Study on the process of chloride invasion and deposition in concrete under dry-wet cycles and continuous loading

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Abstract. Concrete for marine construction is not only eroded by seawater but also affected by ocean tides. The corrosion of the concrete structure is severe in the tidal range zone and the splash zone under the frequent dry-wet cycles environment. In order to investigate the process of chloride invasion and deposition in concrete under continuous loading, this paper applied pre-loading to concrete samples and evaluated pore distribution, chloride ions invade, and deposition of chlorine salts in concrete samples under dry-wet cycles with the use of salt weighing method, X-ray diffraction (XRD) and micro-CT. The results showed that the chloride salt quickly invaded into the samples under the influence of dry-wet cycles. With dry-wet cycles, chlorine salt is deposited in the pores of the samples, and the amount of chloride salt deposition increased with time. The pre-applied stress loading condition inhibited the salt deposition process. The results of the XRD analysis showed that chloride ions combined with calcium ions and deposited in the cracks and pores of the concrete after penetrating into concrete.

Introduction

With the development of the national marine strategy and the construction of many marine projects, lots of marine structures have been put into service, and the research on the durability of concrete structures in the marine environment has received extensive attention. In particular, in the service
process of concrete structures in tidal range area, they are not only affected by the dry-wet cycles due
to the influence of the tide but also damaged by invasion ions such as Cl$^-$ and Mg$^{2+}$ and SO$_{4}^{2-}$ in
seawater, making tidal range area the fastest and most serious damage area for marine construction$^{[1]}$.
By penetrating the concrete, chloride ions cause the corrosion of the steel bar and then destroys the
concrete structure, and failing the whole engineering structure. Therefore, it is vital to study the
mechanism of chloride ions invasion into concrete structures.

Many researchers have studied the invasion of chloride ions into concrete from the perspectives,
including temperature, relative humidity, and pore saturation of concrete structures$^{[2-5]}$. The influence
of aggregate properties and mix ratios on the chloride ions invasion of concrete is also shown$^{[6,7]}$. In
addition, it is also found that there is a strong influence of the saturated state of concrete and the water
environment on the transmission characteristics of chloride ions when invading into the concrete$^{[8,9]}$.

Nowadays, more and more attention has been paid to the factors such as continuous loading and
dry-wet cycles. Experimental studies showed that the dry-wet cycles significantly reduced the chloride
ion transmission resistance of concrete and coarsened the pore structure of concrete surface$^{[10]}$. Under
the influence of concrete pore structure and water distribution, chloride ions are enriched in the
sample's surface$^{[11]}$, and finally about 65% of the chloride solution intruding into the concrete sample
would be deposited inside the sample$^{[12]}$. Meanwhile, along with the increase of the loading level, the
chloride ions permeability would undergo a weaken stage before the increase due to a lot of
micro-cracks generations$^{[13-15]}$.

Therefore, a study on the process of chloride invasion and deposition in concrete under dry-wet
cycles and continuous loading is conducted, and presented in this paper. Concrete samples are exposed
to continuous loading under a dry-wet alternation system. The amount of chloride ions deposited is
tested by the weighing method. The pore distribution and salt deposition distribution after chloride
ions invasion are obtained by micro-CT scanning, the phase changes of concrete samples before and
after invasion are obtained by XRD. It uses these methods to realize the exploration of chloride ions
invasion and deposition process and sediment distribution and composition in concrete under
continuous loading.

1. Experiment setup
In order to understand the invasion process of chloride ions to concrete, saltwater exposure
experiments of concrete samples are conducted. Considering the requirement of the penetration
capacity of micro-CT on the sample size, the size of samples made in the test is Φ25mm×50mm. The
cement used for sample preparation is P.O 42.5 ordinary Portland cement produced by Huaxin Cement
Co. LTD and GB/T 19671-1999 standard sand produced by Xiamen ISO Standard Sand Co. LTD. The
mix proportion of concrete is determined according to the General Concrete Mix Proportion Design
Specification JGJ55-2011$^{[16]}$, as shown in Table 1.

| Table 1. Mix proportion of concrete(kg/m3) |
|------------------------------------------|
| W/C | W | CT | Stone | Sand | WR (%) |
| 0.4 | 180 | 450 | 980 | 700 | 1 |

After 28d standard curing, the strength test results are 53.89~56.43MPa, and it conform to the
strength standard of concrete structures in the marine environment stipulated in the Code for Design of
Concrete Structures in Waterborne Engineering JTS 151 – 2011$^{[17]}$. 


1.1 test procedure

After the prepared samples reach the curing age of 28d, the dry-wet cycles test is started immediately, and at the same time, random samples are taken from 0d samples for the XRD test. The samples of each group are numbered according to the stress state and test days. The unloaded group is Group C, and the loaded group is Group F, so the two groups taken out on the 10th day are numbered as C10 and F10, respectively. The test lasts for 100 days in total, and the amount of chloride released in group C and group F is tested by the weighing method every 10 days for 10 rounds. Finally, the micro-CT scan and XRD test of C50 are performed.

1.2 Dry-wet cycles system and continuous loading

The customized 80*80 mm stainless steel plate fixture was used to carry out continuous axial loading on the samples of Group F, as shown in Figure 1(a). The test used a torque wrench to tighten the nut when installing the fixture to realize the control of the loading level of the sample. The loading level was 50% of the compressive strength of the 28-day sample, and the loading was continued during the experiment.

The samples were immersed in 5% NaCl solution, and the dry-wet test was carried out in a cycle every 24h, as shown in Figure 1(b). Each alternating cycle includes 3 stages: soaked at 30°C for 17 h, dried at 80°C for 6 h, and cooled for 1 h.

1.3 Invasion amount of chloride ions test

The amount of chloride deposited is measured by the weighing method, and the details are demonstrated as follows. Firstly, the test sample is pre-treated. The sample is ground flat with a polishing mill to measure the actual dimensional parameters of the sample. After the sample size is measured, the sample is placed in the oven and dried at 80°C for 24h. After cooling, the samples are weighed to obtain the mass before chloride salt precipitation from the samples. The sample is dried again for 24h after washing with UP water shock for 5min. The mass of the sample after chloride precipitation is obtained by weighing again and using the mass difference to denote the mass of chloride precipitation.

1.4 Micro-CT and XRD test
The extracted C50 sample is scanned by a Zeiss Xradia 410Versa micro-CT scanner, manufactured by Carl Zeiss (Shanghai) Management Co. Ltd., with the power of 140kv72μA and the sweep rate 2.5s/p for 1600 layers. After the scanning, visualization software Avizo is used to process the scanning data and analyze the state of the sample after 50 days of chloride ions invasion.

Cross-sections about 5mm thickness are cut in the middle of 0d and 50d samples and pounded and ground into powder firstly. Then the XRD is used to carry out the diffraction test with the angle 5-70° and a sweep rate of 0.02°/s.

2. Results and discussion

2.1 The invasion amount of chloride ions

In Figure 2, chloride ions in group C invaded very quickly before the 20th day, and the precipitation amount of salt reached 1.747 mg/mm3. During the same period, the precipitation amount of Group F was only 0.597 mg/mm3. Before the 70th day, the precipitation of chloride ions in Group C was generally higher than that in Group F. From the 50th day, the increase rate of chloride ion precipitation in Group F started to accelerate, and exceeded Group C by 2.345 mg/mm3 at the 90th day.

![Figure 2. The invasion amount of chloride ions](image)

By taking the chloride ions invasion amount of each group at the 100th day as the standard, the precipitation amount in each round of the two groups can then be expressed as percentages. It is clearly shown that Groups C invades very quickly before the 30th day. The precipitation amount of Group C reaches 50.12% on the 30th day, as 3.276 mg/mm3. While at the same time, the precipitation amount of group F is only 2.105 mg/mm3, as 24.43%. Group C grows slowly from the 30th day to the 60th day, and then rapidly increases from the 60th day to the 80th day, reaching 78.03%. After that, the growth rate slows down until the 90th day. At the same time, Group F grows slowly from the 20th day to the 50th day, and then the growth rate accelerates continuously till the 80th day, when it reaches 51.90%, and exceeds Group C by 2.345 mg/mm3 at the 90th day.
In the process of dry-wet cycles, the sample exhibits periodic chloride ions saturations. After a short period of rapid accumulation of chloride ions, a stable period appeared in both groups. After that, the rapid increase and stable precipitation of chloride ions occurred alternately. In addition, Group F with continuous loading appeared before Group C without a continuous loading in each cycle. That is because chloride ions can only enter the concrete through existing channels, while continuous loading can effectively close off the intrusion channel, but the dry-wet cycles can constantly open the entry channel of chloride ions. The effects of continuous loading and dry-wet cycles are reflected in the change of the growth rate of chloride ion precipitation in the sample. The slower growth rate indicates that the effect of continuous loading is stronger than the dry-wet cycles. The acceleration of the growth rate indicates that the dry-wet cycles is stronger than the continuous loading.

2.2 Microstructure test – Micro-CT

The threshold segmentation method is adopted to process the micro-CT scan result. And the pore distribution and sedimentary salt distribution of the C50 sample are obtained, as shown in Figure 3.

![Figure 3. C50 chloride deposition and internal pores](image)

Many chloride ions intruded into the sample's interior after experiencing accelerated dry-wet cycles in a chloride solution. The salt is deposited in the pores on the sample's surface to form fluid-like salt blocks shown in Figure 3(b). Chloride ions that invade into the sample interior and accumulate on the pore wall. Some of the smaller pores had been filled in. At the same time, the gap between chloride ions filled mortar in the area where the mortar at the upper part of the sample is relatively concentrated forms cloud deposition as shown in Figure 3(c). No noticeable connected pores are found in the sample. The pores existed wholly and independently as shown in Figure 3(d). Most of the salt deposited in the pore area is enriched on the pore wall, and a small amount is deposited in the mortar gap near the pore as shown in Figure 3(e).

Apparent chloride deposition is seen on the sample's surface, but no obvious connected holes are found inside the sample. Therefore, the chloride ions invaded into the sample through the tiny pores between the mortar due to the concentration gradient and penetration effect. Moreover, it is deposited in the pores. Continuous loading compacts the mortar caused the pores between the mortars narrowing
and impeding the invasion of chloride ions.

![Concrete sample](image)

**Figure 4.** Schematic diagram of chloride ion invasion of concrete

The invasion process of chloride ions is as follows (Fig.4): At the early stage, chloride ions quickly invaded through the existing cracks on the surface of the sample due to the dry-wet cycles and concentration gradient action. The cracks in the radial part of Group Loaded are closed which hindered the invasion because of the continuous axial load. However, as the dry-wet cycles continued, chloride ions keep depositing in the surface layer, the existing cracks are continuously widened, which effectively accelerated the invasion of chloride ions; In the middle stage, deposition filled some of the surface cracks and chloride ions invaded slowly mainly depending on the internal concentration gradient of the sample because of the accumulation of chloride. Causing the precipitation amount increased steadily and slowly; In the long run stage, the cracks inside the sample are effectively widened and deepened due to the accumulation of dry-wet cycles. The invasion of chloride ions is gradually accelerated causing the cracks are filled with chloride salts, and the inhibiting effect of the continuous axial loading is continuously weakened. The rapid invasion of Cl\(^{-}\) resulted in a rapid increase in the invasion of chloride ions. It means that when chloride ions invade the concrete, the chloride ions are accelerated by the dry-wet cycles and invaded the sample under the effect of the concentration gradient and osmotic action.

### 2.3 Composition analysis

XRD is used to analyze the compositions of the two samples: 0d before invasion and Group C 50d before invasion. By comparing the changes of XRD patterns, the compositions changes of concrete before and after been eroded by chloride ion in 5% NaCl solution are analyzed.

Figure 5 showed the XRD patterns of 0d and 50d concrete powder. The most significant characteristic peak is SiO\(_2\). The concrete hydration product C-S-H are relatively conspicuous. The characteristic peaks of CaAl\(_2\)Si\(_2\)O\(_8\) and C-S-H are strengthened compared with 0d, verifying the continuous hydration reaction of concrete. The characteristic peak of CaCl\(_2\) appeared on 50d. It means that when chloride ions invade the concrete, the chloride ions are accelerated by the dry-wet cycles and invaded the sample under the effect of the concentration gradient and osmotic action. The chloride ions combined with Ca\(^{2+}\) and deposited in the cracks and pores of the sample. In addition, a small amount of Na\(^+\) intruded into the sample and is combined with other ions in the pore fluid of the sample to form sodium salts. However, due to the small amount of Na\(^+\), there is no prominent expression in the chromatogram. Due to the general solubility of sodium salts, the sodium salts deposited during the
dry cycle are dissolved into the pore fluid again in the tight wet cycle during the dry-wet cycles, which reduces the difference in the concentration of sodium ions in the solution inside and outside the sample and makes the invasion of sodium ions very little.

![XRD line widening](image)

**Figure 5.** XRD line widening

The characteristic peak of calcium chloride is not significant because the chloride ions concentration in the 5% NaCl solution used in the experiment is not high. Even if the concentration of chloride ions inside and outside the sample reaches equilibrium with the deepening of invasion, the concentration of chloride ions inside the sample is still not high. In the samples, SiO₂, CaAl₂Si₂O₈ and C-S-H are the main components from beginning to end. In the deposition process of crystallized salt, there are other chlorinated products, so the amount of CaCl₂ is less, and it is more likely to be disturbed during the X-ray diffraction test, leading to the inapparent characteristic peak.

**3. Conclusion**

In this paper, the seawater environment is simulated and the self-made continuous loading device is used to carry out the saline dry-wet cycle tests with and without loading on the concrete samples. According to the chloride ion intrusion amount weighed, as well as the XRD and CT test results, some important conclusions can be drawn.

The invasion process of the chloride ions into the concrete shows a pattern of periodicity in both the loaded and unloaded samples. In the early stage of invasion, the chloride ions content in the samples is saturated soon after a short period of rapid accumulation of chloride ion. While, along with the dry-wet cycles, the chloride ions invasion amount would increase rapidly again in the late stage of invasion.

The peak of chloride ions invasion amount in the loaded samples is appeared earlier in time as compared to that in the unloaded samples, meanwhile, with a lower total amount shown, indicating that the presence of continuous loading may inhibit chloride ions invasion into concrete.

The chloride ions invasion process into the concrete can be roughly divided into two main stages. In the early stage of invasion, chloride ions mainly deposit on the outer wall and surface layer of the
sample. As more chloride ions invade into the sample, chloride ions would combine with $\text{Ca}^{2+}$ and form $\text{CaCl}_2$ precipitations in the pores and cracks inside the sample in the middle and late stage of invasion.

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