Journal of Materials Science and Chemical Engineering, 2015, 3, 72-81
Published Online November 2015 in SciRes. http://www.scirp.org/journal/msce
http://dx.doi.org/10.4236/msce.2015.311009

Influence of Nano-Barium Sulfate Agglomeration on Microstructure and Properties of the Hardened Cement-Based Materials

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Received 7 October 2015; accepted 21 November 2015; published 27 November 2015

Abstract

The aim of the present work is to study the effect of Nano-barium sulfate additions on the physico-mechanical properties of hardened cement pastes. Nano-barium sulfate was prepared by the precipitation method. Eight mixes of filled cement pastes containing 0.5 wt%, 1.0 wt%, 1.5 wt% and 2.0 wt% of both nano-barium sulfate and micro-limestone were prepared and compared to the base OPC. The hydration characteristics were evaluated by the measure of combined water content, bulk density, total porosity and compressive strength for samples hydrated up to 90 days. The progress of hydration reactions was followed up by XRD analysis. The morphology and microstructure were studied by SEM. Nano-size barium sulfate acted as a nucleating agent and enhanced the hydration of cement pastes up to 2.0% mass content. Also, the microstructure was improved considerably. Accordingly, nano-size barium sulfate can be used successfully in the preparation of filled cement.

Keywords

Nano-Barium Sulfate, Cement Paste, Filler, Compressive Strength, Microstructure

1. Introduction

The use of active mineral admixtures such as condensed silica fume, coal fly ash, natural pozzolana, ground granulated blast furnace slag or fillers such as limestone or quartz, in concrete is an effective way of reducing

How to cite this paper: Saraya, M.E.I. and Bakr, I.M. (2015) Influence of Nano-Barium Sulfate Agglomeration on Microstructure and Properties of the Hardened Cement-Based Materials. *Journal of Materials Science and Chemical Engineering*, **3**, 72-81. http://dx.doi.org/10.4236/msce.2015.311009

the consumption of Portland cement clinker and then reducing the related CO_2 emissions. The durability and mechanical properties of concrete are mainly dependent on the microstructure of the hardened cement paste and the interfacial transition zone through incorporating mineral admixtures [1] [2]. These mineral admixtures are believed to act through three roles [3]: 1) they tend to physically fill the void space between the larger particles, which is otherwise occupied by water that is not free to contribute to fluidity; 2) with time they react chemically with calcium hydroxide (CH) to produce additional material such as pozzolanic C-S-H gels and 3) the pozzolanic C-S-H gels act as seeds to provide nucleation sites for cement hydration products.

Nanotechnology is being used in many applications and it has received increasing attention also in building materials, with potential advantages and drawbacks being underlined [4]. The nano-particles have attracted great interests due to their four major effects [5] [6], including size effect, quantum effect, surface effect and interface effect. The use of nanoparticles can not only change properties by prospect enhancing strength [7] and durability [8] but also by improving new functionality, such as photocatalytic (self-cleaning, pollution reduction and antimicrobial ability) [9], anti-fogging [10] and self-sensing capabilities [11]. Among the types of nanoparticles investigated are titanium dioxide (TiO_2) nanoparticles [12] [13], zinc dioxide (ZnO_2) nanoparticles [14] [15], calcium carbonate ($CaCO_3$) nanoparticles [16], nano-Fe_2O_3 [17] [18], Al_2O_3 nanoparticles [19]-[21] and nanoclays [22], although the majority of studies thus far have focused on nanosilica [23]-[26]. Previous researchers [27] [28] reported that functionalized multi-walled carbon nanotubes were found to improve strength properties of Portland cement.

Taking into account the available data concerning the effect of barium sulfate on cement characteristics along with its inertness in addition to the reported data about limestone filler in Portland cement, the present work aims at investigating the use of nano-size barium sulfate as a filler in Portland cement as compared to limestone filler.

2. Experimental Work

The starting materials were ordinary Portland cement (OPC), limestone of Samalout formation, from Beni-Khalid quarries, El-Minia, Egypt and nano-barium sulfate prepared by the precipitation method [29]. Their chemical analysis was conducted by a Philips X-ray fluorescence equipment model PW/1404 (**Table 1**). The limestone was ground to pass 90 μm sieve. In order to investigate the effect of the nano-size barium sulfate on the physico-mechanical properties of cement pastes, as compared to limestone, eight compositions were prepared in addition to the base OPC (**Table 2**). Each dry mix was homogenized in an automatic agate mortar for one hour.

Table 1. Chemical analysis of the starting materials, mass %.

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	BaO	L.O.I
OPC	20.88	6.08	3.18	63	1.5	1.6	0.02	0.04	1.9
Nano-size barium sulfate	0	0	0	0	0	34.35	0	63.45	2.3
Limestone	0.26	0.16	-	54.59	0.29	0.05	0.11	0.03	43.72

Table 2. Compositions of the investigated mixes, mass %.

Mix	Composition, mass %		
	OPC	Nano-barium sulfate	Limestone
NBS1	99.5	0.5	0.0
NBS2	99.0	1.0	0.0
NBS3	98.5	1.5	0.0
NBS4	98.0	2.0	0.0
LS1	99.5	0.0	0.5
LS2	99.0	0.0	1.0
LS3	98.5	0.0	1.5
LS4	98.5	0.0	1.5

Limestone filled samples were denoted in this work as LS1 up to LS4, while samples mixed with nano-barium sulfate were denoted as NBS1 up to NBS4. Dry mixes were molded into 2 × 2 × 2 cm cubes by the use of the required water of standard consistency [30]. The specimens were demolded after 24 h, casting, and cured up to 90 days under tap water. Their bulk densities were determined according to Archimedes principle [31], while the compressive strength was measured according to ASTM designation: C109-80 [32]. The hydration was stopped by microwave drying technique [33]. Ignition loss test was conducted at 1000˚C in order to determine the combined water content of dried samples. The microstructure was investigated via scanning electron microscope (SEM; JXA-840A electron probe microanalyzer, JEOL, Japan).

3. Results and Discussion

3.1. XRD Results

The reflection intensities of alite (C_3S) diminished greatly with the addition of nano-barium sulfate, while the amount of portlandite (CH) that produced from hydration reaction increased (**Figure 1**). This indicated the good effect of nano-barium sulfate in the enhancement of hydration reactions. Barite reflections were detected in the filled samples and increased in accordance to the added amount of nano-barium sulfate, while the quartz content decreased as the amount of barium sulfate increased. The XRD results confirmed the complete inertness of nano-barium sulfate as no other phases were detected.

3.2. Combined Water Content

Figure 2 represented the combined water contents of the investigated mixes cured up to 90 days. Generally, the progress of curing time was accompanied by higher water contents due to the progress of the hydration of anhydrous clinker phases and the formation of hydration products [34]. Nano-barium sulfate filled cement pastes had the highest combined water contents as compared to OPC and limestone filled samples. Moreover, the increase of the nano-barium sulfate content resulted in higher combined water contents at all addition levels, while

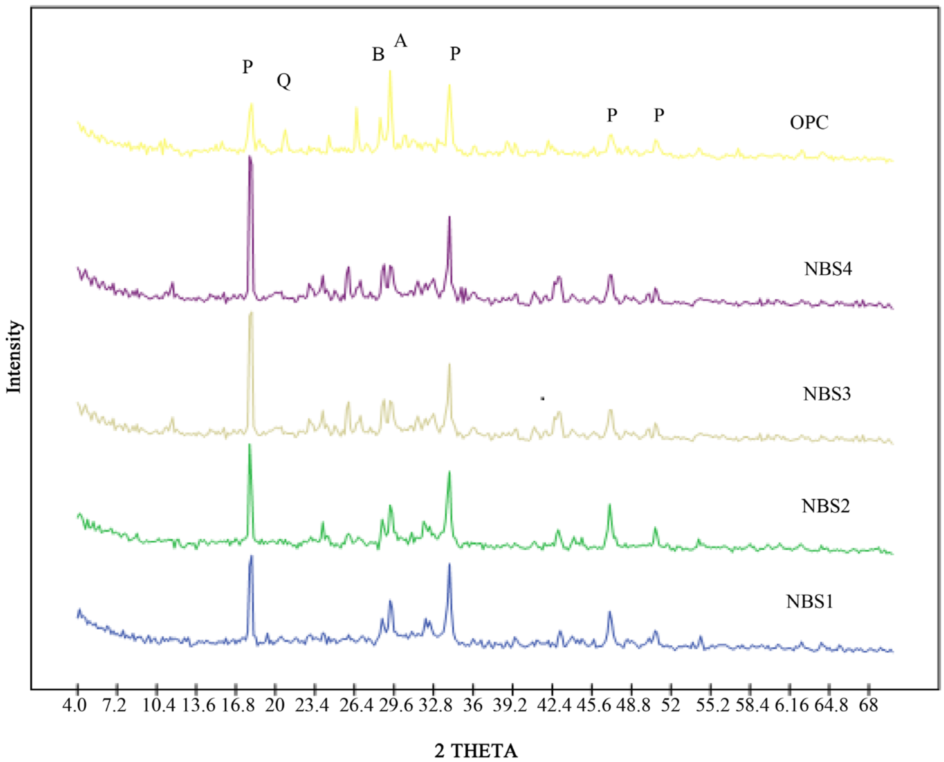

Figure 1. XRD patterns of samples hydrated up to 90 days (P = Portlandite, A = alite, B = Barite, Q = Quartz).

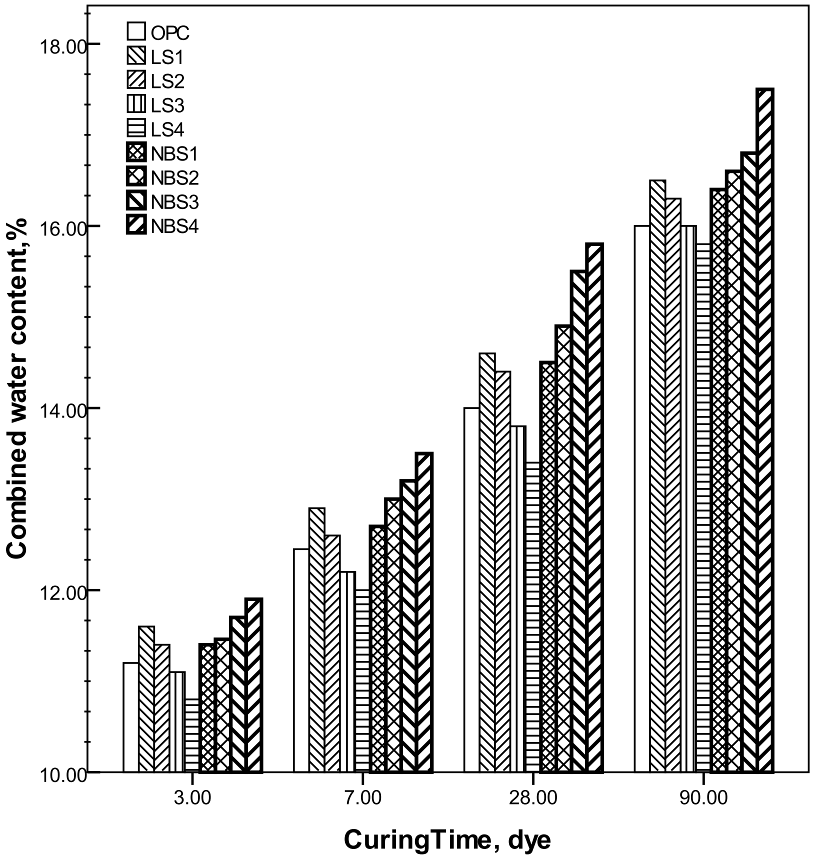

Figure 2. Chemically combined water content of the investigated mixes as a function of curing time.

high additions of limestone (LS3, LS4) resulted in lower combined water contents. This can be understood according to the dilution effect of filler that leads to less hydrated compounds. The continuous increase in combined water content for nano-barium sulfate blended samples is referred to the hydration enhancement, as given by XRD results, and the high fineness which helps in water absorption. These two factors seem to eliminate the dilution effect.

3.3. Bulk Density and Total Porosity

The bulk density increased while the total porosity decreased with the curing time for all hydrated cement pastes, (**Figure 3** and **Figure 4**). As the hydration progressed, hydration products filled some of the pores and led to decrease the porosity and increase the bulk density of the hardened cement pastes. The bulk density values of nano-size barium sulfate filled cement pastes (up to 2%) were higher than those of both OPC and micro limestone filled cement pastes at all ages of hydration. This is mainly due to the progress in the hydration process which is enhanced due to the high surface area of nano-barium sulfate in addition to its high specific gravity [35]. The bulk density of limestone filled cement samples were less than that of OPC and decreased gradually as the amount of limestone increased. Also, their porosities are generally higher than those of OPC at all curing times. On contrary to barium sulfate which is considered as a good stable filler and almost has no reaction with the hydration products, calcite present in limestone filler favors the formation of calcium carboaluminate hydrates with higher amount of water [36]-[39]. The porosity of the pastes typically increases with the water cement ratio. The water enclosed in the microstructure is directly responsible for the porosity of the hardened cement pastes [40].

3.4. Compressive Strength

The compressive strength increased with curing time for all cement pastes (**Figure 5**) due to the formation of

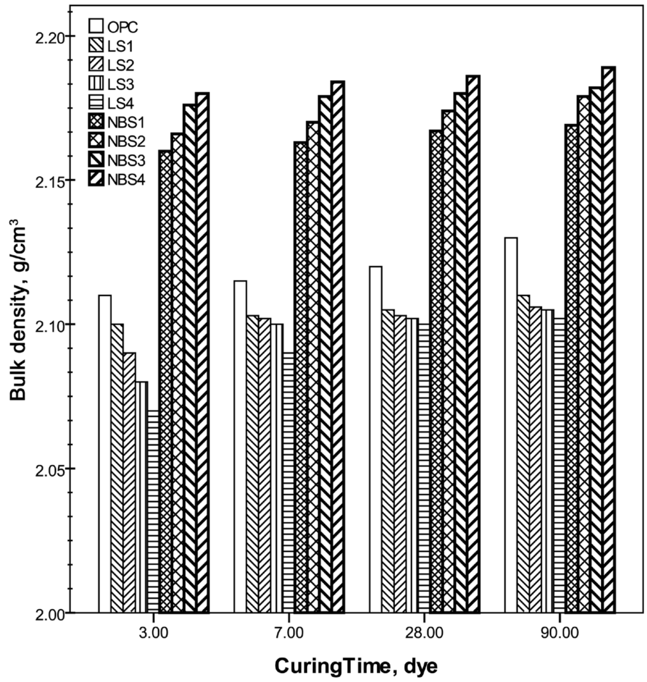

Figure 3. Bulk density of the investigated mixes as a function of curing time.

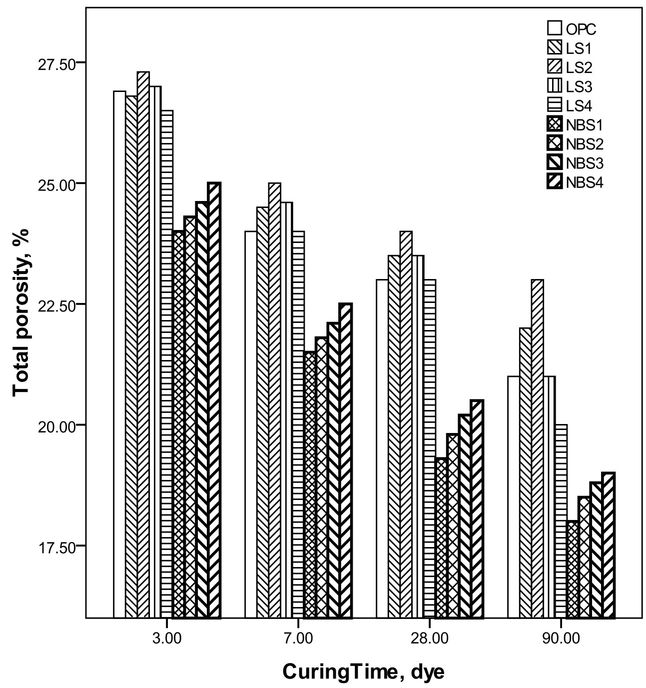

Figure 4. Total porosity of the investigated mixes as a function of curing time.

more cementing materials. Nano-barium sulfate cement pastes revealed higher compressive strength values than both OPC and micro limestone cement pastes. The high surface area of nano-barium sulfate activated the hydration of C_3S and favored the formation of additional amounts of CSH which is the main cementations material responsible for compressive strength gain. The porosity seemed to be the most intrinsic factor affecting the compressive strength. The highest strength values were observed for NBS1 samples which revealed the lowest porosities and its changes were compatible with porosity variations.

The strength activity index (SAI) was found [41] with Equation (1) below to determine the effect of the mineral additions on paste strength:

$$\text{S.A.I.} = \text{Blended cement strength}/\text{Refrence cement strength} \quad (1)$$

A coefficient greater than one therefore means that the mineral addition raised cement strength, while values of less than one denote lower strength in the blended cement than in the control. The SAI values for each age studied are plotted against the filler materials (**Figure 6**) At all ages, the pastes prepared with 0.5%, 1.0%, 1.5%

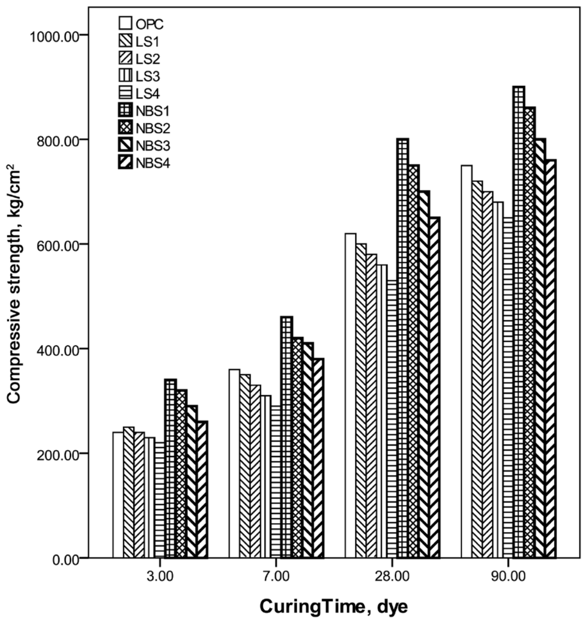

Figure 5. Compressive strength of the investigated batches as a function of curing time.

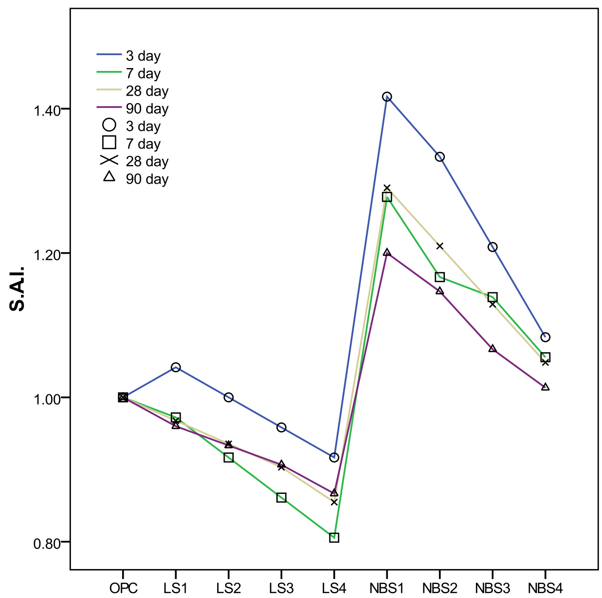

Figure 6. The strength activity index values for each age against the filler materials.

and 2% limestone exhibited lower strength than the OPC paste, except those of 0.5% limestone paste after 3 days exhibited higher strength has a result of acceleration effect of filler on cement hydration. On the other hand, the pastes with nano-barium sulfate content had SAIs of higher than one at all ages, an indication that the addition of barium sulfate had beneficial effect on strength of cement paste. This is mainly attributed to that the nano-barium sulfate acts as seeds to provide nucleation sites for hydration products and accelerate the rate of cement hydration. The highest strength value was achieved after 3 days, while the lowest value was observed after 90 days.

3.5. Morphology and Microstructure

The additions of nano-barium sulfate improved the microstructure considerably. The micrograph of the blank sample (OPC) indicated the formation of an opening pore system (**Figure 7(a)**). On the other hand, the additions of barium sulfate resulted in a dense structure and no macropores were observed (**Figure 7(b)** and **Figure 7(c)**). This can be understood according to packing effect of the nano particles as they filled the spaces inside the skeleton

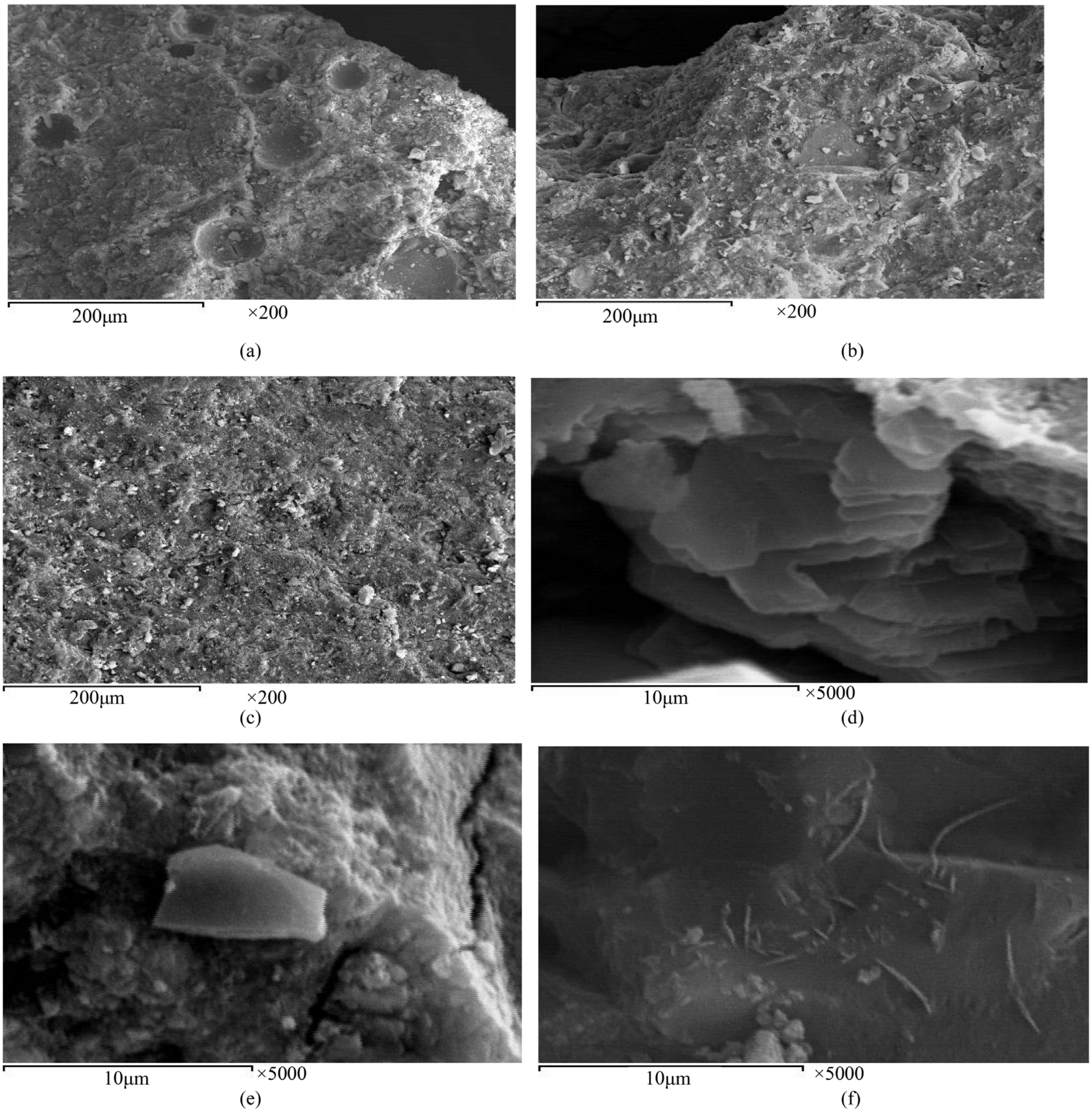

Figure 7. SEM micrographs of OPC, NBS1, and NBS2 Mixes hydrated up to 90 days.

of the cement paste. Platelet-like hydrates of CSH were observed in OPC (**Figure 7(d)**), while the addition of 0.5% barium sulfate led to finer crystals (**Figure 7(e)**). When 1% of barium sulfate was added, the structures became completely compact and smooth (**Figure 7(f)**).

4. Conclusion

The hydration reactions were enhanced by the addition of nano-barium sulfate. The combined water content of nano-barium sulfate filled cement increased progressively up to 2 mass %, while the addition of limestone filler revealed a decrease of the combined water content at amounts higher than 1 mass %. The bulk density, total porosity and compressive strength of nano-barium sulfate filled samples were improved remarkably as compared to both OPC and limestone filled samples at all filler contents. The compressive strength values of hardened cements were compatible with their porosity variations. The nano-barium sulfate filled cements were characterized by finer crystals, compact and smooth microstructure.

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