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Research Article

Removal of High-Concentration Sulfate from Seawater by Ettringite Precipitation

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Due to the worldwide scarcity of fresh water, seawater becomes an alternative base fluid in hydraulic fracturing for oil and gas production. However, the injection of seawater that contains high concentration of sulfate will induce the scale formation and thus reduce hydrocarbon production. One of the most effective ways to solve this problem is to remove sulfate ions from seawater before fracturing application. The objective of this study is to develop an effective and environment-friendly approach to remove sulfate ions from seawater based on coprecipitation of SO_4^{2-} with $NaAlO_2$ and CaO as ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$). Residual sulfate concentration in treated seawater was determined when $NaAlO_2$ and CaO dosed at different molar ratios to sulfate. Results showed the efficiency of sulfate removal was more than 90% (4290 ppm to ~400 ppm) when Al : Ca : S = 2 : 6 : 1. It was found the sulfate precipitation completed in 15 mins with stirring under an alkaline condition (pH ≈ 12) and was not affected by temperature (15°C to 45°C). Increasing the Na^+ concentration from 0 to 25,000 ppm in waters resulted in the increment of residual sulfate concentration from 250 to ~600 ppm, decreasing the removal efficiency. Besides, the analysis of Ca^{2+} and Mg^{2+} in treated seawater showed the Ca^{2+} concentrations were on the similar level as that before the treatment and Mg^{2+} was removed in the precipitation process, which is beneficial to the application of the treated seawater. The morphology and element analysis of the collected precipitates showed that the ettringites were in a layered shape with composition between $Ca_6Al_2(SO_4)_3(OH)_{12}$ and $Ca_4Al_2(SO_4)(OH)_{12}$ at the optimized chemical dosage; therefore, the developed ettringite precipitation method could effectively remove sulfate from seawater without toxic chemicals involved, which benefits seawater hydraulic fracturing in an economic way, and this contributes to water sustainability.

1. Introduction

Hydraulic fracturing technique has been extensively used in the oil and gas industry to produce oil from reservoirs, but it is currently challenged by the limited availability of fresh water for preparing fracturing fluids [1]. Seawater is considered to be an alternative water source for hydraulic fracturing. However, one of the primary challenges is the tendency of scale formation due to the incompatibility between seawater and formation water [2–4]. As the seawater usually contains a high concentration of sulfate ions (>4,000 ppm) and the formation water contains very high concentrations of calcium, barium, and/or strontium ions, $CaSO_4$, $BaSO_4$, and/or $SrSO_4$ precipitates can be formed when these two fluids encounter in the reservoir [5]. The formed sulfate precipitates could lead to severe formation damages, overall reduction in hydrocarbon production capacity, and some other adverse effects [6, 7]. Therefore, the sulfate concentration in seawater should be reduced by >90% for a successful seawater hydraulic fracturing, especially when normal scale mitigation strategies perform poorly in high-temperature reservoirs [8, 9].

Currently, the most effective and popular method applied to remove sulfate from seawater for hydraulic fracturing is nanofiltration [10, 11]. This technology is based on the rejection of sulfate ions when water passing through a membrane with nanometer-sized pores under high pressure (usually 2–15 bar). It has been reported to reduce sulfate

concentration to <50 ppm in field [12–14]; but the disadvantages of nanofiltration, including intensive energy input required to push water through the membrane and high operation cost, hinder the large-scale field applications. Although researchers have devoted years of efforts to develop state-of-art membranes to improve water permeance [15], this technology is still far from mass production and becomes unsuitable for a low-carbon economy nowadays. Compared to nanofiltration technology, chemical precipitation methods show growing potential in seawater treatment as these methods have no energy input required and the operation cost is much lower [16, 17]. The formed precipitates through reactions of the added chemicals and sulfate can be treated as valuable industrial products or recycled in the water treatment process. Thus, it is of great benefit to develop a chemical precipitation method for seawater fracturing.

The $CaSO_4$ precipitation method is one of the most widely applied methods in the industry to remove sulfate in waters through the formation of $CaSO_4$ or gypsum from Ca^{2+} and SO_4^{2-}; but the high solubility of $CaSO_4$ (1,200–2,000 ppm in low-salinity water and 5000~7000 ppm in high-salinity water) results in insufficient removal of SO_4^{2-} and high Ca^{2+} concentrations in treated water, which could significantly degrade the performance of prepared fracturing fluid [2, 18–20]. Another highly effective method is $BaSO_4$ precipitation, in which barium chloride or barium carbonate is used to form barium sulfate ($pK_{sp} = 10$) with SO_4^{2-}. This method could reduce the sulfate concentration to as low as 50 ppm [21, 22]. However, the toxicity of barium turned out to be a compelling problem to the environment, which should be seriously considered before field applications. Therefore, a highly efficient, energy-saving, and environment-friendly method is in urgent need to fulfill the seawater treatment demand for hydraulic fracturing.

The ettringite precipitation method has been reported as a highly effective and popular solution for treating wastewaters containing high-concentration sulfate, such as mine drainage and FGD wastewater [23]. This method is based on the reaction of aluminum and calcium compounds with sulfate to form insoluble ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) [24]. The commonly used aluminum compounds include aluminum chloride ($AlCl_3$), polyaluminum chloride (PAC), aluminum sodium oxide ($NaAlO_2$), aluminum nitrate ($Al(NO_3)_3$), or $Al(OH)_3$, and the calcium compounds include but are not limited to CaO, $Ca(OH)_2$, or $CaCl_2$ in the application [25–28]. The sulfate concentration after treatment is typically 200–1000 ppm, depending on the initial sulfate concentration, pH value, and other contaminants in the water [29, 30]. The advantages of ettringite precipitation method include (i) high sulfate removal efficiency along with a easy and flexible water treatment process; (ii) avoided toxic elements in the whole precipitation process; and (iii) valuable products achieved after the reaction, which were reported to be used for removing other toxic compounds such as arsenate, boron, and heavy metals and also an important component in cement concretes [31–35].

Though ettringite precipitation methods have been successfully used for sulfate removal in some industrial water treatment, the application to remove sulfate from seawater has not been reported. Comparing to previous reports, which usually focused on low-salinity waters (total dissolved solids <10,000 ppm) [17, 26–28], the study on the performance of ettringite precipitation in high-salinity waters (TDS >50,000 ppm) is essential and meaningful.

Aiming to reduce the seawater sulfate concentration by an order of magnitude (from thousands to hundreds of ppm), the capability of the three mentioned precipitation methods with certain chemicals is compared, and the development of ettringite method using $NaAlO_2$ and CaO is further elaborated as the selected method. The efficiency of sulfate removal from a certain seawater sample (TDS of 57,600 ppm, sulfate of 4,290 ppm) was optimized at a series of chemical dosages. It turned out that >90% sulfate in seawater could be removed at an optimized molar ratio of $NaAlO_2$ and CaO to SO_4^{2-}. The influences of stirring time in precipitation, Na^+ concentrations, solution pH, and working temperature have also been systematically studied. Besides, Ca^{2+} and Mg^{2+} ions in treated seawater have been analyzed using an inductively coupled plasma mass spectrometer (ICP-MS), and the results showed the treated water could meet the requirements for fracturing fluid preparation. The collected precipitates formed at different $NaAlO_2$ and CaO dosages have also been characterized through scanning electron microscopy (SEM). In addition, the treated seawater was processed by CO_2 injection to reach neutral pH, and the excess calcium was removed as $CaCO_3$. After all, this work has shown that the developed ettringite precipitation method is an effective way to remove sulfate from seawater, so that the treated water can be used as a base fluid for hydraulic fracturing applications. Besides, this work not only broadens the applicability of the ettringite method at high-salinity conditions but also provides a new seawater treatment option for hydraulic fracturing from a sustainable perspective.

2. Materials and Methods

2.1. Materials. The salts NaCl, $CaCl_2\cdot 2H_2O$, $MgCl_2\cdot 6H_2O$, Na_2SO_4, $NaHCO_3$ $NaAlO_2$, CaO, $BaCl_2$, $Ca(OH)_2$, polymeric aluminum (PAC), and $AlCl_3$ were obtained on analytical grade from Sinopharm Reagent (Beijing) and used as received. The salts were dissolved in deionized water to prepare seawater. The TDS of the seawater was 57,670 ppm with 4,290 ppm sulfate. The detailed composition is shown in Table 1. Seawater preparation is based on the composition in Table 1, and each time 2 L of seawater was prepared. Firstly, the measured NaCl, $CaCl_2\cdot 2H_2O$, and $MgCl_2\cdot 6H_2O$ were dissolved in about 1.2 L deionized water in a 2 L beaker. The measured Na_2SO_4 and $NaHCO_3$ were dissolved in about 300 mL deionized water in another 600 mL beaker. After the salts were all dissolved through stirring, the solution containing Na_2SO_4 and $NaHCO_3$ was mixed with the solution containing NaCl, $CaCl_2\cdot 2H_2O$, and $MgCl_2\cdot 6H_2O$ in the 2 L beaker, and the solutions were further stirred for another 30 mins. This process makes sure the cationic ions and

Table 1: Ion contents in seawater.

Ions	Na^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Cl^-	HCO_3^-	Total dissolved solids
Ion amount, ppm	18,300	650	2,110	4,290	32,200	120	57,670

anionic ions will not precipitate during solution preparation. Then, the solutions were transferred into a 2 L volumetric flask and the solution volume was finalized to 2 L.

2.2. Removal of Sulfate Ions. The steps of ettringite precipitation were performed as follows: (1) 50 mL of seawater was taken in a glass beaker, and a certain amount of chemicals in solid were added to the solution; (2) the solution was stirred at 200 rpm using an IKA mechanical agitator for a certain time; and (3) the precipitates were separated from solutions by sedimentation for 1 h. The upper-layer water was collected as treated seawater for sulfate and other ions analysis. According to the above steps, batch experiments effecting different experimental conditions on sulfate removal were implemented, including CaO dosage (the molar ratios of CaO to sulfate of 2 : 1, 3 : 1, 4 : 1, and6 : 1), $NaAlO_2$ dosage (the molar ratios of $NaAlO_2$ to sulfate of 0.8 : 1, 1 : 1, and 2 : 1), precipitation time (0, 1, 2, 5, 10, 15, 60, 120 mins), Na^+ concentrations (0, 1000, 2500, 5000, 10,000, and 25,000 ppm), and solution temperature (15°C, 30°C, and 45°C). In the dynamic precipitation experiments, the formed precipitates were separated from seawater by filtration through 0.45 μm membrane. The pH value of the solutions was measured using a pH meter (Mettler Toledo).

2.3. Chemical Dosage Optimization. $NaAlO_2$ is added at molar ratios of 0.8:1, 1:1, and 2:1 to SO_4^{2-} in seawater. When the $NaAlO_2$-to-SO_4^{2-} ratio is fixed, the CaO dosages were at molar ratios of 2:1, 3:1, 4:1, and 6:1 to SO_4^{2-}, respectively. After the precipitation reaction, the residual SO_4^{2-} concentrations were determined by ICP-MS to evaluate the efficiency of sulfate removal. After the optimization of the molar ratios of $NaAlO_2$ and CaO, the molar ratio of Al:Ca was set at 1:3, and the dosage of $NaAlO_2$ was set at 0, 3000, 3750, 7500, and 11,250 ppm to determine the optimized dosage.

2.4. Ion Concentrations in Water. The sulfate, calcium, and magnesium concentrations were measured using an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7900). Water obtained from the Thermo Scientific water purification system was used to prepare standard solutions in ICP-MS analysis. For sulfate analysis, Na_2SO_4 was used to prepare the standard calibration solutions and ^{34}S was selected to indicate sulfate concentration. The calibration line of S was prepared in the range between 25 ppm and 500 ppm, presenting SO_4^{2-} is in the range between 75 ppm and 1,500 ppm. In the measurement of Ca^{2+} and Mg^{2+} in the treated water, a mixed standard calibration solution was prepared using $CaCl_2{\cdot}2H_2O$ and $MgCl_2{\cdot}6H_2O$. Specifically, ^{43}Ca and ^{24}Mg were chosen to indicate the ion concentrations, respectively. The dynamic range was set from 1 ppm to 50 ppm for both the ions. The seawater was diluted with appropriate times before analysis.

2.5. Precipitate Characterization. For the collection of the obtained precipitates, the treated water was separated with solids by sedimentation at room temperature 1 h. The sludge was then collected and washed three times using deionized water. Then, the sludge was dried at 60°C for 24 h. The dried solids were crushed into powders. The morphology and element compositions were characterized through scanning electron microscopy-energy dispersive spectroscopy SEM/EDS (Hitachi SU8000, Japan). The samples were Pt sputtering processed before the SEM observation.

3. Results

3.1. Comparison of $CaSO_4$, $BaSO_4$, and Ettringite Precipitation Methods. Although it is known from previous work that $CaSO_4$ precipitation is not so effective compared to $BaSO_4$ and ettringite precipitation methods, it is still worthy comparing the sulfate removal efficiency of the three methods [18, 21]. Preliminary experiments were carried out using six groups of chemicals. The results of the residual sulfate and calcium ion concentrations in the treated seawater, as well as the chemical dosages, are shown in Table 2. For $CaSO_4$ methods, the addition of $CaCl_2{\cdot}2H_2O$, CaO, or $Ca(OH)_2$ lowered the sulfate concentration in seawater to a limited value (>1,500 ppm). It is not surprising that, with the decrease of sulfate concentration, the calcium concentration greatly increased. For example, the overdose of $CaCl_2$ could only lower the sulfate concentration to 1,600 ppm, and the concentration of Ca^{2+} significantly increased from 650 ppm to 5,000 ppm, which could cause compatibility issues and other side effects during fracturing fluid preparation, especially in the case of guar gum-based and slick-water fluids. Thus, the resultant sulfate and calcium concentrations both cannot meet the requirements for hydraulic fluid preparation. And it was concluded that $CaSO_4$ methods were not applicable for sulfate removal in seawater. When $BaCl_2{\cdot}2H_2O$ was used as the precipitation agent, the sulfate concentration can be reduced to as low as 300 ppm, without increasing calcium concentration in resultant waters. This proves that the $BaSO_4$ method is efficient in sulfate removal, but the toxicity remains to be a problem in field applications.

As to ettringite methods, two formulations were selected to perform sulfate removal in seawater. One formulation is $NaAlO_2$ and CaO, and the other is polyaluminum chloride (PAC) with $AlCl_3$ and CaO. The results showed the formulation of PAC/$AlCl_3$/CaO could only reduce 50% of sulfate and resulted in an increase of calcium concentration. This is possibly because of the dissolution problem of PAC in seawater, resulting in an insufficiency of aluminum in the solution and a low precipitation efficiency. On the contrary,

Table 2: Sulfate and calcium concentrations in treated seawater by using $CaSO_4$, $BaSO_4$, and ettringite precipitation methods.

Chemical	Dosage (g/L)	Sulfate (ppm)	Calcium (ppm)	Precipitates
$CaCl_2{\cdot}2H_2O$	9.4	1,677	5,382	$CaSO_4$
CaO	2.5	3,258	1,319	$CaSO_4$
Ca $(OH)_2$	10.4	2,301	2,836	$CaSO_4$
$BaCl_2{\cdot}2H_2O$	9.4	301	506	$BaSO_4$
$NaAlO_2$/CaO	7.5/10.9	402	811	Ettringite
PAC/$AlCl_3$/CaO	2.86/7.2/7.2	2,388	2,434	Ettringite

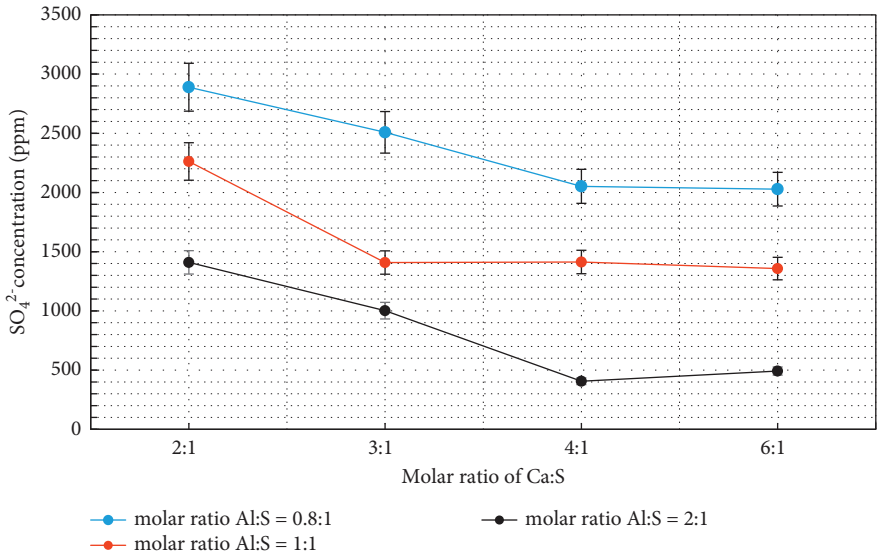

Figure 1: Sulfate concentration in seawater after treatment with various molar ratios of Al : S and Ca : S. The RSD of sulfate concentration is less than 10%.

the other formulation of $NaAlO_2$ and CaO could greatly reduce the sulfate concentration in seawater from 4290 ppm to ~400 ppm. The slight increase of calcium concentration in the treated water is acceptable. Due to the possible environmental influences by toxic barium ions, this work will only focus on the optimization of $NaAlO_2$/CaO for further investigation at this point.

3.2. Effects of $NaAlO_2$ and CaO Dosages. The dosages of $NaAlO_2$ and CaO are one of the key factors in the precipitation reaction and sulfate removal efficiency. The sulfate concentrations in seawater after treatment by adding series of $NaAlO_2$ and CaO are shown in Figure 1. For concision, $NaAlO_2$, CaO, and SO_4^{2-} were abbreviated as Al, Ca, and S, respectively. The molar ratio of Al : S was set from 0.8 : 1 to 2 : 1, and the molar ratio of Ca : S was set from 2 : 1 to 6 : 1. The solutions were stirred for 1 h after chemicals were added to make sure the precipitation reactions completed.

As depicted in Figure 1, sulfate removal was greatly affected by the $NaAlO_2$ dosage. With the same initial calcium dosages, an increase of Al : S from 0.8 : 1 to 2 : 1 led to a significantly lower sulfate concentration. The molecular Al : S ratio found in the chemical formula $Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$ is about 0.67; but, when $NaAlO_2$ was added at a molar ratio of 0.8, the precipitation efficiency was not obviously improved, with the lowest sulfate concentration at 1,800 ppm. With the increase of Al : S ratio, the amount of ettringite generated was reduced and the formation of the monosulfate ($Ca_4Al_2(SO_4)(OH)_{12}$) increased. When the Al : S molar ratio was set at 2 : 1, the sulfate concentrations were lower than the cases of 0.8 : 1 and 1 : 1. And the lowest sulfate concentration is 406 ppm when the added CaO was at a molar ratio of 4 : 1 to SO_4^{2-} in seawater, under which condition, the ratios between the added Al and Ca were close to the monosulfate formula.

When the Al : S molar ratio is fixed, it is found that sulfate removal increased with an increase of CaO at first, and then the curve became flat when the Ca : S was higher than 4 : 1 (shown in Figure 1). The quick drop in the sulfate concentration when the molar ratio of Ca : S increased from 2 : 1 to 4 : 1 can be possibly explained as the increased Ca^{2+} concentration in the solution, which facilitated the precipitation of sulfate in the form of monosulfate. When the molar ratio Ca : S increased to 6 : 1, the excess calcium did not greatly affect the residual sulfate concentration. Although the most efficient chemical dosages for sulfate removal is with the molar ratio of Al : Ca : S at 2 : 4 : 1, the molar ratio of Al : Ca : S at 2 : 6 : 1 was selected because the water recovery at the Al : Ca : S of 2 : 6 : 1 was higher than that at the Al : Ca : S of 2 : 4 : 1 (Figure S1, Supporting Information).

Figure 2 presents the sulfate concentration in the treated seawater when 0, 3000, 3750, 7500, and 11,250 ppm of $NaAlO_2$ were added with a fixed molar ratio with CaO at 1 :

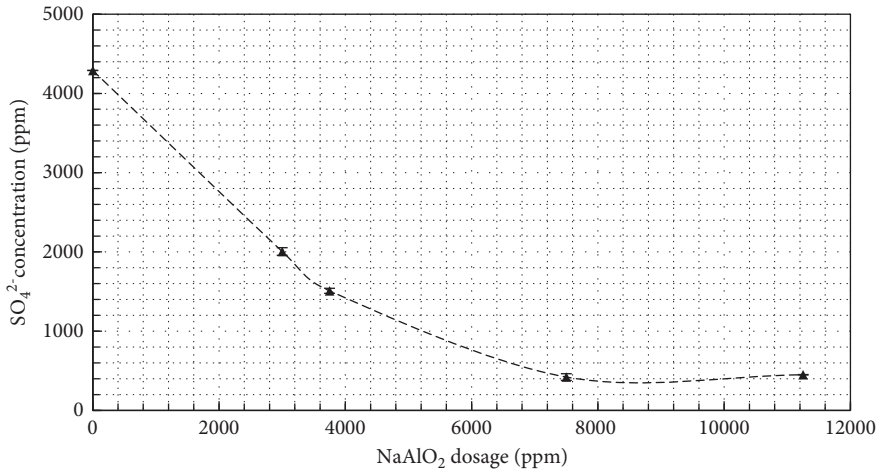

Figure 2: Sulfate concentration in seawater after adding different concentrations of $NaAlO_2$ at a fixed Al : Ca molar ratio of 1 : 3. The RSD of sulfate concentration is less than 10%.

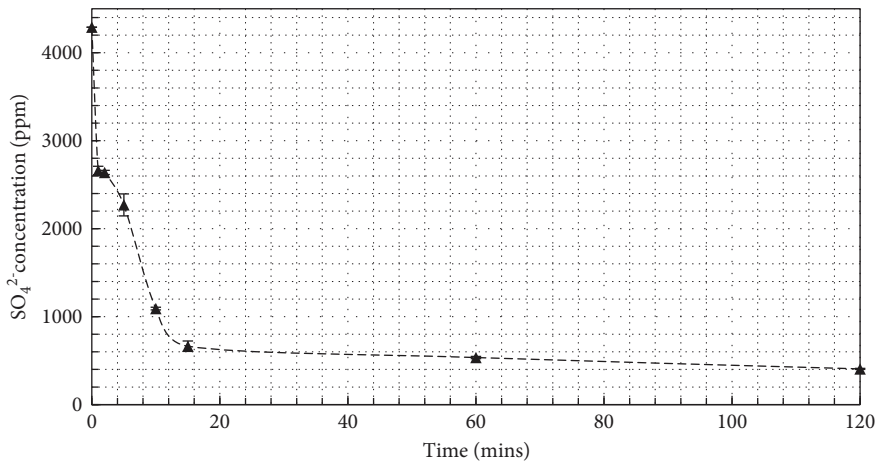

Figure 3: Effect of stirring time in precipitation reactions on the sulfate concentration in treated seawater using the ettringite method. The added molar ratio of Al : Ca : S is 2 : 6 : 1. The RSD of sulfate concentration is less than 10%.

3. The corresponding molar ratio of $NaAlO_2$ to SO_4^{2-} in seawater is 0 : 1, 0.8 : 1, 1 : 1, 2 : 1, and 3 : 1, with the corresponding molar ratios of Ca : S of 2.4 : 1, 3 : 1, 6 : 1, and 9 : 1, respectively. The results showed the sulfate removal efficiency increased with the increasing concentration of $NaAlO_2$ until the dosage was higher than 7,500 ppm. Further addition of aluminum cannot improve the precipitation of ettringite, and thus the optimized $NaAlO_2$ dosage was determined as 7,500 ppm.

3.3. Effects of Stirring Time in Precipitation Reaction. Figure 3 shows the dynamic sulfate concentration in seawater after the addition of $NaAlO_2$ and CaO with a molar ratio of 2 : 6 : 1 (Al : Ca : S)$^{-}$. Seawater was separated immediately with formed precipitates by filtration through the 0.45 μm membrane after a certain period of time of 1, 2, 5, 15, 60, and 120 mins. The results showed that the sulfate concentration dropped very quickly in the first 2 mins. This can be explained that, at the first stage, the hydrolysis of dissolved $NaAlO_2$ and CaO provided a large amount of $Al(OH)_3$ and Ca^{2+}, which led to a high reaction efficiency with SO_4^{2-}. Then, the sulfate reduction continued in a much smoothing pace. After stirring for 15 mins, the decrease of sulfate concentration in the water was quite slow. The results showed that the reaction of aluminum, calcium, and sulfate is a rapid reaction, almost completed within 15 mins, which is acceptable for field applications.

3.4. Effects of Na^+ in the Solution. Applications of the ettringite method for water treatment in mine drainage, FGD water, and textile industry have been discussed in the literature about the effects of pH values and some ions like Mg^{2+} on the sulfate removal efficiency [23, 27]; but the effect of salinity, especially very high salinity such as in seawater, on the removal of sulfate seemed to be never mentioned. Here, the sulfate concentration was fixed at 4,290 ppm and the residual SO_4^{2-} concentration in a series of NaCl solutions was investigated at different concentrations after treatment. The Na^+ ion concentration was set from 0 (deionized water) to 25,000 ppm (~63,600 ppm NaCl). The

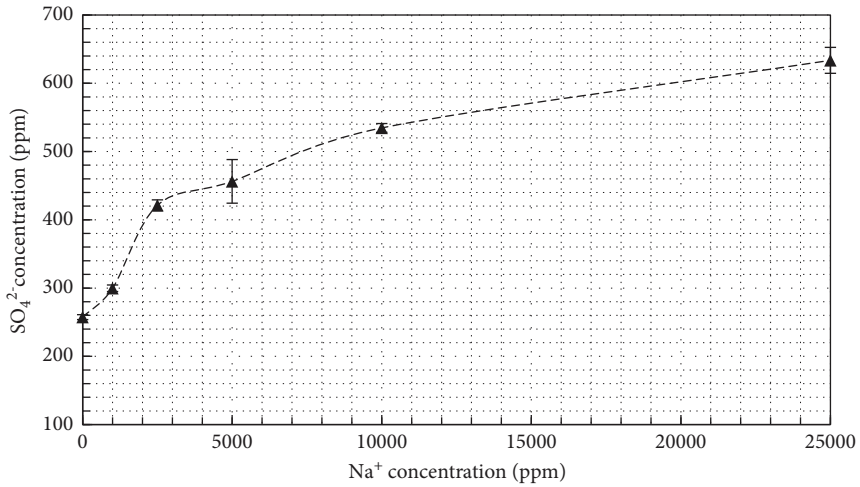

Figure 4: Effects of different concentrations of Na^+ ions on the sulfate concentration in treated NaCl solutions by the ettringite method. The initial sulfate concentration is 4,290 ppm, and the added chemical dosage of Al : Ca : S is at a molar ratio of 2 : 6 : 1. The RSD of sulfate concentration is less than 10%.

results in Figure 4 show an "S" shape curve, and the sulfate concentration in the treated water increased with the increase of Na^+ concentration. When the Na^+ concentration was less than 5,000 ppm, the sulfate concentration increased quickly from 250 ppm to 400 ppm. With the further increase of Na^+ in the solution to 25,000 ppm, the sulfate concentration increased to 600 ppm. The results indicated that a high concentration of Na^+ in the solution could inhibit the ettringite precipitation and lower the sulfate removal efficiency, which should be considered in high-salinity water treatment.

3.5. Effects of the Solution pH Value. The pH value of the solution could be influenced by the hydrolysis of added $NaAlO_2$ and CaO, mainly the CaO. Figure 5 shows the solution pH values after addition of $NaAlO_2$ and CaO at various dosages. It was found that the pH value increased from 9~10 to >12 when the molar ratio of Ca : S increased from 2 : 1 to 6 : 1. When the Ca : S was 2 : 1 or 3 : 1, the pH also slightly increased with the addition of $NaAlO_2$ due to hydrolysis. When the pH was higher than 12, the hydrolysis of $NaAlO_2$ and CaO were inhibited and the pH value did not obviously increase further. The previous results showed the highest sulfate removal efficiency was achieved when the Al : Ca : S was 2 : 4 : 1, with a pH value of 12.2. Under this condition, with the process of precipitation reaction, the consumption of hydroxyl ions and aluminum/calcium ions facilitated the hydrolysis reaction of $NaAlO_2$ and CaO to keep a dynamic equilibrium between these ions and a stable alkaline environment. A possible issue at a high pH value is that the HCO_3^- in seawater would form CaO_3^{2-}, which could react with ettringite to form hydrated carbonated calcium aluminate ($3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O$) [27]. However, the reduction of sulfate removal efficiency at a high pH value was not observed so far. This could possibly be explained by the much lower concentration of bicarbonate than sulfate, and thus the possible influences can be neglected.

3.6. Effect of Working Temperature in Precipitation Reaction. The solution temperature could affect the hydrolysis of $NaAlO_2$ and CaO and the precipitation reaction. For the application of the method in field, it is important to make sure the sulfate removal efficiency is steady regardless the temperature change over the year. Thus, the precipitation reactions were carried out in a water bath with temperature controlled at 15°C, 30°C, and 45°C, respectively. Table 3 shows the sulfate removal efficiency after precipitation was similar and the working temperature had a minimal effect in the tested range.

3.7. Ca^{2+} and Mg^{2+} in Treated Water Using Ettringite Method. Since the divalent ions in seawater after treatment have a great impact on the fracturing fluid properties regarding the added polymers, surfactants, or other chemicals, the concentrations of Ca^{2+} and Mg^{2+} were systematically be analyzed using ICP-MS.

Figure 6(a) shows the residual Ca^{2+} concentration in seawater with different dosages of $NaAlO_2$ and CaO, and Figure 6(b) presents the change comparing to the initial Ca^{2+} concentration. It was found that, when the chemical dosage of Al : S is at 0.8 : 1 and Ca : S is >2 : 1, the Ca^{2+} concentrations were much higher than the initial value, which was possibly due to the lack of Al, leading to the insufficient precipitation of sulfate and a large amount of Ca^{2+} left in the solution. At the exception point when Al : Ca : S was 0.8 : 2 : 1, Ca^{2+} ions were not adequate either and the resultant concentration was quite low. With the increase of Al dosage at the same molar ratio of Ca : S, the residual Ca^{2+} concentration decreased, indicating the increase of sulfate precipitation efficiency. The curves of Al : S at 1 : 1 and 2 : 1 were similar, that the residual Ca^{2+} decreased and then slightly increased with the addition of CaO. As discussed before, with the increasing molar ratio of Al : S, the $Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$ was less generated and the formation of $Ca_4Al_2(SO_4)(OH)_{12}$ increased. The molar ratio of Ca : S in precipitates shifted from 2 : 1 to 4 : 1. When the added CaO was less than the theoretical molar

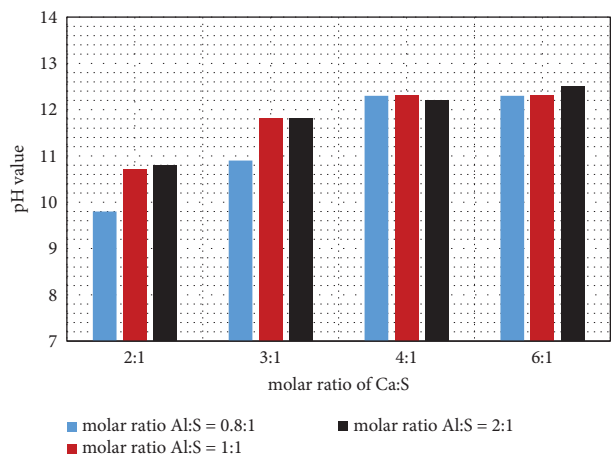

Figure 6: Solution pH value in seawater after addition of $NaAlO_2$ and CaO at series of dosages.

Table 3: Sulfate removal efficiency in seawater at different working temperatures.

Working temperature (°C)	Sulfate removal efficiency (%)
15	86.9
30	88.9
45	87.4

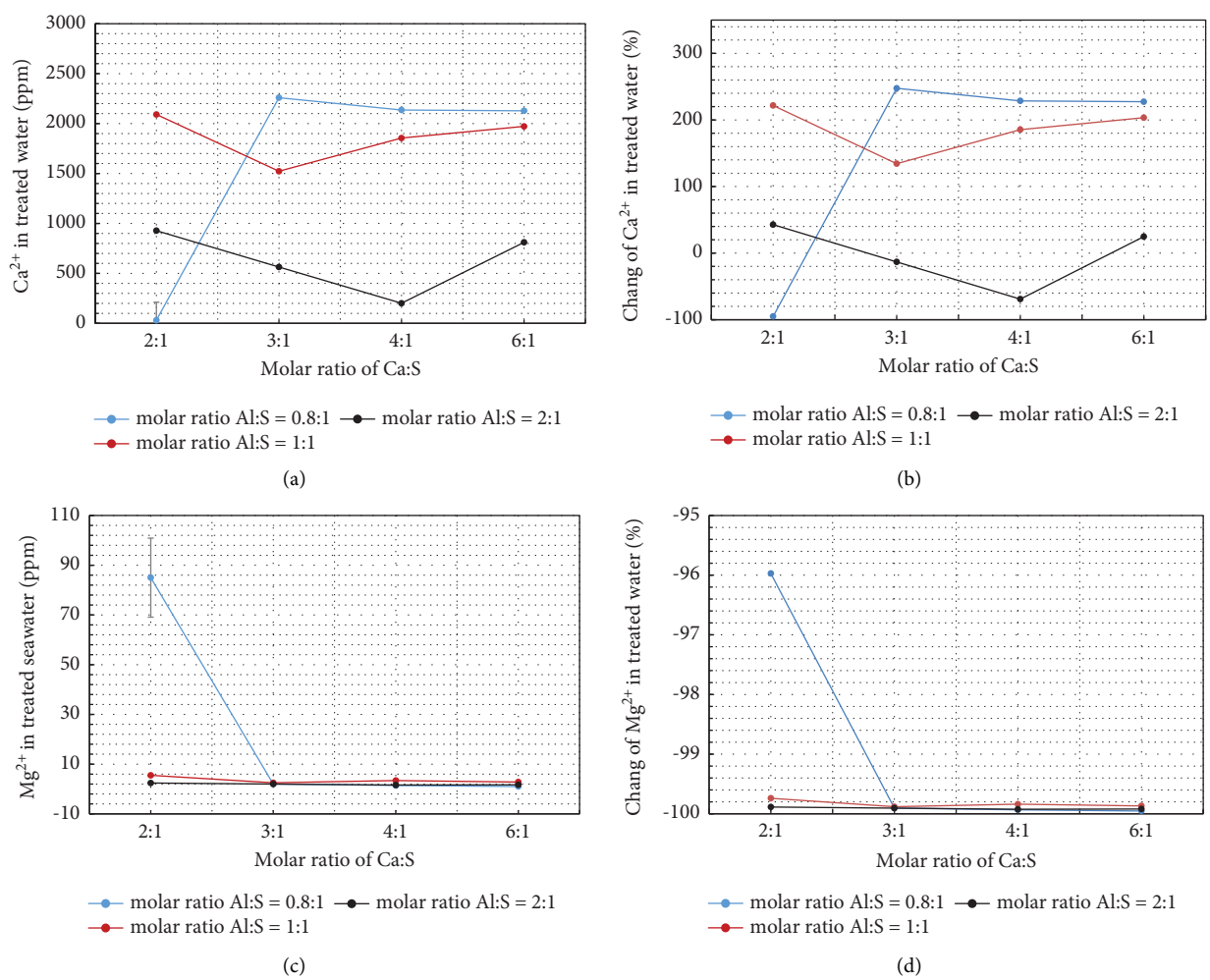

Figure 6: Calcium and magnesium concentrations in treated seawater. The original concentration of Ca^{2+} and Mg^{2+} in seawater is 650 ppm and 2,100 ppm, respectively.

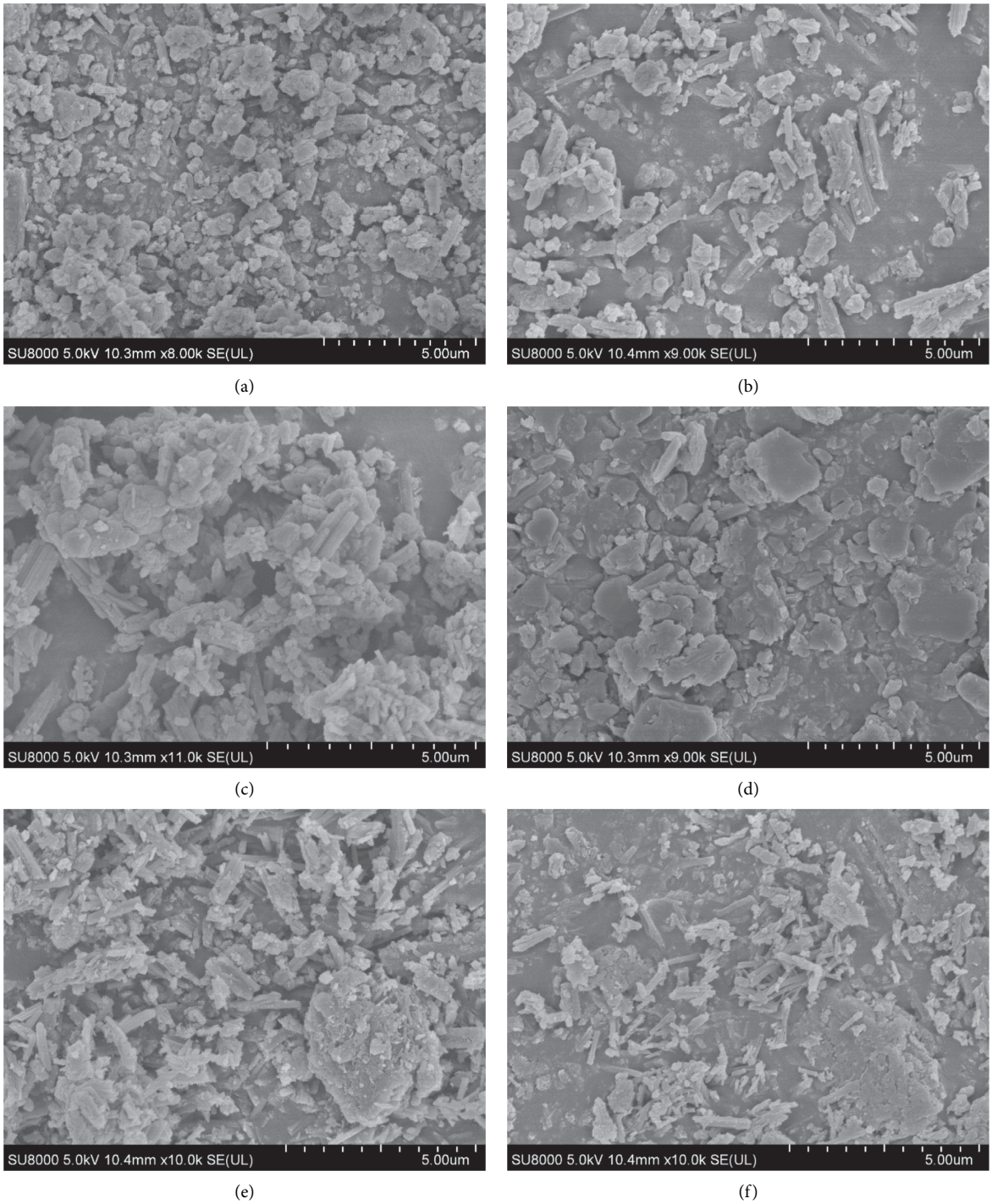

Figure 7: SEM images of the morphology of formed precipitates with the added chemical dosage at Ca : S molar ratios of (a) 2 : 1, (b) 3 : 1, (c) 4 : 1, and (d) 6 : 1, respectively, when the molar ratio of Al : S is 2 : 1; and (e) and (f) present the SEM images of precipitates formed with the chemical dosage of Al : Ca : S at 0.8 : 4 : 1 and 1 : 4 : 1, respectively.

ratio in precipitates, the residual Ca^{2+} decreased. And when the added CaO was higher than the theoretical molar ratio, the excess CaO would lead to the increase of Ca^{2+} in treated seawater. When the molar ratio of Al : Ca : S was 2 : 4 : 1, the residual Ca^{2+} was lower than that in the original seawater, indicating a sufficient precipitation reaction with sulfate.

Figures 6(c) and 6(d) show the Mg^{2+} concentrations were greatly reduced from 2,100 ppm to tens of ppm and more than 96% Mg^{2+} were removed. When the pH value of the solutions are higher than 10 (Figure 5), Mg^{2+} left in the seawater was less than 10 ppm. The extremely low concentration of Ca^{2+} and Mg^{2+} at optimized chemical dosage

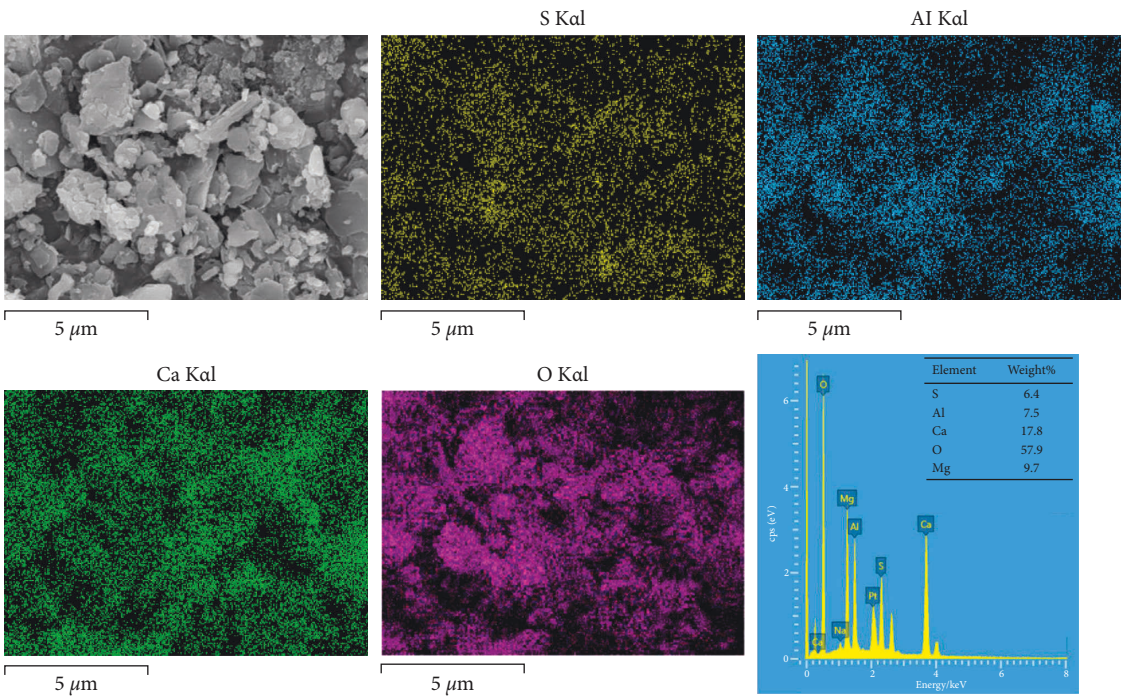

Figure 8: EDS analysis showing elements' distribution in the precipitates when the added molar ratio of Al : Ca : S is 2 : 6 : 1.

made the treated seawater very promising for hydraulic fracturing fluid preparation.

3.8. Characterization of Precipitates by SEM/EDX. The morphology of formed ettringite was reported to be affected by the precipitation conditions in the literature [36, 37]. Here, the precipitates obtained at different dosages of $NaAlO_2$ and CaO were characterized using SEM. Figures 7(a)–7(d) present the SEM images of precipitates with addition of series of Ca : S molar ratios while Al : S was fixed at 2 : 1. The precipitates were stacks of small crystals when Ca : S was 2 : 1. And they changed to rod-like crystals when Ca : S was increased to 3 : 1 and 4 : 1. When the Ca : S was 6 : 1, layered crystals were formed. When Ca : S is fixed at 4 : 1, the SEM images in Figures 7(c)–7(f) show the crystals were all rod-like. The increase of Al : S molar ratio from 0.8 : 1 to 2 : 1 did not show a great impact on the morphology. The results demonstrated that the molar ratio of Ca : S is a dominant factor on the morphology of precipitates.

To confirm that the precipitates were composed of ettringite, the distributions of elements by EDX are presented in Figure 8 when the chemical dosage of Al : Ca : S was at 2 : 6 : 1. It could be clearly observed that aluminum, calcium, sulfur, and oxide were distributed exactly as the flake shape of precipitates. The resultant element composition in precipitates is $Ca_{2.5}Al_{1.5}SO_{18}$, which is between the ettringite form and monosulfate form.

3.9. Injection of CO_2 in Sulfate-Removed Water. After the sulfate in seawater was removed by $NaAlO_2$ and CaO, and separation of precipitates, the pH value of the water is around 12. To make sure the water can be applied in most hydraulic fracturing fluid preparation, the pH was adjusted to ~7 by injection of CO_2 [38, 39]. After CO_2 was injected into the sulfate-removed seawater, the gas will mainly stay as CO_3^{2-} in the aqueous phase due to the high pH value [40]. The formed carbonate ions will precipitate with calcium ions to form calcium carbonate precipitates immediately until the pH value drops to neutral. In the case of bubbling CO_2 into 50 mL sulfate-removed seawater (added Al : Ca : S of 2 : 6 : 1) at a flow rate of 1 L/min for 1 min, the solution became turbid immediately and the pH value dropped from 12.5 to 6.7. The Ca^{2+} concentration decreased from 811 ppm to 678 ppm. The sequestered CO_2 as $CaCO_3$ was estimated at 7.3 mg.

4. Discussion

Ettringite precipitation methods have been widely used in industrial wastewater treatment, and various aluminum and calcium compounds are used for different waters. As far as concerned, this work is a pioneer study on sulfate removal by ettringite methods in high-salinity seawater (TDS >50,000 ppm). After the optimization of the chemical dosage, it turned out that when Al : Ca : S is 2 : 4 : 1 or 2 : 6 : 1, more than 90% sulfate was removed from the water. The Al/S ratio (2 : 1) for sulfate removal was deviated from the theoretical ratio of ettringite (2 : 3) (Figure 1). This finding was in agreement with previous studies that had also reported the optimum conditions of Al : S molar ratio was higher than that in the theory by Fang et al., Tian et al., and Pratinthong et al. [27, 28, 41]. Besides, the Ca : S molar ratio is 4 : 1 ~ 6 : 1, which is also consistent with previous studies in literature. And the formed precipitates are composed ettringite, as well as

monosulfate ($Ca_4Al_2(SO_4)(OH)_{12}$). The EDS analysis of the precipitates showed the molar ratio of Al : Ca : S is 1.5 : 2.5 : 1, which is between ettringite and monosulfate.

The previous reports also investigated the effects of magnesium ions on sulfate removal efficiency, while most Mg^{2+} was removed in the precipitation process [27]. Similar Mg^{2+} removal phenomenon was also observed in this study, that the concentration decreased from 2,110 ppm in seawater to only a few ppm (Figure 5). And Mg was observed in the precipitates by EDS analysis (Figure 8). This is because that Mg^{2+} can react with OH^- to convert to $Mg(OH)_4^{2-}$, which preferentially reacts with hydrolyzed aluminum sulfate to form hydrotalcite-type compound ($Mg_6Al_2SO_4(OH)_{16}{\cdot}nH_2O$), leading to magnesium removal from the water [23].

4.1. Practical Applications and Future Research Prospects. Experimental results in lab have demonstrated the ettringite precipitation methods have the potential to remove 90% sulfate from high-salinity seawater, so that the water can be used for hydraulic fracturing and reduce fresh water consumption. Besides the optimization of the separation process of precipitates from seawater in field applications, there are several prospects to be considered, including (i) development of cheaper aluminum and calcium compounds to further reduce the cost [42]; (ii) optimization of the method with higher salt tolerance and lower resultant sulfate concentration; and (iii) development of the slurry treatment technology to reuse the aluminum compounds or recover the slurry as a new industrial product.

5. Conclusions

The work has developed an efficient ettringite method to remove sulfate ions from high-salinity seawater to meet the application requirements as a base fluid for hydraulic fracturing applications. After comparison among the three precipitation methods ($CaSO_4$, $BaSO_4$, and ettringite), it turned out the ettringite precipitation method using $NaAlO_2$ and CaO was the most promising method, which could reduce sulfate concentration in seawater from 4,290 ppm to around 400 ppm with an optimized chemical dosage. The experiment results also showed the ettringite reaction mostly completed in 15 mins in an alkaline condition and the sulfate removal efficiency was not affected by temperature from 15°C to 45°C. The high concentration of Na^+ in seawater could reduce sulfate removal efficiency. In addition, the characterization of the sulfate-removed water showed that Ca^{2+} concentrations were on a similar value as that before treatment and Mg^{2+} was effectively removed in the precipitation process, so that the seawater could meet the requirements of oil and gas industry applications. The morphology and element analysis of the collected precipitates showed that the ettringites were in a layered shape with composition between $Ca_6Al_2(SO_4)_3(OH)_{12}$ and $Ca_4Al_2(SO_4)(OH)_{12}$ when the chemical dosage at a molar ratio of Al : Ca : S = 2 : 6 : 1. More importantly, the developed ettringite method is an environment-friendly method without any toxic chemicals involved, which could greatly benefit the oil and gas development in a sustainable way.

Data Availability

The authors confirm that the data supporting the findings of this study are available within the article. The main table and figure data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare no conflicts of interest.

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Supplementary Materials

Removal of high-concentration sulfate from seawater by ettringite precipitation. (*Supplementary Materials*)

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