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# Chloride penetration and electrical resistivity of concretes containing nanosilica hydrosols with different specific surface areas



Hesam Madani<sup>a,\*</sup>, Alireza Bagheri<sup>b</sup>, Tayebeh Parhizkar<sup>c</sup>, Amirmaziar Raisghasemi<sup>c</sup>

<sup>a</sup> Civil Engineering Faculty, Graduate University of Advanced Technology, Haftbagh Exp. Way, Kerman, Iran

<sup>b</sup> Civil Engineering Faculty, K.N.Toosi University of Technology, No. 1346, Vali Asr Street, Mirdamad Intersection, Tehran, Iran

<sup>c</sup> Department of Concrete Technology, Building and Housing Research Center (BHRC), Pas Farhangian Street, Sheikh Fazlollah Exp. Way, Tehran, Iran

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### ABSTRACT

In this study, the influence of nanosilica hydrosols with specific surface areas of  $100 \text{ m}^2/\text{g}$ ,  $200 \text{ m}^2/\text{g}$  and  $300 \text{ m}^2/\text{g}$  and silica fume with specific surface area of  $21 \text{ m}^2/\text{g}$  on chloride permeability and electrical resistivity of concrete is investigated. The results indicate that the nanosilicas, especially at higher replacement levels, enhanced the chloride and electrical resistance of concrete at early ages, while silica fume did not have a significant influence on these characteristics at early ages. The results also show that the nanosilicas with lower surface areas had better performance in enhancing the chloride and electrical resistance of concretes compared to the finer ones, especially at 28 days and 90 days. Silica fume achieved a similar performance to the best performing nanosilica at 28 days and surpassed it at 90 days.

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## 1. Introduction

Chloride-induced rebar corrosion is a major concern for reinforced concrete structures, in chlorine environments. In the highly alkaline pore solution of concrete a thin impermeable oxide layer is formed and strongly adhered to the steel surface. This film is stable and makes the steel passive to corrosion. It is well documented that in the presence of sufficient amounts of chloride ions, this protective layer is destroyed and corrosion is initiated [1–9]. Hence, the risk of chloride-induced corrosion increases with ease of migration of Cl<sup>-</sup> through the cement paste.

The corrosion of steel in concrete essentially is an electrochemical process [1-5]. The steel surface can be divided into anodically and cathodically acting areas, which are connected by the electrolyte in the form of pore water of concrete. At anodic sites positively charged ferrous ions Fe<sup>2+</sup> pass into solution and the excess free electrons flow through the steel to cathodic sites where they combine with water and oxygen to form hydroxyl ions. The process is completed by electro migration of hydroxyl ions through the electrolyte and combining them with ferrous ions, leading to formation of a corrosion product [1–4]. Thus, the progress of corrosion is influenced by the resistivity of the concrete between the anode and the cathode [1]. In other words, the electrical resistivity would be a decisive factor in controlling the rate of steel corrosion [1,5,7,10]. Considering the above points, sufficient resistance against chloride ingress and adequate electrical resistivity are essential requirements for durable concretes in aggressive environments.

The electrical resistivity and chloride penetration of concrete are fundamentally related to the pore structure of concrete. A denser microstructure could provide higher electrical and chloride resistances for concrete. Pozzolanic admixtures like silica fume could provide a denser and more discontinuous and tortuous microstructure via the pozzolanic reactions. Thus, these materials could significantly enhance the electrical resistivity of concrete and its resistance against chloride penetration. In this regard, the superior performance of silica fume on enhancing these characteristics has been well established [1,11–18]. It is notable that Gjorv [18] has suggested that even if passivity is breached, the electrical resistivity of concretes containing silica fume may be so high that steel corrosion will not present any practical problem.

Structural similarities of amorphous nanosilica materials with silica fume have lead to a considerable research effort in investigating the influence of nanosilicas on the characteristics of cement composites. In this regard, some researches have investigated the influence of nanosilicas on the chloride resistance of concrete.

Zhang and Islam [19] and Zhang et al. [20] observed that the total passed charges through the fly ash and slag concretes with 2% nanosilica powder (surface area of  $200 \text{ m}^2/\text{g}$  and particle size



<sup>\*</sup> Corresponding author. Tel./fax: +98 342 6226611. *E-mail address:* h.madani@kgut.ac.ir (H. Madani).

of 12 nm) was lower than that of the corresponding reference fly ash and slag concrete at 28 days. However, the difference between the resistances against chloride penetration was not significant between the nanosilica concrete and silica fume concrete at similar replacement level. Ozyilsirim and Zedetosky [21] reported that incorporation of 3% nanosilica hydrosol (particle size of 22 nm) reduced the passed electrical charge through concrete by about 45% as compared with the companion control concrete at 28 days. Chandra and Maiti [22] also observed 72% and 75% lower chloride penetration coefficients of mortars compared to that of control mixture at 3% and 8% replacement levels of cement with a hydrosol (specific surface area of  $80 \text{ m}^2/\text{g}$ ) at 28 days. The most interesting results are those of Ottersetedt and Greenwood [23], who reported that replacing only 0.2% of cement weight with a nanosilica led to about 50% lower passed charge compared to the reference concrete.

In the aforementioned studies, which have investigated the influence of nanosilicas on the properties of cement composites, the nanosilicas used were not of same type and did not have similar surface areas. It is notable that nanosilicas can be produced by various methods, yielding different characteristics. The main types of nanosilicas, which have been used in studies of cement mixtures, include nanosilica hydrosols, pyrogenic nanosilicas can also be produced with different specific surface areas ranging from  $50 \text{ m}^2/\text{g}$  to  $1000 \text{ m}^2/\text{g}$ . Therefore, concentrated studies are required on different types of nanosilicas to characterize their effects on the properties of concrete. The influence of variation in surface areas of nanosilicas on the properties of cement composites should also be considered.

This study was thus carried out to evaluate the influence of addition of monodispersed nanosilica hydrosols with different specific surface areas (100, 200 and 300 m<sup>2</sup>/g) and different incorporation levels on chloride and electrical resistivity of concretes. It should be mentioned that the nanosilica hydrosols are mainly produced through nucleation and growth of silicic acid in the aqueous medium [24–27]. In a previous study, the pozzolanic reactivity of the nanosilica hydrosols in lime pastes and cement pastes were determined through the thermogravimetric studies [26]. It was shown that the nanosilica hydrosols had accelerating influence on the early hydration of cement; however, by progress of hydration and after early ages, less hydration degree of cement was observed compared to the plain paste. It was also observed that hydrosols with finer particles had faster pozzolanic reaction than the coarser ones. The tests performed in this study on the concrete specimens containing the nanosilicas were electrical resistivity test [28], rapid chloride penetration test (RCPT as per ASTM C1202 [29]) and rapid chloride migration test (RCMT as per AASHTO TP 64 [30]). The results were also compared with the results of concretes containing silica fume.

#### 2. Experimental program

## 2.1. Materials and mixture characteristics

Three types of monodispersed nanosilica hydrosols with different specific surface areas including Levasil 100/45, Levasil 200/30 and Levasil 300/30 supplied by H.C. Stark Gmbh were used in this study. These products, according to the manufacture's data, have specific surface areas of 100, 200 and 300 m<sup>2</sup>/g, mean particle sizes of 30, 15 and 9 nm and mass concentrations of 45%, 30% and 30%, respectively. The silica fume, used for the study, was supplied by Azna Ferroalloy Company and complied with ASTMC1240. To utilize silica fume in the mixtures, this material was first mixed with water in mass concentration of 30% and then was dispersed by a high shear mixer for 4 min.

The cement, used for the study, was a type II Portland cement complying with the requirements of ASTM C150. A polycarboxylic ether-based superplasticizer (Gelenium 110) was employed to achieve the desired workability. The physical and chemical properties of the nanosilicas, silica fume and cement are shown in Table 1.

A river sand with maximum nominal aggregate size of 4.75 mm was used as fine aggregate. The coarse aggregate used was a crushed gravel with maximum nominal aggregate size of 19 mm. The specific gravity for both fine and coarse aggregates was  $2550 \text{ kg/m}^3$ .

The concrete mixtures were prepared at a water/binder ratio of 0.45 and cementitious materials content of 395 kg/m<sup>3</sup>. The replacement levels of cement by the solid content of nanosilica hydrosols were (i) 3%, 5% and 7.5% for L100 (ii) 1%, 3% and 5% for L200 and (iii) 1% and 3% for L300. Higher replacement levels were not considered because of the significant increase in superplasticizer demand to achieve similar workability levels for the mixtures. A control concrete without incorporating any pozzolanic material and concrete mixtures with 3%, 5% and 7.5% of cement replaced by silica fume were also made for comparison purposes. Details of mixtures are presented in Table 2. It should be noted that the water content of the nanosilica hydrosols, the silica fume slurry and the superplasticizer was considered as part of mix water.

The mixing procedure used in this study consists of: (i) mixing the dry ingredients with a conventional concrete mixer for 1.5 min, (ii) adding nanosilica hydrosol (or silica fume suspension) and water to the dry ingredients, (iii) mixing the mixture for 2 min (adding superplasticizer to the mixture during mixing) and (iv) mixing concrete for another 3 min.

The workability of all concrete mixtures was kept constant in the slump range 120–140 mm. The difference in water demand of various mixes was accounted for by the use of required amounts of the superplasticizer. After casting, the specimens were covered to minimize water evaporation. They were demolded after 24 h, and cured in water (CH-saturated) at  $23 \pm 2$  °C until testing.

#### 2.2. Test methods

#### 2.2.1. Compressive strength

Compression tests were performed at 1, 3, 7, 28 and 90 days in accordance to BS EN 12390. At each age, four 100 mm cubic concrete specimens were tested for determining compressive strength. The coefficients of variation of compressive strength test results at ages of 1, 3, 7, 28 and 90 days had mean values of 2.9%, 2.4%, 2.6%, 2.6% and 3.2% with maximum values of 4.9%, 5.3%, 4%, 3.5% and 5.6%, respectively.

#### 2.2.2. Electrical resistivity of the concretes

The electrical resistivity was measured using AC current according to the procedure proposed by Swedish national testing and research institute [28] at ages of 7, 28 and 90 days. At 7, 28 and 90 days, the coefficients of variation of electrical resistivity test results had mean values of 2.8%, 2.4% and 4.4% with maximum values of 3.3%, 4.6% and 5.2%, respectively.

#### 2.2.3. Rapid chloride permeability tests (RCPT)

Rapid chloride permeability test (RCPT) was carried out in accordance with the ASTM C1202 [29]. In the current study, the RCPT has been done on 3 specimens. The RCPT results obtained in this study at ages of 7, 28 and 90 days had mean coefficients of variation of 5.8%, 4.3% and 3.3%, respectively. Among the mixtures, the maximum Coefficients of variation at 7, 28 and 90 days were 10.3%, 8.4% and 5.6%, respectively. In the RCPT test the total electrical charge passing through a 50 mm thick concrete specimen

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