Study on new cementitious materials used for pile and stabilized soil in super saline soil

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ABSTRACT

More and more infrastructure have to be built on super saline soil in China, the salt content of which may be as high as 40wt.%. The salt corrodes the cement hydrate of the foundation. This paper reports preliminary research on anti-corrosion cementitious materials for concrete pile and stabilized soil pile. The results are as follows: Strength of magnesium oxychloride cement (MOC) and its hydrate Phase 518 (P5, the contributor of the strength) could develop and keep stable in the chloride brine, the ions other than those forming P5 did not affect P5 forming. So MOC possesses the characteristic of hydraulic cementitious material and the essential stability of corrosion resistance in the brine. Strength of GC (self-made binder) paste and stabilized soil stabilized with GC could develop and keep stable in the chloride brine. Both strength and height of diffraction peak of hydrated calcium silicate (CSH) of the specimen either curing in the brine or mixed with the brine were higher than that mixed with distilled water and standard curing. So the brine is favorable condition for GC hydrate growing rather than corrosion media. GM (self-made binder) didn't include Ca^{2+} , so eliminated the basic element to form expansive ettringite (AFt) when GM immersed in sulfur brine. Sulfur saline soil stabilized by GM curing in the sulfur saline could keep strength and volume stable. Strength of GM paste could keep stably in the sulfate solution.

Keywords: cementitious materials, super saline soil, concrete pile, stabilized soil, durability

1 INTRODUCTION

Super saline soil covered almost half of the northwest of China, salt content of which is 5-10 times as high as seashore saline soil's, even as high as 40 wt. % of the saline soil^[1]. As the Grand Western Development Program of China has been further promoted, more and more infrastructure have to be built on super saline soil.

The salt with such high content in the saline corrode severely concrete-pile or stabilized-soil-pile whose cementitious materials is Portland cement^[2]. In a research on the durability of the concrete foundation used in the saline soil of the Qarhan Salt Lake in Qinghai Province of China done by China Academy of Building Research^[3], it concluded that all kinds of pile foundation and foundation treatment methods containing Portland cement could not be used in the saline soil.

Durability, in such environmental extremes, of the concrete made of Portland cement, high alumina cement, magnesium oxychloride cement, sulphate aluminium cement, slag cement, polymer, polymer cement, silica fume and the concrete treated by

technology such as polymer impregnated, substitution, separation and coating in the surface, and so on have been studied, but the problem can't be solved yet^[3-5]. Currently, technology route of researching anti-corrosion concrete focus on either improving the composition of hydrate or increasing the density of material, but these methods can't solve the root cause that the hydrates of cement clinker minerals such as tricalcium silicate, tricalcium aluminate, are naturally susceptible to corrosion of the salt^[6].

Lacking of high bearing capacity foundation treatment methods such as concrete-pile and stabilized-soil-pile is a big obstacle for the development of this region. This paper reports the preliminary research work about anti-corrosion cementitious materials for concrete-pile and for stabilized-soil pile in the super saline. In the former the salts corrode the hydrates of the cementitious materials, while in the latter the salts react with constituents of the cementitious materials.

2 EXPERIMENTAL

In this research, performance of magnesium oxychloride cement (MOC), a air hardening inorganic binding materials^[7], in brine was investigated;

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durability, in saline environment, of paste and stabilized super saline soil made with GC and GM was investigated. GC and GM are powder of inorganic cementitious mineral made by our group.

2.1 Materials

Light-burned magnesia oxide (MgO) was industrial grade (content of active MgO was 24.2wt.%). MgCl₂·6H₂O, MgSO₄·7H₂O, Na₂SO₄ was analytical pure. The brine A was underground water in Ge’ermu by the Qarhan Salt Lake, and the mass fraction of salt is 40% measured by evaporation. The soak solution was made by diluting the brine with the tap water according to the experimental need. The brine B with mass fraction of salt of 21.8% was made by simulating the brine of salt lake in Xinjiang province. The ionic species of brine A and B is shown in Table 1. Tap water and distilled water were used. The composition and XRD patterns of GC and GM are in Table 2 and Fig.1. Sulfur saline soil sample ZZ was made by adding Na₂SO₄ in soil collected in Beijing. Super chloride saline soil sample C was taken from Qarhan district. Physical properties of C and ZZ are in Table 3. Composition of salt in sample C is shown in Table 4.

Table 1 Ionic species of brine of Qarhan and Xinjiang (wt.%)					
Brine	K ⁺ ,Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻
Qarhan	13.86	1.07	0.71	21.03	3.26
Xinjiang	6.78	0.71	0.93	10.51	2.82

Table2 Chemical composition of GC and GM						
Stabilizer	SiO ₂	Al ₂ O ₃	SO ₃	CaO	MgO	others
GC	25.7	11.1	3.2	55.7	3.3	1.0
GM	30.1	13.7	2.5	37.5	14.5	1.7

Fig.1. XRD patterns of GC and GM

Table 3 Physical properties of soil				
Soil	ω(%)	G _s	W _L (%)	W _p (%)
ZZ	20.9	2.7	29.0	19.8
C	18.7	2.6	23.9	16.7

Table 4 Composition of salt in sample C (wt.%)				
NaCl	Na ₂ SO ₄	CaCl ₂	MgCl ₂	total content
35.2	1.6	1.0	2.2	40.0

2.2 Test method

(1) Preparation and test of MOC paste

Weight the constituents based of molar ratio (active MgO:MgCl₂:H₂O = 5:1:13), dissolve MgCl₂·6H₂O in water and mix it with MgO power adequately. Put the paste in mold of 20×20×20mm, and vibrate adequately. Cover it with plastic film and demould at 4 hours later. Soak specimens of Group A in the chloride soak solution with different concentration respectively after demoulding, soak specimens of Group C in the soak solution after curing in a room with temperature at 20±0.5 °C and relative humidity of 60~70% for 28 days.

The soak solution concentration was 40%, 30%, 20%, 10% (wt.%), and the contrast groups include an air curing group and a fresh water curing group. The identifiers of the specimens’ curing condition were correspondingly 4,3,2,1,5 and 0. The curing condition was in temperature between 5~15°C. The volume ratio of the specimens’ blocks to soaking solution was 1:4. Test the strength of specimens in scheduled day, take the average value of 6 specimens as the result. Preparation method of specimens of GC and GM paste was similar to that of MOC paste, with water to binder ratio of 0.5.

The central of specimens was collected and grinded into powder, which was used for testing by D/Max-2200/PC X-ray diffraction (XRD) instrument, and the instrument condition was 40 kV, 40 mA, Cu/Kα.

(2) Preparation and test of stabilized soil

The stabilizer content was 10% of wet soil weight. Mix stabilizer with soil adequately, put the mixture in mold of 50×50×50mm, and cover plastic film on the surface, demould after 24h. Cure the specimens of stabilized chloride saline soil C in standard curing chamber (20±2 °C , humidity ≥95%), and bury the specimens of stabilized sulfur saline soil in the same sulfur saline soil (soil ZZ with Na₂SO₄ of 2wt.% and 5wt.%); test the strength of them on scheduled day. Expansion increment of specimens was tested by slide calipers.

3 EXPERIMENTAL RESULTS AND ANALYSIS

3.1 Performance of MOC in chloride brine

Strength of specimens of group A and B curing in different environment is in Table 5, XRD patterns of the specimens of 180d is shown in Fig.2 and 3, and that of group A curing in brine of No.4 for 3d and 180d is shown in Fig.4.

Table 5 Strength of specimens curing in different environment		
Curing	Strength of group A(MPa)	Strength of group B(MPa)

condition	3	28	90	180 d	3	28	90	180 d
5	23.5	40.3	49.3	49.6	44.3	48.6	49.6	49.8
4	18.7	34.5	35.3	35.3	41.4	41.9	42.1	42.2
3	17.9	23.6	26.7	26.7	41.3	41.7	42.0	42.0
2	16.1	22.7	23.6	23.7	41.3	41.8	41.9	42.0
1	15.6	21.3	22.5	22.6	41.1	41.6	41.7	41.7
0	8.5	0.0	0.0	0.0	25.1	0.0	0.0	0.0

Fig. 2. XRD pattern of specimens of group A

Fig. 3. XRD pattern of specimens of group B

Fig. 4. XRD patterns of specimens of group A curing in brine 4

Figures 2, 3 show that XRD pattern of A5, A0, B5 and B0 are consistent with existing research^[8], i.e., the hydrate of MOC cured in air is phase 518 (P5) and that cured in fresh water is $\text{Mg}(\text{OH})_2$ but not P5.

Table 5 shows that: for Group A, at the same soaking age, strength of the specimens decreased as the concentration of the soak solution decreased; but in the solution of all concentration, MOC strength continued growing until 60d age and then kept consistent to 180d age; for Group B, strength of all the specimens soaked in soak solution of every concentration was similar and

keeps strength stable as soaking age growth.

Development of strength of the specimens was consistent with development of P5 content. Specimens A0, B0 developed no strength, correspondingly no P5 was in XRD pattern; strength of specimens A5, A4 were higher, and diffraction intensity of P5 were higher too; strength of specimen A2 was lower, and so was its diffraction intensity of P5. The specimens B2, B4, B5 had similar strength, correspondingly the diffraction intensity of P5 of them was almost the same. Above results suggest that strength of MOC in the brine is built by P5, which is consistent with MOC cured in air.

It is known that P5 of MOC have generated completely after curing 28 days in air. For Group B, curing in air for 28d before soaking in the soak solution, both the strength and P5 diffraction intensity of all the specimens soaked in every soak solution with different concentrations were similar respectively, which means that P5 can exist stably in the brine mentioned above.

Fig. 3 shows that P5 quantity of A4 at 3d is much less than that at 180d, and diffraction peak of reactant MgO exists, but no $\text{Mg}(\text{OH})_2$ and other new phase appear; MgO decreased and P5 increased as age growing. This result implies that P5 can generate in the brine.

The XRD patterns show that ions in the brine, other than those forming P5 and $\text{Mg}(\text{OH})_2$, did not involve in the chemical reaction of MOC formation, and no new hydrate generated in the specimens, which suggests that the P5 is not affected by the various ions in the brine.

Based on above analysis, it could be concluded that in the brine MOC possesses the characteristic of hydraulic cementitious material and the essential stability of corrosion resistance.

3.2 Performance of GC in chloride brine

Strength of GC paste specimens are shown in Table 6; where, GC Paste a: GC mixed with distilled water, standard curing; GC Paste b: GC mixed with distilled water, curing in brine of Qarhan; GC Paste c: GC mixed with brine of Qarhan, standard curing. Strength of the stabilized chloride saline soil with GC curing in the saline soil (GC stabilized-soil) is also shown in Table 6.

Condition	Strength (MPa)				
	7 d	28 d	60 d	90 d	180 d
GC Paste a	4.9	19.2	19.5	19.7	20.1
GC Paste b	9.3	36.7	36.9	37.2	37.3
GC Paste c	9.7	36.9	37.5	37.5	37.6
GC stabilized-soil	1.7	8.3	10.5	11.1	11.2

XRD patterns of GC paste of 180d are shown in Fig.5, the height of diffraction peak of CSH in Fig.5 is shown in Table 7.

GC paste curing in the brine developed strength high enough to make concrete, and the strength kept stable till the test ended. Both strength and height of diffraction peak of CSH of the specimen either curing in the brine (Paste b) or mixed with the brine (Paste c)

were higher than that mixed with distilled water and standard curing, which imply that the brine is favorable condition for GC hydrate growing rather than corrosion media.

Strength of the stabilized soil stabilized with GC can increase to 11MPa and keep stable till the test ended.

Fig. 5. XRD patterns of GC paste of 180d

Table 7 Height of diffraction peak of CSH in GC paste

Samples	a	b	c
Height of diffraction peak	180	270	290

3.4 Performance of GM in sulfur brine

The corrosion mechanism of sulfur saline soil to cementitious material is that the corrosion reaction produce expansive ettringite (AFt). The chemical formula of AFt is: $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 32H_2O$.

Because Al^{3+} and SO_4^{2-} are supplied sufficiently in sulfur saline soil, so only if the composition of cementitious material does not include Ca^{2+} , the basic element to form AFt would be eliminated. GM is just such cementitious material.

Strength of GM paste curing in brine B and saturated solution of Na_2SO_4 is shown in Table 8. It shows that GM can exist stably in the both sulfate solution until the test ended.

Table 8 Strength of GM curing in brine of sulfate

Brine	Strength (MPa)	
	28 d	90 d
Brine B	31.7	32.2
Saturated solution of Na_2SO_4	33.9	34.5

The strength and expansion increment of the stabilized sulfur saline soil stabilized by GM and PC of 90d is shown in Table 9.

Table 9 Strength and expansion increment of stabilized soil

Stabilizer	Content of Na_2SO_4 in saline soil (wt.%)			
	2	5	2	5
	Strength(MPa)		Expansion increment(mm)	
GM	2.3	2.4	0	0
PC	0	0	1	1.7

It shows that for both saline soil with Na_2SO_4 content of 2wt.% and 5wt.%, the stabilized soil specimens stabilized with GM can develop rather high strength and keep volume stable, no volume expansion

implying no AFt produced; while those stabilized with PC produced opposite results.

4 CONCLUSION

Strength of MOC and its hydrate P5 (the contributor of the strength) could develop and keep stable in the chloride brine, the ions other than those forming P5 did not affect P5 forming. So MOC possesses the characteristic of hydraulic cementitious material and the essential stability of corrosion resistance in the brine.

Strength of GC paste and stabilized soil stabilized with GC could develop and keep stable in the chloride brine. Both strength and height of diffraction peak of CSH of the specimens either curing in the brine or mixed with the brine were higher than that mixed with distilled water and standard curing. So the brine is favorable condition for GC hydrate growing rather than corrosion media.

GM didn't include Ca^{2+} , so eliminated the basic element to form AFt when GM immersed in sulfur brine. Sulfur saline soil stabilized by GM curing in the sulfur saline could keep strength and volume stable. Strength of GM paste could keep stably in the sulfate solution.

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