro structural properties Recent development on research and development (R&D) in cement based material was done on new admixture for cement at nano scale. The main objective is to enhance physicochemical properties of cementatious products to be more economical and environmental friendly. In the nanotechnology R&D, USA leads by investment of USD 3.7 billion through its National Nanotechnology Initiative (NNI), followed by European Union with USD 1.7 billion in investment [2].

With the advent of nanotechnology,suchnano scale materials have been developed for the application in cementatious or binding building materials namely concrete and mortar. A new synthetic material, namely ultrafine silica orNanoSilica (SiO_2), has been recently produced and available in the market.It is based on silica particles of 5-50 nm and is much smaller than those of silica fume (microsilica) which contains particles as "big" as 0.1-1 μm [1]. Previous studies have shown that due to the very high specific surface area (80-1000 m^2/g) and the spherical shape of the silica particles,NanoSilica, can potentially enhance the performance of cementatious materials mainly due to the pozzolanic reaction of SiO_2 with calcium hydroxide (CH) to develop more of the strength-carrying compound in cement structure: calcium silica hydrate (C-S-H) [3-7]. This reaction has been contributing to the improvement of the microstructure of cementatious material products which in effects solves durability problems in particular efflorescence as shown in Fig. 1.

Efflorescence schematically shown in Fig. 2, is a deposit of crystalized calcium carbonate ($CaCO_3$) on the exposed concrete and cementatious materials manifesting from hazy white layers to thick white crusts [8,9]. This manifestation is caused primarily by the leaching of CH or Portlandite, one of Portland cement hydration products, which is slightly soluble in water, migrating to the concrete surface through the capillary system of the concrete and evaporated to leave the solid CH which thenreacts with atmospheric carbon dioxide (CO_2) to form $CaCO_3$[8 - 12].

Fig. 1: Efflorescence on concrete wall.

Despite the fact that the aesthetic problem is more obvious on coloured surfaces than on the grey ones and causes economical implication due to products rejection by customers, efflorescence is indirectly related to durability problem in a way that theleaching occurred within the concrete can cause an increase in porosity, increase in permeability and decrease in strength, thereby increases its vulnerability to aggressive chemicals ingress [13, 14]. This phenomenon has received much description and discussion in the literature, not to mention speculation as to its causes and prevention; however the concern of this study is the in depth understanding of the underlying mechanism that may lead to creating solution that can mitigate its occurrence and by extension minimize the previously mentioned implication [8, 10]. To date there is no effective method that can guarantee the prevention of efflorescence [14, 15]. Hypothetically, if NMB reacts as pozzolanic material, efflorescence can be mitigated by the minimization of CH leaching. However, there are limited data available in the study of the microstructural interaction of NMB that can possibly reduce efflorescence. Therefore the objective of this study is to investigate the effect of NMB on efflorescence by focusing on the characterization and morphology of CH and CSH in NMB mortar in comparison to conventional mortar.

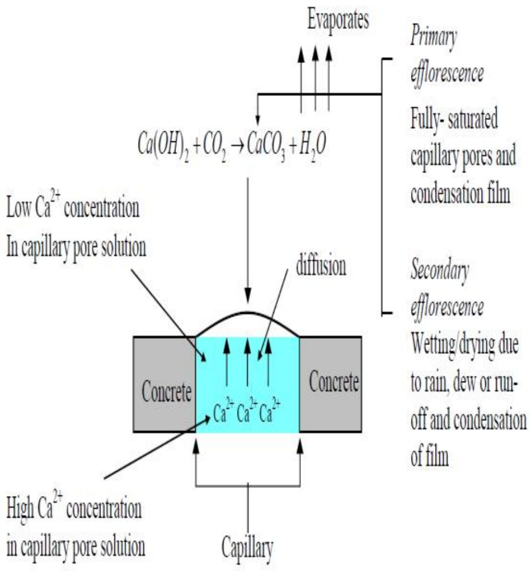

Fig. 2: Schematic diagram of Efflorescence from a cross sectional view of concrete block.

2. Materials and Methods

2.1 Materials and sample preparation

Nano-SiO_2 used in this study was Aldrich Silicon Dioxide Nanopowder of 10-20nm particle size (BET) with 99.5% silica. Binder used was Ordinary Portland Cement (OPC) (ASTM Type 1 recognized by ASTM C150) manufactured by Cahaya Mata Sarawak Cement Sdn. Bhd (CMS) and it exceeds the quality requirements specified in the Malaysian Standard MS 522: Part 1: 1989 Specifications for OPC. The chemical and mineralogical characteristics of the OPC binder are given in Fig. 3. The mix proportion was set at(cement: sand: water) 1:1.67:0.5(w/c)for all samples that were casted into Universal Container 30ml, (28mm diameter x 85mm height) for PT,SCM,XRD and SEM and 150 mm X 150 mm X 150 mm cubes for CS test. All samples wereair-cured in the concrete laboratory with average temperature (T) of 32^{o} C and relative humidity (RH) of 90%. NMB mortar samples were prepared with water-binder ratio of 0.50 and 2%, 3% and 5% of binder replacement by weight.

2.2 Methods

To study the effect of NMB to efflorescence, comparative physicochemical analysis were performed by using Puddle Test (PT), Standard Chemical Method (SCM), Compressive Strength Test (CS), X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM).

2.2.1 Efflorescence Tests

PT and SCM were performed at age of 7, 14, 21 and 28. Puddle test is an accelerated efflorescence test where distilled water of 10 ml was added on samples surfaces in the form of circular drops [6, 7].The water in the circle could vaporized or absorbed by the samples. On specified day, the surface of the samples was scraped to extract powder of 1gram in weight. SCM was used to quantify the amount of $CaCO_3$ from the extracted powder by dissolving it in a diluted hydrochloric acid solution. The dissolved salts was then placed on a filter paper and weighted before it was oven dried for 24 hours at temperature between 90°C-100°C. Then the sample was taken out and weighted again. The weight loss indicated the amount of the dissolved efflorescence formed on the mortar samples surface.

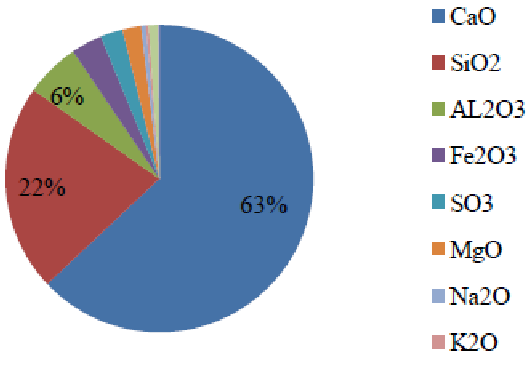

Fig. 3: Chemical Composition of OPC.

2.2.2 Characterization by XRD and SEM

The fine powder samples (passing 75 µm) and polished small samples were prepared and analysed using XRD and SEM at day 28 respectively. Acetone was used to stop the hydration process of these samples.XRD analysis forall prepared samples was performed with PANalytical equipment with CuKα radiation and λ of 0.1546 nm of running kV and 30 mA. The specifications were: count step: 4 sec/step, step size: 0.02 degree step size and range: 50 - 650 2ϴ angle.SEM images for all prepared samples were captured by a Scanning Electron Microscope (JSM-6701F) supplied by JEOL Company Limited, Japan that followed the ASTM C 1723-10 (2010) code of practice.

2.2.3 Mechanical Test

28-day CS test was performed according to BS 1881-116 (1983) on 150 mm cubes samples. It was used to determine the maximum compressive load that a sample can carry per unit area. The compressive strength gave the overall picture of the quality of concrete.

3. Results and Discussion

Fig. 4 shows the percentage of $CaCO_3$ collected from the surfaces of NMB mortar samples of 0.5 w/c ratio for 7, 14, 21, 28 days which shows thatefflorescence intensity on 5%NMB samples were the least most of the time. Besides, Fig. 5 shows that 5%NMB samples exhibited less calcium carbonate ($CaCO_3$) formation in comparison to other samples at day 28.This is in agreement with previous studies that found that showed 5% or more replacement with SiO_2 is required in order to have any significant microstructural improvement [16].

Fig.6 shows the XRD diffractograms of Control and NMB. The well-defined peaks of CH crystalat approximately 19^o 2ϴ appeared on all samples except for 5%NMB. Poor crystalline peak C-S-H appeared at 30^o 2ϴ for all samples except for 2% NMB where the presence of CH was the highest.This indicated that pozzolanic reaction has taken place which prevented leaching of CH to become efflorescence. The results were also confirmed by and reflected in the SEM images in Fig. 7 and compressive strength trend in Fig. 8 where 5%NMB was found to be the strongest.

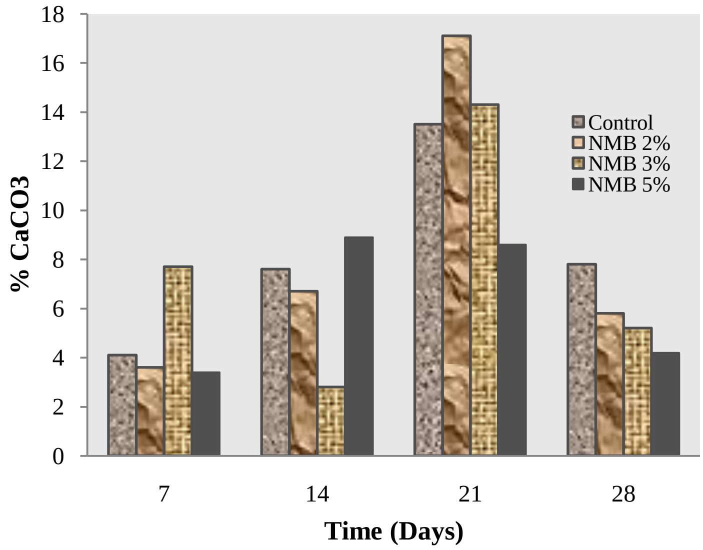

Fig. 4: Comparison of Percentage (%) of $CaCO_3$ versus days forNMB with control.

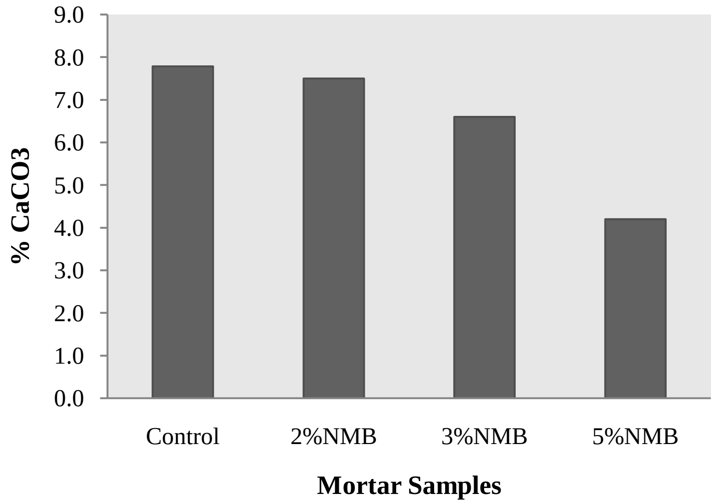

Fig. 5: Comparison of Percentage (%) of $CaCO_3$betweenNMB and control at day 28.

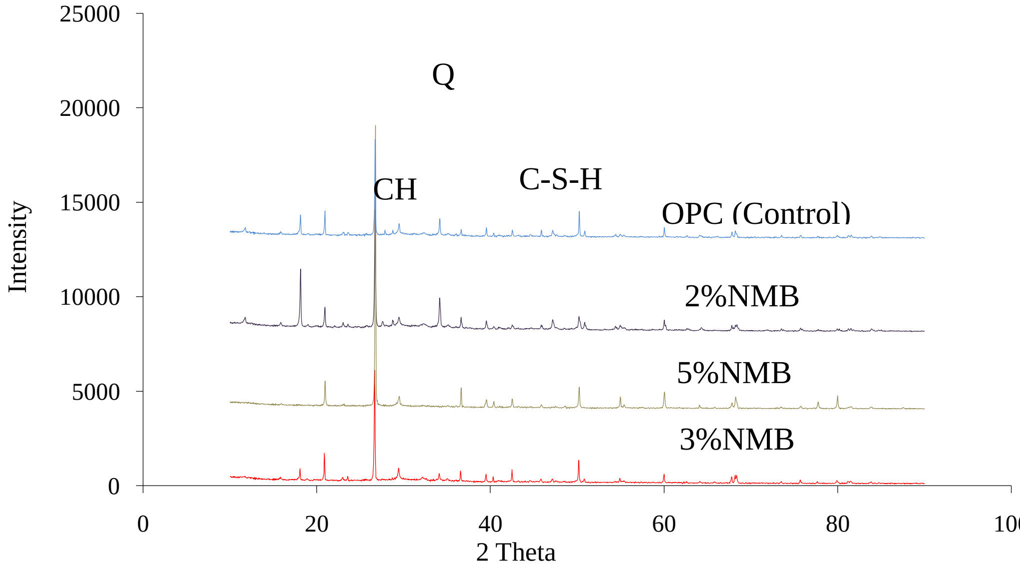

Fig.6:XRD patterns (CuKα radiation) of NMB and control atday 28.

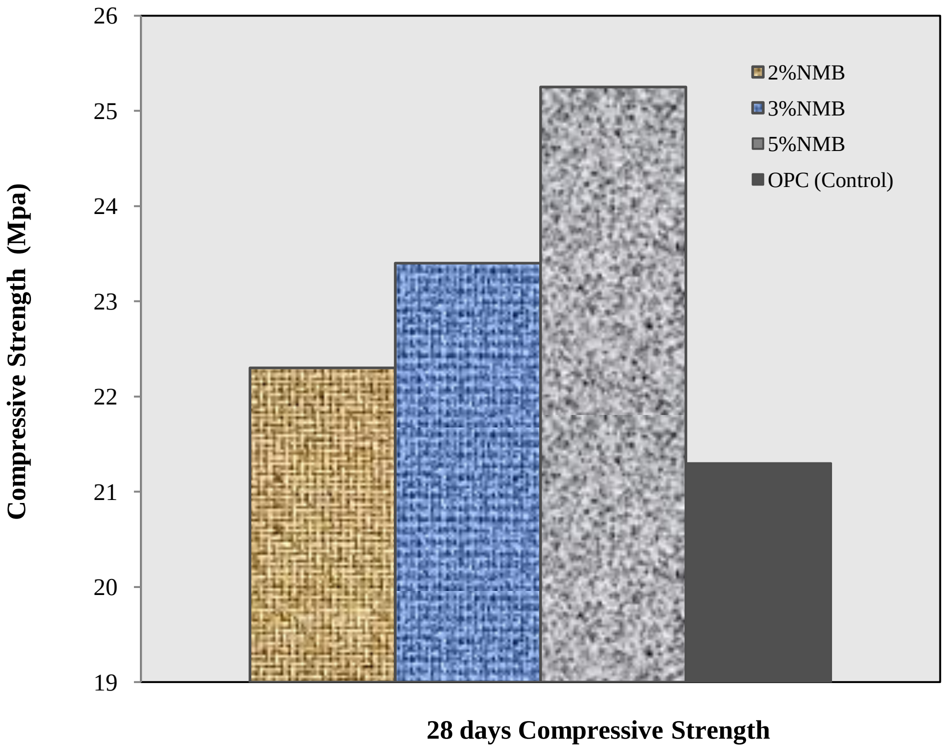

Fig. 7: Comparison of 28 days Compressive Strength betweenNMB and control.

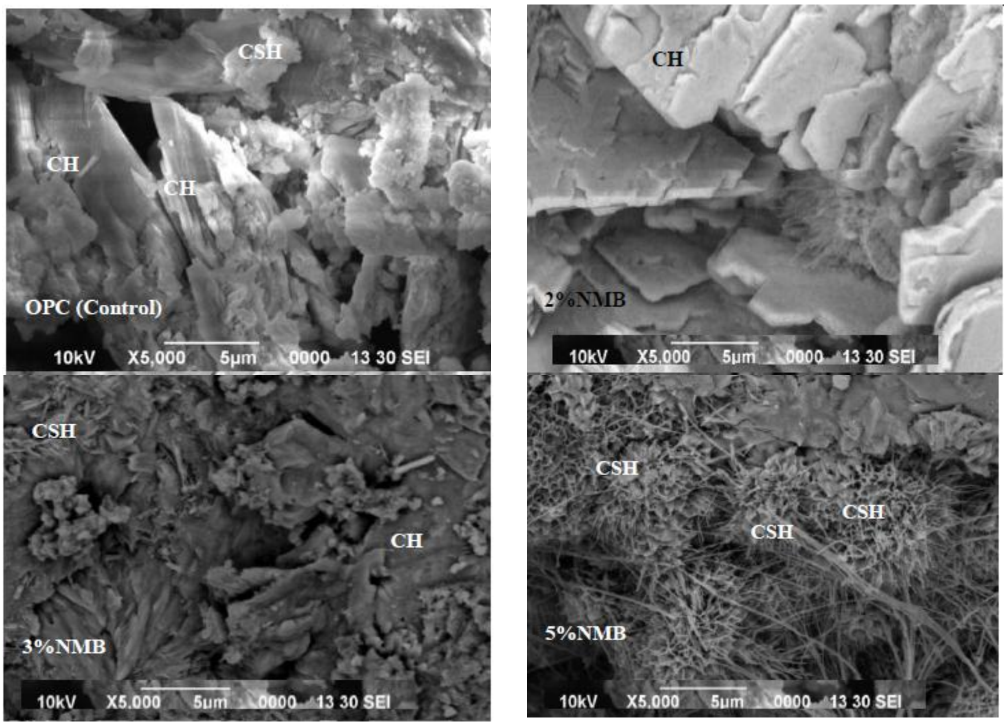

Fig.8: SEM images of OPC, 2%NMB, %3NMB and 5%NMB atday 28.

4. Conclusions

From the PT and SCM investigations performed, it is possible to conclude that NMB has influenced the efflorescence formation on mortar surfaces to a significant extent. The influence was based on pozzolanic reactivity of nS. This behavior was reflected in the XRD patterns, SEM images and the stronger NMB results for CS in comparison to conventional mortar. It was further validated that the optimum level of nS replacement to mortar was 5% by weight. Future investigation on the extent of reactivity of different particle sizes of nS with CH is needed to solve efflorescence phenomenon and indirectly improve concrete durability and sustainability.

5. Acknowledgement

The research work reported in this paper has been funded by the Ministry of Higher Education Malaysia: (FRGS/03(04)/772/2010(53)) and University Malaysia Sarawak (SGS/03(S113)/894/2012(26)).

References

[1] *Research and Markets: Malaysia Cement Industry*. 2012 [cited 2012 04 October]; Available from: http://www.businesswire.com/news/home/20120809005630/en/Research-Markets-Malaysia-Cement-Industry-1H12

[2] *Nano Technology Initiative. 2012* [cited 2012 27 January];Available from: http://www.nano.gov/publications-resources.

[3] Lin D.F, L.K., Chang W.C, Luo H.L and Cai M.Q.*Improvement of nano Silica SiO2 on sludge/ fly ash mortar.* Waste management, 2008,**28**: p. 6.

[4] Bjornstorm J, M.A., Matic A, Borjesson L. and Panas I.*Acclerating effects of the colloidal nano-silica for beneficial calcium-silicate-hydrate formation in cement*,Chem Phys Lett, 2004, **392**: p. 1-3.

[5] Gaitero J.J.*Reduction of the calcium leaching rate of the cement paste by addition of the silica nanoparticles* ,Cement Concrete Research, 2008, **38**(8-9): p. 1112-1118.

[6]Zegetodky, C.O.*Laboratory Investigation of Nanomaterials to Improve the Permeability and Strength of the Concrete*,2010, Virginia Transportation Research Council: Charlottesville.

[7] Arefi, M.R. *Silica nanoparticle size effect on mechanical properties and microstructure of cement mortar*, Journal of American Science, 2011, **7**(10).

[8] Kresse, P. *Efflorescence-Mechanism of Occurrence and Possibilities of Prevention*. Betonwerk+Fertigteil-Technik, 1987, 53:160-168.

[9] Kresse, P., *Efflorescence and its prevention*.Betonwerk+Fertigteil-Technik, 1991, 57: 84-88.

[10] Higgins, D.D., *Appearance* Matters (No.4.), 1982, Cement and Concrete Association.

[11] Neville, A.*Efflorescence-surface blemish of internal problem? Part 2: Situation in practice*, Concrete International, 2002.24.

[12] Neville, A.*Efflorescence-surface blemish of internal problem? Part 1: The knowledge*, Concrete International, 2002, 24.

[13] Bensted, J.*Efflorescence-prevention is better than cure*, Concrete, 2000, 34:40-41.

[14] Kresse, P.*Coloured concrete and its enemy: efflorescence*, Chemistry and Industry, 1989: pp. 93-95.

[15] Dow, C. & Glassier, F.P.*Calcium carbonate efflorescence on Portland cement and building Materials*, Cement and Concrete Research, 2003.33:147-154.

[16] Tobon, J.I., Restrepo, O. &Paya, J., *Comparative Analysis of Performance of Portland Cement Blended with Nanosilica and Silica Fume*, Dyna, 2010, .33:37-46.