Rev. Adv. Mater. Sci. 40 (2015) 72-88

A SYNOPSIS ABOUT THE EFFECT OF NANO-TITANIUM DIOXIDE ON SOME PROPERTIES OF CEMENTITIOUS MATERIALS – A SHORT GUIDE FOR CIVIL ENGINEER

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Received: February 19, 2014

Abstract. Recent developments in many areas of nanotechnology show significant promise in addressing many challenges. Researches and developments have shown that the application of nanotechnology can improve the performance of traditional construction materials, such as concrete. Noteworthy improvements in concrete strength, durability and sustainability are being achieved by using different types of nanoparticles such as nano-TiO_2 (NT). This paper presents an overview of the previous works carried out on the effect of NT on some properties as heat of hydration, workability, setting time, chemical shrinkage, mechanical strength, abrasion resistance, fire resistance, freeze/thaw resistance, water absorption, chloride penetration and permeability of the traditional plain or blended cement systems. In addition, this survey presents a comparison of some properties of the matrix containing NT versus that containing other nano particles. This overview can be considered as a short guide for Civil Engineer.

1. INTRODUCTION

Nanotechnology has recently become one of the hottest areas in research and development worldwide, and has also attracted considerable attention in the media and investment community. Nanotechnology is mainly defined by size and comprises the visualization, characterizations, production and manipulation of structures which are smaller than 100 nm [1]. The structures the dimensions of which range from 100 nm down to approximately 0.1 nm sizes exhibit special mechanical, optical, electrical and magnetic properties which can differ substantially from the properties of the same materials at larger dimensions [2].

Cementitious composites typically exhibit extremely brittle failure, low tensile capacity and susceptible to cracking. These characteristics of cement based materials are serious shortcomings that not only impose constraints in structural design, but also affect the long term durability of structures. To overcome these disadvantages, nanoparticles have been added to the cementitious composites. The addition of nanoparticles into cement paste is gaining an attention due to their high surface area and therefore high reactivity. Recent experiments have shown that nanoparticles improved the mechanical properties of CSH, reduced porosity and modified the durability of cement matrix [3,4].

Concrete containing NT has proven to be very effective for the self-cleaning of concrete as well as de-polluting the environments. NT triggers a photocatalystic degradation of pollutants [5,6]. A clean NT surface in the presence of sunlight enables the removal of harmful NO_x gases from the atmosphere by oxidation to nitrates. The photocatalytic concrete paving stones containing NT were found to be very effective to remove NO_x (source of serious pollution) [7]. In the literature there are a lot

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of review papers regarding to the previous works carried out on the areas of NT photocatalysis, mainly photocatalystic air purification, sterilization, photo-induced superhydrophilic phenomenon involving NT, self-cleaning, water purification, air purification, self-sterilizing surfaces, light-induced superhydrophilicity, thermal control, energy saving, cancer therapy, anti-fogging, anti-corrosion coatings, anti-reflection coatings for glass/windows, anti-bacteria coatings for work surfaces, more durable paints, and anti-graffiti coatings for buildings and structures [8-13]. On the contrary, there is no literature review paper carried out on the effect of NT on some properties of plain or blended traditional cement systems such as heat of hydration, workability, setting time, chemical shrinkage, mechanical strength, abrasion resistance, fire resistance, freeze/thaw resistance, water absorption, chloride penetration and permeability. However, this investigation reviewed these topics. In addition, comparison between NT and other types of nanoparticles such as nano-silica (nano-SiO_2) (NS), nano-zirconium (nano-ZrO_2) (NZ), nano-alumina (nano-Al_2O_3) (NA), and nano-magnetite (nano-Fe_3O_4) (NF) was reviewed. This review paper can be used as a short guide for Civil Engineer.

2. HEAT OF HYDRATION

Lee and Kurtis [14] investigated the effect of NT on the early age, up to 30 h, hydration kinetics of tricalcium silicate (C_3S). Isothermal calorimetry was performed on C_3S pastes with 0%, 5%, 10%, and 15% of NT, by weight. The effect of NT on the early age hydration was also investigated. They reported that the addition of NT provided additional nucleation sites for hydration product formation resulted in acceleration in hydration reaction; higher rate peaks and higher total heat of hydration were observed in both C_3S pastes and PC pastes. For the C_3S pastes, a delay in the rate of hydration was found in 5% NT pastes. Lee and Kurtis [15] studied the hydration rate, up to 90 days, of belite (C_2S) pastes with the addition of NT at levels of 0%, 5%, and 10%, by weight. The results indicated that the addition of NT shorten the induction period and accelerated the hydration beyond 3 days. The addition of NT increased the degree of hydration at age of 90 days by 47% compared to the neat C_2S paste. These results suggested that the addition of NT could potentially promote the early strength gain of C_2S in cement. Lee [16] studied the heat of hydration, up to 80 h, of pastes modified with NT. Cement was partially replaced with NT at levels of 0%, 5%, 10%,

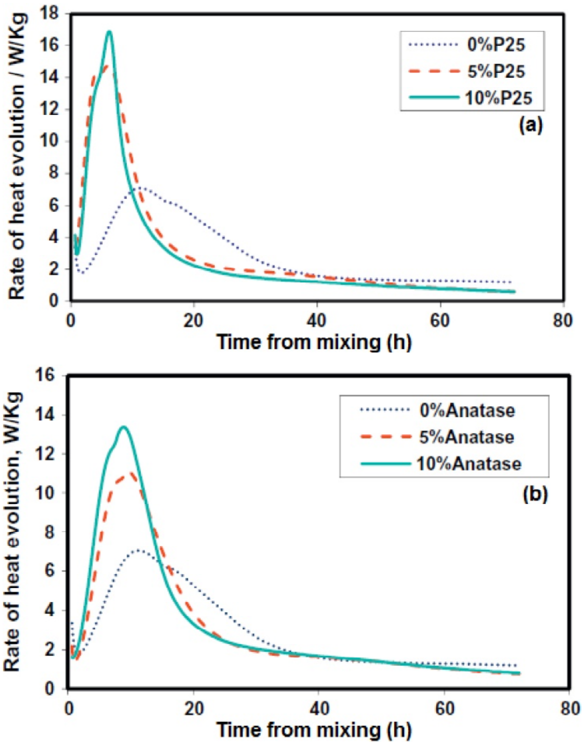

Fig. 1. Rate of heat evolution for different NT content: (a) P25, (b) Anatase. Reprinted with permission from Jun Chen, Shi-cong Kou and Chi-sun Poon // *Cement & Concrete Composites* **34** (2012) 642, (c) 2012 Elsevier.

and 15%, by weight. Fixed w/b ratio of 0.5 was used. The results showed an increase in the degree of hydration with the addition of NT. The higher content of NT showed higher degree of hydration

Chen et al. [17] studied the heat of hydration, up to 72 h, of pastes modified with NT. Two kinds of NT with different crystal phase compositions, P25 (75% anatase and 25% rutile) and Anatase (99% anatase) were used. The NT was used as addition to the cement at levels of 0%, 5%, and 10%, by weight. Fixed w/c ratio of 0.35 was used. The results showed that the addition of NT significantly increased the intensity of the heat peak and shortened its duration of occurrence (Fig. 1). The increase of NT dosage from 5% to 10% enhanced these effects. The incorporation of the NT resulted in a greater cumulative heat release, particularly in the first 30 h. The exothermic hydration process was accelerated more by P25 compared with Anatase. However, it was proposed that nanoparticles could act as potential heterogeneous nucleaction sites for the hydration products and the grain boundary region was densely populated with nuclei and transformed completely early in the overall process of hydration [18,19]. Senff et al. [20] studied the heat of hydration, up to 22 h, of mortars modified with NT. The incorporation of NT was 0%, 1.3, 2.6% and 5.2%, by weight. Fixed w/b ratio was used. The results showed noticeable changes on the extension of the dormant period and the intensity of the main exothermic peak due to the relative amount of NT. During this period, the temperature increased quickly because of the rapid crystallization of CH and formation of CSH gel from C_3S phase. NT tended to accelerate the hydration process and showed the main exothermic peak between 4 and ~ 7 h curing, whilst control mixture exhibited the low peak value, confirming a lower chemical activity.

Nazari and Riahi [21] studied the heat of hydration of pastes modified with NT. Cement was partially replaced with 0%, 1%, 2%, 3%, 4%, and 5%, by weight. The results showed a reduction in the heat release rate with the addition of NT. Nazari and Riahi [22-24] studied the heat of hydration of paste containing 45 wt.% slag. NT particles were used to modify this type of paste mixture. The binder materials were partially replaced with NT at levels of 0%, 1%, 2%, 3% and 4%, by weight. Fixed w/b ratio of 0.4 was used. The results showed that the inclusion of NT in the pastes accelerated the peak time and dropped the heat release. 3% NT showed the highest drop in the heat release. Nazari [25] studied the heat of hydration of pastes modified with NT. Cement was partially replaced with NT at levels of 0%, 0.5%, 1%, 1.5%, and 2%, by weight. Fixed w/b ratio of 0.4 was used. The different pastes were mixed with water or saturated limewater. The results showed a reduction in the heat of hydration with the inclusion of NT. The total heat released decreased with higher content of NT. The heat of hydration of pastes containing saturated limewater sample was lower than that containing water.

Jalal et al. [26] studied the heat of hydration, up to 70 h, of cementitious composites having NT. Cement was partially replaced with NT at levels of 0%, 1%, 2%, 3%, 4%, and 5%, by weight. Fixed w/b ratio of 0.38, fixed dosage of superplasticizer and fixed dosage of viscosity modifying were employed. The results showed a reduction in the heat release rate with the inclusion of NT. Jalal et al. [27] studied the heat of hydration, up to 70 h, of high strength SCCs modified with NT. Cement was partially replaced with NT at levels of 0%, 1%, 2%, 3%, 4%, and 5%, by weight. Fixed w/b ratio of 0.38, fixed dosage of 2.5 kg/m^3 superplasticizer and fixed dosage of 2 kg/m^3 viscosity modifying agent were employed. They reported that the inclusion of NT up to 4% accelerated the appearance of the first peak in conduction calorimetry test which related to the acceleration in formation of hydration cement products.

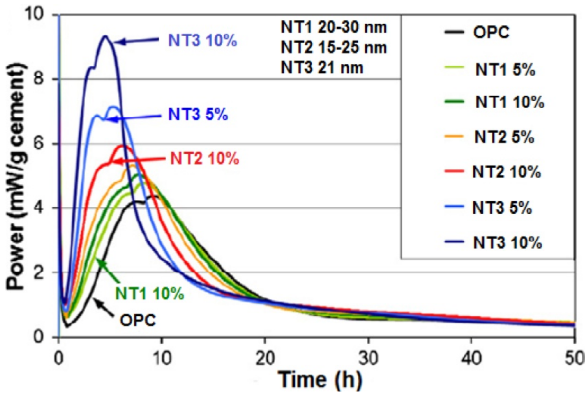

Fig. 2. Effect of NT on the rate oh heat release. Reprinted with permission from Amal R. Jayapalan, Bo Yeon Lee and Kimberly E. Kurtis // *Cement & Concrete Composites* **36** (2013) 16, (c) 2013 Elsevier.

Jayapalan et al. [28] studied the heat of hydration, up to 48 h, of cement pastes modified with different surface areas of NT. NT was added at levels of 0%, 5%, and 10%, by weight. Fixed w/b ratio of 0.5 was used. They reported that the hydration reaction was accelerated and the rate of hydration was increased with the addition of NT. The increase in the rate of reaction increased with increasing the content and the surface area of NT (Fig. 2). In another investigation, Jayapalan et al. [29] studied the heat of hydration, up to 48 h, of cement pastes modified with two different particle sizes (29-30 and 15-25 nm) of NT at replacement levels of 5%, 7.5%, and 10%, by weight. Fixed w/b ratio of 0.5 was used. The results showed that the inclusion of NT increased the heat of hydration and accelerated the rate of reaction at early ages of hydration. This increase was found to be proportional to the percentage addition and the NT fineness. Smaller particles of NT accelerated the reaction more than larger particles. On the same line, higher content of NT accelerated the reaction more than lower content.

From the above discussion it is safe to conclude that the inclusion of NT into the cement increased the heat of hydration and accelerated the rate of reaction at early ages of hydration. Smaller particles of NT accelerated the reaction more than larger particles. Higher content of NT accelerated the reaction more than lower content.

3. WORKABILITY AND SETTING TIME

Noorvand et al. [30] studied the flowability of mortar mixtures modified with NT up to 1.5% containing 10% and 20% untreated black rice husk ash (BRHA) as cement replacement. The results showed a reduction in the flowability with the inclusion of NT.

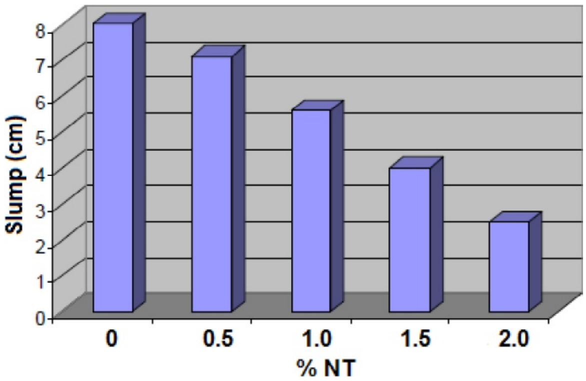

Fig. 3. The effect of NT content on the concrete workability, replotted from [32].

Salemi et al. [31] reported a reduction in the workability of concrete mixture with the inclusion of 2% NT. The slump of control mixture was 120 mm, whilst it was 60 mm for NT mixture. Nazari et al. [32] studied the workability of concrete mixtures modified with NT. Cement was partially replaced with NT at levels of 0%, 0.5%, 1%, 1.5%, and 2%, by weight. Fixed w/b ratio of 0.4 was used. The results showed a reduction in the workability with the inclusion of NT. The workability reduction increased with increasing NT content (Fig. 3). Li et al. [33] studied the workability of concrete mixtures modified with NT. Cement was partially replaced with NT at levels of 0%, 1%, and 3%. Fixed w/b ratio of 0.42 and various dosages of water reducing agents were employed. The results showed a reduction in the workability with the inclusion of NT. The reduction in slump height was about 54.54%. Li et al. [34] and Zhang and Li [35] studied the workability, by slump, of concrete mixtures modified with NT. Cement was partially replaced with NT at levels of 0%, 1%, 3%, and 5%, by weight. Fixed w/b ratio and various dosages of water reducing agents were employed. The results showed a reduction in the workability with the inclusion of NT. The reduction in the slump values was 54.54% with the inclusion of 1% or 3% NT, whilst the reduction was 72.75% with the addition 5% of NT.

Jalal et al. [36] studied the slump flow of SCC mixtures modified with NT. Cement was partially replaced with NT at levels of 0%, 1%, 2%, 3%, 4%, and 5%, by weight. Fixed w/b ratio of 0.38 with various dosages of superplasticizer and viscosity modifying agents were employed. The results showed that the slump flow decreased with increasing NT content. In another investigation, Jalal et al. [27] studied the rheological properties of high strength SCC mixtures modified with NT. Cement was partially replaced with NT at levels of 0%, 1%, 2%, 3%, 4%, and 5%, by weight. Fixed w/b ratio of 0.38, fixed dosage of superplasticizer of 2.5 kg/m^3 and fixed dosage of viscosity modifying agent of 2 kg/m^3 were employed. The results showed a reduction in the workability with the inclusion of NT. As the NT content increased as the reduction in the workability increased. The T_{50}, V-funnel flow time and L-box (H2/H1) increased with increasing NT content. The slump flow decreased with increasing NT content. The reduction in the slump diameter was 1.25%, 2.5%, 5%, 7.5%, and 8.75% with the inclusion of 1%, 2%, 3%, 4%, and 5% NT, respectively.

Senff et al. [20] studied the rheological and flow table of mortar mixtures modified with NT. The incorporation of NT was 0%, 1.3, 2.6%, and 5.2%, by weight. Fixed w/b ratio of 0.51 and fixed dosage of superplasticizer were employed. The results showed an increase in the values of torque and yield stress with the addition of NT. These values increased as the NT content increased. Meng et al. [37] studied the fluidity of mortar mixtures modified with NT. Cement was partially replaced with NT at levels of 0%, 5%, and 10%, by weight. Fixed w/b ratio of 0.5% was used. The results showed that the fluidity of the mixture decreased by 21% and 40% with the inclusion of 5% and 10% NT, respectively.

Chen et al. [17] studied the initial and final setting time of paste mixtures modified with NT. Two kinds of NT with different crystal phase compositions, P25 (75% anatase and 25% rutile) and Anatase (99% anatase). The NT was used as addition to the cement at levels 0%, 5%, and 10%, by weight. The results showed that the setting time was shorter for the pastes with the higher NT content. The addition of P25 particles had shorter setting time. Lee [16] studied the initial and final setting time of paste mixtures modified with NT. Cement was partially replaced with NT at levels of 0%, 5%, and 10%, by weight. Fixed w/b ratio of 0.5 was used. The results showed a reduction in the initial and final setting time with the inclusion of NT. This reduction increased as the content of NT increased. Nazari et al. [38] studied the initial and final setting time of concrete mixtures modified with NT. Cement was partially replaced with NT at levels of 0%, 0.5, 1%, 1.5%, and 2%, by weight. Fixed w/b ratio of 0.4 was used. The results showed a reduction in the initial and final setting time with the inclusion of NT. This reduction increased as the content of NT increased. Essawy and Abd Elhaleem [39] reported that the inclusion of 5%, 7%, and 10% NT in sulfate resisting cement blended with micro silica shortened the setting time. Table 1 summarizes the

Table 1. Effect of NT on the workability and setting time of the mixture.

Author	% NT	Effect
Noorvand et al. [30]	0, 0.5, 1, and 1.5	Decreased flowability
Salemi et al. [31]	0 and 2	Decreased workability
Nazari et al. [32]	0, 0.5, 1, 1.5, and 2	Workability decreased with increasing NT content
Li et al [33]	0, 1, and 3	Workability decreased
Li et al. [34] and Zhang and Li [35]	0, 1, 3, and 5	Workability decreased with increasing NT content
Jalal et al. [27,36]	0, 1, 2, 3, 4, and 5	Workability decreased with increasing NT content
Senff et al. [20]	0, 1.3, 2.6, and 5.2	Torque and yield stress increased with increasing NT content
Meng et al. [37]	0, 5, and 10	Workability decreased with increasing NT content
Lee [16] and Chen et al. [17]	0, 5, and 10	Initial and final setting time decreased with increasing NT content
Nazari et al. [38] NT content	0, 0.5, 1, 1.5, and 2	Initial and final setting time decreased with increasing
Essawy and Abd Elhaleem [394]	0, 5, 7, and 10	Setting time decreased

mentioned studies about the effect of NT on the workability and setting time of the mixture.

From the above review of the literature in this section, it is safe to conclude that the inclusion of NT in the mixture decreased its workability. The workability decreased with increasing NT content. This may be related to the higher surface area of NT particles that needs more water to wetting the cement particles [32]. The reduction in the workability by applying NT in the mixture is one of the shortcoming of using this material which may limit its wide use by engineers.

The initial and setting time of the mixture decreased with the inclusion of NT. As the content of NT increased as the initial and final setting time decreased. This is because with the inclusion of NT there is a rapid consumption of free water speeded up to bridging process of gaps and as a result, the viscosity increased and solidification occurred earlier [17]. Also, the reduction in the setting time might be related to the large surface area of NT that provided a greater availability of nucleation sites, led to faster hydration rate and shorter setting time [16]. The setting time shorting by NT can be considered as advantage or disadvantage. This depends on the application that NT mixture used for.

4. CHEMICAL SHRINKAGE

Lee [16] studied the chemical shrinkage, up to 50 h, of pastes modified with NT. Cement was partially replaced with NT at levels of 0%, 5%, 10%, and 15%, by weight. Fixed w/b ratio of 0.5 was used. The results showed an increase in the chemical shrinkage with the inclusion of NT. The chemical shrinkage increased with increasing NT content. Jayapalan et al. [28] studied the chemical shrinkage, up to 100 h, of cement pastes modified with NT. The addition of NT was 0%, 5%, 10%, and 10%, by weight. Fixed w/b ratio of 0.5 was used. The addition of NT increased the rate of chemical shrinkage compared to the control. The chemical shrinkage increased with increasing NT content (Fig. 4).

It is safe to conclude that the inclusion of NT in the matrix increased the chemical shrinkage. The higher NT content resulted in a greater chemical shrinkage. This results were expected since chemical shrinkage is directly related and proportionally to the degree of hydration in which the chemical

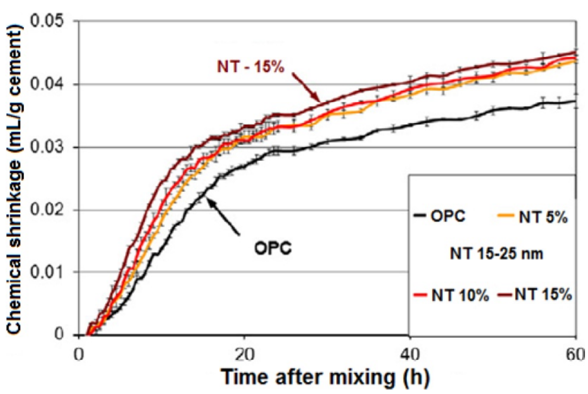

Fig. 4. Effect of NT on chemical shrinkage. Reprinted with permission from Amal R. Jayapalan, Bo Yeon Lee and Kimberly E. Kurtis // *Cement & Concrete Composites* **36** (2013) 16, (c) 2013 Elsevier.

shrinkage refers to the volume reduction associated with the hydration reactions in a cementitious material.

5. MECHANICAL STRENGTH

Li et al. [40] have reported that the inclusion of 1% NT as an additional of cement weight to concrete mixture enhancement its compressive strength by approximately 36%. Nazari [25] and Soleymani [41] studied the flexural strength, at ages of 7, 28, and 90 days, of concretes modified with NT. Cement was partially replaced with NT at levels of 0%, 0.5%, 1%, 1.5%, and 2%, by weight. Fixed w/b ratio of 0.4 was used. Some specimens were cured in water and the others in were cured in saturated limewater. The results showed an increase in the flexural strength with the inclusion of NT for all curing conditions and at all ages. The enhancement in the 28 days flexural strength, for the specimens that were cured in water, was 13.64%, 20.45%, 15.91%, and 11.36% with the inclusion of 0.5%, 1%, 1.5%, and 2% NT, respectively. For the specimens that were cured in saturated limewater, the enhancement in the flexural strength was 36.58%, 48.78%, 56.1%, and 65.85% with the inclusion of 0.5%, 1%, 1.5%, and 2% NT, respectively. The flexural strength for the specimens that were cured in saturated limewater was higher than that were cured in water. The inclusion of 1% NT exhibited the highest flexural strength, for specimens that were cured in water, whilst 2% exhibited the highest flexural strength for specimens that were cured in saturated limewater. Soleymani [42] studied the compressive strength, at ages of 7, 28, and 90 days, of concretes modified with NT. Cement was partially replaced with NT at levels of 0%, 0.5%, 1%, 1.5%, and 2%, by weight. Fixed w/b ratio of 0.4 was used. Some specimens were cured in water and the others in saturated limewater. The results showed an increase in the compressive strength with the inclusion of NT for all curing conditions and at all ages. The enhancement in the 28 days compressive strength, for the specimens that were cured in water, was 13.86%, 17.93%, 15.49%, and 6.79% with the inclusion of 0.5%, 1%, 1.5%, and 2% NT, respectively. For the specimens that were cured in saturated limewater, the enhancement was 21.47%, 29.1%, 35.88%, and 40.96% with the inclusion of 0.5%, 1%, 1.5%, and 2% NT, respectively. The compressive strength for specimens that were cured in saturated limewater was higher than that were cured in water. 1% NT exhibited the highest compressive strength, for specimens that were cured in water, whilst 2% exhibited the highest compressive strength for specimens that were cured in saturated limewater. Similar trend of splitting tensile strength results was obtained by Soleymani [43].

Nazari et al. [41] studied the splitting tensile and flexural strength, at ages of 7, 28, and 90 days, of concretes modified with NT. Cement was partially replaced with NT at levels of 0%, 0.5, 1%, 1.5%, and 2%, by weight. Fixed w/b ratio of 0.4 was used. The results showed that both splitting tensile strength and flexural strength increased with the inclusion NT at all ages. The enhancement in the 28 days flexural strength was 15.91%, 25%, 22.73%, and 15.91% with the inclusion of 0.5%, 1%, 1.5%, and 2% NT, respectively, whilst the enhancement in the 28 days splitting tensile strength was 44.44%, 66.67%, 50%, and 5.55% with the inclusion of 0.5%, 1%, 1.5%, and 2% NT. Nazari et al. [32] studied the compressive strength of the same previous mixtures. The same trend of the previous results was obtained. The enhancement in the 28 days compressive strength was 13.86%, 17.93%15.49%, and 6.79% with the inclusion of 0.5%, 1%, 1.5%, and 2% NT, respectively. Salemi et al. [31] reported an increase in the compressive strength of concretes with the inclusion of 2% NT. The enhancement in the compressive strength was 12%, 22.71%, and 27% at ages of 7, 28, and 120 days, respectively.

Li et al. [29] studied the flexural strength, at age of 28 days, of concretes modified with NT. Cement was partially replaced with NT at levels of 0%,1%, and 3%, by weight. Fixed w/b ratio of 0.42 and various dosages of water reducing agent were employed. The results showed an increase in the flexural strength with the inclusion of NT. The inclusion of 1% NT showed higher flexural strength than that of 3% NT. The enhancement in the flexural strength was 10.27% and 2.93% with the inclusion of 1% and 3% NT, respectively. They also studied the flexural fatigue of the previous concretes. They concluded that the flexural fatigue increased with the inclusion of NT. The inclusion of 1% NT showed the best flexural fatigue performance, the enhanced extent of flexural fatigue performance for the concrete containing 3% NT came in the second place. Li et al. [34] and Zhang and Li [35] studied the compressive and flexural strength, at age of 28 days, of concretes modified with NT. Cement was partially replaced with NT at levels of 0%, 1%, 3%, and 5%, by weight. Fixed w/b ratio of 0.42 and various dosages of water reducing agents were employed. The results showed an increase in the compressive strength with the inclusion of NT. The inclusion of 1% NT exhibited the highest compressive and flexural strength. The enhancement in the compressive strength was 18.03%, 12.76%, and 1.55% with the inclusion of 1%, 3%, and 5% NT, respectively. The inclusion of 1% and 3% NT increased the flexural strength by 10.28% and 3.04%, respectively, whilst the inclusion of 5% NT decreased it by 3.27%.

Nazari and Riahi [21] studied the compressive, splitting, flexural strength, at ages of 2, 7, and 28 days, of SCCs modified with NT. Cement was partially replaced with 0%, 1%, 2%, 3%, 4%, and 5%, by weight. Fixed w/b ratio of 0.4 and various dosages of superplasticizer were employed. The results showed an increase in the all strengths with the inclusion of NT. The enhancement in the 28 days compressive strength was 11.39%, 21.2%, 40.82%, 58.54%, and 54.1% with the inclusion of 1%, 2%, 3%, 4%, and 5% NT, respectively. The inclusion of 4% NT exhibited the optimum content. In a similar investigation, Jalal et al. [27] studied the splitting tensile strength and flexural strength, at ages of 7, 28, and 90 days, of high strength SCCs modified with NT. Cement was partially replaced with NT at levels of 0%, 1%, 2%, 3%, 4%, and 5%, by weight. Fixed w/b ratio of 0.38, fixed dosage of superplasticizer of 2.5 kg/m^3 and fixed dosage of viscosity modifying agent of 2 kg/m^3 were employed. The results showed an enhancement in all strengths with the inclusion of NT. The inclusion of 4% NT exhibited the highest splitting tensile and flexural strength followed by 5%, 3%, 2%, and 1% NT, respectively. The enhancement in the 28 days splitting tensile strength was approximately 8.8%, 18.61%, 27.78%, 36.67%, and 30% with the inclusion of 1%, 2%, 3%, 4%, and 5% NT, respectively, whilst the enhancement in the 28 days flexural strength was 10.58%, 21.75%, 29.4%, 44.67%, and 36.46%, respectively. Senff et al. [44] reported a slight enhancement in the compressive strength of mortar, at age of 28 days, with the addition of 5% NT, by weight. On the other hand, Behfarnia et al. [45] reported that the compressive strength of concrete at age of 28 days decreased with the inclusion of NT. The reduction in the compressive strength was 20.73%, 27.17%, 14%, 15.97%, and 26.33% with the inclusion of 1%, 2%, 3%, 4%, and 5% NT, respectively.

Chen et al. [17] studied the compressive strength, at ages of 3, 7, and 28 days, of mortars modified with NT. Two kinds of NT with different crystal phase compositions, P25 (75% anatase and 25% rutile) and Anatase (99% anatase) were used. The NT was used as addition to the cement at levels of 0%, 5%, and 10%, by weight. The results showed an increase in the compressive strength with the

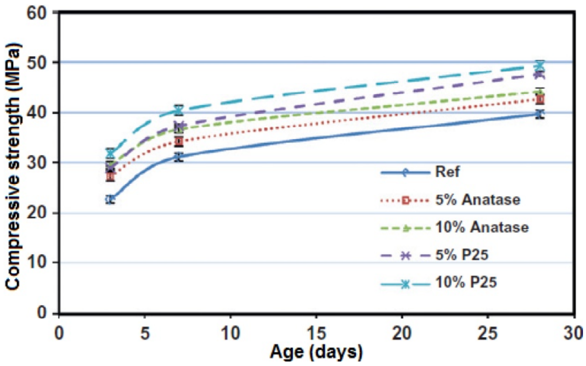

Fig. 5. Compressive strength development of mortars modified with NT. Reprinted with permission from Jun Chen, Shi-cong Kou and Chi-sun Poon // *Cement & Concrete Composites* **34** (2012) 642, (c) 2012 Elsevier.

addition of NT at all ages (Fig 5). Essawy and Abd Elhaleem [39] reported that the inclusion of 5% NT in sulfate resisting cement blended with micro silica increased the compressive strength, whilst the inclusion of 7% and 10% did not lead to any significantly higher strength. Lee [16] studied the compressive strength, at ages of 1, 3, 7, 14, and 28 days, of pastes modified with NT. Cement was partially replaced with NT at levels of 0%, 5%, and 10%, by weight. Fixed w/b ratio of 0.5 was used. The results showed an enhancement in the 1, 3 and 7 days compressive strength with the inclusion of 5% NT, whilst a reduction in the 28 days compressive strength was obtained. An enhancement in the 1 and 7 days compressive strength was obtained with the inclusion of 10% NT, whilst a reduction in the compressive strength at the remaining ages was obtained. The effect of different w/b ratios on the 28 days compressive strength was studied. The results showed an increase in the compressive strength with increasing NT content at w/b ratio of 0.4, whilst it decreased with increasing NT content at w/b ratios of 0.5 and 0.6. Mohammadi et al. [46] reported an increase in the compressive strength of calcium phosphate cement by addition 5% and 10% NT. Meng et al. [37] studied the compressive strength, at ages of 1, 3, 7, and 28 days, of mortars modified with NT. Cement was partially replaced with NT at levels of 0%, 5%, and 10%, by weight (mixture designations were J, P5, and P10, respectively). Fixed w/b ratio of 0.5% was used. The results showed an increase in the early strength and a reduction in evening strength with increasing NT content. The enhancement in the 1 day compressive strength was 46% and 47% with the inclusion of 5% and 10% NT, respectively. On the other hand, the reduction in the 28 days compressive strength was 6% and

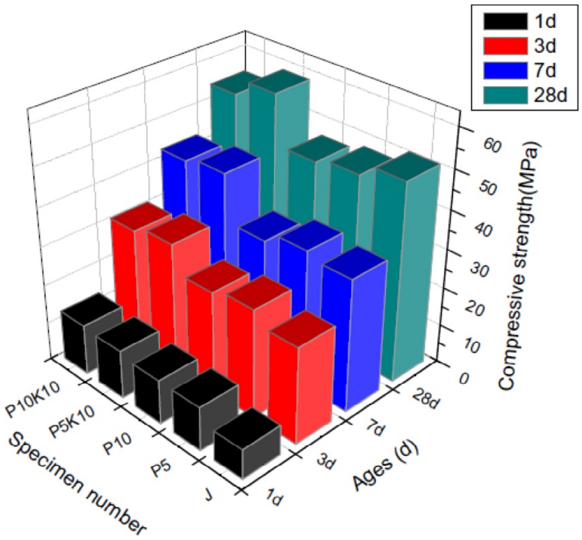

Fig. 6. Compressive strength of mortars modified with NT and NT+slag. Reprinted with permission from Tao Meng, Yachao Yu, Xiaoqian Qian, Shulin Zhan and Kuangliang Qian // *Construction and Building Materials* **29** (2012) 241, (c) 2012 Elsevier.

9% with the inclusion of 5% and 10% NT respectively. They tried to modify the compressive strength of the mixtures containing NT by replacing part of cement with 10% slag with the addition of 2.25 kg/m^3 superplasticizer (mixtures were P5K10 and P10k10). By these modifications the 1 day compressive strength increased by 60% and 68% with the inclusion of 5% and 10% NT, respectively. The compressive strength at age of 28 days increased by 15% and 7% with the inclusion of 5% and 10% NT, respectively (Fig. 6).

Shekari and Razzaghi [47] studied the compressive strength and indirect tensile strength, at age of 28 days, of concretes containing 15% metakaolin (MK), as cement replacement, modified with NT. The addition of NT was 0% and 1.5%, by cementitious weight. Fixed w/c ratio and fixed dosage of superplasticizer were employed. The results showed an increase in the compressive strength and indirect tensile strength with the addition of NT. The enhancement in the compressive and indirect tensile strength was about 22.75% and 17.86%, respectively. Noorvand et al. [30] studied the compressive strength of mortars modified with NT up to 1.5% containing 10%, 20%, and 30% BRHA as cement replacement. The results showed an enhancement in the compressive strength at ages of 7, 28, and 90 days with the inclusion of NT. This enhancement increased with increasing NT content. Farzadnia et al. [48] studied the compressive strength, at ages of 28 days, of mortars containing 5% silica fume (SF) modified with NT. Cement was partially replaced with NT at levels of 0%, 1%, 2%, and 3%, by weight. Fixed w/b ratio of 0.35 and 2% naphthalene sulfonate based superplasticizer were employed. The specimens were cured in lime saturated water for 28 day. The results showed an increase in the compressive strength with the inclusion of NT. The inclusion of 2% NT showed the highest compressive strength followed by 1% and 3% NT, respectively. The enhancement in the compressive strength was 12.5%, 15.8%, and 10.5% with the inclusion of 1%, 2% and 3%, respectively.

Nazari and Riahi [22,23] studied the flexural strength, at ages of 7, 28, and 90 days, of concretes containing different amounts of slag. They found that slag improved the flexural strength up to 45 wt.% at later ages. NT particles were used to modify the concrete with the optimum content of slag. The binder materials were partially replaced with NT at levels of 0%, 1%, 2%, 3%, and 4%, by weight. The results showed an increase in the flexural strength with the inclusion of NT at ages of 7, 28, and 90 days. The inclusion of 3% NT showed the optimum content which exhibited the highest flexural strength at all ages. The enhancement in the flexural strength, at age of 28 days, was 5.56%, 14.81%, 27.78%, and 16.67% with the inclusion of 1%, 2%, 3%, and 4% NT, respectively. In another investigation, Nazari and Riahi [23,24] studied the compressive strength of the same previous mixtures. The same trend of the previous results was obtained. The enhancement in the 28 days compressive strength was 14.19%, 26.54%, 36.38%, and 28.37% with the inclusion of 1%, 2%, 3%, and 4% NT, respectively. Nazari and Riahi [23] studied the splitting tensile strength of the same previous mixtures. The same trend of the results was obtained. The enhancement in the 28 days splitting tensile strength was 9.52%, 23.81%, 33.33%, and 23.81% with the inclusion of 1%, 2%, 3%, and 4% NT, respectively. Table 2 summarizes the mentioned studies about the effect of NT on the mechanical strength of plain and blended PC systems.

From the above discussion, it is evident that the inclusion of NT, in most cases, has positive effect on the strength. The enhancement in the strength with the inclusion of NT may be related to the rapid consumption of crystalline $Ca(OH)_2$ which are quickly formed during hydration of cement specially at the early ages as a result of high reactivity of NT. As consequence, the hydration of cement is accelerated and larger volumes of reaction products are formed [21]. The NT particles recover the particle packing density of the blended cement, directing to

Table 2. Effect of NT on the mechanical strength of plain and blended cement systems.

Author	% NT	Effect
Li et al. [40]	0 and 1	-Increased the compressive strength
Nazari [25] and Soleymani [41]	0, 0.5, 1, 1.5, and 2	(Curing in water) -Increased the flexural strength-1% is the optimum (Curing in limewater) -Increased the flexural strength-2% is the optimum
Soleymani [42]	0, 0.5, 1, 1.5, and 2	(Curing in water) -Increased the compressive strength-1% is the optimum (Curing in limewater) -Increased the compressive strength-2% is the optimum
Soleymani [43]	0, 0.5, 1, 1.5, and 2	(Curing in water) -Increased the splitting strength-1% is the optimum (Curing in limewater) -Increased the splitting strength-2% is the optimum
Nazari et al. [41]	0, 0.5, 1, 1.5, and 2	-Increased the splitting and flexural strengths-1% is the optimum
Nazari et al. [32]	0, 0.5, 1, 1.5, and 2	-Increased the compressive strength1% is the optimum
Salemi et al. [31]	0 and 2	-Increased the compressive strength
Li et al. [29]	0, 1, and 3	-Increased the flexural strength-Increased the flexural fatigue-1% is the optimum
Li et al. [34] and Zhang and Li [35]	0, 1, 3, and 5	-Increased the compressive strength-1% and 3% increased the flexural strength, whilst 5% decreased it-1% is the optimum
Nazari and Riahi [21]	0, 1, 2, 3, 4, and 5	-Increased the splitting and flexural strengths-4% is the optimum
Jalal et al. [27]	0, 1, 2, 3, 4, and 5	-Increased the splitting and flexural strength-4% is the optimum
Senff et al. [44]	0 and 5	-Increased the compressive strength
Behfarnia et al. [45]	0, 1, 2, 3, 4, and 5	-Decreased the compressive strength
Chen et al. [17]	0, 5, and 10	-Increased the compressive strength-Increasing rate at early ages was high that that at later ages
Essawy and Abd Elhaleem [39]	0, 5, 7, and 10	-5% increased the compressive strength
Lee [16]	0, 5, and 10	-5% NT increased the compressive strength at 1, 3 and 7 days, but reduced it at 28 days (w/b = 0.5) -10% NT increased the compressive strength at 1 and 7 days, but reduced it at 3 and 28 days (w/b = 0.5) -Increased the compressive strength with increasing NT content (w/b = 0.4) -Decreased the compressive strength with increasing NT content (w/b = 0.5 or 0.6)
Mohammadi et al. [46]	0, 5, and 10	-Increased the compressive strength
Meng et al. [35]	0, 5, and 10	-Increased 1 day compressive strength -Decreased 28 days compressive strength (Mixture containing 10% slag) -Increased the compressive strength
Shekari and Razzaghi [47]	0 and 1.5	(Mixture containing 15% MK) -Increased the compressive and splitting strength

Noorvand et al. [30]	0, 0.5, 1, and 1.5	(Mixtures containing 10%, 20% and 30% BRHA) -Increasing the compressive strength
Farzadnia et al. [48]	0, 1, 2, and 3	(Mixture containing 5% SF; curing in limewater) -Increased the compressive strength -2% is the optimum
Nazari and Riahi [22,23]	0, 1, 2, 3, and 4	(Mixture containing 45% slag) -Increased the flexural strength -3% is the optimum
Nazari and Riahi [23,24]	0, 1, 2, 3, and 4	(Mixture containing 45% slag) -Increased the compressive strength -3% is the optimum
Nazari and Riahi [23]	0, 1, 2, 3, and 4	(Mixture containing 45% slag) -Increased the splitting strength -3% is the optimum

reduce volume of larger pores in the cement paste and produce compact formation of hydration products (Fig. 7) [21]. Some studies [17] believed that the inclusion of NT increased the strength, but the rate of strength gain of the specimens containing NT was higher at early ages than that at late ages. This may be related to the addition of nanparticles could only have an impact on the early hydration (C_3A and C_3S) and the much slower reaction of C_2S hydration which contributed to longer term properties of hydrated cement pastes might be less affected [17]. Anyway, some studies [25,41-43] reported that 1% NT is the optimum content which exhibited the highest strength for specimens that were cured in water, whilst 2% NT is the optimum for the same specimens that were cured in limewater. Other studies [22-24] reported that 3% NT is the optimum when cement was substituted with 45% slag, other [48] reported 2% NT is the optimum when cement was substituted with 5% SF. This means that the optimum NT content in the matrix is affected by curing condition, curing age, w/b ratio, the type and content of the cementitious material which replaced cement as well as NT particle size.

6. ABRASION RESISTANCE

Li et al. [34] studied the abrasion resistance, at age of 28 days, of concretes modified with NT. Cement was partially replaced with NT at levels of 0%, 1%, 3%, and 5%, by weight. Fixed w/b ratio of 0.42 and various dosages of water reducing agent were employed. The results showed that the abrasion resistance of concrete increased with the inclusion of NT. The addition of 1% NT exhibited the highest abrasion resistance, followed by 3% and 5%, respectively. The enhancement in the surface index of the abrasion resistance was 180.7%, 147.7, and 90.4% with the inclusion of 1%, 3%, and 5% NT, respectively, whilst the enhancement in side index of the abrasion resistance was 173.3%, 140.2%, and 86% with the inclusion of 1%, 3%, and 5% NT, respectively.

7. FIRE AND FREEZE/THAW RESISTANCE

Farzadnia et al. [48] studied the compressive strength, modulus of elasticity, energy absorption and brittleness, at ages of 28 days, of mortars containing 5% SF modified with NT after being exposed to elevated temperatures up to 1o 1000 °C for 1 h. Cement was partially replaced with NT at levels of 0%, 1%, 2%, and 3%, by weight. Fixed w/b ratio of 0.35% and 2% naphthalene sulfonate based superplasticizer were employed. The specimens were cured in lime saturated water for 28 days. NT specimens showed higher residual compressive

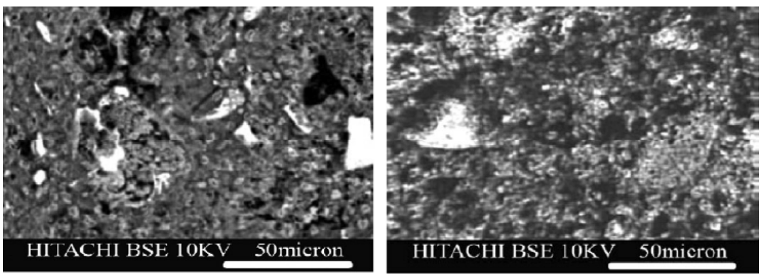

Fig. 7. SEM micrographs of plain SCC (a) and SCC modified with 4% NT (b) at age of 28 days, replotted from [21].

strength than that of control at temperatures up to 600 °C (Fig. 8). The inclusion of 2% NT showed the optimum content. On the other hand, the inclusion of 1% NT showed better effect on the residual modulus of elasticity after being exposed to elevated temperatures. The energy absorption per unit volume increased when 1%, 2%, and 3% NT were included. As temperature increased to 1000 °C, there was a reduction in energy absorption. At temperatures above 300 °C, the reduction in energy absorption was more significant. The inclusion of 2% NT showed the highest energy absorption. The inclusion of NT resulted in brittleness compared to that of control up to 600 °C. The inclusion of 2% NT showed more stable compared to other mixtures exposed to elevated temperatures. They also studied the gas permeability of the mortars after being exposed to 300 and 600 °C. At 300 °C, 1% and 2% NT reduced the permeability, whilst 3% NT increased it. On the other hand, at 600 °C, the addition of NT increased the permeability.

Salemi et al. [31] partially replaced cement in concretes with NT at levels of 0% and 2%, by weight. They exposed the specimens to 50, 150, and 300 cycles of freeze/thaw in water according to ASTM C666A. The results showed high resistance of freeze/thaw cycles of NT concrete specimens. The strength loss and the reduction in the length after 300 cycles of the control were 100% and 28.1%, respectively, whilst they were only 11.5% and 2% for NT concrete, respectively.

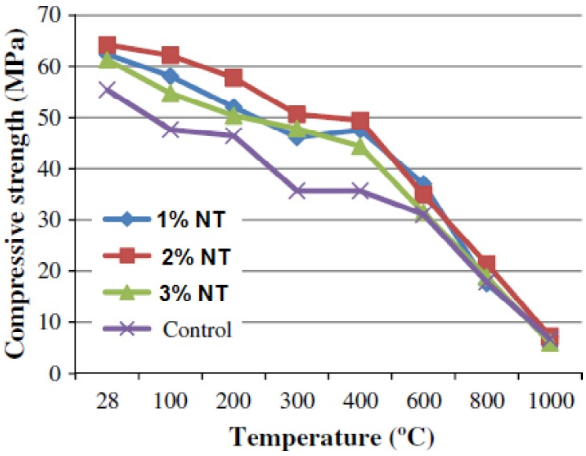

Fig. 8. Residual compressive strength of mortars modified with NT at elevated temperatures. Reprinted with permission from Nima Farzadnia, Abdullah Abang Ali Abang, Ramazan Demirboga and Mohammed Parvez Anwar *// Construction and Building Materials* **43** (2013) 469, (c) 2013 Elsevier.

8. WATER ABSORPTION, CHLORIDE PENETRATION AND PERMEABILITY

He and Shi [49] studied the permeability of cement mortar modified with 1% NT. They reported that NT improved the chloride penetration resistance of mortar where the apparent diffusion coefficients of chloride anion were reduced. Li et al., 2014 [40] reported that the addition of 1% TiO_2 to concrete exhibited better performance than plain concrete in resisting chloride invasion. Salemi et al. [31] reported a reduction in the percentage of water absorption of concrete specimens with the inclusion of 2% NT. This reduction was approximately 22% at age of 28 days. Nazari [25] studied the percentage of water absorption, rate of water absorption and coefficient of water absorption, at ages of 7, 28, and 90 days, of concretes modified with NT. Cement was partially replaced with NT at levels of 0%, 0.5%, 1%, 1.5%, and 2%, by weight. Fixed w/b ratio of 0.4 was used. Some specimens were cured in water and the others in saturated limewater. The results showed a reduction in the percentage of water absorption, the rate of water absorption and coefficient of water absorption with the inclusion of NT for all curing conditions and at all ages. The reduction in the 28 days water absorption, for the specimens that were cured in water, was 59.1%, 54.1%, 51.1%, and 47.5% with the inclusion of 0.5%, 1%, 1.5%, and 2%, respectively. For the specimens that were cured in saturated limewater, the reduction in water absorption was 73.73%, 71.45%, 68.65%, and 65.85% with the inclusion of 0.5%, 1%, 1.5%, and 2%, respectively. The replacement level of 0.5% was the optimum. The specimens that were cured in limewater showed lower water absorption and lower rate of water absorption than that were cured in water. Soleymani [50,51] studied the percentage of water absorption of concretes modified with NT. Cement was partially replaced with NT at levels of 0%, 0.5%, 1%, 1.5%, and 2%, by weight. Fixed w/b ratio of 0.4 was used. Some specimens were cured in water and the others in saturated limewater. The results showed an increase in the percentage of water absorption with the inclusion of NT at age of 7 days, whilst a reduction in the percentage of water absorption was observed with the inclusion of NT at ages of 28 and 90 days at all curing conditions. The specimens that were cured in saturated lime water showed lower percentage of water absorption than that were cured in water. For specimens that were cured in water, the reduction in the percentage of water absorption, at age of 28 days, was 59.11%, 54.11%, 51.1%, and 47.5%, with the inclusion of

0.5%, 1%, 1.5%, and 2% NT , respectively. For the specimens that were cured in saturated limewater, the reduction in the percentage of water absorption, at age of 28 days, was 73.73%, 71.45%, 68.65%, and 65.85% with the inclusion of 0.5%, 1%, 1.5%, and 2%, respectively. The addition of 0.5% NT showed the lowest percentage of water absorption.

Jalal [36] studied the water absorption, and capillary absorption, at age of 14 days, of SCCs modified with NT. Cement was partially replaced with NT at levels of 0%, 1%, 2%, 3%, 4%, and 5%, by weight. Fixed w/b ratio of 0.38 with various dosages of superplasticizer and viscosity modifying agents were employed. The results showed a reduction in the water absorption and the capillary absorption with the inclusion of NT. The addition of 4% was the optimum content of NT in which this level exhibited the lowest value of water absorption or capillary absorption. The chloride ion penetration of the previous mixtures was studied at age of 90 days. The results showed the same trend, where the chloride penetration depth decreased with the addition of NT. The addition of 4% NT was the optimum level which exhibited the lowest chloride penetration depth. In another investigation, Jalal et al. [27] studied the percentage of water absorption, capillary water absorption and chloride ion penetration, at age of 90 days, of high strength SCCs modified with NT. Cement was partially replaced with NT at levels of 0%, 1%, 2%, 3%, 4%, and 5%, by weight. Fixed w/b ratio of 0.38, fixed dosage of superplasticizer of 2.5 kg/m^3 and fixed dosage of viscosity modifying agent of 2 kg/m^3 were employed. The results showed a reduction in the percentage of water absorption, capillary water absorption and chloride penetration depth with the inclusion of NT. The inclusion of 4% NT exhibited the lowest percentage of water absorption, capillary water absorption and chloride penetration depth followed by 5%, 3%, 2%, and 1%, respectively.

Zhang and Li [35] studied the pore structure and chloride permeability of concretes modified with NT. Cement was partially replaced with NS at levels of 0%, 1%, 3%, and 5%, by weight. Fixed w/b ratio and various dosages of water reducing agents were employed. The results showed a reduction of the total specific pore volumes of concretes with the inclusion of NT. The results showed 31%, 19.64% and 11.74% reduction in the chloride permeability coefficient with the inclusion of 1%, 3% and 5% NT, respectively. Nazari and Riahi [21,23] studied the percentage of water absorption, at ages of 2, 7, and 28 days, of SCCs modified with NT. Cement was partially replaced with 0%, 1%, 2%, 3%, 4%, and 5%, by weight. Fixed w/b ratio of 0.4 and various dosages of superplasticizer were employed. The results showed a reduction in the percentage of water absorption with the inclusion of NT, at ages of 7 and 28 days. The inclusion of 4% NT showed the lowest percentage of water absorption. On the other hand, the percentage of water absorption increased with the inclusion of NT at age of 3 days. Behfarnia et al., [45] reported a reduction in the permeability of concretes by partially replacing cement with 1%, 2%, 3%, 4%, and 5% NT. The inclusion of 4% NT exhibited the lowest permeability. Chen et al. [17] studied the porosity, at ages of 3, 7, and 28 days, of pastes modified with NT. Two kinds of NT with different crystal phase compositions, P25 (75% anatase and 25% rutile) and anatase (99% anatase). The NT was used as addition to the cement at levels 0%, 5%, and 10%, by weight. Fixed w/c ratio of 0.35 was used. The results showed that the addition of NT decreased the porosity at all ages. The Anatase type showed lower porosity than that of P25 type. The reduction in the 28 days porosity of the specimens containing 5% and 10% P25 was 11.68% and 14.65%, respectively, whilst it was 21.36% and 21.65% for the specimens containing 5% and 10% Anatase specimens, respectively. However, the nanoparticles seemed to act as effective fillers of voids. With hydration continued, the conglomerations containing the nanoparticles as nucleus expanded and filled up the pore space around them gradually. The presence of these “nuclei” significantly accelerated the hydration reaction rate. Therefore, the hydration accumulated rapidly grew outwards into the water filled voids, resulting in the decrease in porosity. Essawy and Abd Elhaleem [39] reported that the inclusion of 5% NT in sulfate resisting cement blended with micro silica decreased the porosity, whilst the inclusion of 7% and 10% did not lead significantly to lower the porosity. Mohammadi et al. [46] reported a reduction in the total porosity of calcium phosphate cement by adding 2.5%, 5%, and 10% NT, by weight.

Nazari and Riahi [22,23] studied the porosity, at age of 90 days, of concretes containing different amounts of slag. They found that the optimum slag content was 45 wt.% that exhibited the lowest porosity. NT particles were used to modify the concrete with the optimum content of slag. The binder materials were partially replaced with NT at levels of 0%, 1%, 2%, 3%, and 4%, by weight. The results showed that the porosity of the specimens decreased with the inclusion of NT. The addition of 3% NT showed the optimum content of NT which exhibited the lowest porosity. The reduction in the porosity was 1.64%, 4.33%, 5.67%, and 5.07% with the inclusion of 1%, 2%, 3%, and 4% NT, respectively. In another investigation, Jalal [52] studied the percentage of water absorption, at ages of 7, 28, and 90 days, of concretes containing 45 wt% slag. NT particles were used to modify this type of concrete. The binder materials were partially replaced with NT at levels of 0%, 1%, 2%, 3%, and 4%, by weight. The results showed that the percentage of water absorption decreased with the inclusion of NT at all ages. The inclusion of 3% NT showed the optimum content of NT which exhibited the lowest percentage of water absorption. The reduction in the percentage of water absorption, at age of 28 days, was 38.42%, 41.35%, 45.75%, and 43.4% with the inclusion of 1%, 2%, 3%, and 4% NT, respectively.

Shekari and Razzaghi [47] studied the percentage of water absorption and chloride penetration, at age of 28 days, of concretes containing 15% MK, as cement replacement, modified with NT. The addition of NT was 1.5%, by cementitious weight. Fixed w/c ratio and fixed dosage of superplasticizer were employed. The results showed that the percentage of water absorption decreased with the addition of NT. The reduction in the percentage of water absorption was approximately 75.74%. The addition of NT reduced the chloride penetration by approximately 33.64%. Farzadnia et al. [48] studied the gas permeability, at ages of 28 days, of mortars containing 5% SF modified with NT. Cement was partially replaced with NT at levels of 0%, 1%, 2%, and 3%, by weight. Fixed w/b ratio of 0.35% and 2% naphthalene sulfonate based

Table 3. Effect of NT on the percentage of water absorption, permeability, porosity and chloride penetration of plain and blended cement systems.

Author	% NT	Effect
He and Shi [49]	0 and 1	-Improved the chloride penetration resistance
Li et al. [40]	0 and 1	- Resisting chloride invasion
Nazari [25]	0, 0,5, 1, 1.5, and 2	-Reduced the percentage of water absorption and its rate -Reduced the coefficient of water absorption -0.5% is the optimum
Soleymani [50,51]	0, 0.5, 1, 1.5, and 2	-Reduced the percentage of water absorption at ages of 28 and 90 days -0.5% is the optimum -Increased the percentage of water absorption at age of 7 days
Jalal [36]	0, 1, 2, 3, and 4	-Reduced the water absorption and the capillary absorption -Reduced the chloride ion penetration -4% is the optimum
Jalal et al. [27]	0, 1, 2, 3, 4, and 5	-Reduced the percentage of water absorption and capillary water absorption -Reduced the chloride ion penetration -4% is the optimum
Zhang and Li [35]	0, 1, 3, and 5	-Reduced the chloride permeability coefficient -1% is the optimum
Nazari and Riahi [21,23]	0, 1, 2, 3, 4, and 5	-Reduced the percentage of water absorption at ages of 7 and 28 days -4% is the optimum -Increased the percentage of water absorption at age of 2 days
Behfarnia et al. [45]	0, 1, 2, 3, 4, and 5	-Reduced the permeability -4% is the optimum
Chen et al. [17]	0, 5, and 10	-Reduced the porosity -10% is the optimum
Essawy and	0, 5, 7, and 10	-Reduced the porosity

Abd Elhaleem [39]		
Mohammadi et al. [46]	0, 2.5, 5, and 10	-Reduced the porosity
Nazari and Riahi [22,23]	0, 1, 2, 3, and 4	(Mixture containing 45% slag) -Reduced the porosity -3% is the optimum
Jalal [52]	0, 1, 2, 3, and 4	(Mixture containing 45% slag) -Reduced the percentage of water absorption -3% is the optimum
Shekari and Razzaghi [47]	0 and 1.5	(Mixture containing 15% MK) -Reduced the percentage of water absorption -Reduced the chloride penetration
Farzadnia et al. [48]	0, 1, 2, and 3	(Mixture containing 5% SF; curing in limewater) -Reduced the gas permeability -2% is the optimum

superplasticizer were employed. The specimens were cured in lime saturated water for 28 days. The result showed a slightly reduction in the permeability with the attraction of NT which might be due to the nucleus expansion on NT and uniform distribution of hydration products. The inclusion of 2% NT showed the lowest permeability followed by 1% and 3%, respectively. Table 3 summarizes the mentioned studies about the effect of NT on the percentage of water absorption, chloride penetration and permeability of the plain and blended PC systems.

From the above review of the literature in this section, it can be noted that the inclusion of NT, in most cases, reduced the percentage of water absorption, chloride permeability, gas permeability and porosity, but sometimes increased the percentage of water absorption at early ages. The reduction in the percentage of water absorption may be related to the pozzolanic action and filler effect of NT particles [25]. According to the optimum content of NT, some studied [25,51] reported that 0.5% NT is the optimum content which exhibited the lowest percentage of water absorption, whilst others [21,23,27,36] reported 4%. 3% NT is the optimum content with the inclusion of 45% slag [52], whilst 2% NT is the optimum with the inclusion of 5% SF [48]. Anyway, the optimum content of NT in the matrix that exhibited the lowest percentage of water absorption or permeability or porosity not fixed, but varying according to curing condition, hydration age, NT particle size, the type, w/b ratio and the content of pozzolan that replaced part of cement.

9. COMPARISON BETWEEN NT AND OTHER TYPES OF NANOPARTICLES

9.1. NT versus nano-SiO_2

Li et al. [33] studied the workability and flexural strength, at age of 28 days, of concretes modified with either 1% NT or 1% NS, by weight. Fixed w/b ratio of 0.42 and fixed dosage of water reducing agent were employed. The results showed a reduction in the workability of concrete with the addition of either NT or NS, but approximately the same workability was obtained for NT mixture compared to NS mixture. The specimens containing NT exhibited 5.8% higher flexural strength than that containing NS. Zhang and Li [35] compared the compressive strength, flexural strength, pore structure and resistance to chloride penetration of concretes modified with either NT or NS. Cement was partially replaced with either NT or NS at levels of 0%, 1%, and 3%, by weight. The results showed that both compressive strength and flexural strength of concrete containing NT were higher than that containing NS. On the same line, the pore structure and resistance to chloride penetration of concrete containing NT were superior in comparison with that containing NS. Li et al. [32] compared the compressive strength and flexural strength, at age of 28 days, of concretes modified with either NT or NS. Cement was partially replaced with either NT or NS at levels of 0%, 1%, and 3%, by weight. Fixed w/b ratio of 0.42 and various dosages of water reducing agent were employed. The results showed that the specimens modified with NT exhibited higher strengths than that modified with NS. The specimens modified with 1% nanoparticles exhibited higher strength than that modified with 3%. The enhancement in the compressive strength of specimens modified with 1% and 3% NT over that modified with NS was 5.1% and 8.93%, respectively, whilst the enhancement in the flexural strength was 5.8% and 4.85%, respectively.

Li et al. [34] studied the abrasion resistance, at age of 28 days, of concretes modified with NT versus that modified with NS. Cement was partially replaced with either NT or NS at levels of 0%, 1%, and 3%, by weight. Fixed w/b ratio of 0.42 and various dosages of water reducing agent were employed. The results showed that specimens modified with NT exhibited higher abrasion resistance than that modified with NS. The abrasion resistance of the specimens modified with 1% was higher than that modified with 3%. The enhancement in the surface index of the abrasion resistance of specimens modified with 1% and 3% NT over that modified with NS was 15.1% and 45.53%, respectively, whilst the enhancement in the side index of the abrasion resistance of the specimens modified with NT over that modified with NS at levels of 1% and 3% was 24.32% and 57.53%, respectively. Goberis and Abraitis [53] studied the fire resistance of concrete containing either 5% NT or 5% NS. Bauxite components form the basis of the concrete, including fine-ground bauxite, that were introduced into the concrete in identical amounts. The bonding material was aluminate cement. The specimens were exposed to elevated temperatures of 800, 1100, and 1300 °C. The results showed that the compressive strength of the specimens containing NT after being exposed to elevated temperatures was considerably lower than that containing NS. They also studied the chemical resistance of both concrete types by immersing the specimens after treatment in alkali (NaOH) for 24 h at 100-110 °C and 800 °C. The results showed that concrete containing NT had substantially higher chemical resistance.

9.2. NT versus nano-ZrO_2, nano-Al_2O_3, and nano-Fe_3O_4

Shekari and Razzaghi [47] compared the compressive strength, indirect tensile strength, percentage of water absorption and chloride penetration, at age of 28 days, of concretes containing 15% MK, as cement replacement, modified with NT versus that modified with NZ, NA and NF. The additions of nanoparticles were 0% and 1.5%, by cementitious weight. Fixed w/c ratio and fixed dosage of superplasticizer were employed. The results showed that the compressive strength of NT specimens was higher than that of the control and that modified with NZ by 22.75% and 2.16%, respectively. On the other hand, specimens modified with NA or NF showed higher compressive strength that that modified with NT by 26.3% and 5%, respectively. Splitting strength results showed approximately the same trend as compressive strength (Fig. 9). The specimens modified with NF showed the lowest percentage of water

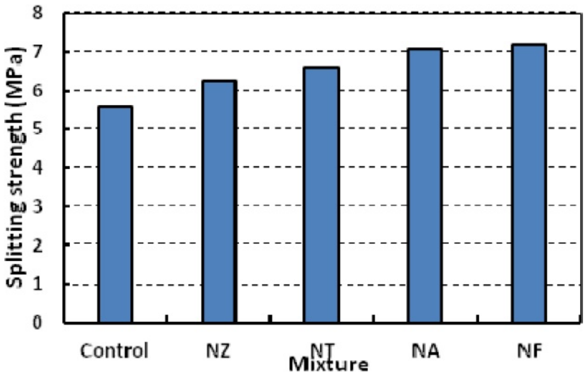

Fig. 9. Comparison between splitting tensile strength of concretes modified with NT versus other types of nanoparticles, replotted from [47].

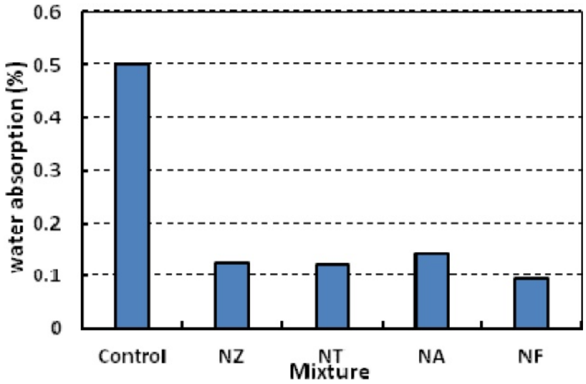

Fig. 10. Comparison between % water absorption of concretes modified with NT versus other types of nanoparticles, replotted from [47].

absorption followed by specimens modified with NT, NZ and NA, respective (Fig. 10). The specimens modified with NT showed lower chloride penetration than that modified with NF. On the other hand, the specimens modified with NT showed higher chloride penetration than that modified with NZ or NA.

10. REMARKS

The current review paper carried out on reviewing the previous works that investigated the effect of NT on some properties (heat of hydration, workability, setting time, chemical shrinkage, strengths, abrasion resistance, fire resistance, water absorption, chloride penetration and permeability) of plain or blended cement systems. However, the remarks of this literature review can be summarized as following:

1. The addition of NT into the cement increased the heat of hydration and accelerated the rate of reaction at early ages of hydration. Smaller particles of NT accelerated the reaction more than larger particles. Higher content of NT accelerated the reaction more than lower content.

2. The workability, flowability, initial setting time and final setting time of cement system decreased with increasing NT content.
3. Chemical shrinkage of cement increased with increasing NT content.
4. In general, the mechanical strength increased with the inclusion of NT, up to specified limit. The optimum content is still controversial from researcher to another, this may be depends on many factors such as w/b ratio, curing condition, curing age, pozzolan type, pozzolan content, chemical admixture and nanoparticle size. However, 1-4% NT in concrete, 2-10% in mortar and up to 10% in paste seemed to be the suitable content that showed good strength.
5. The inclusion of 1-3% NT increased the abrasion resistance of concrete and the inclusion of 2% NT increased the fire resistance of concrete.
6. In general, the inclusion of NT into the matrix reduced the percentage of water absorption, permeability and chloride penetration, but sometimes increased the percentage of water absorption at early ages. Most of studies reported 4% NT is the optimum content, others reported 0.5%, 1%, 2%, and 3%.
7. The inclusion of NT up to 3% into concrete showed higher compressive strength, flexural strength and abrasion resistance compared to concrete modified with the same content of NS, whilst the inclusion of NS up to 5% into concrete showed better fire resistance and chemical resistance compared to the same concrete modified with the same content of NT.
8. The inclusion of 1.5% NT into concrete containing 15% MK showed higher compressive strength and splitting tensile strength than NZ concrete, whilst it showed lower compressive strength and splitting tensile strength than either NA concrete or NF concrete.
9. The addition of 1.5% NT into concrete containing 15% MK showed lower percentage of water permeability than NA concrete, but showed higher percentage of water absorption than NF concrete. NT concrete showed lower chloride penetration than NF concrete, but showed higher than NZ concrete and NA concrete.

REFERENCES

[1] S. Kaluza, J. Klein-Balderhaar and B.Orthen, *Literature review – Workplace exposure to nanoparticles* (EUOSHA-European agency for safety and health at work, 2008).

[2] *Handbook of nanostructured materials and technologies*, ed. by H.S. Nalwa (Academic Press, 2002).

[3] Alaa M.Rashad // *Materials and Design* **52** (2013) 143.

[4] Alaa M. Rashad // *Construction and Building Materials* **52** (2014) 437.

[5] Y. Murata, T. Obara and K. Takeuchi // *Journal of Advanced Oxidation Technologies* **4** (1999) 227.

[6] Jun Chen and Chi-sun Poon // *Building and Environment* **44** (2009) 1899.

[7] K. Kamitani, Y. Murata, H. Tawara and K. Takeuchi, In: Proc. *International Symposium on cement and concrete*, ed. by Z. Wu (International Academic Publishers, Beijing, 1998), p. 751.

[8] Akira Fujishima, Xintong Zhang and Donald A. Tryk // *Surface Science Reports* **63** (2008) 515.

[9] Rowan Leary and Aidan Westwood // *Carbon* **49** (2011) 741.

[10] F. Pacheco-Torgal and Said Jalali // *Construction and Building Materials* **25** (2011) 582.

[11] W. Zhu, P. J. M. Bartos and A. Porro // *Materials and Structures* **37** (2004) 649.

[12] O. Carp, C. L. Huisman and A. Reller // *Progress in Solid State Chemistry* **32** (2004) 33.

[13] Monica J. Hanus and Andrew Harris // *Progress in Materials Science* **58** (2013) 1056.

[14] Bo Yeo Lee and Kimberly E.Kurtis // *J. Am. Ceram. Soc.* **93** (2010) 3399.

[15] Bo Yeon Lee and Kimberly Kurtis // *J. Am. Ceram. Soc.* **95** (2012) 365.

[16] Bo Yeon Lee, *Effect of titanium dioxide nanoparticles on early age and long term properties of cementitious materials* (PhD thesis, Scool of Civil & Environmental Engineering, Georgia Institute of Technology, August 2012).

[17] Jun Chen, Shi-cong Kou and Chi-sun Poon // *Cement & Concrete Composites* **34** (2012) 642.

[18] W. A. Gutteridge and J. A. Dalziel // *Cement and Concrete Research* **20** (1990) 778.

[19] A. M. Poppe and G. D. Schutter // Cement and Concrete Research **35** (2005) 2290.

[20] L. Senff, D. Hotza, S. Lucas, V. M. Ferreira and J. A. Labrincha // *Materials Science and Engineering A* **532** (2012) 354.

[21] Ali Nazari and Shadi Riahi // *Materials Science and Engineering A* **528** (2010) 756.

[22] Ali Nazari and Shadi Riahi // *Materials Science and Engineering A* **528** (2011) 2085.

[23] Ali Nazari and Shadi Riah // *Energy and Buildings* **43** (2011) 995.

[24] Ali Nazari and Shadi Riah // *Science China, Technological Sciences* **54** (2011) 3109.

[25] Ali Nazari // *Materials and Structures* **44** (2011) 773.

[26] Mostafa Jalal, Ali A. Mortazavi and Nemat Hassani // *Journal of American Science* **8** (2012) 391.

[27] Mostafa Jalal, Mojtaba Fathi and Mohammad Farzad // Mechanics of Materials **61** (2013) 11.

[28] Amal R. Jayapalan, Bo Yeon Lee and Kimberly E. Kurtis // *Cement & Concrete Composites* **36** (2013) 16.

[29] A. R. Jayapalan, B. Y. Lee and K. E. Kurtis // *Nanotechnology in Construction* **3** (2009) 267.

[30] Hassan Noorvand, Abdullah Abang Ali Abang, Ramazan Denirboga, Nima Farzadnia and Hossein Noorvand // *Construction and Building Materials* **47** (2013) 1350.

[31] N. Salemi, K. Behfamia and S. A. Zaree // *Asian Journal of Civil Engineering (BHRC)* **15** (2014) 411.

[32] Ali Nazari, Shadi Riahi, Shirin Riahi, Seyedeh Fatemeh Shamekhi and A. Khademno // *Journal of American Science* **6** (2010) 43.

[33] Hui Li, Mao-hua Zhang and Jin-ping Ou // *International Journal of Fatigue* **29** (2007) 1292.

[34] Hui Li, Mao-hua Zhang and Jin-ping Ou // *Wear* **260** (2006) 1262.

[35] Mao-hua Zhang and Hui Li // *Construction and Building Materials* **25** (2011) 608.

[36] Mostafa Jajal, Ali Akbar Ramezaianpour and Morteza Khazaei Pool // *Journal of American Science* **8** (2012) 285.

[37] Tao Meng, Yachao Yu, Xiaoqian Qian, Shulin Zhan and Kuangliang Qian // *Construction and Building Materials* **29** (2012) 241.

[38] Ali Nazari, Shadi Riahi, Shirin Riahi, Seyedeh Fateneh Shamekhi and A. Khademno // *Journal of American Science* **6** (2010) 98.

[39] Amr A. Essawy and El Aleem A. Abd // *Construction and Building Materials* **52** (2014) 1.

[40] Hui Li, Huigang Xiao, Xinchun Guan, Zetao Wang and Lei Yu // *Composites: Part B* **56** (2014) 688.

[41] Farzad Soleymani // *Journal of American Science* **7** (2011) 1.

[42] Farzad Soleymani // *Journal of American Science* **8** (2012) 734.

[43] Farzad Soleymani // *Journal of American Science* **8** (2012) 121.

[44] L. Senff, D. M Tobaldi, S. Lucas, D. Hotza, V. M. Ferreira and J. A. Labrincha // *Composites: Part B* **44** (2013) 40.

[45] K. Behfarnia and A. Keivan // *Asian Journal of Civil Engineering (BHRC)* **14** (2013) 517.

[46] Maryam Mohammadi, Saeed Hesaraki and Masoud Hafezi-Ardakani // *Ceramics International* **40** (2014) 8377.

[47] A. H. Shekari and M. S. Razzaghi // *Procedia Engineering* **14** (2011) 3036.

[48] Nima Farzadnia, Abdullah Abang Ali Abang, Ramazan Demirboga and Mohammed Parvez Anwar // *Construction and Building Materials* **43** (2013) 469.

[49] Xiaodong He and Xianming Shi // *Journal of the Transportation Research Board* **3** (2008) 13.

[50] Farzad Soleymani // *Journal of American Science* **7** (2011) 7.

[51] Farzad Soleymani // *Journal of American Science* **8** (2012) 698.

[52] Mostafa Jalal // *Journal of American Science* **8** (2012) 289.

[53] S. Goberis and R. Abraitis // *Refractories and Industrial Ceramics* **50** (2009) 295.