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Sulfate precipitation treatment for NOM-rich ion exchange brines

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ABSTRACT

Ion exchange (IEX) resins can remove natural organic matter (NOM) from drinking water sources. However, the IEX system produces a waste brine rich of sodium, chloride, NOM and sulfate. The treatment of the waste brine aims to recover a clean solution rich of sodium chloride, that can be reused to regenerate IEX resin. Previous research showed that ceramic nanofiltration partially removes NOM from the waste brine, but sulfate removal requires additional treatment. Sulfate removal by chemical precipitation was previously studied either on brines with low NOM concentrations or water with low concentrations of NOM and salts. The current work focussed on sulfate removal from NOM-rich brines by chemical dosing of (1) $BaCl_2$, resulting in precipitation of barite ($BaSO_4$), and (2) $CaCl_2$, $Ca(OH)_2$ and $NaAlO_2$, resulting in precipitation of calcium sulfate and, subsequently, ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}$). Additionally, the effect of NOM on SO_4^{2-} removal was studied. Modelling and batch experiments were conducted with IEX and synthetic brines within the typical ion strength range of 0.1 to 1 M. With doses of 2.2 g of $BaCl_2$ per g of initial sulfate, $BaSO_4$ precipitation removed more than 83 percent of sulfate, resulting in final concentrations below 0.4 g/L even in the presence of NOM. However, NOM inhibited the precipitation of calcium sulfate and, subsequently, ettringite. With doses of 1.3 g of $CaCl_2$, 0.5–0.7 g of $Ca(OH)_2$ and 0.4–0.6 g of $NaAlO_2$ per g of initial sulfate, calcium sulfate and ettringite precipitation removed between 8 and 95 percent of sulfate from NOM-rich brines, resulting in final concentrations between 0.8 and 2 g/L. As a reference, NOM-free brines required doses of 1.3 g of $CaCl_2$, 0.2–0.7 g of $Ca(OH)_2$ and 0.1–0.6 g of $NaAlO_2$ per g of initial sulfate for 89 to 99 percent of sulfate removal, resulting in final concentrations of 0.2 g/L. The inhibition might be attributed to covering of crystal sites by NOM molecules, and to NOM coagulation with aluminium.

1. Introduction

Anion exchange (IEX) can effectively remove negatively charged natural organic matter (NOM) during drinking water treatment [1]. In IEX processes, resins are reused after cleaning with an electrolyte regenerant solution. In IEX for NOM removal, the regenerant solution is usually NaCl [2–4]. The regenerant solution is then reused several times before disposal, which increases the concentrations of NOM and anions, like sulfate (SO_4^{2-}) [3–5]. The composition of spent IEX brines depends on the quality of the water to be treated, the affinity of negatively charged components with the resin, and the specific IEX system operation. Spent IEX brines obtained by four pilot and full-scale installations had concentrations between 0.04 and 1.6 g/L of dissolved organic carbon (DOC), and concentrations of chloride (Cl^-) and SO_4^{2-} in a broad range of 2.6 to 19.1 g/L and 0.3 to 24.3 g/L, respectively (Supplementary information).

Discharging waste streams with NOM and salts is often problematic. Therefore, water companies aim to limit waste volumes by recovering some of the spent IEX brine components, such as clean water or concentrated NOM [4,6,7]. Additionally, the recovery of clean NaCl regenerant was previously studied [2,7–9]. Previous work has also shown that nanofiltration of brines can remove high levels of NOM, humic substances [2,9,10]. On the other hand, residual SO_4^{2-} was still present in the nanofiltration permeate, giving potential risk of SO_4^{2-} accumulation in the recovered regenerant.

Chemical precipitation can be an option to remove SO_4^{2-} from spent IEX brine. SO_4^{2-} can precipitate with various cations to form sparingly soluble salts, for instance calcium sulfate, barite ($BaSO_4$), and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}$). Calcium sulfate exists in different phases, such as gypsum ($CaSO_4$*$2H_2O$) and anhydrite ($CaSO_4$). Gypsum precipitates at

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lower temperatures and NaCl concentrations than anhydrite. Gypsum was found to precipitate below 25 °C and with NaCl concentrations below 4 M at 25 °C [11], and is therefore potentially relevant for treatment of IEX spent regenerant, that has NaCl concentrations below 2 M [2–4]. A disadvantage of gypsum is its high solubility product, i.e. a log Ksp of −4.31 at 25 °C [12], and, thus, the required low SO_4^{2-} concentrations cannot be reached. $BaSO_4$ has a much lower solubility product, i.e. a log Ksp of −9.96 at 25 °C [12], but it requires the dosage of toxic $BaCl_2$. An alternative is ettringite precipitation. Ettringite is stable at high alkaline conditions, with an optimum pH close to 12 [13], and its solubility product is low, i.e. log Ksp of −44.91 at 25 °C [14]. SO_4^{2-} removal from brines by ettringite precipitation has been frequently studied, mostly subsequent to calcium sulfate precipitation [15–19]. Generally, very low concentrations of SO_4^{2-} could be obtained by chemical precipitation. However, to the authors' knowledge, brines with high NOM concentrations were not studied before.

Based on other applications, some NOM interference on chemical precipitation could be expected. NOM and polymaleic acid, which is a synthetic surrogate of the fulvic fraction of humic substances [20], for instance, has been found to inhibit chemical precipitation in studies for water recycling in cooling towers [21,22]. In addition, Banz and Luthi [21] found that NOM of wastewater origin inhibited calcium sulfate precipitation, which was attributed to complexation of Ca^{2+} and NOM. However, NOM and salts concentrations in cooling tower water are much lower than in spent IEX brine and different mechanisms might be involved.

In the present study we therefore studied chemical precipitation as an alternative to remove SO_4^{2-} from NOM-rich spent IEX brines. In particular, the focus was on the performances of $BaSO_4$ precipitation, and the combination of calcium sulfate and ettringite precipitation to obtain low concentrations of SO_4^{2-}. The impact of NOM on chemical precipitation in brines and the mechanisms involved were also investigated. We studied spent and synthetic brines with varying NOM, sodium (Na^+), Cl^- and SO_4^{2-} concentrations within the typical ion strength range of 0.1 to 1 M, by means of laboratory experiments and modelling.

2. Materials and methods

2.1. Analyses for NOM and ions' concentrations

NOM was measured as dissolved organic carbon (DOC) by a total organic carbon analyser (TOC-VCPH, Shimadzu, Japan) after filtration of the sample. For some of the analyses, the Cl^- and SO_4^{2-} concentrations were determined by ionic chromatography using an ion-exchange column (A Supp 150/4.0, Metrohm AG, Switzerland). Other experiments required direct measurement results for SO_4^{2-}. Therefore, test cell kits (NOVA 60 Spectroquant, Merck, Germany; or LCK 311/153 with spectrophotometer DR 3900, Hach, Germany) were used. For both DOC and anion measurements, the samples were filtered with 0.45 μm filters and diluted when needed.

2.2. Brines

2.2.1. Preparation of synthetic brines

For the synthetic brines, Na_2SO_4 and NaCl were weighted and dissolved in demineralized water. The pre-set anion concentrations divided the synthetic brines into two groups: (1) low concentration brines, in the range of 0.2 to 5 gCl^-/L and 0.2 to 2 gSO_4^{2-}/L; and (2) high concentration brines, in range of 9 to 18 gCl^-/L and 8 to 16 gSO_4^{2-}/L. In addition, for the synthetic brines with NOM, concentrated NOM (HumVi, Vitens) was added to obtain concentrations of 0.5 and 2 gDOC/L. The NOM of HumVi has groundwater origins and was recovered from spent IEX regenerant brine. HumVi was also used and described in previous research [10,23].

2.2.2. Characterisation of spent IEX brine

A spent IEX brine was provided by a drinking water facility in Sweden (Sweden brine). This facility piloted suspended ion exchange (SIX®), as described by Galjaard and Koreman [24]. The NOM of the brines was characterized using liquid chromatography-organic carbon detection (LC-OCD), according to the procedure from Huber et al. [25]. LC-OCD gave the chromatographic fractionation of organic carbon (CDOC), being the sum of the concentrations of five NOM fractions. In decreasing size, the fractions are biopolymers (BP), humic substances (HS), building blocks (BB), low molecular weight acids (LMWa) and neutrals (LMWn) [25].

2.3. Precipitation experiments

Sweden brine and the synthetic brines of Table 1 were tested in duplicate for $BaSO_4$ precipitation. Samples for NOM and anion measurements were taken before and after precipitation. First, 150 mL of brine in a plastic container was stirred on a magnetic plate (speed 9%, Labinco, the Netherlands). The acidity (measured by Multi 3630 with SenTix 940 electrode, WTW, Germany) was adjusted to pH 8 by adding 0.1 M NaOH, to the brines. While stirring, $BaCl_2{\cdot}2H_2O$, dissolved in ultrapure water, was added in the Ba:SO_4 moles proportion of 1:1, considering the pre-set SO_4^{2-} concentration of the synthetic brines and the initial SO_4^{2-} concentration measured in the Sweden brine. After the $BaCl_2{\cdot}2H_2O$ was added, the brines were mixed for 30 min, and the precipitate was allowed to settle for another 30 min. The supernatant was then filtered to collect the samples to be analysed, according to Section 2.1.

Sweden brine and the synthetic brines of Table 2 were tested for calcium sulfate precipitation and subsequent ettringite precipitation, similar to the work of Almasri et al. [15]. All the experiments were in duplicate. Samples for NOM and anion measurements were taken before calcium sulfate precipitation, and before and after ettringite precipitation. For the calcium precipitation, 150 mL of brine in a plastic container was stirred on a magnetic plate (at 9% speed, Labinco, the Netherlands). While stirring, $CaCl_2$ was added in the Ca:SO_4 moles proportion of 1:1, considering the pre-set SO_4^{2-} concentration of the synthetic brines and the initial SO_4^{2-} concentration of the Sweden brine. The plastic container was closed directly after the addition of $CaCl_2$, and the stirring continued for 2 h. The pH before the addition of $CaCl_2$ and after precipitation was 7.6 ± 1.2 and 8.3 ± 0.7 (average ± standard deviation), respectively. The solid content in the plastic container after calcium sulfate precipitation was separated using gravity glass fibre filters. The supernatant was then filtered to collect the samples to be analysed, according to Section 2.1. For the subsequent ettringite precipitation, 115 mL of the filtered brine was again stirred on the magnetic plate. While stirring, $NaAlO_2$ and $Ca(OH)_2$ were added as solids in the Al:SO_4 and Ca:SO_4 moles proportion of 0.67:1 and 1:1, respectively, considering the concentration of the brines after gravity filtration. Afterwards, the stirring continued for 2 h. The supernatant was then filtered to collect the samples to be analysed, according to Section 2.1. The pH before the addition of $NaAlO_2$ and $Ca(OH)_2$ and after precipitation, was 8.2 ± 0.6 and 11.8 ± 0.1 (average ± standard deviation), respectively. The final

Table 1
Synthetic brines (with different ionic strength) and IEX brine tested for $BaSO_4$ precipitation experiments.

Brine	Ionic strength, IS (M)	Cl^- (g/L)	SO_4^{2-} (g/L)	NOM (gDOC/L)
1. 0gNOM/L-low IS	0.1	1.8	1.6	0
2. 0gNOM/L-mid IS	0.5	9	8	0
3. 0gNOM/L-high IS	1	18	16	0
4. Sweden brine	~0.2	5	2	0.5

Table 2
Pre-set concentrations of synthetic brines tested for calcium sulfate and subsequent ettringite precipitation experiments.

Brine	Ionic strength, IS (M)	Cl^- (g/L)	SO_4^{2-} (g/L)	NOM (gDOC/L)
0gNOM/L-low IS	0.2	5	2	0
0gNOM/L-high IS	1	18	16	0
0.5gNOM/L-high IS	1	18	16	0.5
2gNOM/L-high IS	1	18	16	2
Sweden brine	~0.2	5	2	0.5

pH was in the range for ettringite formation according to Almasri et al. [15] without further adjustment, except for Sweden brine. For Sweden brine, the pH before ettringite precipitation was increased from 8.1 to 11.9 with addition of 1 M NaOH. The chemicals used for the precipitation experiments have a purity ≥ 93 percent.

2.4. PhreeqC model

The results of the precipitation experiments of the synthetic brines without NOM were compared to the results modelled with PhreeqC, a geochemical modelling software. Solutions with high salinity can be modelled using the Pitzer database, as an alternative for the default PhreeqC database [26]. The PhreeqC script for calcium and ettringite precipitation was validated using the data from Almasri et al. [15]. According to the reasoning in Chapter 1, the calcium sulfate precipitate in the model was gypsum. Our scripts of the models and their validation are presented in the Supplementary Information.

3. Results and discussion

3.1. Brines characteristics

The NOM in the Sweden brine and in the synthetic brines consisted mostly of HS and BB (Table 3), because these fractions are preferentially removed by IEX from natural water [27–30].

3.2. Modelling of sulfate precipitation with BaSO4, calcium sulfate and ettringite

The scripts for the PhreeqC model, and the procedure of its validation are presented in the Supplementary Information. Model simulations are shown in Figs. 1–3, including the validation points of $BaSO_4$ and calcium sulfate precipitation. The model shows that, in Na_2SO_4 solutions with an ionic strength of 0.1 to 1 M, SO_4^{2-} precipitation with calcium sulfate depends on the initial SO_4^{2-} concentration (Fig. 1). The low SO_4^{2-} removal at low ionic strength is explained by the relatively high solubility product of calcium sulfate, that puts a theoretical limit on the achievable minimum concentration of SO_4^{2-} to 1.5 g/L [31]. In the same SO_4^{2-} range, precipitation with $BaSO_4$ and ettringite, that have low solubility products, only depends on stoichiometry (Figs. 2 and 3).

Table 3
LC-OCD fractionation of NOM in HumVi (used for the synthetic brines), NOM in the Sweden brine, given as carbon percentage of the CDOC.

NOM sample	Biopolymers	Humic Substances	Building Blocks	Low molecular weight neutrals	Low molecular weight acids
	≫20,000 Da	~1000 Da	300–500 Da	<350 Da	<350 Da
HumVi	0.0%	88.7%	6.8%	4.5%	0.0%
Sweden brine	0.3%	74.7%	16.0%	9.0%	0.0%

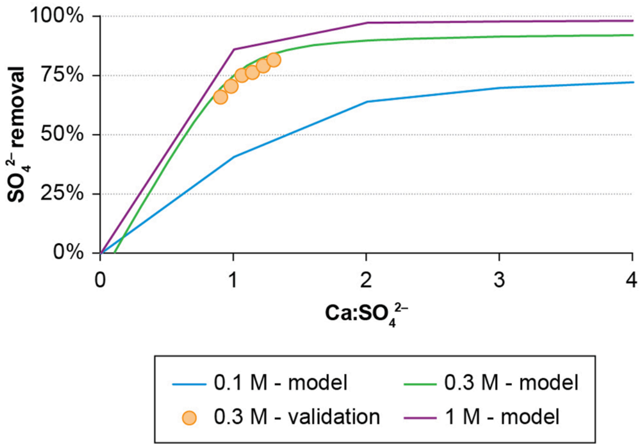

Fig. 1. PhreeqC model of calcium sulfate precipitation for Na_2SO_4 solutions with ionic strength between 0.1 and 1 M, for varying Ca to SO_4 molar ratio.

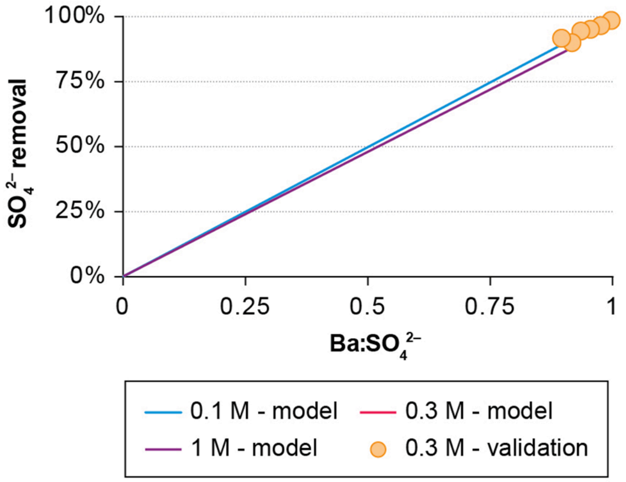

Fig. 2. PhreeqC model of $BaSO_4$ precipitation for Na_2SO_4 solutions with ionic strength between 0.1 and 1 M, for varying Ba to SO_4 molar ratio.

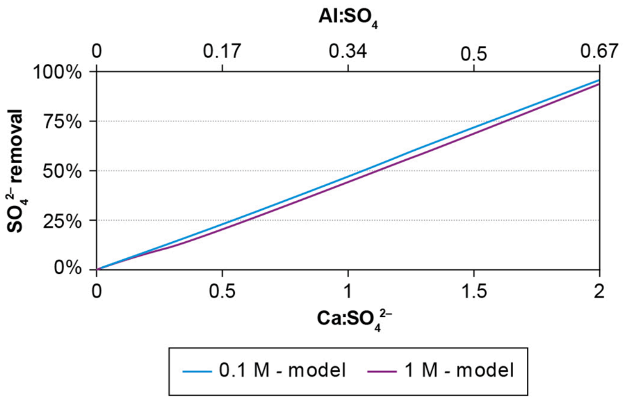

Fig. 3. PhreeqC model of ettringite precipitation for Na_2SO_4 solutions with ionic strength between 0.1 and 1 M, for varying Ca and Al to SO_4 molar ratio.

3.3. SO_4^{2-} removal and effect of NOM during $BaSO_4$ precipitation

For $BaSO_4$ precipitation, 2.2 g of $BaCl_2$ was dosed per g of initial SO_4^{2-} in the brine. With initial SO_4^{2-} concentrations between 1.3 and 14.5 g/L (and ionic strengths between 0.1 and 1 M), SO_4^{2-} removal from the synthetic brines without NOM was above 98 percent, resulting in SO_4^{2-} concentrations below 0.2 g/L (Table 4). Table 4 includes the SO_4^{2-} concentration of Sweden brine before and after precipitation with $BaSO_4$, and for the modelled brine without NOM as a reference. The SO_4^{2-} of Sweden brine decreased by 84 percent, from 2 to 0.3 g/L, showing that the presence of NOM slightly inhibited $BaSO_4$ precipitation, probably attributed to the antiscalant properties of NOM [32,33]. During $BaSO_4$ precipitation of Sweden brine, also NOM was removed by 23 percent, which could be a potential problem in case NOM recovery is desired.

Another application issue is linked to the toxicity of barium. The toxicity is linked to its chemical form [42]. In particular, barium salts with low solubility, such as $BaSO_4$, are generally considered less dangerous than free Ba^{2+} and readily soluble barium salts. Therefore, residual Ba^{2+} in the treated brine should be measured. The EPA drinking water standard for barium from 2002 was 2 mg/L [43]. However, ecotoxicity studies derived lower limits for environmental quality standards [44]. In the Netherlands, the maximum concentration of Ba^{2+} in surface water intended for drinking water production is 200 μg/L [45].

3.4. SO_4^{2-} removal and effect of NOM during calcium sulfate and ettringite precipitation

Calcium sulfate and subsequent ettringite precipitation without NOM, removed 89 to 99 percent of SO_4^{2-}, resulting in a final SO_4^{2-} concentration of 0.2 g/L for synthetic brines of both low and high initial SO_4^{2-} concentrations (1.8 to 14.8 g SO_4^{2-}/L, with ionic strength between 0.2 and 1 M). However, the presence of NOM affected the precipitation (Figs. 4 and 5).

At low initial SO_4^{2-} concentration (Fig. 4), calcium sulfate precipitation removed only<7 percent of SO_4^{2-} for both synthetic brine without NOM and Sweden brine, due to high solubility of calcium sulfate (see Section 3.2). However, NOM in Sweden brine inhibited the subsequent ettringite precipitation, resulting in an overall SO_4^{2-} removal of only 7.5 percent and a final SO_4^{2-} concentration of 1.7 g/L.

At high initial SO_4^{2-} concentration (Fig. 5), calcium sulfate precipitation removed 75 percent of SO_4^{2-} from the synthetic brine without NOM. However, calcium sulfate precipitation was inhibited by NOM, and the average removed SO_4^{2-} dropped to 35 and 6 percent in the synthetic brines with 0.5 and 2 gDOC/L, respectively. Similar to the case of $BaSO_4$, inhibition of calcium sulfate precipitation by NOM was attributed to the antiscalant properties of NOM [34,35]. Due to the fact that calcium sulfate precipitation only removed 3 to 4 percent of NOM from the synthetic brines, SO_4^{2-} removal by subsequent ettringite precipitation was inhibited by NOM as well. The dose of chemicals for ettringite precipitation was dependent on the remaining SO_4^{2-} concentration after calcium sulfate precipitation. Therefore, considerably more $NaAlO_2$ and $Ca(OH)_2$ were dosed in the NOM-rich synthetic brines than in the brine without NOM (Fig. 5). Nevertheless, the overall SO_4^{2-} removal was between 86 and 95 percent, although the final SO_4^{2-} concentrations for the NOM-rich synthetic brines were still above 0.8 g/L.

Table 4
SO_4^{2-} and NOM concentrations before and after $BaSO_4$ precipitation of brines: brines without NOM, NOM-rich Sweden brine, and PhreeqC-modelled brine without NOM.

Brine for $BaSO_4$ precipitation	Ionic strength, IS, (M)	Initial SO_4^{2-} (g/L)	Final SO_4^{2-} (g/L)	Initial NOM (gDOC/L)	Final NOM (gDOC/L)
0gNOM/L-low IS	0.1	1.34	<0.01	0	–
0gNOM/L-mid IS	0.5	7.86	<0.01	0	–
0gNOM/L-high IS	1	14.50	0.19 ± 0.02*	0	–
Sweden brine	~0.2	2.02	0.33 ± 0.05*	0.44	0.34 ± 0.01*
Model-low IS	0.2	2.00	0.00	0	–

*average ± standard deviation of duplicate measurement.

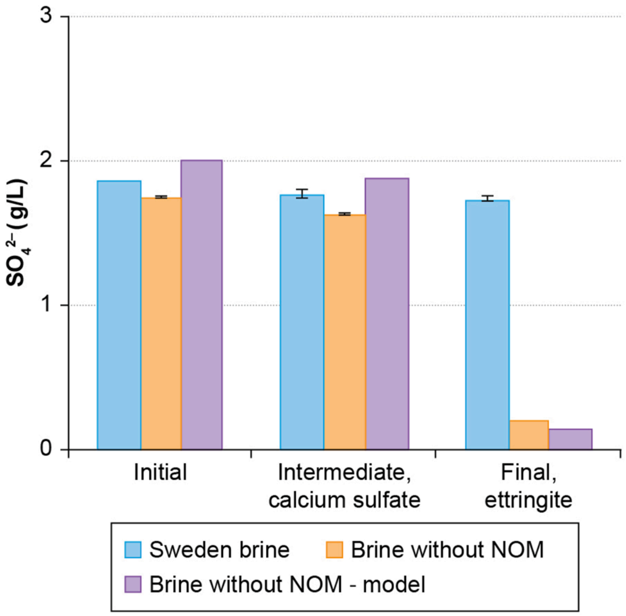

Fig. 4. SO_4^{2-} concentration before and after $CaSO_4$ and subsequent ettringite precipitation of brines at low ionic strength: NOM-rich Sweden brine, and synthetic brine without NOM. The doses of chemicals are 2.2 g/L of $CaCl_2$ for the intermediate calcium sulfate precipitation step, and 1.3 to 1.4 g/L of $Ca(OH)_2$ and 1.1 to 1.2 g/L of $NaAlO_2$ for the final ettringite precipitation step. A PhreeqC model calculation of the brine without NOM is included.

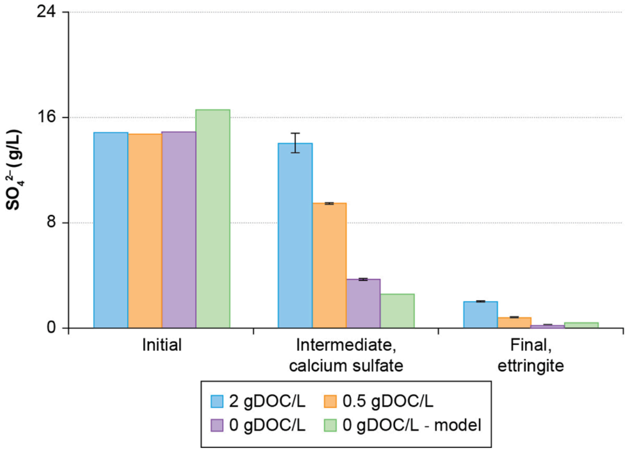

Fig. 5. SO_4^{2-} concentration before and after $CaSO_4$ and ettringite precipitation of synthetic brines at high ionic strength (1 M) and different NOM concentrations. For the intermediate calcium sulfate precipitation step, the dosed $CaCl_2$ was 20 g/L for all brines. For the final ettringite step, $Ca(OH)_2$ and $NaAlO_2$ were dosed. For the 2 gDOC/L brine, the dose was 11 g $Ca(OH)_2$/L and 9 g $NaAlO_2$/L. For the 0.5 gDOC/L brine, the dose was 8 g $Ca(OH)_2$/L and 6 g $NaAlO_2$/L. For the 0 gDOC/L brine, the dose was 3 g $Ca(OH)_2$/L and 2 g $NaAlO_2$/L. A PhreeqC model calculation of the brine without NOM is included.

The overall NOM removal from the NOM-rich brines was between 23 and 67 percent (Table 5). The calcium sulfate precipitation step only removed between 3 and 11 percent of NOM. The ettringite precipitation step removed 14 percent of the residual NOM from Sweden brine with low initial SO_4^{2-}, and between 51 and 65 percent of the residual NOM from the two NOM-rich synthetic brines with high initial SO_4^{2-}, likely due to coagulation of NOM by $NaAlO_2$ [36,37].

Table 6 summarises the initial NOM/sulfate ratio of the brines, the

Table 5
NOM concentrations during calcium sulfate and subsequent ettringite precipitation.

Brine	NOM before $CaSO_4$ precipitation (gDOC/L)	NOM before ettringite precipitation (gDOC/L)	Final NOM (gDOC/L)
Sweden brine, 0.5gDOC/L	0.48	0.43	0.37
High ion strength, 0.5gDOC/L	0.48	0.46	0.16

percentage of removal and chemicals dosed per initial sulfate concentration (specific dose). Calcium sulfate and subsequent ettringite precipitation is the most suitable for NOM-free brines with high ionic strengths, as indicated by the relatively low specific dose of chemicals and high SO_4^{2-} removal. However, brines with low ionic strength required a relatively high specific dose of $Ca(OH)_2$ and $NaAlO_2$.

When applied to NOM-rich brines, calcium sulfate and subsequent ettringite precipitation removed hardly any SO_4^{2-} at high initial NOM/sulfate ratio, or required a relatively high dose of chemicals.

The potential effect of the initial NOM/sulfate ratio in practice was to see in our experience with additional spent IEX brines. The percentage of sulfate removed was higher in brines with less NOM and higher initial sulfate concentration than Sweden brine (Supplementary Information), indicating that calcium sulfate and ettringite precipitation were more suitable for IEX brines with low initial NOM/sulfate ratio.

The inhibition of precipitation of Ca^{2+} or SO_4^{2-} crystals caused by NOM and organic acids could be attributed to Ca^{2+} complexation or covering of nucleation and growth crystal sites [33,35,38–40].

Table 7 shows that the Ca^{2+} that can potentially be consumed by complexation was negligible compared to the available Ca^{2+}, i.e. below 10 percent. Therefore, similar to the experiments of Lee et al. [35], covering of crystal site by NOM molecules is suggested as precipitation inhibition mechanism during our experiments. PhreeqC models the interaction between NOM and ions is modelled as complexation and the antiscalant properties of NOM are not considered. Therefore, PhreeqC could not be used to model the NOM-rich brines of our experiments.

An application issue is linked to the purity of the chemical used for the precipitation of the sulfate salts. Natural limestone (calcium carbonate) contains magnesium in case of dolomitization [46], and therefore, Mg^{2+} ions can be present as impurity in the produced $CaCl_2$. In our experiments, $CaCl_2$ had high purity, but the presence of Mg^{2+} should be checked in application. Previous studies showed that Mg^{2+} can maintain SO42- in the soluble form $Mg(SO_4)$ [47,48].

4. Conclusions

Chemical precipitation of SO_4^{2-} to $BaSO_4$, calcium sulfate and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}$) was studied for brines with varying NOM and ionic strengths, and initial concentrations between 2 and 16 gSO_4^{2-}/L. Sulfate removal with $BaSO_4$ precipitation was above 98 percent for NOM-free brines, and 84 percent for the NOM-rich spent IEX brine. This resulted in final concentrations below 0.4 g SO_4^{2-}/L, even in the presence of NOM. In addition, 23 percent of NOM was removed from the spent IEX brine, which could decrease the potential for NOM recovery. For application, the residual concentration of dissolved barium, that is toxic, should also be investigated.

At low initial SO_4^{2-} concentration, calcium sulfate and subsequent ettringite precipitation removed overall 89 percent of SO_4^{2-} from the NOM-free brine, resulting in a final concentration of 0.2 g SO_4^{2-}/L. However, the calcium sulfate precipitation step was limited by its high solubility, and the subsequent ettringite precipitation step required a relatively high dose of $NaAlO_2$ and $Ca(OH)_2$. In the NOM-rich spent IEX brine, hardly any removal of SO_4^{2-} was observed at low initial SO_4^{2-} concentration.

At high initial SO_4^{2-} concentration, inhibition of calcium sulfate and subsequent ettringite precipitation by NOM was observed as well. Without NOM, the overall SO_4^{2-} removal was 99 percent, resulting in a final concentration of 0.2 gSO_4^{2-}/L. When NOM was present, SO_4^{2-} removal was between 86 and 95 percent, with final concentrations above 0.8 g SO_4^{2-}/L, even with a relatively high dosage of chemicals for the ettringite precipitation. The inhibition might be attributed to covering of crystal sites by NOM molecules, and to NOM coagulation with aluminium.

CRediT authorship contribution statement

Irene Caltran: Conceptualization, Methodology, Data curation, Writing - original draft. **Floriana Ayumurti Kukuh:** Conceptualization,

Table 6
Summary of initial NOM/SO_4^{2-} ratio of the brines, the percentage of SO_4^{2-} removal, and chemicals dosed per amount of initial SO_4^{2-}

Brine	Initial NOM/SO_4^{2-} ratio (gDOC/gSO_4^{2-})	Overall SO_4^{2-} removal (-)	Dose $CaCl_2$ per initial sulfate (g$CaCl_2$/gSO_4^{2-})	Dose $Ca(OH)_2$ per initial sulfate (g$Ca(OH)_2$/gSO_4^{2-})	Dose $NaAlO_2$ per initial sulfate (g$NaAlO_2$/gSO_4^{2-})
NOM-free, high ionic strength	0	99%	1.3	0.2	0.1
NOM-free, low ionic strength	0	89%	1.3	0.7	0.6
0.5 gDOC/L, high ionic strength	0.03	95%	1.3	0.5	0.4
2 gDOC/L, high ionic strength	0.14	86%	1.3	0.7	0.6
Sweden brine	0.25	8%	1.3	0.7	0.6

Table 7
Calculation of the charge potentially consumed by NOM in several brines, compared to the charge of dosed Ca^{2+}.

Brine	NOM (gDOC/L)	Charge density NOM (-meq/gDOC)	Charge NOM (-meq/L)	Dosed Ca^{2+}(mmol/L)	Charge Ca^{2+} (meq/L)	Charge NOM/Charge Ca^{2+}
Sweden brine, 0.5gDOC/L	0.5	5–15*	2–7	20 ($CaCl_2$) 19 ($Ca(OH)_2$)	76	3–9%
High ion strength, 0.5gDOC/L	0.5	5–15*	2–7	153 ($CaCl_2$)99 ($Ca(OH)_2$)	505	0–1%
High ion strength, 2gDOC/L	2	5–15*	10–30	154($CaCl_2$) 146 ($Ca(OH)_2$)	600	2–5%

*Charge density range for humic substances according to Edzwald [41].

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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