

The study of releasing dynamics of composite chlorine dioxide wells blockage relieving agent

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Abstract: Composite chlorine dioxide blockage relieving agent is a kind of new blocking remover. This paper studies its releasing kinetics. Get the microscopic releasing dynamics laws of different releasing stages: in the initial releasing stage, similar to first order reaction and the dynamics equation is $\ln CA = 0.6020t + 1.8692$; the metaphase releasing stage similar to zero order reaction and the dynamics equation is $CA = 0.9t + 0.695$; while the telophase releasing stage it is second order reaction and the dynamics equation is $1/CA = -0.0079t + 0.2460$.

Keywords: Chlorine dioxide; Blockage relieving agent; Dynamics; Release

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Chlorine dioxide is internationally recognized as a new generation of strong oxidizing agent with powerful abilities to oxidatively degrade polymers, kill microorganisms, and dissolve sulfides [1-6]. When combined with acids, chlorine dioxide can effectively serve as a composite blockage relieving agent for oil wells, improving injection and production rates and enhancing recovery efficiency [7-11]. This paper primarily discusses the release dynamics of the composite blockage relieving agent by investigating its activation and release process [12-14].

1 Experimental Section

Weigh approximately 2.0 g of the blockage relieving agent sample, accurate to 0.2 mg. Place it into a 250 mL iodine volumetric flask that has been pre-filled with 50 mL of water. Add 2 g of potassium iodide and perform a titration using sodium thiosulfate standard solution (0.1 mol/L). Near the endpoint, add 1-2 mL of starch indicator solution and continue titrating until the blue color disappears, indicating the endpoint. Also, conduct a blank test and record the volume as V1. Then add 3 mL of sulfuric acid solution (1:1), mix thoroughly, and place the mixture in a dark place for 10 minutes. Perform the titration again using sodium thiosulfate standard solution (0.1 mol/L). Near the endpoint, add 1-2 mL of starch indicator solution and continue titrating until the blue color disappears, indicating the endpoint. Record the volume as V2 and also perform a blank test.

The chlorine dioxide content (X) in the sample, expressed as a percentage by mass, is calculated as follows:

$$X1 = (V1 - V0)C \times 0.01349 / m \times 100\%$$

$$X2 = (V2 - V0)C \times 0.01349 / m \times 100\%$$

Where:

V1 — Volume of sodium thiosulfate standard solution consumed during the titration, mL

V0 — Volume of sodium thiosulfate standard solution consumed during the blank titration, mL

C — Actual concentration of sodium thiosulfate standard titration solution

m — Mass of the sample (g)

2 Results and Discussion

First, prepare a chlorine dioxide blockage relieving solution with a concentration of 4000 mg/L and let it sit for 10 minutes at room temperature. Measure the chlorine dioxide content. Then, place the solution in a 30°C water bath and measure the chlorine dioxide concentration every half hour. The results are shown in Figure 1.

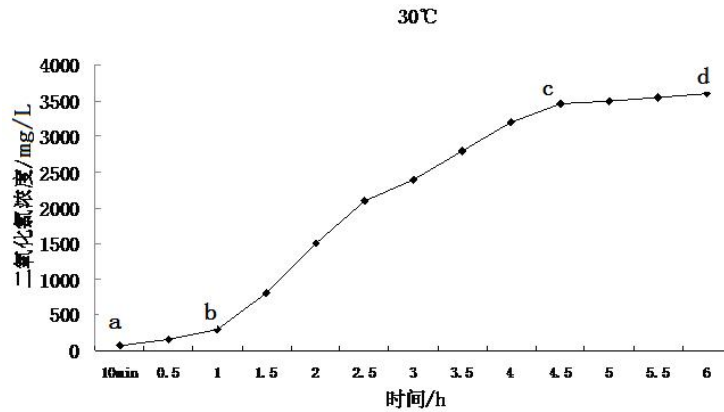


Fig.1 The relationship of chlorine dioxide concentration and time

From the above figure, it can be seen that during the a—b stage, the release of chlorine dioxide is slow. After that, there is an accelerated release process in the b—c stage. After 4.5 hours, the release begins to level off in the c—d stage.

3 Release Kinetics Study^[15]

In the initial stage, the logarithm of chlorine dioxide concentration is plotted against time for the first hour, as shown in the figure below:

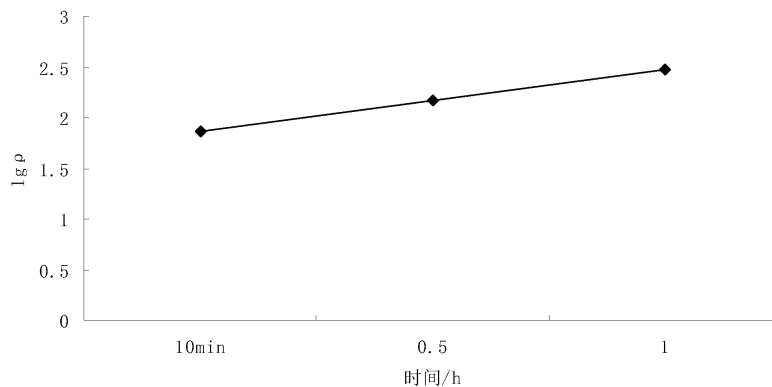


Fig.2 Dynamics equation of a-b stage

As shown in the figure, the logarithm of the chlorine dioxide concentration $\ln CA$ is proportional to the release time t . This indicates that the reaction is a first-order reaction in the initial stage. The reaction rate is given by $u_A = -dCA/dt = kACA$, with the dynamics equation: $\ln CA = 0.6020t + 1.8692$. During the initial stage, due to the presence of surfactants in the blockage relieving agent, the concentration of surfactants is high. The surfactants form micelles, encapsulating the reactants inside. The reactants need to break free from the micelle's confinement before the reaction can occur, which delays the reaction time.

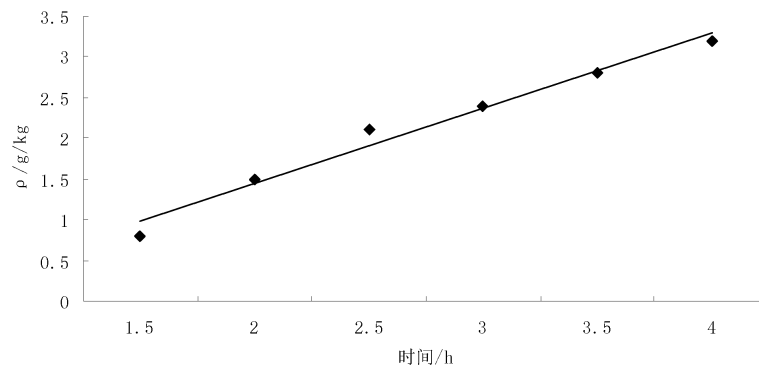


Fig.3 Dynamics equation of b-c stage

As shown in the figure, the chlorine dioxide concentration CA is proportional to the time t . This indicates that the reaction follows a zero-order process in this stage. The reaction rate is given by $u_A = -dCA/dt = k_A$, with the dynamics equation: $CA = 0.9t + 0.695$. As the reaction progresses, more and more reactants break free from the surfactants' confinement, significantly increasing the probability of effective collisions. Therefore, the reaction rate increases with time.

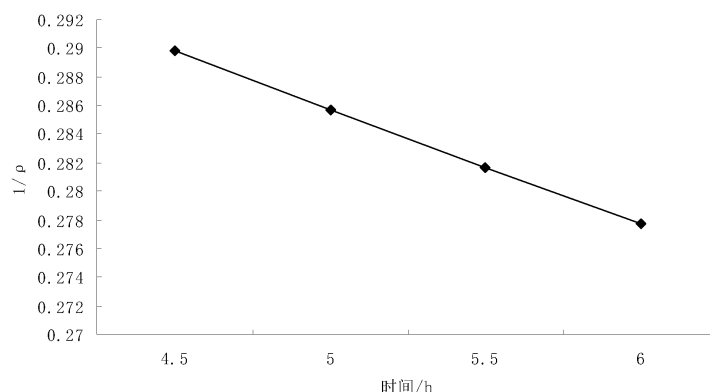


Fig.4 Dynamics equation of c-d stage

As shown in the figure, the inverse of the chlorine dioxide concentration $1/CA$ is proportional to time t , indicating that the reaction is a second-order reaction during the final stage. The reaction rate equation is $u_A = -dCA/dt = k_A CA CB$, with the dynamics equation: $1/CA = -0.0079t + 0.2460$. In the final stage of the reaction, as the concentration of reactants decreases, the frequency of effective collisions drops rapidly. No new chlorine dioxide is produced, and the concentration stabilizes. Over time, the concentration may even decrease further.

4 Conclusion

From the above experiments, it can be concluded that during the initial stage, the release of chlorine dioxide is slow and essentially inactivated, with the reaction following a first-order kinetics equation: $\ln CA = 0.6020t + 1.8692$. During the mid-release stage, the reaction behaves approximately as a zero-order reaction, with the dynamics equation $CA = 0.9t + 0.695$. In the final stage, the reaction follows second-order kinetics, with the dynamics equation $1/CA = -0.0079t + 0.2460$.

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