MONITORIZAREA DEGRADĂRII BETONULUI ÎN TIMPUL LIXIVIERII, CUPLATĂ CU CICLURI DE ÎNGHEȚ-DEZGHEȚ, PRIN MĂSURAREA REZISTIVITĂȚII ELECTRICE

DAMAGE EVOLUTION OF CONCRETE BY ELECTRICAL RESISTIVITY MONITORING METHOD AFTER A LEACHING PERIOD COUPLED WITH FREEZE-THAW CYCLES

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The leaching behaviour of hydraulic concrete can't be ignored for its long-term exposure to surrounding water resulting in irreversible damage of durability, such as strength loss and porosity increase. The coupled effect of leaching and freeze-thaw cycles on the durability of hydraulic concrete in severe cold regions is a bigger challenge. For the quite slow process of natural leaching, electrochemical accelerated leaching method (EALM) was proposed to investigate the damage evolution under two test schemes (scheme one is only leaching for 50 days and scheme two is first 100 rapid freeze-thaw cycles and then leaching for 50 days) designed in this work. The electrical resistivity and calcium oxide dissolved mass were measured through electrode impedance spectroscopy (EIS) and EDTA titration method, respectively. Based on electrical resistivity measurement, the measurable damage can be discussed during above-mentioned single and coupled tests. The results indicate that compared with single leaching the coupled leaching with the freeze-thaw cycling leads to over 50% electrical resistance loss, the largest difference of both calcium oxide dissolved mass and pH in cathode room on the 21st day.

Keywords: *leaching, hydraulic concrete; coupled effect; EALM; damage evolution; EIS; calcium oxide dissolved mass*

1. Introduction

In recent 30 years, concrete has been widely used as the most important building material in water conservancy project, especially in large-scale hydraulic project, such as water gates and dams. Hydraulic concrete refers to concrete normally used in hydraulic buildings and structures which are periodically or constantly exposed to surrounding mineralized or acid water during its service life and therefore the leaching behavior of hydraulic concrete can't be neglected. The technical requirements for hydraulic concrete vary from purposes to purposes. When it comes to hydraulic concrete in cold regions, the permeability resistance and frost resistance are both demanded.

Leaching is a combined diffusion-precipitation phenomenon when hydraulic concrete is involved in working conditions, resulting in dissolving of hydration products from the matrix, subsequent structure degradation even finally deterioration. As many literatures shown, the most direct damages of leaching to concrete structures include strength loss and porosity increase [1-8]. H. Saito [2] found by electrochemical accelerated leaching device, that leaching led to the porosity of mortar specimens increasing to of1.6 to 2 times. The compressive strength of mortar samples decreased gradually along with the similar electrochemical leaching process [1]. Although porosity and compressive strength can reflect directly the damage extent of internal structure, common methods to measure them are destructive which produces inconvenience for monitoring in-use concrete structures. Johannesson [9] pointed out the necessity for studying the frost resistance of hydraulic concrete and micro-cracks caused by the frozen stress will inevitably form the leakage passage and aggravate the leaching behavior of hydraulic concrete, especially in cold regions. As a result, the research on the damage evolution of hydraulic concrete under leaching coupled with freeze-thaw cycles is an urgent task.

The natural process of leaching is usually

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very slow [10], the degradation of cement paste due to dissolving rarely affects common concrete structures, but it grows relevant to hydraulic structures, such as dams and radioactive disposal facilities, wherein long-term durability must be guaranteed [10-11]. The accelerated method used includes chemical attack with de-ionized water under applied voltage [1, 2, 12, 13] or a more aggressive solution (extensively 6 M/L ammonium nitrate solution) [14-16]. The electrochemical accelerated leaching method (EALM) was proposed to conduct the leaching process for the hydraulic concrete in this study. Most researchers focused their attention on studying the Ca leaching behavior of cement or mortar. Although some references [12,13] aim at discussing the leaching mechanisms and performance of concrete, the published works involving hydraulic concrete under the coupled factors of leaching and freeze-thaw cycles are rare.

The hydraulic concrete structures in cold regions are constantly subjected to coupled actions of leaching and freeze-thaw cycles, which lead to degradations of microstructures harmful for the durability of structures. Based on electrical resistivity and dissolved calcium hydroxide content, the performance of hydraulic concrete under single leaching and coupled with freeze-thaw cycles respectively were studied in this paper. Compared with the compressive strength and porosity, electrical resistivity measurement is a nondestructive method for characterizing degradation of the internal structures during leaching process. Chung [17-20] has verified the electrical resistivity measurement using the Wenner method to represent and interpret the freeze-thaw cycles damage evolution by systematic tests. In addition, Electrochemical impedance spectroscopy (EIS) method [21-23] has been adopted to analyze the electrochemical behavior of cementitious materials by built corresponding equivalent circuit.

The aims of this work are to (i) study the damage evolution of hydraulic concrete in cold regions under two test schemes by measuring the electrical resistivity and calcium accumulated dissolution oxide dissolved mass and (ii) to demonstrate quantitatively the non-ignorable damage caused by coupled effect of rapid freeze-thaw cycles and leaching.

2. Experimental

2.1. Materials

The chemical compositions of cement and fly ash used for all concrete samples in this study are presented in Table 1. According to the design code for mix proportions of hydraulic concrete (DL/T 5330-2005), the concrete specimens were fabricated at with water-binder ratio (W/B) of 0.6. The fly ash was used to replace cement in a mass ratio of 20%. The mix proportion of concrete specimen (called 6F20) is shown in Table 2. To improve the properties of concrete, polycarboxylate superplasticizer with 20% water reduction and an air entraining entraining admixture named SJ-2 were mixed into all specimens added with dosage of 0.8% and 0.02%, respectively. Cylindrical specimens of 100mm diameter and 50mm height were prepared. After removal of from the mould, they were cured in a standard curing room (temperature 20±2°C and relative humidity over 95%) for 28 days before test.

2.2. Electrochemical accelerated leaching method (EALM)

The principle of EALM method is to accelerate cement hydrates dissolution by increasing the movement speed of calcium ions in the pore solution under the applied constant voltage across a concrete specimen in contact with water. The balances between the main hydrates ($Ca(OH)_2$ and C-S-H gels as equation 1) and general equation 2) show) and their component ions in pore solution, are interrupted and therefore calcium ions in the pore solution migrate steadily outwards to the aggressive solution according to equilibrium law.

Table 1

Chemical composition of materials

Oxide	Cement (%)	Fly Ash (%)
SiO_2	21.07	66.57
Al_2O_3	5.48	18.95
Fe_2O_3	3.95	4.44
CaO	62.28	3.05
MgO	1.74	1.22
SO_3	2.64	0.31
R_2O	0.49	-
Loss on ignition(LOI)	1.62	3.10

Table 2

Mix proportion of hydraulic concrete

Specimen	W/B	Cement (kg/m^3)	Water (kg/m^3)	Fly ash (kg/m^3)	Sand (kg/m^3)	Gravel (kg/m^3)	Water-reducer agent (g/m^3)	Entraining admixture (g/m^3)
6F20	0.6	210	158	53	850	1030	2.11	52.7

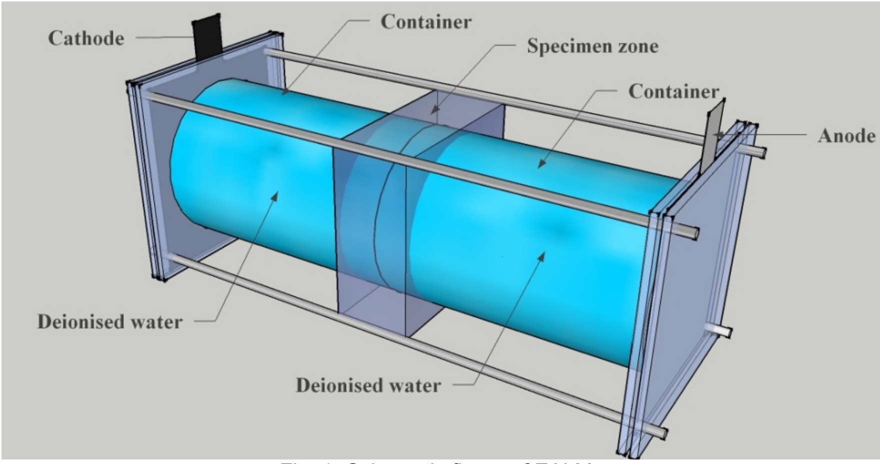


Fig. 1- Schematic figure of EALM .

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \quad (1)$$

$$C\text{-}S\text{-}H \rightarrow Ca^{2+} + 2OH^- + SiO_2 \quad (2)$$

The self-designed EALM device in this paper is given in Figure 1. As Figure 1 shows, this device mainly includes three parts, namely cathode zone, anode zone and specimen fixed zone. The two main containers of the device made by polymethyl methacrylate were filled with de-ionized water which was chosen as the leaching medium. The cathode is ferritic stainless steel plate and the anode material is MMO (MMO is a single-sided titanium alloy electrode plate with metal oxide coatings made by Xi'an Taijin Industrial Electrochemical Technology co. Ltd in Shanxi Province, China) separately.

The conditions of hydraulic concrete fixed into EALM were: an applied DC voltage of 30V, constant room temperature of 25°C and immersion in de-ionized water both anode room and cathode room. In addition, only two bottoms of specimens were exposed to leaching, their lateral face being sealed with waterproof materials. In this sense, the contact surface between de-ionized water and concrete specimens was rounded of 100mm diameter.

2.3. Test schemes

All specimens prepared in this paper were divided into two groups and used for two test schemes, namely single test and coupled test. Single test is only leaching for 50 days. The procedure of coupled test includes first 100 rapid freeze-thaw cycles and then EALM leaching for 50 days. During the coupled test, leaching parameters, including the calcium oxide dissolved mass and pH variation in the cathode room as well as electrical resistivity, were measured and compared with the same parameters of the single leaching test. Note that the rapid freeze-thaw test in this work was conducted according to the standard for testing methods of long-term performance and durability of ordinary concrete (GB/T 50082-2009) using non-standard specimens, namely cylinders of 100mm diameter and 50mm height rather than prisms of 100mm×100mm×400mm.

Compressive strength was measured according to standard for test method of mechanical properties on ordinary concrete (GB/T 50081-2002) to study quantitatively the effect of different test schemes on mechanical performance of concrete. It has to be mentioned that the size of specimen was not standard used for compressive strength test to fit the EALM device and demonstrate quantitatively the non-ignorable damage caused by coupled effect of rapid freeze-thaw cycles and leaching.

2.3.1. pH measurement

The pH variation of the cathode room during leaching process was monitored by pH electrodes and PCIS-10 chlorine meter, produced by KangYi YiQi co. Ltd, Shanghai City, China. The pH value of water sample taken out from the cathode room should be measured before the calcium ions dissolved measurement because such procedure won't alter the ingredients of water sample. pH electrodes need calibration before each test in order to get accurate data.

2.3.2. Calcium ions measurement

The concentration of dissolved Ca^{2+} ions into the de-ionized water from concrete specimens was measured by EDTA (Ethylene Diamine Tetra-acetic acid) titration method. Specific steps are as follows. 50mL water solution sample from the cathode end drawn by filter water was putted into the beaker flask with 250mL. After mixing three drops 1:1 hydrochloride acid, the mixtures were heated until boiling last for 30 seconds. When the solution cooled naturally below 50°C, potassium hydroxide solution and mixed indicator by calcein and phenolphthalein were added in sequence. Lastly, the titration end point arrived once the yellowish green of the solution changed to red in colour.

For each dissolved Ca^{2+} ions concentration, three titration tests were performed. The concentration of calcium ions in sample was converted into the dissolution mass of calcium oxide denoted by X (named by calcium carbonate, mg/L) according to equation 3).

$$X=\frac{V\times M\times 100.08\times 1000}{V_w} \quad (3)$$

Where V is the consumed volume of EDTA standard solution, ml; M is the EDTA standard solution concentration, M/L; V_w is solution sample volume, ml and 100.08 is the molar mass of calcium carbonate.

2.3.3. Electrical resistivity measurement

One thing to note is that all specimens should be water-saturated by vacuum treatment before leaching test to ensure uniform conditions for electrical resistivity measurement which partly eliminates the errors from moisture content of concrete samples.

The electrical resistivity measurements were performed by RST5200 electrochemical system (produced by KeRui YiQi co. Ltd. Gongyi City, Henan Province, China) using the two-electrode AC impedance method (Lu *et al.* 2010; 2011). Figure 2 depicts the connection graph of electrode plates and specimens to measure electrical resistivity before the specimens were fixed in the EALM device. In practice, in-situ measurement of electrical resistivity can be achieved by direct junction of electrode plate terminal and three-electrode system of RST5200 during the leaching process.

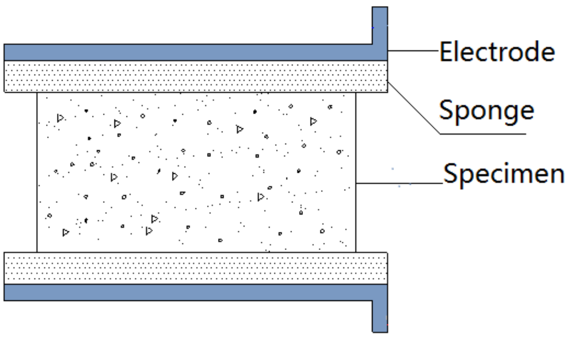


Fig. 2- Connection graph of electrode and specimens for electrical resistivity measurement.

To achieve the electrical resistivity measurement in Figure 2, the electrical contacts were stainless plate in conjunction with copper wires. In order to get a good contact between specimens and electrodes and further eliminate the negative influence of the interface, two pieces of thin and wet sponge containing 3% sodium chloride solution were placed between them. The test frequencies ranged from 0.1Hz to 10K Hz, and the potential amplitude was 10mV. Electrical resistivity was measured for six times and the result was an average value of six measurements.

3. Results and Discussion

3.1. Comparison of damage evolution for single and coupled factors

To analyse quantitatively the damage extent of two test schemes, such indices as pH variation in cathode room, calcium oxide accumulated mass and electrical resistivity were compared. Furthermore, the scanning electron microscope analysis (SEM, Quanta 200F environment SEM) was also used for obtaining information regarding the microstructure alterations of hydraulic concrete under test procedures.

3.1.1. pH variation in cathode room

Under the applied voltage, the H^+ ions move towards the cathode and starts hydrolysis process as equation 4) shows which explains the reasons for which the cathode solution becomes alkaline. Similarly, the calcium ions also move towards to the cathode room and therefore only the pH variation in cathode room was measured and discussed here to investigate the leaching behavior.

$$2H^+ + 2e \rightarrow H_2 \quad (4)$$

The pH of cathode room under single leaching and coupled factors is shown in Figure 3.

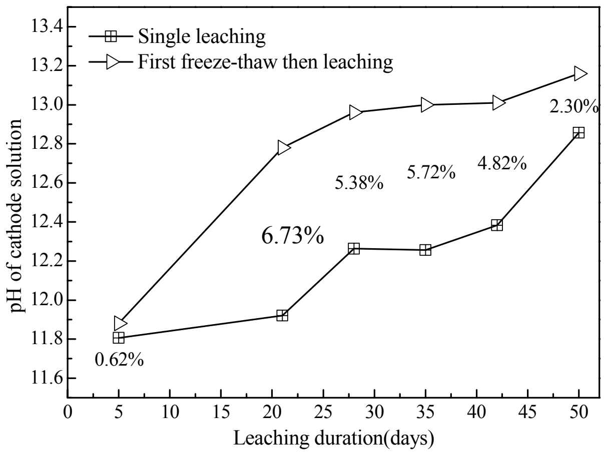


Fig. 3 - Comparison of pH variation in cathode room between single test and coupled test.

According to test data, the pH value in cathode room changes from 6.70 (initial pH value of de-ionized water) to 12.86 for single leaching test. If the same concrete specimens undergone to 100 rapid freeze-thaw cycles, the amplitude of pH variation becomes larger. After freeze-thawing coupled with leaching the pH value exceeds 13. During the whole test period, the largest pH difference between the two test schemes with 6.73% appears at the 21st day while the smallest value was 0.62% at the 5th day. After then the pH difference in cathode room decreases gradually which means that the effect of freeze-thaw cycles on leaching resistance of hydraulic concrete is a downward parabola with vertex at (21, 6.73%).

3.1.2. Calcium oxide accumulated mass by hydrolysis

The calcium oxide dissolved mass of specimens in conditions of the two test schemes was measured and the data are given in Figure 4. The results indicate that the leaching for 50 days after 100 freeze-thaw cycles evidently amplifies the calcium ions dissolving compared with single leaching during of the same period. From the point view of 50 days leaching, the difference of calcium ions dissolved between the two test conditions initial increases until 21 days and decreases afterwards, which is in accordance with the pH variation trend in the cathode room. The effect of freeze-thaw cycles on the leaching damage can't be neglected because the dissolved calcium oxide under coupled factors is larger than the single leaching by at least 20%, significant for hydraulic concrete durability. For this reason, improving of the frost resistance and impermeability or optimizing the mix proportions have to be considered to prevent hydraulic concrete in cold regions from freeze-thaw cycles coupled with leaching damage.

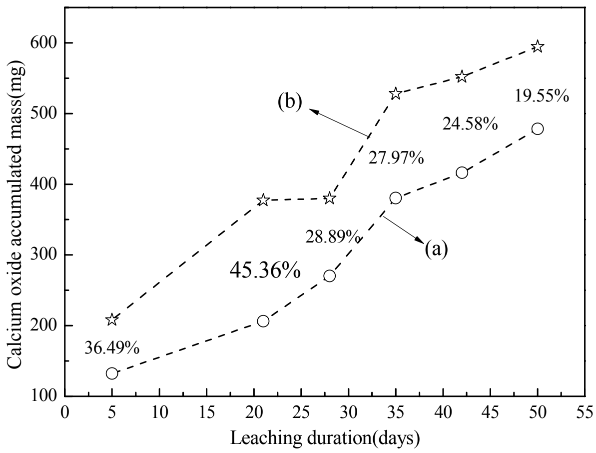


Fig. 4 - Calcium oxide accumulated mass (a) single test and (b) coupled test.

3.1.3. Electrical resistivity

The electrical resistivity of leached and un-leached specimens before freeze-thaw test, for 25, 50 and 100 freeze-thaw cycles was measured correspondingly. The test data are given in Table 3.

From the Table 3, it can be concluded that along with freeze-thaw cycles, the electrical resistivity of un-leached and leached concrete specimens decreases gradually as consequence of the expansion stress during the freeze-thaw cycles. But the falling range of corresponding value is over 50% after leaching test which indicates that the coupled factors of freeze-thaw cycles and leaching caused a great effect on the electrical resistivity. The electrical resistivity can directly reflect the internal degradation and therefore allows evaluation of the damage extent in-situ during the freeze-thaw cycles and leaching process. The double degradation due to coupled test conditions, including the on-going dissolution and precipitation of hydrate products and micro-cracks, aggravates damage of the internal structures. If the early-stage monitoring and repair works are missed, the irreversible destruction is inevitable. Meanwhile, the electrical resistivity of concrete matrix will decrease from 1500~2000ohmm to 500~1000ohmm, accompanied by the decrease of compactness.

The compressive strength and electrical resistivity after single and coupled test schemes decreased sharply compared with the 28 days value. Loss ratios of electrical resistivity caused by different factors are evidently larger than that of compressive strength. From Table 4, it can be concluded that the freeze-thaw cycle is more harmful for durability of hydraulic concrete than single leaching. What's more, the damage extent of coupled factors is more than simple superposition of leaching and freeze-thaw cycles which further validate the complexity of coupled test conditions.

Table 3

Electrical resistivity of specimens with different freeze-thaw cycles

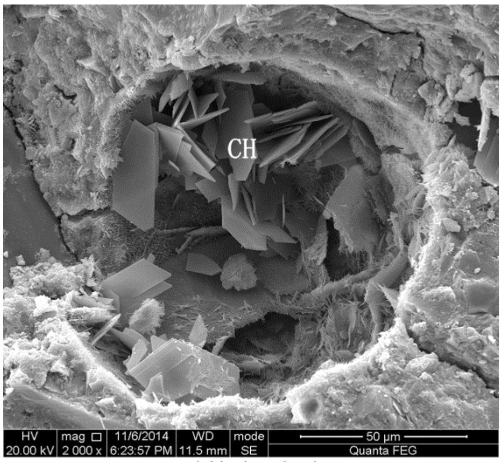
Specimens	Freeze-thaw cycles				Total reduction ratio (%)
	0	25	50	100	
Un-leached	1063.5	890	694	656	38.3
leached	612	496	344	275	55.1

Table 4

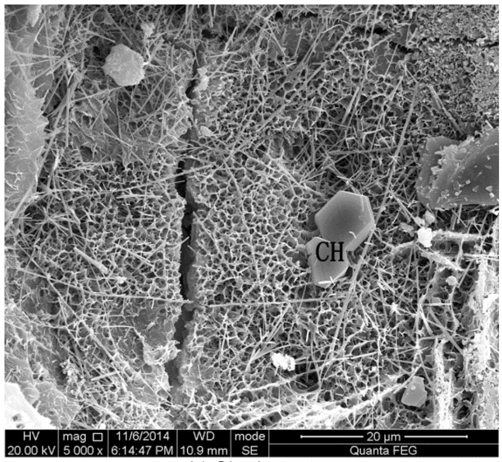
Electrical resistivity and compressive strength change

Characteristics	Values for sample after 28days	Values determined by scheme one	Values determined by scheme two	LLR (%)	FLR (%)	CLR (%)
Electrical resistivity (Ohmm)	1063.5	612	275	42.5	55	74.1
Compressive strength (MPa)	34.5	26.9	15.6	22	42	54.8

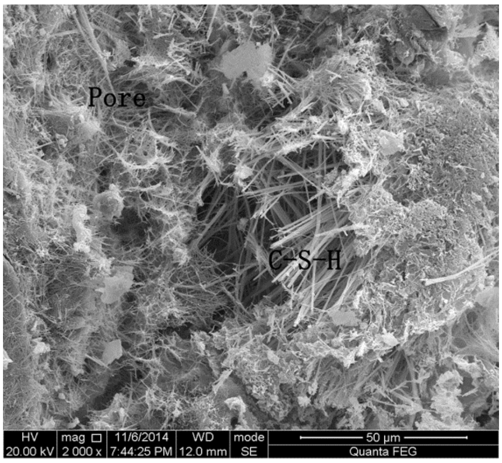
Note: LLR, FLR and CLR mean the loss ratio of indices caused by leaching (LLR), freeze-thaw cycles (FLR) and coupled factors (CLR) correspondingly.

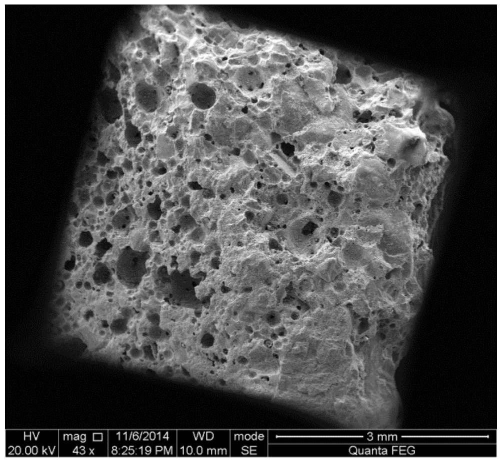


a) Un-leached



b) Single test





c) Coupled test

Fig. 5 - SEM images of a) un-leached specimen, b) single test and c) coupled .

3.2. SEM of hydraulic concrete after leaching test

SEM analysis was conducted to search the microstructure differences between the two test schemes. The SEM images are shown in Figure 5.

In Figure 5, it can be seen that porosity of all hardened cement matrix after two test schemes increased evidently. As seen from Figure 5 a, the compactness of specimen is obviously high and a cluster of calcium hydroxide crystals exist in the pore. The pore size of cement matrix for single leaching test seems to be smaller and there still exists integrity crystal structure of calcium hydroxide as shown in Figure 5 b. Even though the magnification is just 43×, large and dense pores distribute uniformly at the surface of the cement matrix undergoing freeze-thaw cycles coupled with leaching test (Fig. 5c). In Figure 5 c, the remaining hydrated phases after dissolution of calcium hydrate become smaller like " new branches " sprouting from columnar calcium silicate hydrate which are direct reflection of the different damage extents. Above all, the coupled actions aggravate the degradation of concrete specimens just as the calcium oxide dissolved mass and pH showed.

4. Conclusions

Two test schemes were designed to analyze the damage extent by the freeze-thaw cycles coupled with leaching on the hydraulic concrete through monitoring of three indices, including pH variation in cathode room, calcium oxide dissolved mass as well as electrical resistivity of specimen matrix. The main conclusions are as follows.

Whether from the microscopic level or macroscopic level, the coupled action of freeze-thaw cycles and leaching indeed aggravates the damage extent of hydraulic concrete.

The largest difference values of both pH in the cathode room and calcium oxide dissolved mass between single test and coupled test appear at the 21st day during the electrochemical accelerated leaching process, the former with 6.73% and the latter 45.36%.

After coupled action, the electrical resistivity and compressive strength of concrete matrix decreases over 50% which is non-ignorable for practical engineering. The loss ratios of them caused by freeze-thaw cycle are larger than that by leaching and the damage extent of coupled factors is more than simple superposition of leaching and freeze-thaw cycle.

The results of SEM analyse indicate that the freeze-thaw cycles coupled with leaching test conditions truly aggravate the dissolution of calcium hydroxide and the increase of porosity.

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