Enhanced removal of scaling cations from oilfield produced water by carrier mineral flotation

Hao Sun, Yuwen Liu, Dandan Liu, Shaomin Li, Xiaqing Li, Haitao Chen, Zhongying Han, Lei and Xiaobing Li

ABSTRACT

This work reports a novel carrier flotation protocol for removing scaling cations from an oilfield produced water source which significantly reduces the collector consumption by employing natural minerals such as quartz, montmorillonite and talcum as the scaling cations carriers. The scaling cations uptake onto all carrier minerals exhibited homogeneous and monolayer adsorption, which was mainly dominated by physical adsorption. After adding oleate collector, the scaling cations removal rate was further enhanced, which was attributed to its high affinity with the scaling cations. Notably, the talcum flotation process simultaneously offered high scaling cations removal rate (76.1%) and mineral recovery rate (98.3%), which achieved a sediment yield reduction of 72.2%. By summarizing the characterization results, the scaling cations removal mechanisms were also proposed. Moreover, high regeneration efficiencies (86.1% and 84.8% for quartz and talcum regeneration within 3 cycles) were achieved by the proposed regeneration protocol. This carrier flotation protocol with its low collector consumption offered technical promise for scaling cations removal from oilfield produced water.

Key words: adsorption, carrier flotation, natural mineral, produced water, scaling

INTRODUCTION

As most oilfields entered the high and ultra-high water cut development period, tertiary oil recovery technology has been developed and promoted, which greatly improves the oil recovery. However, in the face of massive produced water, how to achieve the water quality stabilization to meet the reinjection standard has become a tremendous challenge (Kamal et al. 2018; Sun et al. 2020). Notably, scaling is one of the most severe problems in water controlling in oil field. Due to the incompatibility of injected water and formation water, inorganic salt precipitation will generate after mixing in water flooding production process (Li et al. 2016). The produced water contains HCO₃⁻, SO₄²⁻, CO₃²⁻ and Ca²⁺, Mg²⁺, Sr²⁺, Ba²⁺ and other ions that are able to scaling. When Ca²⁺, Sr²⁺ and Ba²⁺ combine with SO₄²⁻, sulfate scale will produce immediately. Moreover, the scale produced in oil field contains a part of corrosive FeSO₄ and FeS (Olajire 2015). Scaling can occur in almost all parts of the formation and oil pipeline, which is considered to be the main cause of premature abandonment of wells and strata. Scaling will reduce the water cross-section area, increase the flow resistance and energy, and result in the increase of cleaning cost and shutdown maintenance time (Tam & Elefsiniotis 2009). In addition, the deposition of scale will cause the corrosion of equipment and pipeline, and the oil pipeline will be damaged by perforation in a short
term (Zhang et al. 2019). When scaling occurs in the formation, it will block the formation and decrease the permeability of the reservoir, thus affecting the oil recovery. Therefore, the scaling of produced water should be effectively controlled.

Various protocols have been proposed to inhibit oilfield scale, mainly divided into reinjection water quality adjustment and chemical methods (Ghalib & Almallah 2017; Al-Ghouti et al. 2019). Al-Samhan et al. (2020) mixed the produced water with seawater in a compatible ratio to reduce the risk of scaling potential and well formation damage. When treating the North Kuwait effluent water, they pointed out that the barium sulfate concentration drops and consequently the scale risk reduced at 70% seawater concentration. Nevertheless, this method was more practicable for those countries with easy access to seawater. Chemical treatment, such as adding chemical scale inhibitors, is more prevalent in oil fields. These scale inhibitors are threshold inhibitors which can delay the scale formation kinetics. The molecular structures of these scale inhibitors were referenced to contain phosphonate, carboxylate, or sulfonate groups, which prefer to interact with group II cations (Mpelwa & Tang 2019). Although some scale inhibitors containing phosphorus appear with significant achievements, researchers shrink back at the sight of its toxicity. Also, in some extreme formation environment, the scale inhibitor will lose its efficacy (Belattar et al. 2021).

Compared to the above scale control methods, removing the scaling cations, is believed to be the most effective and thorough to inhibit scale. Ali et al. (2018) combined the microfiltration and membrane distillation to treat the produced water and recover various salts such as sodium, calcium, magnesium and barium. Thus, favorable anti-scaling conditions are realized and the treated water was more suitable for reinjection. However, more efforts should be made to stabilize membrane flux, reduce membrane fouling and prolong the membrane lifetime (Kusworo et al. 2018). Flotation is an economic and effective method to separate coal, ores, oil and ions from the aqueous solutions (Ahmadi et al. 2014; Etchepare et al. 2017). In some specific conditions, divalent cations such as Ca\(^{2+}\), Mg\(^{2+}\), Cu\(^{2+}\) and Pb\(^{2+}\) could serve as the activators for minerals (quartz, wolframite, magnesite, et al.) flotation, which promote the adsorption of collector on mineral surface and thus improve mineral hydrophobicity (Li et al. 2020). Based on previous research, ion flotation has also proved effective for divalent cations removal and can be selective using specific anionic collectors. Generally, heavy metal ions have a better affinity for the anionic collector since they have smaller hydrated radius (Agnieszka et al. 2021; Luong & Liu 2021). Flotation possesses several advantages over other conventional methods in terms of larger treatment capacity, low energy consumption and better space utilization ratio. However, a mass of anionic collectors could be consumed when treating the scaling cations of the produced water.

To effectively remove the scaling cations from the produced water and reduce the collector dosage, the authors proposed a carrier flotation protocol which consuming the scaling cations in the minerals flotation process. This protocol employed natural minerals as the scaling cations carrier and anionic surfactants as the flotation collector, which was inspired by the facilitation of coarse particles on the flotation of fine or ultrafine minerals (Muhammad et al. 2021). Therefore, the objectives of this research herein have been to: (a) select suitable carrier minerals and optimize the operation parameters for the carrier flotation technique; (b) investigate the scaling cations removal mechanisms during the carrier flotation process; (c) explore a regeneration method for the exhausted carrier minerals.

**MATERIALS AND METHODS**

**Materials**

Three kinds of commercial natural minerals, included quartz, talcum and montmorillonite, were supplied by Crystal mining area (Donghai, China), Lianshanguan mining area (Benxi, China) and Longkou mining area (Yantai, China), respectively. Before adsorbing the scaling cations, we ground and sieved them to a standard mesh size of 325 × 400 (45 × 38 μm). XRD patterns (Fig.S1 in the supplementary materials) showed that all these minerals had high purity. The produced water used in this research was directly sampled from the Bin 2# water-injection station, Binnan oil recovery plant of Shengli oil field. This produced water sample (pH = 7.1) was taken after the advanced oil-water separation process, and it was found to contain 616.2 mg/L Ca\(^{2+}\), 126.6 mg/L Mg\(^{2+}\), 7,227.1 mg/L Na\(^+\),183.8 mg/L K\(^+\), 10,901.3 mg/L chloride, 44.7 mg/L nitrate (as NO\(_3\)), 726.2 mg/L bicarbonate (as HCO\(_3\)), 31.8 mg/L sulfate (Standardization Administration of China GB/T 15452-2009). It suggests that the main scaling cations are Ca\(^{2+}\) and Mg\(^{2+}\).

The sodium oleate, ethylenediamine tetraacetic acid disodium salt (EDTA), sodium hydroxide and calconcarboxylic acid were ordered from Sinopharm Chemical Reagent Co.,Ltd (China).

Scaling ions adsorption tests

Batch adsorption tests were conducted to obtain the scaling cations adsorption isotherm data. Primarily, various masses of mineral adsorbents were added to an array of bottles that contained 20 mL of the fresh produced water to be treated. The initial adsorbent levels were selected as 1.0, 3.0, 5.0, 8.0 and 10.0 g/L. These mixtures were sealed in bottles and shaken on a water bath thermostatic oscillator for 24 h to equilibrium under different temperature conditions. After this, the mineral particles were filtered out through 0.2 μm nylon fiber filters, and then the aqueous filtrate Ca$^{2+}$ and Mg$^{2+}$ concentrations ($C_e$) were measured according to the National Standards of P.R.C (EDTA titration method). Each test was repeated three times, and duplicates varied by less than 3–5%.

Carrier flotation tests

Carrier flotation experiments were conducted in a XFD flotation cell, 500 mL in volume, and air was sucked into the cell due to the negative pressure formed by high speed rotating impeller, so as to generate air bubbles. Initially, carrier mineral was dosed into the produced water and then dispersed at 1,500 rpm for 10 min. Then, 200 mg/L of sodium oleate was added into the mixture as the collector and frother. Finally, the conditioned pulp was floated at 0.20 m$^3$/h of aeration rate for 5 min. The flotation products were separated and dried for subsequent characterization and the cations levels of the residual solutions were further analyzed.

Characterization

The pore volume distributions and surface area of these natural minerals were monitored by an automated specific surface area analyzer (BELSORP-max, MicrotracBEL, Japan), while N$_2$ was employed as the adsorbent. Fourier transform infrared spectroscopy (FTIR, Thermo Scientific, USA) was used to characterize the surface functional groups composition of the minerals. The surface elemental compositions of the minerals were monitored using an X-Ray Photoelectron Spectrometer (ESCALAB 250Xi, Thermo Fisher, USA), which employed CASAXPS software to analyze the obtained spectrums. Variation of the zeta potential of the minerals was measured using a Zetasizer Nano Analyzer (Zetaplus, Bröokhaven, Germany).

Carrier minerals regeneration

After the scaling cations-capturing, we aimed to find an efficient method to regenerate the spent carrier minerals. To achieve the objective, the spent carrier minerals were packed into a 2.65 mL plastic column, where it was successively rinsed by a prepared ethanol solution (30 wt%) and a HCl solution (0.1 mol/L) regenerant for 3 h at 5.3 mL/min flow rate (360 bed volume); and then rinsed with deionized water so as to remove the residual regenerant onto the minerals surface. It should be noted that the ethanol and HCl solutions were employed to remove the organic collector and scaling cations from the minerals surface, respectively. After this, the regenerated minerals were again processed through a carrier flotation test, while using the same produced water source as previously.

RESULTS AND DISCUSSION

Pore structure and texture properties of carrier minerals

Several characterization protocols were employed to investigate the basic pore structure and texture properties of the carrier minerals. Representative SEM photographs were presented to shown textural structure and approximated size of quartz, montmorillonite and talcum particles, respectively. It was observed that the quartz particles have a smooth surface with few pores (Figure 1(a)). Montmorillonite exhibited a coarse surface with an obvious stratified structure. Also, long channels of various widths were considered to be more favorable to pollutants adsorption (Figure 1(b)). Then, talcum exhibited a more compact stratified structure than montmorillonite, so there are relatively few pores on the surface (Figure 1(c)). These results were also consistent with the BET results presented. The montmorillonite particle was characterized as a microporous material that about 80% of the total pore volume belongs to microporous structure, and its specific surface area reached 26.2 m$^2$/g (Figure 1(d)). On the contrary, talcum has a high mesoporous ratio, and the specific surface area is only 2.4 m$^2$/g. In the case of quartz particles, there are almost no pores on the surface.

Scaling cations adsorption thermodynamics

Batch adsorption tests were completed with each carrier mineral at 298, 308 and 318 K, so as to evaluate the scaling cations adsorption capacities (Figure 2). It should be noted that all minerals adsorbed Ca$^{2+}$ in preference to Mg$^{2+}$, so the single component adsorption thermodynamics models were employed. This result is also consistent with the conclusion reported in the
previous literatures (Sangdae 2011; Atouei et al. 2016). The isotherm results were fitted to the Langmuir and Freundlich models which can be described by the following equations (Sun et al. 2019).

\[
\frac{1}{Q_e} = \frac{1}{Q_m K_L C_e} + \frac{1}{Q_m}
\]

\[
\ln Q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e
\]

where \(K_L\) (L/mg) is the Langmuir adsorption constant; \(C_e\) (mg/L) is the equilibrium concentration of scaling cations; while \(Q_e\) and \(Q_m\) (mg/g) represent the equilibrium and Langmuir maximum adsorption capacity, respectively; \(K_F\) (mg/g (L/mg)\(^{1/n}\)) and \(1/n\) are the Freundlich model constants.

In all cases, the Langmuir modeling of the experimental data yielded a correlation coefficient \(R^2\) of more than 0.99, which represented the best fit of the scaling cations adsorption equilibrium data (Table 1). This manifested that the scaling cations uptake onto all carrier minerals exhibited homogeneous and monolayer adsorption. It was noted that the montmorillonite exhibited the highest adsorption capacity. In particular, at 298 K, the montmorillonite achieved a 109.9 mg/g maximum monolayer adsorption capacity, which was greater than that for quartz (79.4 mg/g), or talcum (101.0 mg/g). These results highlighted the importance of micropore structure of montmorillonite for adsorbing scaling cations.

*Figure 1* | SEM images of pristine (a) quartz, (b) montmorillonite and (c) talcum and (d) accumulative pore volume curves of the carrier minerals.
The adsorption thermodynamics were conducted to further explore the scaling cations adsorption mechanism. The enthalpy change ($\Delta H$), Gibbs free energy change ($\Delta G$), and entropy change ($\Delta S$) for the adsorption process were computed by the following formulas (Sun et al. 2019):

$$\Delta G = -RT \ln K$$  \hspace{1cm} (3)

$$\ln K = \Delta S/R - \Delta H/RT$$  \hspace{1cm} (4)

**Figure 2** | Langmuir model plots (a) and Freundlich model plots (b) of scaling cations adsorption onto the carrier minerals at various temperatures.

**Table 1** | Scaling cations (mainly Ca$^{2+}$) adsorption thermodynamics parameters of the natural minerals at three temperatures

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T$ (K)</th>
<th>$Q_m$ (mg/g)</th>
<th>$K_L$ (L/mol)</th>
<th>$R^2$</th>
<th>$\Delta G^0$ (KJ/mol)</th>
<th>$\Delta H^0$ (KJ/mol)</th>
<th>$\Delta S^0$ (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>298</td>
<td>79.4</td>
<td>155.9</td>
<td>0.9996</td>
<td>-12.5</td>
<td>-16.9</td>
<td>98.3</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>71.9</td>
<td>172.1</td>
<td>0.9988</td>
<td>-13.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>59.2</td>
<td>240.0</td>
<td>0.9990</td>
<td>-14.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>298</td>
<td>109.9</td>
<td>119.8</td>
<td>0.9909</td>
<td>-11.9</td>
<td>-6.0</td>
<td>54.6</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>107.5</td>
<td>128.5</td>
<td>0.9979</td>
<td>-12.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>98.0</td>
<td>139.6</td>
<td>0.9929</td>
<td>-13.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Talcum</td>
<td>298</td>
<td>101.0</td>
<td>132.8</td>
<td>0.9918</td>
<td>-12.1</td>
<td>-4.2</td>
<td>60.0</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>91.7</td>
<td>136.3</td>
<td>0.9983</td>
<td>-12.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>82.6</td>
<td>147.8</td>
<td>0.9953</td>
<td>-13.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
where \( R \) (8.314 J/mol K) is the universal gas constant; \( T \) is the solution temperature in Kelvin units; and \( K \) (L/mol) represents the distribution ratio, which was converted from the Langmuir \( K_L \) value.

As Table 1 illustrates, the negative values of \( \Delta G \) revealed the spontaneous nature of scaling cations adsorption process onto all the carrier minerals. Generally, the adsorption processes have been attributed to physical adsorption when \( \Delta G \) values is between \(-20\) and \(0\) kJ/mol; while \( \Delta G \) values in the range of \(-400\) to \(-80\) kJ/mol have been attributed to chemical adsorption (Chen et al. 2021). For scaling cations adsorption, the \( \Delta G \) values are all in the range of \(-11.9\) to \(-14.5\) kJ/mol; thus indicating that the scaling cations uptake is dominated by physisorption. Since physical adsorption is currently identified as the prevalent phenomenon with the adsorbents, it also demonstrated the better regeneration possibility of the spent adsorbents. The negative \( \Delta H \) values for carrier minerals revealed the exothermic nature of the scaling cations adsorption process. The positive \( \Delta S \) revealed that the scaling cations uptake increased the randomness of the adsorption system—which is mainly attributed to exchange ions being released.

**Carrier flotation tests**

Carrier flotation and blank flotation (without carrier minerals) tests were employed to evaluate the scaling cations removal performance at a series of collector concentrations. When treating the produced water by blank flotation, the scaling cations removal rate was found to be positively correlated with the collector concentration (Figure 3(a)). It was noted that the

![Figure 3](http://iwaponline.com/wst/article-pdf/doi/10.2166/wst.2021.478/954826/wst2021478.pdf)

Figure 3 | Effect of collector concentration on (a) scaling cations removal rate of blank flotation, (b) scaling cations removal rate of carrier flotation at 5 g/L mineral dosage, (c) carrier minerals yields, (d) sediment yields prediction model at various scaling cations removal rate at formation pressure of 44.5 MPa and temperature of 90 °C.
negatively charged sodium oleate collector interacts with $\text{Ca}^{2+}$ more strongly than $\text{Mg}^{2+}$ in the produced water environment (Sun et al. 2021). After adding 5 g/L carrier minerals, the collector consumption significantly decreased under the condition of comparable removal rate, which was considered to be more economical than traditional ion flotation process (Figure 3(b)). The carrier montmorillonite flotation offered the highest scaling cations removal rate, which was mainly attributed to the outstanding scaling cations adsorption capacity of montmorillonite. When discerning the scaling cations removal rate of 75%, we noted that only 300 mg/L of collector was consumed in carrier montmorillonite flotation process; and this was about one-seventh for that (2,000 mg/L) in blank flotation. Whereas in the talcum flotation process, 400 mg/L of oleate collector was required to achieve the scaling cations removal rate of 75%.

After the carrier flotation process, the floating minerals were collected and the minerals recovery rates were shown in Figure 3(c). Previous research has stated that $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ are favorable to oxide mineral flotation, which generates more binding sites for collector adsorption (Solongo et al. 2020). During the talcum flotation process, most of talcum (more than 95%) was recycled, even at low collector concentration. This was largely ascribed to the natural hydrophobicity of talcum and the enhanced adsorption capacity of collector on the scaling cations loaded talcum surface (Mai et al. 2021). For quartz flotation, a recovery rate of 85.5% was achieved at 400 mg/L dosage. Montmorillonite was characterized as a polar groups-rich and hydrophilic mineral, which achieved the lowest recovery rate. Among these three carrier minerals, talcum can achieve a high recovery rate which also ensuring an acceptable scaling cations removal rate. This means that the subsequent clarification process requires only a lower investment, so talcum was considered to be the most appropriate for the carrier minerals.

The sediment yields of the produced water at the formation pressure of 44.5 MPa and temperature of 90 °C were calculated using the Visual Minteq software. At this formation environment, the saturation index was calculated to be positive, which indicates that scaling is unavoidable when scaling cations exist. For the raw produced water, 1,024.7 mg/L of sediment was required to achieve the scaling cations removal rate of 75%.

FTIR analysis
These three carrier minerals were also appraised for their FT-IR spectrums (Figure 4) between 4,000 and 400 cm$^{-1}$. For all the spectra, the peak at 460, 776 and 1,060 cm$^{-1}$ were identified as the bending vibration symmetric stretching vibration and asymmetric stretching vibration of the Si-O bond, separately. The quartz exhibited characteristic peak at 3,553 cm$^{-1}$ (OH stretching), while talcum and montmorillonite exhibited -OH stretching peak at 3,676 and 3,621 cm$^{-1}$, respectively (He et al. 2017). The characteristic peak at 3,587 cm$^{-1}$ for talcum and 3,436 cm$^{-1}$ for montmorillonite were attributed to the interlayer water stretching. Moreover, the peaks appeared at 1,456 cm$^{-1}$ for talcum and for montmorillonite were identified as the $-\text{OH}$ bending vibration after adsorbing water molecules.

After adsorbing scaling cations, all the spectra show reduction of hydroxyl group (-OH), which indicates that the irreplaceable role of hydroxyl group on scaling cations adsorption (Figure 4(a)–4(c)). After the flotation process, spectra of all the minerals show a new stretching peak at 2,853–2,923 cm$^{-1}$, which was identified as the alkyl (CH$n$) peaks in the oleate molecules, respectively. As shown in Figure 4(a), the reduction on Si-O peak intensity indicated the aggregation of collector on the quartz surface. In other words, scaling cations and collector were mainly adsorbed on the external surface of quartz. Whereas in Figure 4(b) and 4(c), the peaks at 460, 670 (vibration of Mg-O) and 1,026 cm$^{-1}$ for talcum and 460, 873 (bending vibration of Al-Mg-OH) and 1,060 cm$^{-1}$ for montmorillonite all exhibited remarkable stretch, which illustrates that the scaling cations and collector was inserted into the interlayers of talcum and montmorillonite. This was corresponded to the interlayer ion-exchange mechanism. As a result, more clusters appeared on the surface of quartz than that on talcum or montmorillonite, which was considered as the complex that composed of oleate and scaling cations (Figure 4(d)–4(f)).

Surface element composition and zeta potential analysis
X-ray Photoelectron Spectroscopy (XPS) measurements discerned the surface functionality variations in these carrier minerals (see Fig.S3 in the supplementary materials). As shown in Table 2, all these pristine minerals hosted a certain amount of organic impurities. After the adsorption process, Na and C inevitably increased on the minerals surface due to the high salinity and residual oil in produced water. Also, more Ca and Mg were introduced onto the minerals surface, which indicates...
the scaling cations adsorption by minerals. Moreover, the increase in Ca was greater than the increase in Mg. This means that all these minerals preferably adsorbed the Ca$^{2+}$, which was consistent with the above adsorption thermodynamics results. It also should be noted that montmorillonite obtained the lowest Ca promotion (0.1% to 0.3%), which was mainly due to the adsorption in pores, while the scaling cations adsorption of quartz and talcum was mainly concentrated on the external minerals surface. After the flotation process, the C ratio further raised because of the collector adsorption onto the minerals. Additionally, further increase of Ca ratio indicates that the carrier minerals captured more scaling cations.

Table 2 also listed the zeta potential values of the minerals during the carrier flotation process. The results manifested that all these pristine minerals were negatively charged. After adsorbing scaling cations, the electronegativity of these minerals exhibited an appreciable reduction. In particular, the negative charged surface of talcum transformed into positive charged. After absorbing the anionic collectors, the surface electronegativity was partially restored.

![Figure 4](https://iwaponline.com/wst/article-pdf/doi/10.2166/wst.2021.478/954826/wst2021478.pdf)

*Figure 4* | FTIR spectrums of (a) quartz, (b) talcum, (c) montmorillonite following each step of the carrier flotation process and the SEM images of (d) quartz, (e) talcum, (f) montmorillonite after carrier flotation.
Discussion on scaling cations removal mechanisms

It was confirmed that carrier flotation process was more cost-effective than the traditional ion flotation technique to remove the scaling cations from the oilfield produced water. During the carrier flotation process, over four-fifths of the anionic collector was replaced by low-cost natural minerals, so as to simultaneously enhance the scaling cations removal rate and operation economy. By summarizing the above scaling cations adsorption thermodynamics, carrier flotation and characterization results, we proposed the scaling cations removal mechanisms as described in Figure 5.

During the carrier flotation process, the scaling cations removal mainly divided into the following mechanisms. Primarily, scaling cations were adsorbed by the carrier minerals via electrostatic attraction or ion exchange. For quartz and talcum, scaling cations adsorption mainly occurred on the external surface, while the adsorption onto montmorillonite and talcum mainly occurred in the interior pores and interlayers, as exhibited in the FTIR and XPS characterizations. Afterwards, the anionic oleate collector was mixed into the slurry and adsorbed onto the minerals which enhanced the minerals floatability. The hydrophobic associated multilayer oleate restored the negative charges (−6.6 to −17.0 mV for quartz) of carrier minerals and attracted more scaling cations (1.2%–3.5% onto quartz), as indicated by zeta potential and XPS test. Furthermore, air bubbles were introduced into the flotation cell to float up the hydrophobic scaling cations-loaded minerals. Simultaneously, the negatively charged bubbles were also favorable to remove more scaling cations from the produced water.

Carrier minerals regeneration

In this research, ethanol solution and HCl combination was employed to restore the spent carrier minerals. Following regeneration, carrier flotation runs were re-conducted to evaluate the regeneration efficiency (see Figure 6). Quartz and talcum

Table 2 | Surface elemental composition and zeta potential of the carrier minerals following each step of the carrier flotation process

<table>
<thead>
<tr>
<th>Carrier minerals</th>
<th>Si</th>
<th>O</th>
<th>Na</th>
<th>Ca</th>
<th>Mg</th>
<th>Al</th>
<th>C</th>
<th>Zeta potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pristine</td>
<td>29.5</td>
<td>66.0</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>4.5</td>
<td>−26.1</td>
</tr>
<tr>
<td>Cations loaded</td>
<td>24.1</td>
<td>53.8</td>
<td>1.9</td>
<td>1.2</td>
<td>0.3</td>
<td>ND</td>
<td>18.7</td>
<td>−6.6</td>
</tr>
<tr>
<td>Floating</td>
<td>2.8</td>
<td>17.9</td>
<td>0.4</td>
<td>3.5</td>
<td>0.3</td>
<td>ND</td>
<td>75.2</td>
<td>−17.0</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pristine</td>
<td>17.5</td>
<td>58.1</td>
<td>2.5</td>
<td>0.1</td>
<td>5.0</td>
<td>2.1</td>
<td>14.7</td>
<td>−30.5</td>
</tr>
<tr>
<td>Cations loaded</td>
<td>17.0</td>
<td>54.8</td>
<td>3.5</td>
<td>0.3</td>
<td>5.1</td>
<td>6.4</td>
<td>12.9</td>
<td>−5.5</td>
</tr>
<tr>
<td>Floating</td>
<td>7.6</td>
<td>29.5</td>
<td>1.2</td>
<td>1.8</td>
<td>1.5</td>
<td>3.9</td>
<td>54.5</td>
<td>−21.2</td>
</tr>
<tr>
<td>Talcum</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pristine</td>
<td>16.2</td>
<td>55.0</td>
<td>ND</td>
<td>ND</td>
<td>25.7</td>
<td>ND</td>
<td>5.1</td>
<td>−11.4</td>
</tr>
<tr>
<td>Cations loaded</td>
<td>14.1</td>
<td>53.2</td>
<td>1.0</td>
<td>2.5</td>
<td>25.0</td>
<td>ND</td>
<td>4.2</td>
<td>0.9</td>
</tr>
<tr>
<td>Floating</td>
<td>13.3</td>
<td>45.0</td>
<td>1.0</td>
<td>3.4</td>
<td>16.0</td>
<td>ND</td>
<td>21.3</td>
<td>−2.4</td>
</tr>
</tbody>
</table>

*ND means not detected.

![Figure 5](https://example.com/f5.png)

Figure 5 | Schematic diagram of the scaling cations removal mechanisms.
were found to be more favorable and stable for regeneration. After three regeneration cycles, the regeneration efficiency of quartz and talcum still reached 86.1% and 84.8%, respectively. However, appreciable reduction on scaling cations removal capacity was observed during the montmorillonite regeneration process.

Based on the proposed scaling cations removal mechanisms, we anticipated that the regeneration process included two steps: (a) the organic collector (binding with a part of scaling cations) was desorbed by ethanol due to their high affinity; (b) the residual scaling cations on the minerals surface were eluted by the HCl solution. For quartz or talcum flotation process, scaling cations primarily loaded onto the external surface via electrostatic attraction which could be easily eluted. While for montmorillonite, the adsorbed scaling cations onto the mineral interlayers were considered to be difficult to release by the regenerant. Moreover, the organic collector could block the pores and inhibit scaling cations desorption. Combined with the scaling cations removal performance, we believed that talcum exhibits the great potential to be the recyclable carrier mineral.

CONCLUSIONS

In this research, the scaling cations were removed by carrier flotation and the scaling cations removal mechanisms were systematically investigated. By exploring the scaling cations adsorption thermodynamics, it was found that all the $\Delta G$ values fall into the $-11.9$ to $-14.5$ kJ/mol range, thus indicates the physisorption process. Montmorillonite showed its superiority in scaling cations adsorption due to the abundant surface functional groups and relatively developed pore structure. Only 500 mg/L of oleate collector was dosed to achieve the scaling cations removal rate of 75% in the montmorillonite flotation process, which is one seventh of that in traditional cations flotation. However, the montmorillonite recovery rate was relatively low. Talcum flotation process was found to be simultaneously achieved high scaling cations removal rate and minerals recovery rate, which shows better industrial application potential. By exploring the scaling cations removal mechanisms, it was concluded that the enhanced scaling cations removal performance was mostly attributed to the synergistic capture effect of carrier minerals and oleate collector. The anionic oleate adsorption onto the minerals surface could partially restore the negative surface potential and further enhanced the scaling cations capture capacity onto the carrier minerals. These results highlight the importance of carrier flotation in removing scaling cations from the produced water. Results also exhibited an efficient and practical regeneration method that employed an ethanol and HCl solutions. These results showed that this carrier flotation protocol would be technically acceptable for removing scaling cations from the oilfield produced water.

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All relevant data are included in the paper or its Supplementary Information.


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