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Chloride penetration and sulfate resistance of concrete incorporating nano-silica (nano-SiO2), micro-silica (micro-SiO2) and fly ash

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In this study, effects of nano-silica (nano-SiO2), micro-silica (micro-SiO2) and fly ash on chloride penetration, sulfate resistance and water permeability were investigated based on the results of electrical indication of concrete's ability to resist chloride iron penetration test (ASTM standard C1202-10) and length change of hydraulic cement mortars exposed to a sulfate solution test (ASTM standard, C1012-02). The addition of nano-silica (nano-SiO2), micro-silica (micro-SiO2) and fly ash in concrete causes a remarkable reduction in chloride iron permeability. These effects may be due to primarily to microstructural changes both in the cement paste phase and in the interracial zone around aggregates. In concrete with nano-silica (nano-SiO2) and micro-silica (micro-SiO2), Nano-SiO2 can behave as nucleus tightly bond with cement hydrates. A stable gel structures can be formed and the mechanical properties of hardened cement paste can be improved when a smaller amount of these materials are added.

Keywords—nano-silica, micro-silica, durability of concrete, chloride penetration, sulfate resistance

I. Introduction

Supplementary cementitious materials (SCM)s are commonly used in concrete mixtures as a replacement of a portion of clinker in cement or as a replacement of a portion of cement in concrete. Most widely used SCMs in cement and concrete are; blast furnace slag, siliceous or calcareous fly ash, natural or natural calcined pozzolana, burnt shale, limestone and silica fume. According to European standard EN 197-1: 2000, 27 different cement types are described. Blast furnace slag up to 95%, fly ash and pozzolana up to 55%, burnt shale and limestone up to 35% and silica fume up to 10% can be used as clinker replacement [1]. This practice is favorable to the industry, generally resulting in concrete with low cost, low environmental impact, high long-term strength, and improved long-term durability [2]. In general, the use of mineral admixtures such as fly ash, silica fume and slag has been shown to enhance concrete durability [3-5]. Mortar containing sufficient low-calcium fly ash or relatively low levels of ultrafine fly ash can improve the sulfate resistance of mortar [6].

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The use of nano silica with other widely used SCM combinations of fly ash and micro silica (micro-SiO2) is rare and still under laboratory studies. It has been observed that optimum quantity of nano silica to be used in concrete is still contradictory [5].

SCMs behave mainly in three different ways within the concrete. SCMs act as nucleation sites to accelerate reactions that helps to generate more Calcium Silicate Hydrate (CSH) in the pozzolanic reaction with Ca(OH)2 and provides denser concrete due to better particle packing. Mostly an efficiency factor of 2 (1 kg of silica fume can be set equal to 2 kg of cement) can be applied to silica fume and effective factor of fly ash is typically 0.4 [7].

A. *Chloride Penetration Resistance of Concrete*

Durability of concrete can be achieved in many stages in different ways and depends on exposure conditions. EN 206-1: 2000 defines five exposure classes for different environment conditions; No risk of corrosion or attack, Corrosion induced by carbonation, Corrosion induced by chlorides other than from sea water, Corrosion induced by chlorides from sea water, Freeze/thaw attack with or without de-icing agents, and Chemical attack [8]. Corrosion due to Chloride Penetration is one of the most critical issues in reinforced concrete.

B. *Sulfate Resistance of Concrete*

When durability is concerned, sulfate resistance is one of the most critical issues in concrete. There are three types of tests on sulfate attack that can be found in the literature; Internal attack, External attack under constant exposure and Partial or cyclic exposure [9]. Currently, ASTM describes two accelerated test methods to evaluate the performance of hydraulic cements in sulfate-rich environments [10]: ASTM C452 Standard Test Method for Potential Expansion of Portland-Cement Mortar Exposed to Sulfate [11] and ASTM C1012 Test Method for Length Changes of Hydraulic-Cement Mortar Exposed to a Sulfate Solution [12].

II. Materials and Methods

A. *Material used*

Ordinary Portland cement (OPC) 42.5 grade conforming to Sri Lanka standard SLS 107 and European standard BSEN 197-1 was used in the present study. It has 64.2 % C3S, 10.4 % C2S, 7.2 % C3A and 9.9 % Tetracalcium Aluminoferrite (C4AF) with fineness of 3,450 cm2/g. Class

F fly ash with low in lime 5.55% (under 15%), and contained a greater combination of silica, alumina and iron up to 84.34% (greater than 70%) bought from Norochcholai Power Plant in Sri Lanka was used in the study. The other materials used were: Nano silica having average particle size of 10 nm and purity 99.59% bought from China and Micro silica having purity of 99.59% and average particle size of 150 µm produced locally. Chemical composition of cement, nano silica, micro silica and fly ash is given in Table I.

TABLE I. CHEMICAL COMPOSITIONS OF CEMENT AND SUPPLEMENTARY CEMENTITIOUS MATERIALS (FLY ASH, NANO SILICA AND MICRO SILICA)

	Table Column Head			
	Cement	**Micro silica**	**Nano silica**	**Fly ash**
SiO_2 (%)	20.38	98.93	99.59	52.03
Al_2O_3 (%)	4.79	-	-	32.31
Fe_2O_3 (%)	3.26	0.31	0.33	7.04
CaO (%)	64.4	-	-	5.55
MgO (%)	0.98	0.17	0.06	1.3
SO_3 (%)	2.21	-	-	0.07
K_2O (%)	0.04	-	-	0.68
Na_2O (%)	-	0.57	-	1
Cl (%)	0.01	-	-	-

B. *Sample Preparations for RCPT*

C 40 concrete, most used industrial concrete for durability applications is used for trials with different percentage replacement of cement with SCM as described from Test C1 to Test C10 in Table II. In Test C1, pure Ordinary Portland cement (OPC) was used in concrete mix. In Test C2, Portland fly ash cement with 25% fly ash was used. In Tests C3 and C4, 15% and 20% (weights) of cement was replaced by fly ash. In Test C5, 10% (weight) of cement was replaced by micro silica. In Test C6 and C7, 3% and 10% (weights) of cement was replaced by nano silica. In Test C8, 8% (weight) of cement was replaced by micro silica and 3% (weight) of cement was replaced by nano silica. In Test C9, the cement replacement was, 15% fly ash, 8% micro silica and 3% nano silica. In Test C10, cement replacement was, 15% fly ash and 8% micro silica. These mixes were decided based on the previous studies on compressive strength and workability of fly ash, of micro silica and nano silica in concrete [13].

TABLE II. CHEMICAL COMPOSITIONS OF CEMENT AND SUPPLEMENTARY CEMENTITIOUS MATERIALS (FLY ASH, NANO SILICA AND MICRO SILICA)

Concrete Mix	**Cement OPC (Kg)**	**Cement PPC (25 % FA)**	**Sand (Kg)**	**Coarse aggregates (kg)**	**Water (l)**	**Chemical admixture (ml)**	**Fly Ash (kg)**	**Micro Silica (Kg)**	**Nano Silica (Kg)**
C1	13.5		24.1	31.9	5.4	135.4			
C2		13.5	24.1	31.9	5.4	135.4			
C3	11.5		24.1	31.9	5.4	135.4	2.0		
C4	9.5		24.1	31.9	5.4	135.4	4.1		
C5	12.2		24.1	31.9	5.4	135.4		1.4	
C6	13.1		24.1	31.9	5.4	135.4			0.4
C7	12.2		24.1	31.9	5.3	135.4			1.4
C8	12.1		24.1	31.9	5.2	135.4		1.1	0.4
C9	10.0		24.1	31.9	5.2	135.4	2.0	1.1	0.4
C10	10.4		24.1	31.9	5.4	135.4	2.0	1.1	-

C. *Sample Preparations for Sulfate Resistance Test*

Mortar bars of 300 mm × 25 mm × 25 mm were prepared with 2.75 cement : sand mortar mix, 0.5 water : cementitious materials ratio (w/cm), different percentage replacement of cement and SCM as described from Test SR1 to Test SR10 in Table 6. In Test SR1, pure Ordinary Portland cement was used in concrete mix. In Test SR3, Portland fly ash cement with 25% fly ash was used. In Tests SR2 and SR4, cement was replaced with fly ash of weight 15% and 30% respectively. In Test SR5, cement was replaced by micro silica of weight 10%. In Test SR6 and SR7, cement was replaced by nano silica of weight 3% and 10%. In Test SR8, cement was replaced by micro silica of weight 8% and nano silica of weight 3% . In Test SR9, cement was replaced by fly ash of weight 15%, micro silica of weight 8% and nano silica of weight 3%. In Test SR10, cement was replaced by fly ash of weight 15% and micro silica of weight 8%. These mixes were decided based on the previous studies on compressive strength and workability of fly ash, of micro silica and nano silica in concrete [13].

TABLE III. DIFFERENT MORTAR MIXES USED FOR SULFATE RESISTANCE

Concrete Mix	Cement OPC (Kg)	Sand (Kg)	Water (l)	Fly Ash (Kg)	Micro Silica (Kg)	Nano Silica (Kg)
SR1	0.74	2.04	0.36			
SR2	0.63	2.04	0.36	0.11		
SR3	0.56	2.04	0.36	0.19		
SR4	0.52	2.04	0.36	0.22		
SR5	0.67	2.04	0.36		0.07	
SR6	0.72	2.04	0.36			0.02
SR7	0.67	2.04	0.36			0.07
SR8	0.66	2.04	0.36		0.06	0.02
SR9	0.55	2.04	0.36	0.11	0.06	0.02
SR10	0.5 7	2.04	0.36	0.11	0.06	

III. Results Discussions

A. *Rapid Chloride Permeability Test*

Rapid Chloride Permeability Test (RCPT) results are presented in Table IV. These results can be interpreted according to Table V and as described in ASTM C1202-10.

TABLE IV. RESULTS OF RAPID CHLORIDE PENETRATION TEST (RCPT) OF CONCRETE

Mix	Solution temperature (oC)	Applied voltage (V)	Shunt resistance (W)	Total charge (c)	Total corrected charge (c)	Measured depth of pen. (mm)	Dnssm (x10-12 m2/s)
C1	35	60	0.05	3428	3110	17	16.6
C2	30	60	0.05	1000	907	6	5.3
C3	35	60	0.05	2586	2346	16	15.3
C4	32	60	0.05	1059	961	6	5.4
C5	28	60	0.05	432	392	3	2.4
C6	34	60	0.05	3146	2855	15	14.5
C7	34	60	0.05	655	595	4	3.4
C8	34	60	0.05	660	598	6	5.3
C9	34	60	0.05	704	639	5	4.3
C10	34	60	0.05	786	713	6	5.3

TABLE V. RATING OF CHLORIDE PERMEABILITY OF CONCRETE ACCORDING TO THE RCPT BASED ON CHARGED PASSED

Chloride Permeability range	Charge Passing Coulombs	Measured Values	Concrete Mixes	SCM (%)
High	> 4000			
Moderate	2000 to 4000	3110	C1	Ordinary Portland Cement
		2346	C3	15% fly ash replacement
		2855	C10	3% nano silica replacement
Low	1000 to 2000			
Very Low	100 to 1000	392	C2	PPC with 25% FA
		907	C4	30% fly ash replacement
		961	C5	10% micro silica replacement
			C6	3% nano silica replacement
			C7	10% nano silica replacement
Negligible	< 100			

According to results presented in Table IV and guideline given in Table V following conclusions could be made. Moderate chloride permeability (charged passed 2000 - 4000 coulombs) was observed in concrete samples with Ordinary Portland Cement, 15% fly ash replacement and 3% nano silica replacement. Very low permeability (charged passed 100 - 1000 Coulombs) was observed in concrete samples with 25% fly ash, 30% fly ash, 10% micro silica, 10% nano silica and in all the double and triple blend samples (i.e. 8% micro silica with 3% nano silica, 15% fly ash with 8% micro silica, 15% fly ash with 8% micro silica and 3% nano silica).

Measured depth of penetration was very low and about 3~6 mm in concrete samples with 25% fly ash, 30% fly ash, 10% micro silica, 10% nano silica and in all the double and triple blend samples (i.e. 8% micro silica with 3% nano silica, 15% fly ash with 8% micro silica, 15% fly ash with 8% micro silica and 3% nano silica. Measured depth of penetration is high as 15~17mm in concrete samples with Ordinary Portland Cement, 15% fly ash replacement and 3% nano silica replacement. Pl refer Figure 5 to Figure 11 for visual presentation of penetration depths after splitting samples.

Then non steady state migration coefficient (Dnssm) was calculated according to Eq. (8). Migration coefficient was 14.5 × 10-12 ~16.6 × 10-12 m2/s in concrete samples with 25% fly ash, 30% fly ash, 10% micro silica, 10% nano silica and in all the double and triple blend samples (i.e. 8% micro silica with 3% nano silica, 15% fly ash with 8% micro silica, and 15% fly ash with 8% micro silica and 3% nano silica). Migration coefficient was 2.4 × 10-12 ~ 2.4 × 10-12 m2/s in concrete samples with Ordinary Portland Cement, 15% fly ash replacement and 3% nano silica replacement.

It can be concluded that concrete samples with Ordinary Portland Cement, 15% fly ash replacement and 3% nano silica replacement were not good for chloride resistance and all other samples (in concrete samples with 25% fly ash, 30% fly ash, 10% micro silica, 10% nano silica and in all the double and triple blend samples; 8% micro silica with 3% nano silica, 15% fly ash with 8% micro silica, and 15% fly ash with 8% micro silica and 3% nano silica) showed significant reduction in terms of chloride permeability, depth of penetration and migration coefficient.

B. *Sulfate Resistance*

Length change of hydraulic cement mortars exposed to a sulfate solution according to ASTM X1012-02 is given in Table VI.

TABLE VI. LENGTH CHANGE OF HYDRAULIC-CEMENT MORTARS EXPOSED TO A SULFATE SOLUTION ACCORDING TO ASTM 1012-02.

Concrete Mix	Length change (%) at 45 days	Length change (%) at 90 days	Length change (%) at 180 days
SR1	0.06	0.07	0.12
SR2	0.06	0.06	0.1
SR3			0.04
SR4			0.04
SR5	0.03	0.04	0.04
SR6	0.04	0.05	0.06
SR7	0.02	0.03	0.03
SR8			0.04
SR9			0.02
SR10			0.03

According to limits, mortar having 180 day expansion of less than 0.05% meet the requirements for a severe sulfate environment, mortars with a 180 day expansion of 0.10% or less meet the requirements for a moderate sulfate environment and mortars with 180 day expansion exceeding 0.1% are only applicable in mild environments [14,15,16].

With that guideline, mortar with 25% fly ash, 30% fly ash, 10% micro silica, 10% nano silica and in all the double and triple blend samples (8% micro silica with 3% nano silica, 15% fly ash with 8% micro silica, and 15% fly ash with 8% micro silica and 3% nano silica) can be used for sever sulfate environment. Mortar samples with 3% nano silica replacement are suitable for moderate sulfate environment. Other two mortar samples with Ordinary Portland Cement, 15% fly ash replacement are suitable only for mild environments.

C. *Overall Effect of Fly ash, Micro silica and Fly ash*

Micro silica was found good for structural purposes in 1950 and it took 20 years to be commercialized in 1970. Turnaround came with the introduction of the Canadian Standard in 1987. This year also ACI published its first attempt at a report on silica fume, a number of countries including Japan, Australia, France, Brazil etc., have developed standards that are very important for the local use of silica fume [9]. Similarly it takes another decade to use nano silica in concrete. Key challenges are to bring down the cost of materials.

Triple blend of OPC, fly ash and micro silica was used in world famous Petronas towers in Malaysia in 1996 for grade 80 and 60 concrete, pumped up to 88 storey height [9]. 350 000 m3 high strength concrete (80 and 60 MPa spec) with ternary blend of OPC, fly ash and micro silica was used in Burj Al Arab tower, pumping all the way in single stage in 2008. In this construction, the content of micro silica used was from 5% to 9% by weight (15 kg to 50 kg for cubic meter of concrete) and fly ash was from 12% to 24% by weight (60 kg to 112 kg for cubic meter of concrete). A clear differentiation of using blended materials can be found in analysis of all the mixes used in Burj Al Arab in Dubai [17] i.e., Concrete with 23% fly ash and 7% micro silica was used for piles, concrete with 57% slag and 5% micro silica is used for pile cap foundations and retaining wall etc. However, high strength pumpable concrete was made with 12~19% fly ash and 5~9% micro silica to achieve both strength (up to C50~C80) and pumpability [17].

ACI 318-08 limits the total replacement ratio of fly ash and silica fume 25% and 10% by weight [38]. EDOT specifies 18% to 22% class F fly ash replacement ratio for regular concrete structures and 18% to 50% for mass concrete, and 7% to 9% weight for micro silica. High volume fly ash concrete with replacement ratio up to 85% by mass has been reported [39]. Limits for use of nano silica in these applications are not given in standards yet. According to previous studies of the authors, it can be recommended that nano silica can be effectively used up to 1% to 3% effectively when strength of the concrete is concerned.

IV. Conclusions and Recommendations

It can be concluded that concrete with Ordinary Portland Cement, 15% fly ash replacement, 3% nano silica replacement show moderate chloride resistance, usually not good for high chloride environment, and all other samples (concrete samples with 25% fly ash, 30% fly ash, 10% micro silica, 10% nano silica and in all the double and triple blend samples; 8% micro silica with 3% nano silica, 15% fly ash with 8% micro silica, and 15% fly ash with 8% micro silica and 3% nano silica) show significant reduction in terms of chloride permeability, depth of penetration and migration coefficient.

Concrete with 25% fly ash, 30% fly ash, 10% micro silica, 10% nano silica and in all the double and triple blend samples; 8% micro silica with 3% nano silica, 15% fly ash with 8% micro silica, and 15% fly ash with 8% micro silica and 3% nano silica can be used for sever sulfate environment. Concrete with 3% nano silica replacement are suitable for moderate sulfate environment. Concrete with Ordinary Portland Cement, 15% fly ash replacement are only suitable only for mild sulfate environments.

This implies that durable structures (resistance to chloride penetration & sulfate resistance) can be achieved using different percentage of SCMs in different ways. Specially, when cost of material is concerned; usually cost of fly ash is 1/2 of cement price, cost of micro silica is 8~10 times higher than cement price, and cost of nano silica is 200~500 times higher than cement price (these can be varied according to quality, source of material, logistic to location etc.). So, it implies that economical concrete mix design can be made to last longer with different mixes.

Optimization of mixes give better performance and cost optimization; it is recommend always to start optimization with cheapest blend, first with very good fly ash, then with fly ash and micro silica, last with fly ash, micro silica and nano silica. It is myth that expensive material give better results, it shows that mix design optimization will end better performance concrete with optimum price.

Micro silica was found good for structural purposes in 1950 and it took 20 years to be commercialized in 1970. Similarly it will take considerable time to (at least another decade) to use nano silica in concrete. Key challenges are to bring down the cost of nano silica to be effectively used in concrete. With the better performance shown in this study and previous studies by other authors, it is recommend including nano silica in concrete standards to use for interested users.

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