Effect of Nano-Alumina (N-Al) and Nanosilica (NS) As Admixtures on Concrete Behavior

Saba Jahangir, and Seyed Kazemi

Abstract— In order to study the effect of nano-alumina (n-Al) and Nanosilica (NS) as admixtures on concrete behavior, the compressive strength of concrete, oxygen permeability and porosity, setting time, and sulfate attack were investigated. In this study, the n-Al was synthesized by sol-gel method, also its characteristics was determined using scan electron microscope (SEM), FTIR and X-Ray Diffraction (XRD). The tests were done by three different mortars and with specimens in cast size of 100×100×50mm at different ages. Based on the results of experiments, the compressive strength of specimens was increased by incorporating nano-alumina and NS into matrix. When the n-Al and NS were added to samples, the setting time was increased while by using only NS, porosity of control samples was reduced by a maximum percentage of 21.2% at 28 days. In the case of combined use of NS and n-Al, porosity was reduced by a maximum percentage of 38.3% at 180 days. The NS admixture in sample 2 seeNS to reduce permeability of concrete to an extent lower than the permeability of control sample. When used in conjunction with n-Al admixture, the permeability reduction is considerable. In the sodium sulfate attack tests, using NS and n-Al have positive effect on the corrosion phenomenon and reduce concrete corrosion, but in the case of magnesium sulfate attack, NS addition increases the corrosion, but n-Al has still positive effect on the concrete corrosion.

Keywords----Nano-alumina, Nanosilica, Permeability, Sol-gel method, Sulfate attack, Corrosion.

I. Introduction

THE uses of mineral admixtures in cement-based materials have grown in recent years, due to sustainability action and environmental issues or due to the technical advantages reached on the ultimate product [1–3]. By incorporating nano-materials into matrix to improve mechanical properties emerged as a promising research field of nano-composite. Compared with the case of dense structure matrix such as polymer, the situation is quite different in the area of cement- matrix composites, because cement-matrix has relative loose structure. Between the cement and the aggregate there are nano-sized air voids which may have significant effects on the nano-composite's mechanical properties. There exists much room for improvement of cement composites by incorporating nano-materials into the cement-matrix [4, 5].

Improvement of concrete strength and durability by incorporation of pozzolans in mixes has been of interest to researchers in the field of construction materials in period of utilization.

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In most cases, the use of pozzolans in concrete with optimal proportion results in reduction of early strength but increment in late strength was observed.

The optimal proportions always require high replacement contents of pozzolans [6–9]. A sulfate attack is one of the most aggressive forNS of environmental deterioration that affects the long-term durability of concrete structures. Concrete attacked by sulfated suffers from expansion, cracking, and deterioration; many engineering structures such as bridges, piers, foundations, or concrete daNS are always exposed to sulfate environment. The sulfate ions in solution, which come from the soil, ground water, and seawater, are found in combination with other ions, such as sodium, potassium, magnesium and calcium ions. The sulfate attack is generally attributed to the reaction of sulfate ions with calcium hydroxide and calcium aluminate hydrate to form gypsum and ettringite. When the gypsum and ettringite are formed as a result of a sulfate attack, significantly more voluminous (1.2–2.2 times) than the initial reactants was occurred [10-16].

In this study the effects of Nano-Alumina (n-Al) and Nano-Silica (NS) on the concrete properties such as compressive strength, concrete oxygen permeability, porosity, setting time, resistant against the sodium sulfate attack and magnesium sulfate are investigated.

II. Materials and Methods

Instrumentation

In this study, scanning electron microscope ((SEM) model XL30) was used to characterize the surface of the n-Al at very high magnification. The n-Al was coated with gold and palladium by a sputter coater with conductive materials to improve the quality of micrograph. The thickness of the coating was 30.00 nm, and the density was 19.32 g/cm^3. Functional groups in n-Al were determined by the Fourier transform infrared (FTIR) spectroscopy. Spectra were collected with a spectrometer using KBr pellets. In each case, 1.0 mg of dried n-Al sample and 100 mg of KBr are homogenized using mortar and pestle thereafter pressed into a transparent tablet at 200 kg$_f$/cm^2 for 5 min. The pellets are analyzed with a FTIR Spectrometer (Shimadzu 4100) in the transmittance (%) mode with a scan resolution of 4 cm^{-1} in the range 3500–500 cm^{-1}. The XRD diagraNS were obtained with a Miscience NH18XHF diffractometer using Fe Ka.

Raw material

Portland cement

The most common type of cement used by concrete manufactures is Portland cement, which is prepared by combining a mixture of materials. The Portland cement, ordinary CEM type I, is derived from the Firuzkuh factory. The Portland cement composition is shown in Table 1.

TABLE 1
CHEMICAL COMPOSITIONS OF PORTLAND CEMENT

Constituents	Content (wt. %)
SiO_2	22.7
Al_2O_3	5.9
Fe_2O_3	2.8
CaO	60.38
MgO	2.91
SO_3	2.1

Pozzolanic Material

Most parts of mineral admixture are artificial pozzolan that produced by industry. Nano-Silica (NS) is a pozzolanic material that was produced in the electrical arc furnace in silicon production flow by exposing silica alloy specially Ferro-Silica. So, the chemical component of NS depends on the main order in furnace. The chemical component of NS is shown in Table 2.

TABLE II
CHEMICAL COMPOSITIONS OF SILICA FUME

Constituents	Content (wt. %)
SiO_2	92.5
Al_2O_3	2.75
Fe_2O_3	1.12
CaO	0.25
MgO	0.38
SO_3	0.24
Average diameter	180 nm
Specific surface area	2700 m^2kg^{-1}

Preparation of specimens

In accordance with the objective of the study, 2 different types of mortars are produced. The material proportion of the mortars are showed in the Table 3. The preparation of samples involved: (a) weighing of components of different materials in the mortar, (b) dry mixing aggregates with mortars inside a plastic bag for 10 minutes, (c) adding water in step by step progressive and (d) mechanical mixing for 40 minutes. The temperature of laboratory in stage of mixing material is 25±2 °C and relative humidity is 38 %. The mixtures were cast into the cubic mold (100×100×50mm). Every mold was filled with concrete in two layers. Each layer was compacted using vibration table for 10 seconds in medium speed. After filling the molds, the samples are keep in laboratory temperature (about 23~27 °C) for 24 hours. After that, the specimens were removed from the molds and the specimens were water-curved for the required testing age. The temperature of curving water was maintained at 23±2 °C using a thermostat and a small circulation pump. For every composition of the mortars, two samples are prepared. The mix proportion of this research is given in the Table 3.

TABLE IIII
THE PROPERTIES OF SAMPLES

Samples	Cement (kg)	nano-Silica(kg)	Nano-Alumina(kg)	W/C
sample 1	1	-	-	0.25
sample 3	1	0.1	0.05	0.25

Test procedures

Concrete compressive strength test

The compressive strength tests were carried out on concrete samples based on standard ASTM C39- 83. At the testing age, samples were removed from the curving tank and weighed. The samples were centrally placed in a compression testing machine and load was applied at rate of 1.7 KN/s. In order to centrally placed compression and eliminate effect of load eccentricity, the end surface of all specimens were planished and axis was made vertical before experiment. For decreasing the friction force between loading surface and specimens, lubricants was coated. Compressive strengths were determined at curving ages of 3,7 and 28 days.

Chemical test

The compressive strength tests were carried out on concrete samples based on standard ASTM C39- 83.The concrete samples' chemical resistant to the sulfate attack was investigated at 25±2 °C (the amount of sulfuric acid in the solution were 10% wt). For achieving this reason, three samples with different mortars as mentioned above are exposed to a sulfuric acid. This test continued to 3,7 and 28 days. The length and weight of each sample (after that stainless steel studs had been mounted on both ends of the specimen) were measured. Their weight was recorded after surface-drying the samples with cloth.

III. RESULTS AND DISCUSSION

Characterization of n-Al

Figure 1 shows the XRD pattern of synthesized nano γ–alumina powder, the three main reflections of nano γ-Al2O3 phase are obviously observed as broad peaks at 2θ angles around 38.0◦, 46.0◦, and 66.0◦ which correspond to the (3 1 1), (4 0 0), and (4 4 0) planes, respectively.

The peaks in the pattern are significantly indicated the formation of nano sized γ-Al2O3 crystallites.The main index of n-Al is shown in Table 4.

Fig. 1. XRD pattern of n-Al

TABLE IV
THE MAIN CHARACTERISTICS OF N-AL

Crystal phase	Purity (%)	Average size (nm)	Specific surface (m^2/g)	Density (cm^3/g)
γ	>99	<180	12	0.4-0.5

Compressive strength

Compressive strength measurement was made on eight samples after 3, 7 and 28 days that consistent with conventional concrete testing convection. For every age of

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concrete, two samples are experiments and the average results are shown in Fig. 1. By comparing the result, it's clear in sample 3 that the combinations of the 10% NS and 5% n-Al can improve the compressive strength at every age in proportion to other mortars, but this increase is not significant related to sample 2.

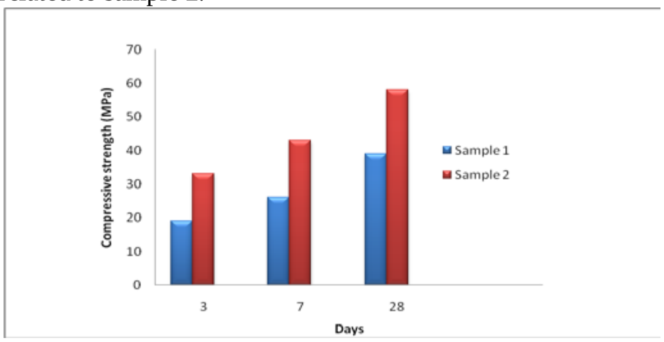

Fig. 2. Compressive strength of different samples

Mortars combine of composite with the three phases including cement paste, aggregate and interfacial transition zone. The main sources that affect strength of mortar are related to the water cement ratio and hydration degree of cement, composition and content of mineral in mortars and distribution of capillary. As mentioned in others researches, the most well-known effect of NS is the increase in concrete compressive strength [6-9]. The strength is due to the pozzolanic activity of NS causing improved strength of the cement paste, the increased density of the mortar resulting from the fineness of NS and the consequent efficient reaction to from hydration products which fill the capillaries between cement paste and aggregates. These effects cause by the densification of the interfacial zone between paste and aggregate. The use of both NS and n-Al enhances the compressive strength because combination of the n-Al with NS can decrease the capillary more; so, the density of the interfacial zone increase and the compressive strength of the concrete improve higher than the only using of the NS.

Effect of admixture on concrete oxygen permeability and porosity

As shown in Fig. 3, reduction in permeability was observed for samples due to age of curing from 28 to 180 days. In this experiment the samples as mention in Table 3 were used. Sample 2 showed a highly remarkable decrease in permeability over this period. As can be seen in Fig.3, the NS admixture when used in conjunction with n-Al admixture, the permeability reduction is considerable. n-Al admixture reduced permeability of concrete when used with NS admixture by up to 21% at 28 days and up to 38% at 180 days for the 5% n-Al proportion as seen in Fig. 3.

As shown in Fig. 4, porosity of sample (1) was highest against all other samples, at both 28 and 180 day ages. Samples prepared with both NS and n-Al admixtures in their mixes exhibited lower porosity than sample with only cement admixture.

Al admixtures, porosity was reduced by a maximum percentage of 33% at 180 days for sample 2 (10%NS+5% n-Al). In this study, use of the pozzolans NS and n-Al must have reduced continuity in pore distribution of the samples making the concretes less permeable.

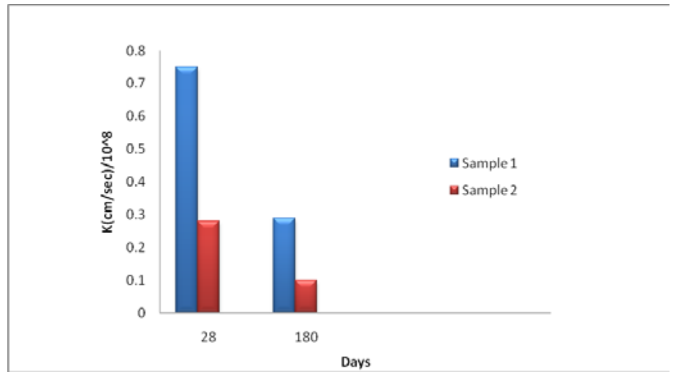

Fig. 3. Permeability of different samples

Fig. 4 shows that, In the case of combined use of NS and n-

Sulfate attack

The effect of sulfates on the released calcium hydroxide from cement compounds is interpreted as sulfate attack. In the polluted environment with sulfate, the reaction of calcium hydroxide with solution sulfates produce plaster. Plaster combines with available aluminuNS in cement paste and produces hydrous sulfa aluminates. Both causes swelling and concrete fault [8].

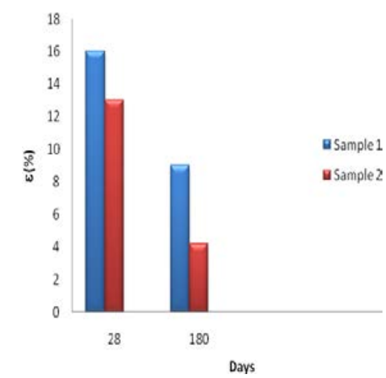

Fig.4.Porosity of different samples

In a typical experiment the samples as mention in Table 3 were exposed against solution with 5 % sodium sulfate and 5 % magnesium sulfate. Fig. 5 shows

When these samples are exposed to magnesium sulfate attack, most of above mention results for sodium sulfate attack have changed. As can be seen from Fig. 9, the best performance is observed in sample 1 because the lowest amount of expansion has happened in this sample in comparisons with the other samples.

By comparing the results between sample 2 and sample 3, it is clear that sample 3 has less amount of expansion when they are in exposure of magnesium sulfate attack; so the use of nano particle (n-Al) in combination of ordinary cement and NS can improve the performance of ordinary cement when it is in exposure of magnesium sulfate attack. By comparing the results it was clear that the addition of NS to ordinary cement has both positive and negative effect on the amount of expansion related to the sort of chemical attack of concrete. When sample 2 with the component of NS is exposing to sodium sulfate attack, the positive behavior in the experiments is observed and the amount of expansion decrease but on the other hand by exposing this sample to magnesium sulfate attack, the amount of expansion increase and the positive effectiveness has changed to the negative one.

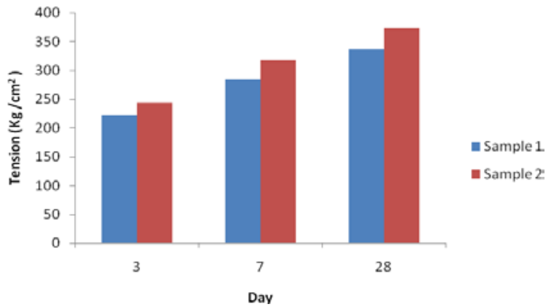

Fig. 5

The reason of above mention result is that the magnesium sulfate converts hydrated calcium silicate into the hydrate magnesium silicate which hasn't any role in cement specifications. In accordance with high tolerance of cements with NS and n-Al are after water absorption, so this phenomenon is probably caused to production of Al $(OH)_3$ that this substance acts as a gelatinous preserver.

IV. Conclusion

In this paper, the effect of proportion and type of admixture on the concrete behavior was investigated and three type of mortar with two type of admixtures at different ages were considered.

Results show that using the combinations of the 10% NS and 5% n-Al can improve the compressive strength at every age in proportion to other mortars, but this increase is not significant related to sample without n-Al.

Reduction in samples permeability was observed due to age of curing from 28 to 180 days. Samples with n-Al and NS showed highly remarkable decrease in permeability.

Samples with 10% NS content seem to reduce permeability of concrete to an extent lower than the permeability of control sample and when used in conjunction with n-Al admixture, the permeability reduction is considerable. n-Al reduces permeability of samples when used with NS by up to 25% at 28 days and up to 41.7% at 180 days for the 5% n-Al proportion.

Porosity of the control sample was highest against all other samples, at ages of both 28 and 180 day and samples prepared with both NS and n-Al admixtures in their mixes exhibited lower porosity than sample with only NS admixture.

All samples satisfied final setting time but requirements of ASTM C 595 and ASTM C 1157 weren't satisfied for samples prepared with NS and with NS and n-Al at initial setting time and setting time of these samples are higher than control sample, so curing of these samples during the setting time needs to a lot of consideration.

Samples were exposed against solution with 5 % sodium sulfate and 5 % magnesium sulfate. Results show after a dormant period of about 52 weeks, the expansion rate suddenly increase and all the specimens containing no NS expand in two steps [20–23]. And expansion of samples containing NS and also containing both NS and n-Al are lower than control sample when samples exposure to sodium sulfate attack and last samples show less expansion.

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