D-2-1 Corrosion behavior of internal curing concrete in saline soil environment

Zuquan Jin

School of Civil Engineering, Qingdao University of Techonlogy, Qingdao, China. jinzuquan@126.com

Peng Chen

School of Civil Engineering, Qingdao University of Techonlogy, Qingdao, China.

Tiejun Zhao

School of Civil Engineering, Qingdao University of Techonlogy, Qingdao, China. ztjgp@263.net

ABSTRACT: Sulfate and chloride ions penetration into reinforced concrete is the major threat to durability of concrete structure in saline soil environment. The sulfate ions transportation mechanism of concrete with super absorbent polymer (SAP) exposed to Ocean saline soil area was studied. Experimental results shown that 1kg/m3 of SAP would help enhance the resistance capacity of corrosion ions penetration and delay strength attenuation of concrete in saline soil environment. And the compressive strength of internal curing concrete in saline soil environment decreased firstly, and then increased with corrosion time, lastly decreased to failure. The ration of reacted sulfate ions in concrete was higher than 91.6%, entraining SAP and decreasing cement dosage reduced the reacted ration of penetrating sulfate ions. The amount of transported sulfate ions in concrete increased with corrosion environment to the formation of estringite and its Young's modulus could be ignored, but the MgSO4 in saline soil environment would promote the generation of gypsum and decrease the Young's modulus of ettringite.

KEY-WORDS: Internal curing concrete, compressive strength, sulfate ions, ettringite.

INTRODUCTION

Degradation of structural concrete components placed in sulfate-bearing environments has been of concern to the concrete technologists since the early years of the 19th century [1-3]. There are more than 1000 salt lakes scattering in the Northwest of China and amounts of coastal saline soil area in Shandong Province, where lots of concrete constructions are severely deteriorated and lost its function only in several years, which is mainly caused by chloride-induced rebar corrosion and sulfate-induced expansive spalling of concrete [4-5]. And the deterioration of concrete used in mountain tunnels and dam attacked by sulfate ions were reported in the Southwest of China [6-7]. With ocean strategy development in China, lots of marine projects including underground, subsea tunnel and civil plaza were constructed on seaside even on ocean back-filled areas. And sulfates ions present in soils and groundwater pose a major threat to the durability of concrete structure exposed to such environments. Therefore, high performance concrete with low w/b, high volume mineral admixture such as fly ash and GGBS, even new chemical admixture or sulfate resistance cement was developed and used in major projects in sulfate environments [8-9]. Besides sulfate ions, high concentration of chloride ions and different types of cation ions were also existence in saline soil. It was difficult to reveal the corrosion mechanism and behavior of concrete in saline soil environment due to these complicated ions.

High volume cementitious materials in high performance concrete, and low RH, high wind speed in environment easily lead to great autogenous and drying shrinkage of concrete in salt lake and saline soil areas[10]. Conventional external curing methods, such as watering and covering with wet burlap, were difficult to have obvious effects. The Superabsorbents Polymers (SAP), which proposed by Jensen as internal curing agents in high performance concrete (HPC) for reduction of shrinkage was one new trend in concrete practice [10-11]. SAP was effective in reducing the internal relative humidity decrease and the shrinkage of concrete [12-13]. However, SAP' s water absorption and desorption as cement hydrates however would leave micro voids within the concrete which could

decrease the mechanical properties of concrete[14-15]. The water desorption behavior of SAP was also easily influenced by ions, the strength reduction and corrosion behavior of concrete with SAP in saline soil environment would distinguish from normal environment due to existence of these complicated ions.

The overall aim of this paper is to reveal strength evolution and corrosion behavior of concrete with different dosage of SAP in saline soil. And then, the mechanics properties of corrosion products and suitable dosage of SAP to concrete exposed to saline soil were proposed.

EXPERIMENTAL

Materials and mix proportions

P.I.52.5 Portland cement in accordance with Chinese standard GB175-2007, with a compressive strength of 59.8 MPa at the age of 28 days, was used for preparation of concrete. The coarse aggregate was the crushed granite with a maximum size of 25 mm. River sand with a fineness modulus of 2.6 was used as the fine aggregate. A polycarboxylic ether-based superplasticizer was used, and its dosage was adjusted to keep the slump of fresh concrete in the range of 180mm to 220 mm. An air-entraining agent was used and its dosage was adjusted to keep the air content of fresh concrete in the range of 3-5%.

Solution-polymerized SAP of irregular particle shape and particle sizes $\leq 63 \mu$ m in the dry state were used as internal curing agent. The L50 and C30 were control concrete without internal curing agent, and other concretes were mixed with 1-1.5 kg/m³ of SAP. The SAP was absorbed water firstly before use, and the water absorbency was 30g water/1g SAP. The mixture proportions and the corresponding compressive strengths of concrete cured in standard room (T=20±3°C, RH=95%) were given in Table 1.

| No. | Kg/m ³ | | | | Compressive strength (MPa) | | | | |
|--------|-------------------|------|-----------|-------|----------------------------|-------|-------|-------|------|
| | Cement | Sand | Aggregate | Water | SAP with water | 3d | 7d | 28d | 90d |
| L50 | 480 | 730 | 1095 | 160 | 0 | 35.45 | 40.5 | 43.41 | 51.8 |
| L50SP1 | 480 | 730 | 1095 | 130 | 30 | 31.86 | 41.13 | 44.3 | 55.3 |
| L50SP2 | 480 | 730 | 1095 | 115 | 45 | 27.47 | 36.5 | 42.07 | 43.8 |
| L50SP3 | 480 | 730 | 1095 | 100 | 60 | 27.92 | 36.9 | 43.1 | 44.6 |
| C30 | 376 | 750 | 1126 | 195 | 0 | 23.8 | 30 | 34.1 | 36.6 |
| C30SP1 | 376 | 750 | 1126 | 165 | 30 | 20.87 | 25.47 | 35.4 | 37.9 |
| C30SP2 | 376 | 750 | 1126 | 135 | 60 | 19.1 | 23.1 | 32.1 | 35.1 |

Table 1. The mix proportion and compressive strength of concretes

Experiment method

Concrete specimens with size of $100 \times 100 \times 100$ mm³ were prepared to monitor the development of compressive strength and corrosion ions transportation in saline soil environment. All specimens were cast at room temperature in module for the first 24hours. After demolding, all specimens were cured in a condition of 20±3°C and 95% of relative humidity for a period of 28 days. After curing, five sides of concrete samples were coated with epoxy and were buried into saline soil completely. Saline soil from Dongying in Shandong Province was placed in the closed box, which the main chemical components were shown in Table 2.

| Table 2 chemical composites of saline soil | | | | | | | | | | | | |
|--|------|-------------------|-------------------|------------------|-----------|----------------|-----------------|--|--|--|--|--|
| constituent | Cl- | SO4 ²⁻ | CO3 ²⁻ | Ca ²⁺ | Mg^{2+} | \mathbf{K}^+ | Na ⁺ | | | | | |
| /% | 0.71 | 0.80 | 0.42 | 7.74 | 7.88 | 3.1 | 1.3 | | | | | |

After 30d, 60d, 120d, 180d and 360d of corrosion, the concrete specimens were taken out and their surface was washed. The powder sample was ground with the 1-5 mm layer from the surface to the inner of specimens. The water soluble sulfate ion and acid soluble sulfate ion in concrete were measured by turbidimetry [16]. And the phase composites of corrosion products were analyzed by XRD and TG-DSC.

RESULTS AND DISCUSSION

Compressive strength of concrete

Compressive strength of concretes stored into saline soil for 360 days was tested and shown in Fig.1. Obviously, the compressive strength of control concrete including L50 and C30 increased by 10-20% in the firstly 60 days, and then decreased with corrosion age. And this result was in accordance with that concrete exposed to sulfate solution cycling in drying-immersion [17]. However, the compressive strength of internal curing concretes decreased in the firstly 30-60 days, and then increased with time, lastly decreased with corrosion age.



Fig.1. Compressive strength of concretes in saline soil environment

The above mentioned results could be explained by that SAP released pre-absorbed water faster in seawater environment than that in atmosphere environment, which shown in Fig. 2. Therefore, micro voids were left within the internal curing concrete exposed to saline soil due to water desorption of SAP, which would decrease its compressive strength firstly. With the migration of sulfate ions into concrete, the expansion corrosion products including ettringite and gypsum would compact the micro void and refine the pore structure, which would increase the compressive strength of internal curing concrete [18].



Fig.2. The water desorption process of 1g SAP which has pre-absorb water for 2 hours

The compressive strength loss of L50SP1 and C30SP1 specimens was 7.4% and 8.0% when concrete under attacked of saline soil for 360 days, which was less than that of other concretes. That was to say concrete with 1kg/m³ of SAP could improve its resistance capacity of saline soil corrosion, but more SAP, earlier and more serious damage by saline soil.

Sulfate ion distribution in concrete

Fig.3 shown the acid soluble sulfate ion concentration profiles at different depth intervals of concretes exposed to saline soil for 120 days. It was clear that the concentration of sulfate ion decreased from surface to the interior of concrete, and reached to a steady value at a depth of 5 mm to 10 mm. The acid soluble sulfate ions content and its penetration depth of concretes with 1kg/m³ SAP was the minimum.



Fig.3. Acid soluble sulfate ions content of internal curing concrete exposed to saline soil

The reacted sulfate ions content could be gained the acid soluble sulfate ions minus the water soluble sulfate ions [16]. Because the reacted sulfate ions increased with acid soluble sulfate ions linearly, the linearly regression coefficient was named as sulfate reaction parameters, which shown in Fig.4. It was clear that the sulfate reaction parameters of control concretes were highest, nearly reached to 0.93-0.96. When 1kg/m³ SAP was mixed into L50 concrete, the sulfate reaction parameters decreased to 0.916. Similarly, the sulfate reaction parameters would decrease by 4-11% when 1-2 kg/m³ SAP was added into C30 concrete. This means that SAP could reduce the expansion corrosion products content, which would lighten the damage of concrete induced by sulfate ions.



Fig.4. Sulfate reaction parameters of internal curing concrete exposed to saline soil environment



Fig.5. Acid soluble sulfate ions content of concretes exposed to saline soil for different time

The sulfate ions content evolution of L50SP1 and C30SP1 concrete exposed to saline soil for different age was tested and plotted in Fig.5. The sulfate ions penetration depth into concrete increased with corrosion time, and the depth was 9mm and 20mm for L50 and C30 concrete exposed to saline soil for 360 days. Therefore, the sulfate ions penetration into concrete could be depicted by Fick's 2nd Law when it stored to saline soil.

And the sulfate reaction parameters of L50 SP1 and C30SP1 concrete were shown in Fig.6. The sulfate reaction parameters of concrete increased with corrosion time firstly. After 360 days of corrosion, the reacted sulfate ions content was about 95% of total penetrated sulfate ions of concrete. Moreover, the reacted sulfate ions content of L50 was higher than that of C30 due to more dosage cement in L50 concrete. And the sulfate resistance capacity of L50 concrete was higher than that of C30 due to lower w/b of L50 concrete.



Fig.6. Sulfate reaction parameters of internal curing concrete exposed to saline soil environment for different time

Corrosion production

Pastes with same w/b as L50 was stored in saline soil for 120 days, the XRD spectrums of paste powder was shown in Fig.7(a). Obviously, the ettringite and gypsum were mainly corrosion production of concrete exposed to saline environment. In order to investigate the mechanics properties of ettringite formed in different environment, the pure ettringite was prepared by saturation Ca(OH)₂ reaction with [Al 2(SO4)₃·18H₂O] for 7 days as Eq (1) [19]. And the XRD spectrums was shown in Fig.7(b).

$$Al_{2}(SO4)_{3} \cdot 18H_{2}O + 6Ca(OH)_{2} \rightarrow 3CaO \cdot Al_{2}O_{3} \cdot 3CaSO_{4} \cdot 32H_{2}O$$
(1)

And then the ettringite preparation in 0.5%NaCl, 1%NaCl and 0.5%MgSO4 solutions was carried out. These ettringite powder was pressure moulding as $\phi 23*10$ mm³ cube specimens with 84.3-132.4MPa [20]. The stress-strain curve of these pre-press powder specimens was tested and the Young's modulus could be calculated by Eq (2) and shown in Fig.8.



It was clear that the Young's modulus of ettringite formed in NaCl solution was about 9.3-9.4 GPa, which was nearly equal to that of pure ettringite. However, the Young's modulus of ettringite prepared in $MgSO_4$ solution was 8.4GPa, which less than that of pure ettringite. These results indicated that expansion ration of ettringite in sulfatechloride bearing environment was same as that in sodium sulfate environment, but the Mg^{2+} in sulfate bearing environment would increase the expansion ration of ettringite and induced more serious damage than that in sodium sulfate environment.

$$y = \frac{A_1 - A_2}{1 + e^{(x - x_0)/dx}} + A_2 \tag{2}$$



Fig.8. Young's Modulus of ettringite powder prepared in different environment

Paste with same w/b as L50 concrete and mixed with 0, 1 and 2 kg/m³ of SAP was exposed to sulfate solution with 60 cycles of drying-wetting. The corroded paste powder was tested by XRD and TG-DSC, and shown in Fig.9 and Fig.10. Obviously, the ettringite and gypsum were mainly corrosion production of concrete exposed to sulfate environment. But the ettringite and gypsum content in corroded paste decreased with increasing SAP dosage.



The decomposition temperature of ettringite, gypsum and $Ca(OH)_2$ was about $80\sim130^{\circ}C$, $130\sim150^{\circ}C$ and $400-500^{\circ}C$. The mass loss of paste with 0, 1 and 2 kg/m³ of SAP in $80\sim150^{\circ}C$ was 5.58%, 5.32% and 5.06%. And their $Ca(OH)_2$ content was 4.99%, 5.12% and 5.66%, respectively. This was means that SAP was added to concrete would decrease the generation of corrosion products in sulfate bearing environment.

CONCLUSIONS

The compressive strength evolution, sulfate ions penetration and reaction of internal curing concretes with different dosage of SAP was tested and presented in the current research. By comparing the mechanics and transportation properties of internal curing concrete, it became evident that these properties of internal curing concrete were influenced by dosage of SAP, w/b and corrosion age. To further clarify the corrosion mechanism of internal curing concrete in saline soil environment, corrosion products of paste and pure ettringite were analyzed by XRD and TG-DSC. Overall, based on the experimental results and research findings as they were described in this paper, it could be concluded that:

- 1. SAP's fast water desorption when it encountered seawater in saline soil, which left amounts of micro void within the internal curing concrete, induced the compressive strength decreased firstly. And generation of expansion corrosion products induced by penetrated sulfate ions would compact the micro void and refined the pore structure lead to increasing of compressive strength of concrete.
- Acid soluble sulfate ions penetration into concrete could be depicted as Fick's 2nd Law. Low w/b and 1kg/m³ SAP added into concrete would contribute to improve the sulfate resistance capacity of internal curing concrete in saline soil.
- 3. The ettringite and gypsum were mainly corrosion products of concrete was buried into saline soil, and existence of chloride ions didn't change the Young's modulus of ettringite, but the MgSO₄ in saline soil environment would promote the generation of gypsum and decrease the Young's modulus of ettringite.
- 4. The reacted sulfate ions content was higher than 91.6% and 82% for L50 and C30 series of concretes, respectively. And SAP in concrete reduced the reacted sulfate ions content and decreased the generation of gypsum and ettringite.

ACKNOWLEDGMENT

This work is a part of a series of projects financially supported by the Chinese National Natural Science Foundation (NSF) Grant No. 51378269, 51678318 and No.51420105015, and the Chinese National 973 project Grant No. 2015CB655100. Besides, this work is also supported by National 111 project. All these supports are gratefully appreciated.

REFERENCES

- [1] RASHEEDUZZAFAR, Influence of cement composition on concrete durability. J. ACI Mater. 89 (1992): 574-586.
- [2] Paulo J.M. MONTEIRO, E. K. KIMBERLY, *Time to failure for concrete exposed to severe sulfate attack*. Cem.Concr. Res. 33(2003): 987-993.
- [3] X. B. ZUO, W. SUN, H. LI, *Modeling of diffusion-reaction behavior of sulfate ion in concrete under sulfate environments*. Comp. Concr. 10 (2012): 79-93.
- [4] X.M. SHI, N. XIE, K. FORTUNE. Durability of steel reinforced concrete in chloride environments: An overview. Construct. Build. Mater. 30 (2012): 125-138.
- [5] Z.Q. JIN, X. ZHAO, T. J. ZHAO, Y. LI. Corrosion and 3D crack-propagation Behaviors in Reinforced Concrete Subjected to Bending Load in Simulated Marine Environment, International Journal of Electrochem. Sci, 11 (2016): 8779 - 8796.
- [6] Z.Q. LIU, F.Y. ZHANG, D.H. DENG, *Physical sulfate attack on concrete lining–A field case analysis*, Case Stu Construct. Mater. 6 (2017): 206-212.
- [7] X.J. GAO, B.G. MA, Z.M. ZHAO. On attack product and corrosion mechanism of hydraulic concrete after long-term exposure to natural environment in western China, J. Chin. Soc. Corros. Prote, 25 (2005): 299-302.
- [8] M. NEHDI, M. HAYEK. *Behavior of blended cement mortars exposed to sulfate solutions cycling in relative humidity*, Cem. Concr. Res. 35(2005): 731-742.
- [9] Z.Q. JIN, W. SUN, B.R. HOU, P. ZHANG. *Key parameters of constructed lining concrete in Jiaozhou Bay Subsea Tunnel*, Journal of Central South University (Science and Technology), 42 (2011): 810-816.

- [10] H. YAZICI, M.Y. YARDIMCI, S. AYDIN, A.S. KARABULUT. Mechanical properties of reactive powder concrete containing mineral admixtures under different curing regimes, Construct. Build. Mater. 23 (2009): 1223-1231.
- [11] O.M. JENSEN, P.F. HANSEN. Water-entrained cement-based materials: I. Principles and theoretical background, Cem. Concr. Res. 31 (2001): 647-654.
- [12] J.H. LIU, C.J. SHI, X.W. MA. An overview on the effect of internal curing on shrinkage of high performance cement-based materials, Construct. Build. Mater. 146 (2017): 702-712.
- [13] J. JUSTS, M. WYRZYKOWSKI, D. BAJARE. Internal curing by superabsorbent polymers in ultra-high performance concrete, Cem. Concr. Res. 76 (2015): 82-90.
- [14] B. J. OLAWUYI, W. P. BOSHOFF. Influence of SAP content and curing age on air void distribution of high performance concrete using 3D volume analysis, Construct. Build. Mater.135 (2017): 580-589.
- [15] J.M. LIU, Z.W. OU, J.C. MO. The effect of SCMs and SAP on the autogenous shrinkage and hydration process of RPC, Construt. Build. Mater. 155(2017): 239-249.
- [16] Z.Q. JIN, H.S. CHEN, T.J. ZHAO, S. GAO. Damage and ion penetration in concrete subjected to sulfate frost, J. Build. Mater. 18(2015): 493-498.
- [17] Y.J. GENG, Z.Q. JIN, B.R. HOU, T.J. ZHAO, S. GAO. Long term behavior of fiber reinforced concrete exposed to sulfate solution cycling in drying-immersion, Journal of Wuhan University of Technology-mater. Sci. Ed. 32(2017): 875-881.
- [18] Z.Q. JIN, W. SUN, Y.S. ZHANG. Interaction between sulfate and chloride solution attack of concretes with and without fly ash, Cem. Concr. Res. 37 (2007): 1223-1232.
- [19] D.Y. YANG, W. SUN, Z.Y. LIU. Thermal decomposition kinetics of ettringite crystal, J. Chin. Cera. Soc, 35(2007):1641-1656.
- [20] M.H. ZHANG, J.K. CHEN, J. ZHU, J.Y. CHEN, Experimental evaluation on modulus of equivalent homogeneous ettringite, Acta. Mech. Solid. Sinica, 22 (2009): 320-327.