

## Article

# Influence of the Concentration of Seawater on the Early Hydration Properties of Calcium Sulphoaluminate (CSA) Cement: A Preliminary Study

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**Abstract:** This research investigates the effect of seawater of different concentrations on the hydration process and microstructure of calcium sulphoaluminate (CSA) cement. It studies the CSA cement pastes via experiments carried out to determine the initial and final setting times, mechanical strength and chemical shrinkage with X-ray diffraction (XRD), scanning electron microscopy (SEM) and simultaneous differential thermal-thermogravimetric (DTA-TG) analysis. The DTA-TG and XRD results showed that the main hydration products were ettringite (AFt) and aluminum hydroxide in the CSA cement paste mixed with both freshwater and seawater, while a small amount of ettringite (AFt) became monosulfate (AFm) in the freshwater-mixed CSA cement. The SEM results demonstrate that seawater can improve the microstructure of CSA cement paste in the early stage of hydration (1 d) but impairs the microstructure of the CSA cement matrix in the later stage of hydration (7 d). The experimental results also indicate that a high concentration of seawater can extend the setting time, increase the chemical shrinkage and decrease the mechanical strength of CSA cement.

**Keywords:** calcium sulphoaluminate cement; concentration of seawater; ettringite; hydration process; mechanical property; microstructure



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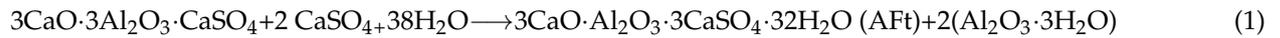
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## 1. Introduction

Calcium sulphoaluminate (CSA) cement is a kind of cement with ye'elimite (anhydrous calcium sulphoaluminate is the artificial clinker phase of ye'elimite), anhydrite and belite as the main clinker minerals. It possesses the merits of a short setting time, early high strength [1], micro-expansion, low water impermeability [2,3], low chloride diffusion [4–7] and high sulfate corrosion resistance [2,8,9], as well as its lower energy consumption [10–12] and lower CO<sub>2</sub> emissions [2,9,13,14]. Furthermore, it also possesses the properties of small drying shrinkage and a low solution pH [15–17]. The hydration products of CSA cement are mainly ettringite (3CaO·Al<sub>2</sub>O<sub>3</sub>·CaSO<sub>4</sub>·32H<sub>2</sub>O) and aluminum hydroxide (Al<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O) via the reaction displayed in Equation (1) [18,19]. Therefore, CSA cement has good corrosion resistance against sulfate attacks [20], making it particularly suitable for the construction of offshore engineering constructions. Furthermore, CSA cement has been considered for a potential approach to repair the deteriorated concrete in Cl<sup>-</sup>-rich environments which can improve the durability of concrete [21]:



Island engineering constructs are generally far away from land and lack freshwater and river sand. If the concrete can mix with seawater and sea sand taken from the island locally, it can not only save resources and reduce costs but also ensure construction progress. Furthermore, the application of seawater and sea sand in coastal and offshore engineering is a potential development trend in China [22].

Many researchers have revealed that seawater can be applied in the production of concrete [23–25]. However, most of the investigations were conducted on the concrete made of Portland cement [26,27], and studies on the seawater-mixed CSA cement are still lacking. Seawater mainly contains chloride and sulfate ions, which influence the chemical reaction in the hydration process and produce unfavorable hydration products, limiting its application in concrete engineering [28]. Though it has already been recognized that seawater can influence the mechanical performance of concrete, it is still uncertain whether its application has favorable or unfavorable effects [29–35].

Presently, there are many papers on the hydration of sulphoaluminate cement mixed with freshwater [36–38]. The hydration of CSA cement in freshwater has been studied and understood thoroughly [38,39]. However, the hydration process between CSA cement and seawater has not been investigated comprehensively. Only a few examples of research were carried out on the influence of seawater [40,41]. It is known that there is a quick chemical reaction when CSA clinkers meet with water and  $\text{CaSO}_4$  [42], and there exists a large number of free sulfate ions in seawater, which may produce an effect on the hydration process and change the hydration products of CSA cement [43]. Studies on the effect of the concentration of seawater on the hydration process of CSA cement are seldom conducted. The process of hydration and the mechanical properties are not well known yet.

The purpose of this research is to find out the influence of seawater of various concentrations on the hydration process and products of CSA cement. Tests on the initial and final setting times, mechanical performance, chemical shrinkage, hydration products and microstructure of CSA paste were carried out.

## 2. Experiments

### 2.1. Experiment Materials

(1) Sulphoaluminate cement: calcium sulphoaluminate cement 42.5 was used. Its main chemical compositions are displayed in Table 1, while Table 2 shows its primary properties. Its XRD patterns are displayed in Figure 1. The XRD patterns show that the main mineral components of the CSA clinkers were ye'elimite ( $3\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot \text{CaSO}_4$ ), belite ( $2\text{CaO}\cdot \text{SiO}_2$ ), anhydrite ( $\text{CaSO}_4$ ), mayenite ( $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ) and calcite ( $\text{CaCO}_3$ ). The particle size distribution of CSA cement is shown in Figure 2.

**Table 1.** Chemical compositions of the CSA cement (wt %).

MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
1.85	6.71	25.52	12.02	45.96	4.35	1.36

**Table 2.** Properties of the CSA cement.

Fineness Gravity (m <sup>2</sup> /kg)	Setting Time (min)		Strength in 1 d (MPa)		Strength in 3 d (MPa)	
	Initial	Final	Flexural	Compressive	Flexural	Compressive
408	15	30	6.3	35.8	6.6	45.8

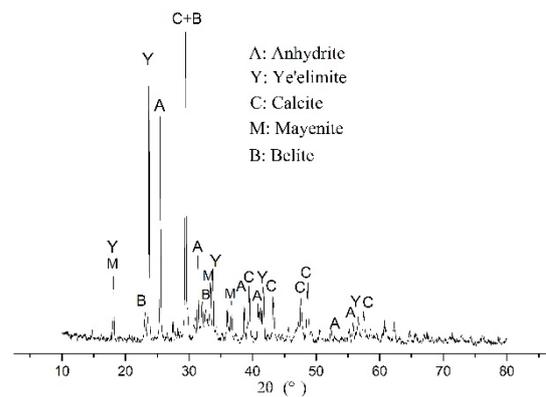


Figure 1. XRD patterns of the CSA cement.

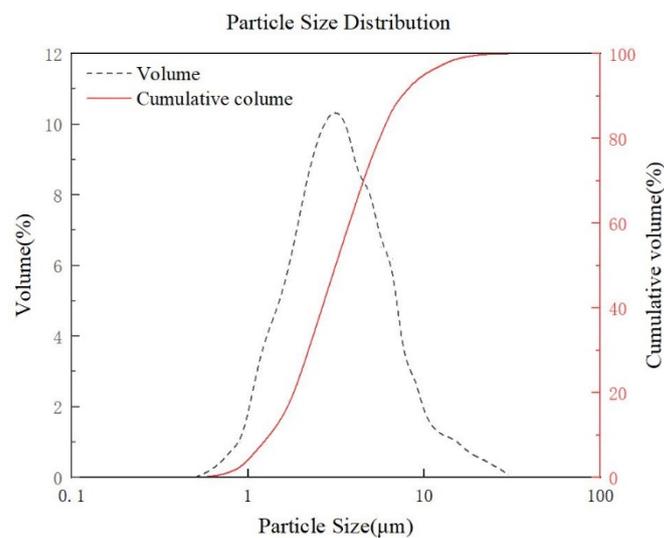


Figure 2. CSA cement particle size distribution.

(2) Mixing water: the seawater was made manually, and Table 3 shows its main chemical compositions. Tap water provided by the municipality of Shantou was used as freshwater.

Table 3. Composition of the artificial seawater (g/L).

NaCl	MgCl <sub>2</sub>	Na <sub>2</sub> SO <sub>4</sub>	CaCl <sub>2</sub>	KCl
24.36	5.12	4.02	1.16	0.69

## 2.2. Specimen Preparation and Curing

In this research, a water-to-cement ratio of 0.4 was applied. As the main focus of this research was on the early hydration of CSA cement, therefore, only CSA cement paste was prepared. Freshwater and seawater were mixed separately with CSA and stirred for 4 min to produce CSA cement paste. Concentration of 2 times, 3 times, 4 times and 5 times the normal amount of seawater were considered to study the effect of the seawater concentration on the hydration process and products of CSA. Abbreviations with capital letters were applied to distinguish each specimen. FW denotes the CSA paste made of freshwater, while *n*SW represents the CSA paste made of seawater with *n* times the normal concentration of seawater and 0SW represents freshwater. All samples were cured in a 20 °C steaming curing box for 12 h, 1 d, 3 d and 7 d.

### 2.3. Test Method

#### 2.3.1. Setting Time

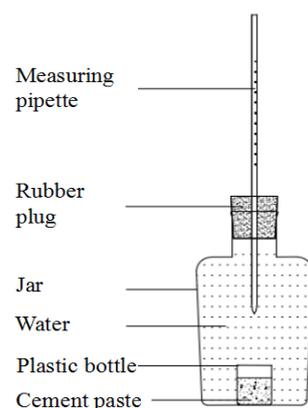
The initial and final setting times were carried out based on the Chinese code “Test methods for water requirement of normal consistency, setting time and soundness of the Portland cement” (GB/T 1346-2011).

#### 2.3.2. Compressive Strength Tests

The compressive strength test was carried out on a cube with a dimension of 50 mm. The test was conducted based on the Chinese code “Method of testing cements-Determination of strength”. The specimens were compressed with a loading speed of 2.4 kN/s. The average of the values of three samples was taken as the final compressive strength.

#### 2.3.3. Chemical Shrinkage

The chemical shrinkage test of the CSA paste is carried out according to the American Standard ASTM C1608-12 (see Figure 3). First of all, the proper amount (10–15 g) of prepared CSA paste was put into a soft plastic bottle and vibrated gently to discharge bubbles. Then, we put the soft plastic bottle into a glass jar and slowly injected curing fresh water into the bottle until the water surface was close to the mouth of the bottle. Then, the jar was sealed with a rubber plug, and a measuring tube was inserted into the rubber plug. After that, the test equipment was sealed with paraffin wax at every joint. Then, the device was moved into a 20 °C water bath for curing.



**Figure 3.** Chemical shrinkage device for the CSA cement paste.

#### 2.3.4. X-ray Diffraction (XRD) Analysis

XRD was applied to identify the hydration products of CSA cement mixed with seawater at various concentrations. The samples were taken from the center portion of the specimen after the compressive strength test and then ground into fine powder using an agate mortar. The fine powder was then soaked in absolute ethyl alcohol (20 mL) for 24 h. The ethyl alcohol was changed every 2 h. After that, the fine powder was moved to an oven and dried for 24 h at a temperature of  $45 \pm 1$  °C. The measurement was performed on a diffractometer provided by Bruker at 40 kV and 40 mA between  $10^\circ$  and  $80^\circ$  ( $2\theta$ ) at a step size of 0.0333 degrees.

#### 2.3.5. Scanning Electron Microscopy (SEM)

The samples with dimensions of 2 mm × 5 mm × 5 mm were taken from the inner area of the specimens after the compressive tests, and then the pieces were soaked in absolute ethyl alcohol for 24 h. The ethyl alcohol was changed every 2 h. After that, the samples were moved to an oven and dried for 24 h at a temperature of  $45 \pm 1$  °C. The sample was adhered to a standard stub with carbon tape and coated with gold palladium. The SEM investigation was performed with a JEOL JSM 6360LA. An acceleration voltage

of 10 kV and a working distance of 12 mm were applied. A spot size of 36 nm was set for the electron beam.

### 2.3.6. Thermogravimetric Analysis (TGA)

TGA measurement was carried out on equipment provided by Shimadzu with a heating rate of 10 °C/min. The temperature ranged from 20 °C to 1000 °C. The technique was able to identify ettringite, gypsum, calcium silicate hydrate, aluminum hydroxide and calcium hydroxide based on their specific dehydration endothermic peaks [38,44].

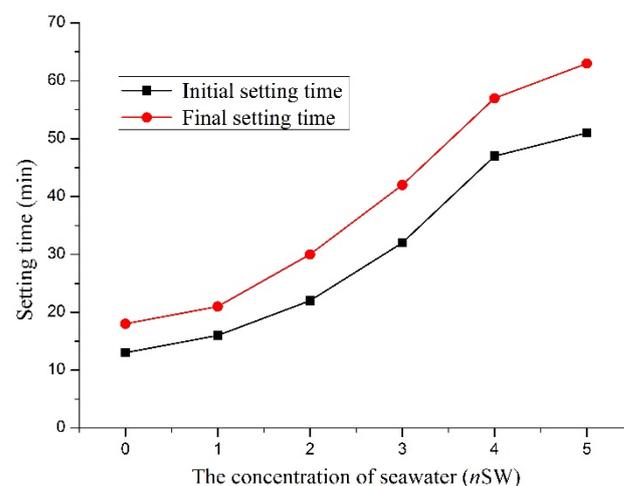
## 3. Results and Discussion

### 3.1. Influence on the Initial and Final Setting Times

The influence of the concentration of seawater on the initial setting and final setting times of the CSA paste is displayed in Table 4. Figure 4 demonstrates that the CSA cement had a very short setting time, and the difference between the initial setting time and the final setting time was relatively short. Aside from that, the initial and final setting times of the CSA cement were retarded when seawater was used as the mixing water, and the higher the concentration of seawater, the greater the retarding effect on the CSA cement, and the influence of the concentration of seawater on the initial setting time was more remarkable than that on the final setting time. Furthermore, Table 4 shows that the concentration of seawater could affect the time difference between the initial and final setting of CSA cement. The higher the concentration of seawater, the longer the time difference between the initial and final setting.

**Table 4.** The influence of the seawater concentration on the setting time of CSA cement.

The Concentration of Seawater ( <i>n</i> SW)	Initial Setting Time (min)	Final Setting Time (min)	(Final-Initial) Setting Time (min)	Improvement on Initial Setting Time (%)	Improvement on Final Setting time (%)
0	13	18	5	-	-
1	16	21	5	23.0	16.6
2	22	30	8	69.2	66.6
3	32	42	10	146.1	133.3
4	47	57	10	261.5	216.6
5	51	63	12	292.3	250.0



**Figure 4.** The influence of the seawater concentration on the setting time of CSA cement.

The previous experimental results indicate that the setting time of CSA cement could be retarded by seawater. The main reason for this is that the  $\text{SO}_4^{2-}$  in seawater plays an important role. There is a large amount of free  $\text{SO}_4^{2-}$  in seawater, and these ions

rapidly combine with  $\text{Ca}^{2+}$  in CSA cement to form gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) [43]. Gypsum can combine with the  $\text{C}_4\text{A}_3\bar{\text{S}}$  in CSA cement to develop insoluble ettringite (see Equation (1)), which quickly precipitates on the surface of cement particles and retards the further hydration of CSA cement [43]. Moreover, the higher the concentration of seawater, the more gypsum was produced via hydration, and the more obvious the effect of retarding on the setting of CSA cement.

Previous research [35–41] found that seawater can reduce the setting time of Portland cement, which is contrary to this research. The main reason for this is the different hydration process of CSA cement versus Portland cement.

### 3.2. Affect on the Compressive Strength

Figure 5 shows the influence lines of seawater of various concentrations on the compressive strength of CSA cement cured for different ages. The results indicate that the CSA cement possessed the merit of a high early strength. The compressive strength of the CSA cement cured for 12 h could reach 80% of the maximum compressive strength whether freshwater or seawater with different concentrations was used as the mixing water. The figure also illustrates that the concentration of seawater played an essential role in the hydration process of CSA cement. To be more precise, when normal seawater (1SW) was applied, the early hydration reaction of CSA cement was slightly promoted, resulting in slightly higher compressive strength than that of freshwater-mixed CSA cement. However, in the later hydration stage (7 d), the compressive strength of the CSA cement mixed with seawater was slightly lower than that of the freshwater mix. When the concentration of seawater was increased, the strength of the CSA paste was adversely affected by seawater, and the higher the concentration, the lower the strength. Although the strength of the CSA cement mixed with seawater of higher concentrations increased slightly from 12 h to 3 d, the compressive strength decreased by different degrees after being cured for 7 d. Figure 6 also shows that the higher the concentration of seawater, the lower the mechanical performance of the CSA cement.

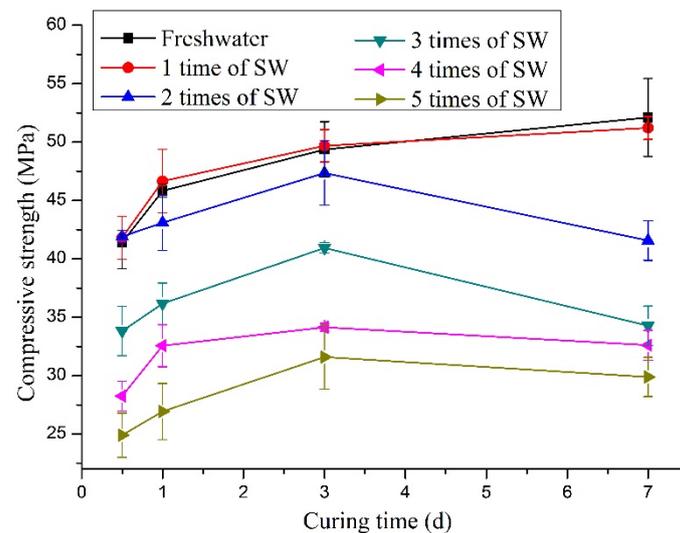
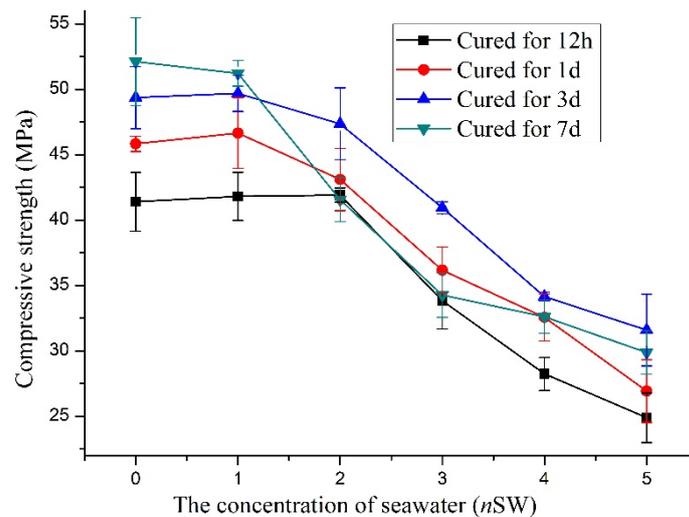


Figure 5. The strength development of CSA cement mixed with seawater at different concentrations.



**Figure 6.** Influence of seawater concentration on the compressive strength of CSA cement.

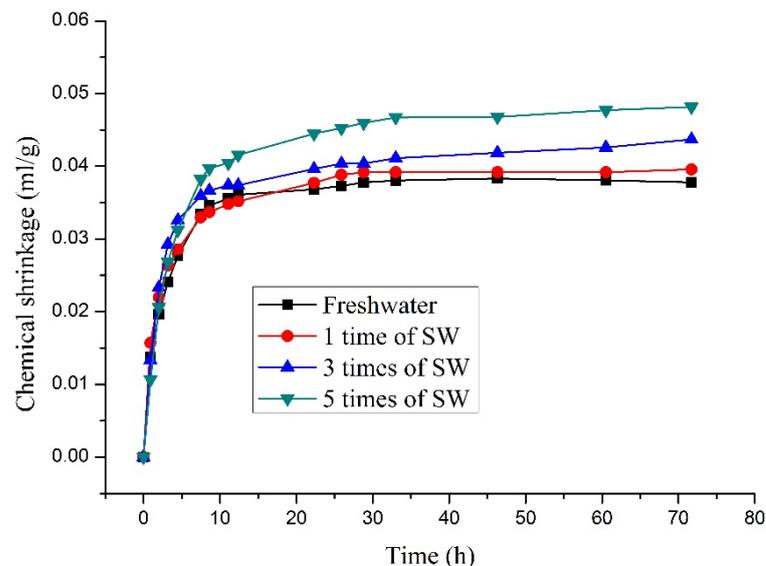
The above experimental results illustrate that at a lower concentration, the salinity could promote the early hydration of CSA cement, but it produced an adverse effect in the later stage. Seawater of a high concentration had an adverse impact even on the early hydration reaction, and a higher concentration provided a more obvious effect. Higher concentrations could even cause strength inversion in CSA cement. This experimental phenomenon was mainly due to the large number of inorganic salts in seawater, mainly including  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$ . These inorganic salts change the types and concentrations of ions in the CSA cement slurry, affect the formation of ettringite and finally affect the hydration process of CSA cement. The free  $\text{SO}_4^{2-}$  in seawater can provide a large amount of sulfate ions for the hydration of CSA cement, which can react with CSA cement rapidly to form insoluble AFt (see Equation (1)). The AFt precipitates on the surface of cement particles to prevent the further hydration. In the early hydration stage of CSA cement, the rapid formation of ettringite can promote the strengthened formation of CSA cement. However, if the concentration of seawater is increased, then more CSA particles will be covered in the early hydration phase, which means fewer cement particles will participate in the hydration reaction, thus resulting in the lower strength of CSA cement mixed with seawater of a higher concentration.

In the later stage of hydration, the CSA paste mixed with seawater can produce more ettringite, which expands the CSA cement paste. Microcracks occur during expansion, resulting in the decline in strength in the later stage. Additionally, the higher the concentration of seawater, the more intense the hydration reaction, the faster the ettringite production speed, and the higher the expansion rate of CSA cement, which results in lower strength for the CSA cement mixed with seawater of a higher concentration and even presents the retrograde strength phenomenon in the later stage.

### 3.3. Influence on Chemical Shrinkage

The chemical shrinkage of CSA cement mixed with seawater with different concentrations is displayed in Figure 7. The figure displays that the hydration speed of the CSA cement was quick, and the chemical shrinkage of CSA cement in the first 12 h reached almost 80% of the final chemical shrinkage. The shrinkage was nearly stable after 24 h. The figure also shows that the concentration of seawater had different effects on the chemical shrinkage. The higher the concentration of seawater, the greater the chemical shrinkage. After being cured for 48 h, the shrinkage of the CSA cement mixed with 1SW, 3SW and 5SW was 7.89%, 15.21% and 26.54% higher than that of the freshwater-mixed CSA cement, respectively. When the CSA cement reacts with water and  $\text{CaSO}_4$ , the volume of the hydration products becomes smaller, and the volume reduction is called chemical shrinkage. The free  $\text{SO}_4^{2-}$  in seawater promotes the hydration reaction of CSA cement, and the higher

the concentration, the more rapid the reaction. The CSA cement mixed with seawater of a higher concentration resulted in more significant chemical shrinkage. In the later stage of hydration, the reaction was basically completed due to the lack of free water in the calcium sulphoaluminate cement, so the shrinkage of the CSA cement tended to be stable. Furthermore, the shrinkage of the cement paste was also largely due to the development of porosity [45,46]. The seawater of higher concentrations contained more salts. When the cement paste was soaked in freshwater, as shown in Figure 2, the salts would ooze out slowly and leave pores inside of the paste, and the higher concentrate, the more pores were produced, thus resulting in greater shrinkage.

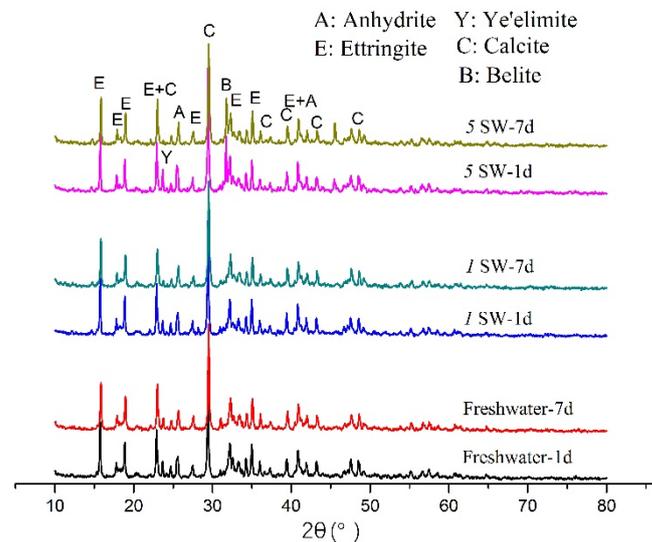


**Figure 7.** Influence of the seawater concentration on the chemical shrinkage of CSA cement.

### 3.4. XRD Analysis

Figure 8 displays the XRD patterns of the CSA paste. The figure displays that the hydration product of the CSA paste cured for 1 d with different types of mixing water was mainly ettringite (AFt). At the initial stage of hydration, the CSA powders reacted rapidly with gypsum and water to generate large amounts of ettringite crystals and aluminum hydroxide (see Equation (1)). Specifically, the concentration of seawater had a particular effect on the hydration products of the CSA cement. In the CSA paste mixed with 5SW, the peak of the XRD pattern of ye'elimite was higher, which indicates that there were more unhydrated CSA clinkers in the matrix. According to the analysis, as mentioned earlier, this was because a large amount of ettringite rapidly formed and precipitated on the surface of the cement particles when seawater of a higher concentration was applied, thus preventing further hydration. In addition, the XRD pattern peak of gypsum in the CSA paste mixed with 5SW was higher than that of the other two samples. The main reason is that there was more  $\text{SO}_4^{2-}$  in the seawater of higher concentrations which could produce more gypsum. After being cured for 7 d, the main hydration products of the CSA cement did not obviously change, and ettringite was still the main hydration product. However, the figure shows that the non-hydrated CSA paste mixed with seawater decreased gradually to an even lesser degree than the ones mixed with freshwater, which indicates that the hydration of seawater-mixed CSA cement was more complete. This is because the anhydrite kept dissolving continuously, and the osmotic pressure of the solution made the ettringite film produced in the previous stage rupture, so the ettringite kept generating in large quantities again. However, there were more sulfate ions in the seawater, and more gypsum was produced by hydration. When the gypsum was depleted, the CSA crystal continued to react with the water, resulting in the continuous formation of monosulfate (AFm) and

AH<sub>3</sub> (Equation (2)). However, the crystallinity of AFm was poor at the early stage, and no diffraction peak was found via XRD:



**Figure 8.** XRD patterns of the hydration products of CSA cement mixed with freshwater and seawater and cured at 1 d and 7 d.

The figure also displays that the hydration process of CSA cement was different when it was mixed with freshwater and seawater. There were some non-hydrated cement particles in the freshwater-mixed CSA cement after 7 d, which indicates that there was still room for improvement for the strength development of the CSA cement mixed with freshwater. However, when the CSA cement was mixed with 1SW, the non-hydrated cement particles were significantly reduced after 7 d of hydration, which indicates that the hydration degree of the CSA cement was improved. When mixed with 5SW, there were no non-hydrated cement particles in the CSA cement matrix, which implies the hydration was almost complete. The conclusion proves that a higher concentration of seawater is beneficial to the hydration of CSA cement.

Table 5 shows the Rietveld results (wt %) for the CSA cement mixed with different types of water and cured for 1 d. Table 5 proves that the concentration of seawater had an influence on the hydration product of the CSA cement. The concentration of 1SW helped to improve the hydration of the CSA cement, as the amount of belite and ye'elimite was lower and the amount of ettringite was higher. However, when the concentration of seawater reached 5SW, the seawater slightly impaired the hydration of the CSA cement, as the amount of ettringite became lower while the non-hydrated belite and ye'elimite remained higher. The results agreed well with the qualitative analysis based on the XRD patterns.

**Table 5.** Rietveld results (wt %) for the CSA cement mixed with different types of water and cured for 1 d.

Specimen	Ettringite	Calcite	Belite	Ye'elimite	Anhydrite
Freshwater, 1 d	45.5	25.4	26.4	2.7	0.0
1SW, 1 d	46.4	26.1	23.6	2.5	1.4
5SW, 1 d	42.0	27.2	25.7	3.2	1.9

Compared with the compressive strength test results, there exists a contradiction, as the compressive strength test results indicate that seawater of a higher concentration

was detrimental to the mechanical performance of the CSA cement. In contrast, the XRD results show that seawater of a high concentration helped with hydration. However, better hydration does not equal higher strength, as the strength of cement is related to a lot of factors, such as the water-to-cement ratio, microcracks and hydration products. If ettringite is generated too fast during the hydration, it will cause expansion damage in the paste. At this time, the slurry structure is not well developed and has a high porosity. Therefore, although the amount of ettringite generated by the CSA cement mixed with seawater was greater, there were many microcracks in the cement matrix, which hindered the further development of its mechanical properties.

### 3.5. DTA-TG Analysis

Figure 9 shows the thermogravimetric analysis results of the CSA cement under different conditions. The figure demonstrates that the primary hydration products of CSA cement are AFt and aluminium hydroxide [18,19]. The calcite is the original material that does not participate in the hydration. Figure 9a shows that whether freshwater or seawater was used for mixing, a large amount of ettringite was produced after 1 d of hydration. However, the amount of ettringite produced by freshwater was slightly greater than that produced by seawater, which can also be seen in Figure 10a. The reason for this, as was explained previously, is that the ettringite rapidly produced by seawater precipitated on the surface of the CSA particles and prevented hydration. When the CSA cement was cured for 7 d, the quantity of ettringite produced by seawater nearly reached that of freshwater, which can also be seen in Figure 9b. Figure 9c displays that the amount of ettringite of the CSA cement mixed with freshwater decreased after being cured for 7 d. The reason for the decline of ettringite in freshwater is that some of the ettringite was changed to monosulfate (AFm) via Equation (2) if the gypsum was depleted. However, the crystallinity of AFm was poor in the early stage, and no diffraction peak was found in the XRD analysis. In Figure 9d, the amount of ettringite in the seawater-mixed CSA cement samples did not significantly change after being cured for 7 d. This is because the seawater could continuously provide sulfate ions to form calcium sulfate. Therefore, the hydration products of the CSA cement mixed with seawater existed mainly in the form of AFt. Figure 10b proves that the amount of ettringite was almost the same both in the specimens cured for 1 d and 7 d if they were mixed with seawater.

### 3.6. SEM Analysis

Figure 11 displays the microstructure diagrams of the CSA cement in different conditions. It can be seen that under the action of various mixing water, a large amount of ettringite was produced after being cured for 1 d, indicating that the hydration speed of the CSA cement was very fast. However, the hydration products and microstructures of the CSA paste differed with different types of mixing water. Compared with Figure 11a,c,e, it can be seen that acicular and lamellar ettringite were produced after 1 d of hydration of the CSA cement mixed with freshwater, and the interior of the matrix was relatively loose. However, the CSA cement mixed with 1SW produced some acicular ettringite after hydration for 1 d with a denser matrix. When the concentration of the seawater was increased by five times, the acicular ettringite decreased. Due to the rapid formation rate of hydration products in the early stage, the hydration products lacked the time to form a uniform and dense network structure but formed heterogeneous porous paste joints with a large porosity.

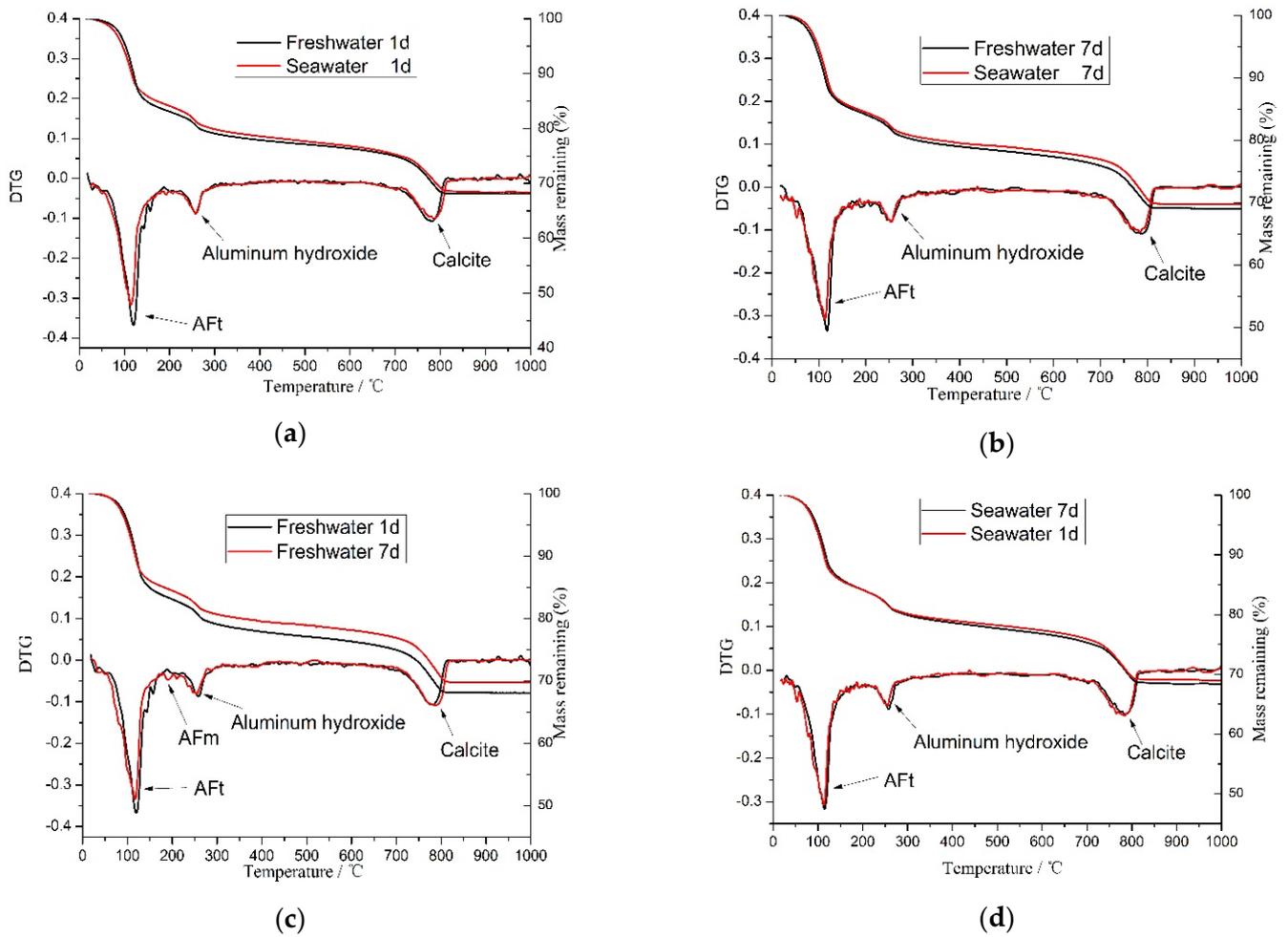


Figure 9. TG–DTG curves of CSA cement mixed with different types of water at 1 d and 7 d.

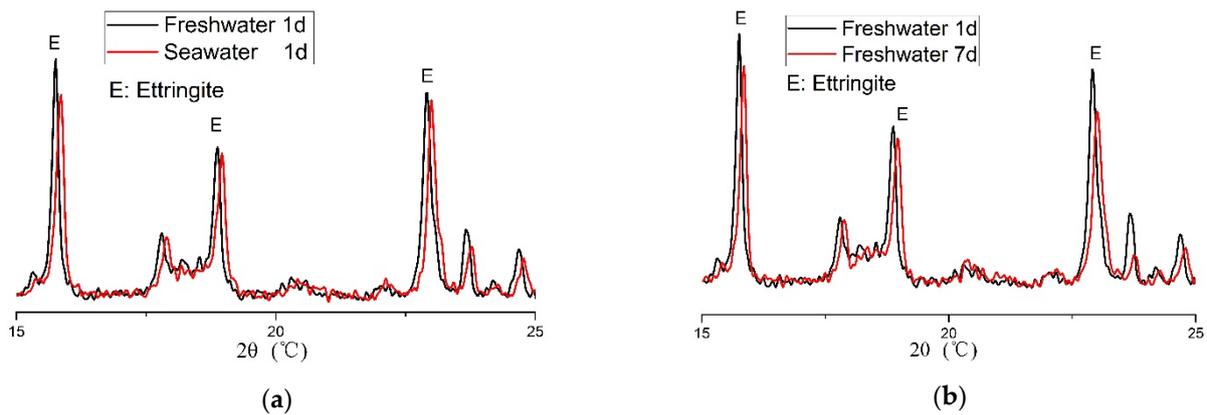
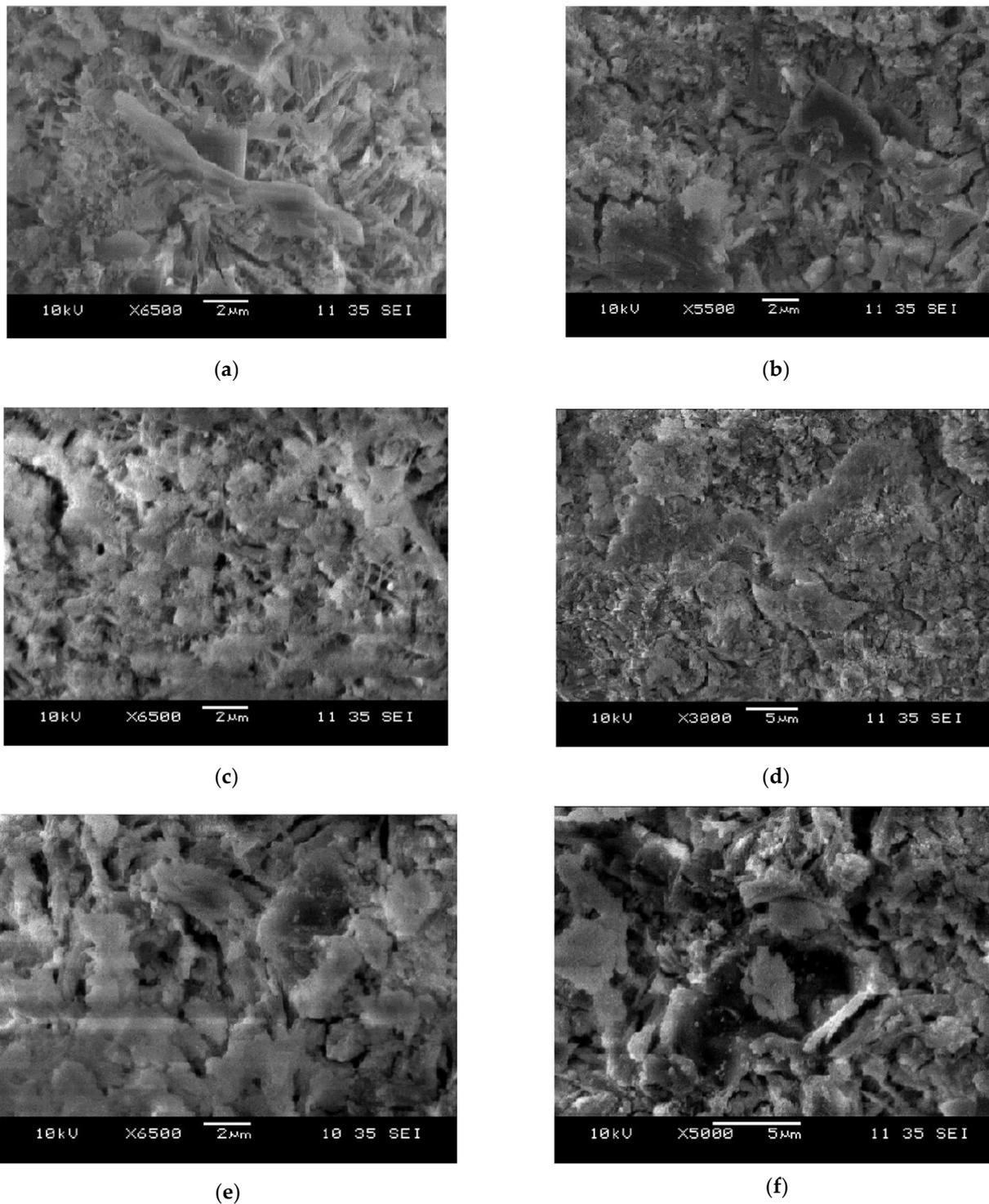


Figure 10. XRD patterns of CSA cement mixed with freshwater and seawater (a) cured for 1 d or (b) cured for 7 d.



**Figure 11.** SEM diagrams of CSA cement mixed with different types of water and cured for different times: (a) freshwater cured for 1 d, (b) freshwater cured for 7 d, (c) 1SW cured for 1 d, (d) 1SW cured for 7 d, (e) 5SW cured for 1 d and (f) 5SW cured for 7 d.

Compared with Figure 11b,d,f, the hydration process of the CSA cement cured for 7 d was changed under the action of different mixing water. The acicular ettringite of the CSA cement mixed with freshwater gradually decreased, and the internal compactness of the matrix was further improved, which indicates that the strength of the matrix was improved. The acicular ettringite of the CSA cement mixed with seawater gradually disappeared, and the compactness of the matrix was improved. However, microcracks

gradually appeared in the cement matrix. This phenomenon was caused by the generation and expansion of ettringite, which made the cracks in the cement matrix increase gradually. The microstructure of the CSA cement mixed with 5SW did not change significantly, which indicates that most of the hydration reaction was completed in 1 d. The SEM diagram reflects that the microstructure of this CSA cement was looser and more porous than those of the other two samples, which is the reason why it had a lower mechanical strength.

#### 4. Conclusions

In this study, an experimental investigation on the effect of the seawater concentration on the early hydration of CSA cement was carried out. Based on the experimental study, the following conclusions can be drawn:

- (1) The hydration reaction of CSA cement occurs quickly. The primary hydration products are AFt and aluminium hydroxide, while a small amount of ettringite (AFt) becomes monosulfate (AFm) in the freshwater-mixed CSA cement.
- (2) A low concentration of seawater can promote the hydration of CSA cement. Sulfate ions can accelerate the hydration reaction to produce AFt. The early strength of the CSA cement mixed with seawater of a lower concentration is higher than that of freshwater-mixed CSA cement. However, the strength of the samples mixed with high concentrations seawater will decrease significantly, and the higher the concentration is, the greater the decrease will be.
- (3) Seawater retards the setting time of CSA cement, and the higher the concentration, the more pronounced the delay. Seawater can increase the chemical shrinkage, and the higher the concentration of seawater, the greater the chemical shrinkage.
- (4) According to the analysis of SEM, XRD and TGA,  $\text{SO}_4^{2-}$  in seawater can accelerate the hydration reaction and produce insoluble AFt to precipitate on the surface of CSA cement particles and prevent their further hydration. Moreover, the higher the concentration is, the faster ettringite is formed and the more non-hydrated the sulphoaluminate cement is. Aside from that, a lot of AFt is generated in a very short time, which makes the cement matrix expand and produces microcracks in the cement matrix, resulting in the lower compressive strength of the cement paste.

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