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EFFECT OF NANO POLYMER MICROSPHERES ADSORPTION ON NEGATIVELY CHARGED SIO_2 SURFACE: MOLECULAR DYNAMICS SIMULATION AND EXPERIMENTAL STUDY

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ABSTRACT

As a major profile control method for low permeability reservoirs, nano polymer microspheres (NPM) are used for thousands of wells in Changqing Oilfield every year， and have achieved excellent effect of EOR. Different from the profile control particles optimized based on the theory of matching between particle and pore throat size, the main mechanism of NPM is to increase the flowing resistance after adsorption on the pore throat surface.

However, there is a lack of quantitative research on the adsorption law of NPM, and the double-layer HPAM molecular model, without considering electrical properties, used by scholars cannot reflect the real formation charge properties and the expansion characteristics of NPM, and cannot reveal the adsorption law of NPM, which seriously affects the efficient application in the field.

In this paper, the dynamic adsorption capacity of NPM in sandstone reservoir is studied by QCM-D. Then, a customized SiO_2 coupon is used to simulate the cumulative static adsorption capacity of NPM at a certain position of the reservoir. At the same time, above two experimental methods were used to study the effects of different expansion time, different expansion ratio NPM combination and salinity on dynamic and static adsorption capacity. Finally, by changing the mass fraction of H_2O and HPAM to simulate NPM with different expansion time, a three-layer molecular model of "NPM + mineralized water + negatively charged SiO_2" was constructed to verify the experimental results and reveal the adsorption mechanism of NPM from the molecular scale.

The results show that the maximum static and dynamic adsorption capacities of NPM are 9.26 $\mu g \cdot cm^{-2}$ and 0.18 $\mu g \cdot cm^{-2}$ respectively. The aggregates in NPM solution will adsorb the monomer on the surface of SiO_2 coupon, so there are both adsorption and desorption happened. The maximum cumulative static adsorption capacity reached 150 $\mu g \cdot cm^{-2}$ after 3 days of expansion. The combination of different expansion time and new NPM has synergistic effect, which can double the adsorption capacity of expanded NMP. The adsorption capacity of NPM increases with the increase of salinity, and NPM can reduce the mineral adsorption capacity of pore surface.

The research results of this paper quantitatively characterize the adsorption capacity of NPM under different conditions, which lays a foundation for the establishment of adsorption characteristic model in the numerical simulation study of NPM profile control. It also can guide significance for the determination of NPM combination type and the judgment of NPM adsorption position, i.e. flow diversion position, in the field application.

Keywords: nano polymer microspheres; absorption; Molecular Dynamics Simulation; experimental study; negatively charged sio_2 surface

1. INTRODUCTION

Most Low-permeability Oilfields in China are also in the middle and late stage of development, facing the situation of surge of water cut and aggravation of reservoir heterogeneity, but there are still a large number of remaining oil not started. Polyacrylamide (HPAM) nano particles have the properties of deep profile control and flooding because of their small particle size, large molecular weight, aging, water absorption and expansion, elasticity and deformation,

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and can effectively play a role in high permeability water channeling. At present, more than 5000 wells have been implemented in Changqing Oilfield[1, 2], and excellent profile control and flooding effect has been produced[3] . The majority of scholars believe that the adsorption of profile control particles in the formation pore throat is one of the important factors affecting their sealing effect[4]. However, for nano scale particles, adsorption is one of the main modes of action. Adsorption at a suitable formation position plays a positive role in the formation of stable and effective bridging and plugging of particles. There are gaps in the research on the adsorption mechanism and influencing factors of nanoparticles at home and abroad, and there are few molecular dynamics simulations of HPAM nanoparticles with different water absorption and expansion time.

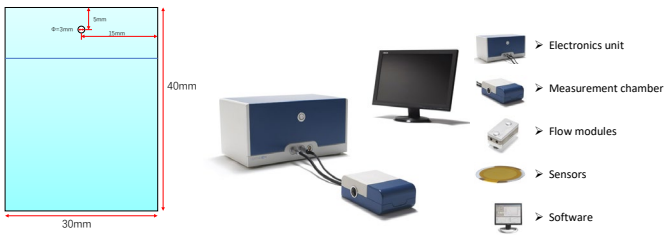
In this paper, the adsorption law of HPAM nanoparticles at different aging time, different particle size combination and different mineralization was studied by SiO_2 coupon and quartz crystal microbalance experiment. Using materials Studio software, the molecular dynamics simulation method of "HPAM + formation water + SiO_2" three-layer model was used to explore the adsorption mechanism at different aging times. This paper has certain guiding significance for the application of HPAM nanoparticles in low permeability reservoirs.

2. EXPERIMENTAL

2.1 Materials

Customized high-purity SiO_2 coupon were used in the experiment, as shown in Fig.1a. the SiO_2 content was greater than 99.99% and the effective adsorption area was 30 × 2mm. The nanoparticles used in the experiment are WQ 50nm particle emulsions (provided by Changqing oil and Gas Technology Research Institute).

In this experiment, simulated formation water is used to configure formation water according to Chang 6 reservoir ($CaCl_2$ type, salinity 89850mg / L, Ca^{2+} 20710mg / L, (K^+ + Na^+) 12220mg / L, Ba^{2+} 648mg / L, Cl^-56105mg / L, HCO^{3-}83mg / L).



a. SiO_2 coupon b. QCM-D

Fig 1 experimental materials

The equipment used in the experiment is mainly quartz crystal microbalance (manufacturer: Biolin scientific; model: qsense analyzer / qsense auto), as shown in Fig.1b. the equipment includes SiO_2 chip sensor, peristaltic pump, test tube, etc.

2.2 Methods

2.2.1 Experimental method

Customized high-purity SiO_2 coupon were used in the experiment, as shown in Fig.1a. the SiO_2 content was greater than 99.99% and the effective adsorption area was 30 × 2mm. The nanoparticles used in the experiment are WQ 50nm particle emulsions (provided by Changqing oil and Gas Technology Research Institute).

The experimental methods used in the silica coupon experiment are as follows: ① prepare the solution; ② Wash the SiO_2 coupon with deionized water, and weigh it with a balance; ③ After fully stirring the HPAM nanoparticle solution, pour it into the beaker with SiO_2 coupon to the liquid adding line and stand for 30min. ④ Take out the SiO_2 coupon, wash and dry it; ⑤ Weigh the completely dried SiO_2 coupon and calculate the mass difference of the coupon before and after adsorption.

Quartz crystal microbalance is a measurement and analysis technology that uses piezoelectric effect of quartz crystal to reflect surface quality changes of quartz crystal in real time. Due to its nack-level sensitivity, it is very suitable for the mechanism research of nanomaterials, and has been widely used in medicine [8], chemistry, biology and other fields. In order to simulate the adsorption law of HPAM nanoparticles in flowing state and verify the correctness of SiO_2 coupon experiment, the dynamic adsorption experiment of quartz crystal microbalance was carried out. The steps are as follows: ①Deionized water was injected at the rate of 100 μL·$min^{-1}$to establish the deionized water base line; ② For the experimental groups with different salinity, the simulated formation water is injected to establish the simulated formation water base line; ③ Inject fully stirred HPAM nanoparticle solution, and stop the experiment after the frequency is stable; ④ Sort out the data and calculate the adsorption capacity of HPAM nanoparticles by using the following formula:

$$\Delta m = -\frac{C\Delta f}{n}$$

Symbol notes: Δm—mass change，ng·cm^{-2}; Δf—-change of resonance frequency; C—constant, C= 17.8 ng·cm^{-2}·Hz^{-1};n—harmonic number, n=3 in this paper.

2.2.2 Molecular simulation method

Scholars at home and abroad have constructed layers of polyacrylamide molecular chain and water and conducted molecular dynamics simulation of HPAM with different mineral components [5]. This simulation method is suitable for mechanism study of sewage treatment and other aspects [6], but not suitable for spherical HPAM nano-particles. In this paper, quantitative HPAM and different H_2O molecular weight in the same layer is used to simulate HPAM nanoparticles after aging water absorption expansion. The effect of oil on the adsorption of nano-particles is not considered in this paper because nano-particles mostly act on water channelling layer. The three-layer model as shown in Figure X was constructed to study the conditions of different aging time and different salinity, verify the correctness of the adsorption experiment, and reveal the adsorption law and mechanism of SiO_2.

The model construction and analysis steps are as follows: ① HPAM molecular chain with chain number of 50 is established by using build polymers module; ② Using the construction function in amorphous cell module, HPAM and H_2O molecules, NaCl and H_2O molecules are established into cubic cells, and the solution density is 1g/cm^3; ② Use the build layers module to establish the "HPAM solution + SiO_2" double-layer model and the "HPAM solution + salt solution + SiO_2" three-layer model respectively. The size of SiO_2 in the bottom layer is 39.30nm×34.04 nm×14.93 nm, the length and width of other layers are the same as that of SiO_2 bottom layer; ③ In order to avoid the low energy potential trap, the force calculation module is used for geometric optimization until the energy is minimized; ④ Use the force calculation module for simulation. It does not correspond to the indoor experiment. First use the room temperature (298K) for 500psnvt simulation.

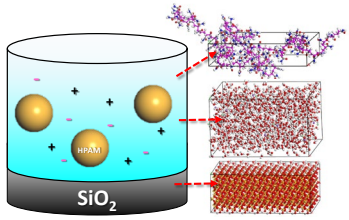


Fig 2 three-layer molecular model

Firstly, SiO_2 and mineralized water layer are simulated, and HPAM nano particle layer is added for simulation to truly reflect the behavior of nano particles when entering the formation.

2.3 Results and discussion

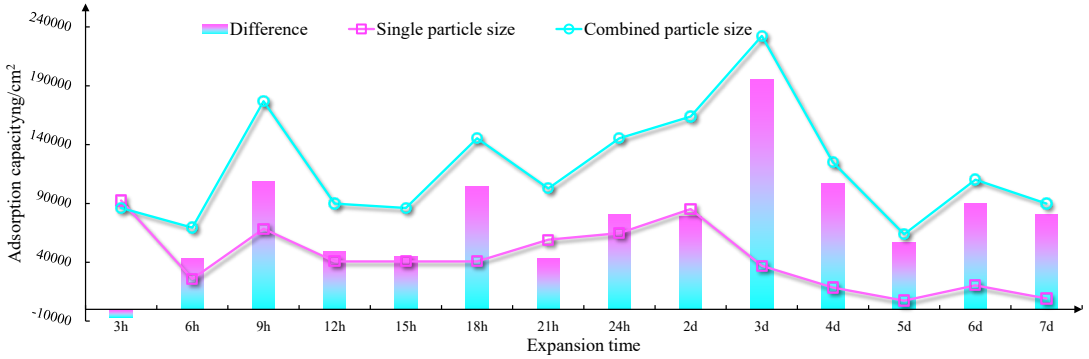


Fig 3 Comparison of combined adsorption and single particle size adsorption

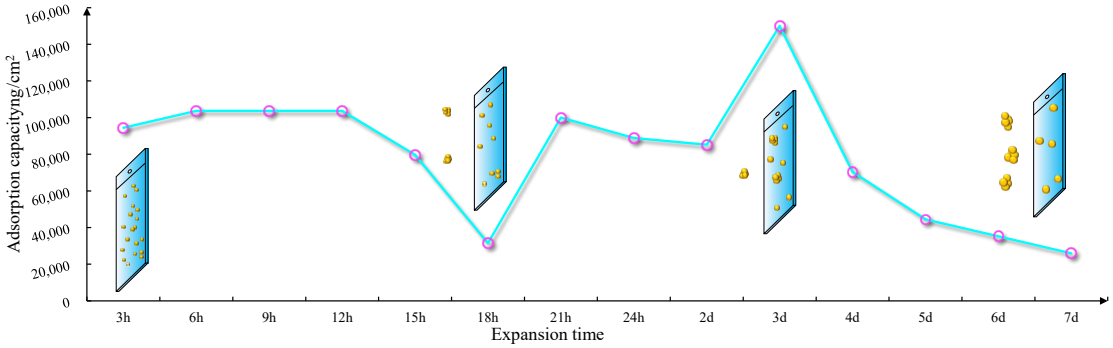


Fig 4 Cumulative adsorption of HPAM nanoparticles

2.3.1 Adsorption characteristics of NPM with different aging time

The results showed in Fig3 that the curve trend was basically the same as that of the single particle size adsorption experiment, but the maximum value changed from 3 hours of single particle size adsorption aging time to 3 days of combined adsorption.

According to the bar chart of single particle size adsorption and combined adsorption difference, except for the 3-hour point, the elastic particles with initial particle size can act synergistically with the aging particles for a certain period of time, such as the electrical opposite to enhance the adsorption capacity of the aging particles.

In field use, the plugging effect of slug 1 can be enhanced by adding the second slug 3 days after the aging of the first slug. To make the deep migration of slug 1, the effect of two slug 2 should be reduced. Slug 2 can be injected within 3 hours of the first slug injection to reduce the interaction between the two and make the deep migration of slug 1 maintain the maximum molecular weight. Results should be clear and concise.

2.3.2 Cumulative adsorption of NPM

The results show that the cumulative adsorption curve of NPM does not always increase, indicating that both adsorption and desorption still exist at the same time even under static conditions. At first, a large number of NPM were stirred and dispersed to adsorb on the SiO_2 hanging sheet. As the particles in the solution agglomerate, the particles that have been adsorbed on the hanging plate have an effect, leading to their desorption. Molecular dynamics simulation can also prove this point of view. As shown in Fig4, the adsorption capacity of HPAM layer with high molecular weight is stronger than that of SiO_2. As the aggregate tends to be stable, the aggregate begins to adsorb on the surface of the hanging plate. However, the aging water absorption and expansion of the particles lead to the decrease of the adsorption area between the agglomerates and the hanging sheet, and gradually desorption begins.

3. CONCLUSIONS

The results show that the maximum static and dynamic adsorption capacities of NPM are 9.26 $\mu g \cdot cm^{-2}$ and 0.18 $\mu g \cdot cm^{-2}$ respectively. The aggregates in NPM solution will adsorb the monomer on the surface of SiO_2 coupon, so there are both adsorption and desorption happened. The maximum cumulative static adsorption capacity reached 150 $\mu g \cdot cm^{-2}$ after 3 days of expansion. The combination of different expansion time and new NPM has synergistic effect, which can double the adsorption capacity of expanded NMP. The adsorption capacity of NPM increases with the increase of salinity, and NPM can reduce the mineral adsorption capacity of pore surface.

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