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Anti-scaling study on phosphate rock flotation wastewater

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ABSTRACT

Static experiments were carried out to study the pipe scale behavior with phosphate rock flotation wastewater. The performance of an anti-scalant that can be regarded as composition of 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA), 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) was validated. Its scale inhibiting mechanism could be viewed as investigation with zeta potential, turbidity value, X-ray diffraction (XRD) as well as scanning electron microscope (SEM). The experimental results demonstrated that the compound of PBTCA and HEDP has more favorable properties of scale inhibition than its components for simulative wastewater and actual flotation wastewater. The effects of hardness, alkalinity, pH and temperature of solution on the scale inhibition rates of the anti-scalant are comparatively high. The $CaSO_4$ samples were analyzed and prepared after addition of the anti-scalant, which indicated that the inhibition efficiency reached the maximum and the absolute value of zeta potential reached the maximum, whilst the turbidity value of solution was minimal. XRD and SEM results indicated that the inhibitor caused the $CaSO_4$ crystal lattice of scale to be distorted, then the regularly dense crystal acicular structure transformed into amorphous loose granulation.

Keywords: Flotation wastewater; Anti-scaling; Calcium sulfate

1. Introduction

The flotation can be regarded as the main method for processing medium and low-grade phosphate rock. In the course of the progress of picking up ore backwater in phosphate rock, the complex ions mainly come from the outlet water in flotation [1]. In order to solve or alleviate the issue of water shortage and water pollution, the most effective way can be regarded as to reuse flotation wastewater in mineral processing after treatment [2]. However, scaling on the surface of pipeline and the equipment is inevitable in reusing phosphate rock flotation wastewater process. On industrial plants, we use scale inhibitors as currently acceptable methods to prevent scale formation [3].

Davey et al. [4] presented a review on the role of scale inhibitors in precipitation processes. He classified the various agents studied into four groups: First, low molecular weight organic substances, such as succinic, tartaric acid, citric; Second, low molecular weight inorganic substances, such as sodium triphosphate rock and sodium pyrophosphate rock; Third, long-chain polymeric materials with hydroxyl side groups, such as polyacrylic acid, 1-hydroxyethylidene-1,1-diphosphnic acid (HEDP), 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA) and polyglutamic acid; The last group is proteinaceous materials, such as gelatin and phosphoproteins. He concluded that the active scale inhibitors generally extend the induction time. He interprets that the presence of scale inhibitors in the system may result in adsorption onto embryo that reduces the rate of nucleation.

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Table 1
Wastewater property

Wastewater	Ca^{2+}	Mg^{2+}	SO_4^{2-}	F^-	Suspended	COD	pH
1	2,500	125	3,201	1.21	156	34	6.9
2	1,004	390	3,446	1.7	59	105	5
3	2,607	143	3,520	2.08	827	53	5.8
4	1,500	353	5,058.4	40.1	354	82	4.1

The X-ray diffraction (XRD) results depicted that the ingredient of the scale samples taken from Guizhou province of China can be regarded as mainly dihydrate calcium sulphate ($CaSO_4 \bullet 2H_2O$). The phosphate rock flotation wastewater in the main pipe contained Ca^{2+}, SO_4^{2-}, Mg^{2+}, F^- and PO_4^{3-}, as shown in Table 1. The surface fouling was mainly composed of dihydrate calcium sulphate. The Ca^{2+} and SO_4^{2-} in the high concentration wastewater was the main cause of pipe scaling.

Zhao et al. [5] studied that the induction time of the growth of the crystal nucleus and crystal morphology were influenced by carboxylic acid as calcium sulfate scale inhibitor, and the factors which affect scale inhibition efficiency are Ca^{2+}, Mg^{2+}, SO_4^{2-} concentration, temperature and acidity. Cao [6] investigated that HEDP and PBTCA interact with calcium sulfate to generate complex which is not easily to scale on the metal surface. With others, Wang Gengping and PU Yu [7] further studied that the property of two kinds of scale inhibitors (HEDP and PBTCA). As a consequence, the vital factors that influence scale inhibition efficiency are acidity, concentration of impurity ions and temperature. In accordance with Kazi [8], scale inhibitors may act to hinder scale formation by several ways. They were likely to change the precipitation's chemical potential by adsorption, and be adsorbed onto growing crystals for inhibiting scale nucleation, or be adsorbed onto precipitating ions for generating complex and for distorting crystal lattice. It is possible that the active inhibitors function through one or more of the above ways.

Scaling on the surface of pipeline and equipment is inevitable in reusing phosphate rock flotation wastewater process. Currently, the objective is that little material can be viewed as available for anti-scaling study on phosphate rock flotation wastewater [9]. This paper takes the static scale inhibition method to investigate the performance of compound of PBTCA and HEDP to the pipe scale behavior of phosphate rock flotation wastewater. The anti-scalant's performance to phosphate rock flotation wastewater has been evaluation under various conditions to explore its inhibition mechanism. Our research may provide some certain basis data for anti-scaling in the reusing process of practical phosphate rock flotation wastewater.

2. Experimental procedure

2.1. Materials

Calcium chloride and sodium sulfate were in analytically pure grade and used without further purification, unless specified. HEDP was in technical pure grade (50%). PBTCA was in technical pure grade (60%). Sodium ethylenediaminetetraacetic acid (EDTA) was prepared as standard solution.

2.2. Methods

2.2.1. Static scale inhibition tests

Static scale inhibition method is used to evaluate the efficiency of scale inhibition [10]. 0.05 mol/L $CaSO_4 \bullet 2H_2O$ saturated solution was prepared by dissolving calcium chloride and sodium sulfate. It can be measured that the concentration of Ca^{2+} and SO_4^{2-} of solution are 2,000 and 4,800 mg/L. Solution was stored in sealed condition at 50°C in thermostat water bath for 8 h. $CaSO_4 \bullet 2H_2O$ was prepared by simulative wastewater as shown in the following reaction equation [11]:

$$Na_2SO_4 + CaCl_2 + 2H_2O \rightarrow CaSO_4 \bullet 2H_2O + 2NaCl.$$

The supersaturation ratio (S) was calculated as follows [12]:

$$S = \frac{c}{c^*} \tag{1}$$

where S is the ratio of supersaturation; c is the $CaSO_4 \bullet 2H_2O$ concentration, %; c^*, which is the $CaSO_4 \bullet 2H_2O$ (solute) solubility under the experimental conditions, is 3.1 g/L of high purity water, which is determined experimentally.

The Chinese national standard method (GB/T 16632-2008) was used to measure the concentration of Ca^{2+}. The scale inhibition rate calculation formula is given below [13]:

$$\eta = \frac{c_x - c_0}{c - c_0} \tag{2}$$

where η can be regarded as the efficiency of scale inhibition; c_x is the concentrations of Ca^{2+} in the presence of the inhibitor, mg/L; c_0 is the concentrations of Ca^{2+} in the absence of the inhibitor, mg/L; c is the total concentrations of Ca^{2+}, mg/L.

2.2.2. Equipment

0.05 mol/L $CaSO_4 \bullet 2H_2O$ saturated solution was prepared by dissolving calcium chloride and sodium sulfate in high purity water. The different concentrations of scale inhibitor, 0, 2, 10 and 14 mg/L were added to the prepared solution. It was stored in sealed condition at 50°C in thermostat water bath for 8 h. For the first time, the solid sample of calcium sulfate (probably in dihydrate calcium sulphate form) was placed in the oven after drying for 5 h at 50°C. Thermostat water bath is a multifunctional type circulation constant temperature water bath used not only to provide a constant temperature bath but also for a variety of low (20°C) and high (80°C) temperature test. A 0.75 L single slot laboratory flotation machine

(XFD-3) was used to produce and collect practical flotation wastewater. The high purity water was prepared by deionized water preparation machine (Exceed-E). The value of the zeta potential of $CaSO_4\bullet 2H_2O$ catalysts was characterized by zeta potential measurement instrument (Delsa^{TM} Nano). The $CaSO_4\bullet 2H_2O$ saturated solution after measuring zeta potential was used to turbidity analysis. The value of the turbidity of $CaSO_4\bullet 2H_2O$ saturated solution was characterized by turbiditor (WZS-200). The morphology of $CaSO_4\bullet 2H_2O$ catalysts was characterized by SEM (ZEISS-EVO-18). The crystal structure of $CaSO_4\bullet 2H_2O$ catalysts is characterized by XRD (X'Pert Pro XRD PANalytical Delsa^{TM} Nano).

3. Results and discussion

3.1. Influence of the ratio of PBTCA and HEDP

It can be concluded from Fig. 1 that when the dosage of PBTCA was 10 mg/L, the scale inhibition rate reached 96.5%. When the HEDP dosage reached up to 12 mg/L, the scale inhibition rate reached 95.0%. When the dosage of anti-scalant (PBTCA and HEDP ratio is 4:1) was 10 mg/L, the inhibition rate reached 99.9%. Compared with PBTCA and HEDP use individually, the scale inhibition rate increased by 7.7% and 18.8%, respectively.

In the range of 2–6 mg/L, with the dosage of the scale inhibitor increasing, the inhibition rate was on the rise. This is explained by that the number of functional groups of inhibitors, phosphonic acid $[(OH)_2OP–]$ and carboxylic acid groups [–COOH], can be regarded as effective inhibition groups on the $CaSO_4\bullet 2H_2O$ scale.

In the range of 6–10 mg/L, the scale inhibition rate did not change significantly. The main reason is that the phosphoric acid and carboxylic acid groups of the scale inhibitor react with Ca^{2+} in the $CaSO_4\bullet 2H_2O$ crystal embryo (composed of Ca^{2+} and SO_4^{2-}) and Ca^{2+} in the solution. With the increase of dosage, the amount of compound adsorbed on the surface of $CaSO_4\bullet 2H_2O$ crystal embryo also increases and more Ca^{2+} in the solution react with the scale inhibitor until reaching saturation. If the scale inhibitor is added further, the scale inhibition rate would not increase, due to the threshold effect.

When the dosage of the compound agent was more than 10 mg/L, the scale inhibition efficiency illustrated a decreasing trend. The dosage of anti-scalant should be controlled in the range from 8 to 12 mg/L to ensure great effect. What caused by this over-additive which we used turns out to be huge. Overusing agent can cause self-polymerization, flocculation and scale inhibition rate decline [11].

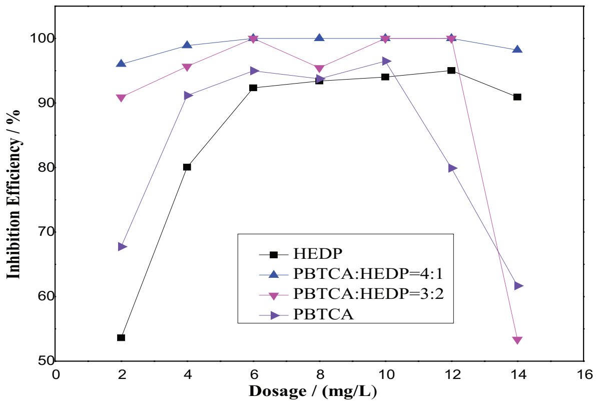

Fig. 1. Influence of PBTCA/HEDP quality ratio on calcium sulfate scale inhibition.

3.2. Influence of temperature

The effect of temperature on the calcium sulfate scale inhibition performance was investigated under the conditions of PBTCA:HEDP (4:1) dosage adopted 10 mg/L, with 8 h of water bath time. The results are demonstrated in Fig. 2 that with the increase of temperature, first, the scale inhibition rate to $CaSO_4\bullet 2H_2O$ to flatten out, then it falling rapidly. When the temperature was less than 50°C, the inhibition rate was above 95%. Since it contains PBTCA and HEDP structure carboxyl, it can be chelated with two or more Ca^{2+} into a five-membered ring or double five-membered ring structure. HEDP contains two phosphonate groups which can be well combined with Ca^{2+}. Then it forms a loose complex which hindered the development of crystals of $CaSO_4\bullet 2H_2O$. When the temperature is higher than 50°C, the scale inhibition effect of $CaSO_4\bullet 2H_2O$ decreases obviously. Because the scale inhibitor which is adsorbed onto the active sides of the $CaSO_4\bullet 2H_2O$ crystal surface is unstable in high operation temperature, the scale inhibition rate decreases crucially [14].

Calcium sulfate is one of the most commonly encountered scale deposits and occurs in three different crystalline forms: $CaSO_4$ (anhydrite), $CaSO_4\bullet 0.5H_2O$ and $CaSO_4\bullet 2H_2O$. In reusing flotation wastewater systems, gypsum is the most commonly encountered calcium sulfate scale [15]. The solubility of $CaSO_4$ (anhydrite), $CaSO_4\bullet 0.5H_2O$ and $CaSO_4\bullet 2H_2O$ is different in water solution [16]. Temperature was proved to have vital effects on scale inhibition. Higher temperature speeds up scaling process. One of the reasons for this could be change in solubility of $CaSO_4$ in water as the temperature increases due to the shift from $CaSO_4\bullet 2H_2O$ to $CaSO_4\bullet 0.5H_2O$ or $CaSO_4$ (anhydrite) as the most insoluble phase. Another reason for this behavior could be that higher temperature provides enough energy to the $CaSO_4\bullet 2H_2O$ molecules to overcome the activation energy of the precipitation reaction and speed up the transport of scale components from bulk solution to the crystal surface [17].

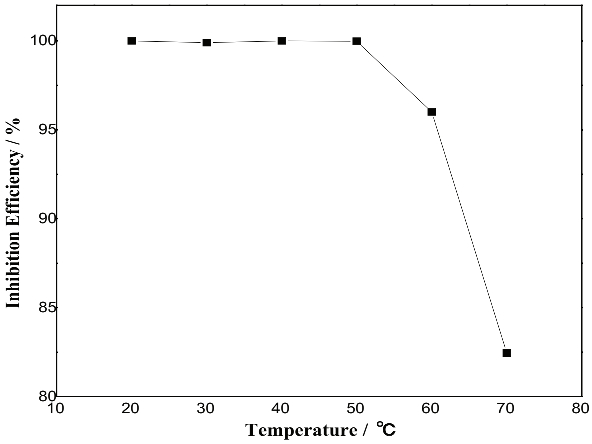

Fig. 2. Influence of temperature on calcium sulfate scale inhibition at a level of 10 mg/L PBTCA/HEDP (4:1).

3.3. Influence of pH value

The actual pH values of the flotation wastewater ranges 4.1–6.9 from Table 1. The range of pH value was from 3.0 to 9.0. In accordance with the date of actual flotation wastewater, the experiments studied the influence of pH value on the calcium sulfate scale inhibition by anti-scalant (PBTCA/HEDP [4:1]), and the solution temperature was 50°C. The results are demonstrated in Fig. 3. The anti-scalant illustrated superior inhibition ability to calcium sulfate precipitation.

Calcium sulfate inhibitory power rises from 23% to 97% rapidly with the increasing of pH value of the solution from 3.0 to 6.0. It indicates that the scale inhibition efficiency to $CaSO_4•2H_2O$ is influenced greatly by the system acidity [18]. One of the reasons could be that hydrolyzed functional groups have been inhibited. With the increase of pH value, the concentration of H^+ decreases. The equilibrium between OH^- and H^+ breaks up. It directly leads to that phosphoric acid groups and carboxylic acid groups become deprotonated. There are more amount of deprotonated groups that take part in calcium sulfate precipitation. The growth of $CaSO_4•2H_2O$ crystals can be viewed as disturbed and the scale inhibition efficiency increases [19].

3.4. Influence of concentrations of Ca^{2+}

The influence of the concentration of Ca^{2+} on the scale inhibition to $CaSO_4•2H_2O$ was conducted in this experiment and the results are illustrated in Fig. 4. The range of the concentration of Ca^{2+} was from 1,000 to 7,000 mg/L in accordance with the date of flotation wastewater. With the increase of the concentration of Ca^{2+}, the concentration of Ca^{2+} from 1,000 mg/L increases to 7,000 mg/L, the scale inhibition efficiency of the anti-scalant (PBTCA/HEDP (4:1)) decreases gradually, the scale inhibition efficiency decreases from 98.5% to 89.2%. After the Ca^{2+} concentration increasing to a certain amount, the scale inhibitor reaches "chelating saturation." Especially, the decreasing relative concentration of scale inhibitor has caused the scale inhibitor rate decline. According to the above analysis, the concentration of the Ca^{2+} is an crucial factor on scale inhibition performance. The reasons for this could be the dosage of the inhibitor was constant and the increase of calcium ion concentration exceeded the polymer's "cation chelation" for it [20].

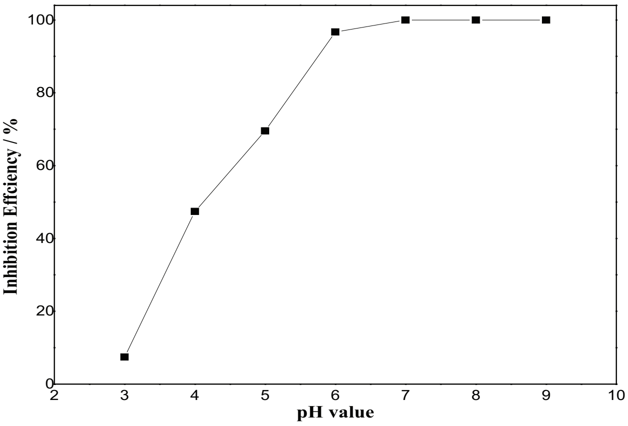

Fig. 3. Influence of pH value on calcium sulfate scale inhibition at a level of 10 mg/L PBTCA/HEDP (4:1).

3.5. Influence of concentrations of SO_4^{2-}

The influencing rules of the concentration of SO_4^{2-} on the scale inhibition efficiency were tested in this experiment and the results are demonstrated in Fig. 5. With the increase of the concentration of SO_4^{2-}, the scale inhibition efficiency of the anti-scalant (PBTCA/HEDP [4:1]) to $CaSO_4•2H_2O$ gradually decreases. The concentration of SO_4^{2-} from 2,400 mg/L increases to 8,400 mg/L, the scale inhibition efficiency decreases from 98.8% to 9.2%. Inhibition efficiency decreased gradually as the concentration of SO_4^{2-} increased. The influence of the calcium ion concentration was compared with sulfate ion. The results of the test have demonstrated that these two trends are quite different. The influence of sulfuric acid ion is greater than the calcium ions. This tendency of scale inhibition also indicates that the concentration of the SO_4^{2-} is a significant factor on scale inhibition test.

According to the analyses of the above experiments and results, The anti-scalant's performance was closely influenced

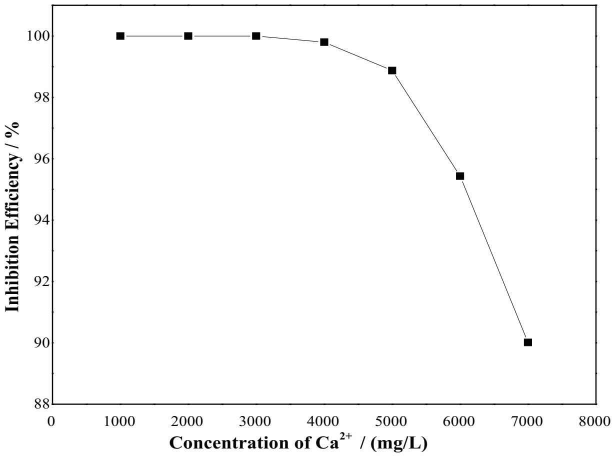

Fig. 4. Influence of concentration of Ca^{2+} on calcium sulfate scale inhibition at a level of 10 mg/L PBTCA/HEDP (4:1).

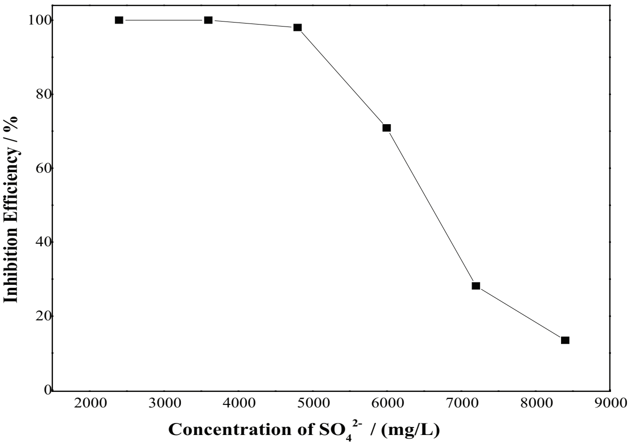

Fig. 5. Influence of concentration of SO_4^{2-} on calcium sulfate scale inhibition at a level of 10 mg/L PBTCA/HEDP (4:1).

by crystal nucleation rate. Nucleation rate can be viewed as defined as the number of formed nuclei per unit time per volume. It can be calculated in accordance with the following relation [21].

$$J = F\,\exp\left[\frac{-\beta\gamma^3 V_m^2 N_A f(\theta)}{(RT)^3 \ln^2 S}\right] \quad (3)$$

where J is the rate of nucleation and F is a frequency constant which is known as the pre-exponential factor and has a theoretical value of 10^{30} nuclei/cm^3 s. β is a geometric (shape) factor of 16 π/3 for the spherical nucleus and $f(\theta)$ is a correction factor. When purely homogeneous nucleation takes place, $f(\theta) = 1$, and when heterogeneous nucleation occurs, $f(\theta) = 0.01$. V_m is the molar volume (74.69 cm^3/mol for $CaSO_4$•$2H_2O$), T is the absolute temperature (K), R is the gas constant (J/mol K), γ is the surface energy (J/m^2) and N_A is the Avogadro's number (mol^{-1}).

By knowing the surface energy of $CaSO_4$•$2H_2O$ crystals (γ), the nucleation rate can be determined by these factors, pH and temperature affect surface energy by affecting the adsorption capacity, the concentrations of Ca^{2+} and SO_4^{2-} affect the crystal nucleation rate by affecting the ratio of supersaturation, to name only a few. Scale inhibition ability in certain conditions, the anti-scaling efficiency was affected [22].

3.6. Scale inhibition effect on actual flotation waste water

Experiments of actual flotation wastewater were collected from reversing flotation on a magnesium–calcium phosphate rock with low grade from Guizhou province. In accordance with the phosphate rock ore properties, regulator uses H_2SO_4 and collector uses GJBW (homemade in Guizhou University) in reverse flotation [23]. The property of PBTCA/HEDP (4:1) as anti-scalant was discussed by encoding standard method (GB/T 16632-2008) to actual flotation wastewater. It can be measured that the concentration of Ca^{2+} and SO_4^{2-} of wastewater sample 1 solution is 1,214.5 and 3,780.5 mg/L. The concentration of Ca^{2+} and SO_4^{2-} of wastewater sample 2 solution is 1,786.4 and 5,040.5 mg/L. The pH value is 5.5 and 4.9 of two samples, respectively. Experimental temperature is at 50°C. In accordance with Fig. 6, the scale inhibition efficiency is on the rise until reaching the maximum 98.4%. Then declines with the increase of dosage of scale inhibitors from 2 to 14 mg/L. PBTCA/HEDP (4:1) as anti-scalant has a great effect on laboratory flotation wastewater. When the dosage of 10 mg/L was used, the efficiency reached the maximum. When the dosage is more than a certain amount it will produce high dose effect, which comes into being flocculation. This trend can be regarded as consistent with simulated wastewater of flotation of phosphate rock.

3.7. Zeta potential analysis

Hydrolysis of the PBTCA/HEDP (4:1) as anti-scalant produces phosphonic acid groups and carboxylic acid groups both with negative charge. During a collision between the PBTCA/HEDP (4:1) as anti-scalant and the $CaSO_4$•$2H_2O$ crystallite in simulative solution, physical or chemical adsorption phenomena occurred on the surface of $CaSO_4$•$2H_2O$ crystallite. Then it lead to the formation of electrical double layer with negative charge on the surface of microcrystal. As demonstrated in Fig. 7, the compound inhibitor was attracted to the surface of $CaSO_4$•$2H_2O$ crystallite, so it made zeta potential (ζ) of crystal surface to decline. There exists more amount of deprotonational groups with increasing additives' dosage. Deprotonation of PBTCA and HEDP can interact with the metal ions, such as Ca^{2+}, to form electrical double layer. The value of the zeta potential of $CaSO_4$•$2H_2O$ crystallite reaches the minimum when the dosage of the PBTCA/HEDP (4:1) as anti-scalant is 10 mg/L. When we continue to add anti-scalant into solution, the value will increase. It means that the ability of adsorption on the surface of the $CaSO_4$•$2H_2O$ crystallite is weaken. The degree of hydrolysis reaches saturation. In addition, with the content of carboxyl groups in solution increased, which can be regarded as easy to have an interaction with the other divalent ion in the water, come out the function of bridging. It is easy to produce gel precipitation, resulting in the decrease of the relative content of inhibitors [24]. These characteristics can be proved in the following experiments.

The change of surface potential reflects the change of surface energy. On the basis of the theory of classic homogeneous

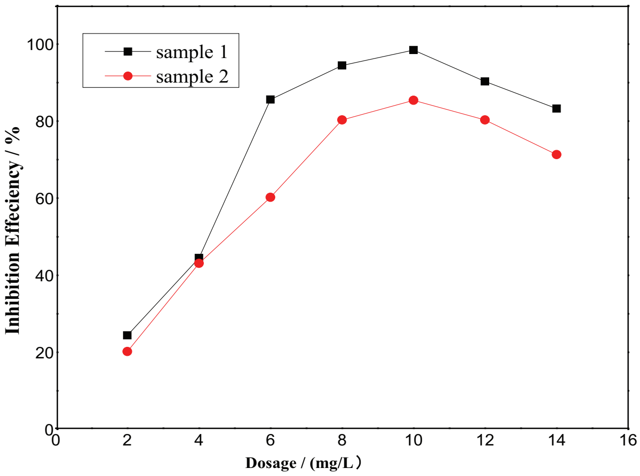

Fig. 6. Scale inhibition efficiency of PBTCA/HEDP (4:1) on actual flotation waste water.

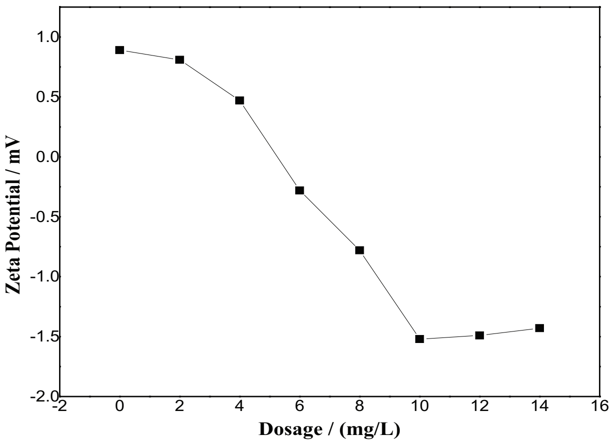

Fig. 7. Relationship between compound dosage and zeta potential value.

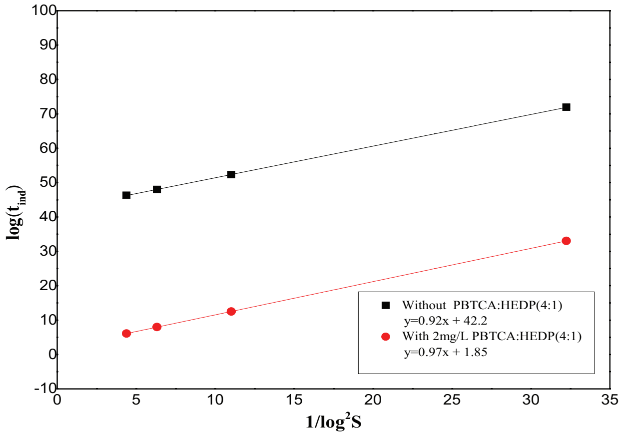

Fig. 8. Relation between log induction time and 1/log² super saturation, without and with 2 mg/L compound of PBTCA/HEDP (4:1).

nucleation, the induction time can be regarded as related to the ratios of supersaturation as the following correlation [21]:

$$\log\left(t_{\text{ind}}\right) = A + \frac{B}{T^3\left(\log^2 S\right)} \tag{4}$$

where A is an empirical constant (dimensionless) and B depends on the number of variables and is given by:

$$B = \frac{\beta\gamma^3 V_m^2 N_A f(\theta)}{\left(2.3R\right)^3} \tag{5}$$

While all of the parameters are as described above. According to the Fig. 8 and Eqs. 3, 4 and 5, surface energies are 1.513 × 10^{-2} and 1.595 × 10^{-2} J/m² without and with PBTCA/HEDP (4:1), respectively. It is clear that the surface energy is increased with PBTCA/HEDP (4:1) as anti-scalant. Generally, the surface energy for more soluble salts is less than that for less or sparingly soluble salts. Decreasing the surface energy leads to increasing the nucleation rate of $CaSO_4•2H_2O$ crystals.

3.8. Turbidity analysis

The vital role of anti-scalant (PBTCA/HEDP [4:1]) in the flocculation of Ca^{2+} with polymer was described. The flocculation of Ca^{2+} with polymer will rise the turbidity value eventually. Turbidity method was used to investigate the inhibition efficiency of PBTCA/HEDP (4:1) as anti-scalant. In accordance with Fig. 9, turbidity value reduced at first and then increased with the increase of dosage. The result illustrated that inhibition efficiency was gradually improved with the increase of scale inhibitor concentration. Nevertheless, when the concentration was more than 10 mg/L, threshold value effect appeared, the turbidity was on the decline until reaching the minimal value 0.3 NTU, then came out increasing trend with increasing the dosage of scale inhibitors from 10 to 14 mg/L. Turbidity value is expressed as raising trend in high dose, because of continuing to add scale inhibitors, the adsorption amount of scale inhibitor on the surface of $CaSO_4•2H_2O$ embryos reached saturation. It caused flocculation phenomena. That is consistent with zeta potential analysis results [25].

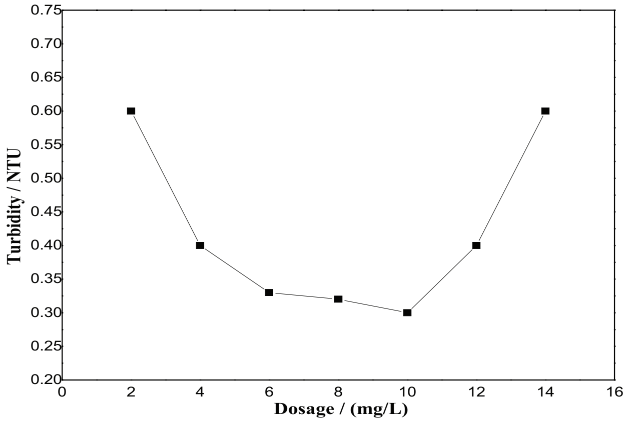

Fig. 9. The relationship between compound dosage and turbidity.

3.9. SEM and XRD analysis

As demonstrated in Fig. 10, the results for scale formation are discussed concisely and four scale samples taken from different dosage are analyzed. The concentration of PBTCA/HEDP (4:1) as anti-scalant is 0, 2, 10 and 14 mg/L. The X-ray diffraction pattern illustrated that there exists no significant difference with the blank control group, the peak intensity at 12.046° is weaker with adding dosage, but the absorption peak do not change. It indicated that scale sample components is not changed, which remain contains calcium sulfate dihydrate and calcium sulfate hemihydrate, the anti-scalant does not form other crystal.

With the resolution boosted over 100 times, the morphologies of deformed specimens were observed by scanning electronic microscope. Through the SEM observation as Fig. 11, the morphology of the crystal has changed. The crystal without any scale inhibitor was needle-shaped, this shape was more likely to scale on the solid surface; after adding scale inhibitor it became granular or short flat, which was not conducive to the formation of fouling on the solid surface [5].

The growth of calcium sulfate crystals can be viewed as in strict accordance with a certain crystal lattice forming a dense and hard crystal. After adding scale inhibitor, the scale inhibitor is adsorbed on the crystal and doped in the lattice. The disturbance of $CaSO_4·2H_2O$ crystal growth caused the increase of crystal internal stress, so the morphology of the crystal has changed. The surface becomes loose porous, the crystal is easy to break into a granular or short flat shape and hinder the growth of calcium sulfate scale [26].

4. Conclusions

Preliminary experiments have been initiated to study the influence of the ratio of PBTCA and HEDP, hardness, alkalinity, pH and temperature of solution on simulative wastewater. By optimizing the proportion of PBTCA, HEDP, the best quality ratio is 4:1. When the dosage reaches 10 mg/L, the inhibition efficiency can be 99.98%.

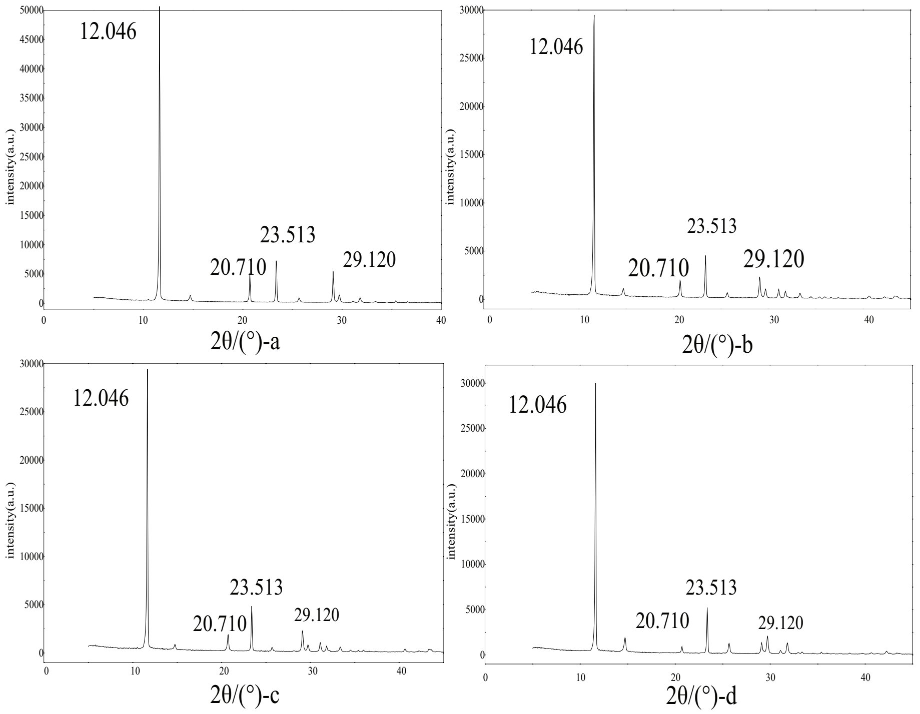

Fig. 10. XRD spectrum in different compound scale inhibitor dosage (a) 0 mg/L, (b) 2 mg/L, (c) 10 mg/L, (d) 14 mg/L.

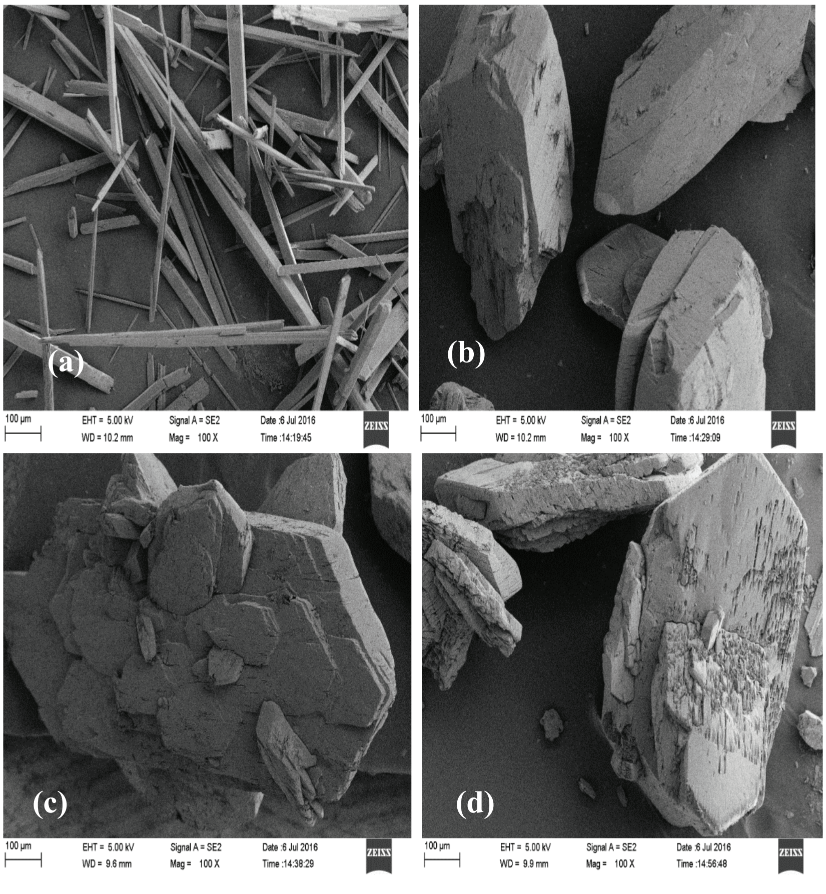

Fig. 11. SEM image in different compound scale inhibitor dosage (a) 0 mg/L, (b) 2 mg/L, (c) 10 mg/L, (d) 14 mg/L.

The property of PBTCA/HEDP (4:1) as anti-scalant was discussed by encoding standard method (GB/T 16632-2008) to actual flotation wastewater, while the scale inhibitor has a better effect on laboratory reverse flotation wastewater. When the dosage reaches 10 mg/L, the scale inhibition rate is 98.45% by static scale inhibition method, which has a much better effect.

Supersaturated solution 0.05 mol/L $CaSO_4•2H_2O$ was selected for initial mechanism analyses of scale inhibition. The influence on crystal modifications has been evidenced by SEM analyses. Through the observation of SEM and XRD diffraction pattern, it is not difficult to know the distribution of scale inhibitor produce morphology distortion on $CaSO_4•2H_2O$, and during the progress of crystal nucleus growth. It brings on physical and chemical adsorption with $CaSO_4•2H_2O$ microcrystal, which makes the surface of $CaSO_4•2H_2O$ form electric double layer with negative charge.

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Symbols

η — Efficiency of scale inhibition,%
c_x — Concentrations of Ca^{2+} in the presence of the inhibitor, mg/L
c_0 — Concentrations of Ca^{2+} in the absence of the inhibitor, mg/L
c — Total concentrations of Ca^{2+}, mg/L
S — Ratio of supersaturation
J — Rate of nucleation
F — Frequency constant, 10^{30} nuclei/cm^3 s
β — Geometric (shape) factor, $16\pi/3$
$f(\theta)$ — Correction factor, $f(\theta) = 1$, or $f(\theta) = 0.01$
V_m — The molar volume for $CaSO_4•2H_2O$, 74.69 cm^3/mol
T — Absolute temperature, K
R — Gas constant, J/mol K
γ — Surface energy, J/m^2
N_A — Avogadro's number, mol^{-1}
t_{ind} — Induction time, h

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