Scaling measurement of oil production wastewater as a comprehensive environmental engineering experiment

Tao Yu1,a, Xiaofei Zhang2,b, Bo Yang1,c, Jinling Li1,d, Gang Chen1,2,e and Chengtun Qu1,2,f,*

1 College of Chemistry and Chemical Engineering, Shaanxi Province Key Laboratory of Environmental Pollution Control and Reservoir Protection Technology of Oilfields, Xi’an Shiyou University, Xi’an, 710065 China
2 State Key Laboratory of Petroleum Pollution Control, CNPC Research Institute of Safety and Environmental Technology, Beijing, 102206 China

a 180708@xsyu.edu.cn, b Zhang-xiaofei@cnpc.com, c yangbo@xsyu.edu, d lijinling@xsyu.edu.cn, e gangchen@xsyu.edu.cn, *, f Corresponding author e-mail: xianquct@xsyu.edu.cn

Abstract. In the process of scaling the measurement of oil production wastewater using the bottle test method, the deposition and attachment of scaling crystals on the bottle wall lead to a small measurement result and a large error compared to the actual measurement. The scaling amount of oil production wastewater is measured by adding quantitative clay and inducing adsorption, gathering, and deposition of scaling crystals onto the surface of clay particles. Comparing with the theoretical value, the determination result is more accurate than the result of the bottle test method. The comprehensive experimental design described in this paper applies various topics of colloid and interface chemistry, such as scale crystal growth, clay diffusion double electric layer, and micelle structure. We believe that this design will help students majoring in environmental engineering to master the measurement method of scaling the amount of oil production wastewater and strengthen their ability to solve practical problems.

Key words: scaling measurement; adsorption-induced scaling; comprehensive experiments.

1. Introduction

Oil production wastewater with a high content of Ca2+, Mg2+, SO42-, CO32-, and other scaling ions has a strong scaling tendency and large scaling volume, making it a high scaling production wastewater that easily produces CaSO4, CaCO3, and other scaling crystals. There are two reasons for scaling oil production wastewater. First, the dissolution equilibrium of scaling ions in sewage fluctuates with changes in the thermodynamic conditions (such as temperature, pressure, etc.), which leads to the precipitation of scaling crystals. Second, water that is produced at different oil layers with large differences in scaling ions is mixed on the ground, resulting in a large amount of scaling crystal precipitation due to ion reaction [1, 2].
The surface of clay particles is electronegative due to lattice substitution. When Ca\(^{2+}\), Mg\(^{2+}\), and other scaling ion content in sewage is high, they are adsorbed on the surface of electronegative clay particles, making the concentration of these ions on the surface of clay particles higher than their concentration in the solution, thus accelerating nucleation and deposition of scaling crystals onto the surface of clay particles [3-5].

The conventional measurement method used for scaling crystals in oil production wastewater is the bottle test method. In this approach, a certain amount of filtered oil production wastewater is kept at a certain temperature (the actual onsite water temperature) for 72 h. After all the scaling crystals are deposited, the crystals are filtered out, and the scaling amount of oil production wastewater is obtained by measuring the qualitative difference before and after the filtering. In the process of measuring the scale amount using the bottle test method, some of the scale crystals deposit onto the bottle’s walls, resulting in small measurement results and large errors, which will have a great impact on the accurate judgement of the scaling properties of oil production wastewater. However, by applying the principle of scaling crystal adsorption, aggregation, and deposition onto the surface of clay particles and adding a certain amount of clay, the deposition of scaling crystals onto the bottle’s walls can be avoided, improving the accuracy of the measurement results. Experiments have proved that this method—the adsorption–aggregation method—is feasible [6-10].

As a comprehensive experiment for students majoring in environmental engineering at petroleum and petrochemical colleges and universities, this experiment can help students to understand the scaling properties of oil and gas field production from sewage and grasp a useful scaling amount measurement method. By comparing the conventional scale measurement method (the bottle test method) with the adsorption–aggregation method, students can acquire colloid and interface chemistry knowledge, such as the scale crystal growth process, the electrical double layer structure of clay diffusion, and the structure of a micelle, and gain the ability to apply that specific knowledge to solve practical problems.

2. Design of the experiment

2.1. Purpose

(1) Master the two methods of measuring the scale of oil production wastewater: the bottle test method and the adsorption–aggregation method.

(2) Understand the basic content of scale formation in oil production wastewater and the mechanism of the accumulation and deposition of scale crystals on the surface of clay particles.

(3) Learn to explain the basic principle of the adsorption–aggregation method to determine the scale amount of oil production wastewater by applying colloid and interface chemistry knowledge, such as the scale crystal growth process, the adsorption property of the surface of clay particles, the theory of the electrical double layer in diffusion, the structure of a micelle, and charge theory.

2.2. Principle

2.2.1. Clay particles’ surface adsorption properties and the electrical double layer diffusion theory. (1) Clay particles’ surface adsorption performance.

The basic composition of clay is the montmorillonite, with the structure of Na\(_{0.7}(Al_{3.3}Mg_{0.7})Si_{8}O_{2}(OH)_{4}·nH_{2}O\), which is composed of two layers of Si-O tetrahedron sandwiched between an Al-O octahedron. In the process of lattice substitution, part of the Si in the Si-O tetrahedron can be replaced by low-price Al\(^{3+}\) and Fe\(^{3+}\), and part of Al\(^{3+}\) in the Al-O octahedron can be replaced by low-price Mg\(^{2+}\) or Ca\(^{2+}\), which results in the absence of positive charge in the crystal cells and a negative charge on the surface of the clay particles in the solution. In order to maintain the electrically neutral solution, some positive ions must be adsorbed on the surface of the clay, hence the surface of a clay particle has an adsorption property [11,12].

(2) Electrical double layer diffusion on the surface of clay particles
According to the theory of the electrical double layer diffusion, the counterions in the diffusion layer on the surface of clay suspension particles can be divided into two layers: one is the adsorption layer (also known as the Stern layer), which is close to the surface of clay particles, and the other is the diffusion layer [13,14].

(3) Zeta potential on the surface of clay particles
Zeta potential refers to the electrokinetic potential generated during the movement between the adsorbed layer and the diffusion layer on the surface of a particle in a clay suspension. Zeta potential can reflect the charge on the surface of the particles in the clay solution and indicate the aggregation property of the suspension system. The lower the Zeta potential, the more stable the suspension system. On the contrary, a higher Zeta potential indicates that the suspension system is unstable and could easily coagulate[15].

2.2.2. Micelle structure and charge theory. The scaling crystal nucleus exists in the form of a micelle (1 nm–100 nm), the structure of which consists of a micelle nucleus, an adsorption layer, and a diffusion layer. Taking the micelle structure of the CaSO₄ scaling crystal as an example, it can be expressed as 
\[(CaSO₄)m•nCa²⁺•2(n-x)Cl⁻\]²⁺•2xCl⁻. The outer layer of the micelle is negatively charged, and SO₄²⁻ can promote the growth of the CaSO₄ scale crystal by replacing the outer layer of Cl⁻.[16]

2.2.3. The aggregation–deposition mechanism of scale crystals on the surface of clay particles. Based on the theories of scaling crystal growth, electrical double layer diffusion on the surface of clay particles, and micelle structure and charge, this paper takes the deposition process of the CaSO₄ scaling crystal on the surface of clay particles as an example to explain the deposition–accumulation mechanism of scaling crystals on the surface of clay particles (hereinafter referred to as the “sedimentation–accumulation mechanism”) as follows.

At the first stage, the surface of clay particles adsorbed Ca²⁺ from the solution to form an adsorption layer, and the concentration of Ca²⁺ in the adsorption layer on the surface of clay particles was higher than that in other parts of the solution. When SO₄²⁻ is introduced, under the action of stirring and diffusion, SO₄²⁻ approaches the adsorption layer on the surface of the clay particles, leading to local CaSO₄ being in a state of supersaturation. This stage is the induction stage of CaSO₄ scaling crystal deposition on the surface of clay particles.

At the second stage, when SO₄²⁻ diffuses across the surface of clay particles and reaches a certain degree, a supersaturated solution is formed in the adsorption layer. The solution is in an unstable state, and the CaSO₄ scaling crystal nucleus begins to precipitate, covering the surface of the clay particles and forming the first layer of CaSO₄ scale crystals. This process is monolayer adsorption and an exothermic reaction. At this stage, there is scale nucleation formation during the deposition of CaSO₄ scaling crystals onto the surface of the clay particles.

At the third stage, the CaSO₄ scaling crystal nucleus is in the colloidal state on the surface of the clay particles, the CaSO₄ scaling crystal particles are adsorbed on the surface by excess Ca²⁺ ions, the structure is 
\[(CaSO₄)m•nCa²⁺•2(n-x)Cl⁻\]²⁺•2xCl⁻, the colloidal outer shell is electronegative, and SO₄²⁻ will replace Cl⁻ in the supersaturated solution, combine with Ca²⁺, and promote scaling crystal growth, so that the scaling crystals are angled along the crystal nucleus monolayer growth, growing up gradually. This is the growth stage of the CaSO₄ scaling crystal in the deposition process on the surface of the clay particles [3, 17-21].

2.3. Experimental materials
Analytically pure anhydrous calcium chloride and anhydrous sodium sulfate were obtained from Chongqing Chemical Engineering Group Co., Ltd., China. Clay was sourced from the domestic market.

The main instruments are a vacuum pump (SHB-III), an electronic analytical balance (CP114), an electric thermostatic drying oven (101), and so on.
3. Theoretical calculation and measurement

3.1. Calculation of the theoretical scaling amount
The theoretical scaling amount refers to the scaling amount of sewage calculated using the ion reaction equation according to the ion concentration of the scaling substance in the sewage. Taking CaSO₄ as an example, the theoretical amount of CaSO₄ scaling formation refers to the chemical reaction between SO₄²⁻ and Ca²⁺ in accordance with Formula 1 to generate CaSO₄ scaling crystal precipitation in an ideal state. The amount of CaSO₄ scaling crystal production is calculated using Equations 2 and 3.

\[
Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4 \downarrow
\]  

When \( n_{Ca^{2+}} \geq n_{SO_4^{2-}} \) in a mixture with water, the theoretical scale amount of CaSO₄ is

\[
m_T = m_{SO_4^{2-}} \times \frac{136}{96}
\]  

When \( n_{Ca^{2+}} \leq n_{SO_4^{2-}} \) in a mixture with water, the theoretical scale amount of CaSO₄ is

\[
m_T = m_{Ca^{2+}} \times \frac{136}{40}
\]

where \( m_T \) is the theoretical scaling amount in mg/L. The atomic masses of S, O, and Ca are 32, 16, and 40, respectively.

3.2. Determining the scaling amount of oil production wastewater using the conventional method (the bottle test method)
The so-called conventional method refers to the sewage scaling amount measurement method that is often used in the laboratory; that is, the weight method is used to measure the scaling crystal precipitation amount in undeposited sewage water in a conical flask after it is placed at a certain temperature for a certain time. This is referred to as the bottle test method. The specific experimental method is as follows[2]:

1. The oil production sewage is filtered through the filter membrane (0.45 μm) to remove suspended particles.
2. Put 200 mL of filtered water into a conical flask, seal it with plastic wrap, and place it at a certain temperature (the actual onsite water temperature) for 72 h.
3. According to the method for determining suspended matter in the Recommended Indexes for Water Quality of Water Injected into Clastic Rock Reservoir (SY/T5329-1994), the scaled water is filtered, dried, and weighed with a filter membrane (0.45 μm) to determine the amount of scaling deposition, that is, the conventional method for determining the amount of scaling.

The equation for calculating the scaling amount measured using the conventional method is shown in Equation 4:

\[
m = m_2 - m_1
\]

where \( m_1 \) is the quality of the filtration membrane before filtration, g; \( m_2 \) is the total weight of the filtration membrane and the scale after filtration, g; and \( m \) is the scaling amount using the conventional method.

3.3. Determining the scaling amount of oil production wastewater using the adsorption–aggregation method
The adsorption–aggregation method can be used to determine the scaling amount of oil production wastewater by using clay to adsorb the scaling crystals, which will accumulate and deposit on its surface,
so as to avoid the error caused by the deposition of scaling crystals on the test bottle’s walls. The specific experimental method is as follows:

① Clay particles of 80 mg–100 mg and 30 μm–50 μm were placed in 1000 mL of sewage and stirred slowly for 72 h at a certain temperature (the actual onsite water temperature). After filtration, drying, and weighing, the total scaling amount could be obtained.

② After a certain amount of clay adsorbed with scaling crystals is acidified to pH 1–2 and filtered, dried, and weighed, the scaling formation amount of CaSO₄ can be obtained.

The equation for the adsorption–aggregation method is given by Equation 5 below:

\[ M = M₂ - M₁ - M₀ \]  (5)

where \( M₀ \) is the mass of added clay, g; \( M₁ \) is the quality of the filtration membrane before filtration, g; \( M₂ \) refers to the total mass of the filtration membrane, the scaling crystals, and clay after filtration, g; and \( M \) is the scaling amount using the adsorption–aggregation method, g.

3.4. A comparison of the scaling measurement methods

Ca²⁺ solution and SO₄²⁻ solution were prepared to mix different proportions of simulated water, which would then be fouled. By calculating the theoretical scaling amount (Section 3.1), the conventional scaling amount (Section 3.2), and the adsorption–aggregation method scaling amount, the degree of similarity between the measured and theoretical scaling amount as obtained using different methods was compared to judge the accuracy of the methods.

The simulated water was prepared according to Table 1, and nine groups of experiments were designed to calculate the theoretical scaling amount. The conventional method (the bottle test method) and the adsorption–aggregation method were used to measure the scaling amount of the simulated water. The calculations and experimental results are summarized in Table 2.

Table 1. List of preparation experiments for the simulated water

| Serial number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---------------|---|---|---|---|---|---|---|---|---|
| Simulated water | 1  | 0.1 | 0.2 | 0.3 | 0.5 | 1  | 2  | 3  | 4  |
| Ca²⁺/mmol/L    | 0.1 | 0.2 | 0.3 | 0.5 | 1 | 2 | 3 | 4 | 5 |
| SO₄²⁻/mmol/L   | 0.1 | 0.2 | 0.3 | 0.5 | 1 | 2 | 3 | 4 | 5 |

Table 2. Theoretical calculation and measurement results

|                | Theoretical scaling amount/mg/L | Bottle test method/mg/L | Adsorption–aggregation method/mg/L |
|----------------|---------------------------------|-------------------------|-----------------------------------|
|                | 13.6                            | 27.2                    | 54.4                              |
|                | 68                              | 136                     | 272                               |
|                | 408                             | 544                     | 680                               |
|                | 7                               | 16                      | 31                                |
|                | 45                              | 109                     | 224                               |
|                | 271                             | 375                     | 498                               |

As shown in Table 2, because scaling crystals were deposited onto the surface of the clay particles, a reduced amount of scaling crystals was deposited onto the container’s walls. The results of the adsorption–aggregation method were greater than those measured using the conventional scaling method, and the former’s results were also closer to the theoretical scaling amounts. Therefore, the adsorption–aggregation method can be used to determine the scaling amount with high accuracy, that is, closer to actual scaling.

During comprehensive experimental teaching, students can be placed into groups of five. Before the experiment, the students will work together to design the experiment, which mainly involves preparing the experimental reagents and instruments, outlining the experimental steps, and cooperating and dividing labor within the group. The instructor can carry out related experiments after the review. When assessing the completed experiment, the students’ experimental process and results are to be observed according to each group’s experimental design report. However, students should receive individual feedback.
4. Questions and exercises

(1) In this experiment, the constant temperature time is 72 h. How is the time determined and is it accurate? Please design the experiment to determine the constant temperature time for the sewage scaling measurement process.

(2) Is it possible to simulate the dynamic scaling process using a constant temperature shaking table in this experiment? Please design an experiment to compare the results of the static experiment (in the oven) and the dynamic experiment (in the shaker) and explain the advantages of the dynamic experiment.

(3) What is the effect of the addition of clay on the measurement results in this experiment? Design experiments to compare the experimental results produced with different clay dosages, and explain the reasons for the effect of various clay dosages and the principles for determination.

(4) In the process of determining the scaling amount of sewage using the adsorption–aggregation method in this experiment, how is the CaCO3 scaling amount calculated? Please refer to the literature for scale analysis methods.

5. Conclusion

Efficient scaling measurement of oil production sewage is an important index for evaluating its scaling performance of oil production sewage. Innovation and mastery of the scaling measurement method is an essential skill for the personnel in the field of petroleum and petrochemical environmental engineering. Based on the knowledge of colloid and interface chemistry, this work analyzes the basic principle of the adsorption–aggregation method for determining the scaling amount and outlines its advantages over the bottle test method. We believe that this study will allow students to master the scaling measurement method and apply this knowledge to solve practical problems. The development of this comprehensive experiment will help improve the spirit of teamwork, motivate innovation, and facilitate the application of theoretical concepts.

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