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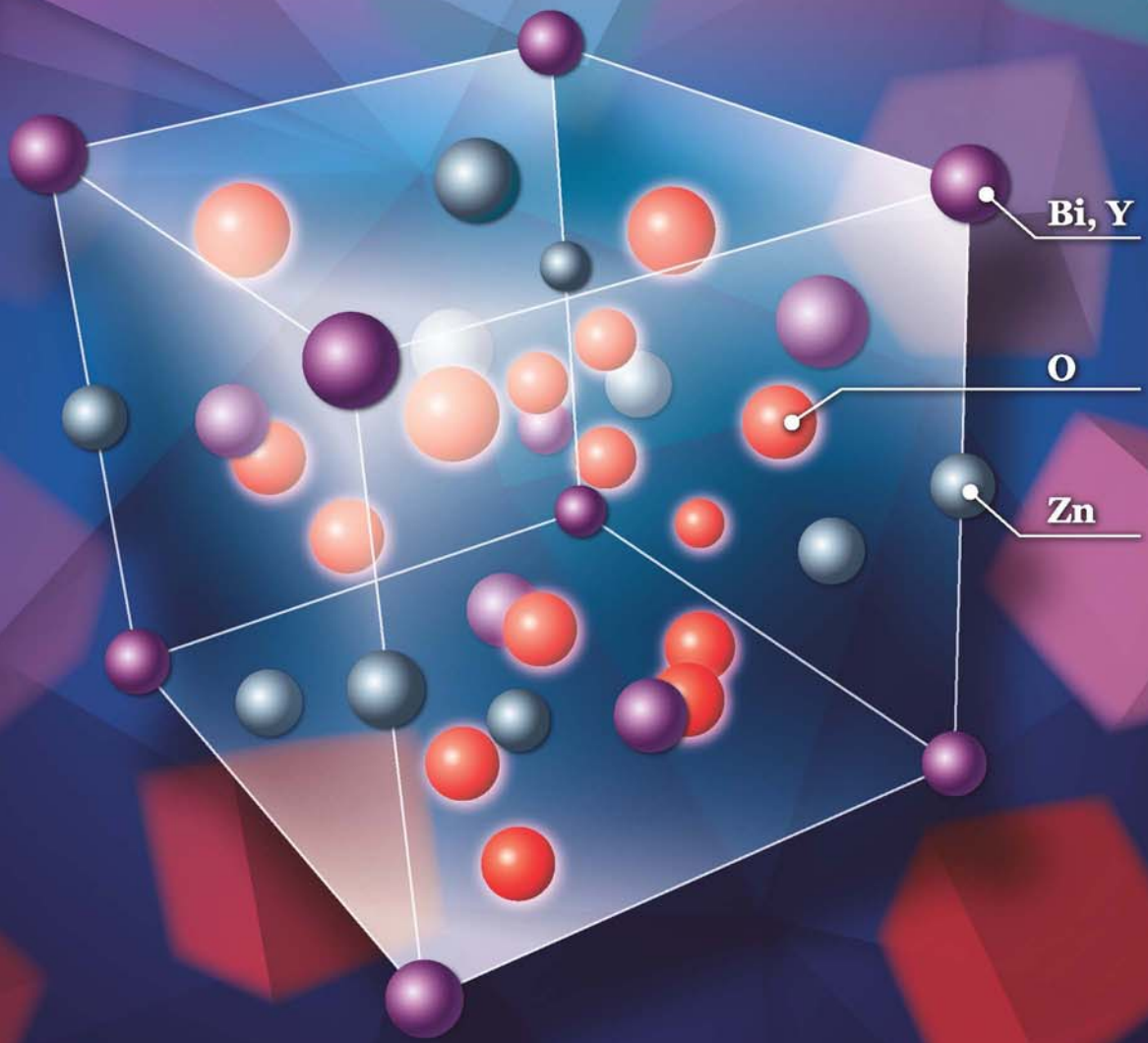

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Effect of six kinds of scale inhibitors on calcium carbonate precipitation in high salinity wastewater at high temperatures

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ABSTRACT

Precipitation of calcium carbonate ($CaCO_3$) scale on heat transfer surfaces is a serious and expensive problem widely occurring in numerous industrial processes. In this study, we compared the scale inhibition effect of six kinds of commercial scale inhibitors and screened out the best one (scale inhibitor SQ-1211) to investigate its scale inhibition performance in highly saline conditions at high temperature through static scale inhibition tests. The influences of scale inhibitor dosage, temperature, heating time and pH on the inhibition efficiency of the optimal scale inhibitor were investigated. The morphologies and crystal structures of the precipitates were characterized by Scanning Electron Microscopy and X-ray Diffraction analysis. Results showed that the scale inhibition efficiency of the optimal scale inhibitor decreased with the increase of the reaction temperature. When the concentration of Ca^{2+} was 1600 mg/L, the scale inhibition rate could reach 90.7% at 80°C at pH 8. The optimal scale inhibitor could effectively retard scaling at high temperature. In the presence of the optimal scale inhibitor, the main crystal structure of $CaCO_3$ changed from calcite to aragonite.

Introduction

In recent years, more attention has been paid to the reuse of refinery wastewater in the petroleum industry after advanced treatment (Liu et al., 2011a, 2011b). Compared with natural water, there are a considerable number of inorganic ions and organic substrates in refinery wastewater, which would lead to easier scale formation in circulating cooling water systems (Liu et al., 2013). Scale formation on heat transfer surfaces is a severe problem widely occurring in numerous industrial processes including batch precipitation, power generation, water transport and oil or gas production (Demadis et al., 2007; El Dahan and Hegazy, 2000; Gu et al., 2012; Suharso et al., 2011). It will reduce the efficiency of heat transfer, increase energy consumption and cause unscheduled equipment shutdowns (Yang et al., 2001).

The most common and effective scale inhibition method is to use scale inhibitors. Scale inhibition derives from complex physical processes, such as adsorption, nucleation and crystal growth processes, rather than chemical reactions (Ketrane et al., 2009). There is little understanding of the fundamental inhibition mechanisms, especially in quantitative aspects. Generally, researchers believe that the main mechanisms of scale inhibition include: (1) the threshold effect; (2) crystal distortion effect; (3) dispersion and (4) chelation (Darton, 2000; Lisitsin et al., 2005). Among them, threshold inhibition is the most appropriate method to control scale formation (Shakkthivel and Vasudevan, 2006). In other words, even a trace amount of inhibitor can prevent a scale layer from growing or adhering to a flow surface. Such low dosages are far less than the concentration of the scaling species, so chemical additives are also called "threshold inhibitors".

In recent years, because of the strong chelation of their functional groups with metal ions and superior dispersion characteristic of macromolecules, copolymers have been regarded as satisfactory scale inhibitors and received much attention (Wang et al., 2009). A series of studies have proved that various

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polyelectrolytes can retard crystal growth effectively (Al-Shammiri et al., 2000; Hasson et al., 1997, 1998; Smith, 1967). During crystal growth, different degrees of growth retardation for different crystal faces result in the formation of irregular crystals. The distortion of the crystal structure could increase the internal stress of crystals, which results in crystal fractures and prevents the deposition of microcrystals (Yang et al., 2001).

Polyphosphates, polyphosphonates and polycarboxylic acids are three popular copolymer scale inhibitors. Early research indicated that phosphate-containing additives had been adopted in over half of the drinking water treatment utilities in the United States (Casale, 2001). The phosphate-containing additives can sequester calcium and inhibit $CaCO_3$ scale precipitation even under the condition of calcite oversaturation (Marshall and Greaves, 1988). Polycarboxylic acids are another kind of copolymer scale inhibitor with cyclic or linear structure that can effectively inhibit $CaCO_3$ scale formation (Reddy and Hoch, 2001). The functional groups of polycarboxylic acids can chelate with Ca^{2+} ions to inhibit the formation of $CaCO_3$ crystals and distort the crystal lattice to generate irregular crystals.

Though in recent decades many scientists have been studying scale inhibition, few have focused on scale inhibition in high salinity and oily wastewater at high temperature. In this research, we compared the inhibition effect of six kinds of commercial scale inhibitors and screened out the optimal one to investigate its scale inhibition performance on $CaCO_3$ scale using the static scale inhibition method. Compared with other scale inhibition methods, the static scale inhibition method is widely used because it requires simpler devices and shorter testing time than other methods. The influences of scale inhibitor dosage, reaction temperature, heating time and pH on scale inhibition efficiency of $CaCO_3$ precipitation were investigated. The morphology and crystal form of $CaCO_3$ scale were characterized by scanning electronic microscopy (SEM) and X-ray powder diffraction (XRD) analysis, respectively.

1. Experimental

1.1. Reagents and instruments

Potassium sulfate (K_2SO_4), magnesium chloride ($MgCl_2$), ethylenediamine tetraacetic acid disodium salt (EDTA-2Na), ethanol and triethanolamine were supplied by Tianjin Guangcheng Chemical Reagent Co., Ltd. (Tianjin, China). Calcium chloride anhydrous ($CaCl_2$), sodium chloride (NaCl) and sodium bicarbonate ($NaHCO_3$) were purchased from Tianjin Bodi Chemical Reagent Co., Ltd. (Tianjin, China). Eriochrome black T was obtained from Tianjin Damao Chemical Reagent Factory (Tianjin, China). Ammonium nitrate (NH_4NO_3) was purchased from Chengdu Kelong Chemical Reagent Factory (Chengdu, China). EDTA-magnesium disodium salt and ammonium chloride (NH_4Cl) were supplied by Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China). Ammonium hydroxide ($NH_3{\cdot}H_2O$) was purchased from Laiyang Kangde Chemical Reagent Co., Ltd. (Laiyang, China). The six scale inhibitors are: scale inhibitor SQ1211 (Shandong TianQing Science and Technology Development Co., Ltd., China); scale inhibitor 190, 265 (Nalco Company); and LinHai-4, LinHai-1 and LinHai-3 (Shandong LinHai Science and Technology Co., Ltd., China). All the reagents above are analytical reagent grade. Deionized water was used throughout the experiment.

1.2. Evaluation of the scale inhibition efficiency of inhibitors against $CaCO_3$ scale

In order to screen out the best scale inhibitor among six kinds of commercial scale inhibitors against $CaCO_3$ scale, a preliminary screening test was carried out. The experiment was performed according to the Chinese oil and gas industry standard evaluation method (SY/T 5673-1993). The oilfield wastewater in Shengli Oil Field (China) was used. The composition and analysis of the oilfield wastewater are shown in Table 1.

Experiments were carried out in 250 mL conical flasks heated at 80°C for 24 hr. First, a certain amount of oily wastewater was added into the flasks. Then six kinds of scale inhibitors were added into the wastewater, respectively. Next, the specimens were immersed in a thermostatic water bath at 80°C for 24 hr (the level of the water bath should be higher than that of the test solutions). When the solutions naturally cooled down to room temperature, they were filtered using medium-speed quantitative filter paper. The

Table 1 – Compositions and analysis of the oilfield wastewater.

Analyte		c(1/zB^{Z-}) (mmol/L)	ρ(B) (mg/L)	Analyte		c(1/zB^{Z-}) (mmol/L)	ρ(B) (mg/L)
Anion	F^-	0.000	0.00	Cation	Li^+	0.000	0.00
	Cl^-	326.274	11566.42		Na^+	239.990	5279.78
	NO^-_2	0.000	0.00		NH^+_4	0.985	17.74
	Br^-	0.000	0.00		K^+	1.932	75.54
	NO^-_3	1.197	74.21		Mg^{2+}	7.312	88.84
	SO^{2-}_4	5.028	241.35		Ca^{2+}	80.109	1605.39
	OH^-	0.000	0.00		Sr^{2+}	0.000	0.00
	CO^{2-}_3	0.000	0.00		Ba^{2+}	0.000	0.00
	HCO^-_3	1.377	84.02				
Amount		333.876	11966.00	Amount		330.328	7067.29
pH			6.5				
Degree of mineralization ρ(∑B) (mg/L)			19033.29	Permanent hardness ρ($CaCO_3$) (mg/L)			4306.51
Total hardness ρ($CaCO_3$) (mg/L)			4375.43	Temporary hardness ρ($CaCO_3$) (mg/L)			140.13
Total alkalinity ρ($CaCO_3$) (mg/L)			68.92	Negative hardness ρ($CaCO_3$) (mg/L)			0.00

Ca^{2+} concentrations in test and blank solutions were titrated by an EDTA standard solution. The scale inhibition efficiency was calculated as follows:

$$\eta = \frac{\rho_2 - \rho_0}{\rho_1 - \rho_0} \times 100\% \quad (1)$$

where, ρ_0 (mg/L) is the mass concentration of Ca^{2+} in the absence of scale inhibitor in the blank solution after the test. ρ_2 (mg/L) is the mass concentration of Ca^{2+} in the presence of scale inhibitor in the test solution after the test. ρ_1 (mg/L) is the mass concentration of Ca^{2+} before the test.

As a result, the scale inhibitor SQ1211 showed the best scale inhibition effect compared with other inhibitors (Section 2.1) and was used in following experiments.

1.3. Inhibition performance of the optimal scale inhibitor against $CaCO_3$ scale

After the preliminary screening test, the optimal scale inhibitor was used for further study. The scale inhibition efficiency of the optimal scale inhibitor was also determined according to the Chinese oil and gas industry standard evaluation method (SY/T 5673-1993). The composition of the sample solution used in these experiments was based on that of the oilfield wastewater in Shengli Oil Field (China). The exact experimental procedure was described in Section 1.2. The detailed process of preparing the water sample solution was as follows. First, 35 mL of deionized water was added into a 250 mL conical flask. Then, 25 mL of $CaCl_2$ solution (0.2 mol/L), 50 mL of NaCl solution (0.6 mol/L), 1.25 mL of NH_4NO_3 solution (0.1 mol/L) and 5 mL of $MgCl_2$ solution (0.1 mol/L) were added into the conical flask in sequence. In order to investigate the effect of scale inhibitor SQ-1211 on the scale inhibition performance, a SQ1211 sample was added into the above sample solution at 1 g/L and shaken to ensure complete mixing. Then, 5 mL of NH_4Cl–$NH_3{\cdot}H_2O$ buffer solution with pH = 10 was added. Finally, 1.25 mL of $NaHCO_3$ solution (0.1 mol/L) and 2.5 mL of K_2SO_4 (0.1 mol/L) was slowly added (shaking while adding).

1.4. Sample collection of $CaCO_3$ scale

25 mL of $CaCl_2$ solution (0.2 mol/L) was added into a 250 mL conical flask. Then 50 mL of NaCl solution (0.6 mol/L) was added. Next, a scale inhibitor solution sample was added at 1 g/L. Finally, 50 mL of $NaHCO_3$ solution (0.2 mol/L) was slowly poured into the above mixture. Then the blank and test sample were immersed into a thermostatic water bath at 80°C for 10 hr. After that, the samples were dried to collect the $CaCO_3$ scale for further analysis.

1.5. Characterization of $CaCO_3$ crystal

The sample of $CaCO_3$ scale obtained according to Section 1.4 was characterized by SEM and XRD analyses. Micrographs of $CaCO_3$ crystal were taken using a HITACHI S-520 scanning electron microscope (Hitachi Limited, Japan). The samples were pretreated by gold sputtering before imaging. XRD experiments were carried out on a Rigaku D/MAX-rA XRD diffractometer (Rigaku Corporation, Japan) with Cu Kα radiation at λ = 1.54184 Å.

2. Results and discussion

2.1. Preliminary screening test of scale inhibitors

The scale inhibition efficiencies of six kinds of scale inhibitors at different dosages are shown in Fig. 1. When the dosage of SQ1211 was 11 mg/L, the scale inhibition efficiency was as high as 91%, but the scale inhibition efficiency decreased to 57% when the dosage was 20 mg/L. When the dosage was more than 20 mg/L, the scale inhibition efficiency of SQ1211 increased slightly from 20 to 30 mg/L and then decreased with the increase of dosage. When the dosage increased from 10 to 50 mg/L, the scale inhibition efficiency of scale inhibitor 190 and 265 had first increasing and then decreasing trends with the increase of dosage, while scale inhibitor LinHai-4, LinHai-1 and LinHai-3 decreased with the increase of dosage and stabilized finally.

As illustrated in Fig. 1, SQ1211, which consisted of polycarboxylic acids and an organic phosphine-carboxylic acid copolymer, had the best scale inhibition effect compared with other inhibitors, and the highest scale inhibition efficiency could reach 91%.

2.2. Inhibition performance of the optimal scale inhibitor against $CaCO_3$ scale

2.2.1. Effect of dosage and temperature on inhibition efficiency

The effect of scale inhibitor dosage on scale inhibition efficiency was investigated and the results are shown in Fig. 2. A simulated wastewater of high salinity was prepared according to Table 1. The heating time was 10 hr; concentration of $CaCl_2$ and $NaHCO_3$ were 0.04 mol/L and 0.001 mol/L, respectively. It can be seen from Fig. 2 that the scale inhibition efficiency rose with the increase of the scale inhibitor dosage when the dosage was below 11 mg/L. The reason was that a smaller amount of active scale inhibitor contributed to the adsorption of $CaCO_3$ and blocked its formation at low scale inhibitor dosages, thereby $CaCO_3$ precipitated more easily. When the scale inhibitor dosage reached 11 mg/L, it had the highest efficiency. After the dosage of the scale inhibitor exceeded the optimal

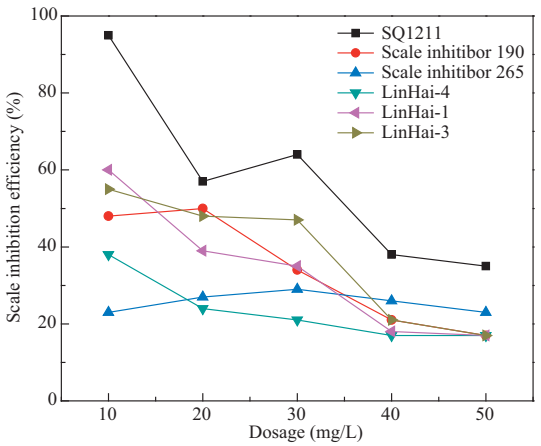

Fig. 1 – Scale inhibition efficiencies of six kinds of scale inhibitors at different dosages at 80°C for 24 hr.

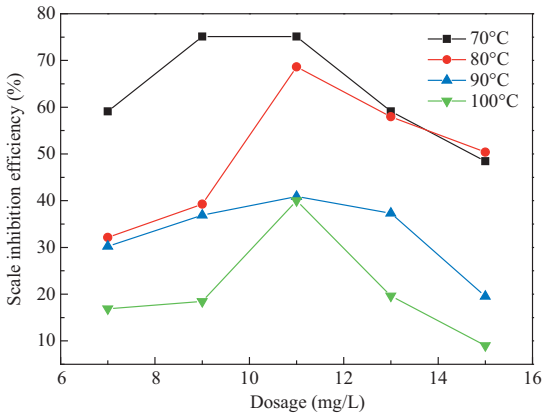

Fig. 2 – Effects of dosage and temperature on scale inhibition efficiency for 10 hr.

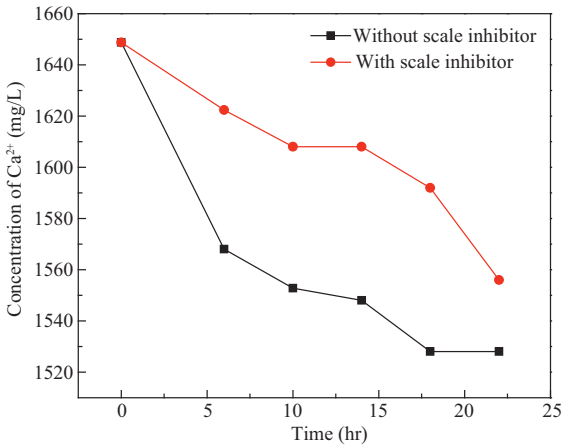

Fig. 3 – Effects of heating time on the concentration of Ca^{2+} at 80°C.

concentration, the scale inhibition efficiency declined as the dosage increased. This phenomenon could be explained by the threshold effect, which indicated that the dosage exceeded the optimal concentration, so that the scale inhibition efficiency did not increase when the scale inhibitor dosage increased.

It can also be observed that the scale inhibition efficiency was significantly affected by the reaction temperature. The scale inhibition efficiency declined with the increase of temperature. The highest scale inhibition efficiency could reach 75.1% and 69% when the temperature was 70 and 80°C, respectively. Moreover, the result showed that when the temperature was over 80°C, the scale inhibition efficiency had an obvious reduction at the optimal concentration. The highest scale inhibition efficiency at 90°C was only 40.9%, which was a little higher than that at 100°C. It is well known that the solubility of $CaCO_3$ decreases with increasing temperature. In addition, the scale layer formed more rapidly and became thicker as temperature increased, which could also reduce the scale inhibition efficiency. So the scale inhibition efficiency decreased as temperature rose from 70 to 100°C.

2.2.2. Effect of heating time on concentration of Ca^{2+}

According to the result obtained from Section 2.2.1, the influence of heating time on concentration of Ca^{2+} was investigated at 80°C, and the concentration of SQ1211 was 11 mg/L. The initial concentration of Ca^{2+} was 1650 mg/L. As observed in Fig. 3, the concentration of Ca^{2+} in solution decreased with the increase of heating time with and without scale inhibitor. The difference is that in the presence of scale inhibitor, the concentration of Ca^{2+} was much higher than that in the blank sample without scale inhibitor. In other words, the scale inhibitor can significantly retard the scaling tendency. The concentration of Ca^{2+} showed a significant declining trend from 1650 to 1568 mg/L during the first 5 hr in the absence of scale inhibitor, while the concentration of Ca^{2+} in the sample only decreased from 1650 to 1622 mg/L when scale inhibitor was used. As heating time went up, it could be clearly observed that the scale inhibitor had a significant effect on slowing down the formation of scaling. The reason may be that the scale inhibitor not only chelated with Ca^{2+} in the solution but also occupied the active growth sites of the crystal surface, which led to lattice distortion. After 18 hr, the concentration of Ca^{2+} in the sample with scale inhibitor declined greatly. This might be caused by the destabilization of the scale inhibitor. However, the concentration of Ca^{2+} in the blank solution began to stabilize, because there was insufficient CO_3^{2-} in the solution to form a precipitate. In conclusion, the scale inhibitor had a good effect on retarding the formation of $CaCO_3$ scale.

2.2.3. Effect of pH on inhibition efficiency

The influence of pH on scale inhibition efficiency was investigated at 80°C with a heating period of 10 hr, and the concentration of the scale inhibitor SQ1211 was 11 mg/L. It can be seen from Fig. 4 that the scale inhibition efficiency increased at first and then decreased with the increase of pH from 6 to 10. The scale inhibitor had the highest efficiency of 90.7% at pH 8. Compared with alkaline conditions, the scale inhibition efficiency was lower under acid conditions, maybe because the scale inhibitor was less stable under acid conditions. In addition, the concentration of Ca^{2+} decreased with the increase of pH without scale inhibitor, while the concentration

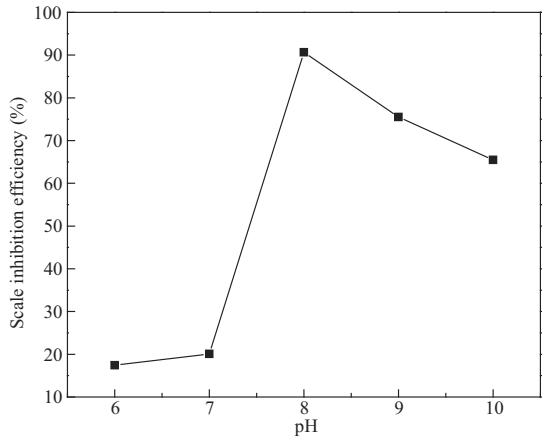

Fig. 4 – Effects of pH on scale inhibition efficiency at 80°C for 10 hr.

of Ca^{2+} remained at a high level at different pH in the presence of scale inhibitor. Hence the scale inhibition efficiency was better under alkaline conditions. With the increase of pH, the concentration of OH^- increased and the reaction equilibrium between OH^- and HCO_3^- shifted to the right, which led to the decrease of HCO_3^- and the increase of CO_3^{2-}. As a consequence, the $CaCO_3$ precipitated more easily and the scale inhibition efficiency decreased. In addition, the carboxylic acid group (–COOH) was unstable in alkaline conditions, because the ionization degree of the carboxylic acid group increased under this condition, and only C═O from the completely protonated scale inhibitor with –COOH groups could form hydrogen bonds with the water molecules from the surface of insoluble salt nuclei. Hence the scale inhibition efficiency decreased as pH increased from 8 to 10.

2.2.4. SEM micrographs of $CaCO_3$ crystals in the absence and presence of scale inhibitor

In order to investigate the effect of the scale inhibitor on the growth and morphology changes of $CaCO_3$ crystals, the $CaCO_3$ scales formed in the absence and presence of the optimal scale inhibitor were characterized by SEM analysis. The scanning micrographs of $CaCO_3$ crystals are shown in Fig. 5. As shown in Fig. 5a, the $CaCO_3$ crystals in the blank sample had regular shape with clear rhombohedral structure. They also had a glossy surface and compact structure. This indicated that the $CaCO_3$ crystals in the blank sample without scale inhibitor were mainly composed of calcite, which was the most thermodynamically stable form of $CaCO_3$ crystal (Xyla et al., 1992). When the scale inhibitor was added into the sample, the $CaCO_3$ crystals changed obviously from regular cube shapes and glossy surfaces with compact structure to flower and rod structures and rough surfaces with relatively loose accumulation (Fig. 5b). It is well known that calcite, aragonite and vaterite have rhomboidal, needle/rod and spherical structures, respectively (Gopi and Subramanian, 2012). So we could conclude that the main crystal structure of $CaCO_3$ had changed from calcite to aragonite after adding the scale inhibitor.

The major components of the optimal scale inhibitor were polycarboxylic acids and organic phosphine-carboxylic acid copolymer. During $CaCO_3$ crystal growth, the $–P(O)(OH)_2$ group could affect the scale inhibition efficiency by occupying the active sites on the surface of $CaCO_3$ crystals and changing the extent of chemical bonding with the surface (Sondi and Matijević, 2001). In addition, the $–P(O)(OH)_2$ group and $–COO^-$ group had a high chelating ability toward calcium ions to form stable chelation compounds (Demadis and Katarachia, 2004; Gal et al., 1996; Hasson et al., 1997). These would interfere with the nucleation and growth of $CaCO_3$ crystals so that the crystals became irregular (Qiang et al., 2013). The distortion in the $CaCO_3$ crystals increased their internal stress, which would lead to crystal fractures and inhibition of deposition of microcrystals. Previous studies suggested that aragonite and vaterite could be more thermodynamically stable than calcite at certain temperatures or in the presence of some inhibitors (Kralj et al., 1997). Thus it was illustrated that the aragonite and vaterite possessed higher thermodynamic stability than calcite in the presence of the scale inhibitor SQ1211. Because aragonite and vaterite have a higher solubility product and free energy than calcite (Knez and Pohar, 2005), the scale was easy to dissolve and can be washed away by water. Consequently, the $CaCO_3$ crystals deposited in the experimental process had difficulty adhering to the surface of the beaker and scale inhibition was obtained.

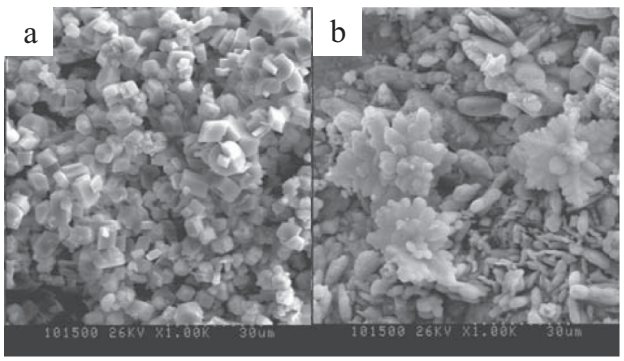

Fig. 5 – Scanning Electron Microscope (SEM) micrographs of the $CaCO_3$ precipitation in the absence of scale inhibitor (a), in the presence of scale inhibitor (b).

2.2.5. XRD analysis of $CaCO_3$ crystals in the absence and presence of the optimal scale inhibitor

The $CaCO_3$ crystals were also characterized by XRD analysis. Fig. 6 presents the XRD images of $CaCO_3$ crystals in the absence and presence of the scale inhibitor. The XRD patterns in Fig. 6a show that calcite was the main crystal form in $CaCO_3$ precipitation without scale inhibitor. The diffraction peak strength of the calcite crystal deposited in the blank sample without scale inhibitor was strongest at 29.242° (the characteristic crystal face 104 of the calcite), which confirmed that the 104 face was the major growth surface without scale inhibitor. In addition, the diffraction peaks at 39.223°, 43.057° and 48.378° corresponded to the calcite crystal faces 113, 202 and 118, respectively. This indicated that calcite was the dominant crystal form in the absence of scale inhibitor. This result was consistent with the conclusion drawn from Fig. 5a. Yet, after adding the scale inhibitor, the characteristic diffraction peaks of calcite observed in Fig. 6a were simultaneously invisible in Fig. 6b, which illustrated that the growth of the crystal faces 104, 113, 202 and 118 was completely inhibited by the scale inhibitor. Instead, the diffraction peak at 31.602° (the characteristic crystal face 006 of calcite) was observed and it had the strongest diffraction peak strength, which illustrated that the face 006 became the major growth surface in the presence of scale inhibitor. In addition, the diffraction peaks of aragonite phase at 45.342°, 56.313° and 66.261° are also visible in Fig. 6b, which correspond to the 221, 042 and 312 crystal faces. This indicated that the scale inhibitor could not only greatly inhibit the crystal growth of calcite but also transform a large amount of calcite phase to the aragonite phase. In other words, the aragonite phase was stabilized kinetically in the presence of the scale inhibitor. A previous study has shown that vaterite was the initial phase formed in $CaCO_3$ supersaturated solution, and it could be transformed to calcite in the absence of scale inhibitor (Chakraborty et al., 1994), which was also confirmed by this study. In the presence of scale inhibitor, most of the vaterite phase was transformed to mixtures of the calcite phase and aragonite phase. It is known that calcite is the most

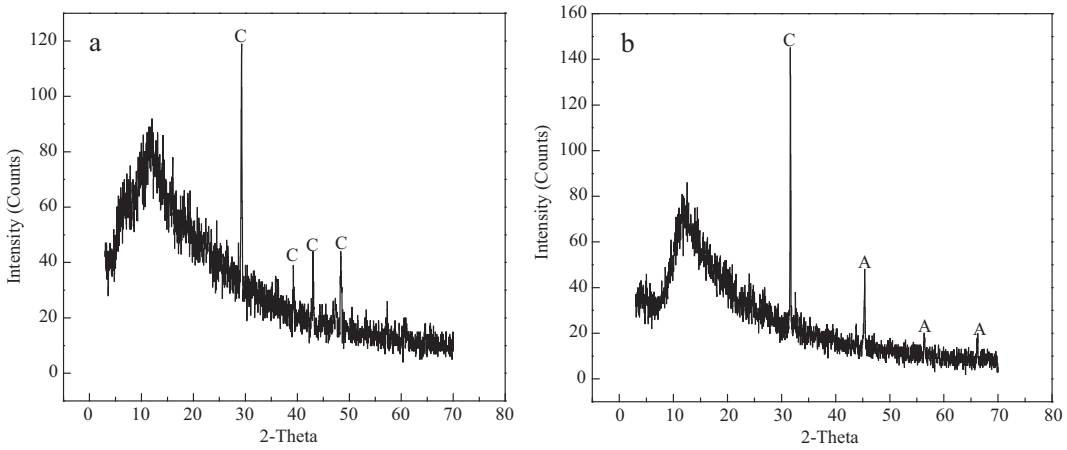

Fig. 6 – XRD images of the $CaCO_3$ precipitate in the absence of scale inhibitor (a), in the presence of scale inhibitor (b). A: aragonite; C: calcite.

thermodynamically stable form of $CaCO_3$, so the formed scale was easy to attach on the surface of the heat exchanger and hard to wash away. However, the scale inhibitor changed the crystal growth habit and destroyed the crystal structure. Compared with calcite, aragonite had loose accumulation and higher solubility product and free energy, which meant that the highly dispersed and unstable crystal was easy to dissolve and can be washed away by water. In conclusion, the loss of heat transfer can be minimized and scale inhibition can be obtained.

3. Conclusion

(1) Of the six kinds of scale inhibitors, the scale inhibitor SQ1211 had the best scale inhibition effect at high temperatures. In the scale inhibition system, the inhibition efficiency was influenced by scale inhibitor dosage, reaction temperature, heating time and pH. (2) The optimal dosage of SQ1211 was 11 mg/L when the concentration of Ca^{2+} was as high as 1600 mg/L. Moreover, SQ1211 can significantly retard the scaling tendency. (3) The scale inhibition efficiency decreased as the reaction temperature (ranging from 70 to 100°C) increased. The scale inhibition efficiency could reach 75.1% at 70°C. (4) Initially, the scale inhibition efficiency increased gradually in the pH range 6–8, and then decreased with pH further increasing. At constant temperature of 80°C, the highest inhibition efficiency was 90.7% at pH 8. (5) In the presence of SQ1211, the highly dispersed and unstable aragonite phase became the main crystal form in $CaCO_3$ scale, which would cause the scale to dissolve and be washed away by water easily. (6) The reason why the scale inhibition effect of SQ1211 in the oilfield wastewater was higher than in the simulated wastewater still needs further study.

Acknowledgments

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