A Model for the Deposition of Scale Crystals on the Surface of Clay Particles

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Abstract. Deposition and aggregation of scale on microbial surface leads to poor stabilization of the treatment of oilfield high-scale oily wastewater. To study the deposition characteristics of scale on the surface of microbial particles, we perform the deposition and aggregation of calcium sulfate on the surface of clay particles as simulators of microbes and establish the deposition-aggregation process model. According to the theory of crystal growth, the diffuse electric double layer theory for clay, and the charged colloid theory, the scale deposition model can be divided into induction period, formative period of scale crystal nucleation, and crystal growth period. When calcium sulfate crystals deposit and aggregate on the surface of clay particles, the zeta potential and the average particle size on the surface of the clay particles increase continuously over time and tend to increase and decrease in cycles. The scale crystals are wrapped divergently around the surface of the clay particles in a needle-like form, such that the clay suspension is in a state of high aggregation. Logarithmic value of the conductivity in the formation of scale crystal has a good linear relationship with time, which conforms to the first-order rate equation. Conductivity curves can better reflect the deposition course of scale crystal on the surface of clay particles, which is divided into the induction period (6 min), transition period (1.5 min), formative period of scale crystal nucleation (10.75 min), rapid growth period of scale crystal (8.5 min), slow growth period of scale crystal (14.75 min), and stationary phase (4.75 min), and with the formation of the scale crystal, the deposition rate constant decreases gradually from 0.00945 min⁻¹ to 0.0001 min⁻¹. The results uncovered that Deposition and aggregation rules of scale on the surface of clay particles and the basis for further studying on microbial surface.

1. Introduction
The exploitation of crude oil into the middle and late stages has led to increased water content, and the oilfield produced water is re-injected into reservoirs after treatment. This is the main water source of oilfield water flooding. Treatment methods for oily wastewater in an oilfield are classified as physical,
chemical, and biological methods. Microorganism methods are widely used for oily wastewater treatment because of its good stability and high efficiency. However, in microbiological treatment is not effective for the treatment of high-scale oily wastewater, as the deposition and aggregation of scale on the surface of the microbial particles inhibits the exchange of microbes with external substances and energy. This would destabilize, or even paralyze, the treatment process, in addition to affecting the normal production of oil fields. Hence, a detailed study on the deposition process and properties of the scale on the surface of microorganisms is very significant for ensuring the stability of oilfield high-scale oily wastewater treatment by microbiological methods.

Recently, studies on microbial treatment of oilfield produced wastewater discussed mainly focused on microbial domestication, cultivation, etc. Studies on the scaling of oil field high-scale produced wastewater largely addressed the amount of scale formation, scaling control, and so on. Research on microbial fouling and its effects were centered on the deposition of microbial particles on the surface of pipeline walls. However, there is hardly any study on the deposition of scale on the surface of microorganisms. In order to study the deposition characteristics of scale on the surface of microbial particles, the paper perform the deposition and aggregation of calcium sulfate on the surface of clay particles as simulators of microbes and establish the deposition-aggregation process model.

According to the crystal growth theory, crystal growth in solution generally involves three stages. Solute is transferred from a metastable state to a supersaturated state in solution in the first stage, which is the induction period of nucleation and the incubation stage of crystal formation. In the second stage, the solute reaches supersaturation state and spontaneous nucleation stage. In the third stage, the crystal begins to grow with crystal nucleus as the core.

There is a double electric layer around each colloidal particle in clay slurry, and the liquid around the colloidal particles is divided into two parts because of this structure: the oppositely charged ions will be tightly bound in the stern layer and loosely bound in the diffusion layer. In the electric field, electrokinetic phenomena exist between the solid and liquid, and the potential difference across the interface between the solid surface and the bulk of the liquid is called the zeta potential, which represents the effective charge of the particles dispersed in water and can characterize the stability of the dispersion system. The smaller dispersed particles in the solution, the greater will be the positive or negative charge taken up by the particles; this is referred to as high Zeta potential. Thus, under high zeta potential, the particles will repel each other due to the electrostatic interactions, so as to achieve the stability of the whole system. On the other hand, if the particles take less positive or less negative charges, which indicates that Zeta potential is very low, then the positive and negative charges will attract each other leading to condensation, so that the entire system will be in destabilized.

The crystal nucleus exists in the state of colloid (1–100 nm), the micelle structure of which consists of a colloidal nucleus, an adsorption layer, and a diffusion layer. Micelle structure of calcium sulfate crystal can be expressed as [(CaSO₄)ₙ•nCa²⁺•2(n-x)Cl⁻]²⁺•2xCl⁻, the outer layer of which is negatively charged. The replacement of sulfate ions with the outer chloride ion can promote crystal growth.

This paper reports the deposition and aggregation of calcium sulfate on the surface of clay particles as simulators of microbes. In addition, we discuss a deposition-aggregation model for scale crystals on the surface of clay particles on the basis of the theory of crystal growth, theory of charged clay and diffuse electric double layer, and the theory of colloid structure and charged colloids. Meanwhile, in order to fully explain the deposition-aggregation model of the scale crystal on the clay particle surface, we observed morphology changes of the calcium sulfate scale during its deposition and aggregation on the surface of clay particles and changes in particle diameter using an optical microscope and a laser particle size analyzer. Zeta potential measuring instrument determinates the electrical properties and trends in changing aggregation properties of the clay particle surface; changes in conductivity are used to reflect the variation of scale ions and the formation of scale crystal on the surface of clay particles in solution.
2. Experiments

2.1. Reagents and Instruments
Primary reagents: Bentonite (screened by 200-mesh sieve, dried for 1 h at 105℃ and placed in a dryer for standby, Shanghai Four Hervey Chemical Co.), anhydrous calcium chloride (≧ 96%, Tianjin Shentai Chemical Reagent Co., Ltd.), anhydrous sodium sulfate (≧ 99%, Guangdong Project Technology Research Exploitation Center for chemical reagent), etc.

Primary instruments: Laser particle size analyzer (LS13 320, Angga instrument (Shanghai) Co., Ltd.), optical microscope (Nikon Ti-S), Zeta potential analyzer (Zetasizer Nan-ZS90, UK Malvern Instruments Ltd), conductivity meter (Mettler), magnetic heating stirrer (CJJ79-1, Beijing Jingcheng Huatai Instrument Co. Ltd.), and electric-heated thermostatic water bath (DK-98-1, Shanghai optical instrument factory), etc.

2.2. Experimental method

2.2.1. Preparation of scaling ion solution. The calcium ion solution was prepared using 0.4 mol/L calcium chloride and 0.01 mol/L sodium chloride. The sulfate solution was prepared using 0.2 mol/L sodium sulfate and 0.01 mol/L sodium chloride. Both solutions were preheated at a constant temperature of 35℃ for standby.

2.2.2. Clay suspension preparation. Bentonite (5 g) was added to sodium chloride solution (0.01 mol/L; 100 mL) and stirred for 4 h, and poured into the column in the static 24h. The column soil sample average was divided into 5 parts, where the middle part was the experimental clay suspension.

2.2.3. Scale deposition-aggregation analysis. 25 mL of the bentonite clay suspension was placed in a beaker and stirred at a constant speed of 150 r/min and constant temperature of 35 ℃. Then, 25 mL calcium ion solution was added after 30 min and 50 mL sulfate solution was added after 60 min for the subsequent experiments.

The Nikon optical microscope is used to observe morphological changes of clay particles and scale crystals in the deposition process of scale crystals. Samples were observed at an amplification of 20x at 0 min (clay suspension), 30 min (addition of calcium solution), and 60 min (addition of sulfate solution). Further, clay scale samples were observed every 10 min.

Zeta potential analyzer, pH meter and laser particle size analyzer are employed to determine zeta potential, pH level and average particle size, respectively, at 0 min (clay suspension), 30 min (addition of calcium solution), 60 min (addition of sulfate solution), and every 10 min after that.

The conductivity was tested by conductivity meter at every 0.05 min, and then dataswere processed to make relationship cures between conductivity and time.

3. Model for Deposition process

3.1. Scale deposition-aggregation model
According to the crystal growth theory and the diffusion theory of clay minerals and charged colloid theory, this paper establishes the deposition and aggregation model (deposition-aggregation model) of scale crystal on the surface of clay particles, taking the deposition of scale crystal of calcium sulfate on the surface of clay particles as an example. The deposition-aggregation model comprises the following three stages.

In the first stage, a Stern layer is formed due to surface adsorption of Ca^{2+} on the clay particles, such that Ca^{2+} concentration on the Stern layer on the surface of clay particles is higher than that in other parts of the solution. When sulfate ion is added, it approaches the Stern layer under the action of stirring and diffusion so that calcium sulfate is formed locally in the supersaturation state. This stage is the
induction period of the deposition of calcium sulfate scale crystals on the surface of clay particles, as shown in Fig. 1.

In the second stage, i.e. the formation stage of the scale nuclei, when sulfate anions diffuse to the surface of clay particles to a certain extent, they form a supersaturated solution in the stern layer, thereby destabilizing it. Scale nuclei begin to precipitate, covering the surface of the clay particles and forming the first layer of calcium sulfate scale crystal, as shown in Fig. 2. This process is called monolayer adsorption.

In the third stage, i.e. the growth stage of the scale crystal, the scale crystal nucleus adopts a colloidal form on the surface of clay particles. The surface of the CaSO₄ scale crystal particles can absorb excess Ca²⁺ counterions; thus, the structure of the colloid is \([\text{[(CaSO}_4\text{)]}_n\cdot n\text{Ca}^{2+}\cdot 2(n-x)\text{Cl}^-\cdot 2x\text{Cl}^-}\), its outer layer being electronegative. The sulfate ion in the saturated solution will combine with calcium ion to replace the chlorine ion and promote scale crystal growth along the crystalline face in the monolayer, as shown in Fig. 3.
3.2. **Analysis of scale deposition and aggregation process**

3.2.1. **Optical microscope observation.** As can be seen from Fig. 4, clay suspension is in dispersed state before the addition of calcium ions. Upon addition of calcium ions after 30 min, the clay particles in solution start to aggregate, when the calcium ions diffuse to the surface of the Stern layer and forms calcium sulfate layer of high concentration. The aggregation continues upon addition of calcium ions after 60 min, when the sulfate ions move into the diffusion layer on the clay particle surface. Scale crystals form on the clay particle surface at 70 min and they grow around the clay particles in one-dimensional and two-dimensional manner in the form of whiskers. These whiskers continue to grow at 80 min and aggregation occurs between the clay particles; some scale crystals detach from the clay particle surface upon stirring at 90 min. Thus, at this stage, scale crystals coexist with clay particles in solution, growing and aggregating. Aggregation occurs due to mutual adsorption between the scale crystals and the clay particles from 100 min to 150 min, so that the scale crystals are wrapped divergently around the clay particles in a needlelike form.

![Fig. 4 Micrograph of deposition process of CaSO₄ scale crystals on the clay particle surface](image)

3.2.2. **Changes of Zeta potential, pH value and average particle size.** Figure 5 shows that zeta potential of clay suspension changes from −32.9 mV to −10.9 mV after the addition of the calcium ion solution, destabilizing the clay suspension. The clay particles in solution change from dispersed state to aggregated state and the average particle size increases from 8.66 µm to 25.12 µm; the zeta potential changes to −5.2 mV after the addition of the sulfate ion solution at 60 min and the clay solution adopts a highly aggregated state. The calcium ion is adsorbed on the surface of the clay particles to form a Stern layer. Sulfate ions diffuse to the Stern layer, resulting in further aggregation. From 70 min to 150 min, calcium ions continuously move to the clay particle surface, resulting in deposition of the calcium sulfate crystal, thereby increasing the Zeta potential and average particle size on the clay particle surface. The solution
is in a highly aggregated state, and mutual aggregation occurs between the scale crystals and the clay particles. Under the effect of stirring, the scale crystals deposited on the clay particle surface will be removed by fluid shear stress and impaction, and the removed parts will act as new nuclei and continue to grow. There are nucleation effect of shear stress and contact nucleation effect and the change law of increase and decrease in circles of Zeta potential and the average particle size on clay particle surface in the solution. During deposition and accumulation, the zeta potential is gradually increased from $-32.9$ mV to 3 mV, and the average particle size is increased from 8.66 µm to 37.66 µm. The relationship between pH value and time in the solution during the deposition and accumulation of calcium sulfate scale crystals on the clay particle surface (Figure 6) shows that the pH gradually decreases from 8 to the neutral pH value of 7.

![Fig. 5 Disposition process of CaSO4 scale crystals on the surface of clay particles](image1)

The relation between Zeta potential, average particle size and time

![Fig. 6 Disposition process of CaSO4 scale crystals on the surface of clay particles](image2)

The relation between pH value and time

3.2.3. Conductivity changes in the deposition process. The conductivity can represent ion content in the solution and the conductivity change in the deposition process with time can reflect changes in ion content during the formation of calcium sulfate scale in the solution. Figure 4 shows that conductivity decreased rapidly from 0– to 1.5 min due to dilution upon initial addition of sulfate ions, remains unchanged from 1.75 min to 8.5 min, decreased rapidly from 8.75 min to 21.25 min, and decreased gradually from 21.5 min to 60 min. According to the deposition-aggregation model of the scale crystal,
1.5–8.5 min is the induction stage and the induction period is 6 min, when no scale crystal is formed; 8.75–21.25 min is the formation stage of the scale nuclei and the period is 12.5 min when electrical conductivity (a) decreases slowly (8.75–10.25 min) and (b) decreases rapidly (10.5–21.25 min). The slow declining stage is the transition period of scale formation of the crystal nucleus, when the nuclei are in equilibrium between precipitation and dissolution; the fast declining stage is stable precipitation stage of scale crystal nuclei on the clay particle surface. The growth period of scale crystals is from 21.5 min to 60 min and the time required is 38.5 min, which is divided three phases: (c) rapid phase (21.5—30 min), (d) slow phase (30.25—45 min) and (e) stationary phase (45.25—60 min).

According to the deposition-aggregation model for the scale crystal, the nucleation stage and the growth stage of scale nuclei are monolayer reactions controlled by surface reaction, which should be described by first-order rate equation. The relationship between solution concentration and time can be expressed by equation (1). The linear relation between conductivity and concentration of the solution can be expressed by equation (2). The logarithmic value of conductivity in the formation process of the crystal nuclei and the growth process of the crystal has a linear relationship with time, as shown by equation (3), and the fitting results are shown in Figure 7.

\[ c = c_0 e^{-K_1 t} \]  
\[ c = B\kappa + D \]  
\[ \ln \kappa = \ln c_0 - K_1 t \]

Here, \( c_0 \) (mol/L) is the initial concentration of ions in solution; \( c \) (mol/L) is the ion concentration in the solution at time \( t \); \( \kappa \) is solution conductivity (μs·cm\(^{-1}\)); \( t \) is reaction time (min); \( K_1 \) is rate constant of scale crystal deposition on clay particles.

Figure 8 shows that the log value of conductivity and time have a good linear relationship at the stages of scale nucleation and growth of the scale crystal, which is consistent with the first-order rate equation and the deposition model. The growth rate constant of scale crystals is determined using the degree of supersaturation. Scale ion concentration and the growth rate constant decreases gradually with continuous precipitation of scale crystal in solution. Rate constants of the transition period (a) and the rapid phase (b) during scale nucleation are 0.00221 min\(^{-1}\) and 0.00945 min\(^{-1}\), respectively, while the rate constants of the rapid phase (c), slow phase (d), and stationary phase (e) during crystal growth are 0.00239 min\(^{-1}\), 0.0007 min\(^{-1}\), and 0.0001 min\(^{-1}\), respectively.

![Fig. 7 The relation between conductivity in deposition process and time](image-url)
4. Conclusion

(1) The present investigation is aimed to uncover the rule of deposition and aggregation of scale crystals on the surface of clay particles for further study of the deposition characteristics of scale on the surface of microbial particles.

(2) In this work, we firstly established the model for the deposition-aggregation of scale crystals on the surface of clay particles, which was divided into three stages: the induction phase, the formation stage of crystal nuclei, and the crystal growth stage.

(3) From the present study, during deposition and aggregation of scale crystals on the surface of clay particles, the zeta potential and the average particle size of the clay suspension increase continuously from \(-32.9\) mV to \(-3.64\) mV, from 8.66 µm to 37.66 µm, respectively, and increase and decrease in cycles.

(4) It is seen that the pH value of the clay suspension is gradually decreased from 7.97 to 7.19 during deposition and aggregation of scale crystals on the surface of clay particles.

(5) From optical microscope observation, the calcium sulfate scale crystals are wrapped divergently around the clay particles in the needlelike form and the scale crystals and clay particles are gathered together due to mutual adsorption.

(6) In the present investigation, the curve of conductivity change is divided into the induction phase, the formation stage of crystal nuclei, and the crystal growth stage.

(7) The logarithmic value of conductivity has a good linear relationship with time in the scale nucleation stage and the growth stage of the scale crystal.

(8) The growth rate constant of the scale crystals decreases gradually with the continuous precipitation in solution.

(9) These results above are basis for revealing the deposition characteristics of scale on the surface of microbial particles and benefit for the stability operation of oilfield high-scale oily wastewater treatment by microbiological methods.

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Conflict of Interest
There are no conflicts of interest to declare.

Ethical Approval
This article does not contain any studies with humans or animals subjects performed by any of the authors.

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