



# Chemical and mineralogical alterations of concrete subjected to chemical attacks in complex underground tunnel environments during 20–36 years



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## ABSTRACT

This paper investigates the chemical and mineralogical alterations of concrete in underground tunnel structures built from 1980 to 1996, located on the China's east seashore. The underground water around the tunnels had once been treated to be not or little aggressive. However, the complex environments in the tunnels had increased the aggressiveness of certain ingredients, thus causing chemical attacks. The chlorides in the leakage underground water cause chloride attack, and the NaCl crystallizations on the surface of the C50 pre-cast concrete segments induce a deeper chloride contamination. When the concrete suffers flowing leakage water, calcium leaching also occurs, leading to decalcification and magnesium incorporation. Under this circumstance, C50 pre-cast concrete shows a higher resistance compared with C30 cast-in-place concrete, mainly due to the low water to binder ratio. Within the C30 cast-in-place concrete facing concentrated leakage water and NaCl crystallizations, a strong magnesium chloride attack is observed. Besides the materials factors, the environmental factors, including the high concentrations of both chloride and magnesium ions, the removal timing of calcium ion, and the water saturation, are believed to take responsibility for the magnesium chloride attack.

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## 1. Introduction

Concrete is a multiphase, porous, and basic material. It is thermodynamically unstable when subjected to aggressive aqueous environments [1,2]. Chemical and mineralogical alterations take place, thus leading to degradation or deterioration. The concretes in the underground tunnel structures are directly exposed to aggressive underground water or water saturated soils, so they usually suffer from potential chemical attacks. The most widely reported types of chemical attacks in these structures are sulfate attack, including thaumasite sulfate attack. Case studies were well conducted in Northern Europe [3–7], as well as in China's western regions [8,9]. Usually, one side of the concrete in tunnel structures are buried with earth. Deterioration potentially occurs where aggressive water comes into contact with the concrete. Hence, reference [3] is an example where water acted from the inner part of the tunnel only, whilst reference [5] is an example where the main degradation of shotcrete took place from the rock mass

behind. In this respect, the degradation of concrete in tunnel structures is difficult to find and study, but it is of great importance.

In aggressive aqueous environments, the chemical attack of concrete—type, depth, speed, and durability—is a complex issue [10,11]. On one hand, it is highly dependent on the environmental factors. For example, in marine environments, typical kinds of chemical attacks, depending on the concentrations of aggressive ions, range from chloride attack (causing corrosion of reinforcing bars) [12,13], sulfate attack [13], thaumasite sulfate attack [7], sulfate magnesium attack [14], and carbonation [15]; while the depth and speed of certain attacks, depending on water velocity, pressure, and moisture, also vary in atmospheric zones, tidal zones, and submerged zones [12,16–18]. On the other hand, the durability of concrete against chemical attacks not only relates to environmental factors, but also to the materials. This viewpoint is highly confirmed in Ref. [19] by observing an inappropriate use of sulfate-resisting cement (ASTM C150 Type V) in a typical sulfate magnesium environment. Contradiction also appears when discussing the effect of supplementary cementitious materials (SCMs) in this environment: the reduction in permeability and the refinement of pore structure are believed to benefit the sulfate magnesium resistance, while the

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complete consumption of calcium hydroxide seems not to make any improvements [13,19–22].

Due to the complexity of chemical attacks, field or in-situ researches are always important to the findings of laboratory studies. On one hand, laboratory studies usually add some extra conditions to accelerate the attacks, e.g. high concentrations [1], auxiliary ingredients [23–25], wet/dry cycles [26,27], or electrochemical techniques [28–30]. Since the side effects of these accelerating methods are probably unknown, they may change the course and mechanism of the attack. A typical example lies in the inappropriate use of magnesium sulfate solutions in the earliest studies on sulfate attack [31,32]. On the other hand, some factors that are believed to be less important are always ignored, but they may also influence the attacks and cause serious problems. Our knowledge on thaumasite sulfate attack explains this point of view: in-situ investigations have made great contributions to unveil the severity, as well as the relation with low temperatures and delivery of carbonates [33–36].

This paper provides a study on the chemical and mineralogical alterations of concrete in underground metro tunnel structures. These tunnels were built from 1980 to 1996, and are the earliest built metro tunnels in China. Located in the seashore area, the underground water contains chloride, sulfate and magnesium. The low concentrations of these ions were once treated to be almost not aggressive by the materials scientists and civil engineers, which is also confirmed by the current Chinese standards [37,38]. However, due to the complex environments in the tunnels, continuous leakages of underground water and severe enrichments of aggressive ingredients were observed in the field investigations. Core samples on certain leakage and enrichment areas were drilled, and the chemical and mineralogical alterations of the concrete were studied. Based on the test results of scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS), X-ray diffractometry (XRD), and X-ray fluorescence spectrometry (XRF), various kinds of chemical attacks were found, mainly including chloride attack, calcium leaching, magnesium attack, and magnesium chloride attack. By comparing the different environmental and materials characters, factors causing the diversification of the chemical attacks were further analyzed.

## 2. Background information

### 2.1. Field investigations

The concrete samples in this study were cored from underground metro tunnel structures in a city on the China's east seashore. The constructions of the tunnels last from 1980 (earliest trial constructions) to the recent years. From 2015 to 2016, field investigations were conducted on eight different tunnel sections (a section is about 1 km–2 km long). During the field investigations, structural problems were found and recorded, and in-situ measurements were conducted. Generally, most of the concrete structures were in good conditions, and deteriorations were scarcely observed. However, a small number of structural problems existed, due to the complex environments in the tunnel structures. The most widely observed structural problems were water leakages located in concrete cracks and structural joints, and salt crystallizations caused by aggressive ions enrichment. Based on in-situ test results and the observed structural problems, several core samples were drilled. These samples were then detailed tested in the laboratory. The results showed different types of potential or existing chemical attacks. The authors have made careful comparisons among these samples, and presented four cases that can reflect the types of the observed chemical attacks which are caused by typical environmental and materials factors.

### 2.2. Selected cases

The concrete structures in the four selected cases were constructed in 1991 (Case 1), 1980 (Case 2), 1990 (Case 3), and 1996 (Case 4), but the starting time of the structural problems which had caused the attacks could not be confirmed. Therefore, these cases were classified on the basis of the environmental and materials factors, causing typical types of attacks (to be discussed in section 4). The speeds of these attacks would not be discussed quantitatively in this paper.

Case 1 reflects a most commonly found structural problem of the pre-cast shield segments. As shown in Fig. 1(a), the underground water percolated in tiny streams through the structural joint between two segments. Due to the low humidity in the tunnels (to be shown in section 2.3), water evaporated fast, and salts crystallized on the surface of the segments along the joints. The concrete underneath the deposit was cored and studied as Case 1.

Case 2 shows a pre-case concrete segment suffering from flowing water. As shown in Fig. 1(b), water percolated through an embedded part, flowed down through a steel suspension link, and finally to the concrete surface. Different from Case 1, no crystallized salts were found. The leakage water seemed to be changing with the underground water level or the soil moisture content, so no flowing water was observed during the field investigation. The concrete surface was rough and loose. It was covered with a thin layer of rust produced by the steel suspension link. The concrete was cored as Case 2.

Case 3 is about a cast-in-place concrete wall located about 60 m near the exit of a tunnel, as shown in Fig. 1(c). A small crack can be observed and water percolated inside. The leakage was still on, and a thin water film could be found on the surface of the concrete. The concrete suffering from this flowing leakage water was cored.

Case 4 is a cast-in-place concrete in the drainage system at the bottom of a tunnel. This site has been investigated twice. During the first investigation, a leakage point covered with yellow pouring mud could be found, and the drainage system was filled with water, as shown in Fig. 1(d). The aggressive ions in the water had been concentrated due to the water evaporation, which will be shown in section 2.3. In the second investigation, leakage stopped possibly due to the variation of underground water level or the soil moisture content, and the concrete of the drainage system was covered with a thick layer of black deposits. When these deposits were knocked off, a big number of salt crystallizations could be found near the concrete surface, as is shown on the top right picture of Fig. 1(e). The cement matrix of the concrete on the outmost 5 mm–10 mm layer appeared to be white and non-cementitious, and could be easily peeled off, as shown on the below right picture of Fig. 1(e). The loose paste and peeled aggregates were collected, and the concrete below was cored as Case 4. It should be noted that the peeling of the concrete usually relates to some serious chemical attacks. However, this should be treated as a local problem concerning the materials in this case, because the deterioration of the concrete in the drainage system will not evidently affect the structural performance of the tunnels.

### 2.3. Air conditions

As has been described in section 2.2, the concrete structures in Case 3 locate near a tunnel exit, so the air conditions are believed to be similar to those in the open air. According to the data [39], the month average temperature in the city ranged from 4.3 °C to 28.2 °C from 1981 to 2010. The temperature seldom falls below zero, so freeze-thaw cycles scarcely happen. The rainfall is sufficient, and the month average relative humidity ranged from 74% to 82% [39].

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