Cement & Concrete Composites 36 (2013) 16–24

Contents lists available at SciVerse ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Can nanotechnology be ‘green’? Comparing efficacy of nano and microparticles in cementitious materials

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ARTICLE INFO

Article history:
Received 31 January 2012
Received in revised form 7 November 2012
Accepted 8 November 2012
Available online 24 November 2012

Keywords:
Titanium dioxide
Limestone
Nanoparticle
Chemical shrinkage
Calorimetry
Life cycle cost

ABSTRACT

The use of nano-sized particles in cementitious materials introduces a myriad of potential innovations from new functionality to enhanced mechanical performance, but such materials can be energy-intensive to manufacture. With increasing emphasis on sustainable development, it is important to investigate and understand benefits and costs of using nanomaterials compared to relatively less energy-intensive microparticles. The current research investigates the effect of chemically inert nano and microparticles (i.e., titanium dioxide (TiO_2) and calcium carbonate (limestone)) on early age properties and behavior of cement-based materials. Results indicate that the early age hydration rates, shrinkage, and pore structure of cement-based materials can be modified and optimized by tailoring the size of fillers. Life cycle analysis indicates that photocatalytic reactivity of TiO_2 could offset initial higher environmental impacts. Thus, optimally sized nanoparticles could revolutionize the construction industry by allowing tailoring of structure and properties of cement-based composites, with environmental sustainability preserved through the selection of lower embodied-energy particles.

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1. Introduction

The construction industry, like other science and engineering fields, is examining developments in nanotechnology to identify potential novel applications. In particular, the use of nanoparticles in construction materials is of increasing interest. The use of nanoparticles can not only modify properties by potentially enhancing strength [1–3] and durability [4,5] but also by introducing new functionality, including photocatalytic (self-cleaning, pollution reduction and anti-microbial ability) [6], anti-fogging [7] and self-sensing capabilities [8].

While the use of nanoparticles could increase in the construction industry [9], such materials, especially when engineered and manufactured, can be energy-intensive to produce and thus direct economic costs and environmental impacts could be high [10]. With an increasing emphasis on sustainable development in many sectors including the construction industry [11], it is important to understand the costs and benefits associated with the use of nanomaterials when compared to relatively less energy-intensive microparticles. Particles considered in this research include fillers which are largely non-reactive in the presence of Portland cement; as a result, the effect of particle size and dosage of the filler can be isolated. It should be noted that some researchers have noted marginal reactivity of limestone powder with cementitious minerals [12,13]. However, in the current research the reactivity of limestone powder is considered negligible as compared to the reactivity of fine pozzolanic fillers such as micro-silica and henceforth in this manuscript both limestone particles as well as TiO_2 particles will be categorized as ‘inert’ or ‘fillers’.

The presence of chemically inert mineral fillers or additives alters cement hydration by at least three different mechanisms: (1) the introduction of additional sites for heterogeneous nucleation, (2) a dilution effect, and/or (3) changes in the particle size distribution and porosity of the system [14]. The inclusion of very fine (nano-sized) inert fillers, like titania (TiO_2), have been found to increase the rate of cement hydration [15,16] by heterogeneous nucleation, particularly during the early reaction of tricalcium silicate [17]. Researchers have noted that nucleation seeding of cement with well-dispersed calcium silicate hydrate (C–S–H), which is considered a nanomaterial, and ultrafine alumina and quartz also increases the rate of cement hydration [18,19]. The increase in the rate of cement hydration could be beneficial for the construction industry by shortening the time to setting for cement and concrete. Faster setting of cement could increase the throughput of precast plants and also reduce formwork removal time and total time of construction, which would have direct economic benefits. By inducing the shorter setting time through the use of inert particles, additional benefits in mechanical properties, durability, and sustainability are also possible, but these must be balanced with the additional costs – both economic and environmental – associated with their use.

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0958-9465/$ - see front matter Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.cemconcomp.2012.11.002

For guidance, examination of the use of nano and microscale silica particles in concrete may be helpful. (Although such materials are not inert and are typically pozzolans, lessons learned in this area bear some relevance to inert particles, particularly when considering the relative effects of nano and microparticles). Use of silica fume in cement-based materials, with sizes in the tens to hundreds of nanometer, affects particle packing and size distribution and with time by its pozzolanic reaction further densifies the microstructure; as a result, the structure and properties of the cement-based material are altered by the introduction of these particles which are much finer than cement [9,20]. Even smaller nano-SiO_2 particles have been shown to enhance strength and interfacial transition zone properties greater than ordinary silica fume [21], suggesting the potential benefits in decreasing reactive particle sizes below the upper range of nanoscale. However, in part because of this accelerated early hydration and also because of alteration of the pore size distribution in the cementitious system, these reactive particles have also been found to increase shrinkage. For example, researchers have observed that the use of nano-SiO_2 increased 7 day shrinkage by 80% compared to an equivalent mix with micro-silica [22]. Thus, this examination suggests that nano and microparticles of the same composition can have different effects on structure and behavior in cement-bases systems because as the particle size decreases from micro to nanoscale the surface area increases considerably.

In this research, the effects of inert nano and microparticles of inert mineral fillers on properties of cement-based materials compared through heat of hydration studies, measurement of chemical shrinkage, surface area and pore size distribution. Specifically, two inert particle types are examined – TiO_2 and limestone – because of increasing interest in the practical use of these minerals in cementitious materials and products [23–26]. Because both materials are chemically inert (or practically so) [27] with cements, these data can be compared to examine the influence of particle size on the potential for partial cementitious replacement on the structure and property development. In addition, analyses of the potential environmental impact of cementitious materials with TiO_2 and limestone additive is conducted through a life cycle analysis (LCA) [11]. Although the NO_X binding ability of photocatalytic TiO_2 is a potential environmental benefit [28], a comprehensive investigation that includes all factors including total embodied energy, emissions including CO_2 and NO_X among other factors associated with the production of these particles, is required to evaluate the impact (especially on the environment) of their usage.

2. Research methodology

2.1. Materials

Three TiO_2 powders (T1, T2 and T3) and three limestone powders (L1, L2 and L3) of different particle sizes (or surface areas) were used for making the lab-blended cements with ordinary Portland cement. The properties of the TiO_2 and limestone powders are given in Table 1; T1 and T2 were obtained from Cristal Chemical Company (previously Millennium Inorganic Chemicals), T3 from Evonik Industries, and limestone powders (L1, L2 and L3) were obtained from Omya Inc. Although the nominal particle size of the TiO_2 powders are similar, T3 was more well-dispersed in water as experimentally observed using a Zetasizer Nano dynamic light scattering particle size analyzer. The increasing dispersion and decreasing agglomerate size of the TiO_2 particles was in the order T1 > T2 > T3 (Table 1). The cement used was a commercially available ASTM C 150 Type I Portland cement with a composition as given in Table 2. The median diameter of the cement particles used for the experiments was 10.08 μm.

2.2. Mix design and sample preparation

A water/solids ratio (w/s) was maintained at 0.50 for all the mixes (i.e., those used for calorimetry, chemical shrinkage and surface area analysis). Representative mix design details for the different mixtures are given in Table 3. The inert fillers (limestone or TiO_2) were added to cement at 5%, 10% and 15% of the weight of cement. Cement paste samples used for isothermal calorimetry, chemical shrinkage and specific surface area analysis were prepared according to ASTM C 305 [29]. For the mixes with inert filler additives, the filler was initially mixed at medium speed with the entire quantity of water for 1 min. The cement was then added to the filler-water mixture and further mixing continued according to ASTM C 305 standard.

2.3. Isothermal calorimetry

Isothermal calorimetry is used to study the rate and amount of heat evolved in an exothermic chemical reaction such as hydration of cement paste. The effect of various additives can be studied by comparing the hydration curves of the rate and total heat evolved by the cement-filler mixes with control mix. The tests were conducted according to ASTM C 1679 [30] using an eight channel micro-calorimeter (TAM AIR, TA instruments), which has precision of ±2 μW. The test was conducted at 25 °C for at least 72 h and was conducted on triplicate samples. The time of addition of cement to water is considered as the starting time of reaction for each sample. The data for initial 10 min of the tests were discarded to ensure that capsule reached thermal equilibrium with the calorimeter. The results are normalized per gram of cement in each mix.

2.4. Chemical shrinkage

Deformation resulting from early hydration was measured by chemical shrinkage according to ASTM C 1608 [31] Procedure A using glass vials and capillary tubes. The test was conducted for at least 100 h and was conducted on triplicate samples. Cement pastes was poured into the glass vials and the vials were filled with de-aerated water. A rubber stopper with a graduated capillary tube was used to measure the change in volume of the cement paste. The sealed vials were placed in an environmental chamber at a constant temperature of 23 °C and measurements were taken every 30 min. The water level in the capillary tube at 60 min after the paste was mixed is considered as the zero reading, to allow the vials with the sample to reach thermal equilibrium with the environmental chamber. The change in volume was normalized per gram of cement in the paste to measure the chemical shrinkage per unit mass of cement.

2.5. Specific surface area (SSA) analysis

Nitrogen adsorption and desorption technique for porosity measurements was conducted using a Micromeretics ASAP® 2020 accelerated surface area and porosity analyzer. The relative pressure range used for the adsorption and desorption was from 0.002 to 0.995. Surface area was calculated using the BET [32] analysis method, over a relative pressure range of 0.05–0.30 on the adsorption isotherm. Total pore volume available to nitrogen (in the size range 3–40 nm pore radius), average pore width are pore size distribution were calculated using the Barrett, Joyner, Hallenda (BJH) [33] method using the data from the desorption isotherm.

Although researchers have noted that surface area measurements vary with technique, adsorbate and sample preparation [34], the use of nitrogen adsorption–desorption technique and comparison of results using BET surface area and pore size analysis

Table 1
Properties of TiO_2 (T) and limestone (L) additives.

	Particle size[a] (nm)	Agglomerate size (μm)	Surface area[a] (m^2/g)	Purity[a] (%)
L1	20,000	–	0.24	95
L2	3000	–	0.5	95
L3	700	–	12	98
T1	20–30	1.5	45–55	>97
T2	15–25	1.2	75–95	>95
T3	21	0.58	50 ± 15	99.5

[a] Manufacturer specified data.

Table 2
Composition of Type I cement.

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	MnO_2
Percentage	20.38	5	3.09	61.82	3.66	0.07	0.5	0.25	0.13
Component	P_2O_5	SrO	BaO	SO_3	LOI	C_3S	C_2S	C_3A	C_4AF
Percentage	0.06	0.04	0.03	2.62	2.35	51.3	19.73	8.01	9.41

Table 3
Mix design details for ordinary Portland cement mix and various filler-cement mixes.

	0%	5%	10%	15%
Cement (g)	100	100	100	100
Filler (g)	0	5	10	15
Water (g)	50	52.5	55	57.5

using BJH desorption is regularly used for comparing among companion cement samples [35]. The variations due to sample preparation were eliminated in this research by preparing samples using the same methodology. The samples used in this research were prepared similarly by curing for 28 days at 100% relative humidity. The samples were then freeze dried and stored under sealed conditions until further testing. The results from the 28-day cured samples could be used to compare long-term surface area and pore structure of the ordinary Portland cement and filler-cement mixtures.

2.6. Life-cycle analysis methods

A life cycle assessment (LCA) was performed to examine the overall impact of the TiO_2 and limestone replacement for cement on the environment in comparison to ordinary Portland cement. LCA is a technique that incorporates environmental impact and considers all energy and emissions of the various stages of a product or process from raw material production stage through end of life disposal or recycling (cradle-to-grave approach) [36]. In the current research, SimaPro LCA analysis software was used along with BEES (developed by NIST) [37] as a preliminary method for impact assessment, with a primary goal of providing data for comparing the relative impacts of nano and microparticle additions. It should be noted that processing techniques and hence environmental impacts of materials vary with each individual product and manufacturer. But LCA analysis is typically conducted utilizing databases compiled with data from several material manufacturers. Thus LCA analysis can provides an overall impact, especially a comparison of the environmental impact of different classes of materials.

Mix design data for the different materials were input into the SimaPro LCA software, which conducted the life cycle impact analysis that includes classification, characterization, normalization and weighting steps. The analysis conducted in this research considered only the materials production, including raw material acquisition and processing of the components used in the cementitious mixes. The environmental impact due to the various materials used in this research was obtained from the database from the SimaPro software. In the classification step of LCA, BEES assessment method categorized the impact of the materials into the following categories: acidification, criteria air pollutants, ecotoxicity, eutrophication, fossil fuel depletion, global warming, habitat alteration, human health-cancer, human health-noncancer, indoor air quality, ozone depletion, smog, and water intake. Also, further investigation was performed to account for the NO_X binding capability of TiO_2-cement, which could offset a part of the environmental impact of the production of the TiO_2 nanoparticles. The time required to offset the initial NO_X emissions from material was also estimated.

A functional unit of 1000 kg of the cementitious mixture was used for all of the analysis. A generalized processing of TiO_2 and limestone based on data obtained from the respective manufacturers were considered for the material manufacturing in this research. The mixes with a w/s of 0.50 and addition rate of 5% of TiO_2 and limestone were considered for the LCA analysis and compared with the ordinary Portland cement paste.

3. Results and discussion

Isothermal calorimetry was conducted on ordinary Portland cement as well as blended TiO_2 and limestone cements to study the effect of filler replacement level and particle size on the early hydration reaction. Chemical shrinkage tests according to ASTM C 1608-07 were conducted to study the effect of addition of TiO_2 and limestone on extent of shrinkage of cement paste during the early stages of hydration. Specific surface area analysis was conducted using a nitrogen adsorption–desorption experiment on paste samples cured for 28 days at 100% relative humidity. Life Cycle Analysis using SimaPro software and BEES assessment method was conducted to assess the environmental impact of the filler-cement mixtures and was compared to the results from the ordinary Portland cement mix.

3.1. Isothermal calorimetry

Figs. 1a and 2a show the variation of the rate of hydration of ordinary Portland cement and the TiO_2-blended and limestone-blended cements at 5% and 10% replacement levels respectively. For the graph of ordinary Portland cement, the first peak after the acceleration zone of heat release corresponding to the reaction of C_3S can be observed from ~1 to ~8 h. This peak is followed by a

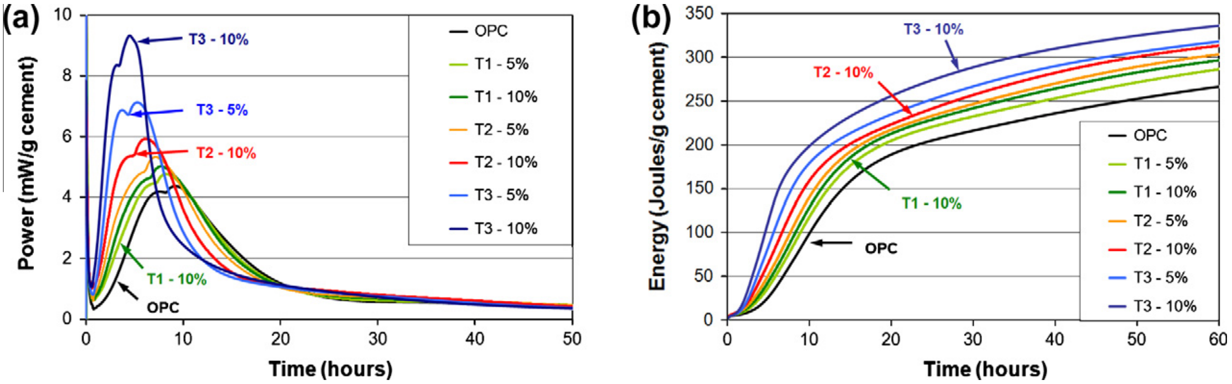

Fig. 1. (a) Rate of heat release and (b) total heat release by TiO_2-cement mixtures.

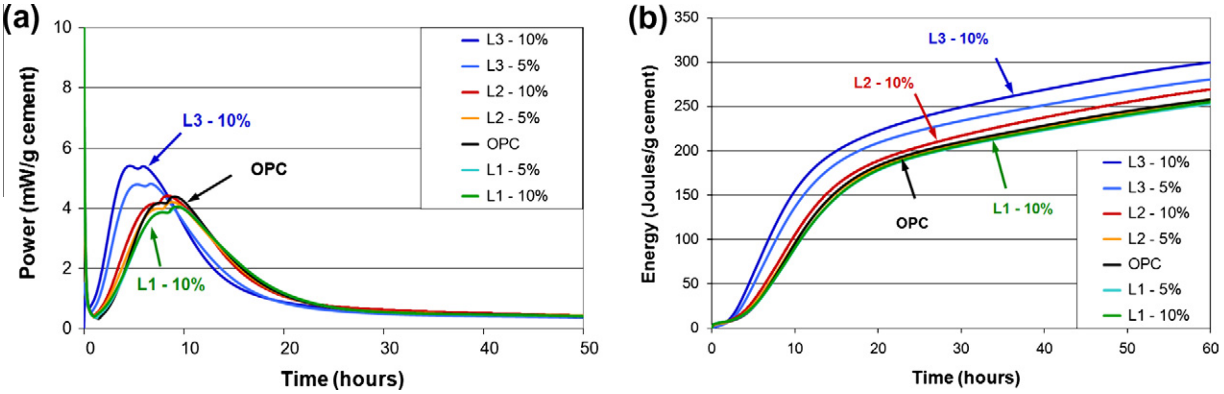

Fig. 2. (a) Rate of heat release and (b) total heat release by limestone–cement mixtures.

secondary peak corresponding to C_3A hydration. Figs. 1b and 2b show the variation of cumulative energy released of ordinary Portland cement and the lab-blended TiO_2 and limestone cements respectively. For the graph of ordinary Portland cement it can be seen that after the initial dormant period there is a rapid increase in the total energy released, which corresponds to the peaks of C_3S and C_3A hydration.

The addition of TiO_2 nanoparticles resulted in an acceleration of the hydration reaction as observed in Fig. 1. There was a decrease in the dormant stage as well as a decrease in the time when the peak of the hydration rate curve is observed. Comparing the peaks of the hydration curves it can be observed that 10% mixes of T1, T2 and T3 accelerated the rate of cement hydration by approximately 80, 180 and 280 min compared to ordinary Portland cement. The TiO_2 fillers also caused an increased rate of reaction of the cement. The total heat evolved over the 60 h test period was also higher in all the TiO_2 mixes compared to ordinary Portland cement mix. The addition of 10% of T1, T2 and T3 increased the total heat evolved by 18%, 27% and 34% respectively, when comparing values at 60 h of hydration. An increased acceleratory effect was observed when the more well-dispersed TiO_2 was used, with greatest acceleration produced by T3. Thus, increasing dosage and the better dispersed TiO_2 produced greater acceleration, higher rates of reaction as well as higher total heat evolved over the test duration. In the case of TiO_2, the increase in rate of early reaction shows that nucleation effects dominate any dilution effect.

The influence of addition of limestone powders on rate of heat release and total heat released is as shown in Fig. 2. Addition of L3 (with highest surface area among the limestone powders) increased the rate of reaction and accelerated cement hydration. By comparing the peaks of the hydration curve, it can be observed that 10% addition of L3 accelerated the reaction by approximately 125 min compared to ordinary Portland cement paste. This indicates a dominant nucleation effect compared to dilution effect. Thus sub-micron sized particles like L3 could be used to increase the rate of cement hydration by heterogeneous nucleation. By observing the calorimetry curves for L2 and L1, it can be concluded that a marginal acceleration of hydration was observed in finer L2 mixes, whereas relatively "coarse" L1 reduced the rate of cement hydration. Thus, a dilution effect was dominant in the case of coarse fillers and beyond a certain particle size there seems to be no effect on cement hydration, as observed in the total heat of hydration curve. The differences between the curves of L1, L2 and ordinary Portland cement paste is marginal and thus the rate of cement hydration is maintained when coarser microparticles are used. It can be concluded that the inclusion of coarser microparticles (L1 and L2) does not produce any significant changes compared to the ordinary cement paste.

Comparing data in Figs. 1 and 2, it can be observed that the submicron-sized limestone particles L3 produced similar effects to that of the nanoTiO_2 particles, albeit to a lesser extent. The increase in the peaks of the rate of hydration curves of L3 can be compared to that of T1 and T2. While 10% addition of L3 accelerated the hydration reaction by 125 min, the addition of T1 and T2 accelerated hydration by 80 and 180 min approximately. When 5% filler addition rate is evaluated, it was observed that T1, T2 and L3 accelerated hydration rate by 60, 120 and 80 min respectively. The acceleratory effect of these particles in increasing order is T1, L3 and T2. Thus the increase in reaction rate, as noted by the shift in peaks of the hydration curve to the left, indicates similar effects by the limestone L3 and the TiO_2 powders, despite the nominally finer size of the TiO_2. A possible explanation for this could be the TiO_2 agglomeration into micron or submicron-sized particles; the phenomena of nanoparticle agglomeration in cements has been widely reported [9,38,39].

Thus, it can be concluded that nanoparticle additives could be even more effective accelerators if dispersion difficulties could be overcome. Comparison of calorimetry data for the microscale limestone L3 and the nominally nanoscale TiO_2 particles indicates that a nanoparticle might not be necessary in the field to produce a meaningful increase in the cement hydration rate. Rather, a particle of approximate size 1 μm (for the parameters used in this research) could be sufficient to produce an equivalent increase in hydration rate as well as acceleration of hydration similar to that of nanoparticles, without the need for special dispersion techniques.

3.2. Chemical shrinkage

Fig. 3 shows the chemical shrinkage of the ordinary Portland cement paste and the lab-blended cement pastes with TiO_2 particles (T2), and limestone particles (L1 and L2). For ordinary Portland cement, a rapid decrease in the volume of the paste is found up to 20 h, which corresponds to the main hydration peaks for the reaction of C_3S and C_3A in the cement paste (Figs. 1a and 2a).

From Fig. 3a, it can be observed that the TiO_2 fillers increased the rate of chemical shrinkage compared to the ordinary cement paste mix. Increasing chemical shrinkage was observed in all the TiO_2-cement mixtures as the dosage was increased. The shape of the graph for chemical shrinkage was similar to the graph of cumulative energy released (Figs. 1b and 2b), which suggests that the decrease in volume of the cement paste is directly related to the energy released during hydration and hence the degree of reaction. Thus the decrease in volume of the cement paste mix should also be considered when designing and using cement paste mixes with nanoparticles.

Similar results were observed for the finer limestone powder as shown in Fig. 3b. However, the coarse filler tested (L1) resulted in a decrease in the chemical shrinkage. This can be related to the dominant dilution effect, as previously discussed. Although there was no significant decrease in the degree of hydration for the filler L1 compared to ordinary Portland cement (Fig. 2), the chemical shrinkage was reduced, which is beneficial for early age dimensional stability. This suggests that (for the parameters used in this research) fillers with size about 20 μm can replace cement up to 10% with enhanced dimensional stability without compromising degree of hydration. Thus, the particle size of the filler could be selected to avoid and decrease chemical shrinkage that occurs in the filler-cement system.

3.3. Specific surface area analysis

Table 4 shows the results from the nitrogen adsorption–desorption tests conducted after 28 days of curing filler-cement paste samples at 100% relative humidity. The BET surface area, BJH desorption pore volume and BJH desorption average pore width are listed for the ordinary Portland cement paste and the lab-blended cement pastes with TiO_2 particles (T1 and T3) and limestone particle L3.

Compared to the ordinary Portland cement paste mix, all the other mixes considered exhibited a higher surface area and pore volume. This could indicate the addition of the fine fillers encourages the formation of a higher surface area C–S–H. Similar increase in surface area was observed by Juenger and Jennings [35] when a chemical accelerator (calcium chloride) was added to cement paste. The larger surface area of the inert filler could also be contributing to an increase in the surface area of the filler-cement paste mix.

However, the increase in pore volume should be examined more critically [40], as larger scale porosity can decrease permeability and compromise durability [41]. It should be considered, for example, if the increase in effective water/cement ratio (since water to solids ratio was kept constant in the mixes) could contribute to an increased pore volume.

Fig. 4 shows the pore size distribution or variation of the pore volume with average pore width. These data can be examined to better explain the increase in BET surface area and pore volume of filler-cement mixes. The range of pore sizes shown in Fig. 4 is typical for capillary pores in cementitious materials [41]. Fig. 4 indicates that, compared to the ordinary Portland cement mix, the TiO_2-cement mixes had a higher pore volume of small (<4 nm) and medium sized (4–20 nm) pores and a lower volume of larger pores (>20 nm). (The definition of small, medium and large capillary pore sizes is according to Juenger and Jenniungs [35]). Thus, in the case of TiO_2-cement mixes there is a refinement of the capillary pores since the relative volume of small and medium sized capillaries increases, despite the greater total pore volume. This is also supported by the fact that the average pore width decreases for the TiO_2 mixes (Table 4), with the finest TiO_2 (T3) exhibiting the greatest reduction in pore width. The C–S–H interlayer porosity (with size < 2.5 nm) could also be affected, but the measurement of C–S–H porosity was beyond the capability of the SSA analyzer used.

The implication of the refinement of capillary pores is that the pores could become disconnected and hence the permeability (which depends on connectivity of larger capillary pores) could decrease. Thus, the use of nanoparticles could result in a decrease in permeability of cementitious materials. Additional testing is necessary to verify this supposition.

On the other hand, the limestone–cement mix exhibited a higher pore volume for all sizes of pores considered as shown in Fig. 4. Table 4 indicates that for L3, the pore volume and surface area values increased compared to ordinary Portland cement mix but the calculated average pore size width was similar to that of ordinary

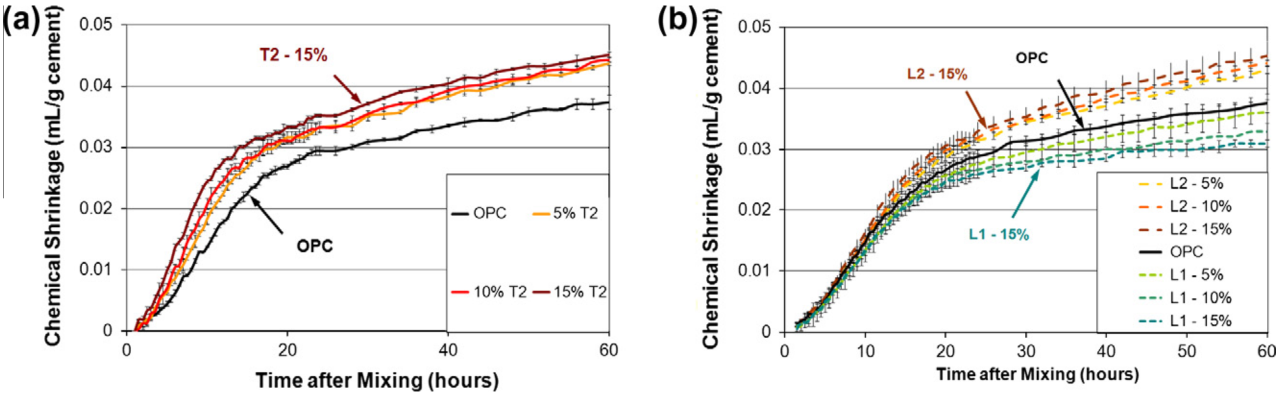

Fig. 3. Chemical shrinkage of (a) TiO_2-cement mixture (with T2) and (b) limestone–cement mixture.

Table 4
Results from specific surface area nitrogen adsorption–desorption experiments.

	OPC	T1-10%	T3-10%	L3-10%
BET surface area (m^2/g)	21.93	25.77	33.10	29.62
BJH desorption pore volume (cm^3/g)	0.088	0.099	0.115	0.117
BJH desorption average pore width (nm)	11.44	10.86	8.77	11.23

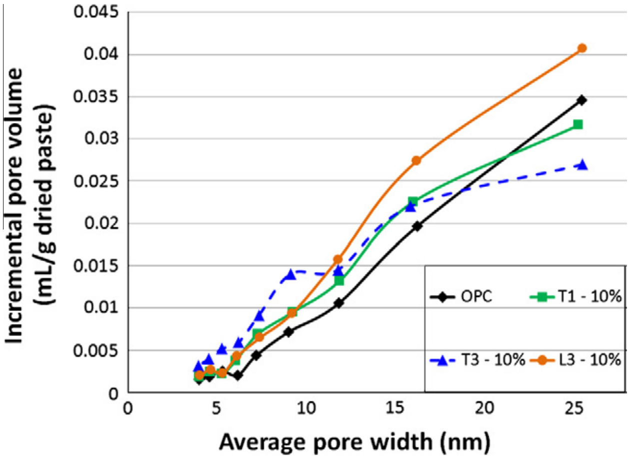

Fig. 4. Pore size distribution of ordinary cement paste and filler-cement mixtures.

Portland cement mix. These results tend to indicate that the total porosity (in the size range measured in these experiments) is greater for the limestone-blended cement and that the porosity is coarser than in the ordinary cement paste. Further research and permeability experiments are necessary to better understand the effect of limestone powder on the pore size distribution, surface area, permeability and hence on the durability of cementitious mixtures.

3.4. Life cycle analysis

In addition to assessing the impact of nano and microparticle additions on performance, it is also relevant to examine the environmental impacts of the use of these materials in concrete. Life cycle analysis is a technique for analyzing environmental performance over the life cycle of a product, or, specifically in this case, for assessing the overall impact of variations in the composition of the product. The limitations of LCA are well-documented and include reliance on data (often industry-reported) which may be inaccurate, highly variable, or limited [11,42,43]. The goal with the preliminary LCA performed here is not to provide absolute quantitative assessments of environmental impacts, but rather to form a basis for a generalized comparison of nano and microparticle additions to concrete as well as to examine the potential effects of further research.

Fig. 5 shows the results from the LCA analysis for ordinary Portland cement and cement containing 5% TiO_2 or 5% limestone filler. As previously described, the analysis was performed using SimaPro software that uses BEES impact assessment method. The total utilized resources and smog creation due to the use of 1000 kg (functional unit) of ordinary Portland cement paste and cement-filler mixes with 5% addition of limestone and titanium dioxide is shown in Fig. 5. This analysis considers only the materials production, including raw material acquisition and processing of the components used in the cementitious mixes. It is clearly evident that the limestone–cement mixes have a lower environmental impact compared to plain cement paste mix, whereas TiO_2-cement mixes have considerably higher environmental impacts (“costs”). The reason for high environmental impact by the TiO_2-cement mix is because of the significantly higher energy and emissions “costs” of TiO_2 manufacturing process compared to cement production [42,44]. By comparing the environmental “costs” of the ordinary Portland cement mix and limestone–cement mixture, it can be observed that the addition of 5% limestone results in almost a 5% decrease in the various impact categories, as might be expected. This suggests that compared to ordinary Portland cement, the energy and emissions of limestone powder is negligible. This can partly be explained due to the fact that limestone is used as a raw material in cement production and most of the energy and emissions from the cement production is due to the clinkering and grinding processes [42]. Hence, the replacement of cement with a lower embodied energy filler, such as limestone powder, is one pathway to enhance sustainability of the construction industry.

However, the potential benefits associated with nanoparticle addition should not be set aside completely based upon this preliminary LCA [45]; here, some pathways for sustainable nanoparticle utilization are proposed. First, for example, fine particles which are naturally occurring or are by-products of industrial or commercial processes potentially would have significantly lower environmental cost than manufactured nanoparticles and should be examined for applications in cement and concrete. The advantage of using such nano, or even fine microparticle fillers, would be that the environmental impacts as well as economic costs would be extremely low, when compared to processed and manufactured nanoparticles. Thus, toward attaining sustainability by reducing environmental “costs”, the utilization of naturally-occurring or by-product nano and finer microparticles should be the subject of further examination. Further extensive research is needed to optimize the potential benefits for the construction industry from using natural nanoparticles in cementitious materials.

One such naturally-occurring material, and one which may become a widely available is a bio-energy by-product [46,47] – diatomaceous earth (DE), the silicon-rich remains of certain forms of algae. To examine whether DE could be used effectively in cements in a manner similar to the other particles assessed here, preliminary isothermal calorimetry experiments were conducted (Fig. 6). Commercially available flux-calcined diatomaceous earth (CAS# 68855-54-9) with an average particle size of 3 μm was used for these tests. From Fig. 6 it can be observed that the addition of 10% and 15% of diatomaceous earth increased the rate of cement hydration and accelerated the reaction marginally compared to the ordinary Portland cement paste. While these results are not entirely satisfactory, other naturally occurring fine fillers, for example a finer diatomaceous earth, should be examined. Such particles, when identified, could increase the rate of cement hydration possibly even similar to the extent observed with the TiO_2 particles used in this research. As demonstrated below, cement-savings could be the net result of the acceleratory effects observed with nano and fine microparticle addition.

The LCA results of the TiO_2 blended cements indicate that the environmental costs due to TiO_2 addition is significantly higher than ordinary cement paste. But interestingly, the results from calorimetry (Fig. 1) indicate that 5% addition of TiO_2 filler to cement increases the cumulative heat evolved in significant excess of this addition rate – by 21% at 48 h of hydration. Similar acceleratory effects have been measured during cement replacement with titania nanoparticles [15]. Since the increase in total energy evolved can directly be related to degree of hydration, these results suggest that nanoparticles could effectively replace a higher percentage of cement than that tested in this research, while achieving a similar degree of hydration as that of ordinary Portland cement paste.

Combining this concept with the notion that inert filler materials could be selected such that the life cycle cost of the filler is negligible compared to the cement or TiO_2 suggests that identification

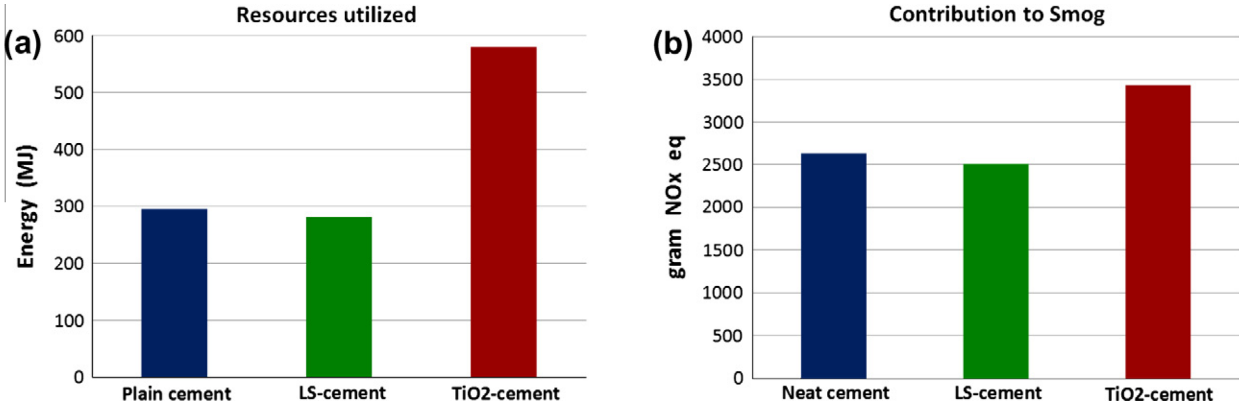

Fig. 5. LCA results showing (a) utilized resources and (b) contribution to smog (due to NO_X emissions) by ordinary Portland cement paste and cement-filler mixes with 5% addition of filler.

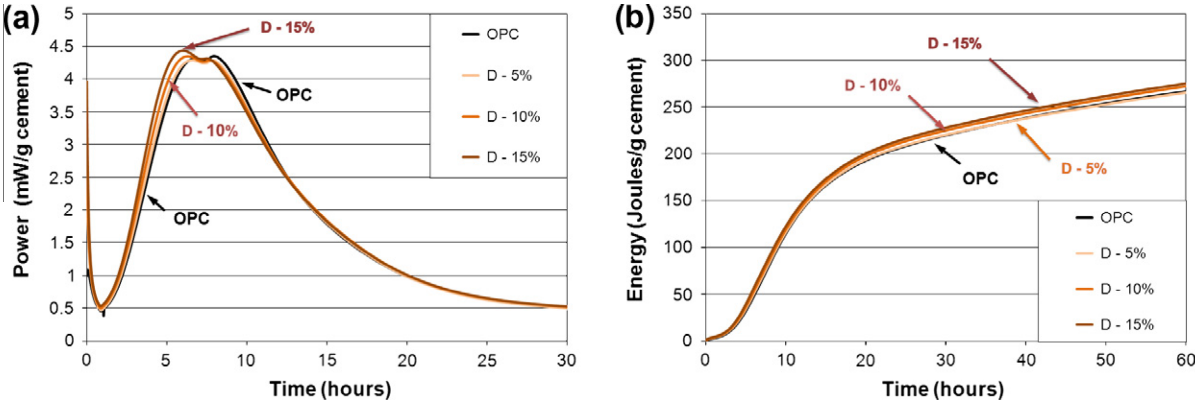

Fig. 6. (a) Rate of heat release and (b) total heat release by 5%, 10% and 15% mixture of diatomaceous earth and cement.

of an “optimum” inert filler material, from both particle size and embodied energy perspectives, should be the subject of further investigation. If such a filler were added to TiO_2-blended cements to reach similar degrees of hydration as ordinary portland cement at 48 h, the maximum replacement rate is calculated to be approximately 17%. For such a mix, the total environmental impact could be much lower compared to the TiO_2-cement mix.

Now, if the capability of TiO_2 to bind pollutant gases (e.g. NO_X, SO_X and VOC’s) is considered, a part of the impacts – (e.g. the NO_X emissions) – can be offset with time. Further analysis was performed based on the conditions in Atlanta, USA to calculate the time required to offset the NO_X from TiO_2 production. Atlanta, USA with an average sunshine per day of 7.25 h was selected because of the location where this research was conducted as well as its relevance to urban environmental conditions. The annual NO_2 concentration in Atlanta was reported 17.0 ppb in 2004 [48]. When 5% of TiO_2 was used as an additive to cement by mass and 5 mm thick surface layer is used, 2.12 years (776 days) are required to offset the initial NO_X emissions by the TiO_2-cement mixture. If the surface is frequently washed, as with rainfall or dew, as expected during the life of TiO_2-cement surfaces, the photocatalytic activity could be renewed and hence these surfaces could perform well throughout the life of the structure.

The results from the analytical calculations for the TiO_2-modified cement indicates that pollutant gas (NO_X) concentration could be reduced, urban air quality could be improved and smog creation reduced, if TiO_2-containing cementitious materials are used in these localities. Thus in the long term, TiO_2 modified cement could be beneficial to decrease the initial higher environmental impact because of production “costs”. Further research and development of TiO_2 with enhanced efficiency for pollutant gas binding (e.g. by doping TiO_2 with transition metal ions [49,50]) is required. Lower energy-production of photocatalytic TiO_2 [51] could also make these nanoparticles more favorable from an environmental impact perspective. The use/production of nanoparticles with a lower embodied energy and emissions could usher a new era of increased nanoparticle usage in the construction industry even when considering life-cycle costs. Thus the introduction and optimization of additional functionalities such as photocatalytic properties (binding pollutant gases, antimicrobial effect), self-sensing capability and development of lower-embodied energy nanoparticles could enhance sustainability and result in a sustainable construction product.

4. Conclusions

The effect of the addition of nano and microparticles of TiO_2 and limestone powders on the cement properties was studied as a part of this research using isothermal calorimetry, chemical shrinkage and LCA analysis. When TiO_2 and limestone of different particle sizes were added to cement, it was observed that the hydration reaction was accelerated and the rate of hydration increased for nano and submicron particles. The increase in the rate of reaction was proportional to the dosage of the TiO_2 and limestone. Smaller particles of TiO_2 were found to accelerate the reaction more than larger particles. Heterogeneous nucleation effect was found to be dominant compared to the effect of dilution when inert TiO_2 and fine submicron sized limestone particles were added to cement. When larger microparticles (L1 and L2) were added to cement the rate of cement hydration was maintained or marginally reduced. A dilution effect was dominant in the case of addition of larger microparticles, above 3 μm in this research. Therefore, these results show that the positive effects of non-dispersed nanoparticles can be obtained with finer microparticles. Use of such fine microparticles can result in lesser energy use as well as emissions if such particles were obtained in a manner that does not require extra processing, such as generally required for nanoparticle manufacture.

Chemical shrinkage test results indicate that the addition of nanoparticles increase the shrinkage in cement paste and the increase in shrinkage is proportional to the percentage replacement of the cement. The addition of coarser microparticle (of size 20 μm, in this research) resulted in a decrease in the chemical shrinkage of the cementitious mixture. Again, the particle size of the filler could be selected to avoid chemical shrinkage and possible cracking due to high chemical shrinkage. Thus, an optimum particle size and dosage of the nanoparticles and microparticle can be used to balance the positive effect of acceleration of hydration reaction and the negative effect which results in decrease in volume of the cement paste.

Surface area and pore size distribution analysis conducted on cement mixtures with nano-TiO_2 and fine limestone (L3) indicates that total BET surface area and pore volume increases when compared to ordinary Portland cement mix. The relative increase in the small and medium sized capillary pores in the filler-cement mixtures indicates a pore refinement due to the addition of the inert fillers. Pore size refinement was also evident by the decrease in the average pore width of the TiO_2-cement mixtures tested. Because the decrease in the size of the pores can have implications for decreasing permeability by the pores becoming disconnected, there is potential for increasing durability of cementitious composites.

The results from the LCA and photocatalytic properties analysis indicate that there could be various pathways for enhancing sustainability in construction materials. The use of natural or by-product nanoparticles or a filler with lower embodied energy and lower emissions (such as limestone) is one such potential pathway to attain greater sustainability. The use of microparticles (with size near 1 μm) can impart similar properties as that of non-dispersed nanoparticles and cause significant increase in the rate and degree of hydration, especially in the first day of cement hydration. Thus, the use of highly dispersed nanoparticles might not be required for significant increase in the rate and degree of hydration as indicated by the use of the submicron sized limestone powder (L3) in this research. The introduction of additional functionalities to cementitious materials, which could decrease the environmental impact of construction materials, is another pathway to increase sustainability. The introduction of TiO_2 powder with photocatalytic properties such as pollutant gas binding, anti-microbial properties and self-cleaning capability, has the potential to thus improve the sustainability of construction materials. Potential improvement of photocatalytic efficiency and development of lower-energy production processes through ongoing research will also significantly enhance the environmental sustainability index of TiO_2-cement composites.

Acknowledgments

This material is based upon work supported by the National Science Foundation under Grant No. CMMI-0825373. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation.

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