Available online at www.sciencedirect.com

ScienceDirect

Materials Today: ProceedingsXX (2016) XXX–XXX

www.materialstoday.com/proceedings

PMME 2016

Effect of nano-SiO_2 on physical and electrical properties of PPC cement using complex impedance spectroscopy

Nikesh Ganesh Rathod[a], N. C. Moharana[a], S. K. S. Parashar[b]*

[a]*School of Civil Engineering, KIIT University, Bhubaneswar-751024, India*
[b]*Nanosensor Lab,School of Applied Sciences, KIIT University, Bhubaneswar-751024, India*

Abstract

The aim of this study was to investigate the effect of nano-SiO_2 incorporated in cement blended with 30% class F fly ash on consistency, setting times, compressive strength, chloride penetration, complex impedance spectra and conductivity at 10 kHz. The composite cement was composed of nano-SiO_2 in 0, 1, 2 and 3% by weight of cement. The consistency was found to be increasing with the increase in nano-SiO_2 content whereas retarding effect was observed for setting time. The compressive strength of cement mortar cube sample was found to be less than the control samples. Depth of chloride penetration was also found decreasing with the increasing dosage of nano-SiO_2. Complex impedance spectra are found in semicircle shape in later hours due to the formation of hydration products. Conductivity of all samples found to be decreasing because of the dissolution of ions and formation of hydration products. A good correlation between conductivity and setting time was observed with the help of complex impedance spectroscopy.

Selection and Peer-review under responsibility of International Conference on Processing of Materials, Minerals and Energy (July 29th – 30th) 2016, Ongole, Andhra Pradesh, India.

Keywords: Consistency; Composite; Impedance.

1. Introduction

Fly Ash (FA) is a waste product produced from coal fired power station is used in cement with limited replacement to make concrete [1] owing to its ability to reduce carbon footprint, lowering down hydration heat, improvement of

* Corresponding author. Tel.: +0-000-000-0000 ; fax: +0-000-000-0000 .
*E-mail address:*sksparasharfpy@kiit.ac.in, sksparashar@yahoo.com

Selection and Peer-review under responsibility of International Conference on Processing of Materials, Minerals and Energy (July 29th – 30th) 2016, Ongole, Andhra Pradesh, India.

later age strength, enhancement in durability and available at cheaper rate [2]. Particle size distribution play substantial role on reactivity of FA. More the quantity of fine particles more the surface area and consequently, greater reactivity and greater compressive strength [3]. The spherical shape of particles (size in microns) covers three prime effects [4]: morphological, micro-aggregate and pozzolanic effect. For general construction purpose, the amount of FA is restricted to 15-25% of total cement [5]. Researchers attempted the use of FA more than 50% in OPC which is termed as High Volume Fly Ash (HVFA) [6]. HVFA proved useful for the improvement of sustainability and workability of cementitious material however the early compressive strength of cementitious materials is compromised which can be improved using nano-SiO_2.

Nanotechnology provides an avenue to enhance the chief properties of conventional construction material, improve functionalities to present materials, introduces novel materials to bridge up existing needs, reduces the environmental influence and energy strength of structures and also increases safety thereby decreasing cost of constructions by tailoring the materials at nano-scale [7]. Nano-silica (nano-SiO_2) has been recently introduced in construction materials and has proved very beneficial because of its high fineness and reactivity. Nano-SiO_2 in cementitious materials yields three vital effects: filler, nucleation and pozzolanic effect which improves the microstructure and early age compressive strength of cementitious materials. Several researches are conducted throughout the world but the optimum amount of nano-SiO_2 is still unknown because of the fact that the nano-SiO_2 used in different studies are of different types with different particle size, specific surface area and associated production method. In addition, uniform dispersion of nano-SiO_2 in cementitious materials is another issue [8].

Complex Impedance Spectroscopy (CIS) was used for the characterization of electro-kinetic properties of cementitious materials. With this technique evolution of microstructure of cementitious materials, change in conductivity and setting time can be studied. In this paper, the effect of nano-SiO_2 on physical properties of cementitious material like consistency, setting times, compressive strength and chloride penetration in addition to conductivity are discussed.

Nomenclature

FA	Fly Ash
OPC	Ordinary Portland Cement
PPC	Portland Pozzolana Cement
HVFA	High Volume Fly Ash
SiO_2	Silicon Dioxide or Silica
CIS	Complex Impedance Spectroscopy
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction
C-S-H	Calcium Silicate Hydrate
$Ca(OH)_2$	Calcium Hydroxide

2. Experimental Program

2.1. Materials and mixture proportions

Portland Pozzolana Cement (PPC) of Ultratech Ltd. containing 30% fly ash confirming to Indian Standard code IS 1489 (Part 1): 1991 [9] was used for the experimental purpose. The batch number of cement bag was W50 M12 Y15.Micro silica of particle size 2 microns and purity >99.9% was synthesized using High Energy Ball Milling technique. The machine for the synthesis of nano SiO_2 was Retch PM 400 and Top-Down approach was utilizedStandard sand of grade I (2mm > particle size> 1mm), grade II (1mm > particle size > 500µm) and grade III (500µm > particle size > 90µm) confirming to Indian Standard code IS 460 (1)-1985 [10].

The test of consistency and setting paste were conducted on cement of 300 gm using Vicat apparatus. Cement mortar cubes of size 7.06cm X 7.06cm X 7.06cm with a cement to sand ratio of 1:3 were casted to conduct physical test like compressive strength and chloride penetration test. CIS was conducted on cement pellets of diameter 13.5 mm and 3.5 mm thick. The mixture proportion for cement paste and mortar samples with different percentage of nano-SiO_2 is tabulated in Table 1 and Table 2 respectively.

Table 1. Mixture proportion for PPC cement pellets.

Sr. No.	Mix code	% nano SiO_2	Consistency (in %)	Amount of Cement (in gms)	Amount of nano-SiO_2 (in gms)
1	NS0	0	34	50	0
2	NS1	1	34	49.5	0.5
3	NS2	2	37	49	1
4	NS3	3	38	48.5	1.5

Table 2. Mixture proportion for PPC cement mortar.

Sr. No.	Mix code	% nano SiO_2	Consistency (in %)	Initial Setting Time (min)	Final Setting Time (min)	Amount of Cement (in gms)	Amount of nano-SiO_2 (in gms)	Amount of Sand I, II, III each (in gms)
1	NS0	0	34	175	370	600	0	600
2	NS1	1	34	160	355	594	6	600
3	NS2	2	37	150	350	588	12	600
4	NS3	3	38	135	335	582	18	600

2.2. Test procedure

Synthesis of nano-SiO_2 was done by Top-Down approach. The dry weight of 49 balls (in each jars) were measured and ball to powder ratio of 10:1. The machine was then calibrated to rotate at 300 rpm for 5 hrs. with 1 hr. interval.

Complex Impedance spectroscopy was studied by conducting experiment on cement pellets. The sample was tested in Hioki 3532-50 LCR HiTESTER, in the frequency range from 1 kHz to 1 MHz.

3. Experimental Program

3.1. Consistency

The variation of required water of standard consistency for fresh PPC cement paste containing nano-SiO_2 in 0, 1, 2 and 3% composition by weight of cement is presented in Table 2. It can be observed that the water demand for the cement paste is increasing with increase in percentage of nano-SiO_2 [11]. Cement particles have particle size of 50µm and fly ash particles have 5-10 µm in size. Addition of nano-SiO_2 of 40 nm in size increases the surface area requiring more water to wet the surface and hence increasing the standard consistency of cement paste with increasing amount of nano-SiO_2.

3.2. Setting times

From Table 2, increasing percentage of nano-SiO_2 is resulting in retardation of initial and final setting time of cement paste. Setting of cement is primarily associated with the generation of calcium sulpho-aluminate hydrates. The generation of Alumina Ferric-oxide mono-sulphate (Al_2O_3-Fe_2O_3 mono) and Alumina Ferric-oxide tri-sulphate (Al_2O_3-Fe_2O_3 tri) depends on the amount of aluminate phases reaction velocity and calcium hydroxide liberation during hydration of cement paste [11].

3.3. Compressive Strength

The compressive strength results of PPC cement mortar blended with different percentage of nano-SiO_2 is shown in Fig. 1. PPC cement is a class F fly ash based cement which is rich in SiO_2 content. Further addition of nano-SiO_2 to this cement increases the silica content in blended cement. Nano-SiO_2 consumes the early formed $Ca(OH)_2$ leaving lesser amount in later ages for fly ash causing decrease in compressive strength of cement mortar at those ages. From Fig. 1., the strength for all the samples blended with nano-SiO_2 are showing lower value than the control sample [12]. Another possible reason for the decrease in strength is due to inadequate dispersion of nano-SiO_2 causing them to form clusters i.e. to agglomerate [13].

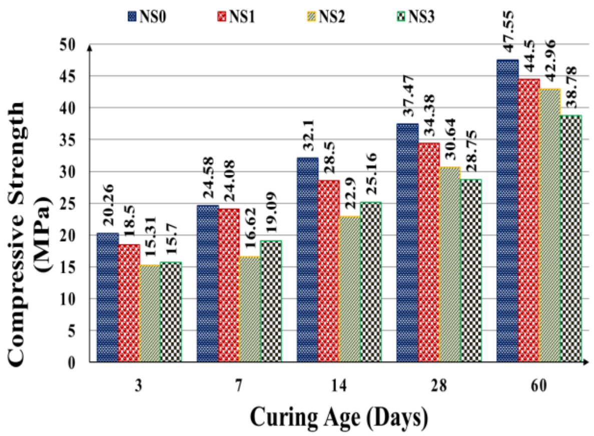

Fig. 1. Compressive strength of PPC cement mortar

3.4. Chloride penetration depth

Fig. 2. shows the chloride penetration depth test results of PPC cement mortar with different percentage of nano-SiO_2. It is observed that, chloride penetration in cement mortar without nano-SiO_2 content is upto full depth of mortar cube (7.06 cm). The reason for this phenomenon is explained by the following mechanism:

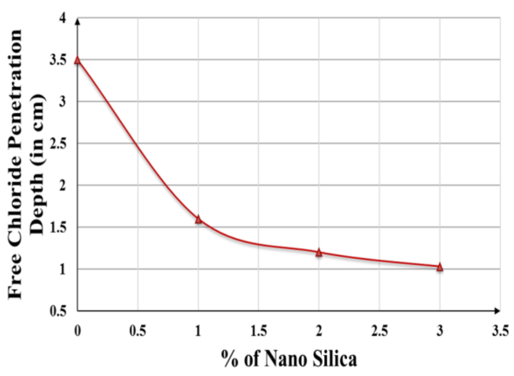

Fig. 2. Chloride penetration test of PPC cement mortar

In the beginning, the soluble chloride reacts with the aluminate phase (C_3A) to form Fridel's salt which is known as chloride binding. Friedel's salt is also known as calcium chloroaluminate ($[Ca_2Al(OH)_6]Cl.2H_2O$ or $C_3ACaCl_2.10H_2O$).

After the chloride bind capacity of cement mortar is over, the left chloride bounds with the C-S-H gel (formed during hydration process of cement). Still, there remains some amount of chloride in pores of mortar known as free chloride. Corrosion in cementitious material is caused because of the free chloride content and not due to the bound chloride. Penetration depth of free chloride is obtained using color indication method and not the total chloride which is a sum of free chloride and bound chloride.

From Fig. 2. It was observed that, free chloride penetration depth gets reduced with the addition of nano-SiO_2 indicating the resistance of mortar towards the chloride penetration. In PPC cement mortar, fly ash content is about 30% reducing the original OPC content by 30% and thus the C_3A content. Therefore, chloride binding capacity of PPC is higher than that of OPC [14].

3.5. Complex Impedance Spectroscopy

The complex impedance spectra of PPC cement paste with 0, 1, 2 and 3 percent of nano-SiO_2 is shown in Fig. 3.

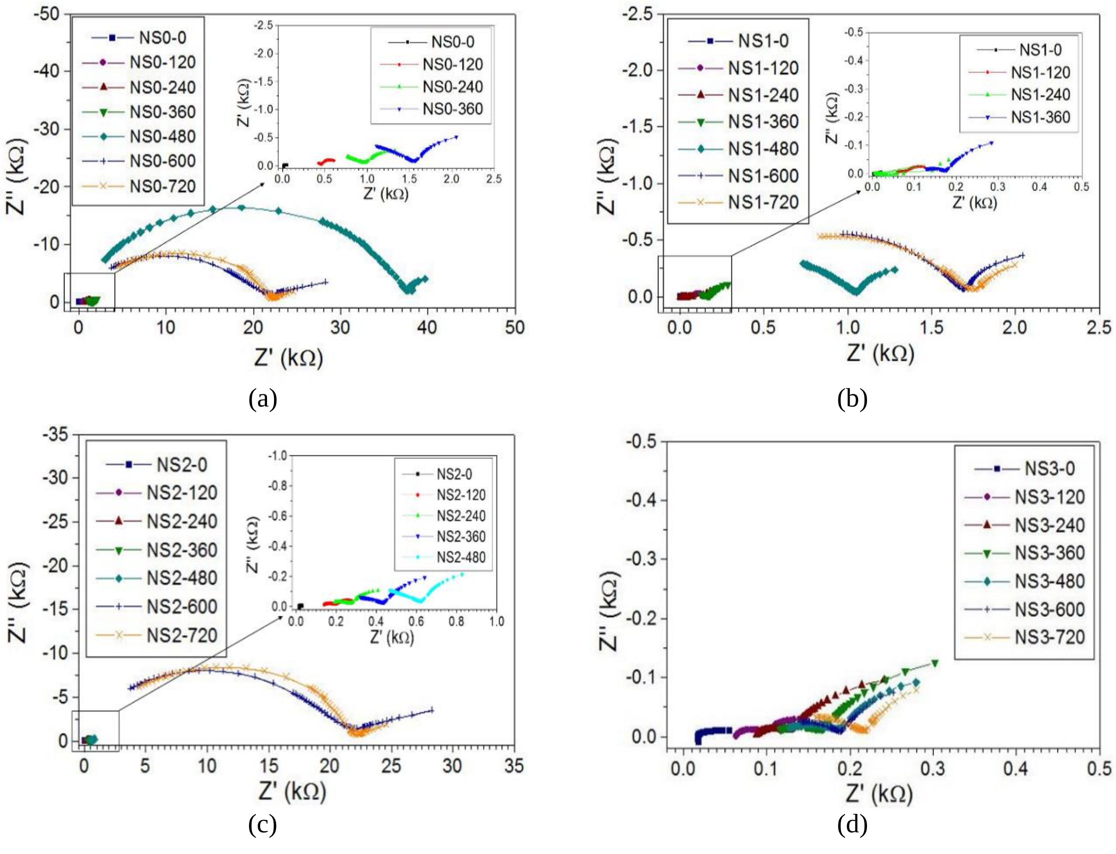

Fig. 3. Impedance spectra for different % of nano-SiO_2 in PPC cement paste for (a) 0, (b) 1, (c) 2 and (d) 3

CIS test for all these samples were conducted from 0 minutes to 720 minutes at an interval of 30 minutes. As seen in all graphs, with the increase in time the impedance curve is increasing its diameter [15]. This can be attributed to formation of hydration products increasing the bulk resistance of sample. At the very beginning, the impedance is very low because dissolution of cement grains given in inset of Fig.3 (a – c). In the dissolution stage, cement particle behaves individually causing impedance due to the grain boundary. With the progress in hydration process, these grains get hydrated forming products like C-S-H gel and $Ca(OH)_2$. The purpose of addition of nano-SiO_2 is to increase the rate of hydration termed as acceleration effect of nano-SiO_2.

3.6. Conductivity Vs Time

The electrical conductivity vs time of PPC cement paste with and without nano-SiO_2 at 10kHz is shown in Fig. 4. The initial decrease of conductivity with time is due to drying of cement. It can be observed that, the slope of curve is abruptly changing from 0 to about 100 minutes and then slope changes which indicates increase in resistance due to starting of setting of cement [16]. On the other hand, the initial setting has been found to be around 110 minutes by Vicat apparatus method (in Table 2). Similarly, at about 300 minutes, the slope changes to a constant value indicating constant resistance. Also it indicates end of setting of cement. It is also found by Vicat apparatus final setting time is about 300 minutes. It is to be noted that, gypsum (3-5%) is added to in cement to retard the hydration process and the setting starts after the reaction between water and gypsum is completed. This initial setting time is about 100-120 minutes. From this discussion, it can be made clear that electrical conductivity vs time using complex impedance spectroscopy is helpful to calculate the setting time of cement paste.

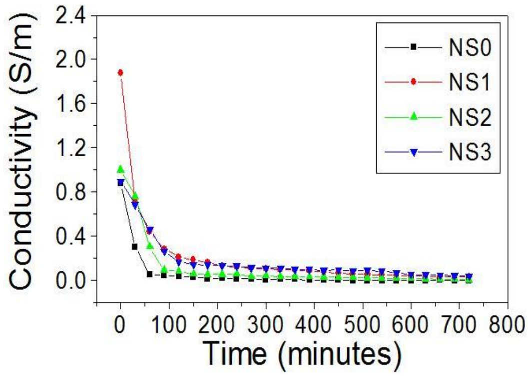

Fig. 4. Conductivity Vs Time at 10kHz

4. Conclusion

From the results and discussions, the following conclusion can be made:
The consistency of cement paste was found to be increasing with the increase in % of nano-SiO_2. Nano-SiO_2 sets retarding effect in setting time of cement paste. In early age, nano-SiO_2 consumes the $Ca(OH)_2$ leaving less amount in later age for fly ash. Therefore, the compressive strength for all control sample was found to be more than the other samples. Filler effect of nano-SiO_2 resulted in the gradual decrease of free chloride penetration depth. From the impedance spectra, the acceleration effect of nano-SiO_2 can be studied. Conductivity Vs time of cement sample can be correlated to setting time obtained by Vicat apparatus.

5. References

[1] Shaikh, Steve W.M. Supit, Constr. Build. Mater. 99 (2015) 208–225.
[2] J.Zhu, C.Feng, H.Yin, Z.Zhang, S. P.Shah, Constr. Build. Mater. 101 (2015) 246–251.
[3] P. S.Deb, P. K.Sarker, S.Barbhuiya, Constr. Build. Mater. 101 (2015) 675–683.
[4] P. Zhang, Ya-Nan Zhao, Qing-Fu Li, Tian-Hang Zhang and Peng Wang, Curr. Sci. 106 (I. 11) (2014) 1529-1537.
[5] H. Dua, Du S., Liu X., Constr. Build. Mater. 82 (2015) 114–122.
[6] F. U. A. Shaikh, S.W.M. Supit, P. K. Sarker, Mater. Des. 60 (2014) 433–442.
[7]M. J. Hanus, A. T. Harris, Prog. Mater. Sci. 58 (2013) 1056–1102.
[8] M. Sonebi, E. García-Taengua, K.M.A. Hossain, J. Khatib, M. Lachemi, Constr. Build. Mater. 84 (2015)269–276.

[9] Indian Standard code IS 1489 (Part 1): 1991, (Reaffirmed 2005), Indian Standard Portland-Pozzolana Cement Specification, (Part 1) Fly Ash Based (Third Revision), Bureau of Indian Standards, May 1991.
[10] Indian Standard code IS: 460 (Part 1): 1985, Indian Standard Specification for Test Sieves (Part 1) Wire Cloth Test Sieves (Third Revision), Bureau of Indian Standards, October 1985.
[11] Mohamed Heikal, A. I. Ali, M. N. Ismail, S. Awad, N. S. Ibrahim, Constr. Build. Mater. 70 (2014) 339–350.
[12] G. Li, Cem. Concr. Res. 34 (2004) 1043-1049.
[13] S. Rao, P. Silva, J. De Brito, Constr. Build. Mater. 96(2015) 508–517.
[14] M. F. Montemor, A. M. P. Simoes, M. G. S. Ferreira, Cem. Concr. Compo. 25 (2003) 491–502.
[15] L. Kong, L. Hou, X. Bao, Constr. Build. Mater. 82 (2015) 332-340.
[16] P. Hou, S. Kawashima, D. Kong, D. J. Corr, J. Qian, S. P. Shah, Compo. Part B 45 (2013) 440-448.