

A REAL TIME MONITORING MODEL OF THE CALCIUM CARBONATE FOULING INDUCTION PERIOD BASED ON THE CONDUCTANCE TITRATION

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ABSTRACT

A new method has been developed to monitor the calcium carbonate fouling induction period (CCFIP) in real time. Based on the conductance titration, this paper investigated the forming process of CCFIP by a static-dynamic combined simulation experiment unit. With the help of titration analysis (that is titrimetry), an accurate definition of CCFIP and the corresponding real time monitoring model were built up. The investigation results show that the proposed model applies not only to measure the CCFIP in real time, but also applies to an investigation of the influence of various factors on the CCFIP.

INTRODUCTION

As the crystallization fouling accounts for over 25% of the fouling problems encountered (Mwaba et al., 2006), a thorough investigation of the crystallization fouling induction period (CFIP) is important both in pursuing the new learning and developing anti-fouling techniques,

So far, in all the works related to fouling hold the identical view that the "crystallization fouling" crystallize on heat exchange surface but not deposit on it, such as Taborek et al. (1972), Epstein, (1979), Yang et al. (2004), Mwaba et al. (2006) and so on.

As to the measurement of CFIP, especially when you're going to measure the fouling thermal resistance, it is difficult to distinguish the CFIP from particulate fouling induction period (PFIP) in determining fouling thermal resistance at the moment. As a matter of fact, according to Epstein's fouling classification (Epstein, 1979), fouling is usually classified into six categories depending on the key physical or chemical process essential to the particular fouling mechanism. The categories are crystallization, particulate, corrosion, biological and solidification in which the crystallization and particulate coexist in conductance titration. Therefore, in the conductance titration, it would be more precise if changed the CFIP into the CCFIP.

Several researchers engaged in studying new methods and experiment techniques for determining the CCFIP. Yang et al. (1994) established a model of the CCFIP without consideration of the time forming pseudo-steady state crystal embryo, Aoun et al. (1999) showed that many methods for determining the nucleation and growth rate from a batch of precipitation experiments were inaccurate.

Considering those, this article aims to study the CCFIP forming process by means of conductance titration, to built

up an accurate definition and corresponding measurement for CCFIP and to develop a static-dynamic combined simulation experiment unit, the latter can also evaluate the performance of the techniques for the prevention and mitigation of fouling.

EXPERIMENT

•Reagent (CAO et al. , 2007; Drela et al. , 1998)

The reagents used in the experiment included the titrate --analytically pure CaCl_2 solution, the titrant -- analytically pure Na_2CO_3 solution and desalted water.

•Static measurement unit

The static measurement unit was made up of a thermostatic cell with conductivity detector and magnetic stirrer shown in Fig.1. The experiment began to put 200 ml titrate in the thermostatic cell with a volume of 300ml and its temperature remained at a level of $25 \pm 0.1^\circ\text{C}$. The amount of titrant adjusted by the peristaltic pump revolution speed. The static measurement results expressed by curve shown in Fig. 3 were derived from the following conditions: the titration velocity $v = 8.36 \times 10^{-6} \text{ mol}/(\text{L} \cdot \text{S})$, the concentration

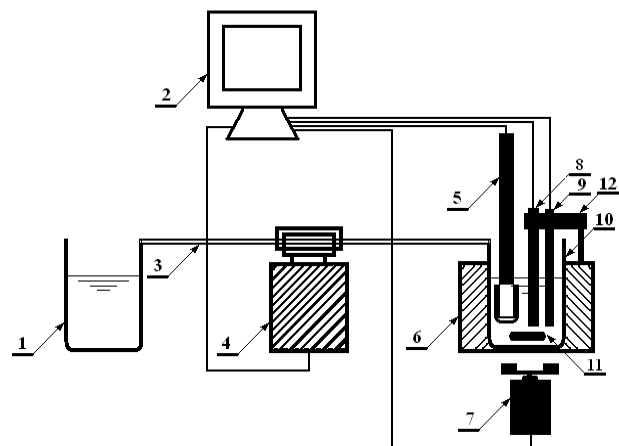


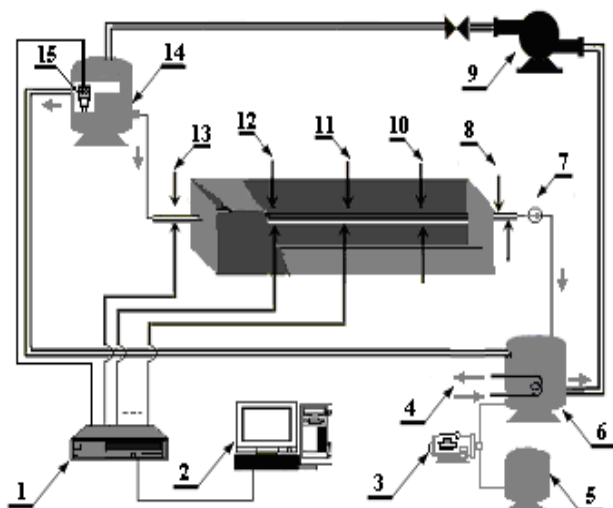
Fig. 1 Static measurement unit

1. titrate solution container; 2. computer; 3. fitting pipe; 4. peristaltic pump; 5. conductivity detector; 6. cozy; 7. stirring motor; 8. heating rod; 9. RTD; 10. thermostatic cell; 11. stirring bar; 12. interval regulator

of titrate is 0.0126mol/L of CaCl_2 solution, the concentration of titrant is 0.115mol /L of Na_2CO_3 solution.

Dynamic simulation measurement unit (XU et al., 2005)

The so-called static-dynamic combined simulation measurement unit, its dynamic part actually is a simulated heat exchanger composed of a circulation loop in a hot water tank. In the tank the static water remain hot by an electric heater with a temperature regulator (as shown in Fig.2).



In accordance with the definition of fouling induction

Fig.2 Schematic of static-dynamic combined simulation experiment unit.

1. data acquisition ; 2. computer; 3. dosing pump; 4. cooling water; 5. titrant tank; 6. low flush tank; 7. flow-meter; 8. exit temperature; 9. circulating pump; 10,12. wall temperature; 11. temperature of water bath; 13. inlet temperature; 14.upper tank; 15. conductivity sensor

period, to measure the CCFIP with the aid of titrimetry, one has to measure the fouling thermal resistance by virtue of the simulated heat exchanger. To begin with, only the titrate flowed through the test tube for exchanging heat with hot water, at this phase, no CaCO_3 appeared on the heat exchange surface, so the fouling thermal resistance would be zero. Then, the titration follows the above phase, the titrant was titrated into the titrate, for short, hereinafter the mixed fluid blended the titrate with titrant is called test medium. As the titration was going, the calcium carbonate CaCO_3 accumulated on the heat exchange surface gradually, so long as the value of fouling thermal resistance achieved more than the threshold of dynamic simulation measuring

unit, the terminal of induction period was determined. The details were shown in the following.

The temperature of wall and test medium at inlet and outlet of test tube are measured by RTD or TC. An anti-fouling flow meter is used for measuring the flow rate of test medium. When the experiment unit is running, the pump transmit the test medium from the lower tank to the upper tank, then it is conveyed from the upper tank to test tube by the static head and an overflow pipe keeps constant of the static water head in it. All of the measured data acquire by a data acquisition and control system (DAC) which are connected with computer by I/O, with the result that all the above mentioned process perform automatically by a computer.

MONITORING MODEL

It's well known that the calcium carbonate fouling processes by several phases: supersaturation (nucleation process), crystal growth and deposition. In each process, the variation of test medium conductivity in the test cell is shown in Fig. 3.

Before the titration experiment, there are Ca^{2+} , Cl^- and few H^+ , OH^- in the aqueous solution. In first experiment process, because there are less CO_3^{2-} in the test medium, the Ca^{2+} and CO_3^{2-} concentration product is less than the K_{sp} of the CaCO_3 in 25°C , no CaCO_3 engender nearly. But the total amount of ions and the concentration of CO_3^{2-} in the solution are increasing to keep pace with the titration, the former result in accretion of the conductivity. As the concentration product of Ca^{2+} and CO_3^{2-} began to exceed K_{sp} , the test medium is in supersaturation which is the necessary but not sufficient conditions for producing CaCO_3 . Along with the increasing titrant quantity, the supersaturation increased gradually, and the crystal nucleus began to appear and proceeded to grow in number. When the rate of crystallizing of CaCO_3 increased to some values, the conductivity dropped at once from the maximum and the conductivity-time curve declined obviously. While the increasing rate of conductivity caused by titration exceeded the decreasing rate of conductivity by crystallizing, the conductivity-time curves got the minimum point, after that, along with the increasing of titrant, the conductivity increased again. As the quantity of CaCO_3 crystal increased obviously, the solution in thermostatic cell became more turbid, the crystal began to deposit on the test tube surface and to form gradually crystallization fouling as well as fouling thermal resistance which could be detected by the dynamic detector.

In briefly, the conductivity-time curve could be used for illustrating precisely every phase of forming process of

calcium carbonate fouling: pre-saturation, saturation, supersaturation (nucleation), crystal growth and deposition. If the concentration of titrant and the titration rate are known, the real-time CaCO₃ concentration of the whole titration process can be figured out by means of conductivity measurement.

As the above mentioned, the test medium is the in pre-saturation and its interval is θ_0 ; K_1 is the conductivity of test medium at the nucleation process, corresponding interval is $\theta_1 = \tau_1 - \tau_0$. So, the interval θ_1 was considered as the nucleation induction period; K_2 is the test medium conductivity for crystals growth process, its interval is $\theta_2 = \tau_2 - \tau_1$, then the interval θ_2 was treated like crystal growth process. ; K_3 is the test medium conductivity during deposition process, the interval of the last phase is $\theta_3 = \tau_3 - \tau_2$, the interval θ_3 was referred to as deposition induction period.

At the moment τ_3 , the fouling thermal resistance increased to a threshold that could be detected by the dynamic simulation unit. In view of the facts, we can define the CCFIP as the sum of intervals of each process mentioned above:

$$\theta_{cf} = \theta_0 + \theta_1 + \theta_2 + \theta_3 \quad (1)$$

The corresponding test medium conductivity in each process can be determined as follows. For a strong electrolyte dilute solution, the solution conductivity was caused by all ion motion brought by the electric field of the electrode (FANG, 2000). From the Faraday's Law of Electricity, the solution conductivity in titration process can be expressed as:

$$K = F \sum_{i=1}^4 |z_i| c_i u_i \quad (2)$$

Where F is Faraday's constant, z_i is the charge number for i ion, c_i is the concentration of i ion, and u_i is the mobility of i ion, and further, u_i can be expressed as follows:

$$u_i = \frac{z_i e}{6\pi\eta r_i} \quad (3)$$

Where e is the charge of electron, r_i is radius of i ion, η is the dynamic viscosity of test medium. Usually, η depends on temperature only. So for given kinds of ions, the test medium conductivity is related linearly to a kind of ion concentration as follows:

$$k_i = U_i c_i \quad (4)$$

Comparing Eq.(4) with Eq.(2), we let

$$U_i = z_i \frac{z_i e}{6\pi\eta r_i} F \quad (5)$$

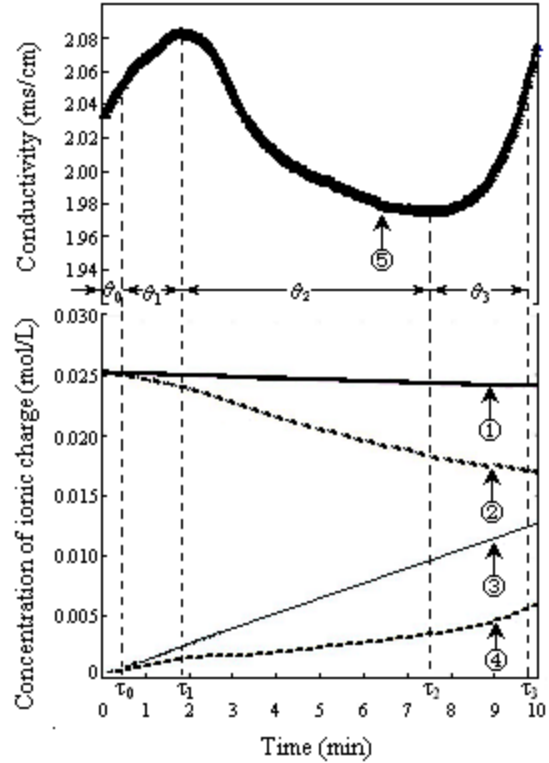


Fig. 3 Curves of conductivity/ concentration - titration time

- ① Concentration of chloride ion; ② Concentration of calcium ion; ③ Concentration of sodium ion; ④ Concentration of CO₃²⁻ ion; ⑤ test medium conductivity

The experimental curve in Fig. 3 was derived from the conditions as the mentioned above. The self-made static-dynamic combined simulation experiment unit was used in the above experiments, the accuracy of conductivity measurement was $\pm 0.1 \mu\text{s/cm}$, the electrode constant of the measuring conductivity was 0.9983.

Now, let us suppose the volume of titrate to be V, the titration rate to be v , the total conductivity of test medium to be K_t , the corresponding calcium carbonate

(CaCO₃) concentration C_t can be figured. By the way, C_t is also the concentration of ions Ca²⁺ or CO₃²⁻ had been consumed due to the crystallization until the moment τ_i . Then,

$$K_t = C_{Cl^-} U_{Cl^-} + (C_{Ca^{2+}} - C_t) U_{Ca^{2+}} + \left(\frac{vt}{V+vt} - C_t\right) U_{CO_3^{2-}} + \frac{vt}{V+vt} U_{Na^+} \quad (6)$$

$$C_t = \int_{\tau_0}^{\tau_i} \frac{\partial C_{Ca^{2+}}}{\partial \tau} d\tau = \int_{\tau_0}^{\tau_i} \frac{\partial C_{CO_3^{2-}}}{\partial \tau} d\tau \quad (7)$$

Here, U_i can be determined by Eq. (5). i is from 0 to 3.

Now there is such a relationship, we can determine the CCFIP by means of measuring the test medium conductivity K_t .

The calculating results are shown beneath the Fig.3. For comparing it with the variation in conductivity shown in top of Fig.3, we replaced the ordinate concentration with the charge number so that the variation of each ion concentration can compared with the variation in conductivity measured at the same measure. The comparison at every corresponding time show that the calculating results agreed with the measuring data reasonably.

It must be pointed out that the above static-dynamic combined simulation unit and corresponding monitoring model can also be used for studying the influence of various kinds of factors on the induction period in much the same way, more details had been published in CAO et al. 2007.

CONCLUSIONS

(1) Based on the conductance titration, the present paper proposed an accurate definition and corresponding monitoring model of the CCFIP, and measured the solution conductivity real time by a static-dynamic combined simulation experiment unit;

(2) The monitoring model of the CCFIP applies also to an investigation into the influence of various factors on the CCFIP.

(3) The theory model based on the mechanism of nucleation, crystal growth and deposition rates of the crystallization fouling remain to be solved.

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NOMENCLATURE

R_f	thermal resistance K/W
K	Conductivity $\mu\text{s}/\text{cm}$
τ_{1-3}	The titration time s
θ_{0-3}	Titration interval s
θ_{cf}	The CCFIP min
F	Faraday's constant $\text{C}\cdot\text{mol}^{-1}$
z_i	The number of charge for i ion
c_i	The concentration of i ion mol/L
u_i	The mobility of i ion m/V
e	The charge of electron C
r_i	Radius of i ion m
η	The dynamic viscosity of solution Pa.s
C_t	The concentration of ions Ca ²⁺ or CO ₃ ²⁻ mol/L