Research Article

Estimation of the Occurrence Time of Thaumasite Sulfate Attack on Tunnel Lining Concrete

Chongbang Xu,1,2 Xiaojing Gao,1,2 Xuefeng Li,1,2 and Kaishun Zhang3

1Bridge and Tunnel Research Center, Research Institute of Highway Ministry of Transport, Beijing 100088, China
2Research Institute of Highway Ministry of Transport Research and Development Center of Transport Industry of Technologies and Equipments for Intelligent Design, Construction and Maintenance of Underwater Tunnel, Ministry of Transport, Beijing 100088, China
3The 5th Engineering Co. Ltd. of China Railway 11th Bureau Group, Chongqing 400037, China

Correspondence should be addressed to Xiaojing Gao; xiaojing.gao1990@foxmail.com

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The thaumasite sulfate attack (TSA) on tunnel concrete structure has been reported increasingly in the past decades. Previous investigations on the formation of thaumasite were focused on identifying the deterioration products and reaction mechanisms, while the occurrence time of TSA on tunnel concrete structures was not reported. A highway tunnel exposed to TSA was reported in the present study. The development of tunnel diseases and results of experimental tests conducted in the tunnel and in the laboratory were analyzed to investigate the occurrence time of TSA on concrete. Results revealed that the thaumasite was formed in a range of 18 to 36 months after the construction of Dugongling tunnel. The preconditions for the formation of thaumasite on tunnel concrete structures are available in Shanxi Province, China, due to the special conditions of stratum lithology and climate. The compositions of corrosion products of lining concrete under TSA varied for site studies and for laboratory tests. Site investigations on TSA on tunnel lining concrete should be paid more attention in further research.

1. Introduction

The rapid economic development urges the construction of high-speed transportation in China. Due to the different environment and geological conditions, there exist various geologic hazards. Some of the hazards are related to the rock masses (including the discontinuities) [1–5], and others are related to the engineering structures (such as the concrete). Sulfate attack has a significant effect on the long-term durability of concrete, which has been largely studied in the concrete industry. The formation of sulfate can generate expansion, cracking, spalling, loss of strength, and severe degradation. Generally, conventional sulfate attack on cement-based materials refers to the formation of corrosion products including ettringite and gypsum [6]. However, thaumasite sulfate attack (TSA) is another type of sulfate attack, which is greatly different from other sulfate attack types and has been widely investigated over the past years [7–10].

Thaumasite, \( \text{Ca}_6[\text{Si(OH)}_6]_2 \cdot (\text{SO}_4)_2 \cdot (\text{CO}_3)_2 \cdot 24\text{H}_2\text{O} \), is a naturally occurring mineral and can be artificially synthesized in the laboratory under proper conditions. As a special form of sulfate attack, the thaumasite is typically formed according to the sulfate ions reacting with calcium silicate hydrates (C-S-H) gel in hydrated paste. Excessive thaumasite formation transforms cementitious material into a mushy, noncohesive gray-white mass without any binding, resulting in a loss of strength on cement-based materials [8]. Compared with the ordinary type of sulfate attack, TSA leads to more serious damage to concretes or mortars and has been increasingly reported [11].

Given the danger of TSA on concrete structure, the composition, mechanism, and influencing factors were widely investigated. There are two different formation mechanisms of TSA. One is the direct formation, and the thaumasite is formed through the reaction among C-S-H, calcite, unbound sulfate ions, and moisture [12–14]. For the
indirect formation, the thaumasite is formed through the reaction among ettringite which forms first, C-S-H, carbonate, and water [15]. In the presence of carbonates in the cement-based materials with abundance of water in a low-temperature environment, the formation of thaumasite will occur [16–18]. Results of field and laboratory tests show that the extent of TSA depends on multiple critical factors including type and concentration of sulfate, change of temperature, relative humidity, type of cement, inclusion of limestone materials, and type and dosage of supplementary cementitious materials [19]. The cool and wet conditions provided in underground buildings and tunnels are favourable to the formation of thaumasite, which result in increasing reports about TSA damaged concrete structures in tunnels [10].

TSA on the tunnel concrete lining can cause the degradation of concrete material and a decrease in the integral bearing capacity, and the reduced safety reliability of the tunnel structure after degradation [20, 21]. The occurrence of TSA has been reported for tunnel concrete structures in Germany, Norway, Switzerland, China, Korea, and Austria [22–25]. Field studies in tunnels were conducted to investigate the mechanisms of thaumasite formation, reaction processes of TSA, and mineralogical composition of damaged concrete materials. Tunnels are considered as the important structure of transportation infrastructure. Due to the implementation of the China Western Development Strategy, an increasing number of road and railway tunnels under the condition of complicated geology are being constructed. Erosive substances, for instance, gypsum and anhydrite widely exist in the formations of Western China [26]. The special stratum in Western China may increase the occurrence of TSA on tunnel concrete structures. The severity of concrete deterioration is related to the risk of failure of the construction and to the costs of repair. The costs for tunnel renovations are extremely high. It is important to understand the deterioration processes of tunnel concrete structure and determine the occurrence time of thaumasite in order to initiate protective countermeasures against TSA.

In this research, the instance of a tunnel concrete structure suffered from TSA in Western China was introduced. The damage of this tunnel was observed for a long time, and experimental tests in the tunnel environment and in the laboratory were conducted to investigate the occurrence time of TSA on the tunnel concrete. X-ray powder diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy were applied to identify and quantitatively analyze the compositions of concrete corroded by sulfate attack.

2. Overview of the Tunnel Project

Dugongling tunnel is located in Pingshun County, Shanxi Province, China, with a design velocity of 80 km/h. The tunnel is a double-route tunnel and the distance between the two routes is 27 m. The total length of the left tunnel and the right tunnel are 2474 m and 2515 m, respectively. The maximum buried depth of tunnel is approximately 231 m. The pile numbers of the left tunnel and the right tunnel are from ZK 33 + 226 to ZK 35 + 700 and from YK 33 + 227 to YK 35 + 742. A curved section with 3 centers of circles was adopted to construct the inner contour of the tunnel, as shown in Figure 1. The net width of the tunnel is 10.25 m.

2.1. Hydrogeological Conditions. The strata of Dugongling tunnel are mainly composed of loessial silt and gravelly soil of Quaternary Holocene (Q4t+p1), mudstone of Benxi formation in the Middle Carboniferous (C2b), and marlstone and limestone of the upper Majiagou formation in the Middle Ordovician (O2S1 and O2S2) [27]. The marl stratum contains irregular gypsum. In order to obtain the distribution of marble rock containing gypsum, the composition of minerals in rock which was drilled from the tunnel surrounding rock were analyzed, as shown in Figure 2. Total 225 rock samples taken from 121 tunnel sections were measured. The measured results show that the composition of tunnel surrounding rocks are calcite, quartz, dolomite, plagioclase, potash feldspar, gypsum, and anhydrite. The percentage of gypsum and anhydrite in sample of tunnel surrounding rock can be as large as 90%. Among the 225 rock samples, there are 67 rock samples containing anhydrite. Among the 121 tunnel sections, it is found that the surrounding rock in 42 tunnel sections containing anhydrite. The distribution of these sampled tunnel sections containing anhydrite is discontinuous. Considering the complexity of formation lithology, it can be concluded that the development of gypsum rock in the longitudinal direction of Dugongling tunnel is irregular.

The area of Dugongling tunnel belongs to midtemperate semiarid continental climate. The temperature and rainfall of Pingshun County, where the Dugongling tunnel is located, were measured from 2013 to 2017 and from 2010 to 2017, respectively. The average temperature of every month is shown in Figure 3. The temperatures of three months were recorded between 5 to 15°C which are favorable to the occurrence of thaumasite. The average rainfall of every month is shown in Figure 4 which indicates that rainfall mainly accumulates between May and September. The annual rainfall of 582 mm can provide abundant water for sulfate attack on tunnel concrete structures. The main type of groundwater of tunnel area contains carbonate fracture, karst water and perched water, which directly affect the moisture content of surrounding rock.

2.2. Tunnel Disease Conditions. In addition to the softening and swelling characteristics, the gypsum rock presented significantly corrosive characteristics on tunnel reinforced concrete, as shown in Figure 5. When the groundwater flows through gypsum strata, it carries a lot of sulfate ions which react with hydrated calcium aluminate to form ettringite. This poses a sulfate attack on the tunnel concrete structures and leads to corrosion expansion, strength loss, reduction of structural bearing capacity and damage on tunnel concrete structures.

The occurrence of thaumasite form of sulfate attack on concrete requires a source of sulfate, carbonate, abundance of water, and low temperature [9]. Considering the formation lithology and hydrogeology of Dugongling tunnel,
the preconditions for TSA are present in this tunnel. Excessive thaumasite formation transforms tunnel lining concrete into a pulpy and noncohesive gray-white mass, which leads to serious damage to tunnel concrete structures.

The construction of Dugongling tunnel was started in March 2010 and completed in December 2011. Tunnel diseases such as lining cracks and cable trench movement gradually appeared after the tunnel has been constructed, as shown in Figure 6(a). The length of the damaged tunnel is 1447 linear meters after about 5 years from the completion of tunnel. Tunnel damages, such as lining cracks, spalling, and swelling deformation, continued to develop in the process of tunnel renovations, as shown in Figure 6(b). The exposed humid concrete of initial lining behaves like soft pulp, which

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**Figure 1:** Typical cross-section for Dugongling tunnel (unit: cm).

**Figure 2:** Core selection scheme and field photo.

**Figure 3:** Temperature of Dugongling tunnel site.

**Figure 4:** Rainfall of Dugongling tunnel site.
indicated that the strength of concrete decreases significantly.

The XRD test was performed to determine the composition of the corroded concrete which behaves like soft pulp. From Figure 7, the main composition of the corrosion products collected from the damaged lining concrete are gypsum, calcite, ettringite, thaumasite, quartz, and dolomite. It is found that the TSA occurred on the tunnel lining concrete.

3. Estimate the Occurrence Time of TSA by Development of Tunnel Diseases

Considering the preconditions for TSA, it is found that the TSA on the lining concrete of a tunnel section will not occur until the construction of this tunnel cross-section has been finished. Two sections of Dugongling tunnel were selected to estimate the occurrence time of TSA on concrete structures based on the development of tunnel diseases and the construction dates of tunnel cross-sections.

The main development of tunnel diseases is as follows:

(1) Longitudinal cracks of secondary tunnel lining (Figure 8) occurred in the left tunnel at sections from ZK 34 + 935 to ZK 35 + 180 and in the right tunnel at sections from YK 34 + 800 to YK 35 + 005 in March 2012.

(2) In December 2012, longitudinal cracks and floor heave appeared on pavement in the left tunnel at sections from ZK 35 + 260 to ZK 35 + 300. Cracking of secondary tunnel lining were continuously developing in the right tunnel (Figure 9) at sections from YK 34 + 810 to YK 34 + 840 and from YK 34 + 955 to YK 34 + 985.

(3) In November 2013, tunnel diseases, such as lining cracking, floor heave, and movement of cable duct, became serious in the left tunnel (Figure 10) at sections from ZK 34 + 300 to ZK 34 + 400 and from ZK 34 + 700 to ZK 35 + 550, in the right tunnel at sections from YK 34 + 450 to YK 34 + 650 and from YK 34 + 700 to YK 35 + 250. The tunnel structures suffered from severe damage and led to the Dugongling tunnel closing.

Based on the development of tunnel diseases, two assumptions were made:

(1) The occurrence time of thaumasite formation in tunnel lining concrete was ranging from December 2012 to November 2013 because the tunnel concrete structures were seriously damaged during that time.

(2) The section ZK 35 + 260 in the left tunnel and the section YK 34 + 820 in the right tunnel were selected as the typical sections to predict the occurrence time of TSA on tunnel lining concrete.

Based on the dates when TSA appeared and the constructions of the typical sections of tunnel were finished, the occurrence time of TSA on tunnel lining concrete for section ZK 35 + 260 and YK 34 + 820 are in a range of 25–36 months and in a range of 18–30 months, respectively, as shown in Table 1. The earliest time that TSA appeared on Dugongling tunnel was selected as 18 months. Results of the composition of tunnel surrounding rock show that the distribution of gypsum rock varies with the tunnel section. Also, the natural water content of tunnel surrounding rock is different for different tunnel sections. Therefore, the time of TSA on lining concrete varies with the tunnel section. In order to reduce the error between the actual time and the

Figure 5: Corrosion of tunnel lining concrete.

In March 2010, the construction of Dugongling tunnel started from the entrance and exit. In December 2011, the construction was finished in the middle of the tunnel. The construction time of Dugongling tunnel is 21 months. The average construction speed is 119 m/month, and the average construction speed of the left tunnel or the right tunnel is 59.5 m/month. The distance between the typical section ZK 35 + 260 in the left tunnel and tunnel portal is 440 m, and the distance between the typical section YK 34 + 820 in the right tunnel and tunnel portal is 992 m. The construction dates of the typical sections ZK 35 + 260 in the left tunnel and YK 34 + 820 in the right tunnel were finished in November 2010 and June 2011, respectively.
estimated time, a wide range of time was selected. The minimum and maximum value of the occurrence time of TSA on the two tunnel sections were selected and the occurrence time of TSA on Dugongling tunnel was estimated as a range of 18 to 36 months after the tunnel section has been built up.

4. Estimate the Occurrence Time of TSA by Experimental Tests

Experimental tests were conducted in the tunnel and in the laboratory to investigate the occurrence time of TSA on tunnel lining concrete. The mix proportion and materials of concrete tested in the tunnel environment are the same as those of Dugongling tunnel lining concrete, as shown in Table 2. A P·O type 42.5 Portland cement, limestone sand, and limestone with diameter ranging from 5 to 10 mm, and polycarboxylate superplasticizer were used to prepare concrete specimen in the experimental study. The mix ratios of cement to coarse and fine aggregate was 1:2.3:2.6, respectively. The w/c ratio was 0.5.

4.1. Experimental Test in Tunnel. The concrete paste were cast into a mould with dimensions of $100 \times 300 \times 400$ mm (Figures 11(a) and 11(b)) and stored at a moist environment for 24 h. After that, the concrete together with the mould were cured under the standard conditions of $20 \pm 2^\circ C$ with a relative humidity less than 95%. After curing, the concrete was cut into cube specimens with dimensions of $100 \times 100 \times 100$ mm. The concrete specimens were soaked in a plastic box which contained gypsum rock and water obtained from the tunnel drainpipe (Figure 11(c)). The gypsum rock was the waste slag rock from tunnel excavation, in which the percentage of gypsum was larger than 90%. The plastic box was put in the tunnel to keep the actual environmental temperature.

The appearance of concrete samples was carefully observed every two months. Obvious corrosion was not
Figure 7: XRD pattern of tunnel lining concrete under TSA.

Figure 8: Longitudinal cracks of secondary tunnel lining.

Figure 9: Tunnel diseases in December 2012. (a) Floor heave. (b) Longitudinal cracks on pavement.
observed on the concrete appearance after 10 months (Figure 12(a)), while phenomena including local separation and spalling were observed after 16 months and 20 months, as shown in Figures 12(b) and 12(c).

FTIR was used to identify the composition of corrosion products of concrete under sulfate attack. The FTIR spectra of immersion samples for 16 months and 20 months are shown in Figure 13. $[\text{SiO}_6]$, $\text{CO}_3^{2-}$, and $\text{SO}_4^{2-}$ are the characteristic peaks of thaumasite. Typically, the variation peaks at 500 cm$^{-1}$, 670 cm$^{-1}$, and 750 cm$^{-1}$ band are attributed to the characteristic peaks of $[\text{SiO}_6]$ in thaumasite [28]. The peaks of $\text{CO}_3^{2-}$ occur at 875 cm$^{-1}$ and 1425 cm$^{-1}$. The vibration peaks of $\text{SO}_4^{2-}$ are at bonds of 1140 cm$^{-1}$, 1120 cm$^{-1}$, and 600 cm$^{-1}$ [29]. $[\text{AlO}_6]$ is the characteristic peak of ettringite $\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3\cdot26\text{H}_2\text{O}$, indicating that aluminium is coordinated with six hydroxyls. The peaks of $[\text{AlO}_6]$ occur at 450 cm$^{-1}$ and 850 cm$^{-1}$, corresponding to the bending vibration and stretching vibration of $[\text{AlO}_6]$ [30]. From Figure 13, the band at approximately 500 cm$^{-1}$ band revealed that thaumasite was formed on the damaged concrete surface after 20 months. Composition of deterioration products were shown in Table 3 based on the FTIR analysis, which revealed that the time when TSA on tunnel concrete occurred was in a range of 16 to 20 months.

| Typical sections | Finished date of construction | Occurrence date of TSA | Occurrence time of TSA |
|------------------|------------------------------|------------------------|------------------------|
| ZK 35 + 260      | Nov. 2010                    | From Dec. 2012 to Nov. 2013 | Ranging from 25 to 36 months |
| YK 34 + 820      | Jun. 2011                    | From Dec. 2012 to Nov. 2013 | Ranging from 18 to 30 months |

Table 2: Concrete mix proportion scheme (kg/m3).

| Cement | Water | Admixture (limestone powder) | Coarse aggregate | Fine aggregate | Superplasticizer |
|--------|-------|------------------------------|------------------|----------------|------------------|
| 374    | 190   | 48                           | 864              | 974            | 5.64             |

Figure 10: Tunnel diseases in November 2013. (a) Lining cracking. (b) Movement of cable duct.

Figure 11: Preparation and maintenance of concrete specimens in tunnel environment.
4.2. Laboratory Test. Laboratory tests were conducted to investigate the TSA on lining concrete in China Building Materials Academy. To accelerate the speed of sulfate attack on concrete, 10 percent of magnesium sulfate was added in the concrete materials to provide \( \text{SO}_4^{2-} \) which is the precondition for TSA. Concrete specimens were cast into a mould with dimensions of 100 x 100 x 100 mm and stored at a moist environment for 1 day. After that, the concrete specimens were soaked in the water under the conditions of 5 ± 1°C.

The appearance of all concrete specimens was carefully observed every month. The damage of the specimens under sulfate attack at 6, 9, and 11 months was representative. Images of the concrete specimens immersing in water after 6, 9, and 11 months are shown in Figure 14. From the appearances of the concrete exposed to the water containing sulfate ions for 9 months and 11 months, visible cracking and spalling occurred on the surface of the concrete specimens, respectively.

XRD was carried out to analyze the compositions of corrosion products of concrete under sulfate attack after 6 months, 9 months, and 11 months. Figure 15 shows the XRD test results. From Figure 15(a), the deterioration materials generated on the damaged surface of concrete after 6 months were mainly composed of ettringite, portlandite, calcite, C2S, C3S, and C4AF. Figure 15(b) showed that the compositions of the main corrosion products of concrete exposed to sulfate ions after 9 months were quartz, calcite,
Figure 14: Appearance of corroded concrete specimens exposed to sulfate ions in the laboratory. (a) 6 months. (b) 9 months. (c) 11 months.

Figure 15: XRD patterns of concrete specimens exposed to sulfate ions in the laboratory. (a) 6 months. (b) 9 months. (c) 11 months.
ettringite, portlandite, and thaumasite. Results in Figures 15(a) and 15(b) showed that the content of ettringite decreased and the content of thaumasite increased after 9 months compared to the corresponding content after 6 months, suggesting that the thaumasite was formed from ettringite. From Figure 15(c), the content of quartz was greater than the contents of the other deterioration products, revealing that quartz was the main production of TSA on the lining concrete. From Figure 15, the content of ettringite and portlandite decreased with an increase in generation of thaumasite, indicating that ettringite and portlandite were the reactants of TSA. XRD results in Figure 15 indicated that the time when laboratory concrete exhibit TSA was ranging from 6 months to 9 months in present research.

5. Estimate the Occurrence Time of TSA on Dugongling Tunnel Concrete

Results of experimental tests in Figure 15 showed that the occurrence time of TSA on concrete ranged from 6 months to 9 months. The 10 percent of magnesium sulfate in concrete accelerated the corrosion of concrete for laboratory tests. It is reasonable that the time determined by corrosion tests in the laboratory was shorter than that obtained from the analysis of tunnel diseases. Results of corrosion tests proved the rationality of the time estimated by tunnel diseases.

Results of experimental tests shown in Figure 13 indicated that the time when TSA occurred was in a range of 16 to 20 months. The time determined by experimental tests at the tunnel and the time estimated by tunnel disease overlaps by two months. The concretes tested in the tunnel were totally immersed in the engineering water. However, it is not clear if the tunnel lining concretes were totally contacted with the underground water in the actual tunnel engineering environment. Considering the potential influence of immersion conditions, the average of 16 and 20, namely, 18 months were considered as the time that TSA occurred on experimental concrete. Meanwhile, taking the complexity of the stratum lithology of tunnel site into consideration, a wide range of time, 18–36 months, was determined as the occurrence time of TSA on tunnel concrete structure.

The occurrence time of TSA on Dugongling tunnel lining concrete was in a range of 18 to 36 months by considering the development of tunnel disease and results of experimental tests.

6. Conclusions

In this study, the occurrence time of TSA on Dugongling tunnel lining concrete was estimated based on the development of tunnel diseases and experimental corrosion tests conducted in the tunnel and in the laboratory. The main conclusions of this research were obtained as follows:

(1) Gypsum rock existing in stratum, lower temperatures (lower than 15°C), and seasonal precipitation can provide preconditions for TSA in Shannxi Province, China. The occurrence time of TSA on Dugongling tunnel lining concrete was in a range of 18 to 36 months.

(2) The typical tunnel diseases which occurred before the formation of thaumasite on Dugongling tunnel lining concrete were cracking and local expansion. The tunnel lining structures were seriously damaged with the spalling of concrete and floor heave, corresponding to the thaumasite form of sulfate attack.

(3) Results of laboratory corrosion tests indicated that the route for thaumasite formation was indirect, and ettringite acted as the precursor for thaumasite formation. Quartz, calcite, and dolomite were the productions of TSA, ettringite, and portlandite were the reactants of TSA.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare no conflicts of interest.

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