# Durability reduction pattern of concrete against sulfate attack under dry-wet cycles

Xu Cundong, Ding Lianying, Liu Hui, Wang Rongrong, Wen qinyu and Lian Haidong

The concrete structure in the coastal area and the salinized zone in the west of China is eroded by hazardous chemical ion, such as sulfate, chloride salt etc. Besides, it is also damaged by the synergistic effect of the dry-wet cycle, which reinforces the durability reduction of the concrete structure. This durability reduction leads to damages made by erosion, such as cracks and scaling, which should occur in a later stage, and has a negative influence on the maintenance and the service life of the structure. This paper used field survey, accelerated laboratory test and theoretical analysis according to the characters of durability reduction of concrete under attack. In the accelerated laboratory test, the contrast test of the different erosions made by sulfate, mixed salt (sulfate+chloride salt) and water in the dry-wet cycle was conducted with the relative dynamic modulus of elasticity as the evaluation standards. The influence of different erosions, erosion medium, water-cement ratios and fly ash on the durability reduction of concrete structure under attack was analyzed. The study shows that dry-wet cycle can accelerate the erosion of the concrete by sulfate; sulfate erosion can make more damages than mixed salt with the sulfate attack in dry-wet cycle; and the concrete with 20% fly ash can better reduce the erosion made by salt crystals.

## 1 INTRODUCTION

Sulfate erosion is one major factor that causes the damage of the concrete structure. It damages the concrete structure mainly by reducing the strength of it [1, 2, 3], which occurs when the dilatant produced by the chemical reaction between sulfate ions and the hydration product of the concrete causes cracks in the concrete. According to the environmental investigation, some harbours, offshore projects, undersea tunnels and cross-sea bridges along the coastline have been eroded and damaged by hazardous ions [4, 5, 6]. The concrete structure of a large number of water conservancy and hydropower projects, such as Yanwoxia project, Bapanxia hydroelectric power station, and Liujiaxia hydroelectric power station on the Yellow River, Chaoyang hydroelectric power station in Qinghai province, and Jingtai electric power's pumping irrigation project, and Xiben electric power's pumping irrigation project in Gansu province, is under the sulfate attack [7]. In addition, some concrete structures, for instance, bridges, roads, pipelines and utility poles in Xinjiang, Qinghai, Xizang Gansu, Ningxia and Inner Mongolia provinces which have a vast salinized land in the west, are also damaged by sulfate attack, which need high maintenance cost to keep normal operation just after being put into use for a few years [8, 9].

Concrete performance under dry-wet cycle is one vital aspect in studying the durability of concrete. It has been perceived that the concrete in dry-wet cycle is more vulnerable to the erosion made by salt [10,11]. Sahmaran and Erdem and other scholars [12] studied the long-term performance of concrete under sulfate attack and dry-wet cycle, and the result indicated that in either sulfate attack or dry-wet cycle, the mechanical property of concrete improves before it deteriorates; while the mechanical property of concrete under erosion of both dry-wet cycle and sulfate attack deteriorates more rapidly. Sun Yingshao and Niu Ditao [13] analysed the concrete damage under sulfate attack and dry-wet cycles, and the result shows that with the increasing numbers of dry-wet cycles, the concrete damage becomes more severe, the thickness of the damage layer increases, and the conduction speed of ultrasonic wave decreases. The more rapidly the conduction speed decreases and the higher the density becomes, the more severe the damage is. The above results can provide important evidence for theoretical analysis and experiments in this field. However, in domestic and foreign literature, a mature theory of mixed salt in dry-wet cycle, that is adding chorine salt into sulfate and replacing certain proportion of concrete with fly ash, has not been established. Therefore, conducting the research to analyze the factors that can influence the durability reduction of concrete under attack has great importance [14, 15].

## 2 TEST METHOD

The mix proportion keeps to *The Mix Proportion Design of Ordinary Cement (JGJ55-2000/J64-2000)*, with general engineering practice and design requirement taken into consideration. Also, considering fly ash's influences upon concrete's resistance of sulfate attack, three concrete mix proportions are designed. The mixture of fly ash into the concrete adopts equivalent replacement method [16]. The concrete mix proportions are shown in Table 1.

The dynamic modulus of concrete's structure can evaluate the degradation and invalidation of concrete's performance accurately. Hence, concrete blocks' relative dynamic modulus of elasticity is chosen as the evaluation indicator of concrete's durability reduction [17]. The relative dynamic modulus of concrete is :

$$E_{rd} = \frac{E_n}{E_0} \times 100\%$$

where, $E_n$ is the dynamic $E_n$ modulus when the experiment has been conducted for n times under dry-wet cycle and $E_0$ is the dynamic modulus before the experiment is conducted. When the relative dynamic modulus of elasticity decreases to 60%, the concrete blocks will be regarded as damaged.

The size of test specimens is 100 mm × 100 mm × 400 mm. After the test specimens are shaped, to avoid evaporation of water, they are covered with a layer on surface and placed in an environment of 20±5°C for about 24h. After form stripping, the test specimens will be conserved in concrete curing room (temperature at 20±2°C and humidity over 95%) for 28d, about 20 mm between each two of them.

Experiments that concrete blocks of three mix proportions (A, B, C) are attacked by three chemical mediums (10%$NaSO_4$, 10%$NaSO_4$+5%NaCl, $H_2O$) chronically under dry-wet cycle were conducted. Concrete blocks' relative dynamic modulus of elasticity is measured at different stages to explore influences caused by different ways of erosion, erosion mediums, water-cement ratio and fly ash upon the durability of concrete.

Dry-wet cycle: test specimens are soaked in attack liquor for 14h, then dried in the air for 1h, baked in oven under 80°C [18] for 8h and in the end refrigerated for 1h, which process takes 24h in all. The liquor is changed once per month. During the erosion, the dynamic modulus is measured and its relative modulus of elasticity is calculated per 10 days. The whole experiment went through 120 dry-wet cycles, that was, 120d.

**Table 1. The concrete mix design**

| Specimen number | | A | B | C |
|---|---|---|---|---|
| Water-cement ratio (W/C) | | 0.5 | 0.4 | 0.4 |
| Sand ratio | | 36% | 36% | 36% |
| Fly ash ratio | | 0 | 0 | 20% |
| Water reducer ratio to cementing material | | 0 | 0.60% | 0.60% |
| Materials used in concrete (Kg/M³) | Water | 182 | 158 | 158 |
| | Cement | 362 | 394 | 315.2 |
| | Sand | 662 | 644 | 644 |
| | Pebble | 1188 | 1145 | 1145 |
| | Fly ash | 0 | 0 | 78.8 |
| | Water reducer | 0 | 1.092 | 1.092 |

## 3 RESULTS AND ANALYSIS

### 3.1 The influence of erosion methods on concrete $E_{rd}$

Use the group B of test specimens with the water-cement ratio being 0.4 as test objects and 10% sodium sulfate solution as erosion medium to research on the durability reduction patterns of concrete's $E_{rd}$ under two different erosion methods: long-term immersion and dry-wet cycle. The results are shown in Figure 1.

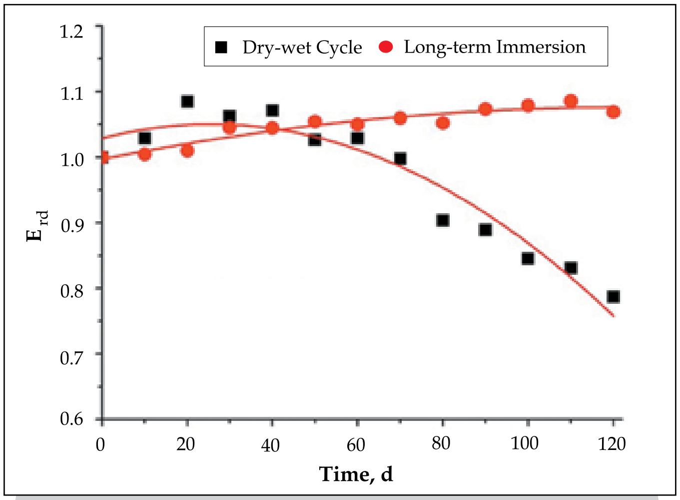


*Figure 1. $E_{rd}$ curve of concrete under different erosion methods*

The Figure 1 shows that dynamic modulus of concrete under long-term immersion in 10% sodium sulfate increases slightly and steadily, $E_{rd}$ having increased by 6.9% when the 120 days ends. There are researches showing that the $E_{rd}$ of concrete which is immersed in 10% $Na_2SO_4$ will increase at the beginning, remain steady on around 20 d, and then follow the trend of slight decrease [19,20]. For the test blocks in long-term immersion, on the one hand, hydration reaction happens in internal concrete produces hydration products which make concrete's inner structure more compact; on the other hand, with the invasion of attacking ions, sulfate radical's erosion effects appear gradually, and chemical reaction will happen between the sulfate radical and the hydration productions of cement, which leads to certain amount of attacking products (gypsum, ettringite, etc.) and thus to some extent works filling effects. The resultant force caused by the two factors above makes concrete's $E_{rd}$ increase, which takes a long time. According to the experiment results, during the long-term 120-day immersion, what the statistics suggests is exactly $E_{rd}$'s changing rules at early stage when the concrete is in natural immersion condition. It is shown that $E_{rd}$ increases quite slowly and ends at 1.07. Different from long-term immersion, dry-wet cycle together with sulfate concrete causes obvious fluctuations of test concrete specimen's $E_{rd}$. Under dry-wet cycle, test concrete's $E_{rd}$ experiences increase and then sharp decrease at the early stage, ending at 0.79 after 120 d. For test specimens under dry-wet cycle, since the external environment is relatively dry during baking, the water molecules in the test concrete move reversely and evaporate outside, which leads to that sulfate content in the pore solutions on concrete's surface increases. Therefore, a content gradient of sulfate ions is formed between concrete's interior and surface. According to the theory of free ions diffusion, saline matter in the multi-pore solutions of concrete in turn diffuses into concrete's interior in the form of liquid. As time goes, most of the pore water on concrete's surface and middle layer is evaporated and extra saline matter crystallizes and separates out. In this way, sulfate ions gather quickly in the interior while water moves outside during baking. During immersion in next step, there will be more saline matter gathering into concrete's surface capillary interstice. Saline solutions on concrete's surface continuously experience the circle of "baking-evaporation-concentration-crystallization-baking". $SO_4^{2-}$ makes the sulfate ions in concrete, after reaching the "threshold value" immediately triggers erosion reactions and products, such as ettringite, come out in advance. Besides, during baking, ettringite decomposes under heat and generates calcium monosulfate aluminate hydrate (AFm) and $CaSO_4$. More serious damage will be caused in next immersion.

## 3.2 The influence of erosion medium on concrete $E_{rd}$

Relative dynamic modules of elasticity of three test block sets (A, B, C) under dry-wet cycle in different erosion mediums are shown in Figures 2, 3, and 4 respectively.

It can be seen in Figures 2 t o 4 that under dry-wet cycle, the dynamic modulus of concrete in sulfate and mixed salt increases a little at early stage. When the cycles repeats, dynamic modulus in three sets all decreases. Among them the dynamic modulus of the test specimen in 10% $Na_2SO_4$ decreases most sharply, whose $E_{rd}$ decreases to 0.71 at the end. Compared with that in sulfate, $E_{rd}$ of concrete in mixed

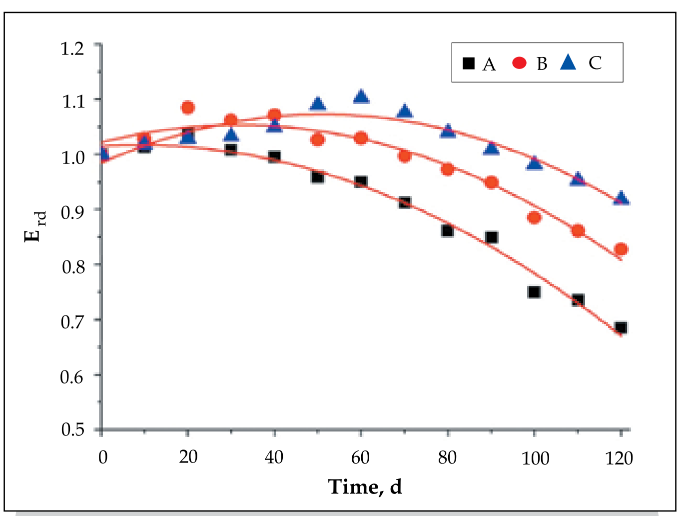


*Figure 2. $E_{rd}$ curve of concrete in sodium sulfate*

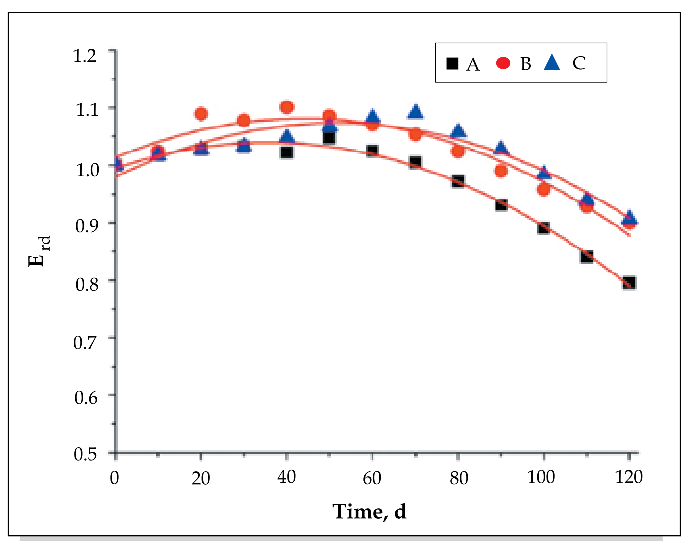


*Figure 3. $E_{rd}$ curve of concrete in mixed salt*

salt peaks at early stage, although later, and after reaching the peak, the decreases slowly and ends at 0.84. This suggests that the addition of chlorine salt brings some help in slowing the damage of dry-wet cycle [21,22]. The $E_{rd}$ of test concrete block in water generally remains steady, almost no damage being made.

Under dry-wet cycle, concrete $E_{rd}$ in water starts with slight increase and decreases a little at later stage, but still larger than 1. The reasons could be that the constant hydration in concrete makes its inner structure more compact and that the concrete in water suffers from corrosion too. Due to the calcium hydroxide produced from hydration, the interior corrodes gradually because calcium hydroxide reaction with sodium sulphate to form expanding gypsum. When the baked concrete surface is immersed in water, it absorbs water through capillary until saturation. Frequent "baking-immersion-baking-immersion" cycles fasten calcium hydroxide's corrosion, causing damage on concrete's inner structure.

As what is shown above, under dry-wet cycle, sodium sulfate solution has considerable effects on concrete's dynamic modulus of elasticity. According to the theory of sulfate ions' erosion, sulfate ions go through the capillaries and cracks to infiltrate or diffuse into concrete's porous continuous structure. The speeds of infiltration and diffusion are influenced by factors such as porosity, pore structure, environment temperature, mediums, etc.

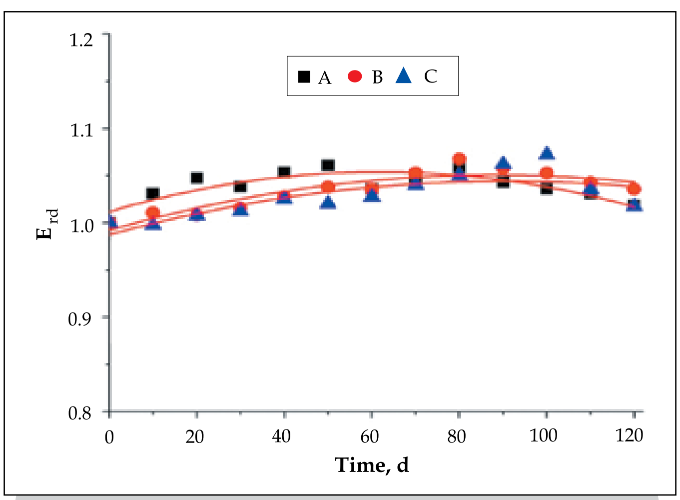


*Figure 4. $E_{rd}$ curve of concrete in water*

### 3.3 The influence of water-cement ratio on concrete $E_{rd}$

This experiment used test specimens with two different water-cement ratio (W/C=0.5, 0.4). The size was 100 mm × 100 mm × 400 mm. There were 3 pieces of test specimens in each erosive medium. The dynamic modulus was measured per 10d and then the mean was calculated and analyzed. The Figure 5 and 6 show how concrete's relative dynamic modulus of elasticity ($E_{rd}$) changes along with the number of times of dry-wet cycle under two different water-cement ratios.

Compare Figure 5 and 6 and it can be seen that the concrete blocks are damaged more quickly when the water-cement ratio is higher (W/C=0.5). Under the attack of 10% $Na_2SO_4$, the $E_{rd}$ of concrete whose water-cement ratio was 0.50 declined to 0.71 after 120 cycles, while that of concrete whose water-cement ratio was 0.40 declined to 0.79; the test specimens were partially damaged. As for other two mediums, changes of test specimens' $E_{rd}$ followed similar rules: test concrete blocks with higher water-cement ratio were damaged more quickly, whereas the difference was more remarkable when concrete was attacked by sulfate. No matter with what water-cement ratio, $E_{rd}$ always follows the trend that it grows first and then declines.

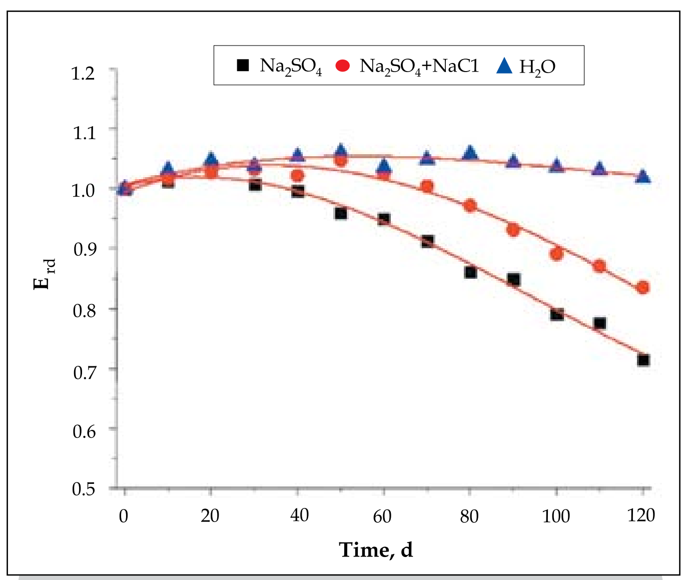


*Figure 5. $E_{rd}$ curve of A set concrete blocks*

In summary, water-cement ratio has evident influences upon concrete's erosion under dry-wet cycle. Concrete with low water-cement ratio has more gel and thus is more compact, where anti-infiltration ability is stronger and therefore their durability under dry-wet cycle is also more qualified, but concrete with high water-cement ratio goes inversely. Sulfate attack is superimposed on dry-wet cycle: dry-wet cycle not only fastens the speed of sulfate ions' infiltration and diffusion but also provides room for erosive products' growth. It can be said that dry-wet cycle is an effective method of researching on concretes against sulfate attack.

### 3.4 The influence of fly ash on concrete $E_{rd}$

As for B and C block sets, under 10% sulfate attack and dry-wet cycle, the changing processes of their relative dynamic modulus of elasticity were shown in Figure 7.

The experiment considered two conditions that nothing was added into the test specimens (B set) and only 20% fly ash (C set) was added when the water-cement ratio W/C=0.4.

The Figure 7 suggests that $E_{rd}$ of each test concrete block experienced a period of initial growth and later declination during the experiment. $E_{rd}$ of C set concrete blocks declined slowly and its transition moment of declination was later. Till the experiment ended, its $E_{rd}$ decreased to 0.88, while that of B set descended to 0.71 in the end. Comparing the two sets, it can be detected that $E_{rd}$ of C set concrete blocks reached its peak relatively slower and its increasing range was small. Generally speaking, concrete's resistance of

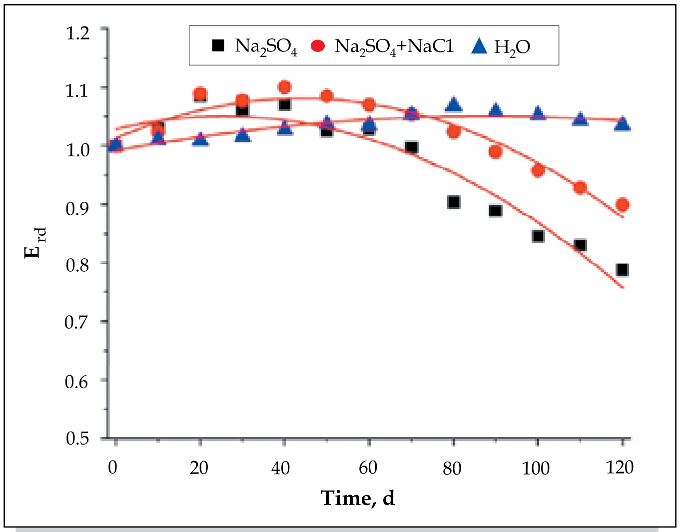


Figure 6. $E_{rd}$ curve of B set concrete blocks

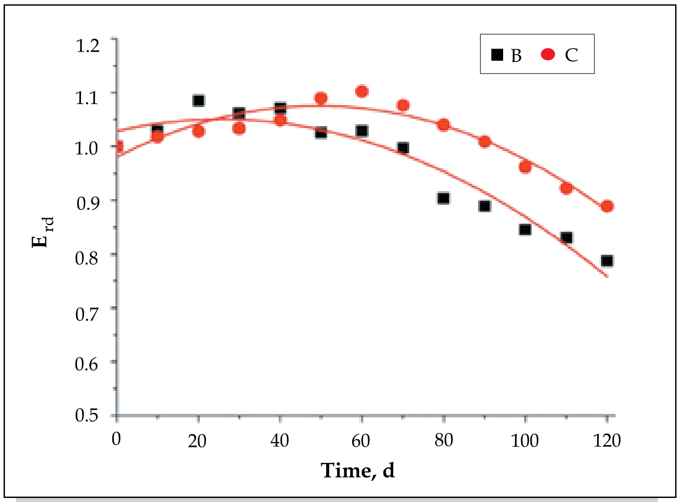


Figure 7. $E_{rd}$ curve of B and C set concrete blocks

sulfate attack increases remarkably after fly ash is added in. According to the theory of ettringite sulfate attack, the basic precondition of producing ettringite is the existence of non-hydrated tricalcium aluminate ($C_3A$) and its hydrated products. But by replacing cement with equivalent amount of fly ash, the content of $C_3A$ in cement is reduced effectively, which thus reduces ettringite sulfate attack and strengthens concrete's resistance of sulfate attack [23]. For another thing, in the second hydration, fly ash's pozzolanic activity is made prominent and the more production of gel makes concrete more compacted, besides in the fly ash pozzolanic reaction it will produce calcium aluminate hydrates (CAH) that will de-stabilize ettringite and convert it to less expanding AFm. It will also consume calcium hydroxide so less gypsum will be formed in the first stage of sulphate attack as well. As fly ash's second hydration reaction continues, concrete's infiltration decreases and correspondingly, sulfate's invasion gets less. Therefore, to some extent, adding appropriate amount of fly ash helps to strengthen concrete's resistance against salt crystallization attack.

## 4 CONCLUSIONS

Based on the above studies the conclusions are given below.

1. The chemical erosion of concrete structures is influenced by various factors in salty regions. The effects of dry-wet cycle and sulfate attack are superimposed together. Dry-wet cycle can fasten sulfate attack on concrete structures; under dry-wet cycle and sulfate attack, sulfate erosion is more

noticeable than that of mixed salt, mainly because the chloride salt in mixed salt reduce the generation of ettringite , which to a certain degree can delay the damage upon concrete.

2. Seen from the $E_{rd}$ curves of each group, the process of concrete's degradation can be divided into three stages: initial degradation of performance; improvement of performance; rapid degradation. Analysis shows that the higher the water-cement ratio is, concrete suffers more from sulfate attack, but adding fly ash can help to improve concrete's resistance against sulfate attack.

3. Researches on the factors influencing durability reduction of concrete only considered four factors, including the methods of erosion, erosion medium, water-cement ratio and the addition of fly ash, but in costal and northwestern arid regions of China, influences of freeze thaw and static-dynamic load cannot be ignored either. Further study on the durability of concrete is expected.

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**Dr. Xu Cundong** holds a PhD and is a Professor at North China University of Water Resources and Electric Power, Henan Province, Zhengzhou, China. He is mainly engaged in the study of hydraulic structure optimization design and hydraulic concrete durability.

**Ding Lianying** is a postgraduate student and a Lecturer at North China University of Water Resources and Electric Power, Henan Province, Zhengzhou, China. He is mainly engaged in the study of hydraulic concrete durability.

**Liu Hui** is a postgraduate student at North China University of Water Resources and Electric Power, Henan Province, Zhengzhou, China. He is mainly engaged in the study of hydraulic concrete durability, pump station flow optimization and structure simulation.

**Wang Rongrong** is a postgraduate student at North China University of Water Resources and Electric Power, Henan Province, Zhengzhou, China. She is mainly engaged in hydraulic concrete irrigation water and salt migration.

**Wen Qinyu** is a postgraduate student at North China University of Water Resources and Electric Power, Henan Province, Zhengzhou, China. He is mainly engaged in hydraulic concrete irrigation water and salt migration.

**Lian Haidong** is a postgraduate student at North China University of Water Resources and Electric Power, Henan Province, Zhengzhou, China. He is mainly engaged in the study of hydraulic concrete durability.