Effect of Polymer Static Adsorption during Polymer Flooding in *Bohai* Oilfield

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ABSTRACT

Polymer flooding technology as one of the effective ways to enhance oil recovery has been widely used and achieved great results in Bohai oilfield in China since 2003. It can improve the area swept efficiency not only in the macro scale but also in the micro scale. However, when polymer flowed in porous media, the surface adsorption and the interactions of polymer molecules would affect oil displacement. In this paper, based on the analysis of polymer adsorption mechanism, by using starch-cadmium iodide method, different clay minerals were measured on the adsorption of hydrophobic polymer in Bohai Oilfield. Concentration, temperature, salinity, and other factors were analysed when the adsorption capacity of clay minerals was influenced. A unit mass of clay minerals on the variation of polymer adsorption were obtained. The experiment results indicate that with the increase of unit mass of polymer concentration, water salinity and rock grain size, adsorption capacity gradually increases; while with the increase of unit mass of temperature, adsorption capacity gradually decreases. The obtained analytical solutions may could help the application design for a chemical flooding process.

KEYWORDS: Polymer flooding; static adsorption; the starch-cadmium iodine method; Bohai oilfield

INTRODUCTION

During the development of water injection in oilfield, the low waterflood sweep efficiency is caused by reservoir heterogeneity and unfavorable mobility ratio [1-2]. Adding polymer can significantly increase the viscosity of injection fluid, improve the mobility of fluid, increase the waterflood sweep efficiency, and eventually enhance oil recovery [3]. However, due to the surface adsorption, mechanical trap, hydrodynamic trap and the interaction between polymer molecules during the flooding of polymer in porous media, the available polymer to actually mobilize trapped oil is reduced badly. Polymer adsorption during polymer flooding is always one of the main drivers of polymer flooding performance [4] . Indeed, together with the effects of the dispersion and adsorption, considerable part of injected polymer solution can't gel in the reservoir, or had low viscosity after gelling [5]. There are many factors related to the static adsorption of polymer, accurately measuring the static adsorption of polymer is the foundation of polymer flooding, ASP flooding and weak gel displacement [6-7].

In this study, by using starch-cadmium iodide method, different rocks in each well of SZ36-1 oilfield were measured on the adsorption of polymer AP-P4. Researching the static adsorption quantity change rules when the concentration, temperature, salinity and the size of rock changed, providing a theory basis for efficient polymer flooding technology of Bohai oilfield.

POLYMER ADSORPTION MECHANISM

Polymer adsorption in the reservoir can be due to different mechanisms, the main reason is the interaction between polymer molecules and solid surface, the solvent medium is water, polymer molecules bonded to the surface of solid by physical adsorption which named electrostatic interaction and hydrogen bonding [8-9].

1) Electrostatic interactions

Sodium carboxyl group ionization after polymer molecules dissolved in water, forming negatively charged ions. The negatively charged groups -COO- and –COONa in the ionization equilibrium state, the carboxyl group of hydrolyzed polyacrylamide negatively charged after acid amide ionizing, it might be due to the electrostatic interaction between mineral and adsorption.

2) Hydrogen bonding

The surface of reservoir rocks produce hydroxyl through hydroxylation reaction under the condition of water invasion for a long time. This hydroxyl groups can be connected with the root of carboxylic acid and amide by hydrogen bonds. There are a large number of groups on the polymer chains can form hydrogen bonding groups, what are adsorbed on the particle surface is only point contact, in the form of macromolecular chains places line groups present in the solution. The hydrophilic properties of the amide group and carboxyl group in hydrolyzed polyacrylamide absorb large amounts of water, thereby inhibiting the flow of water.

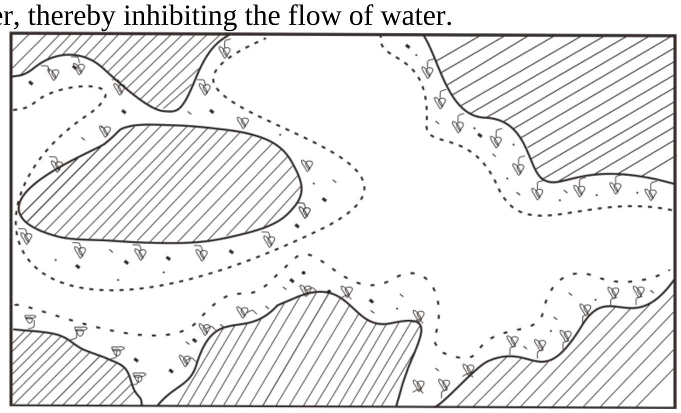

Figure 1: Polymer Adsorption in Porous Media [10]

MATERIALS AND METHOD

Materials

Polymer AP-P4(Mw=1000×10^6g/mol, solid content 88.02%);water used in the test was simulative formation water(salinity 1679.09mg/L), main ion content were shown in **Table 1**; buffer solution of 2.5% $C_2H_3NaO_2.3H_2O$ and 0.075% $Al_2(SO_4)$ .18H_2O, pH value of 3.5; 1% HCOONa solution;

1.1%CdI_2 and 0.25% starch solution; each interval mineral of Bohai oil field(A2-1, A2-2, A8-1, A8-2, A19-1, A19-2).

721 spectrophotometer; TD-L60B centrifuge (speed 3000 r/min, 10min); JJ-1 power blender; analytical balance (0.0001g).

Table 1: The Ion Content of Water Used in the Test

Ion	Na^++K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}
Content(mg/L)	1454	12	36	948	38	1651	342

Method

Standard curve drawing

Experiments by using starch-cadmium iodide colorimetric method by measuring the absorbance of different concentration of polymer solution, the method based on the first step transformation of amide into amine which named HOFMANN rearrangement reaction, the reactive as shown in **type (1)** [11]. Respectively prepared the polymer solution by formation water with concentration of 5mg/L, 10mg/L, 15mg/L, 20mg/L, 25mg/L, 30mg/L, 35mg/L, 40mg/L, 45mg/L, 50mg/L, 55mg/L, 60mg/L; Adding 1g polymer sample and 5g buffer into container which container capacity is 100mL; distilled water was added to about 35g and mixed evenly; put in 5g 1%CHOONa solution after adding 1g bromine water and reaction for 15min, let stand for 5min reaction, finally added 5g starch cadmium iodide chromogenic reagent, mixed and diluted to 50g; the reaction solution thoroughly until the color; the solution was measured absorbance at 610nm wavelength by spectrophotometer, using the blank adjusting instrument absorbance is zero before testing. Based on test data drawing the polymer concentration-absorbance curve.

$$
\begin{gathered}
R\text{—}CONH_2+Br_2 \rightarrow R\text{—}CONHBr+HBr \\
R\text{—}CONHBr+H_2O <=> R\text{—}CONHB_2+HBrO \\
HBrO+2I^-+H+ \rightarrow I_2+Br^-+H_2O \\
I_2+I^-+Starch \rightarrow I_3^-Starch\text{（Blue Compound）}
\end{gathered} \tag{1}
$$

Preparation of detection solution

Preparation a certain concentration (the initial concentration was C_0) of polymer solution; adsorbent using the rock in each well of SZ36-1 oil field . Added some of polymer solution and sorbent into the tube by a certain ratio, seal after shaking evenly; the reagent is placed in the constant temperature of 60℃ water-bath for 48h, again during every once in a while to oscillations tubes, which makes adsorbent and polymer solution released fully. Took out the tube after 48h and pull the upper-middle-class supernatant into a centrifuge tube, after centrifugal supernatant fluid as the polymer detection fluid, according to the standard curve drawing method in the experiment operation after the polymer solution absorbance.

Computational formula

This experiment tested the static adsorption capacity of different rocks in SZ36-1 oilfield in different condition by immersion method. Static adsorption quantity according to the calculated by

type (2):

$$\Gamma = \frac{V(C_0 - C_e)}{G} \quad (2)$$

Where Γ is the static adsorption quantity of rock, means per gram of rock powder polymer adsorption milligrams, mg/g; V is the volume of polymer solution, L; C_0 and C_e are the initial and final concentration of the polymer solution, mg/L; G is the weight of rock, g.

RESULTS

Standard static adsorption curve

By measuring the absorbance of different concentration polymer solution, polymer AP-P4 standard curve drawing is shown in **Figure 2**. According to the curve to fitting the standard curve equation: y=0.0229x+0.1028, the standard deviation R2=0.9955.

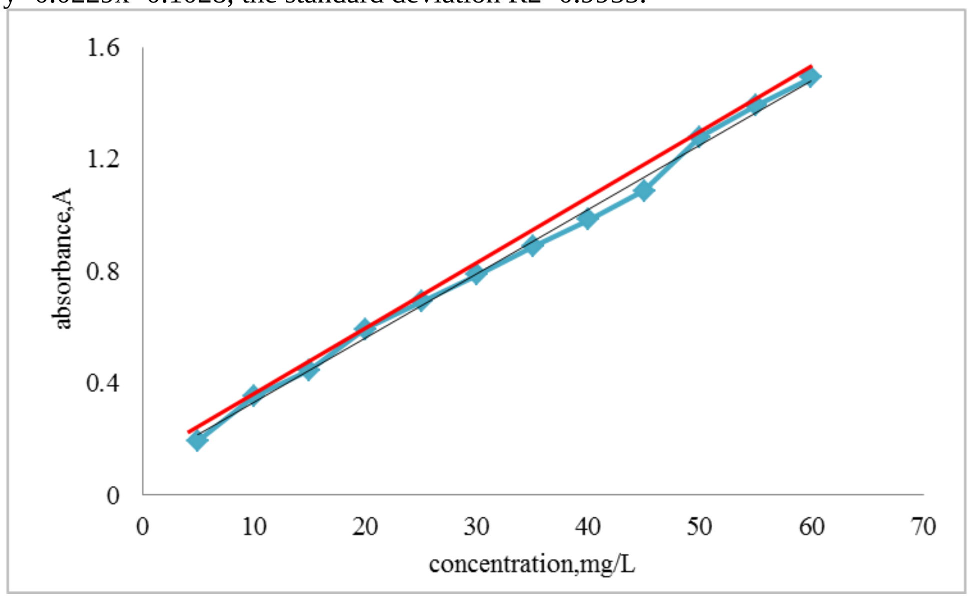

Figure 2: Standard curve of polymer AP-P4

Effect of AP-P4 concentration

Respectively joined the concentration of 100mg/L, 300mg/L, 600mg/L, 1200mg/L, 1500mg/L, 1750mg/L, 2500mg/L, 3000mg/L of the polymer AP-P4 solution in six kinds of rock (100 mesh) at 60℃, **Figure 3** shows the effect of polymer concentration on polymer adsorption. The result shows that at low polymer concentrations, with the increase of concentration, hydrophobic association of polymer reaction mainly occurs within the molecule, in the form of a monolayer adsorbed on the surface of various mineral, which makes the adsorption quantity low; When the concentration of polymer is high (> 1500mg/L), as the increasing of the new hydrophobic association reaction occurs between molecules, polymer adsorbed on the surface of the mineral by hydrophobic group, thus forming a multilayer adsorption which leads to the increase of static adsorption quantity. However the coverage fraction (the coverage fraction of solute on the surface of the adsorbent) of polymer in the surface of mineral decreased, leading to the increase of adsorption but not increase rapidly; with the increase of polymer concentration, the unit quality clay mineral adsorption quantity also gradually increased.

There is an agreement between simulation and experimental results studied the influence of polymer concentration on polymer adsorption and permeability reduction by testing residual resistance factor (RRF) values with different polymer concentrations. Their results also showed an increasing in adsorption quantity with an increase in polymer concentration[12-13].

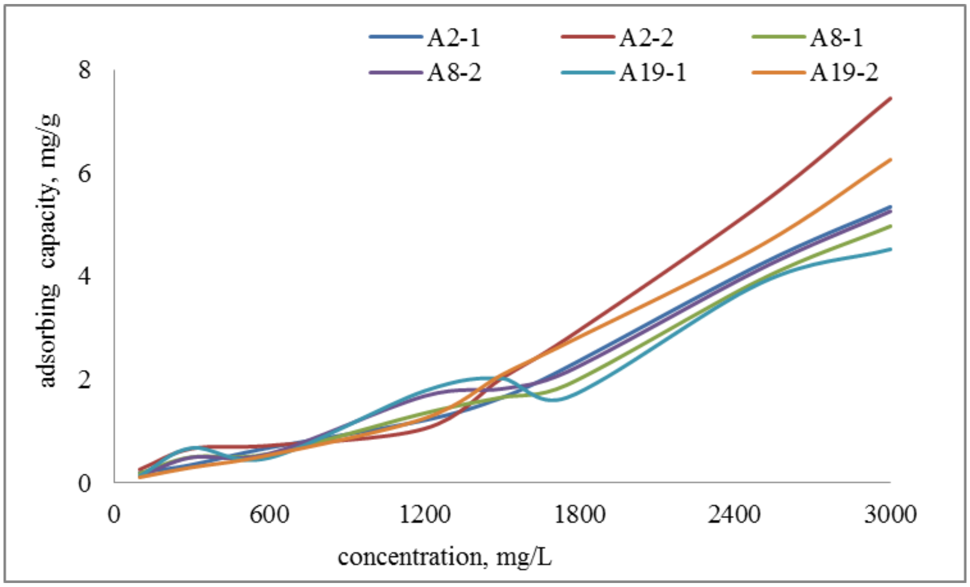

Figure 3: Effect of AP-P4 concentration on polymer adsorption

Effect of temperature

Respectively joined the concentration of 100mg/L of the polymer AP-P4 solution in six kinds of rock (100 mesh) at 30℃、40℃、50℃、60℃、70℃、80℃, measured the units mass adsorption amount after the end of the reaction. Measurement results are shown in **Figure 4**. With increasing of temperature, adsorption capacity per unit mass of rock was gradually decreased. As the temperature raised, the solubility of polymer AP-P4 increased, led to the adsorption quantity decreased; at the same time the increased of temperature intensified the interaction between the hydrophobic groups and the association of polymer enhanced; while thermal motion of ionic groups increased which weakened the electrostatic interactions, thus molecular chain extended and hydrophobic micro area ordering degree increase, increased the adsorption of polymer on the rock. Meanwhile, high temperature also makes the hydrophilic group of hydration abate, molecular chain was contracted, hydrophobic micro area disordering degree increase, decreased the adsorption of polymer on the surface of rock. The two effects cancel each other out, resulting in decreased the amount of adsorption of polymer.

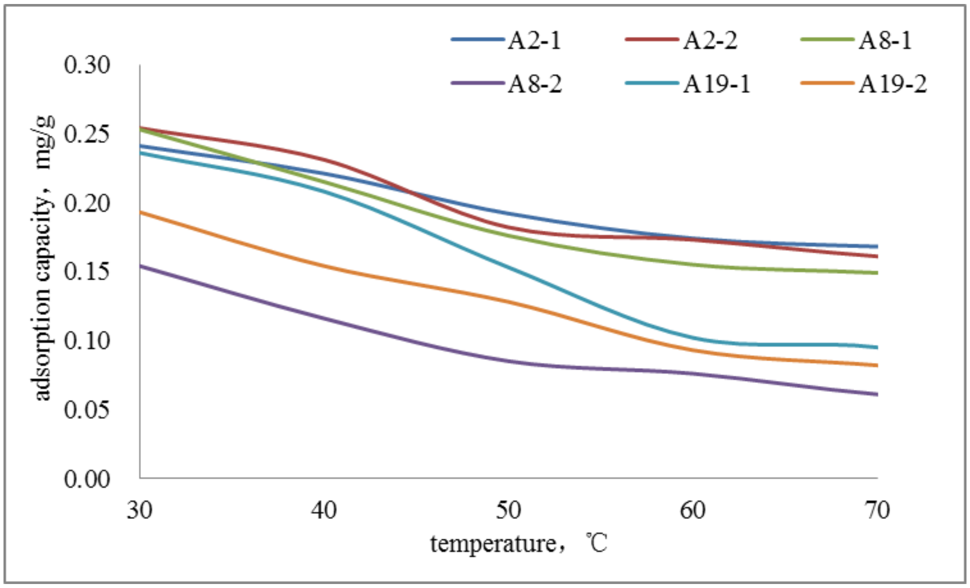

Figure 4: Effect of Temperature on Polymer Adsorption

Effect of water salinity

Respectively prepared polymer solution in concentration of 100mg/L with formation water which salinity were 6400mg/L、7841mg/L、9652mg/L、10387mg/L、12800mg/L, measured the adsorption capacity at 60℃. **Figure 5** shows the effect of water salinity on polymer adsorption with six kinds of rock. Research shows that increasing the brine concentration reduces the residual factor (RF) and residual resistance factor (RRF), and it means that polymer adsorption increases with an increasing of salinity. Moreover, with the increase of water salinity, the polarity of solution enhanced, and the shielding effect of charge stretched the polymer molecular chain, reduced the critical associating concentration of polymer, and increasing the ordering of hydrophobic micro area, resulting in the increase of adsorption quantity in unit mass rock. Hence, to ensure the effect of polymer flooding, polymer flooding process uses low salinity water for preparation of polymer solution at best.

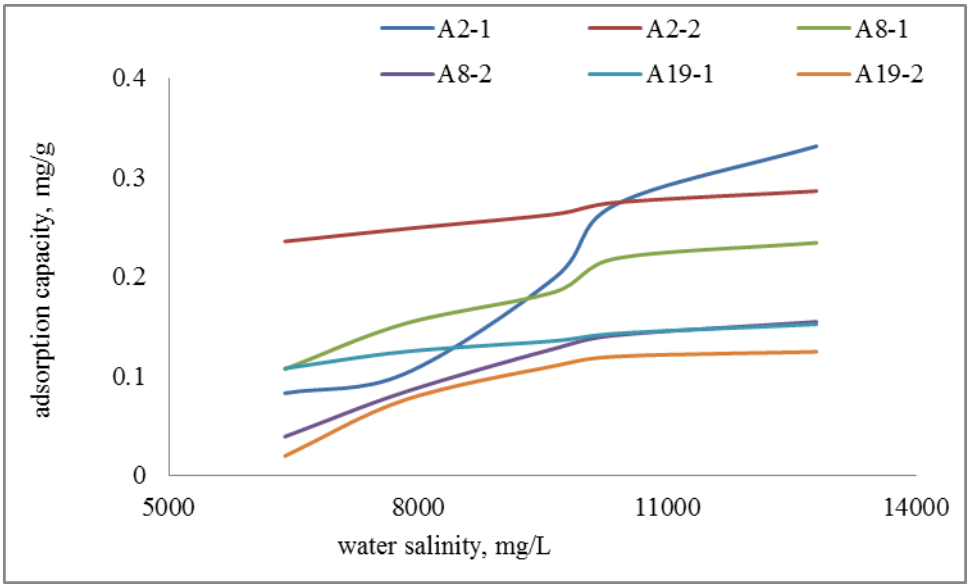

Figure 5: effect of water salinity on polymer adsorption

Effect of rock grain size

The experimental result is shown in **Figure 6**, with the increasing of particle size, unit mass adsorption capacity increased. With the increase of particle size, specific surface also increased, thus enhanced the contact area between rock and polymer, results in the gradually increase of unit mass adsorption capacity of rock.

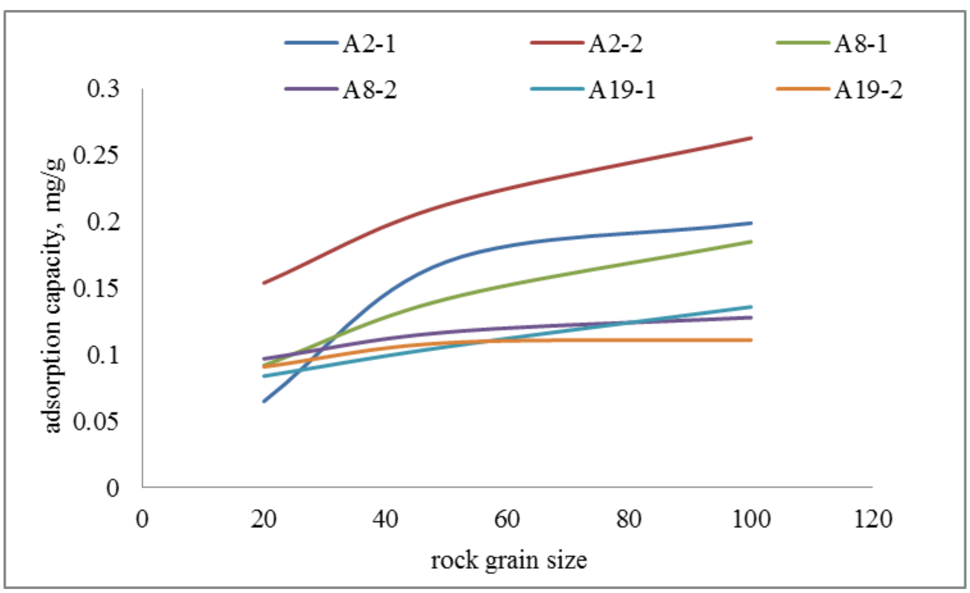

Figure 6: Effect of rock grain size on polymer adsorption

Effect of reservoir heterogeneity and wettability

Research shows that permeability also has great effect on polymer adsorption. The higher permeability rock has the higher RF and RRF or higher polymer adsorption, and also higher permeability reduction. Normally, with high permeable rocks, the adsorbed layer thickness is nearly constant at a low shear rate and increases when the shear rate increases above a critical value. The high rough surface deduces the higher adsorption mass [9].

Polymer adsorption is a function of the surface area in contact with the flooding fluid. Therefore, fine-grained sands adsorb much more polymer than coarse-grained sands. The wettability also has a significant effect on polymer adsorption. The water-wet sand offers an additional adsorbing surface to the polymer, while the oil-wet sand presents a strong decrease in adsorption.

CONCLUSION

This paper presents a comprehensive investigation of polymer adsorption in the chemical polymer flooding process. The main conclusion can be summarized as follows:

1) It is simple and accurate to measure the concentration of polymer solution by starch - cadmium iodide colorimetric method. The application of this method is relatively mature and it has great help for measuring the concentration of hydrophobic associating polymer solution.

2) The results of experiment show that static adsorption of AP-P4 in the formation are mainly affected by concentration of solution, reservoir temperature, salinity of formation water and the size of rock grain.

3) The static adsorption of polymer is obvious and cannot be ignored during polymer flooding, so we recommend that inject some surfactant before polymer flooding, by varying the surface wettability of rock and then reducing adsorption of polymer in the rock surface.

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