The Effect and Analysis on Cr^{3+} Gel Improving Profile Control in Alkalescent Alkaline/Surfactant/Polymer Flooding

Xiangguo Lu, Lanlan Zhao, Ke Zhang

Key Laboratory on Enhanced Oil and Gas Recovery of Ministry of Education of China, Daqing Petroleum Institute, Daqing 163318, People's Republic of China

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ABSTRACT: The emulsification of produced fluid and the scaling along production system have always been one of the most difficult problems in NaOH/surfactant/polymer flooding. To decrease those influences on production, the pilot test of Na_2CO_3/surfactant/polymer flooding was developed in Daqing Oilfield. The results show fluid emulsification and scaling of production system were prevented effectively, but scaling along the injection system appeared and reservoir heterogeneity was aggravated. This is becoming a new technical problem. By analyzing scaling mechanism and the property of profile control agent, the author presents a technical solution that using Cr^{3+} polymer gel is improving fluid entry profile of injection well in Na_2CO_3/surfactant/polymer flooding. Optimization of formula and evaluation of its property and its compatibility with Na_2CO_3/surfactant/polymer flooding system were investigated and a pilot test was conducted in well B2-1-P56 of Daqing Oilfield. The results shows polymer gel has dual function, i.e., removing scale and plugging off high permeability zone. The scale in the instrument of injection, pipes and well-side of wellbore is thoroughly cleared up. The fluid entry into high permeability layer is decreased from 100 to 64.9%, and fluid entry in low and intermediate permeability layer is increased from 0 to 35.1%. The profile control of injection well is effectively improved. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2773–2780, 2009

Key words: compatibility; cross-linking; dynamic light scattering; macroporous polymers; microstructure

INTRODUCTION

Alkali/surfactant/polymer (ASP) is a new technique of enhanced oil recovery after polymer flooding. At present, industrial pilot test and application of ASP is or will be implemented in most oilfields, mainly in Daqing. Aiming at scaling problems in injection instruments of strong alkali ASP flooding,[1–3] the study and application of weak ASP is appreciated by petroleum technical workers. The industrial pilot test of weak alkali (Na_2CO_3) ASP flooding is firstly developed in Beisanxi area of Daqing Oilfield, to evaluate the effect of enhanced oil recovery and the condition of scaling of weak alkali ASP prepared by α-alkene petroleum sulfonates.[4]

The pilot test was started from August 3, 2002. A slug of 0.018 pore volume (PV) of polymer solution was firstly injected as preflush fluid. Main slug of 0.315 PV weak alkali ASP system was injected form November 8, 2002. The pilot test is still in process now. The current production statistics shows the stage oil recovery is increased by 13.23%, and oil production is considerably enhanced. However, some problems are also exposed in pilot test such as scaling along injection system and aggravation of reservoir heterogeneous. Effective techniques of scale cleaning and profile control are urgently needed.[5,6] Based on the analysis of mechanism of scaling in weak alkali ASP flooding and characterization of present profile control technique, the author proposes a technique to use Cr^{3+} polymer gel to improve the entry profile of injection well in weak ASP flooding. Formula optimization, property evaluation and compatibility of polymer gel with weak alkali ASP system were studied through experiments. A pilot test was implemented and its effect was evaluated.[7]

THE COMPATIBILITY BETWEEN CR^{3+} GEL AND WEAK ALKALI ASP SYSTEM

When Cr^{3+} gel is used in the injection well of weak alkali ASP, Cr^{3+} gel is bound to contact with weak alkali ASP. Whether they are compatible influences not only the effect of profile control of polymer gel, but also the increment of oil production of weak alkali ASP. As an extreme case, organic chromium is

Correspondence to: L. Zhao (zhaolanlan840806@163.com).

TABLE I
The Results of Water Quality Analysis

Ion composition (mg/L)	Ca^{2+}	Mg^{2+}	Na^{+}	CO_3^{2-}	HCO_3^{-}	CL^{-}	SO_4^{2-}	Salinity
Produced water	32.1	7.30	1265.0	210.1	1708.6	780.1	9.6	4012.7
Fresh water	34.1	24.3	231.2	90.0	225.1	88.7	36.0	729.3

directly added into weak alkali ASP system. Cr^{3+} gel directly contacts with weak alkali ASP. The property of weak alkali ASP system is tested and the compatibility between Cr^{3+} gel and weak alkali ASP system is evaluated.

MATERIALS

Polymer is partially hydrolyzed polyacrylamide from Daqing Reagent Factory, China, the active content and hydrolysis of which are 90.48 and 24.02%, respectively. Its viscosity averaged molecular weight is 25×10^6. Alkali was sodium carbonate (Na_2CO_3) and its active content was 98%. Surfactant is α-alkene petroleum sulfonates from Dong Hao corp. of Daqing Petroleum Administration Bureau and used in Beisanxi pilot of Daqing Oilfield. Its active content is 50% and other components include salt, alcohol and water. Cross-linking agent is chromium acetate [Cr ($CH_3COO)_3$] whose active content of which is 2.7%. Fresh water and produced water are all from the third oil production factory of Daqing oilfield. Water quality is shown in Table I. Core is made of quartz sand and epoxy resin through cementation. The size of cylindrical core is $\Phi 0.025 \times 0.1$ m. Average Permeability (K_g) is from 0.9 to 1.0 μm^2.

APPARATUS

TC-201 Brookfield viscometer is used to measure viscosity. Model HJ-6 Magnetic stirring apparatus agitated polymer solutions. All the samples are placed in the model HW-III incubator. Model Hake 100 rheological instrument, model XZD-3 interfacial tension instrument and electronic balance are also used in this experiment. Model 668 vacuum chambers saturated cores. And other ancillary instruments are vacuum pumps and microbe checkout test set, etc.

TABLE II
Chemical Composition of ASP System

No.	Polymer (mg/L)	Surfactant (%)	Podium carbonate (%)	Cr^{3+} (mg/L)
1	1400	0.25	1.2	–
2	1400	0.25	1.2	140.0
3	1400	0.25	1.2	70.0
4	1400	0.25	1.2	35.0
5	1400	0.25	1.2	17.5

EXPERIMENTAL PROGRAM

To evaluate the flooding effect, six kinds of ASP system are designed in this experiment (see Table II). For each of them, the parameters including viscosity, interfacial tension, resistance factor, residual resistance factor, viscoelasticity, and profile control effect are tested regularly.

EXPERIMENTAL

According to Table II, five types of ASP solutions are made up and the viscosity and interfacial tension are tested regularly;

Resistance factor and residual resistance factor of five kinds of ASP solutions are tested regularly;

Rheology and viscoelasticity of five kinds of ASP system is tested regularly by model Hake 100 rheological instrument;

"System 1" and "system 2" are chosen to do the experiment of core flooding and oil recovery is compared.

RESULTS AND DISCUSSION

Viscosity

The relationship of viscosity of ASP system versus time is shown in Figure 1. Figure 1 shows that the viscosity of all of five kinds of ASP solution increases at first. However, with time increasing, the

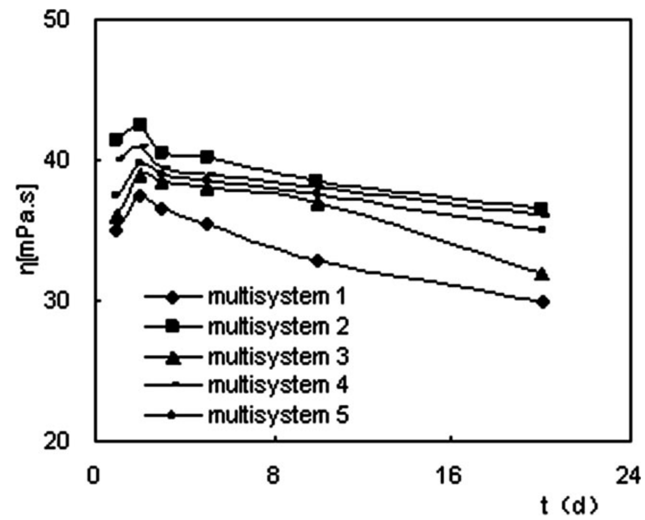

Figure 1 The relative curve of system viscosity and time.

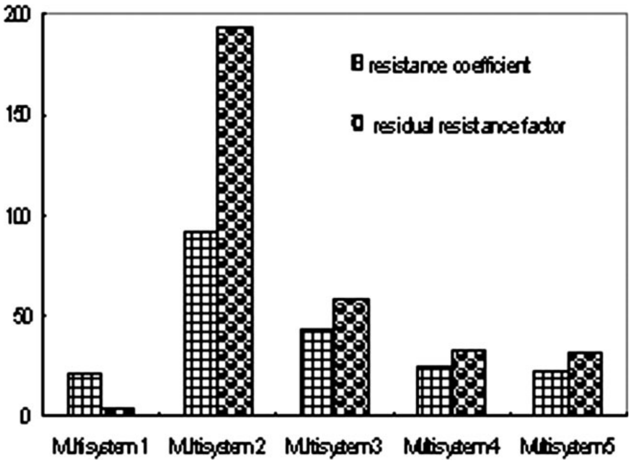

Figure 2 The bar chart of resistance factor and residual resistance factor.

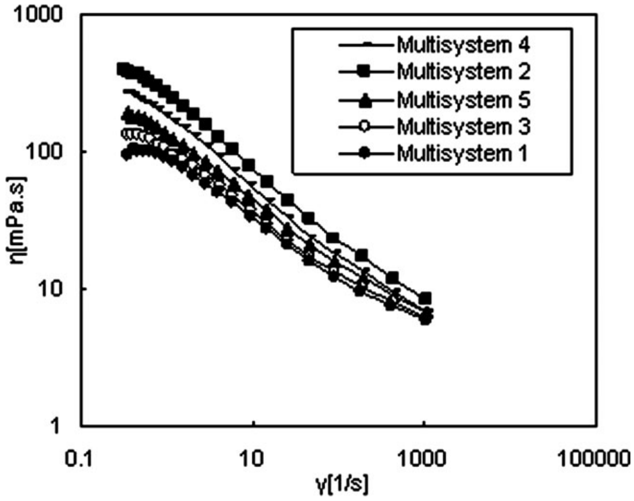

Figure 4 The rheological characteristic of the five systems.

viscosity of them decreases slowly from 3rd to 20th day. Seen from the final value, the viscosity of ASP system with Cr^{3+} is higher than that of common ASP. The sequence of final value of them is as follows: "system 1"<"system 3"<"system 5"<"system 4"<"system 2." We can see that Cr^{3+} has no any influence on the viscosity of ASP system, and on the contrary it can increase viscosity to some extent.

Resistance factor and residua resistance factor

To illustrate the influence of Cr^{3+} on the flow property of ASP system, resistance factor and residual resistance factor are selected as evaluation indexes.

The result of the resistance factor and residual resistance factor of the five systems is shown in Figure 2.

Seen from Figure 2, the ion of Cr^{3+} has great influence on resistance factor and residual resistance factor of ASP system. The resistance factor and residual resistance factor of system with Cr^{3+}, including "system2," "system3," "system4," "system5," is higher than that of system without Cr^{3+} (system1). The result shows that addition of the ion of Cr^{3+} leads to cross-linking the molecular chains of polymer in ASP system. Besides, reaction mainly happens in different branch chain of same one polymer molecular, forming polymer gel by intramolecular cross-linking. That phenomenon causes the retention of ASP in pore media increasing and flow resistance increases. So, mobility control ability is improved obviously.

Interfacial tension

The relationship of interfacial tension versus time is shown in Figure 3.

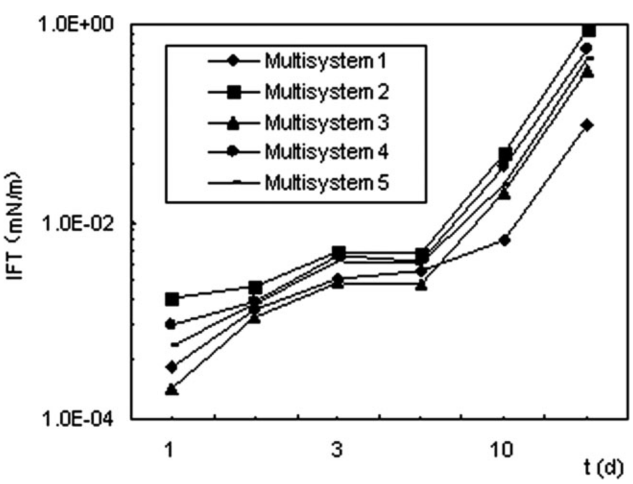

Figure 3 The relationship curve of interfacial tension versus time.

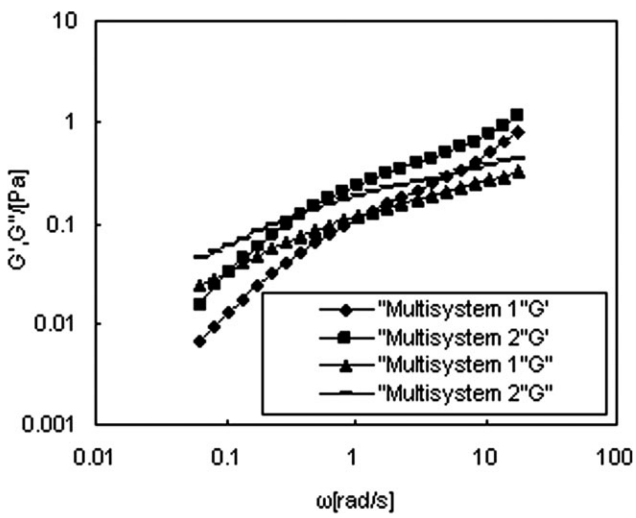

Figure 5 The viscoelasticity curve.

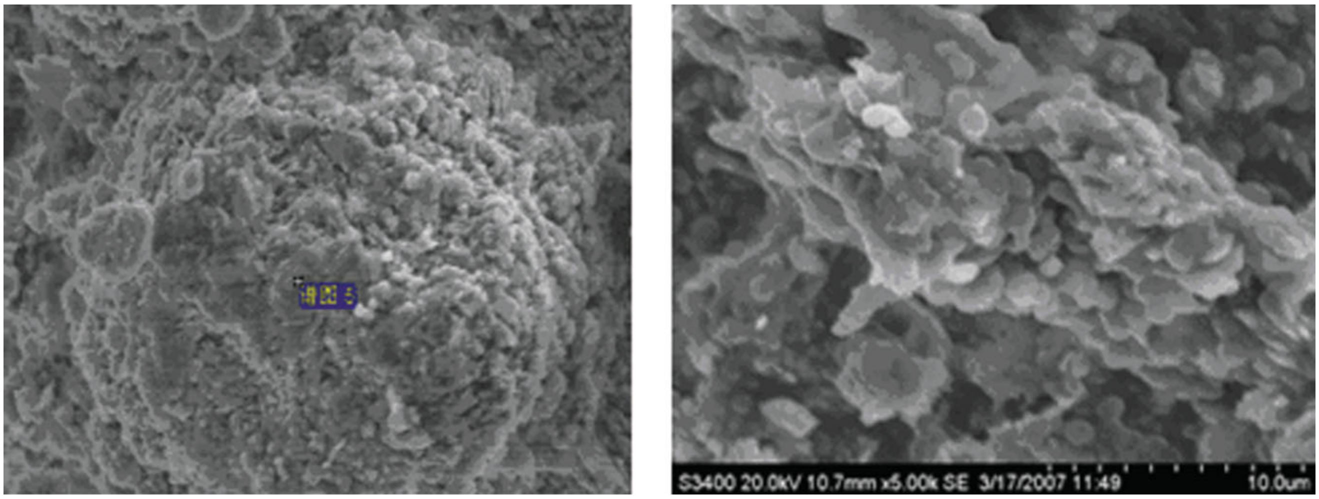

Figure 6 SEM image of calcium scale. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The ion of Cr^{3+} has influence on interfacial tension of ASP system, showing in Figure 3. The interfacial tension between combination system and crude oil is low at first (First–Fifth day). However, interfacial tension increases from 5th to 20th day. The data show the ion of Cr^{3+} can increase the interfacial tension, but the influence is very small.

Rheology and viscoelasticity

The rheological characteristic is shown in Figure 4.

Seen from Figure 4, with sheer rate increasing, the viscosity of five kinds of system decreases. The viscosity of ASP with ion of Cr^{3+} is higher than that of "pure" ASP system. As a result, ion of Cr^{3+} do not affected the property of non-Newtonian fluid of ASP.

The curve of viscoelasticity is shown in Figure 5. (G′) stands for storage modulus and (G″) stands for loss modulus.

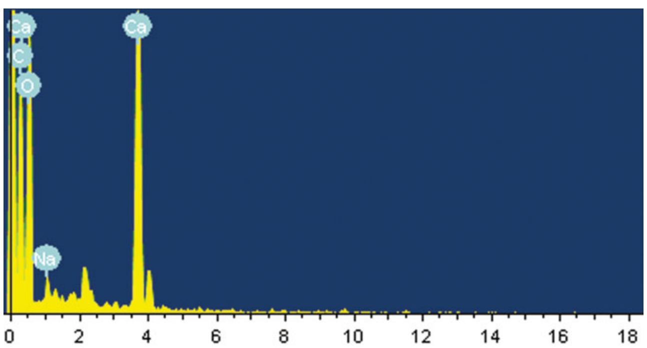

Figure 7 EDS spectrum of calcium scale. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Seen from Figure 5, with angular frequency increasing, storage modulus and loss modulus of "system1" and "system2" gradually increase. Storage modulus and loss modulus of "System2" added by ion of Cr^{3+} is higher than that of "system1." Ion of Cr^{3+} can lead to cross-linking of branch chains of polymer molecule; causing the viscosity of system increasing and mobility control ability improving. Further analysis shows that, there is a cross point between the curves of storage modulus and the curves of loss modulus. When the value of angular frequency is lower than that at the cross point, loss modulus is higher than storage modulus. Otherwise, storage modulus is higher than loss modulus.[8,9]

Analysis of the composition of scale

Excessive hydrochloride is added to scale sample and they interact dramatically, a large amount of bubbles was produced. The scale dissolved completely in a short time. Test shows the produced gas is carbon dioxide. So we can deduce that the scale contains large amount of carbonate.[10,11] To further determine its chemical composition, scanning electron microscopy (SEM) is made. The picture of SEM is shown in Figure 6.

TABLE III
Weight and Atom Percentage of Calcium Scale

Element	Quality percentage	Atomic percentage
C K	29.22	38.86
Ca K	15.22	6.07
Na K	1.30	0.90
O K	54.25	54.17
Total	100.00	100.00

TABLE IV
Relationship Between Concentration of Calcium Ion and Time (mg/L)

No.	t/d 1d	30d
Sample 1	2.39	2.39
Sample 2	0.15	0.19
Sample 3	0.24	0.31
Sample 4	2.30	2.11
Sample 5	2.94	12.65

Seen from Figure 6, crystal size is very small. On the macro, it is thick flakes for one collection of ball shaped, it is sphere (diameter of it is from a few microns to tens of microns). On the micro, its form is as a honeycomb and its structure is not stabile, known as the six-party ball calcite. In the microstructure (Fig. 6), a point is chosen for EDS quantitative analysis of the functional elements (Fig. 7).

Element composition is showed in Table III.

Seen from Table III and Figure 6, the scale is crystals of calcium carbonate, which contains calcium, carbon, oxygen and trace of element of sodium. It content of calcium is 15.22% and that of carbon is 29.22%.

DE-SCALING EFFECT OF CR^{3+} POLYMER GEL

Laboratory experiment

The composition of sample as follows:

Sample 1: Produced water in oilfield;

Sample 2: Weak alkali ASP, i.e., polymer (1650 mg/L) + surfactant (0.3%) +sodium carbonate (1.2%);

Sample 3: One percent scale is added to sample 2;

Sample 4: Polymer gel, i.e., polymer (1650 mg/L) + Organic chromium 27.5 mg/L);

Sample 5:One percent scale is added to sample 4.

To analyze scaling of weak alkali ASP and de-scaling mechanism of polymer gel, the method of atomic absorption detection is used to test concentration of calcium of five samples above. The results are shown in Table IV.

Seen from Table IV, as produced water contains calcium ion, sample 2 and 3 only contain a trace of calcium ion. At 1st and 30th, calcium concentration changes little. When sample 3 is added to 1% scale, calcium concentration also changes little. It shows scale sample is virtually insoluble in weak alkali ASP. Samples 4 and 5 are polymer gel. At first, calcium concentration of them is the same, 2.30 and 2.94 mg/L, respectively. The calcium concentration at 30th is the same as that of 1st. However, calcium concentration of sample 5 has substantially increased to 12.65 mg/L. The results show Cr^{3+} gel has strong dissolution ability to clean scale in pipes and formation generated by weak alkali ASP system.

PILOT TEST

General condition of the pilot area

Pilot area of weak alkali ASP flooding locates in PuI1-4 large unite of Beisanxi block in Daqing Oilfield. Five-spot well pattern is used. Permeability distribution is from 0.12 to 1.2 μm^2. Well B3-6-44 is chosen to analyze heterogeneous characteristics. Variation coefficient of permeability is 0.69. It is between 0.718 Variation coefficient of compound rhythm and 0.668 variation coefficient of normal rhythm. Heterogeneity is relatively serious vertical. Water flooding was made from December 1998 to August 2002. Cumulative water injection of thirteen wells was 0.402 pore volume (PV), and oil recovery is 9.6%. Preflush slug of polymer was from August 3, 2002 to November 8, 2002. The total injection of polymer is 5.7145×10^4 m^3, the same as 0.018 PV. The injection of weak alkali ASP main slug begins from November 8, 2002. The concentration of polymer is 1400 mg/L, the concentration of alkali is 1.2% and the concentration of surfactant is 0.25%. The viscosity of ASP is 30 mPa.s. Until May 2006, the total injection of weak alkali ASP system is 0.315 PV. A total of 45.6% of the whole program is completed. The injection rate is 0.07 PV/a.

Profile control and the effect

Design of implementation

As long-radius profile control implementation of Daqing is from 1/3 to 1/2 of well spacing, so the radius of our profile control is designed as 1/3 of well spacing about 78 m. The numerical simulation

TABLE V
Design of Slug (Polymer: Cr^{3+} = 30 : 1)

Well No.	Pre-flush slug Polymer (mg/L)	Pre-flush slug Volume (m^3)	Main slug Polymer (mg/L)	Main slug Volume (m^3)	Protection slug Polymer (mg/L)	Protection slug Volume (m^3)
B2-1-P56	1600	2000	1800	2000	2000	3000

TABLE VI
Design of Injection Parameter

Well No.	Radius of profile control/m	Thickness of profile control/m	Injection rate /(m^2/d)
B2-1-P56	70.0	3.1	110.0

software of chemical flooding is used to simulate ASP flooding and profile control flooding. And analysis of experimental results, the composition and size slug and injection parameters of the profile control are obtained (Tables V and VI).

Pilot test of profile control by Cr^{3+} polymer gel is from December 27, 2006 to March 11, 2007.

Injection pressure

Variation of injection pressure with time during pilot test is shown in Figure 8.

Seen from Figure 8, the relation between injection pressure and time can be divided into three stages. With time increasing, injection pressure gradually increases, until it reaches its peak 12.6 MPa. In the middle stage of profile control, injection pressure is relatively stable. In the late stage, injection pressure decreases with time. Compared with conventional profile control, this pressure variation trend is opposite. The result shows the ability of entry fluid is improved.

Fluid entry profile

Figure 9 shows fluid entry profiles both before and after our treatment of profile control.

Seen from Figure 9, the entry profile is improved obviously after profile control. Before profile control, only layer of PI2-3 can sucks fluid and PI1, PI3, and PI4 can not. After that, fluid entry into PI2-3 decreases to 64.9%, that of PI1 and PI3increases to 10.4 and 34.7%, respectively.

Effect analysis of descaling

Before the treatment of profile control, the condition of scaling inside the feeding pipes of injection well B 2-1-P56 and the nylon components of flow meter in the well P48 (no profile control) is shown in Figure 10.

Seen from Figure 10, before profile control, the inner-wall of feeding pipes in injection pump and the nylon components of flow meter in well P48 contact no polymer gel, so their surface has a great deal of scale. Its thickness is about 0.003–0.005 m. It is deduced that whose injection system of weak alkali ASP system, well bore and porous medium have a large amount of scale too.

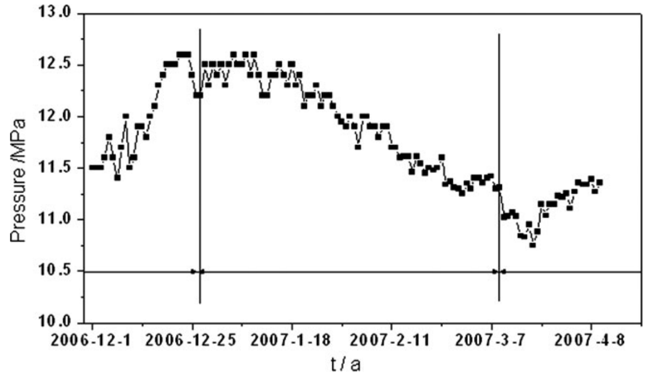

Figure 8 Variation of injection pressure with time during pilot test.

After the treatment of profile control, the condition of them is shown in Figure 11.

Seen from Figure 11, after more than 2 months of treatment by Cr^{3+} polymer gel, the scale inside the flow meter is cleared completely. Similarly, when polymer gel contacts with the wall of pores, scale is also cleared. Permeability is restored.

Comprehensive analysis

As mentioned above, on the one hand, polymer gel can dissolve the scale. After that, the permeability is restored. Besides, flow resistance decreases and entry fluid increases. On the other hand, the retention of polymer gel in porous media can reduce permeability. Resistance increases and entry fluid decreases.[12,13] Therefore, injection pressure during the process of profile control and variation of entry profile control are the overall response to both of the two hands.

Before profile control (September 13, 2006), the picture of entry profile shows PI2-3 layer unit sucks fluid (Fig. 4) and PI1, PI4, and PI5 not. Besides

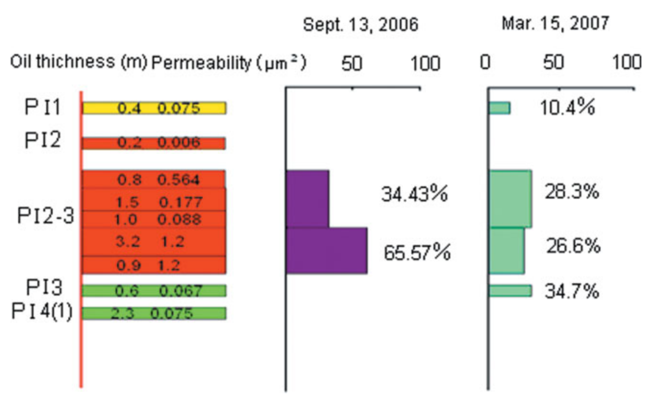

Figure 9 Sketch map of fluid entry profile before and after profile control. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

a Inner wall of feeding pump b Nylon component

Figure 10 Scaling state before profile control. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

serious heterogeneity, the permeability of well bore region is decreased by scale is a main reason. By the treatment of profile control, the scales in the deep of layer PI2-3 and wellbore of low permeability are also cleared by polymer gel. After profile control, the permeability of medium and low permeability layer is restored. Polymer gel does not have negative impact on permeability and the ability of fluid intake is recovered obviously. The penetration of high permeability is restored to some extent. But retention of Polymer gel lowers permeability. The latter has much greater influence than the former. So the ability of fluid intake of high permeability decreased.

a Inner wall of feeding pump b Nylon component

Figure 11 The sealing state after profile control. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

1. Cr^{3+} can not influence the viscosity, interfacial tension and viscoelasticity of weak alkali/surfactant/polymer (ASP); however, it can increase the resistance factor and residual resistance factor.
2. Cr^{3+} polymer gel is compatible with weak alkali ASP.
3. The main component of scale in injection system of weak alkali ASP is calcium carbonate. The formation process as follows: aqueous solution→ saturated solution→ crystal precipitation→ crystal growth→ scaling.
4. Cr^{3+} polymer gel can interact with scale of weak alkali ASP to dissolve and clean it. Thus effective permeability is restored.
5. Cr^{3+} polymer gel has dual function of cleaning scale and profile control to improve fluid entry profile of injection well.

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