THE FAILURE PROCESS OF MORTARS DURING SULFATE ATTACK

Kaiwei Liu[1] - Aiguo Wang[1*] - Daosheng Sun[1] - Yan Li[1] - Jinhui Tang[2]

[1]Anhui Key Laboratory of Advanced Building Materials, Anhui Jianzhu University, Hefei, China
[2]College of Materials Science and Engineering, Southeast University, Nanjing, China

ARTICLE INFO	Abstract:
	External sulfate attacks on concrete structures may cause serious damage and it has attracted a wide range of attention from numerous researchers over the past decades. However, many studies have been concentrated on the sample which has been already destroyed. This paper investigated the entire deterioration process of mortars that were immersed in Na$_2$SO4 solution containing 3 gSO$_4^{2-}$/L and 33.8g SO$_4^{2-}$/l at 20 ^{o}C up to 600 days. The study on time-varying regularity of expansion, cracks, compressive strength and mineral phases was investigated. Back scattered electron image was used to further examine the evolution of microstructures of the mortars during the attack process. The results showed that damage process of mortars can be described as induction stage, surface damage, bulk damage and then completely damage stage. Fine ettringites that were formed in restricted spaces, approximately 2-5 μm, result in surface damage. At the bulk damage stage, cracking was the main characteristic of mortar which leads to obvious expansion. In this stage, some large ettringite crystals (>20μm) were just deposited in the formed cracks. At the later stage, gypsum can be easily formed at interfacial transition zones as the consumption of calcium hydroxide, which mainly contributed to completely strength failure rather than expansion.

1 Introduction

Sulfate attack can be described as a series of chemical interactions that occur between hardened cement paste and sulfates. The degradation of cement-based materials in sulfate-bearing environments has been of concern to concrete technologists since the early 19th century [1-3]. In

most cases, the deterioration that was caused by the sulfate attack resulted in formation of ettringite or gypsum. Sulfate ions can react with tricalcium aluminate, hydrated calcium aluminate, or monosulfate to form ettringite [4]. Sulfate ions also can react with calcium hydroxide to form gypsum. The formation of ettringite or gypsum is

* Corresponding author. Tel.: +86 13637056646
E-mail address: wag3134@126.com.

accompanied by spalling, cracking, softening, expansion and various other forms of damage [5-7]. Due to its complicated mechanisms, research related to the effects of sulfate ions on the products formed in concrete has remained in progress [8]. Generally, expansion that results from sulfate attack is attributed to the formation of ettringite. In addition, several theories have been proposed regarding the expansion mechanisms of ettringite [9-11]. However, it is still a controversy that ettringite crystals observed in cracks are the reason for expansion [12]. Mather [5] believed that the gypsum was formed in the solution and it was therefore non-expansive. However, Tian [13] thought it could lead to expansion. Irassar et al. [14] and Yu et al. [15] tend to support the former with the application of scanning electron microscopy (SEM) in microstructure analysis. Although it remains disputable whether the formation of gypsum leads to expansion, the precipitation of gypsum can lead to the consumption of calcium hydroxide and decalcification of calcium silicate hydrate and cause a strength loss in concrete.

In the existing test procedures, resistance of binders to external sulfate attacks is assessed on the mortar prisms. Different approaches were developed by engineers and researchers over the past century to overcome and understand the mechanisms behind the degradation of concrete by external sulfate sources. Most countries have established national standards to evaluate the sulfate resistance of cement-based materials. Acceleration is often obtained by increasing sulfate concentration: 34g/L in ASTM C1012[16] and NF P 18-837[17], 20.4g/L in GB/T 749[18]. Groundwater or sea water is a natural sulfate source to which buried concrete can be exposed to. However, these waters typically have low sulfate content, usually about 2.7 g/L in seawater, 0.2 to 6 g/L in groundwater. The advantages of obtaining test results in a relatively short period are accompanied by questions regarding the changes that occur during the process of deterioration [19]. Skalny [12] described that gypsum become an issue at sulfate concentrations above 3g/l. Santhanam [20] also thought that the mechanism of sulfate attack could be changed with a change in the concentration of sulfate solution. So, sulfate concentration may be an important impact on the deterioration mechanism.

In this study, mortars prepared with Portland cement containing 6.6% C_3A were immersed in sodium sulfate solutions for up to 600 days. The two levels of the sulfate concentration (3g/L and 33.8g/L) have been taken into account to investigate the phase changes (Portlandite, ettringite and gypsum) and microstructure evolution throughout the entire attack process. Macro-performances on specimens are further studied at different periods. These results are of great importance for the understanding of deterioration mechanism of structures submitted to sulfate attack in different conditions.

2 Experimental

2.1 Materials

Portland cement PII42.5R (GB) manufactured by China Cement Corporation was used to prepare the mortar specimens. The quartz sand was used for the mortar mixture with a particle size of 0.5 mm-1 mm. The chemical composition of the cement is shown in Table 1. The analytical reagent anhydrous sodium sulfate was used to prepare the sulfate solutions.

2.2 Specimen processing

According to GB/T 749 (2008), the mortar specimens were cast with a cement: sand ratio of 1:2.75 and a water to cement ratio of 0.65. All of the specimens were demolded after casting in the molds for 24 h and then cured for 28 days in limewater at 20±2°C. Thereafter, the samples were immersed in the Na_2SO_4 solutions for up to 600 days at 20°C and the solutions were exchanged every month. The length change and the compressive strengths of the specimens with the size of 25 mm × 25 mm × 280 mm and 40 mm × 40mm × 160mm were recorded at regular intervals.

2.3 Test methods

In addition, X-ray diffraction (XRD) was conducted on powder sample using an ARL X' TRA diffractometer with Cu Kα radiation. Scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS, JSM-5900, S-3400N) was used to investigate the microstructure.

Table 1. *Chemical composition of Portland cements /wt.%*

Material	SO_3	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	K_2O	Na_2O	L.O.I.
Cement	2.78	21.98	3.33	4.62	63.18	0.81	0.94	0.19	1.34

3 Results and discussion

3.1 Physical aspects

From visual examination of mortars after 450 days' exposure in Na_2SO_4 solution of 33.8 g/L (Fig. 1), the samples show obvious expansion and cracking. The sample in Na_2SO_4 solution of 3 g/L showed slight cracking at the edges and the reference sample appear no affected. Surface cracks are the main migration paths of sulfate ions and the formation and evolution of cracks obviously affected the ingress rate of sulfate ions even durability of structures. So, it is very important to pay attention to the change of cracks during the entire attack process. The surface cracks of mortars at different immersion time were studied with nondestructive testing by optical microscope (Fig.2). With the increase of immersion time, the cracks progress from the surface of the sample towards the bulk. Many more cracks were formed on the surface, and the sample shows a disintegration of the surface.

Figure 1. *Appearance of the mortars after immersion in the Na_2SO_4 solutions for 450 days.*

In addition to the surface change, expansion was measured to describe damage of the bulk, as shown in Fig.3. The length changes of the reference samples immersed in water showed no obvious changes. The sample immersed in Na_2SO_4 solution of 3 g/L showed steady and slow expansion. The expansion of the samples was still significant after

600 days of exposure. The accelerating expansion pattern of the mortars was observed following 210 days' immersion in Na_2SO_4 solution of 33.8 g/L. The mortar immersed in 33.8 g/L sulfate solution suffered greater expansion, and this might be because more sulfate ions can permeate and diffuse into the inner part to form expansion products. The lengths of the mortars could not even be measured because the nail heads of all three samples fell off at 500 days.
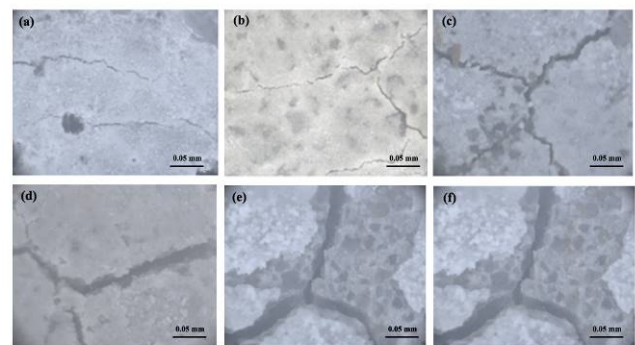

Figure 2. *Surface cracks of mortars immersed in 5% Na_2SO_4 solution for different periods (a)90d (b)150d (c)210d (d)360d €450d (f)600d.*
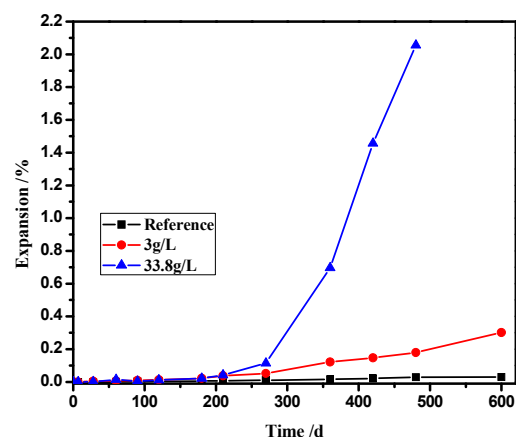

Figure 3. *Expansion of mortars immersed in the Na_2SO_4 solutions for different period.*

Fig. 4 shows the compressive strengths of the mortars after immersion in Na_2SO_4 solutions for different periods. The specimens immersed in

solutions of 3g/L and 33.8g/L showed greater strength than the referenced one after 60 days of immersion. This might be attributable to the space filling with the formation of ettringite in pores at the initial stage. The compressive strengths of the reference samples immersed in the limewater show an increase due to hydration. When the samples were exposed to the Na_2SO_4 solutions, hydration and deterioration from sulfate ingress had competitive effects on the compressive strength. The samples that were immersed in sulfate solutions of 3g/L had slightly greater compressive strengths before 210 days, and then, a slight loss in compressive strength was observed. The samples that were immersed in the accelerated test solution (33.8g SO_4^{2-}/L) had a greater compressive strength at 90 days, and then, a slight loss of compression was observed. After 210 days of immersion in the test solution, a large decrease in the compressive strength was observed. These results indicated that the immersion of the samples in the accelerated test solution accelerated the destruction of the mortars due to sulfate attack.
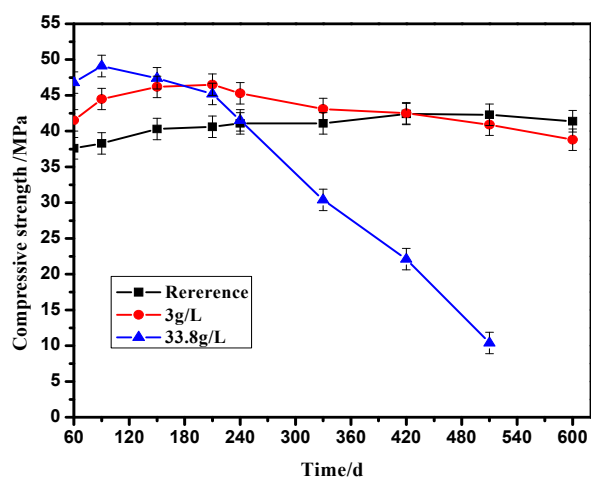

Figure 4. Compressive strengths of mortars immersed in the Na_2SO_4 solutions for different periods.

3.2 The products formed during sulfate attack

The XRD patterns of the mortars that were immersed in sulfate solution of 3 g /L for 150, 210, 360 and 600 days are shown in Fig. 5.
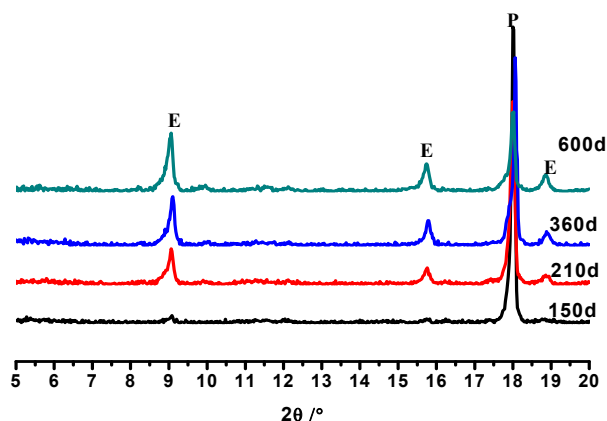

Figure 5. XRD patterns of the mortars after immersion in solutions containing 3g SO_4^{2-}/L for different periods (P: portlandite; E: ettringite).

In this diagram, quartz peaks were avoided by focusing on the patterns between 5°-20° to show the changes in the compounds during sulfate attack. Three X-ray diffraction angles (Cu Kα, 2θ) were used to characterize the phases: ettringite at 9.1, gypsum at 11.6, and Portlandite at 18.0. After 90 days of exposure, only Portlandite was detected and no visible ettringite diffraction peak was observed. Ettringite diffraction peak was observed obviously when the mortars were immersed in the solution for longer, such as 210, 360 and 600 days. However, no gypsum was detected in the mortar even it was immersed in the solution for up to 600 days. These results indicated that sulfate ions diffused into the mortars continuously and reacted with the Al-phase to form ettringite rather than forming gypsum at the low sulfate concentration of 3 g/L.

Fig. 6 showed the XRD patterns of the mortars after immersion in sulfate solution of 33.8 g/L for 150, 210, 360 and 600 days. This XRD pattern shows that gypsum peak was detected after 210 days of immersion. The result indicated that higher sulfate concentration in the solution was favorable for the formation of gypsum. Additionally, the peaks of ettringite and gypsum can be observed obviously while the peak of Portlandite was obviously decreased in the mortar at 600 days of immersion compared with the 150 days of immersion.

3.3 Microstructure of the mortars

Fig. 7 shows the microstructures of the mortar after immersion in sulfate solution of 33.8 g/L for 360 days. Bundles of needles ettringites were observed

surrounding the cement particles (mainly Al-phase) in the mortar. These fine ettringite crystals were approximately 2-5 μm and destroyed the matrix microstructure, which can result in expansion and cracking when they grew towards the surrounding solids. It can be conducted that sulfate ions firstly reacted with the Al-phase in the surface layer. The formation of ettringite can cause the formation of gaps between the pastes and aggregates due to the expansion of the paste. The presence of cracks potentially accelerated the diffusion and deterioration because they provided direct pathways for the diffusion of sulfates ions into the mortar.
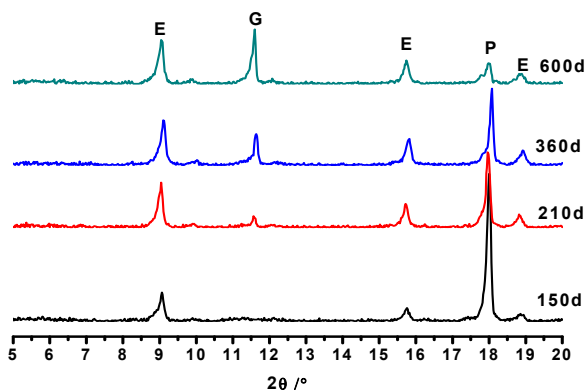

Figure 6. XRD patterns of the mortars after immersion in solutions containing 33.8 g SO_4^{2-}/l for different periods (P: portlandite; E: ettringite; G:gypsum).
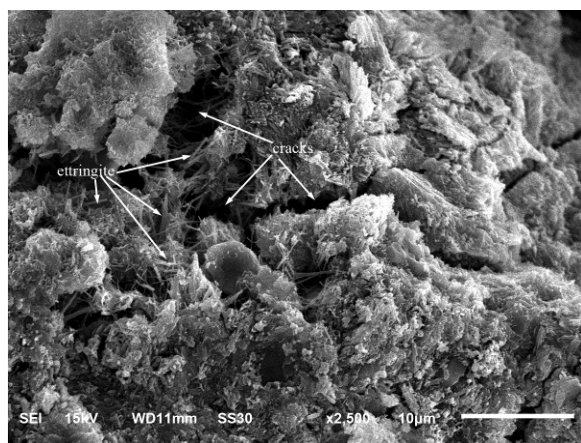

Figure 7. Fine ettringtite(2-5μm) formed in mortar immersed in Na_2SO_4 solution of 33.8 g/L.

Fig. 8 shows the microstructures of the mortars that were immersed in sulfate solution of 33.8 g/L for 600 days. Large ettringite crystals, more than 20μm in length, were observed in cracks or pores. Large

ettringite are often observed in cracks zone (already destroyed). These large crystals are generally considered to be formed in free space through solution without expansion. And it was contributed to little or no expansion. Thus, the formation of fine ettringite(2-5μm) was likely the main reason for the observed expansion and cracking (macro-behavior).
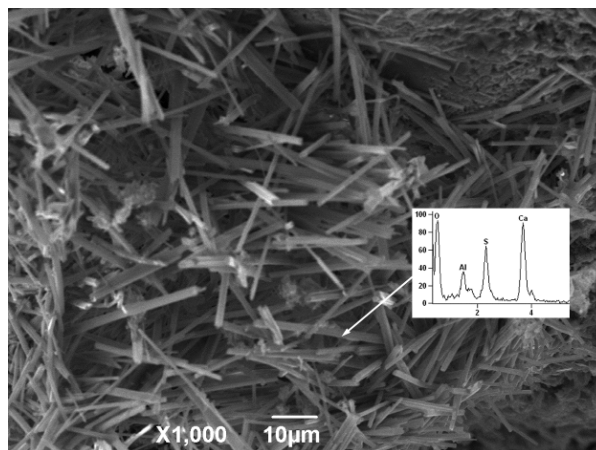

Figure 8. Large ettringtite crystals (>20μm) formed in mortar immersed in Na_2SO_4 solution of 33.8 g/L.

Fig. 9 shows the backscattered electron images of mortars that were immersed in Na_2SO_4 solution of 33.8 g/L for different periods.
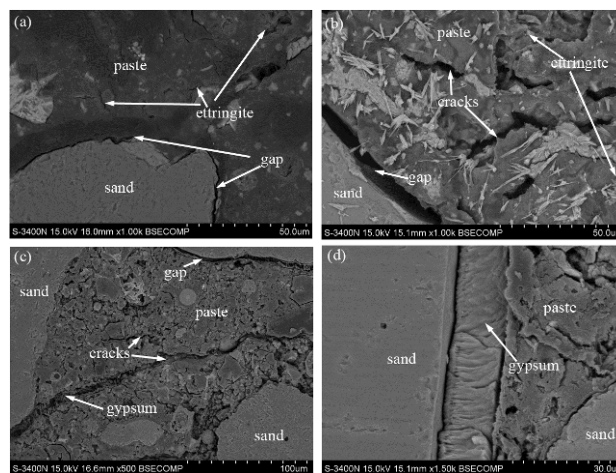

Figure 9. Backscattered electron images of the mortars after immersion in solutions containing 33800 mg SO_4^{2-}/l for different periods (a) 150d (b) 210d (c) 360d (d) 600d.

After 150 days of immersion, as shown in Fig. 9(a), fine ettringite was formed in the paste, which

resulted in expansion and caused some gaps between the sand and paste. At 210 days of exposure, as shown in Fig. 9(b), more cracks were formed in the paste and the gaps between the sand and paste become wider. The formation of fine ettringite in the paste might be responsible for these gaps since gypsum was not observed in the gaps at this stage. With the increase of immersion time, as shown in Fig. 9(c), gypsum was formed in the cracks that were cause by the fine ettringite formation. When the mortars were immersed in the solution for 600 days, as shown in Fig, 9(d), a clear gypsum vein with a thickness of approximately 10 μm was observed in the gaps. In this case, the gypsum was likely deposited in the cracks that originally formed due to the formation of ettringite.

3.4 Discussion

The sulfate concentration affected attack rate and the damage mechanism of sulfate attack may also be affected by sulfate concentration because only ettringite was formed at the sulfate concentration of 3g/L. Gypsum, as well as ettringite, was detected in the samples that were immersed in sulfate solution of 33.8 g/L. According to physical characteristics phase changes and microstructures evolution, the deterioration of mortars immersed in sodium sulfate solution can be described as several stages, as shown in the schematic diagram in Fig. 10.
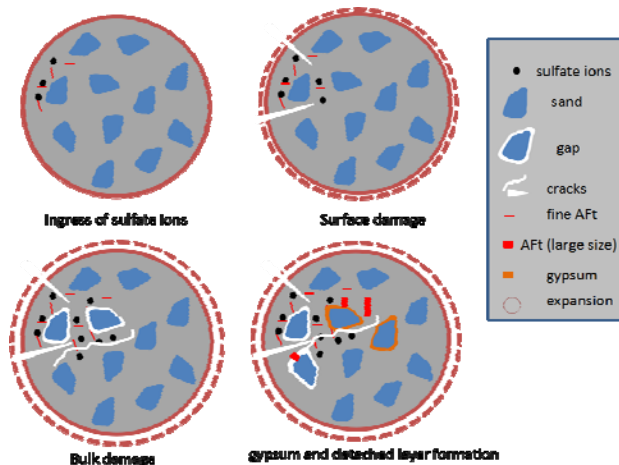

Figure 10. Schematic representation of deterioration process of mortars during sodium sulfate attack.

When the mortars were exposed to sulfate solutions, sulfate ions can react with Al-phase, such as monosulfate and hydrated calcium acuminate, to form small amount of fine ettringite crystals in a high alkaline solution and associate to surface micro-cracking. However, continuous hydration predominates (slight water uptake) resulting in a slight increase in strength and insignificant expansion, which can be referred as induction stage. As the immersion time goes by, many fine ettringites, approximately 2-5 μm, are mainly formed around the cement particles (mainly Al-phase), and it causes cracks in the surface layer. The ingress of sulfate ion starts a slow expansion and a loss of strength as the damage mainly occurred in surface region rather than the inner part, which can be described as surface damage stage. Accompanied by the formation of cracks in surface layer, sulfate ion will continually and quickly move into the inner parts of mortars through the cracks. It is a stage of bulk damage as the formation of more cracks and gaps inside.

Afterwards, much more of sulfate ions migrate into the inside resulting in much more ettringite and gypsum. The typical character of this stage is large ettringite and gypsum crystals deposited in the cracks or gaps that were formed previously. Unlike the fine ettringite formed surrounding the cement particles, the large ettringite crystals in cracks or pores may be formed through solution, and it is believed to be non-expansion. The large ettringite crystals will be formed at the cracks zone (surface layer) as the consumption of portlandite occurs. At the same time, more sulfate ions diffused into the inner part to form fine ettringite at high alkaline environment. The rate and amount of sulfate ions in high sulfate solution (33.8 g/L) will be much higher than that in low sulfate solution (3 g/L). Fine ettringite formed continuously from surface to the bulk, so a large amount of fine ettringite in the inner part of the mortars immersed in 33.8 g/L may be attributed to the large expansion after 210 days exposure.

It can be conducted that the formation of gypsum was from the precipitation of calcium ions (from portlandite) with sulfate ions (from the aggressive environment) since its formation resulted in obvious consumption of portlandite. In order to maintain the calcium balance in the system, the consumption of portlandite caused the decalcification of C-S-H that is source of strength in mortars. Thus, obvious losses of compressive strength could be generally attributed to the decomposition of calcium hydroxyls and to the decalcification of C-S-H. Thus, the gypsum formation contributed to completely

separate the aggregate and paste rather than expansion in the mortars. In addition, the increase of sulfate concentration is a plus for the formation of gypsum. The commonly applied laboratory tests may not be completely suitable for representing the damage that occurs under field conditions.

4 Conclusion

Cracking is the main characteristic of mortar during sodium sulfate attack. Initially, the formation of fine ettringite (2-5μm) surrounding the cement particles contributed to slight cracking along the corners. The degradation process of mortars was from surface damage to bulk damage with the diffusion of sulfate ions through cracks. At the bulk damage stage, more and more fine ettringite crystals that were formed in matrix lead to obvious expansion and cracks. Some gypsum and large ettringite crystals (>20μm) were also observed in the cracks or pores that were formed due to the fine ettringite at this stage. At the later stage, gypsum can be easily formed in interfacial transition zones or matrix, as the consumption of calcium hydroxide or C-S-H, which mainly contributed to a complete failure of mortars rather than their expansion.

Acknowledgements

References

[1] Rasheeduzzafar, A. O. S. B., Abduljauwad, S. N., Maslehuddin, M.: *Magnesum-sodium sulfate attack in plain and blended cements,* Journal of Materials in Civil Engineering, 6 (1994), 2, 201-222.

[2] Kunther, W., Lothenbach, B., Scrivener, K. L.: *Deterioration of mortar bars immersed in magnesium containing sulfate solutions,* Materials and Structures, 46 (2013), 12, 2003-2011.

[3] Whittaker, M., Black, L.: *Current knowledge of external sulfate attack,* Advances in Cement Research, 27 (2015), 9, 1-14.

[4] Rajasekaran, G.: *Sulphate attack and ettringite formation in the lime and cement stabilized marine clays*, Ocean Engineering, 32 (2005), 8, 1133-1159.

[5] Hime, W. G., Mather, B.: *Sulfate attack, or is it*, Cement and Concrete Research, 29 (1999), 5, 789-791.

[6] Santhanam, M., Cohen, M. D., Olek, J.: *Sulfate attack research—whither now*, Cement and Concrete Research, 31 (2001), 6, 845-851.

[7] Thokchom, S., Ghosh, P., Ghosh, S.: *Performance of fly ash based geopolymer mortars in sulphate solution*, Journal of engineering science and technology review, 2010, 3 (1), 36-40.

[8] Feng, P., Garboczi, E. J., Miao, C., Bullard, J. W.: *Microstructural Origins of Cement Paste Degradation by External Sulfate Attack*, Construction and Building Materials, 96 (2015), 391-403.

[9] Mehta, P. K.: *Mechanism of expansion associated with ettringite formation*, Cement and Concrete Research, 3 (1973), 1, 1-6.

[10] Scherer, G. W.: *Stress from crystallization of salt*, Cement and Concrete Research, 34 (2004), 9, 1613-1624.

[11] Flatt, R. J.: *Salt damage in porous materials: how high supersaturations are generated*, Journal of Crystal Growth, 242 (2002), 3, 435–454.

[12] Skalny, J., Marchand, J., Odler, I.: *Sulfate attack on concrete*, Spon Press, London, 2002.

[13] Tian, B., Cohen, M. D.: *Expansion of Alite Paste Caused by Gypsum Formation during Sulfate Attack*, Journal of Materials in Civil Engineering, 12 (2000), 1, 24-25.

[14] Irassar, E., Bonavetti, V., Gonzalez, M.: *Microstructural study of sulfate attack on ordinary and limestone Portland cements at ambient temperature*, Cement and Concrete Research, 33 (2003), 1, 31-41.

[15] Yu, C., Sun, W., Scrivener, K.: *Mechanism of expansion of mortars immersed in sodium sulfate solutions,* Cement and Concrete Research, 43 (2013), 105-111.

[16] ASTM C 1012-13: *Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution.*

[17] NFP18-837: *Produits de calage et/ou scellement à base de liants hydrauliques, Essai de tenue à l'eau de mer et/ou à l'eau à haute teneur en sulphates.*

[18] GB/T 749-2008.: *Test method for determing capability of resisting sulfate corrode of cement, China Standard Committee.*

[19] Bellmann, F., Erfurt, W., Ludwig, H. M.: *Field performance of concrete exposed to sulphate and low pH conditions from natural and industrial sources*, Cement and Concrete Composites, 34 (2012), 1, 86–93.

[20] Santhanam, M., Cohen, M. D., Olek, J.: *Effects of gypsum formation on the performance of cement mortars during external sulfate attack*, Cement and concrete research, 33 (2003), 3, 325-332.