

# The TSA Degradation Process within Cement-Based Materials in the Electrical Field Environment

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## ABSTRACT

*The thaumasite form of sulfate attack (TSA) of cement-based materials is a complex degradation process. The degradation process needs abundant water, carbonate, sulfate and silicate. However, there is no detailed study on the TSA degradation process. X-Ray Diffraction (XRD) and chemical analyses were used to study the TSA degradation process based on the present studies. The results indicated that the degradation process of the electrical field was similar to the full immersion, with the main difference being the degradation rate. The electrical field can obviously accelerate the TSA degradation process. The degradation had progressed to the core of the sample, and the amount of pulp was found at 120 days. The degree of degradation of the  $MgSO_4$  full immersion affected only the surface of the sample at 360 days. The degree of degradation of the  $MgSO_4$  full immersion was the lowest at 360 days. Meanwhile, combining the XRD, chemical analysis data, the degradation rule was summarized as there being a fixed range to generate the pulp (the representative thaumasite form of sulfate attack), and the pH and the Ca/S need to meet the following conditions:  $10.60 < pH < 11.75$  and  $4.00 < Ca/S < 6.35$ .*

**Keywords:** Electrical field; TSA; Cement-based materials; Degradation process

## 1.0 INTRODUCTION

The thaumasite form of sulfate attack (TSA) will occur in cement-based materials when there is an abundance of water, sulfate, and carbonate in a low-temperature environment. The TSA directly destroys the C-S-H gel and turns the cement-based materials into soft pulp. The TSA was first reported by Erlin and Stark (Erlin and Stark, 1965) in the 1960 s. Dozens of TSA cases were subsequently reported (Crammond and Halliwell, 1995). The TSA (thaumasite form of sulfate attack) and thaumasite formation (TF) were proposed by the TEG of England (Longworth, 1999). Considering the danger of the TSA, the composition, structure, and formation mechanism of thaumasite were widely studied. Three formation mechanisms were reported for the TSA: (1) the direct route from a reaction among C-S-H, carbonate, sulfate, and  $Ca^{2+}$  ions (Crammond, 2003); (2) thaumasite formation from ettringite, namely, the woodfordite route (Purnell and Francis, 2003); and (3) thaumasite formation through the heterogeneous nucleation on the surface of ettringite due to the crystalline structure similarities of the two minerals (Köhler and Heinz, 2006).

The electrical field that is found or applied to the cement-based materials had two main aspects: (1) a stray current in rail traffic, which can destroy a reinforced concrete structure (Darowicki and Zakowski, 2004), and (2) an electrical field applied as an acceleration method. The electrical field can accelerate the chloride ion into the sample; this method can be applied to evaluate the permeability of concrete. In addition, the electrical field was applied to accelerate the TSA by our research group. The experimental results from our research group indicated that an electrical field can accelerate decalcification, considering the amount of  $Ca^{2+}$  that migrated from the sample. The C-S-H gel lost stability during decalcification. In addition, the electrical field can accelerate the  $SO_4^{2-}$  migration into the sample, resulting in cracking and a decrease in strength in an ambient-temperature environment (Huang and Wang, 2016). The electrical field can accelerate both the TSA and the generation of gypsum at a low temperature within 120 days (Luo and Wang, 2016). To comprehensively study the TSA in an electrical field and a full-immersion environment, XRD, pH and chemical analyses were used to study the degradation process of the TSA in an electrical field and a full-immersion environment.

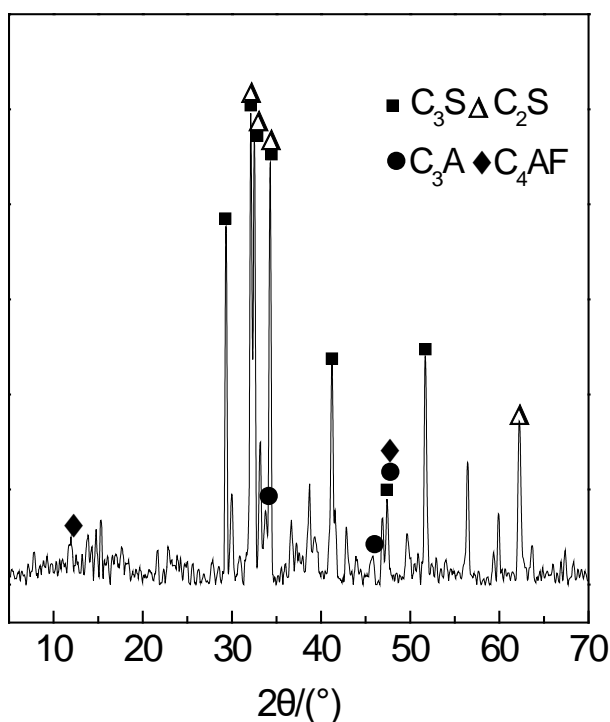
**Table 1.** Chemical components of clinker, gypsum, and limestone powder (wt%)

Materials	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	LOI
Clinker	19.99	2.98	4.80	61.22	3.27	0.23	0.88	0.18	3.52
Gypsum	4.47	0.36	0.99	34.05	1.84	40.61	0.23	0.08	16.87
Limestone powder	0.23	0.21	-	55.46	-	-	-	-	41.75

## 2.0 MATERIALS AND METHODS

### 2.1 Preparation of basic materials

Grade 42.5 R of ordinary Portland cement clinker and 3 wt% dihydrate gypsum were prepared. The chemical components of the cement, gypsum and limestone powder are listed in Table 1. Limestone powder with CaCO<sub>3</sub> ≥ 98 wt% was obtained from Bao Xing Company, Sichuan province, China. The XRD results for the cement clinker are presented in Fig. 1

**Fig. 1.** XRD of cement clinker

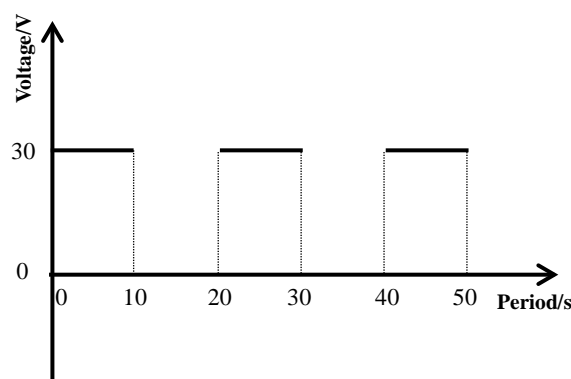
### 2.2 Experiment methods

Cement paste was prepared to test thaumasite formation via the action of an electrical field. The mixture proportions are listed in Table 2. The fresh paste was cast into a PMMA mould with three cube specimens with dimensions of 40 mm × 40 mm × 40 mm and with two end containers for the sulfate solution. The specimens, together with the mould, were cured for 30 days in a moist room at a temperature of (20 ± 2) °C, with a relative humidity of no less than 95% until testing. After curing, the

specimens, together with the mould, were moved into a refrigerating cabinet with a temperature of 5 ± 2 °C, as shown in Fig. 3. Two titanium alloy staffs were used as the anode and cathode materials. An electrical field was applied to accelerate the migration of sulfate ions into the cement-based materials. The electrical voltage was 30 V, and the period was 20 s. The waveform of electrical pulses is shown in Fig. 4.

**Table 2.** Mixture proportions of cement paste

Cementitious materials (wt%)			Water/cementitious materials ratio
Cement	Gypsum	CaCO <sub>3</sub> powder	
67	3	30	0.40

**Fig. 2.** The experiment mold and equipment**Fig. 3.** Oscillogram of electrical field

Some preliminary test results from the authors indicated that TSA deteriorated most rapidly when the

electrical field combination was cathode  $\text{Na}_2\text{SO}_4$  solution-anode  $\text{MgSO}_4$  solution. Therefore, the above electrical field combination was used to test the TSA process for cement-based materials in the electrical field. In addition, the  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$  full immersion control groups were set as the control group. The experimental groups are shown in table 3.

**Table 3.** Experimental groups

Experimental group	Cathode solution	Anodic solution
EF(Electrical field)	$\text{Na}_2\text{SO}_4$	$\text{MgSO}_4$
N	$\text{Na}_2\text{SO}_4$ - full immersion	
M	$\text{MgSO}_4$ - full immersion	

These samples were observed every 30 days, microsamples were created for XRD and chemical analysis. The broken pieces were soaked and rinsed using anhydrous alcohol and oven dried at  $50\text{ }^\circ\text{C}$ . The X-ray diffractometer used was from Ricoh Company, with D/MAX-IIIC and  $\text{CoK}\alpha$  radiation ( $0.2\text{ \AA}$ ).

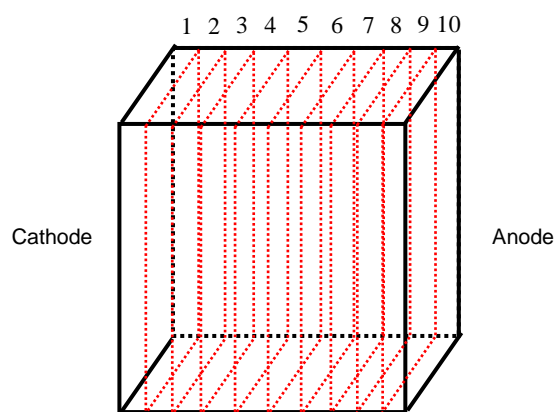
The sample was cut into ten similarly sized pieces for testing using XRD and chemical analysis. Position 1 was the cathode surface of the sample, and position 10 was the anode surface of the sample (shown in Fig. 5). The factors tested by chemical analysis included the  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  contents and the pH value.

### 3.0 RESULTS AND DISCUSSION

#### 3.1 Analysis of degradation process

##### XRD analysis of the electrical field group

The XRD analysis of electrical field group at position 1, position 5 and position 10 within 120 days is shown in Fig. 5. At position 1, the diffraction intensity of ettringite and gypsum was enhanced gradually from 0 day to 60 days, while the diffraction intensity of calcium hydroxide was weakened. The main diffraction peak of ettringite ( $9.72\text{ \AA}$ ) progressively weakened after 60 days. In addition, the peak moved to the left at a distance that was close to the diffraction peak of thaumasite ( $9.56\text{ \AA}$ ). The diffraction peak of thaumasite strengthened after 82 days. In addition, the other peaks of thaumasite were obvious. The gypsum was increased with a longer degradation period. The calcium hydroxide content initially decreased, then increased and showed the lowest value at 82 days, indicating that the calcium hydroxide was first consumed and then generated.



**Fig. 4.** The sliced sample

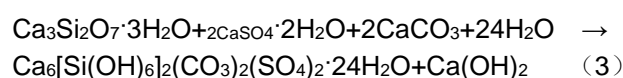
For positions 5, there were obvious diffraction peaks of thaumasite, but the diffracted intensity of these peaks was lower. In addition, the degradation of thaumasite and the gypsum attack were gradually weakening with the depth of the degradation position. The diffracted intensity of  $\text{Ca}(\text{OH})_2$  was lower with an increase in degradation age, and the degradation rule for  $\text{Ca}(\text{OH})_2$  was different from that of positions 1. There was also the same degradation rule for ettringite and thaumasite. The position of the main diffraction peak of ettringite gradually moved to the main diffraction peak of thaumasite, and the diffracted intensity of gypsum became stronger with a longer degradation period.

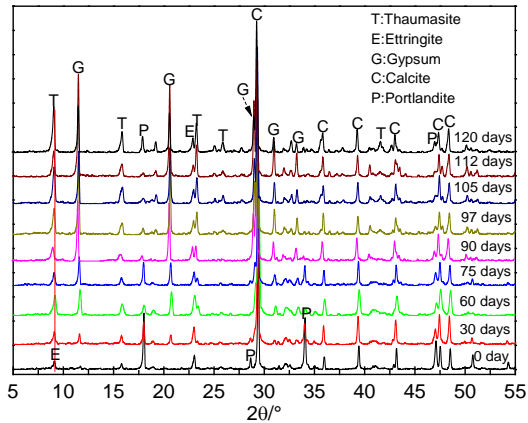
For position 10, the thaumasite production process followed the same rule as did the other positions: first, the ettringite was produced, then the ettringite began to transform the thaumasite, and the thaumasite was produced in large amounts.

Fig. 6 shows the degradation at different positions at 120 days. The diffracted intensity of thaumasite and gypsum gradually weakened from position 1 to position 6, and the diffracted intensity of thaumasite and gypsum gradually increased from position 6 to position 10. Degradation was shown mainly by thaumasite, ettringite and gypsum from the cathode to the core of the sample.

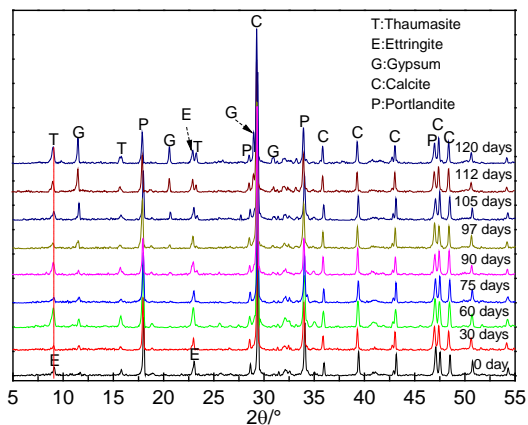
The main thaumasite form of the sulfate attack mechanism is as follows:

1) The direct reaction mechanism: the C-S-H gel reacted directly with carbonate, sulfate and abundant water to form thaumasite (Deng and Xiao, 2005):

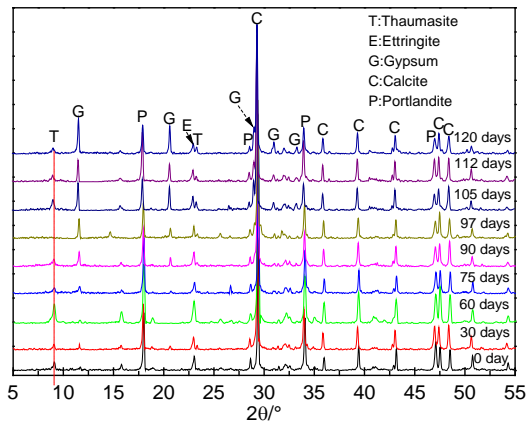




Position 1



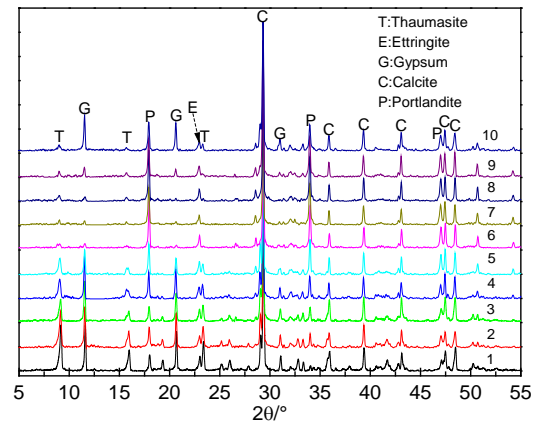
Position 5



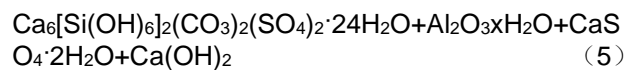
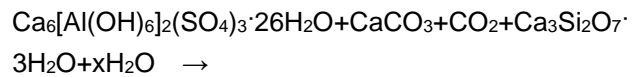
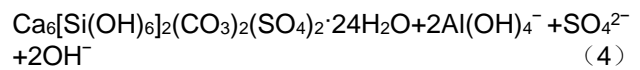
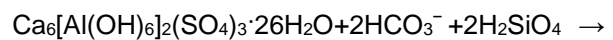
Position 10

**Fig. 5.** Different positions XRD profiles of electrical field in full degradation age

2) The woodfordite mechanism: the ettringite and the C-S-H gel reacted with carbonate and abundant water to form thaumasite. The  $Al^{3+}$  was replaced with  $Si^{4+}$  in ettringite to form thaumasite (Deng and Xiao, 2005):



**Fig.6.** The XRD analysis of the electrical field group at 120 days



$Ca(OH)_2$  was the reaction product with thaumasite in reactions (3), (4) and (5).  $Ca(OH)_2$  can react with  $CO_2$  to form calcite, which provides more carbonate to produce thaumasite. The degradation mechanism of positions 1 was analysed as follows: the main degradation product was ettringite at 60 days. In addition, the  $Ca(OH)_2$  was gradually consumed to form gypsum. The generated amount of gypsum increased continuously, and the main diffraction peak of ettringite began to move to thaumasite. The gypsum was also consumed to form thaumasite. The amount of thaumasite increased continuously. In addition, the  $Ca(OH)_2$  stopped decreasing and began to increase after 97 days. Combined with reactions (3), (4) and (5),  $Ca(OH)_2$  was formed following the thaumasite production process. The  $Ca(OH)_2$  was the reactant for the early degradation age but was the product for the later degradation age. The above results indicated that the two degradation mechanisms both existed and that the process of the ettringite transformation into thaumasite was more serious. The degree of degradation of positions 5 was lower, and the  $Ca(OH)_2$  was always consumed, not produced. The  $Ca(OH)_2$  was mainly consumed to form gypsum. The migrated degradation ions were mainly stranded in the cathode region, resulting in the degradation occurring from the cathode surface to the core. For the amount of gypsum at position 10 due to the degradation process: the anode solution was electrolysed to a high level of  $H^+$ , and the anode

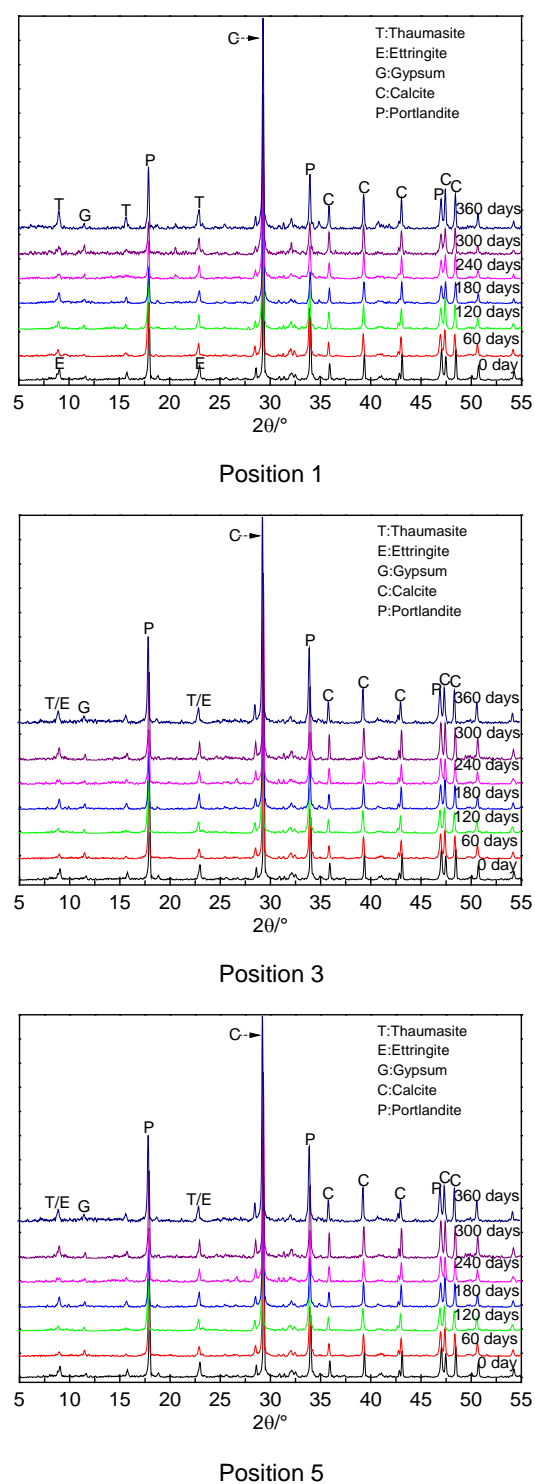
surface of the sample was acidified, resulting in the dissolution of that amount of  $\text{Ca}^{2+}$ . Meanwhile, there was an abundance of  $\text{SO}_4^{2-}$  in the anode solution. Hence, the gypsum was produced at position 10.

#### XRD analysis of the full immersion group

The full-immersion sample was tested every 60 days. The degradation of the full-immersion samples showed no distinction between the 6 faces of the sample. Hence, positions 1, 3 and 5 were tested. Fig. 7 shows the XRD results for the  $\text{Na}_2\text{SO}_4$  full-immersion sample at positions 1, 3 and 5 within 360 days. The degradation of the 3 positions of the sample was the same. The degradation rules for the three directions were the same. The diffraction peak of ettringite was first increased and then decreased, and it was the strongest at 180 days. Then, the diffraction peak of ettringite was weakened. The degradation rule was that the ettringite was produced, then the ettringite transformed to thaumasite, and finally the thaumasite began to be produced. The above full-immersion degradation process was the same with the electrical field.

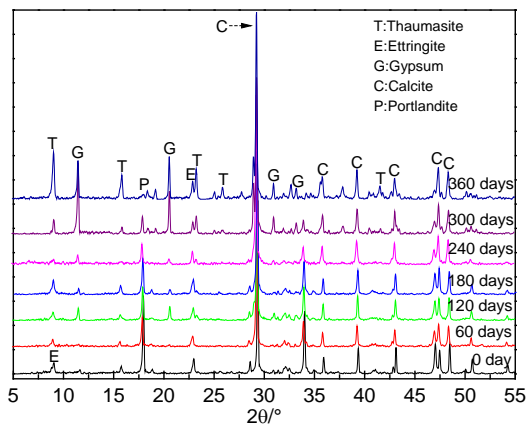
Meanwhile, the diffraction peak of  $\text{Ca}(\text{OH})_2$  was obvious, but there was no diffraction peak for gypsum. These data indicated that there was no serious TSA in the  $\text{Na}_2\text{SO}_4$  full-immersion group at 360 days and that the serious damage in appearance was due to the crystalline fracture. In addition, the diffracted intensity of  $\text{Ca}(\text{OH})_2$  in the surface of the sample was lower than the core of the sample. The main diffraction peak of ettringite began to move after 240 days. These data indicated that the ettringite began to transform into thaumasite.

Fig. 8 shows the XRD results for the  $\text{MgSO}_4$  full-immersion group in positions 1, 3 and 5 within 360 days. The degradation rule was same as that of the  $\text{Na}_2\text{SO}_4$  full-immersion group at position 1. The diffracted intensity of ettringite first was enhanced and then began to weaken. The main diffracted intensity of ettringite was the strongest at 180 days. Then, the thaumasite began to be generated, and the surface of the sample began to produce pulp. The degradation rules for positions 3 and 5 were the same as those for position 1, but the diffracted intensities of thaumasite and gypsum were obviously lower than that of position 1. Meanwhile, the amount of gypsum increased progressively, accompanied by the generation of thaumasite. The degradation rate of the  $\text{MgSO}_4$  full-immersion group was faster than that of the  $\text{Na}_2\text{SO}_4$  full-immersion samples. The degradation rule of the full-immersion samples was similar to the effects of the electrical field. The main distinction was that the degradation rate of the electrical field was faster than that of the full immersion.

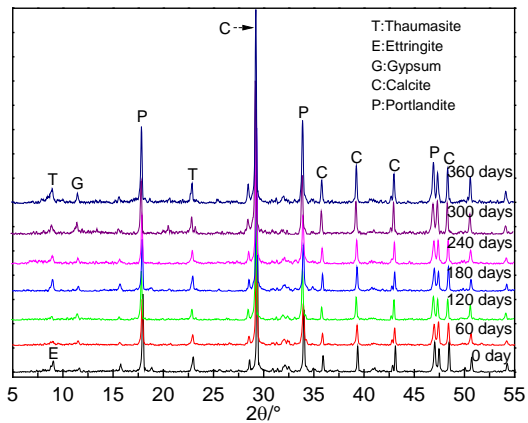


**Fig.7.** Different positions XRD profiles of the  $\text{Na}_2\text{SO}_4$  full immersion in full degradation age

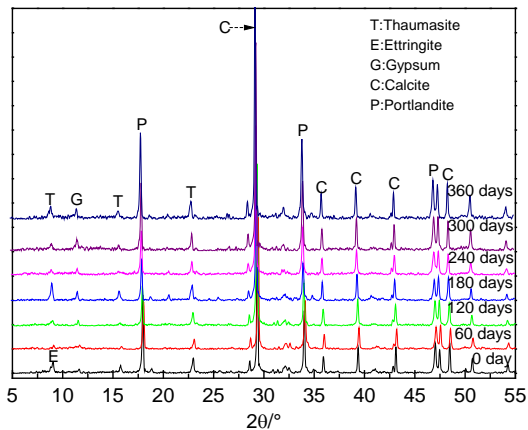
The electrical field groups were compared with the full-immersion groups. There was a similar degradation process: the ettringite was produced first and then began to be transformed into thaumasite. A direct reaction was also present. The change in degradation time was 240 days in the full immersion, and the time was 60 days in the electrical field. The degradation rate of these above samples was the electrical field groups > the  $\text{MgSO}_4$  full immersion >  $\text{Na}_2\text{SO}_4$  full immersion.



Position 1



Position 3



Position 5

**Fig. 8.** Different positions XRD profiles of the MgSO<sub>4</sub> full immersion in full degradation age

### 3.2 The contrastive analysis of the electrical field and the full immersion

The Ca/S of positions 1 to 2 in the electrical field group and of position 1 in the MgSO<sub>4</sub> full-immersion

group was calculated. The Ca/S and the pH are shown in Tables 4 and 5. Combining the above XRD data, the degradation rule is summarized as there being a fixed range for generating the pulp (the representative thaumasite form of sulfate attack). The pH and Ca/S need to meet the following conditions: 10.60 <pH< 11.75 and 4.00 <Ca/S< 6.35. The test data indicated that the degradation of the electrical field and full-immersion groups had a similar degradation rule but that the main difference was the degradation rate. The electrical field can obviously accelerate the degradation process and not change the degradation rule when combined with the full immersion. In addition, the test indicated that the MgSO<sub>4</sub> was more beneficial in causing the TSA.

**Table 4.** The Ca/S and pH of electrical field group at position 1 and 2 under degradation age

Degradation age/days	position 1		position 2	
	Ca/S	pH	Ca/S	pH
0	51.24	12.42	51.51	12.41
30	16.00	12.03	23.39	12.26
60	10.25	11.56	22.41	11.99
75	8.74	12.01	10.81	12.13
82	8.46	11.93	11.10	12.17
90	5.85	11.45	6.82	11.86
<b>97</b>	<b>4.54</b>	<b>11.46</b>	<b>5.52</b>	<b>11.77</b>
105	4.30	11.46	5.54	11.76
113	4.07	11.48	5.33	11.74
<b>120</b>	<b>5.23</b>	<b>11.06</b>	<b>6.07</b>	<b>11.73</b>

**Table 5.** The Ca/S and pH of full immersion groups at position 1 under degradation age

Degradation age/days	MgSO <sub>4</sub> full immersion		Na <sub>2</sub> SO <sub>4</sub> full immersion	
	Ca/S	pH	Ca/S	pH
0	51.24	12.42	51.24	12.42
60	28.43	12.09	30.68	12.31
120	27.26	12.14	26.53	12.23
180	20.85	12.23	24.81	12.21
240	15.28	11.97	17.75	12.1
<b>300</b>	<b>6.32</b>	<b>11.75</b>	14.68	12.07
<b>360</b>	<b>5.12</b>	<b>10.63</b>	14.25	12.18

## 4.0 Conclusions

In this paper, the degradation process of cement-based materials in an electrical field and full-immersion environment was reported, and the following conclusions have been reached:

- (1) The degradation process of the electrical field environment was similar to that of the full-immersion environment. The ettringite was first generated, followed by gypsum and thaumasite. The diffracted intensity of ettringite as first increased and then decreased in the electrical field group at 60 days and in the full-immersion group at 180 days. The degradation rate in the electrical field was faster.
- (2) The pulp began to be generated and the sample deteriorated due to degradation when  $10.60 < \text{pH} < 11.75$  and  $4.00 < \text{Ca/S} < 6.35$ .

The electrical field can obviously accelerate the degradation process. The degradation reached the core of the sample, and the degradation diffused from the cathode to the anode of the sample. The degradation degree only reached the surface of the sample in the  $\text{MgSO}_4$  full immersion group at 360 days. The degradation diffused from the surface to the core of the sample.

### Acknowledgment

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