Journal of China University of Geosciences, Vol. 17, No. 4, p. 342 – 348, December 2006 ISSN 1002 – 0705
Printed in China

Sulfate Attack on Concrete in an Inland Salt Lake Environment

Dong Rongzhen* (董荣珍)
School of Civil Engineering and Mechanics, Huazhong University of Science and Technology, Wuhan 430074, China
Ma Baoguo (马保国) **He Xingyang** (贺行洋) **Zhu Hongbo** (朱洪波)
Key Laboratory for Silicate Materials Science and Engineering, Ministry of Education, Wuhan University of Technology, Wuhan 430070, China
Wei Jun (卫军)
School of Civil Engineering and Mechanics, Huazhong University of Science and Technology, Wuhan 430074, China

ABSTRACT: Several cracks were found on the surface of the concrete foundations that support the steel towers of the Luohe (漯河)-Huaiyang (淮阳) high voltage electricity transmission line that is 20 years old and situated in an inland salt lake environment in North China. To analyze the deterioration mechanism that led to this condition, field investigations were carried out and several tests were conducted on the soil and the affected concrete, including XRD (X-ray diffraction), electric probe analysis, and chemical analysis. The results show that the concentration of sulfates is very high (0.39% wt. – 0.67% wt.) in both the surrounding soil and the material around the coarse aggregates inside the concrete. Hence, sulfate attack could be one of the main causes of concrete deterioration. The percentage of sulfates in the surface layer of the concrete was higher than that in the inner layers of the concrete. The sulfates penetrate into the concrete and react with the hydrates of cement to form ettringite (AFt), which leads to increase in the volume and cracking of the concrete.

KEY WORDS: concrete, inland salt lake, sulfate attack.

INTRODUCTION

Sulfate attack is one of the reasons for concrete structures deteriorating earlier than usual, thus showing poor durability. The SO_4^{2-} from the surrounding environment such as ocean, saline, ground water, and even the concrete itself, reacts with the hydration products of cement, which leads to the deterioration of the concrete (Li et al., 2000; Kang, 1995; Neville, 1983; Samarai, 1976). The deterioration includes three processes: the external swelling, cracking, peeling, and disjointing caused by the formation of ettringite and gypsum; strength and hardness reduction because of the dissolution and decomposition of hydrate CH and C – S – H; and structure disintegration because of the formation of thaumasite.

The Luohe-Huaiyang high-voltage electricity transmission line, with a length of 72 km, is located in North China. Four separate concrete foundations, made of grade C15 – C20 concrete, support each steel tower. The transmission line was completed in 1986. Cracking was discovered on most of the concrete foundations of the tower in January 1999. The largest crack had a width of 45 mm and a depth of approximately 60 mm. The Luohe-Huaiyang high-voltage transmission line is located close to an inland salt lake in which the estimated salt content was 4 000 000 t. Because of the proximity to saline water, the concrete foundations are in salt-contaminated soil that contains many harmful ions such as SO_4^{2-}

This paper is supported by China Postdoctoral Science Foundation (No. 2005038542) and National "973" Project (No. 2001CB610704-3).

* Corresponding author: dongrongzhen@126.com

Manuscript received June 28, 2006.
Manuscript accepted September 15, 2006.

?1994-2017 China Academic Journal Electronic Publishing House. All rights reserved. http://www.cnki.net

and Mg^{2+}. Hence, it is likely that the concrete suffers from sulfate attacks (Yu, 1999).

EXPERIMENTAL PROCEDURE

Preparation of Samples

For analysis and research, the concrete foundation of the 220-kV Luohe-Huaiyang high-voltage transmission line was divided into three layers: (1) The surface layer, approximately 0 – 30 mm below the external surface, in which the concrete has cracked. (2) The transition layer, approximately 30 – 60 mm below the external surface, where only a few cracks were found. (3) The body layer, approximately 60 mm below the external surface, which represents the perfect concrete. During the in situ examination, the investigation and analysis of eight concrete foundations along the line was carried out according to the area and the degree of cracks. On the basis of the three-layer classification, four specimens, each weighing 4 kg, were collected from each foundation. In addition, the characteristics of soil, which is the homologous environment surrounding all the concrete foundations, were evaluated. Samples of soil, weighing 2 kg per sample, were taken at a depth of 80 cm near the tower to avoid the influence of washing off of ions by rain water and the loss of ions due to water evaporation. All the collected soil samples were sealed in black plastic bags.

Preparation of Spot Samples for Analysis

The soil sample was dried at (105±5) ℃. A total of 500 g of dry soil sample was taken and dissolved in 1 000 mL of water. The solution was maintained under constant stirring for 24 h to ensure that the SO_4^{2-} ion dissolved completely in the soil.

The coarse aggregates from the concrete sample were ground into powder with a particle size of less than 0.08 mm. A total of 20 – 25 g of the powder was selected by quartation and was dried. One gram of the dried powder was mixed with 10 mL of HCl solution (1 ∶ 1) such that the SO_4^{2-} ion of the aggregate was completely dissolved. The SO_3 content in the coarse aggregate of the concrete sample was determined using the weight method of barium sulfate (see GB/T14685-93).

The sample of hydrated cement paste containing some fine aggregates was obtained after the coarse aggregate was removed from the concrete specimen. The paste was also ground into powder with a particle size of less than 0.08 mm before analysis.

Research Methods

Chemical analysis

Chemical analysis was carried out to measure the SO_3 content of each of the three layers of the concrete foundation to estimate the extent of SO_4^{2-} invasion in the concrete. The content of pure hydrated cement in the component can be obtained by deducting the content of sand that is mixed with it, which is less and constant because of the differences in the grinding property.

X-ray diffraction analysis

X-ray diffraction (XRD) data were collected at room temperature with a RIGAKU D/MAX-RB diffractometer, using graphite monochromated Cu-K_α radiation. The experiment parameters were as follows: *DS* = 1, *SS* = 1°, *RS* = 0.3 mm, scan speed 10 °/min.

Quantitative X-ray diffraction analysis (QXDA) was applied using the equation proposed by Copeland and Bragg (1958) that relates the ratio of the intensities (I_0 and I_1) of the XRD lines of the two components of a mixture to the ratio of the weight fractions (w_0 and w_1) of those components (Ye, 1994)

$$I_0/I_1 = \alpha w_1/w_0 \quad (1)$$

where α is the proportionality constant.

Electronic probe

An electronic probe (JCXA-733) manufactured by JEOL Co. (Japan) was used to analyze the microstructure of the concrete, and the experimental parameters were as follows: accelerating pressure, 20 kV; electric current, 20 mA.

RESULTS AND DISCUSSION

SO_3 Content inside and outside the Concrete Foundation

The rate of the concrete sulfate attack depends on the category, the concentration of the erosion media, and the SO_4^{2-} concentration inside the concrete. The higher the concentration of the eroding ions, the greater the speed of erosion.

Table 1 shows the classification of the degree of erosion based on the concentration of SO_3 in soil and in groundwater according to the related criterion of America (Gong and Liu, 1990).

Table 2 shows the SO_3 content in the soil around the concrete foundation of the Luohe-Huaiyang high-voltage transmission electricity line. The SO_3 concentration in the soil around the concrete foundation is very high and belongs to the moderate or severe ero-

?1994-2017 China Academic Journal Electronic Publishing House. All rights reserved. http://www.cnki.net

sion grade, the SO_3 may diffuse in the interior concrete as SO_4^{2-} ions and cause the sulfate attack. Table 3 shows the extent of damage of the concrete foundation on spot test. It is seen from Tables 2 and 3 that the degree to which cracks occur in the concrete is proportional to the SO_3 content in the environment, i. e. the higher the SO_3 content in the environment, the more severe the cracking. Therefore, a high SO_3 content in the soil around the concrete foundation may be one of the reasons for the cracking of the concrete.

Table 4 shows the SO_3 contents of the coarse aggregates in the concrete foundations. It is seen that the SO_3 contents of all the coarse aggregates are very low and satisfy the related standard (GB/T14685 93), which advocates that the SO_3 content should be less than 1% of the aggregate weight to avoid sulfate attack inside the concrete.

Table 1 Classification of soil containing sulfate

	Erosion degree	Soluble SO_3 in soil (%)	SO_3 in groundwater (ppm)
0	None	0 – 0.10	0 – 150
I	Weak	0.10 – 0.20	150 – 1 000
II	Medium	0.20 – 0.50	1 000 – 2 000
III	Strong	> 0.50	> 2 000

Table 2 Content of SO_3 and the erosion degree of environment soil of the concrete foundation

No.	026A	039B	041A	095A	101C	107D	128A	135B
SO_3 content (%)	0.67	0.56	0.58	0.53	0.42	0.39	0.45	0.42
Erosion degree	Strong	Strong	Strong	Strong	Medium	Medium	Medium	Medium

Note: 026A indicates the A foundation of iron tower No.026, and so on.

Table 3 Details on the cracks recorded in the concrete foundation

	026A	039B	041A	095A	101C	107D	128A	135B
Maximum length of crack (cm)	85	80	80	75	65	60	65	60
Maximum width of crack (mm)	4.5	3.1	2.0	1.8	1.0	0.4	0.5	0.5
Total number of crack	10	8	9	8	6	4	5	3

Table 4 SO_3 contents of the coarse aggregates of the concrete foundation

No.	026A	039B	041A	095A	101C	107D	128A	135B
SO_3 content (%)	0.43	0.38	0.41	0.29	0.35	0.37	0.30	0.50

SO_3 Content of the Concrete Foundation

The content of SO_3 in hydrated cement in the concrete foundations is determined by deducting the aggregate. The results are shown in Fig. 1.

The following conclusion can be arrived at from the details shown in Fig. 1: (1) The content of SO_3 in the surface layer of the concrete foundations is between 4.5% and 5.5%, and there is a rapid decrease in the SO_3 content from the surface layer to the transition layer, whereas the decrease is comparatively slower from the transition layer to the body layer, wherein the SO_3 content is approximately 2.5%. (2) When compared with the SO_3 content of soil, as shown in Table 2, it can be concluded that the SO_3 content in the surface layer of the concrete is related to that in the soil. A high SO_3 content in soil will lead to a relatively high content of SO_3 in the surface layer of the concrete foundations. An analysis of the SO_3 content of the body layer and the surface layer of the concrete foundations shows that the SO_3 content in the surface layer is considerably higher than the permissible levels set by the standard (GB 175 – 92) (< 3.5%) and that the SO_3 content in the body layer according to the criterion and the variation range of the content is 0.3%. Thus, it can be considered that the SO_3 content in the body layer is appropriate for concrete and is not influenced by the soil.

?1994-2017 China Academic Journal Electronic Publishing House. All rights reserved. http://www.cnki.net

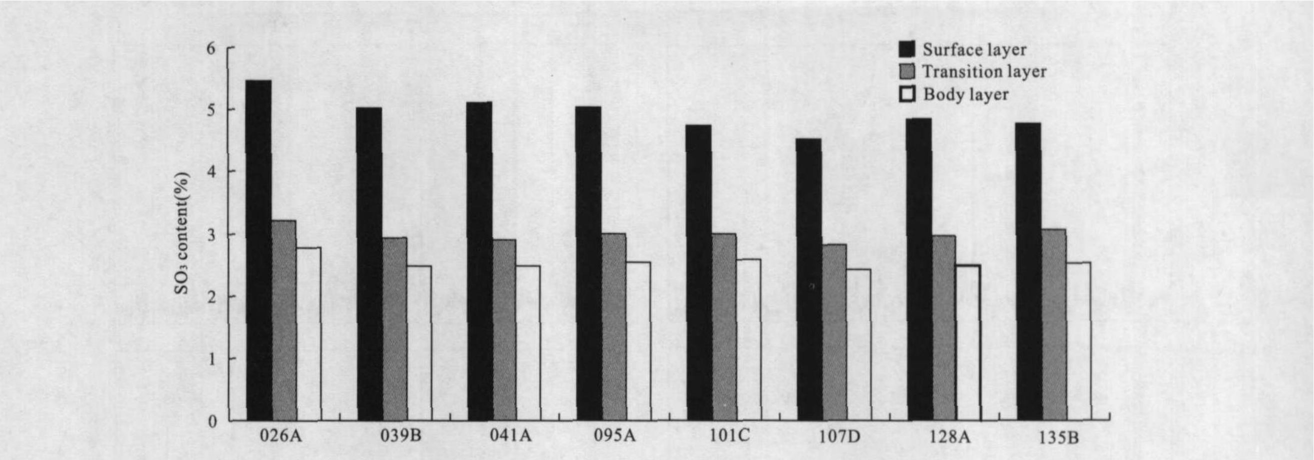

Figure 1. SO_3 **content of the concrete.**

The content of SO_3 in the surface layer increases by at least 2.5% because of the penetration of SO_4^{2-} from the environment. Free water in the concrete foundation and the soil is approximately 2% and 15%, respectively. If the SO_4^{2-} penetrating in the concrete keeps free, then the SO_4^{2-} concentration in the concrete may be seven times that in the soil. According to the principle of diffusion dynamics, ion permeation is nonspontaneous from low concentration to high concentration; hence, the free SO_4^{2-} penetrating the concrete is adsorbed by the products of cement hydration or reacts with them, which leads to a decrease in free SO_4^{2-} concentration and further permeation into concrete from the environment.

Mineral Component of the Concrete Foundation

Powder diffraction patterns from the concrete foundations are shown in Fig. 2. Ettringite was found in each zone, which shows that the SO_4^{2-} penetrating the concrete from the environment reacts with the cement hydration products $C_3A \cdot CS \cdot H_{18}$, $C_3A \cdot CH \cdot H_{18}$, and $Ca(OH)_2$ to convert to ettringite, as shown in the following equation (Taylor, 1990):

$$C_3A \cdot CS \cdot H_{18} + 2CH + 2S + 12H \rightarrow C_3A \cdot 3CS \cdot H_{32} \quad (1)$$

$$C_3A \cdot CH \cdot H_{18} + 2CH + 3S + 11H \rightarrow C_3A \cdot 3CS \cdot H_{32} \quad (2)$$

The relative ettringite content of the different zones of each concrete foundation was estimated using equation (1). The evaluation was carried out using the ratio of the strongest XRD lines of ettringite at $d = 9.7$ Å to the strongest XRD lines of standard mineral at $d = 2.67$ Å. Thus, a set of ratios of the relative weight fraction of ettringite of the specimens was calculated. For convenient analysis, the maximum of the ratio is termed 1 and is divided by the rest in turn and then a group of new relative weight fractions of ettringite is given (see Fig. 3).

The relative ettringite content of the concrete foundations is similar to the SO_3 content in the concrete, which is affected considerably by the SO_3 content of the surrounding soil. The ettringite content of the transition layer is much higher than that in the body layer; however, the situation is reverse between the surface layer and the transition layer. The ettringite is considered to have decomposed under the alkalinity from its stable state ($pH > 10.7$) because of cracking and carbonization. The phenolphthalein test on the plot showed that carbonization occurred partly or entirely in the surface layer, and the pH was lower than 10, in which stable ettringite cannot exist. By comparing Fig. 4 with Table 3, it is seen that the degree of deterioration of the concrete foundations is directly proportional to the ettringite content. The cracks in the concrete foundations are more when the ettringite content is high. Therefore, in the case of the Luohe-Huaiyang high-voltage transmission line, sulfate attack is one of the reasons for the development of cracks in the concrete foundations.

Microstructure of the Concrete

The absorption and the surface state of the aggregate make the water film rise up to the surface of the aggregate in concrete, which results in the formation of a transition zone between the aggregate and the cement stone in hardened concrete. This transition zone is a vulnerable zone that cannot resist the destructive forces or the transmission of harmful ions (Shen et al., 1996).

Figure 4 shows the secondary electron image (left represents aggregate, right represents cement paste). Figure 5 shows the line scan of the chemical

?1994-2017 China Academic Journal Electronic Publishing House. All rights reserved. http://www.cnki.net

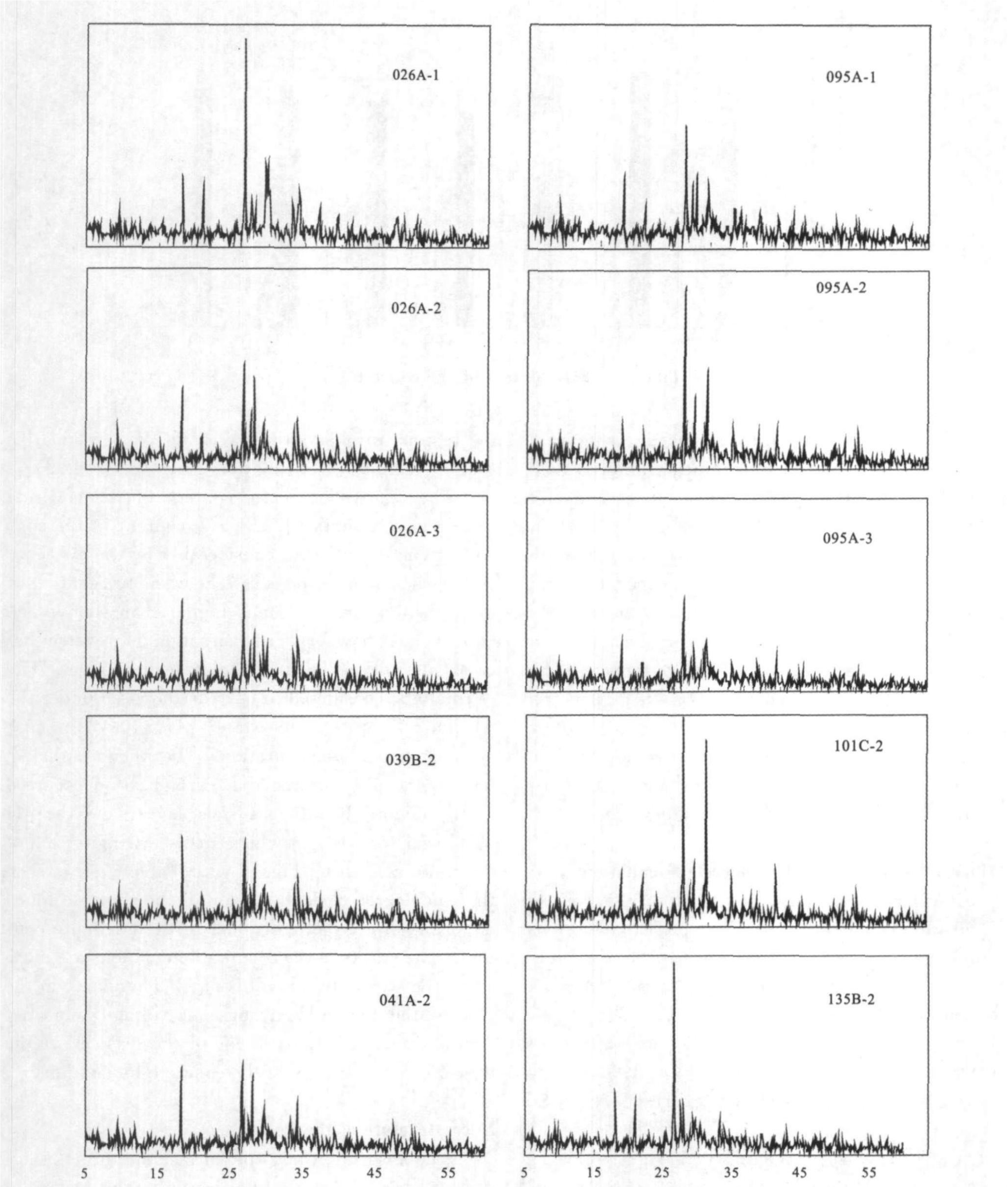

Figure 2. XRD pattern of each concrete foundation.

elements namely Ca, S, and Mg that were identified in Fig. 4. From the figures it can be seen that S and Mg, scanning was from the aggregate to the cement stone, appear in turn in their transition region, i. e. these accumulate in the transition area. There is no obvious peak in the line scans of Ca, which shows that the content in the aggregate (dolomite) and cement is equal. The SO_4^{2-} that permeated from the environment accumulates in the transition region between the cement stone and the aggregate; at the same time, an accumulation of Mg^{2+} that permeated from the environment may occur. By combining with the XRD analysis, it is seen that the expansive ettringite forms in the transition area and leads to

?1994-2017 China Academic Journal Electronic Publishing House. All rights reserved. http://www.cnki.net

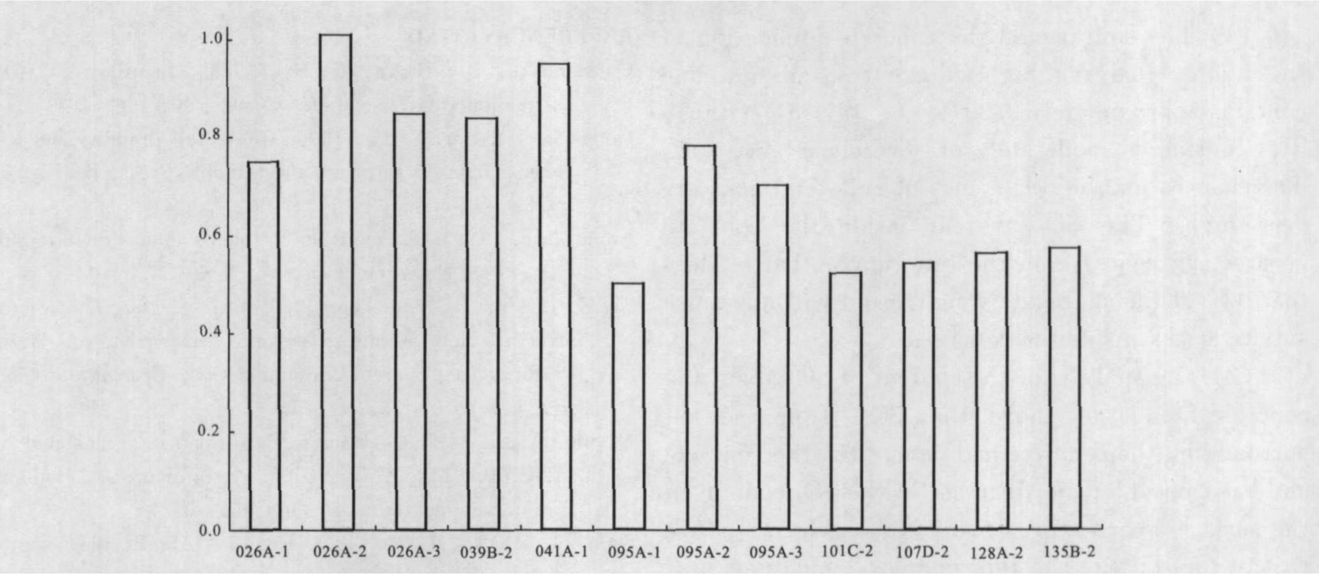

Figure 3. The relative content of ettringite of concrete foundations. 1, 2, 3 are the surface layer, transition layer and body layer respectively.

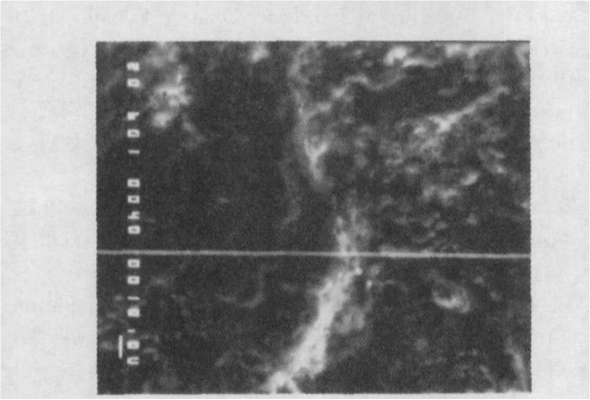

Figure 4. Secondary electron image of transition area (the line is the mark).

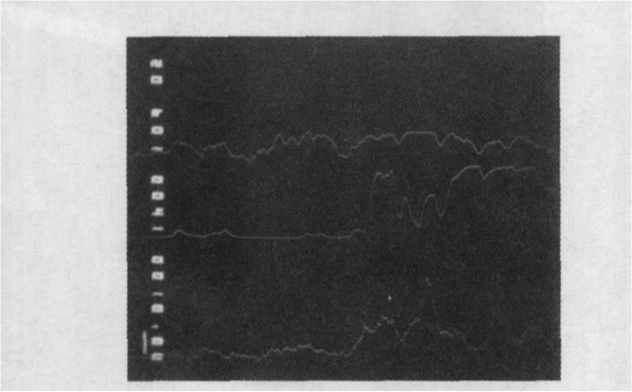

Figure 5. Line scan of Ca, S and Mg elements.

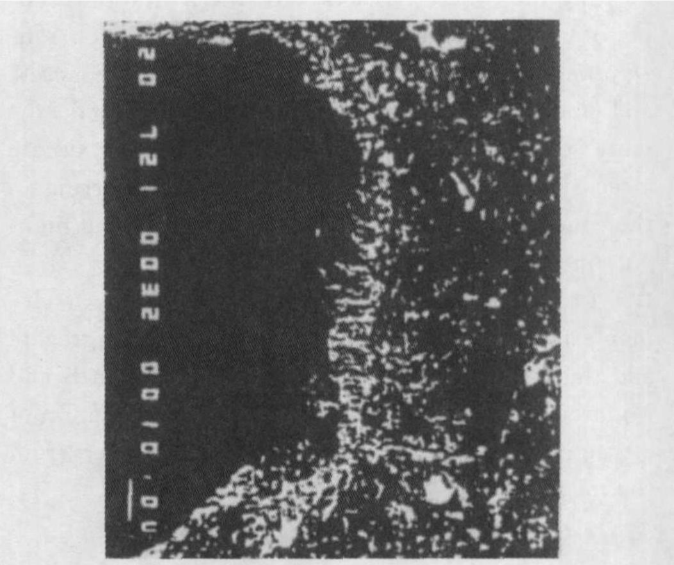

Figure 6. Backscattered electron image of transition area.

cracks when the quantity reaches a certain level because of the accumulation of SO_4^{2-} and the reaction with the cement hydration products. The concrete is peeled off and disintegrated and lowered in strength with the dissolution and decomposition of the hydrate CH and C-S-H. Figure 6 is the backscattered electron image of the concrete foundation No. 026A; several ettringite crystals can be seen in a state of sedimentation around the aggregate, which is caused by the existence of many pores in the transition zone between the aggregate and the cement stone. These pores are the areas where the sedimentation of SO_4^{2-} occurs, and when this sedimentation reaches a certain level, the stress inside the concrete leads to cracking, i.e. the sulfate attack.

CONCLUSIONS

On the basis of the results of this experimental investigation in the inland salt environment, the following conclusions are arrived at

?1994-2017 China Academic Journal Electronic Publishing House. All rights reserved. http://www.cnki.net

(1) The soil around the concrete foundation of the Luohe-Huaiyang high-voltage transmission line contains approximately 0.39% – 0.67% SO_3; thus, it is considered moderately or severely erosive soil. The chances for the occurrence of sulfate attacks are very high. The SO_3 content inside the concrete (coarse aggregate) is in the safe range, that is, less than 1% of the aggregate weight, and will not cause sulfate attack inside the concrete.

(2) The analysis of the content of SO_3 about the concrete foundation shows that SO_4^{2-} from the soil surrounding the concrete had penetrated the concrete and has caused a major increase in the SO_3 content in the surface layer, approximately 5%, which is twice that of the soil close to the concrete foundation.

(3) The XRD analysis of the hydration product of the concrete foundation shows that the SO_4^{2-} permeating the concrete reacts with the hydration product of cement to form ettringite. There is a relationship between the amount of ettringite in the concrete and cracking: the more is the ettringite formed, the more serious are the concrete cracks. Hence, sulfate attack is one of the reasons for cracks occurring in the concrete foundation of the Luohe-Huaiyang high-voltage transmission line.

(4) According to the line scan analysis of elements in the transition zone between the aggregate and the cement stone, the chemical elements S and Mg accumulate in this region and the accumulation of ettringite is very obvious in this area, as seen from the microstructure analysis.

REFERENCES CITED

Copeland, L. E., Bragg, T. H., 1958. Quantitative X-Ray Diffraction Analysis. *Anal. Chem.*, 30: 196 – 201

Gong, L. S., Liu, C. P., 1990. Concrete Durability and Restore. China Architecture and Building Press, Beijing. 51 – 54 (in Chinese)

Kang, J. F., 1995. A Few Basic Problems about Concrete Sulfate Attack Research. *Concrete*, 3: 9 – 17

Li, Z. J., Ma, B. G., Peng, J., et al., 2000. The Microstructure and Sulfate Resistance Mechanism of High-Performance Concrete Containing CNI. *Cement and Concrete Composites*, 22(5): 369 – 377

Neville, A. M., 1983. Concrete Performance. Translated by Li, G. P., Ma, Z. Y.. China Architecture and Building Press, Beijing. 466 – 486 (in Chinese)

Samarai, M. A., 1976. MSC (Eng), MASCE, the Disintegration of Concrete Containing Sulfate Contaminated Aggregates. *Magazine of Concrete Research*, 28: 130 – 141

Shen, Y., Xu, Z. Z., Wu, C. Z., et al., 1996. The Influences of Structure of Interfacial Zone on Sulfate Attack Resistance of Mortar. *Journal of the Chinese Ceramic Society*, 24(6): 119 – 124 (in Chinese with English Abstract)

Taylor, H. F. W., 1990. Cement Chemistry. Academic Press INC, London. 397

Ye, Z. Y., 1994. The Program of X-Ray Quantitative Phase Analysis. *Computers and Applied Chemistry*, 11(3): 184 – 188

Yu, H. D., 1999. State of Art and Development Trend in the Study of Bittern Resisting Concrete. *Journal of the Chinese Ceramic Society*, 27(2): 237 – 245 (in Chinese with English Abstract)

?1994-2017 China Academic Journal Electronic Publishing House. All rights reserved. http://www.cnki.net