CERCETĂRI PRIVIND PENETRAREA IONULUI CLOR ŞI REZISTENȚA LA COMPRESIUNE A BETONULUI HIDROTEHNIC CU CONȚINUT DE NANO-SiO_2
RESEARCH ON CHLORIDE ION PENETRATION AND COMPRESSIVE STRENGTH OF OCEAN HIGH PERFORMANCE CONCRETE DOPED WITH NANO-SiO_2

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The ability to resist at chloride ion penetration and compressive strength of ocean high performance concrete (HPC) with nano-SiO_2 (NS) addition was studied. The 6 hours direct current coulometry method (6-hours DC Method) in ASTM C1202-97 was adopted. The experimental results show that the ability to resist at chloride ion penetration of HPC including NS is heightened effectively, the charge through high-performance concrete with 3%, and 5% NS is reduced with 5% and 15% respectively, and the ability to resist at chloride ion penetration can be heightened gradually with of the age; the charge through high-performance concrete with NS decreases with reducing of W/B of concrete.

Keywords: *nano-SiO_2(NS), ocean engineering, high performance concrete(HPC), chloride ion penetration, compressive strength*

1. Introduction

The emergence of nano science and technology symbolizes that the ability of human being to remodel nature has extended to the atomic and molecular level, and that the science and technology of human being has entered a new era– the era of nano science and technology. Nano science and technology has penetrated into numerous fields such as mechanics, pharmacology, biology, physics, chemistry, materials science, mechanics, etc. [1-3].

Many researchers have investigated mechanical, rheological, durability and micro-structural properties of cement mortar and concrete incorporating SiO_2 micro and nano-particles. B. W. Jo et al. [4] investigated experimentally the properties of cement mortars with nano-SiO_2. It was demonstrated that the nano-particles were more valuable in enhancing strength than silica fume. Based on the results of compressive strength test, it was expected that nano-scale SiO_2 behaved not only as filler to improve mortar cement microstructure, but also as a promoter of pozzolanic reaction. Y. Qing et al.[5] indicated that the compressive strength development of the paste made from $Ca(OH)_2$ and nano-SiO_2, the reaction rate of $Ca(OH)_2$ with nano-SiO_2 and the velocity of C-S-H gel formation from showed marked increases over those of $Ca(OH)_2$ with silica fume. According to T. Ji[6] nano-SiO_2 can react with the $Ca(OH)_2$ crystals, and reduce the size and amount of the $Ca(OH)_2$ crystals, thus making the interfacial transition zone (ITZ) of aggregates and binding paste matrix denser. The nano-SiO_2 particles can fill the voids of the C–S–H gel structure and act as nucleus to tightly bond with C–S–H gel particles, making binding paste matrix denser, and long-term mechanical properties and durability of concrete are expected to be increased.

Impermeability is one of the most fundamental properties of concrete, whereas the durability of concrete mostly depends on its impermeability. A. H. Shekari and M. S. Razzaghi[7] conducted chloride penetration test according to ASTM C 1202-97. Results of this study showed that nano-particles had noticeable influence on improvement of durability parameters. On the basis of the permeability test results, A. N. Givi et al.[8]revealed that the microstructure of the nano-SiO_2 concrete was more uniform and compact than that of the control concrete. M. Jalal et al.[9] summarized that addition of SiO_2 micro and nanoparticles and binder content could be as a result of more packed microstructure achieved. According to the SEM micrographs, more refined microstructure and smaller pores might be achieved by addition of SiO_2 micro and nanoparticles. This could lead to enhanced mechanical, durability and microstructural properties of the high performance self-compacting concrete mixtures.

The higher ability to resist at chloride ion penetration is one of the requirement for ocean

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Table 1

Physical and mechanical properties of cement

Specific surface area ($m^2 \cdot kg^{-1}$)	Fineness (0.08mm sieve residue, %)/	Density (g/cm^3)	Setting time (min)		Compressive strength(MPa)		Bending strength (MPa)	
			Initial	Final	3d	28d	3d	28d
338	1.70	3.12	152	207	31.1	48.7	6.6	8.9

Table 2

Chemical composition of materials(%)

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2Oe*	Ignition loss
cement	64.32	20.81	4.53	3.03	1.05	2.30	0.54	2.65
SF	0.46	92.64	0.33	0.85	0.30	-	0.81	1.8
FA	2.57	52.28	28.22	5.37	0.37	0.15	0.38	3.44

*$Na_2Oe=Na_2O+0.658K_2O$

Table 3

Chemical composition and physical properties of NS

Specific surface area* ($m^2 \cdot g^{-1}$)	Particle diameter* (nm)	Density ($g \cdot cm^{-3}$)	Impurity (%)	Content of SiO_2 (%)
645	12	<0.18	<0.1	>99.9

* the diameter and specific surface area are measured by laser particle size analyzer produced in Dandong

high-performance concrete, as well as one of the determinative factors for durability of ocean reinforced concrete structure. This article focuses on the ability to resist at chloride ion penetration of ocean high-performance concrete added with nano-SiO_2 admixture.

2. Raw materials and mix proportion of concrete

2.1. Raw materials

The cement used in the experiment is P·II 42.5R cement in China. Physical and mechanical properties of cement are listed in Table 1.The stability (Le Chatelier soundness test) of fly ash (FA) produced by Huaneng power plant in Dalian is 1.5mm. The fineness (0.08mm sieve residue) and the water absorption value are obtained as 10% and 0.18%, respectively.Silica fume (SF) having a fineness of about 20000 m^2/kg and the water absorption values as 0.7% is supplied. The chemical composition of raw material (cement, SF and FA) is exhibited in Table 2.

Nano-SiO_2 (NS) is fabricated in China. Refer to Table 3 for its chemical composition and physical properties. The microstructure of nano-SiO_2 is shown in Figure 1. It can be observed that numerous nano-SiO_2 fine particles of approximately spherical shape congregated together.

Fluvial sand with the fineness modulus of 2.74 is used as fine aggregate. It's apparent density is $2.62g/cm^3$ and bulk density is $1520kg/m^3$. Limestone with nominal particle diameter of 5-20mm is used as coarse aggregate, it's fineness modulus[10] is 6.9, It's apparent density $2.85g/cm^3$, and bulk density $1460kg/m^3$. A superplasticizer fabricated in China was used. It has water-reducing rate of 36.5%.

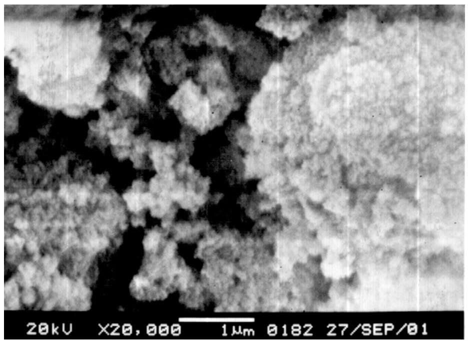

Fig.1 - Microscopic morphology of nano-SiO_2.

2.2 Mix proportion

Details of mix proportions for concrete samples containing silicafume and nano-SiO_2 are given in Table 4. The water-cementitious ratio (W/C) was 0.25, 0.29 and 0.34 respectively, and two contents of nano-SiO_2 particles were used: 3% and 5% by weight of cement. Part of SF is replaced of NS. The dosages of superplasticizer are shown as percentage of the weight of the cementitious materials, and were adjusted according to the effect of the different levels of silica fume and nano-SiO_2 particles. In all mixtures, the amount of superplasticizer was sufficient such that no bleeding or segregation was reported.

Table 4

Mix proportion of concrete

No.	W/B	W	C	NS	Silica fumes	Fly Ash	Sand	Crushed Limestone	Superplasticizer
		(Kg/m^3)							(%)
1-1	0.25	130	416	0	52	52	737	1153	0.06
1-2	0.25	130	416	15.6	36.4	52	718	1172	0.10
1-3	0.25	130	416	26	26	52	700	1190	0.15
2-1	0.29	150	413.6	0	51.7	51.7	737	1153	0.06
2-2	0.29	150	413.6	15.51	36.19	51.7	718	1172	0.10
2-3	0.29	150	413.6	25.85	25.85	51.7	700	1190	0.15
3-1-1	0.34	175	412	0	51.5	51.5	737	1153	0.06
3-1-2	0.34	175	412	15.45	36.05	51.5	718	1172	0.10
3-1-3	0.34	175	412	25.75	25.75	51.5	700	1190	0.15

3. Experimental method

In the test, fine and coarse aggregate must be washed and dried before mixed. In order to well-disperse of nano-SiO_2 into concrete, binding materials (cement, fly ash, nano-SiO_2, and silica fume) were mixed together for 1 min in a blender.

The fresh concrete was cast in 100×100×100 mm cubic and φ95×(51±2)mm cylindrical molds. After one day, all specimens were demoulded and cured in water at a temperature of 20±1°C until the time of the test. The compressive strengths and durability of the concrete samples were determined at 28 and 60 days and the average of two trials was reported.

3.1. Compression test

Cubic samples were used for measuring the compressive strength. All the specimens were tested for each mixture by a hydraulic press with 300 KN capacity. The loading rate was set to 0.3 MPa/s.

3.2. Chloride Ion Penetration test

The research adopted the method of AASHTO T277 (ASTM C1202), which is the most widely used experimental method to test the penetration property of concrete against Cl^-. ASTM C 1202-97 uses electric quantity getting through the sample for 6h for estimate the Cl^- penetration property of concrete, but this fails to identify the coincidence relation[11] between electric quantity and Cl^- penetration coefficient. Feng Naiqian of Tsinghua University and his partners[12] believe that there is a strong linear relationship between the electric quantity and Cl^- diffusion coefficient, and they have concluded that the coincidencerelation between electric quantity and Cl^- penetration coefficient can be obtained by means of regression analysis. The empirical formula [12,13] on high-performance concrete is:

$Y=2.71153+0.00421X$

Where Y is Cl^- diffusion coefficient ($\times10^{-9}cm^2/s$); X is DC electric quantity (Coulomb) which is getting through concrete sample.

4. Experimental results and analysis

4.1. Influence of NS on Compressive strength of concrete

Table 5 shows the compressive strength of HPC specimens containing nano-SiO_2 (NS) after 7, 28, 60 and 90 days of curing which are all increased, especially at the early age. According to the results, the compressive strength increases with NS admixture up to 3.0 wt% and then for 5.0 wt% NS it decreases, although admixture produces specimens with much higher compressive strength with respect to specimens without NS.

According to the Figures 2-4, the compressive strength increase for 3% NS could be due to both a filler effect of NS and a pozzolanic reactions. The pozzolanic activity of NS is better than those of SF. There is a reduced volume of larger pores in the cement paste with NS . However, as indicated, the compressive strength starts to reduce when the volume of NS exceeds 3.0 wt%. Excessive NS leads to the reduction of

Table 5

Compressive strength of concretes

No.	Compressive strength(MPa)			
	7 d	28 d	60 d	90d
1-1	69.0	97.4	109.7	115.4
1-2	73.9	104.9	110.4	120.0
1-3	82	102.3	108.9	117.7
2-1	66.9	87.6	96.7	102.7
2-2	68.7	94.9	104.3	111.9
2-3	77.6	89.0	95.3	105.8
3-1-1	62.1	82.5	92.4	98.0
3-1-2	64.6	86.7	98.1	104.9
3-1-3	70.5	89.3	95.6	100.9

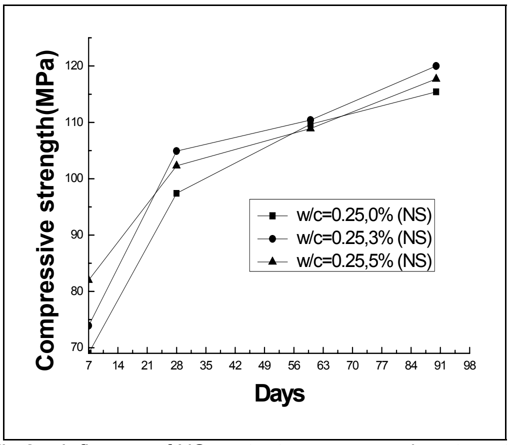

Fig.2 - Influence of NS content on compressive strength (W/B=0.25).

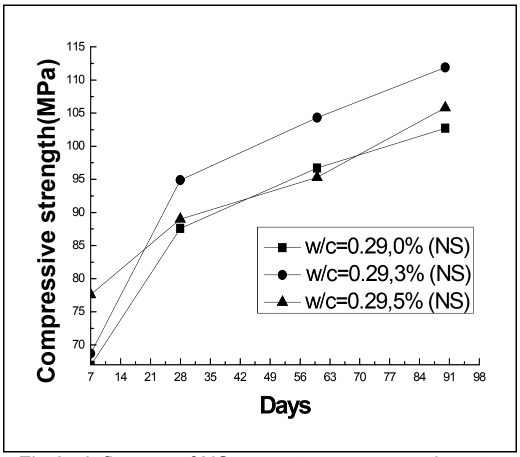

Fig.3 - Influence of NS content on compressive strength (W/B=0.29).

hydrated lime ($Ca(OH)_2$) and the increase of deficiency in the cement paste [14-15].

4.2. Influence of NS on concrete impermeability

Cl^- penetration coefficient and electric quantity are listed in Table 6. Table 7 shows the 6h DC electric quantity of 9 kinds of blending ratios of concrete. Figures 5-7 indicate the influence of NS on 6h DC electric quantity.

It can be seen from Figures 5-7 that in case of 28 days age, the addition of NS can improve the concrete impermeability effectively. This may be

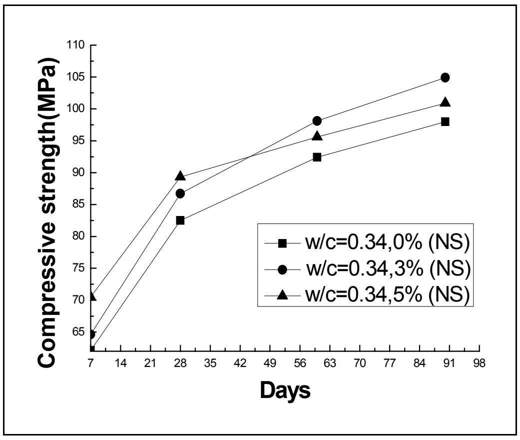

Fig.4 - Influence of NS content on compressive strength (W/B=0.34).

because of the secondary reaction between NS and $Ca(OH)_2$ generated due to the hydration of cement. It reduces the quantity of pores inside the concrete and reduces the connecting degree of pores, and as consequence the movement of Cl^- in concrete is more difficult, and therefore improves the ability of concrete to resist at Cl^- penetrating.

1) The adding of 3% NS can improve the impermeability of concrete with lower W/B (W/B=0.25, 0.29), while the impermeability is equivalent when the amount of NS addition is 3% and 5%. The reason might be the low internal humidity of low W/B concrete which the hinder the secondary reaction between NS and $Ca(OH)_2$, so the NS only play the role of stuffing pores, but not exert the pozzolanic activity to make pores finer.

2) For concrete with W/B=0.34, impermeability of concretes with 5% NS is apparently higher than that with 3% NS. Comparing with reference sample without addition of NS, the former can reduce the electric quantity by about 15%, while the latter can only reduce about 5%. It can be preliminarily confirmed that concretes with lower W/B can reduce DC electric quantity when it contains a small amount of NS, but the reduced quantity is not in proportion to the amount of NS; for concretes with higher W/B will further improve their impermeability when NS is added.

Table 6

6h DC electric quantity and Cl^- diffusion coeficient

No.	DC electric quantity (C)			Cl^- diffusion coefficient (×$10^{-9}cm^2/s$)		
	28 d	60 d	Relative reduction (%)	28 d	60 d	Relative reduction (%)
1-1	371.958	207.642	44.2	4.2775	3.5857	16.2
1-2	337.314	152.430	54.8	4.1316	3.3533	18.8
1-3	331.182	147.744	55.4	4.1058	3.3335	18.8
2-1	572.340	311.652	45.5	5.1211	4.0236	21.4
2-2	447.360	236.892	47.0	4.5949	3.7088	19.3
2-3	439.512	192.288	56.2	4.5619	3.5211	22.8
3-1-1	725.100	409.224	43.6	5.7640	4.4344	23.1
3-1-2	686.940	391.104	43.1	5.6040	4.3581	22.2
3-1-3	610.200	287.766	52.8	5.2810	3.9230	25.7

Table 7

Influence of NS on 6h DC quantity

No.	6h electric quantity for 28 days (C)			6h electric quantity for 60 days (C)		
	Absolute value	Absolute reduction	Relative reduction	Absolute value	Absolute reduction	Relative quantity(%)/
1-1	371.958	0	0	207.6420	0	0
1-2	337.314	34.644	9.3	152.4300	55.212	26.6
1-3	331.182	40.776	11.0	147.7440	59.898	28.8
2-1	572.340	0	0	311.6520	0	0
2-2	447.360	124.98	21.8	236.8920	74.76	24.0
2-3	439.512	132.828	23.2	192.2880	119.364	38.3
3-1-1	725.100	0	0	409.2240	0	0
3-1-2	686.940	38.16	5.3	391.1040	18.12	4.4
3-1-3	610.200	114.9	15.8	287.7660	121.458	30.0

3) As the concrete age increases, their impermeability will be gradually improved, because the degree of hydration of cement will be gradually advanced, pozzolanic activity of NS will further exerted, the quantity of pores in concrete will be gradually reduced, and pore diameters will become further finer, and thus improve the impermeability of concretes.

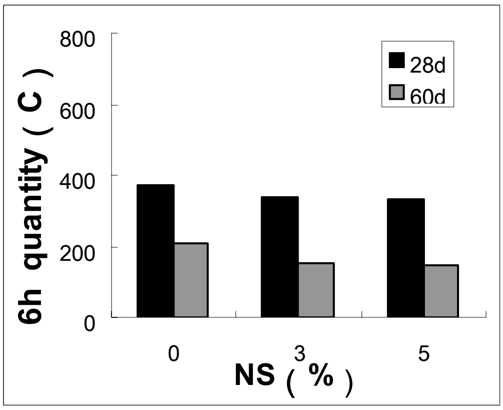

Fig.5 - Influence of NS content on 6h DC quantity (W/B=0.25).

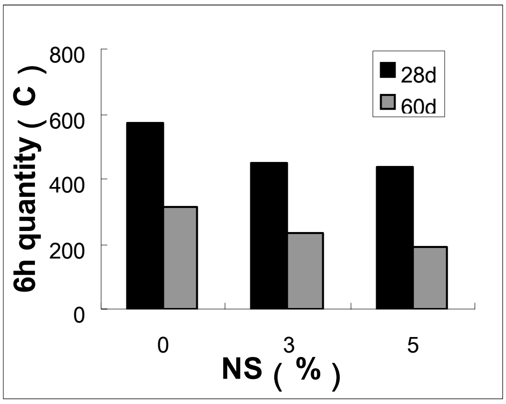

Fig.6 - Influence of NS content on 6h DC quantity (W/B=0.29).

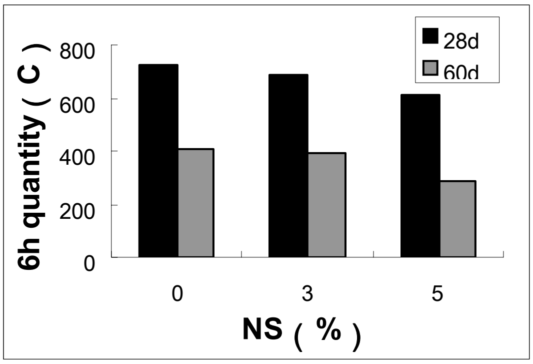

Fig.7 - Influence of NS content on 6h DC quantity (W/B=0.34).

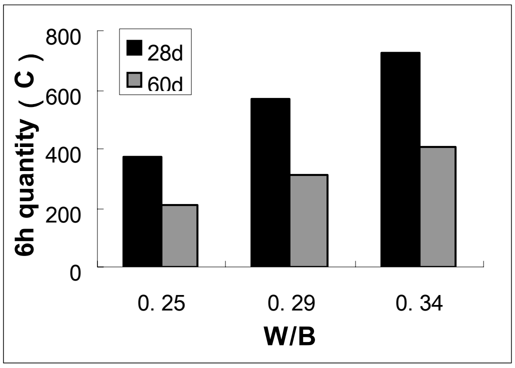

Fig.8 - Influence of W/B on 6h DC quantity (NS=0).

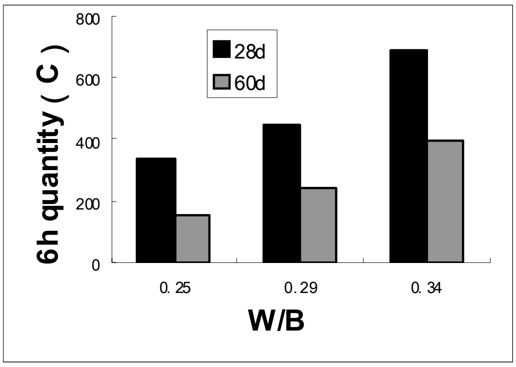

Fig.9 - Influence of W/B on 6h DC quantity (NS=3%).

4.3. Influence of W/B on concrete impermeability

Figures 8-10 indicate the influence of W/B on 6h DC electric quantity. For both 28 days and 60 days concretes, 6h DC electric quantity is reduced in parallel with the decrease of W/B. This is because, with the decrease of water content, some cement cannot completely hydrate, so the ultra fine aggregate will be stuffed between the cement hydrated products, which will reduce the quantity of pores in hydrate products and the connecting degree of pores.

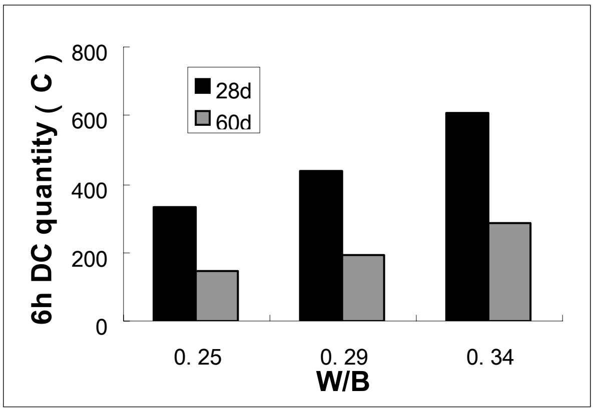

Fig.10 - Influence of W/B on 6h DC quantity (NS=5%).

4.4. Instability of electric current during testing process

See Figures 11-13 for the current-time curves measured by the typical ASTM C 1202 method. We can see from the figures that the electric current has been changing all the time during the measuring process. Such changes can be due to the change in concrete pore solution, or solution of the two electrode ends or copper grid electrode (after this experiment, the bright and shining copper grid becomes gray). In conclusion, the change of electric current reflects the instability of measuring status. In the current-time curve, we can see that the current througe the concretes with NS admixture always reach a stable state earlier than the one without NS.

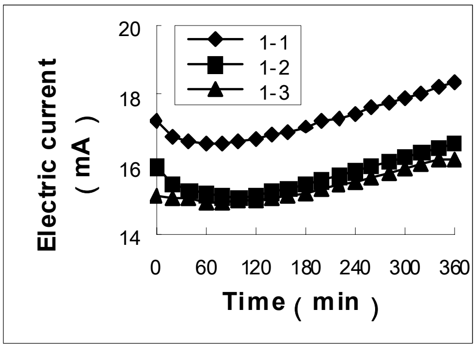

Fig.11 - Instantaneous electric current during the test (W/B=0.25, 28 d).

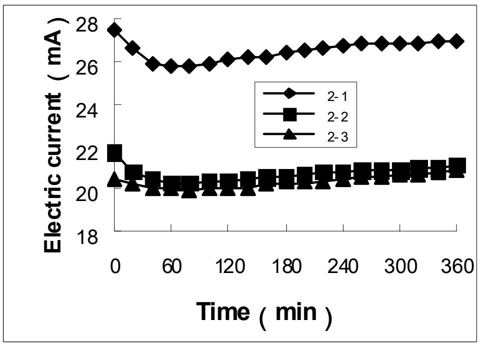

Fig.12 - Instantaneous electric current during the test (W/B=0.29,28 d).

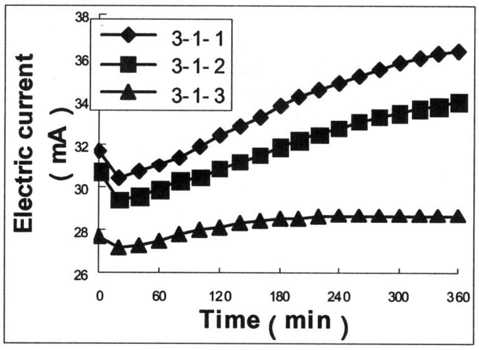

Fig.13 - Instantaneous electric current during the test (W/B=0.34, 28 d).

4.5. Rise in solution temperature during testing process

In the figures 14-16 are showed for the solution temperature–time curves determined by the typical ASTM C1202 method. We can see in the figures that the temperature of NaOH and NaCl solution has been rising during the testing process, but with not large difference from the room temperature. The temperature difference between solution and room temperature increases in parallel with the rise of electric current value. For concretes with lower W/B (W/B=0.25 and W/B=0.29), the temperature difference will not exceed 2^0; for concrete with W/B=0.34, this temperature difference will not exceed 5^0, far lower than the upper limit of 90^0 for stopping the experiment. Therefore, there is small influence on experimental results of this work caused by the rise in solution temperature.

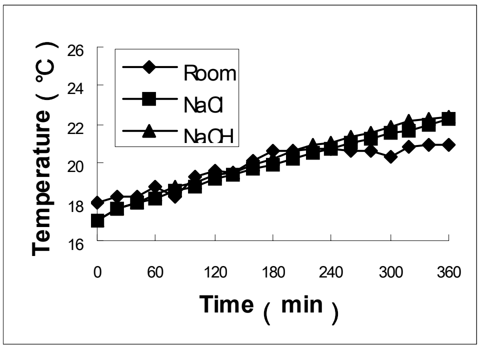

Fig.14 - Trend of solution temperature during the test (W/B=0.25,28 d).

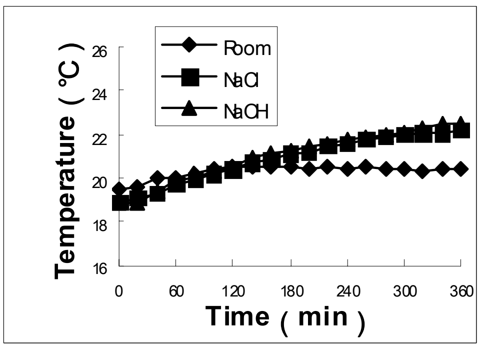

Fig.15 - Trend of solution temperature during the test (W/B=0.29,28 d).

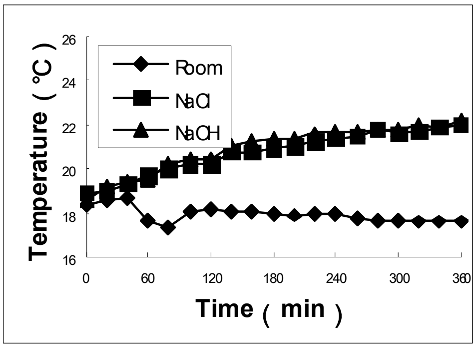

Fig.16 - Trend of solution temperature during the test (W/B=0.34,28 d).

4.6. Microstructure

SEM analysis were made with JEOL JSM-5600 equipment. SEM was used for microscopic morphology investigation and the influence of NS on hardened paste and on interfacial transition zone of concrete;

1) Influence of NS on hardened paste microstructure

In figure 15 shows big tabular C-H crystals and short fibers of C-S-H in pores of 1-1 paste (without NS) can be clearly observed. The microstructure of 1-3 paste (with 5% NS) obviously becomes more compact. The higher strength achieved by concrete mixtures containing NS is due to the rapid consumption of crystalline $Ca(OH)_2$ which quickly are formed during hydration of Portland cement[4,9]. In the case of the concrete with addition of NS, more C-H crystals will form bonding on the surface of NS and produce C-S-H gel, reducing the content of C-H and refining C-H crystals. Also the unreacted NS can disperse in pores between net-shaped C-S-H gels which cannot be filled by SF.

2) Influence of NS on interfacial transition zone (ITZ)

By comparison of Figure 17 with Figure 18 can be seen that different $Ca(OH)_2$ (CH) quantities exist in the ITZ of 3-1-1 concretes. Relatively large, hexagonal CH crystals, sometimes tens of microns across but only one or two microns thick. There are short fibers of C-S-H and clusters of ettringite (AFt) needles around CH. However, there are more cluster-shaped C-S-H gels at interfacial transition zone of 3-1-3 paste, no big C-H crystal is found. The ITZ cement paste has a significantly higher porosity and is weaker than the paste (Fig. 15 with Fig. 16) further away from the aggregates.

5. Conclusions

The following conclusions can be drawn from the obtained experimental data:

1) In general, NS replacing a small part of cement (3%) can improve the compressive strength of the concrete, particularly at early age. The compressive strength decreases with NS increase up to 5.0 wt% after 28d, although 5.0 wt% NS admixture produces better specimens than specimens with silica fume (SF).

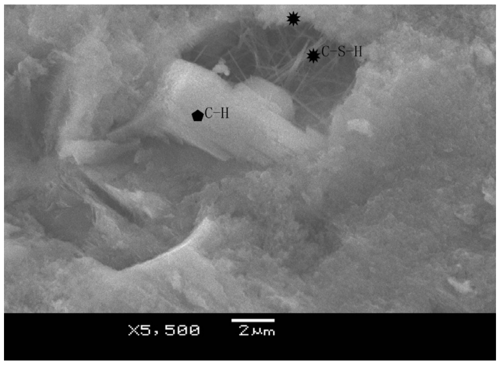

Fig.15 1-1 Paste SEM morphology(3d,W/B=0.25).

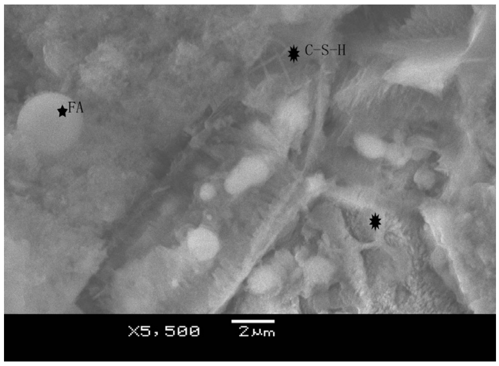

Fig. 16 1-3 Paste SEM morphology(3d,W/B=0.25).

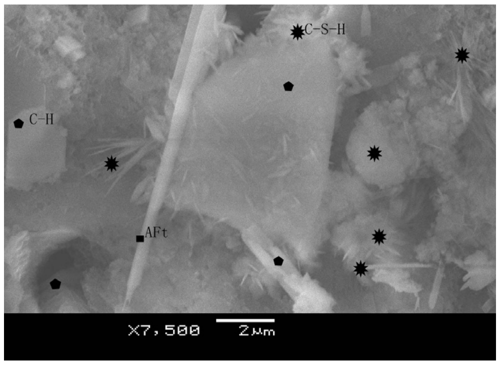

Fig. 17 - 3-1-1 Interfacial transition zone SEM morphology (3d, W/B=0.34).

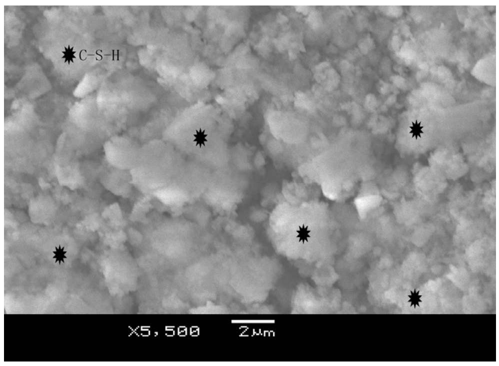

Fig.18 - 3-1-3 Interfacial transition zone SEM morphology (3d, W/B=0.34).

2) Among the 9 groups of concretes prepared for this experiment, all 6h DC electric quantities measured by ASTM C 1202-97 method is smaller than 1000 Coulomb, and all can meet the requirement on penetration resistance of high-performance concrete.

3) The 6h DC electric quantity getting through the concrete sample will decrease in parallel with the increase of NS , for concrete with lower W/B (0.25, 0.29), their impermeability can be improved obviously by adding of 3% NS, for concrete with W/B=0.34; apparent effect can also be achieved if 5% NS is added.

4) The impermeability of concrete is improved for smaller W/B ratio, as well as by increase of the age.

5) During the testing process, the electric current values differ at different moments (there exists a current valley), which indicates that the testing process is under unstable state.

6) The temperature of NaCl and NaOH solutions continue to rise during the testing process; the difference between solution temperature and room temperature becomes larger with the increase of electric quantity, but temperature difference of all tests is within the range of 5^0.

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