CHARACTERISTICS OF NANOCLAY AND CALCINED NANOCLAY-CEMENT NANOMATRICES BY THE COMBINATION OF QXDA AND TGA TECHNIQUES

[1]HAKAMY A, [2]SHAIKH, [3]F.U.A., [4]LOW I.M

[1]Department of Imaging & Applied Physics, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
[2]Department of Civil Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
Email: a.hakmi3@postgrad.curtin.edu.au, s.ahmed@curtin.edu.au, j.low@curtin.edu.au
Email: j.low@curtin.edu.au

Abstract: Theinfluence of nanoclay (NC) and calcined nanoclay (CNC)on themechanical and thermal properties of cement nano-matrices presented. Calcined nanoclay is prepared by heating nanoclay (Cloisite 30B) at 900° C for 2h. Estimation of $Ca(OH)_2$ content in the cement nanomatrixis studied by the combination of Quantitative X-ray Diffraction Analysis (QXDA) and thermogravimetry analysis (TGA) techniques.Results showed thatthe microstructure and compressive strengthof the cement nanomatricesare improved as a result of NC and CNCaddition. An optimumreplacement of ordinary Portland cement with 1 wt% CNCis observed through decreased the porosity and increased compressive strengthof cement nanomatrices.Cost-benefit analysis indicatesthat nanoparticles are expensive but from economic point of view nanoclay is used in very small amount (i.e. 1 wt. %) in cementitious materials. As a result nanoclay does not add any significant cost but improves the mechanical properties significantly.

Index Terms: Nanoclay, Microstructure, Compressive strength, QXDA

I. INTRODUCTION

Nowadays, nanotechnology is one of the most active research areas in the civil engineering and construction materials [1]-[3]. Nanoparticles are used in polymer, ceramic and construction materials in order to produce cement nanomatrices that exhibit superior physical and mechanical properties [4]-[5]. Nanoclay (NC) is a new generation of processed clay for a wide range of high-performance cement nanomatrix [3]-[6]. As a kind of nano-pozzolanic material, nanoclay not only reduces the pore size and porosity of the cement matrix, but also improves the strength of cement matrix. Furthermore, nanoclay particles enhance hardened properties of cement paste and mortar.Farzadnia et al. [7] reported that incorporation of 3% halloysite nanoclay into cement mortars increased the 28^{th} day compressive strength up to 24% compared to the control samples. In this paper, the effect of different amounts of nanoclay and calcined nanoclay on the microstructure and compressive strength of cement nanomatrix is studied. Due to calcination, the amorphous contents of nanoclay is increased, which later reacted with $Ca(OH)_2$ of the cement hydration products and formed additional calcium-silica-hydrate (CSH) gel. The benefit of the use of CNC is the improvementof microstructure of thecement nanomatrix.

II. EXPERIMENTAL PROCEDURE

A. Materials

The nanoclay platelets (Cloisite 30B) used in this investigation is a natural montmorillonite modified with a quaternary ammonium salt, which was supplied by Southern Clay Products, USA.Ordinary Portland cement (ASTM Type I) was used in all mixes.

B. Thermal Treatment of Nanoclay

Calcined nanoclay (CNC) was prepared by heating the nanoclay at 800, 850 and 900° C for 2 h in an electric furnace with a heating rate of 10° C/min.It is found in this study that nanoclay transferred to amorphous state (calcined nanoclay) at 900 °C.Also many platelets in calcined nanoclay were destroyed and some of them broken to small nanoparticles ranging 3-8 nm.

C. Sample Preparation:Cement Nanomatrix, Curing and Test of Specimens

Ordinary Portland cement(OPC) is partially substituted by nanoclay (NC) or calcined nanoclay (CNC) of 1, 2 and 3 % by weight of OPC. The OPC and NC or CNC were first dry mixed for 5 minutes in a Hobart mixer at a low speed and then mixed for another 10 minutes at high speed until homogeneity was achieved. The binder is either nanoclay-cement dry powder or calcined nanoclay-cement dry powder. The cement nanomatrixpaste was prepared through adding water with a water / binder ratio of 0.485. The cement paste (C) was considered as a control. The mix proportions are shown in Table 1.Regarding each series, five cubes of size 50×50×50 mm in dimension were cast. All specimens were demolded after 24 h of casting and kept under water for approximately 56 days. Compressive strength of specimens was tested according to ASTM: C109 using a loading rate of 0.33 MPa/s. the apparent porosity (%) was tested according to ASTM C-20 Standard.

D. Material Characterisation

The XRD patterns and the Quantitative X-ray Diffraction Analysis (QXDA) was done on a D8 Advance Diffractometer (Bruker-AXS) using Cu Ka

(λ = 1.5406 Å) radiation. Scanning electron microscopy (SEM) imaging was obtained using a NEON 40ESB, ZEISS. Thermogravimetry analysis (TGA) was done by A Mettler Toledo TGA 1 star system analyser.

Table 1
Mix proportions of specimens

Sample	Mix proportions (wt %)			
	Cement	NC	CNC	Water/binder
C	100	0	0	0.485
NCC1	99	1	0	0.485
NCC2	98	2	0	0.485
NCC3	97	3	0	0.485
CNCC1	99	0	1	0.485
CNCC2	98	0	2	0.485
CNCC3	97	0	3	0.485

III. RESULTS AND DISCUSSION

A. Calculation of $Ca(OH)_2$ Content in Cement Nanomatrix by the Combination of QXDA andTGA Techniques

The XRD patterns of cement paste, cement nanomatrices containing 1, 2 and 3 wt% CNC and also 1 wt% NC are shown in Fig. 1 (a-e) that included Corundum [Al_2O_3] phase as the internal standard. Table 2 shows the results of quantitative analysis (QXDA) with Rietveld refinement of cement paste and cement nanomatrix containing NC and CNC.
The $Ca(OH)_2$ contentisalso calculated from the TGA curves using the following equation [8]:

$$CH(\%) = WL_{CH}(\%)\frac{MW_{CH}}{MW_{H_2O}}$$

Where $WL_{CH}(\%)$ is corresponds to the weight loss attributable to $Ca(OH)_2$ decomposition, MW_{CH} is the molecular weight of CH (74.01 g/mol) and MW_{H_2O} is the molecular weight of H_2O (18 g/mol). The thermograms (TGA) ofcement paste and cement nanomatrix containing CNC and NCare shown inFig. 2.Table 2summarises the CH content of abovemeasured by QXDA and TGA techniques.

It can be seen that there is good agreement between the two techniques, where both measured amounts are very close to each other. However, the amounts of CH by TGA are slightly lower than the QXDA. This observation is in agreement withthe work done byScrivenera et al [9] and Korpa et al. [10], in which they reported that this discrepancy could be attributed to the possible error sources of each method itself that were difficult to quantify.The TGA and QXDA results in Table 2 confirm the reactivity of 1 wt% CNC in reducing the CH content in cement nanomatrix. The CNC is mainly amorphous material and behaves as a highly reactive artificial pozzolan. The CH content by the TGA and QXDA in cement nanomatrix containing 1 wt% CNC was 10.7 and 12.1 wt%,respectively.It is also be seen that the CH content in cement nanomatrix containing1 wt% CNC is reduced significantly when compared to cement paste and cement nanomatrix containing NC and CNC such as cement nanomatrix containing 1 wt% NC . This could be due to the reactivity of 1 wt% CNC in cement nanomatrix and the consumption of CH by the pozzolanic reaction.Shaikh et al. [11] reported that the cement nanomatrix containing 2 wt % nano-silica exhibited less calcium hydroxide than the control cement paste.

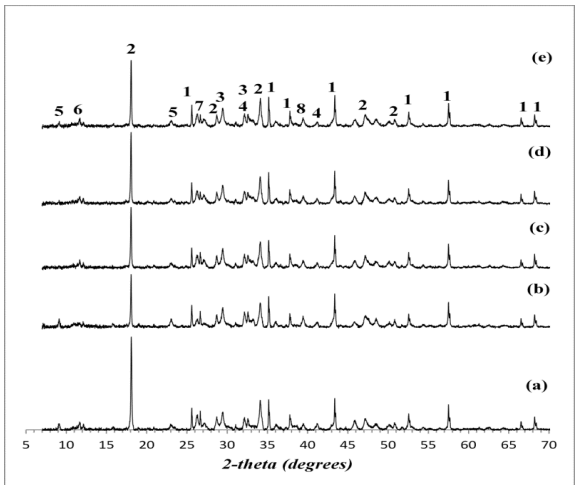

Figure 1 XRD patterns of: (a) cement paste, cement nanomatrix containing; (b) 1 wt% CNC (CNCC1), (c) 2 wt% CNC (CNCC2), (d) 3 wt% CNC (CNCC3), (e) 1 wt% NC (NCC1). Numbers indicate to: 1=Corundum [Al2O3] phase, 2= Portlandite [Ca(OH)2] phase, 3=Tricalcium

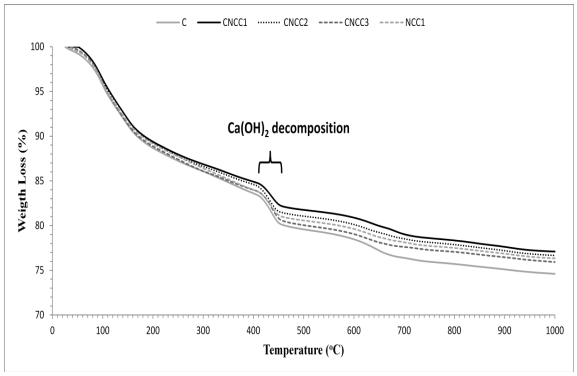

Figure 2 TGA curves of cement paste (C) and cement nanomatrix: CNCC1, CNCC2, CNCC3 and NCC1.

Table 2
Calculation of $Ca(OH)_2$ content in cement paste and cement nanomatrix containing 1, 2 and 3 wt% CNC and 1 wt% NC by QXDA and TGA techniques

Sample	TGA (wt %)	QXRD (wt %)	Difference (wt %)
C	15.5	16.8	1.3
CNCC1	10.7	12.1	1.4
CNCC2	12.1	13.2	1.1
CNCC3	13.0	14.1	1.1
NCC1	12.3	13.8	1.5

B. Porosity

The porosity of cement paste and cement nanomatrix containing NC and CNC are shown in Table 3. It is noticed that the addition of CNC or NC decreases the porosity of these cement nanomatriceswhen compared to control cement paste. In CNCC1 cement nanomatrix, the porosity

decreased by 31.2% compared to cement paste. This indicates that 1 wt% CNC has a filling effect in the porosity of cement nanomatrix. This result is in agreement withthe work done by Jo et al. [12] where the porosity of cement mortar is decreased by the addition of nano-SiO_2particles.

SEM examinations of the microstructure of cement paste, CNCC1and CNCC3 cement nanomatrix are shown in Figs.3 a-b. For cement paste, Fig. 3a shows more $Ca(OH)_2$ crystals and Ettringite as well as more pores which revealed a weak structure. Fig. 3b shows the SEM micrograph of CNCC1, which is different from that of cement paste, the structure is dense and compact with few pores and more C-S-H gel.

Table 3
Porosity and compressive strength values for cement paste (C), (NCC) and (CNCC) cement nanomatrix

Sample	Porosity (%)	Compressive strength (MPa)
C	23.9	53.1
NCC1	18.7	69.8
NCC2	19.6	65.2
NCC3	19.9	61.9
CNCC1	16.5	74.2
CNCC2	17.6	71.5
CNCC3	18.9	68.8

C. Compressive Strength

The compressive strength of the cement paste,cement nanomatrix containingNCC and CNCC are presented in Table 3. It can be noticed from results that the addition of NC and CNC to cement paste increases the compressive strength of all cement nanomatrix pastes. For instance, the cement nanomatrix containing 1 wt % CNC exhibited an enhancement in the compressive strength from 53.1 to 74.2 MPa or 40% increase, whereas in the cement nanomatrix containing 1 wt % NC, the compressive strength reached 69.8 MPa.

The increase in compressive strength of cement nanomatrix containing1 wt % CNC is due to amorphous state of CNC (i.e.small particle size) and extremely large surface area, in which the CNC reacts more quickly with free lime in the hydration reaction than NC and subsequently produced more secondary C–S–H gel and filled the capillary pores in the matrix efficiently[2]-[4]. Thus the microstructure of the matrix is densified by the nanoparticles.Chang [13] reported that the addition of 0.6 wt% nano-montmorillonite into cement paste increased compressive at age of 56 daysfrom 46 to 52.1 MPa (i.e. 13.2% increases) compared to the cement paste.Despite benefits of CNC and NC, it is important to note that the nano particles have a tendency to agglomerate when using at high content (i.e. more 3 wt % CNC) in the mixes [3]-[14]. This agglomeration forms weak zones and consequently prevents the formation of homogenous hydrate microstructure.

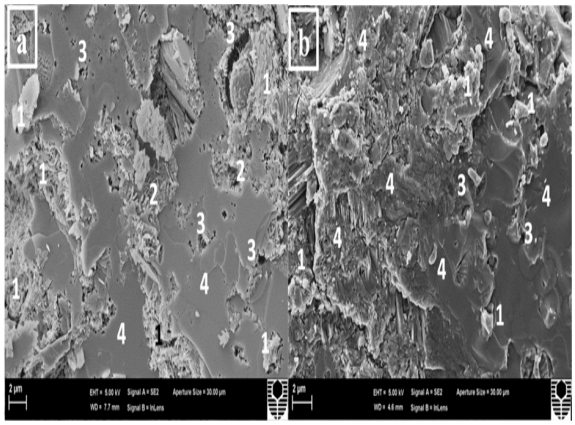

Figure 3 SEM micrographs of: (a) cement paste, cement nanomatrix containing; (b) 1 wt% CNC. Numbers indicate to: 1= [Ca(OH)2] crystals, 2= Ettringite, 3=pores, 4=C-S-H gel.

IV. COST-BENEFIT ANALYSIS AND APPLICATIONS

There is a hugeoptimismon the use of nanomaterials in construction and building applications although the nanoparticles are expensive and could limit their applications [1]-[2]. However, nano particles exhibit unique characteristics which result in new generation of concrete that is stronger and more durable [15]. With progress of manufacturing technologies the cost of nano particles is also expected to drop in future. Moreover, the nanoparticles are used in very small amount in the concrete or other cementitious nanomatrices. For example, in this study1wt% calcinednanoclay in cement nanomatrix led significant improvement in mechanical properties. From economic point of view, the addition of 1% calcined nanoclay in cement nanomatrix will not add any significant cost but improved the mechanical properties by about 40%.

CONCLUSIONS

Results of the combination of QXDA and TGA techniques indicate that TGA is at least as good as QXDA for quantifying the amount of $Ca(OH)_2$.The optimum content of CNC was found to be 1 wt%. The cement nanomatrix containing 1 wt%CNC decreased the porosity (by 31.2%) and increased the compressive strength (by 40%) compared to the control cement paste.However, the addition of more NC or CNC(beyond1 wt %) into cement nanomatrix adversely affected the mechanical and thermal properties. In fact, it could be recommended that much research is needed to overcome the agglomerations of NC or CNCand identify the best method of mixing which leads to good dispersion of CNCin the matrix.

ACKNOWLEDGMENTS

The authors are grateful toMs E. Miller from Applied Physics for assistance with SEM.

REFERENCES

[1] F. Sanchez, and K. Sobolev,"Nanotechnology in concrete – A review," Constr Build Mater, vol. 24, no. 11, pp.2060–2071,Nov.2010.

[2] A. Hakamy, F.U.A Shaikh, and I.M. Low,"Characteristics of hemp fabric reinforced nanoclay–cement nanocomposites," Cem Concr Compos, vol. 50, pp.27–35, July2014.

[3] A. Hakamy, F.U.A. Shaikh, andI.M. Low,"Thermal and mechanical properties of hemp fabric-reinforced nanoclay–cement nanocomposites," J Mater Sci, vol.49, no. 4, pp.1684–1694, Feb.2014.

[4] A. Hakamy, F.U.A. Shaikh, and I.M. Low, "Microstructures and mechanical properties of hemp fabric reinforced organoclay–cement nanocomposites,"Constr Build Mater, vol. 49, pp.298–307, Dec.2013.

[5] A. Alhuthali, I.M. Low, and C. Dong, "Characterization of the water absorption, mechanical and thermal properties of recycled cellulose fibre reinforced vinyl-ester eco-nanocomposites," Compos Part B, vol.43, no. 7, pp. 2772-2781, Oct. 2012.

[6] M. Aly, M.S.J. Hashmi, A.G. Olabi, M. Messeiry, and A.L. Hussain,"Effect of nano clay particles on mechanical, thermal and physical behaviours of waste glass cement mortars," Mater Sci Eng A, vol.528, no. 27, pp. 7991–7998, Oct. 2011.

[7] N. Farzadnia, A. Ali, R. Demirboga, and M. Anwar, "Effect of halloysite nanoclay on mechanical properties, thermal behavior and microstructure of cement mortars,"Cem Concr Res, vol. 48, pp. 97–104, June 2013.

[8] F.U.A. Shaikh, and S. Supit,"Mechanical and durability properties of high volume fly ash (HVFA) concrete containing calcium carbonate ($CaCO_3$) nanoparticles,"Constr Build Mater, vol. 70, pp. 309-321, Nov.2014.

[9] K. Scrivenera, T. Fullmanna, E. Galluccia, G. Walentab, and E. Bermejob,"Quantitative study of Portland cement hydration by X-ray diffraction/Rietveld analysis and independent methods," Cem Concr Res, vol. 34, no. 9, pp. 1541–1547, Sep2004.

[10] A. Korpa, T. Kowald, and R. Trettin,"Phase development in normal and ultra-high performance cementitious systems by quantitative X-ray analysis and thermoanalytical methods,"Cem Concr Res, vol. 39, no. 2, pp.69–76, Feb.2009.

[11] F.U.A. Shaikh, S.W.M. Supit, andP.K. Sarker,"A study on the effect of nano silica on compressive strength of high volume fly ash mortars and concretes," Mater Des, vol. 60, pp. 433–442, Aug. 2014.

[12] B.W Jo, C.H Kim, andJ.H. Lim,"Characteristics of cement mortar with nano-SiO_2 particles,"Constr Build Mater, vol. 21, no. 6, pp. 1351–1355, June 2007.

[13] T. Chang , J. Shih, K. Yang, andT. Hsiao,"Material properties of portland cement paste with nano-montmorillonite," J Mater Sci, vol. 42, no. 17, pp. 7478-7487, May 2007.

[14] S. Shebl, L. Allie, M. Morsy, and H. Aglan,"Mechanical behavior of activated nano silicate filled cement binders," J Mater Sci, VOL. 44, NO. 6, PP. 1600-1606, Jan. 2009.

[15] F. Pacheco-Torgal, andS. Jalali,"Nanotechnology: Advantages and drawbacks in the field of construction and building materials," Constr Build Mater, vol. 25, no. 2, pp. 582–590, Feb.2011.

★★★