Applied Polymer
JOURNAL OF
SCIENCE

Effect of a polymer on chromium(III) diffusion during gelant injection in fractured media

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ABSTRACT: The effect of a polymer on chromium diffusion during gelant injection into fractured media was explored with a polymer/chromium(III) (Cr^{3+}) gelant. The capture and barrier effects are two main affecting mechanisms of polymer molecules on the diffusion of Cr^{3+}, and the formation of the polymer leak-off layer is a key influencing factor. The experimental results show that when the polymer molecular weight (MW) or concentration increased, both the diffusion rate of Cr^{3+} and the leak-off degree of the gelant decreased sharply. This resulted in the delayed initial production and advanced final production of Cr^{3+}. Because of the changing diffusion rate of Cr^{3+} and the dilution effect of brine during gelant injection, the change trends of the Cr^{3+} production from the fracture outlet and matrix ports reversed after the injection volume exceeded a value; this value was named the *critical injected volume*. During gelant injection into the fractures, under the effects of gravity action and the disproportionate diffusion of Cr^{3+}, the chromium diffusion profiles measured at the fracture top and bottom were different. The chromium diffusion profile along the matrix varied with increasing gelant injected volume, but it finally reached the diffusion equilibrium state in the matrix. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43447.

INTRODUCTION

Polymer gel systems, which mainly consist of a polymer and a crosslinker, are widely applied to the plugging of highly permeable water channels to control water production from oil wells, and they have proven their feasibility and practicality in oil fields for decades.[1–3] Their relatively low cost also contributes to the expansion of their application scale, despite the fact that many kinds of new water-plugging agents have been developed in recent years.[4] Anionic polymers, such as hydrolyzed polyacrylamide, are commonly used with crosslinkers to prepare gelling solutions or gelants. Chromium(III) (Cr^{3+}) acetate, which can crosslink the hydrolyzed carboxyl groups attached to the polymer molecular chain, is a commonly used metallic crosslinker.[5,6]

The water-plugging performance of polymer gel systems in heterogeneous reservoirs is satisfactory, but it is unfavorable when they are used in fractured reservoirs. Seright and coworkers[6–9] have investigated the plugging performance of polymer/Cr^{3+} gels in fractures for many years. They found that the diffusion loss of chromium from gelant to brine could greatly reduce the gel strength or even make the gelant ungelled, and finally, it resulted in plugging ineffectiveness. Therefore, Seright and

coworkers held that the application of the "preformed gel," which was aged for a period of time before its injection to form a mobile gel, was an effective method for retarding or eliminating the diffusion loss of chromium ions. Ganguly[10] studied the effect of the leak-off degree of gelant into the matrix on the water-plugging performance in fractures, and he considered that a proper degree of gelant leak-off or chromium diffusion into the matrix could enhance the plugging performance of gels for fracture to some extent. In contrast with the studies of Seright and Ganguly, Zhao et al.[11] held that the influence of the fracture size was significant when hydrolyzed polyacrylamide gels were used for the fracture treatment.

In reality, during the injection of gelant into fractures, the gelant–rock interaction occurred between the gelant and the fracture face.[12] Ghosh et al.[13] found that a cementing force was gradually built between the gelant and fracture face in the process of gel formation, and it contributed to the antiwashout properties of the gel in fracture. Dang et al.[14] held that the matrix surfaces would be covered by polymer molecules because of the polymer adsorption. Both Lipatov et al.[15] and Seyrek et al.[16] studied the structure of the polymer adsorption layer onto the solid surface in detail, and they found that the

adsorption type of polymer molecules onto the solid surface was closely related to the brine salinity, MW, rock constituents, and so on. Except for the polymer adsorption, the diffusion of chromium ions was also critical. Chromium ions could diffuse from the gelant to the brine or from the fracture into the matrix.[17] Ganguly[18] put forward the following five existence types of chromium ions: those that diffuse into brine, those that diffuse into the matrix, those that diffuse into the stagnant pockets of the fracture, those that adsorb onto the sand surface, and those that precipitated because of the increase in pH from fluid–rock interaction. However, few experiments have been conducted to prove the previous hypotheses.

The retarding effect of the polymer on the diffusion of the surfactant or other low molecules has been fully studied; the sharp improvement of the viscosity after the addition of the polymer is mainly responsible for this retarding effect.[19–21] Similarly, the diffusion of chromium ions in the gelant is also greatly affected by the polymer. Bryant et al.[22] held that chromium loss was more critical in matrix formations than in fractured reservoirs because of the high surface area of rock in contact with the gelant. However, the diffusion of chromium ions in fractured reservoirs remains unclear. To systematically explore the effect of the polymer on the chromium diffusion properties in fractured media, we conducted experiments with gelants and fractured cores. Polymers with different MWs or concentrations were used to further investigate the effects of the polymer MW and concentration on chromium diffusion. Meanwhile, the chromium diffusion profiles along the fracture and matrix were also explored in this study.

EXPERIMENTAL

Chemicals and Fluids
Four kinds of commercial partially hydrolyzed polyacrylamide (anionic polymer, Hengju Chemical Co., China), with average MWs of 5000, 8000, 12,000, and 17,000 kDa, were used in the experiments. The hydrolysis degree of four kinds of polymers was about 25%, and the purity exceeded 98 wt %. Chromium acetate (SD107, Shida Oilfield Technical Services Co., China) was used as the crosslinker.

The formation brine, with total salinity of 7706 mg/L, was self-made in the laboratory. The gelant was prepared with certain concentrations of polymer and chromium acetate. The polymer concentration (C_p) in the gelant was varied from 1000 to 5000 mg/L, and it was determined on the basis of the experimental
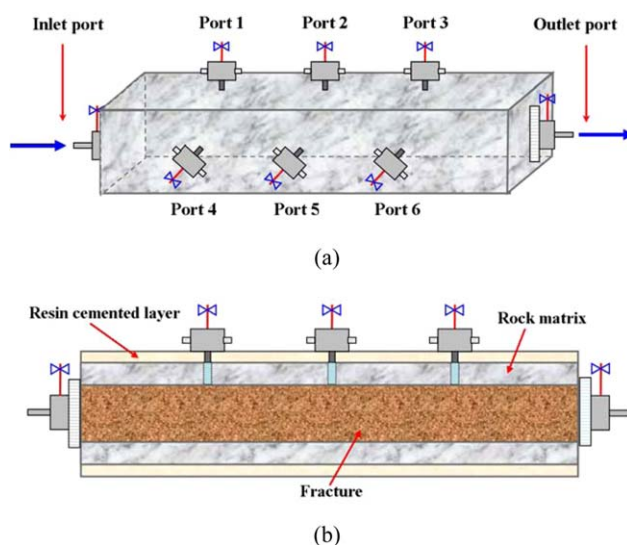

Figure 1. Schematic of the cubic fractured core: (a) general and (b) sectional views. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

objective. The concentration of chromium acetate was always 0.45 wt % to ensure that the effective Cr^{3+} ion concentration in each gelant was 357.5 mg/L.

Fractured Core Preparation
Fractured cores, including cubic fractured cores and cylindrical fractured cores, were prepared and used in experiments, and their schematics are shown in Figures 1 and 2, respectively. Gelant leak-off and chromium propagation tests were conducted with cubic fractured cores with a length of 40 cm, a height of 4.5 cm, and a width of 4.5 cm. A homogeneous fracture with a length of 40 cm, a height of 3.5 cm, and a width of 0.2 cm was prepared in each cubic fractured core. The polymer leak-off layer onto the fracture face was observed visually with the cylindrical fractured cores with a diameter of 2.5 cm and a length of 10 cm, and the fracture size across the core was 10 cm in length, 1.5 cm in height, and 0.2 cm in width. The water permeability of each core matrix was approximately 100 millidarcy.

Chromium Ion (Cr^{3+}) Measurement
The chromium (Cr^{3+}) concentrations of the produced fluids sampled from the fracture outlet and fracture–matrix ports were measured with an ultraviolet–visible spectrophotometer (GBC CINTRA3030) with a wavelength of 358 nm. The typical
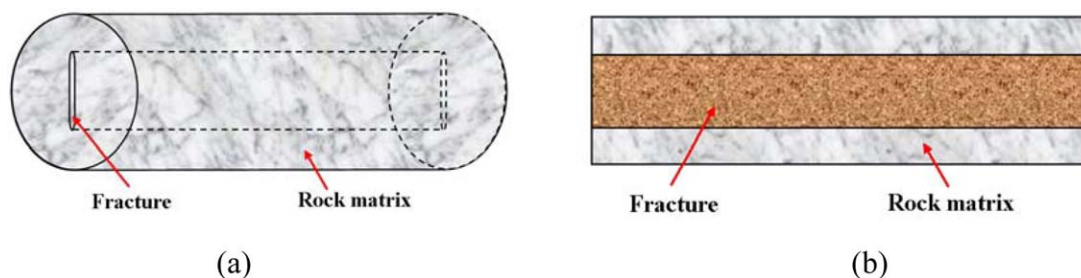

Figure 2. Schematic of the cylindrical fractured core: (a) general and (b) sectional views. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

curve of chromium concentration versus absorbance value had to be achieved before the experiments. During the gelant injection into fractures, the fluids produced from the fracture outlet or fracture–matrix ports were collected at regular intervals, and then, a 5 wt % hypochlorite solution with a weight ratio of 1:2 with samples was added to destroy the polymer molecules, free the chromium ions, and reduce the fluid viscosity. After that, the processed sample was diluted with deionized water to ensure that the chromium concentration was in the range 5–50 mg/L. The absorbance value of chromium in each processed sample was measured, and then, the chromium concentration was achieved with the typical curve and multiple dilution. The normalized chromium concentration was further calculated, and it equaled the ratio of the chromium concentration of the produced fluid to the initial chromium concentration of the fixed gelant (357.5 mg/L).

Gelant Leak-Off Test

During the gelant injection into cubic fractured cores, the gelant leaked off from fracture into the matrix and was produced from the matrix ports (ports 4, 5, and 6), which were vented to the atmosphere. The leak-off volume of produced fluids at each port was recorded, and the leak-off ratio, which was defined as the ratio of the cumulative volume of the fluid produced from the matrix ports to the totally injected fracture volume of the gelant (FV), was calculated. The total leak-off volume of produced fluids collected from all of the matrix ports in real time was used to explore effects of the polymer MW and C_p on chromium diffusion, but the leak-off volume of produced fluids collected from each port was applied when we tested the chromium diffusion profile along the matrix.

When we explored the polymer leak-off layer with the cylindrical fractured cores, the gelant dyed by methylene blue was injected into the fractures. After the gelant injection, the cores were dissected into halves along its fracture length. Microscopic images (magnified 500 times) were obtained with an Anyty microscope (3R-MSUSB601) to visually observe the polymer leak-off layer onto the fracture faces.

Chromium Diffusion Profile Test

The chromium diffusion profile consisted of many diffusion points at which the concentrations of chromium ions were the same. In the initial injection stage, the concentration of chromium measured for this profile was usually lower than its original concentration because of the chromium diffusion. During the gelant injection, fluids produced from the fracture outlet or matrix ports were collected, and the chromium (Cr^{3+}) concentration was measured on the basis of the measuring procedure discussed earlier. When testing the chromium diffusion profile along the fracture, we first placed the cubic fractured core upward (fracture ports upward) and then placed downward (fracture ports downward) to successively make the fluids produce from the top and bottom of the fracture. When testing the chromium diffusion profile along the matrix, we vented all of the matrix ports to the atmosphere, and the fluids produced form each port were collected in real time to evaluate the chromium distribution along the matrix.
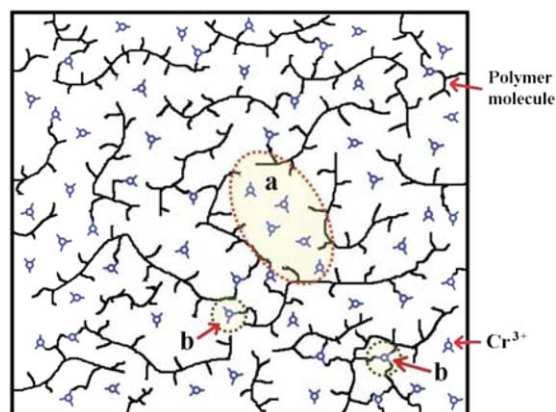

Figure 3. Schematic of the capture effect of polymer molecules on chromium (Cr^{3+}): (a) Cr^{3+} entrapped into molecular clews and (b) Cr^{3+} crosslinked with polymer molecules. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Affecting Mechanism of the Polymer on Chromium Diffusion in the Fractures

Capture Mechanism of the Polymer Molecules on Chromium. When chromium (Cr^{3+}) acetate was mixed with the polymer, because of the huge difference between the physical and chemical properties of two agents, the polymer had a significant effect on the kinetics of the chromium ions. The addition of polymer obviously enhanced the viscosity of the mixed solution and resulted in the deceleration of the diffusion rate of chromium ions, and thus, the capture mechanism of the polymer molecules on chromium ions was responsible for this phenomenon.[22,23] First, polymer molecular clews were formed because of the intermolecular or intramolecular winding and the hydration of the polymer molecules.[24] During the formation of the clews, chromium ions and hydrones were entrapped into the molecular clews, and thus, the freedom degree of chromium ions was reduced, as shown in Figure 3(a). Second, the crosslinking reaction between chromium ions and polymer molecules began as soon as they were mixed, despite the fact that this reaction was weak in the beginning, and thus, some chromium ions were captured and lost their freedom, as shown in Figure 3(b).

Barrier Mechanism of the Polymer Leak-off Layer on Chromium. During the gelant injection into fractures, a polymer leak-off layer was formed; it leaked onto the fracture face and into the adjacent matrix. The formation mechanisms of the polymer leak-off layer in fractures are shown as follows.

Polymer adsorption onto the fracture surface. Electrostatic attraction between fracture surface and charged anionic polymer molecules played a dominant role in polymer adsorption.[14] Anionic polymer molecules often hold negative charges because of the electroionization of carboxylate groups. Electrons on sand surfaces are often negatively or positively charged, and it results in an electrostatic attraction between the polymer and sand. Hydrogen-bonding attraction is another contribution to the polymer adsorption, and it occurs between the hydroxyl groups on the sand surfaces and the carboxylate groups of polymer
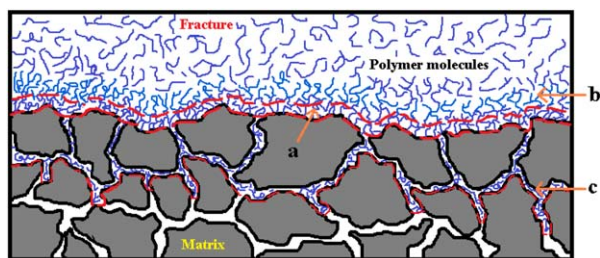
Figure 4. Schematic of the polymer leak-off layer onto the fracture face and the adjacent matrix: (a) adsorption layer, (b) aggregation layer, and (c) retention layer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

molecules.[25] Therefore, the polymer molecules could be adsorbed onto the sand surfaces by virtue of the electrostatic and hydrogen-bonding attractions to form a polymer adsorption layer, which is shown in Figure 4(a). The adsorption type of polymer molecules onto the fracture face followed the adsorption rule of Langmuir; that is, only a single layer of polymer molecules were adsorbed onto the fracture face, and the thickness of the polymer adsorption layer was on the nanometer scale.

Polymer aggregation onto the adsorption layer. After the polymer adsorption onto fracture face reached the equilibrium state, the polymer molecules tended to aggregate onto the polymer adsorption layer because of the continual leak-off of gelant. Because of the partial adsorption of polymer molecules with long molecular chains, the aggregated polymer molecules near the adsorption layer could wind with the adsorbed molecules.[26] Furthermore, other polymer molecules could also wind with the previously aggregated molecules. After a certain amount of polymer aggregation, a polymer aggregation layer was formed onto the polymer adsorption layer, as shown in Figure 4(b).

Polymer retention in the adjacent matrix. During the leak-off process of the gelant, most of the polymer molecules were adsorbed or aggregated onto the fracture surfaces because of the high MW and long molecular chain. However, small molecules could also enter into the matrix pores to form a polymer-retention layer in the adjacent matrix [Figure 4(c)], especially when the pressure differential between the fracture and matrix was high. The lower the polymer MW was, the thinner the retention layer was. The polymer molecules remained in the matrix in two forms: adsorption and entrapment. The polymer molecules could adsorb onto the pore surfaces because of electrostatic and hydrogen-bonding attractions. They could also be trapped because of the roughness of the pore surfaces and the narrowness of the pores; the intermolecular or intramolecular winding further contributed to this entrapment.[27] Both the adsorption and entrapment of polymer molecules in the matrix improved the degree of polymer retention and further led to the formation of the polymer-retention layer.

Therefore, the polymer leak-off layers could be subdivided into three sublayers: the adsorption layer, the aggregation layer, and the retention layer. This played the role of barrier onto the fracture face and into the adjacent matrix to retard the diffusion
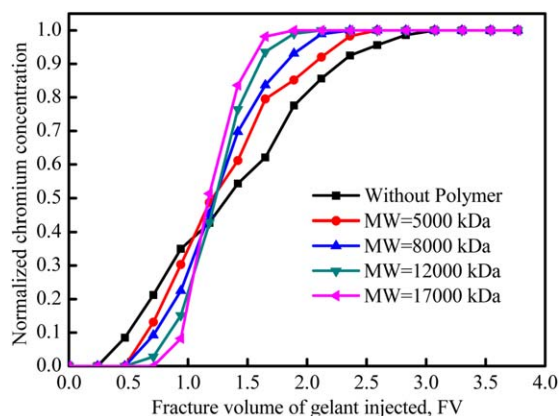

Figure 5. Normalized chromium concentrations of fluids produced from the fracture outlet when the polymer MWs were different. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

rate of chromium ions from the fracture into the matrix and to slow down the leak-off rate of gelant.

Capture Effect of the Polymer on Chromium Diffusion into Brine

Effect of the Polymer MW. To explore the effect of the polymer MW on the diffusion behavior of chromium (Cr^{3+}), the gelants, which consisted of polymers with different MWs (5000, 8000, 12,000, and 17,000 kDa, respectively) and chromium, were injected into fracture cores. A chromium solution without polymer was also used as a contrast. Fluids produced from the fracture outlet were collected, and the chromium concentrations of the produced fluids were measured, as shown in Figure 5. When the polymer MW was certain, the chromium concentration curve could be divided into three subcurves; that is, no chromium was found from the produced fluid when the injected FV was small. With increasing injected volume, the chromium was produced, and its concentration was sharply increased. With a further increase in the injected gelant volume, the growth rate of the curve decreased and the normalized chromium concentration finally leveled off at 1. This was due to the fact that the gelant was diluted and produced together with the formation brine at the initial injection stage; as the formation brine was gradually flooded out, the diluting effect waned, and the chromium concentration in the produced fluid was improved. The data in Table I show that the normalized chromium concentration reached 1 after 3.07 FV of the chromium solution was injected; when the polymer MW was 12,000 kDa, the required gelant volume was only 2.12 FV. This indicated that the larger the polymer MW was, the smaller the gelant volume was that needed to be injected when the gelant filled the fracture.

Table I. Required FVs of Gelants with Different Polymer MWs When the Normalized Chromium Concentration Reached 1

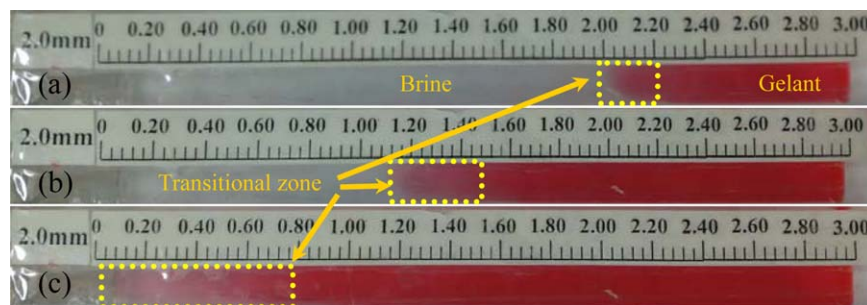| MW (kDa)	0	5000	8000	12,000	17,000
Required FV	3.07	2.59	2.36	2.12	1.89

Figure 6. Propagation states of the gelant with different injection volumes: (a) 0.30, (b) 0.55, and (c) 0.80 FV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Another phenomenon was that there was a similar critical injected FV (1.2 FV) when the polymer MWs were different. When the injected volume was lower than 1.2 FV, after the chromium began to be produced from the fracture outlet, the chromium concentration decreased with increasing polymer MW; on the contrary, it increased with increasing polymer MW after the injected gelant volume exceeded 1.2 FV. The increase in the polymer MW improved the gelant viscosity and further decelerated the diffusion rate of chromium from gelant to brine; therefore, the capture effect of the polymer molecules and the dilution action of brine on Cr^{3+} were mainly attributed to this phenomenon. At the beginning of the gelant injection, when the gelant with low polymer MW was injected, the gelant was easily diluted by the brine, and the diffusion rate of chromium was relatively high. Therefore, chromium was more easily produced from the fracture. With increasing the polymer MW, both the capture effect of the polymer molecules on Cr^{3+} and the dilution action of the brine were accelerated, and this resulted in delayed chromium production. Moreover, the required gelant volumes calculated from the initial production to the final production of chromium (the normalized chromium concentration reached 1) varied when the polymer MWs were different. When the polymer MW was 5000 kDa, the required gelant volume was 1.88 FV, as shown in Table I; it was reduced to only 0.95 FV when the polymer MW was increased to 17,000 kDa. This also proved that the antidilution properties of gelant were intensified with increasing polymer molecules.
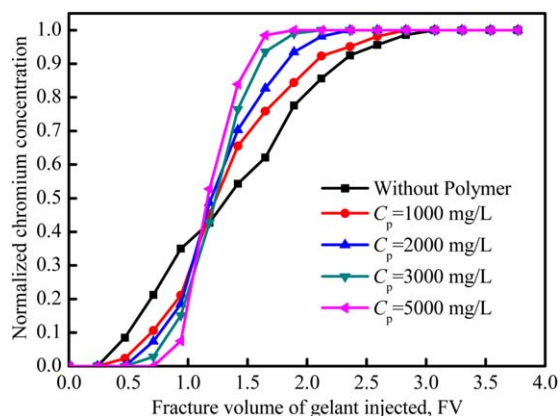
To further investigate the propagation behavior of the gelant in the fractures, a gelant that consisted of 3000 mg/L polymer and 357.5 mg/L Cr^{3+} was injected into a visual fractured model with a fracture width of 2 mm. The polymer MW was 12,000 kDa, and the gelant was dyed red before the experiments. Figure 6 shows the different propagation states of gelant when the injection volumes were 0.30, 0.55, and 0.80 FV, respectively. Three zones were divided during the gelant propagation along the fracture: the gelant zone, the transitional zone, and the brine zone. With the injected gelant volume increasing from 0.30 to 0.80 FV, the volume of the transitional zone gradually became bigger, from 0.24 to 0.76 mL. The diffusion of polymer/chromium and the brine dilution effect were responsible for this phenomenon, and it also proved the discussion of previous experiments.

Effect of C_p. C_p also had a great effect on the gelant propagation and diffusion behaviors. Figure 7 shows the normalized chromium concentrations of fluids produced from the fracture outlet when the C_ps were 1000, 2000, 3000, and 5000 mg/L, respectively. The MW of the polymer was 12,000 kDa, and chromium solution without a polymer was used as a contrast. The change trend of the normalized chromium concentration versus the FV injected curve was similar to that shown in Figure 5. The chromium began to be produced after a certain volume of gelant was injected. The bigger the polymer MW was, the later the chromium began to be produced. On the contrary, the bigger the polymer MW was, the earlier the normalized chromium concentration reached 1. This was due to the fact that the apparent viscosity of the gelant was sharply improved with the increase in C_p. On one hand, the capture effect of the polymer molecules on chromium became more serious, and this resulted in a decrease in the diffusion rate of chromium. On the other hand, when C_p was high, the gravitational differentiation of the gelant in fracture was slight, the propagation profile of the gelant tended to be uniform, and the gelant was uneasily diluted by the brine.[10,28] Therefore, the chromium initial production was delayed, and the final production was advanced compared with that of the gelant with low C_p. The data in Table II show that when C_p was 1000 mg/L, about 2.83 FV gelant was required to be injected when the normalized chromium concentration reached 1, but only 1.65 FV of gelant was required when C_p was 5000 mg/L.

Figure 7. Normalized chromium concentrations of fluids produced from the fracture outlet when the C_ps were different. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Required FVs with Different C_ps When the Normalized Chromium Concentration Reached 1

Concentration (mg/L)	0	1000	2000	3000	5000
Required FV		3.07	2.83	2.36	2.12	1.65

Figure 7 shows that there was also a similar critical injected gelant volume when the C_ps of the gelants were different. When the injected FV was lower than 1.15 FV, with increasing C_p, the chromium concentration in the produced fluid decreased. However, after the injected gelant volume exceeded 1.15 FV, the chromium concentration in the produced fluid increased with the enhancement of C_p. The diluting effect of the formation brine, the diffusion of the chromium, and the retarding effect of the polymer were responsible for this phenomenon. As mentioned previously, the higher the C_p was, the weaker the diluting effect was, and then, the lower the diffusion rate of chromium became. Therefore, with increasing C_p in the gelants, less chromium diffused into the formation brine and matrix, and thus, the chromium produced at the initial injection stage was relatively low.

To visually observe the propagation states of the gelants in the fractures, gelants with C_ps of 1000, 3000, and 5000 mg/L, respectively, were prepared and injected into a visual fractured model with a fracture width of 2 mm. All of the injection volumes of three gelants were 0.5 FV, and the results are shown in Figure 8. When C_p was 1000 mg/L, the volume of the transitional zone was 0.65 mL; with increasing C_p to 3000 and 5000 mg/L, the volumes of the transitional zone gradually decreased to 0.36 and 0.25 mL, respectively. This observation proved that the higher the C_p of the gelant was, the weaker the brine dilution effect on the gelant was. Moreover, the chromium diffusion rate was decelerated with increasing C_p.

Chromium Diffusion Profile along the Fracture. The chromium diffusion profile was studied during gelant propagation along the fractures. Figure 9(a,b) presents the chromium profiles measured at the top and bottom of the fracture when the normalized chromium concentrations were 0.5 and 1.0, respectively. Meanwhile, the experimental data were regressed with data fitting with a zero intercept. When the normalized chromium concentration was 0.5, eqs. (1) and (2) could be used to express the chromium diffusion profiles along the fracture:

$$V_{Cr} = 0.02651 L^{1.05076} \tag{1}$$

$$V'_{Cr} = 0.01649 L^{1.13372} \tag{2}$$

where L is the distance from the fracture inlet (cm), V_{Cr} is the gelant volume required to obtain the chromium subprofile at the top of fracture (FV), and V'_{Cr} is the gelant volume required to obtain the chromium subprofile at the bottom of fracture (FV).

Similarly, when the normalized chromium concentration was 1.0, the chromium diffusion profiles measured at the top and bottom of the fracture could be expressed with eqs. (3) and (4).

$$V_{Cr} = 0.04505 L^{1.04891} \tag{3}$$

$$V'_{Cr} = 0.03594 L^{1.07475} \tag{4}$$

The effect of gravity action was mainly responsible for the difference between V_{Cr} and V'_{Cr}. Under the effect of gravity action, the gelant tends to flow along the bottom of the fracture[29]; therefore, when the distances from fracture inlet to sample points at the fracture top and bottom are same, the chromium concentration of the fluid sampled at the fracture bottom is correspondingly high. Figure 9 also indicates that with the increase in the gelant injection distance away from the fracture inlet, the difference between V_{Cr} and V'_{Cr} was enlarged. In addition to the effect of gravity action, the disproportionate diffusion of chromium ions near chromium profiles was one of the main reasons. The longer the distance from the sample point to the fracture inlet was, the more serious the dilution degree of brine on the gelant was. Therefore, the diffusion rate of chromium increased because of the low viscosity of the gelant, and it contributed to the enlargement of the difference between V_{Cr} and V'_{Cr}.

The difference between eqs. (3) and (1) or between eqs. (4) and (2) reflected the required volume of gelant to increase the normalized chromium concentration from 0.5 to 1.0 at the fracture top or bottom. We also found that when the injection distances of the gelant were same, the difference between V_{Cr} and V'_{Cr} shown in Figure 9(b) was larger than that shown in Figure 9(a), and this indicated both the effect of gravity action and the disproportionate diffusion of chromium at the measured profile became more serious with increasing injection volume.

Barrier Effect of the Polymer on Chromium Diffusion into the Matrix
Effect of the Polymer MW. During gelant propagation along the fractures, the chromium ions not only diffused from the gelant into the formation brine but also diffused from the fracture into
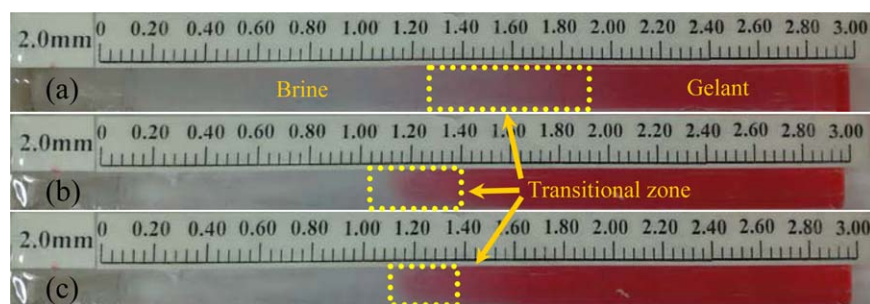

Figure 8. Propagation states of gelants with different C_ps: (a) 1000, (b) 3000, and (c) 5000 mg/L. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
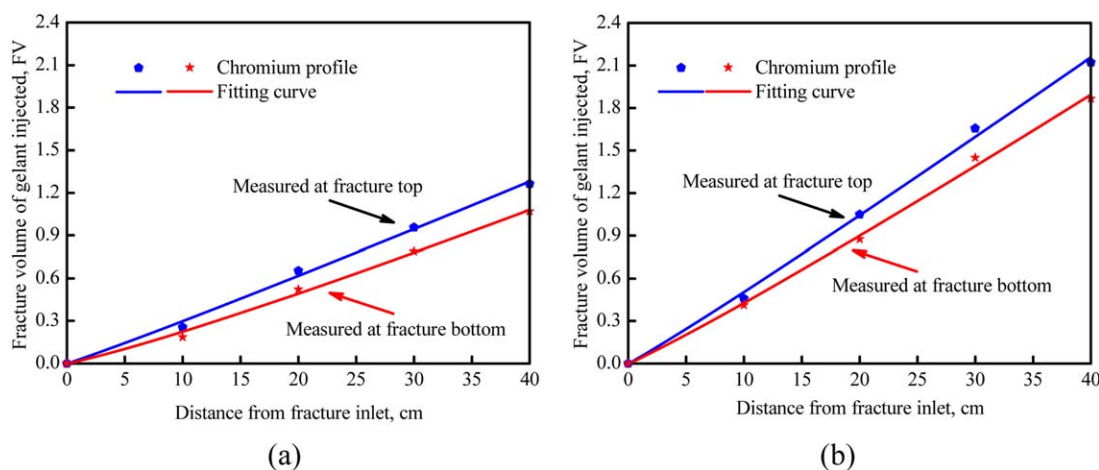
Figure 9. Chromium profiles along the fracture during the gelant injection with normalized chromium concentrations of (a) 0.5 and (b) 1.0. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the adjacent matrix.[18] To explore the effect of the polymer MW on the diffusion behavior of chromium from the fracture into the adjacent matrix, three kinds of polymers with polymer MWs of 5000, 8000, and 12,000 kDa, respectively, were used with 357.5 mg/L chromium to prepare the gelants, and chromium solution without the polymer was also prepared as a contrast. During the injection of gelants and chromium solution into fractures, fluids that leaked off from gelants into matrix were collected at matrix outlets, and the chromium concentrations of the produced fluids were measured and are plotted in Figure 10.
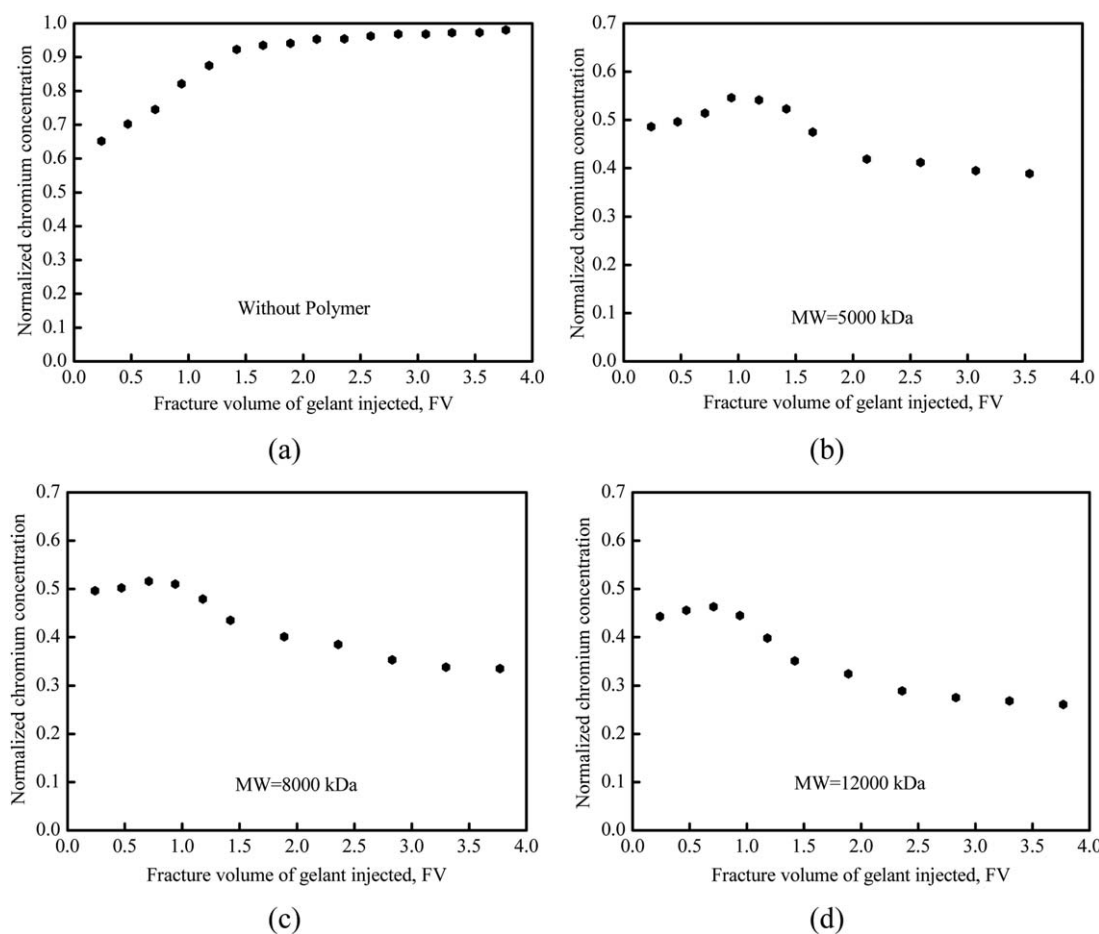

Figure 10. Normalized chromium concentrations of fluids produced from the matrix outlet when the polymer MWs were different.
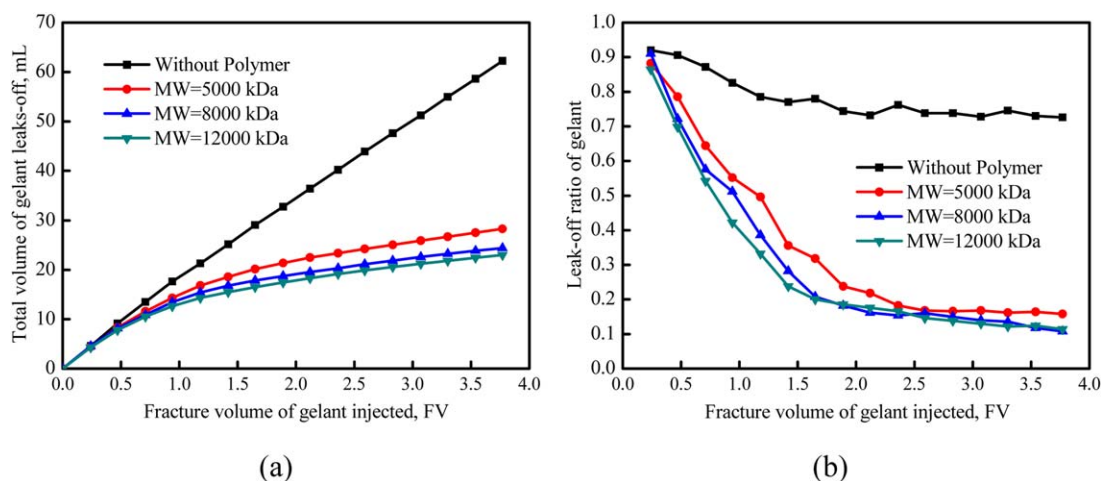
Figure 11. Leak-off volume and leak-off ratio of gelants when the polymer MWs were different. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 10(a) shows that when only chromium was injected into fracture, with increasing injection volume, the normalized chromium concentration first increased and then leveled off. When the polymer was injected together with chromium, the concentration curve first increased, then decreased, and finally leveled off. The difference between the two change trends indicated the different diffusion behaviors of chromium in the gelants and in the chromium solution. When only chromium was injected, chromium ions easily diffused into the matrix along with water because of the concentration and pressure differences. In the initial stage of the diffusion process, some chromium ions adsorbed on the sand surfaces and remained in the matrix pores, and this resulted in the chromium concentration decline in the fluids that were produced early.[30] After a period of gelant leak-off, the degree of adsorption and retention of chromium ions in the matrix declined and finally reached a stable state; therefore, the chromium concentration curve showed a changed trend that first increased and then leveled off. When the polymer was added, because of the higher MW, although few polymer molecules could penetrate into the matrix pores, most of them were adsorbed and accumulated on the fracture surface to form a polymer aggregation layer.[31] At the initial gelant injection, chromium ions easily diffused into the matrix because of the thinness of the polymer layer; with the gradually formation of the polymer leak-off layer, both the gelant leak-off rate and the chromium diffusion rate decreased because of the barrier effect of the polymer layer. Therefore, the chromium concentration in the produced fluid sampled during the later injection stage first decreased and then stabilized.

Figure 10 also reflects that with increasing polymer MW, the diffusion degree of chromium ions from fracture into the matrix decreased. Figure 10 shows that the initial chromium concentrations of both of the produced fluids were about 0.49 when the polymer MWs were 5000 and 8000 kDa, but it decreased to about 0.42 when the polymer MW was 12,000 kDa. The main reason was that the capture effect of the polymer molecules with high MW on chromium ions was strong, and this led to a low diffusion rate of chromium ions. There-

fore, the initial chromium concentration in the produced fluids was low. When the polymer MWs were 5000, 8000, and 12,000 kDa, respectively, the final concentrations of chromium ions after 3.77 FV of gelant was injected were 0.389, 0.335, and 0.261, respectively. This demonstrated that with increasing polymer MW, the diffusion rate of the chromium ions decreased. To further explore the effect of the gelant on the chromium diffusion in the matrix, the leak-off volume and leak-off ratio of gelant were calculated during the gelant leak-off from fracture into the matrix, and the results are shown in Figure 11. It shows that the addition of polymer sharply reduced the degree of gelant leak-off. When only 3.77 FV of chromium solution was injected, the leak-off ratio of gelant was about 0.72; it was reduced to 0.16 when the polymer MW was 5000 kDa, but it changed slightly after the polymer MW exceeded 8000 kDa.

As mentioned previously, both the gelant leak-off and the chromium diffusion from fracture into the matrix were closely related to the formation of the polymer leak-off layers. Polymer leak-off layers formed on the fracture face after the gelant injection was observed when the polymer MWs were 5000, 8000, and 12,000 kDa, respectively, and microscopic images (magnified 500 times) were obtained, as shown in Figure 12(a–c). This obviously showed that the polymer layer became thicker with increasing polymer MW. When the polymer MW was 5000 kDa, some pores and cavities of the matrix still appeared after gelant injection, but they were gradually packed when the polymer MW increased to 8000 and 12,000 kDa; meanwhile, the polymer layer also gradually became thick and rigid; this sharply reduced the diffusion of chromium ions and the degree of gelant leak-off. The result of the visual images was consistent with that of the injection experiments.

Effect of C_p. Figure 13 illustrates the change trends of the normalized chromium concentrations in fluids produced from the matrix outlets when the C_ps were 1000, 2000, 3000, and 5000 mg/L, respectively. This showed that when C_p was 1000 mg/L, the chromium concentration in the produced fluids first increased and then continually decreased. When C_p increased to 2000 mg/L or higher, the change trend of the
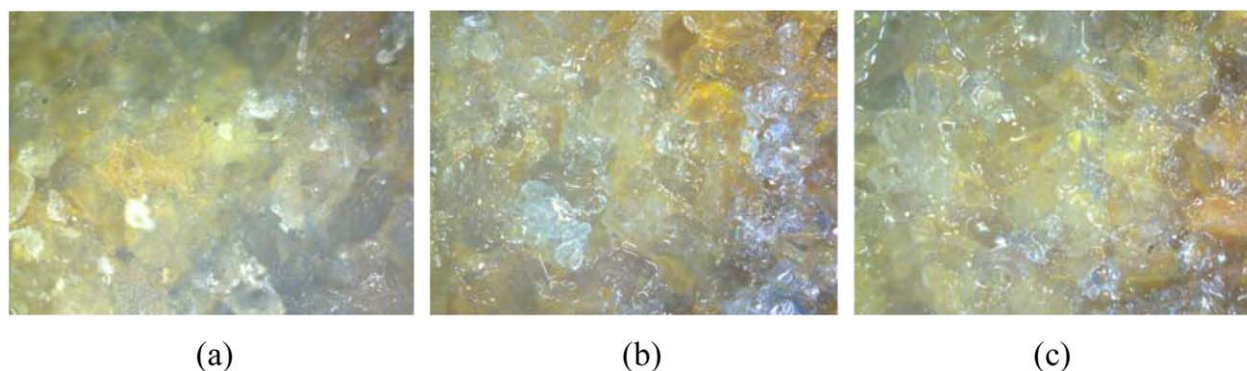
Figure 12. Microscopic images of polymer leak-off layers when the polymer MWs were different (magnification = 500×): (a) 5000, (b) 8000, and (c) 12,000 kDa. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chromium concentration curve first increased, then declined, and finally stabilized. Similar to the discussion of the last Effect of the Polymer MW section, the first increase in the chromium concentration in the produced fluids at the initial injection stage was due to the initial adsorption and retention of chromium ions in the matrix. Microscopic images (magnified 500 times) were obtained to investigate the polymer leak-off layers formed on fracture faces when the C_ps were different, as shown in Figure 14. Figure 14(a) presents that the polymer layer on

the fracture face was relatively thin when C_p was only 1000 mg/L. The barrier effect of this thin polymer layer on the chromium diffusion from the fracture into the matrix was weak, and it was one of main reasons for the continuous decline of the chromium concentration curve. When C_p increased to 3000 and 5000 mg/L, the polymer layers obviously became thick, and meanwhile, most of the pores and cavities of the matrix were fully packed, as shown in Figure 14(b,c). Therefore, the later chromium diffusion was retarded and finally stabilized.
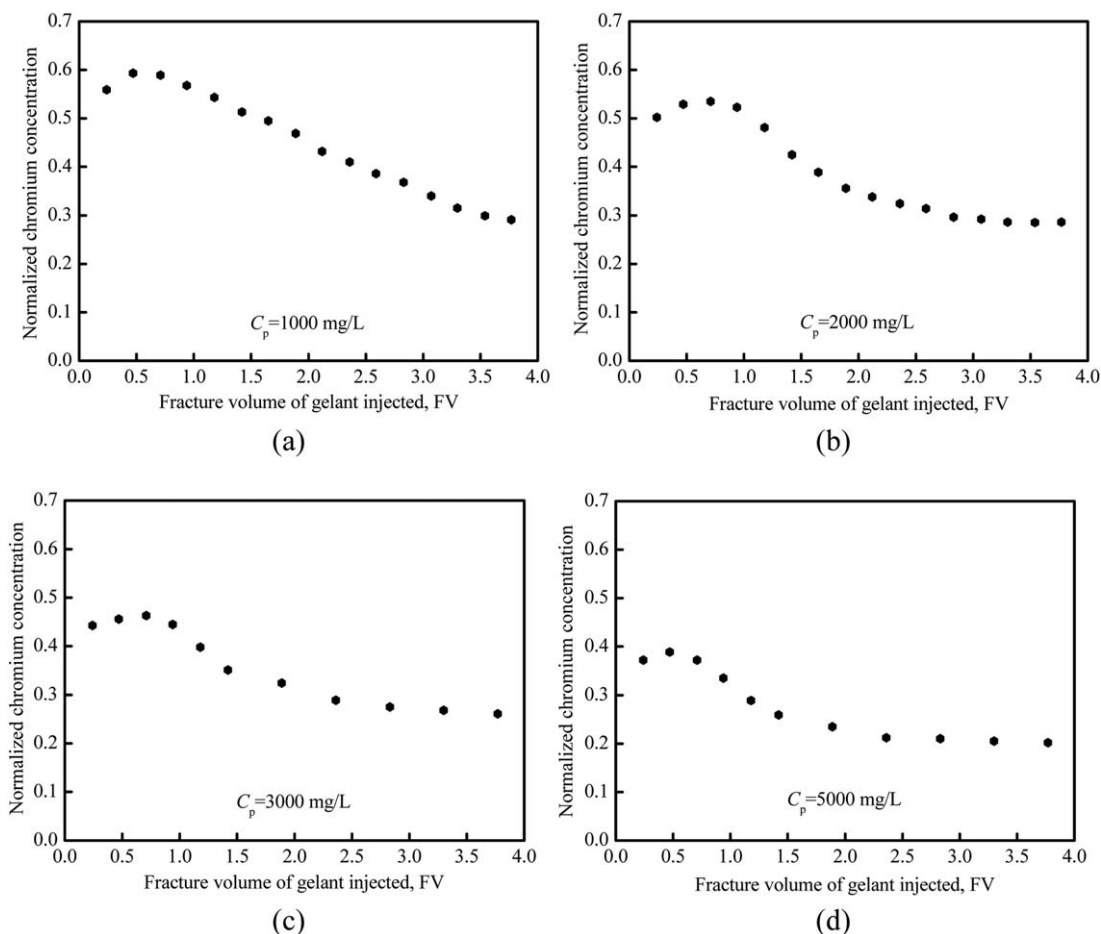

Figure 13. Normalized chromium concentrations of fluids produced from the matrix outlet when the C_ps were different.
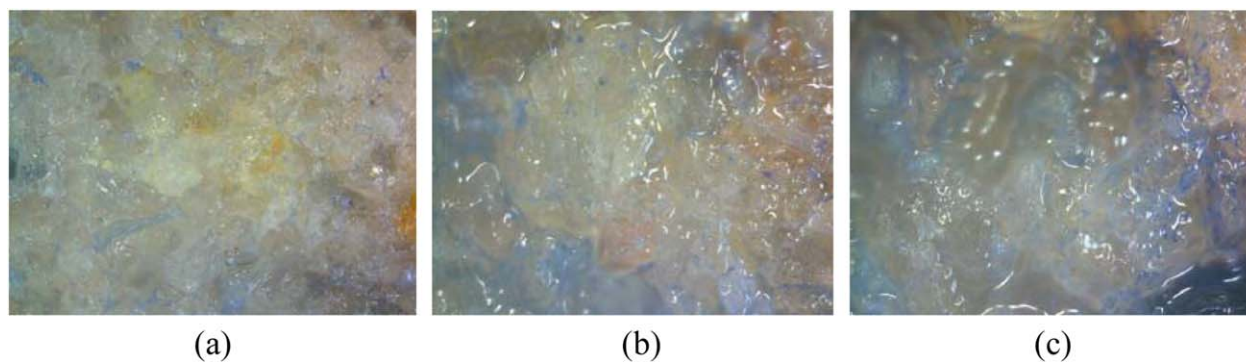
Figure 14. Microscopic images of the polymer layers when the C_ps were different (magnification = 500×): (a) 1000, (b) 3000, and (c) 5000 mg/L. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Because of the difficult penetration of polymer molecules from the fracture into the matrix, only a small amount of polymer molecules could leak off and be produced from the matrix outlets, and the formation of the polymer leak-off layer further reduced the penetration of polymer molecules into the matrix. In contrast, chromium ions could easily diffuse through the matrix as long as they could pass through the polymer leak-off layer. Figure 15 illustrates the leak-off volume and leak-off ratio of the gelants when the C_ps were 1000, 2000, 3000, and 5000 mg/L, respectively. The MW of polymer was 12,000 kDa. It showed that the leak-off degree of the gelant decreased with increasing C_p, but the decreasing rate was gradually reduced. The data also show that the final leak-off ratio of the gelant became stable after certain volumes of gelant were injected; that is, part of gelant still leaked off from the fracture into the matrix after the formation of the polymer leak-off layer, and this resulted in the continual but stable diffusion of chromium ions.[32] Moreover, the change trend of the gelant leak-off was consistent with that of the chromium diffusion rate, and this proved that the diffusion of chromium ions from the fracture into the matrix was always accompanied with the gelant leak-off.[33]

Chromium Diffusion Profile along the Matrix. During the diffusion process of chromium ions from the fracture into the matrix, some chromium ions adsorbed onto sand surfaces, and

some of them remained inside the matrix pores; therefore, the measured chromium concentration in the fluids produced from the matrix outlets was lower than the full diffusion concentration of chromium from the gelants. Moreover, because of the pressure and concentration changes along the fracture, the diffusion degree of chromium ions varied along the fracture, and this resulted in different diffusion rates of chromium ions along the matrix adjacent to the fracture.[34] The chromium diffusion profiles along the matrix were investigated on the basis of the chromium concentration change in the produced fluids.

Figure 16 illustrates the normalized chromium concentrations in fluids produced from the matrix outlets when the injected gelant volumes were 1, 2, and 3 FV, respectively. This showed that when the injected gelant volume was certain, when the distance from the sample point to the fracture inlet increased, the concentration of chromium ions in the produced fluids continually decreased. This reflected the fact that the diffusion degree of chromium ions from the fracture into the matrix decreased with the increase in the injection distance of the gelant. Figure 16 also indicates that with the increase in the injection volume, the chromium concentration in the produced fluids showed a decreasing change trend within the 20 cm L, but it increased without this distance. The different states of the polymer leak-off layer along the fracture were mainly attributed to this
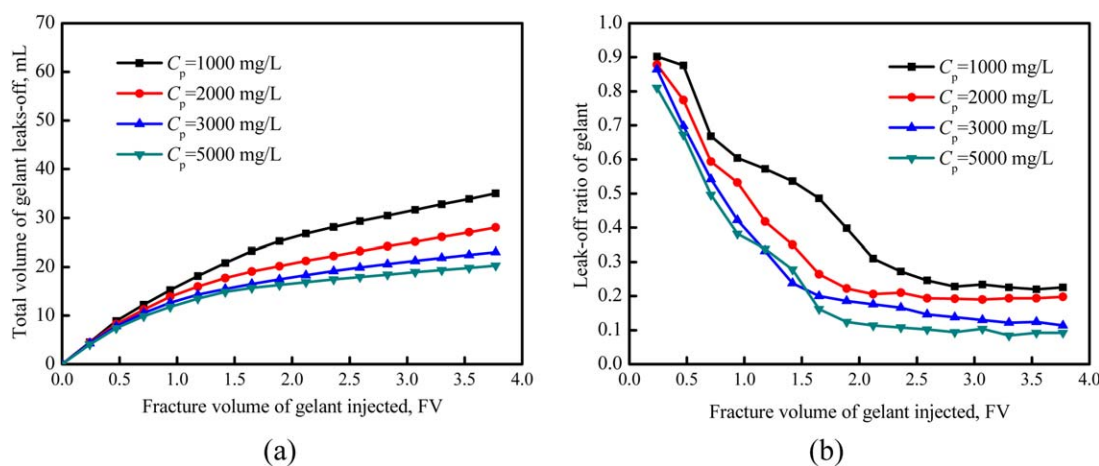

Figure 15. Leak-off volume and leak-off ratio of gelants when the C_ps were different. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
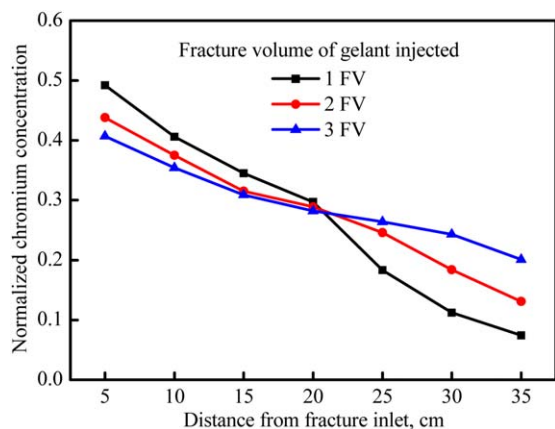
Figure 16. Chromium profile along the matrix during gelant injection. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

phenomenon. When the injected gelant volume was relatively small (1 FV), because of the relatively high injection pressure and the initial formation of the polymer layer near the fracture inlet, both the leak-off ratio of the gelant and the diffusion rate of chromium ions were relatively high. With increasing gelant injection, the polymer layer on the fracture face near the fracture inlet was gradually formed, and the diffusion rate of chromium ions was correspondingly reduced because of the barrier effect of the polymer layer. On the contrary, at the initial injection stage, both the degree of gelant leak-off and the diffusion rate of chromium were relatively low near the fracture outlet. After several volumes of gelant were injected, because of the reduction of polymer leak-off near the fracture inlet, a part of the gelant and chromium ions were forced to leak off from the matrix near the fracture outlet. According to the data shown in Figure 16, it was reasonable to think that the concentrations of chromium ions in the fluids produced from outlets along the matrix finally became the same; that is, the normalized chromium concentration finally did not vary with the change in L, and this reflected the fact that the diffusion equilibrium of chromium ions in matrix were obtained after a period of gelant injection.

CONCLUSIONS

First, the capture effect and the barrier effect are two main affecting mechanisms of polymer molecules on chromium ions in the gelant. The capture effect decreased the diffusion rate of chromium ions from the gelant into the brine, and the barrier effect reduced the diffusion rate of chromium ions from the fracture into the matrix. Moreover, the formation of the polymer leak-off layer onto the fracture face and into the adjacent matrix was responsible for the barrier effect.

Second, when the polymer MW and C_p increased, because of the capture and barrier effects of the polymer on chromium ions, both the diffusion rate of chromium ions from the gelant into brine and that from the fracture into the matrix were sharply reduced; meanwhile, the leak-off degree of gelant also decreased.

Third, the chromium production was closely related to the injected gelant volume because of the effect of the polymer on the diffusion of chromium ions. When the injected volume was lower than the critical injected volume, the chromium concentration of fluids produced from the fracture or matrix outlets decreased with increasing polymer MW; on the contrary, it increased with when the polymer MW increased.

Fourth, the chromium production was also closely related to the polymer MW and C_p. The bigger the polymer MW or concentration was, the later the chromium began to be produced, and the earlier the normalized chromium concentration reached 1.

Fifth, under the effects of gravity action and the disproportionate diffusion of chromium ions, there was a difference between the chromium subprofiles measured at the top of the fracture and that measured at the bottom of the fracture along the fracture, and the difference was enlarged with increasing injection distance of the gelant.

Finally, the chromium diffusion profile along the matrix varied with increasing injected volume of the gelant. It finally did not change along the matrix, and the diffusion equilibrium state of chromium ions in the matrix was obtained after a period of gelant injection.

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