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Chemical Compositions and Viscosity-temperature Characteristics of Produced Fluid from High Concentrated Polymer Flooding

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Abstract: In order to ensure the chemical compositions and viscosity-temperature characteristics of produced fluid from high concentrated polymer flooding, we taking a production zone of high concentrated polymer flooding from Daqing oilfield as an example, this paper systematically analyzes the chemical compositions of produced liquids from the high concentrated polymer flooding by modern analytical devices. The chemical compositions are precisely classified by aqueous phase, oil phase and solid phase. Adopting the method of experimental research, the viscosity-temperature curves for the produced liquid from high concentrated polymer flooding are measured and the properties are revealed.

The results show that firstly, the produced liquid consists of aqueous phase, oil phase, solid phase with domain materials for the phase formation. secondly, insoluble materials in the produced liquid are high and with complicated compositions including self-contained PAM, wax crystal，salinity and bacteria, finally, shown as the viscosity-temperature regularity and property, viscosity is inversely proportional to the temperature with greatly reducing viscosity by raising temperature.

Keywords oilfield; high concentration polymer flooding; produced liquid; viscosity-temperature curve

INTRODUCTION

Polymer flooding[1-3] has been widely applied in modern oil exploration, in this paper we mainly expounded the chemical compositions and viscosity-temperature characteristics of produced fluid from high concentrated polymer flooding, it is of great significance in industrial production.

Oil exploration[4,5] is divided into primary production, secondary recovery[6] and tertiary recovery[7]. Primary production is a mode of oil extraction by oil of its own strength, 5% to 10% recovery; Secondary recovery through artificial recharge to the reservoir by water or gas to add energy so as to get more crude oil. Tertiary recovery is a novel oil extraction methods that can improve the performance of the interaction between water, gas, oil and rock by implanting the specific chemicals. It generally includes the following four aspects: thermal recovery technology[8], gas miscible flooding (or non-miscible flooding) recovery technology[9-11], chemical EOR technology[12,13] and microbial enhanced oil recovery technology[14].

Polymer flooding[15] is a kind of chemical EOR methods, which is very important to industrial production. There are many kinds of polymeric substance, EOR polymers are mainly divided into two categories: HPAM[16-19] and Xanthan Gum[20,21]. But it has been more concerned that the features and applications of partially hydrolyzed polyacrylamide solutions.

Since 2003, Daqing oilfield has launched a high concentration of polymer flooding field test in oil production Plant 1 and 6. The molecular weight of the polymer can up to 25 million, and the concentration is 2000mg/L. Finding a suitable polymer of high molecular weight and high concentration is one of the important measures to further tap the potential of increasing oil polymer flooding, thus, to enhance oil recovery. At present, there is not yet publicly reported high concentrations of polymer applied in the flooding areas. Study abroad is also limited to low-enriched, low molecular weight polymer solution, and less studied on high concentrations of polymer flooding reasonable injection method and parameters. Compared with the ASP flooding[22-25], high molecular weight and high concentration of polymer flooding is more economical at the same flooding effects with no lye and no surfactant[26].

On the one hand, injecting a water-soluble polymer can increase the viscosity of the aqueous phase and reduce the viscosity difference of the water-oil phase, so that oil displacement efficiency is subjoined. On the other hand, the difficulty of wastewater treatment[27,28] growth with the increasing viscosity of the aqueous phase. Produced fluid from polymer flooding is a kind of aqueous solution of HPAM

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varies from different molecular weights, with viscous and adsorption, which increases the content of the insoluble substances. And it is not conducive to the wastewater treatment. In addition, when the the molecular weight and concentration increases, the injection pressure for displacement agent increases. Therefore, the optimal value of the concentration and molecular weight of polymer should be determined to ensure the injection pressure is less than the formation fracture pressure. Optimizing the injection program, putting the research results into the production practice, and adopting viscoelastic polymer flooding instead of ASP flooding, will greatly improve the economic of the oilfield with sustainable development.

With the development of oil exploration, oilfield has entered the secondary and tertiary oil recovery stages. Especially since the implementation of tertiary oil recovery technology, Polymer flooding occupies a very important position in enhancing oil recovery. Currently, Polymer flooding has been widely used in our oil fields, but the fatal flaws of the technology is high integrated moisture content, about 80%. Polymer flooding enhanced oil recovery so as to access to stable and high crude oil, while a large number of polymer flooding wastewater is also produced. The composition of produced fluid is so complex that it is a daunting task to deal with them, let alone the high concentrated polymer flooding technology. Studying the chemical compositions and viscosity-temperature characteristics of produced fluid from high concentrated polymer flooding is of great significance.

MATERIALS AND METHODS

Materials

All aqueous solutions were prepared with distilled double-deionized water. Petroleum ether (XD Chemical Co., LTD), Cadmium iodide (CdI_2, YH Chemical Co., LTD, 99.5%), Chloroform ($CHCl_3$, KM Co., LTD, 98.5%), Hydrochloric acid (HCl, YX Co., LTD, 98%), Sodium hydroxide (NaOH, PK Chemical Co., LTD, 99.5%) and Sulfuric acid (H_2SO_4, LT Chemical Co., LTD, 98%) were used in the solutions.

Analytical methods

1) Calculating CO_3^{2-} and HCO_3^- concentration

Carbonate, bicarbonate concentration can be determined via the volume of hydrochloric acid standard solution (0.05mol/L) consumed by two titrations, using phenolphthalein and bromocresol green-methyl red as indicator.

Firstly, Add phenolphthalein in the produced fluid, and then trickle in hydrochloric acid standard solution slowly until the watery turns to its original color, write down the volume of spent hydrochloric acid V_1. Continue to add 5 drops of bromocresol green-methyl red mixed indicator, watery color changes to blue-green, trickle in hydrochloric acid standard solution slowly until the watery turns to orange-red, write down the volume of spent hydrochloric acid V_2.

For $V_2 > 2V_1$, exist CO_3^{2-} and HCO^{3-}:

$$c_{CO_3^{2-}}(\text{mg/L}) = \frac{60.01 \times c_{HCl} \times V_1}{V} \times 1000 \quad (1)$$

$$c_{HCO_3^-}(\text{mg/L}) = \frac{61.02 \times c_{HCl} \times (V_2 - 2V_1)}{V} \times 1000 \quad (2)$$

For $V_2 < 2V_1$, exist CO_3^{2-} and OH^-:

$$c_{CO_3^{2-}}(\text{mg/L}) = \frac{60.01 \times c_{HCl} \times (V_2 - V_1)}{V} \times 1000 \quad (3)$$

$$c_{OH^-}(\text{mg/L}) = \frac{17.01 \times c_{HCl} \times (2V_1 - V_2)}{V} \times 1000 \quad (4)$$

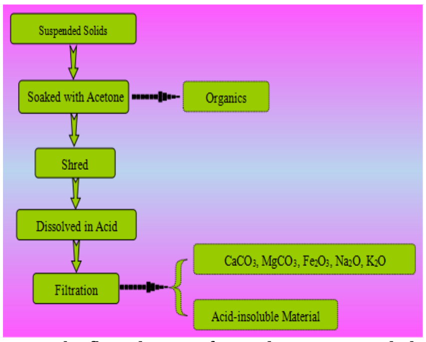
2) Calculating Cl^- concentration

Pipetting 10mL watery to a conical flask accurately, and then add 5 drops of potassium chromate indicator. Drop silver nitrate standard solution in the watery until generate orange-red silver chromate precipitate, write down the volume of silver nitrate, yield Cl^- is determined.

$$c_{Cl^-}(\text{mg/L}) = \frac{35.45 \times c_{AgNO_3} \times V_{AgNO_3}}{V} \times 1000 \quad (5)$$

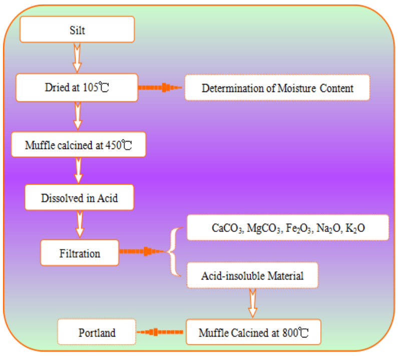
3) Analysis Technology

The suspended solids in the water layer was analyzed accurately by acidification-Calcined-atomic absorption spectrometry technology. The flow chart can be seen from Scheme 1.



Scheme 1. The flow diagram for analyzing suspended solids

Analyzing the composition of the silt (providing by the Daqing oilfield) to determine its compositions and origin. The silt was fired more than 4h, at 800℃ in a muffle furnace, removing moisture and some organics, so as to obtain the scale-like powdery silt. It was inspected by SEM and XRD, the process shows in Scheme 2.



Scheme 2. The flow diagram for analyzing the silt

RESULTS AND DISCUSSION

The chemical compositions in the oil-water phase

The suspended solids in the oil-water phase are composed of organics, hydrochloric acid insolubles, small amounts of carbonate scale and some corrosion products. From chemical analysis, we know that organics is mainly derived from polyacrylamide and emulsified crude oil, accounting for more than 90%; and the hydrochloric acid insolubles is aluminosilicate, accounting for about 3% to 4%, mainly from the formation; It also contains a small amount of carbonate scale ($CaCO_3$, $MgCO_3$). It changes into dirt easily because of the high salinity and the existence of cation (Ca^{2+}, Mg^{2+}) and the anion (CO_3^{2-}). The pH values of produced fluid ranges from 7.68 to 8.75, weak alkaline; The salinity ranges from 2900 to 7100 mg/L.

The content of crude oil in the produced fluid is between 2% and 73%, ranges largely from one oil well to another. Among them, the lowest is the Well L7-AS1721, reaching 2.64% and the highest is the Well 11-PS1901, reaching 72.69%.

The amount of mechanical impurities in the produced fluid from Daqing oilfield is between 2% and 7%, which is very high. In connection with the concentration of the polymer, the completion can be obtained that the content of mechanical impurities volatility increases with increasing number of polymer. The increasing concentration of polymer in the produced fluid makes the viscosity of the produced fluid increases, the particle size of the oil beads decreases, and the emulsification increases, therefore, produced fluid carrying out a large number of mechanical impurities.

The magnitude of the content of acid-insoluble material has large differences in the twenty wells. Among them, the acid-insoluble material in Well L9-PS1233, 9-AS1721 and L10-PS1401 are higher than others. That is, These three wells containing more impurities, emulsified oil and solid particles, etc, which makes the solution containing more suspended solids than the remaining wells. In addition to these three wells, combination the concentration of polymer in produced fluid , you will find that the content of suspended solids increased with increasing polymer volatility. While intercepting the acid-insoluble material by 0.45 μm membranes in different recovery wells can also prove the above conclusions. Observed with the naked eye, with increasing polymer, the color of the membrane is gradually deepened, indicating that the suspension is gradually increased.

The FT-IR spectrum of the suspension is shown in Figure 1, were characteristic peaks for -N-H, -C=O, -$C(CH_3)_3$, -C-N,etc. The following functional groups were observed. The strong 2069 cm^{-1} peak can be assigned to the -C=O stretch vibration band. The major peak at 1452 cm^{-1} arises from -C-N stretch vibration band (amide Ⅲ band). The peak at 1635 cm^{-1} is assigned to the C-OH bending vibrations, and the peaks at 3456 cm^{-1} can be attributed to the stretching vibrations of -N-H. The peak at 1122 cm^{-1} denotes -$C(CH_3)_3$ stretching vibration. Besides, 692 cm^{-1}, 549 cm^{-1}, 426 cm^{-1} on behalf of $BaCO_3$ (SiO_2), Fe_2O_3, $CaSO_4$ characteristic peaks, respectively.

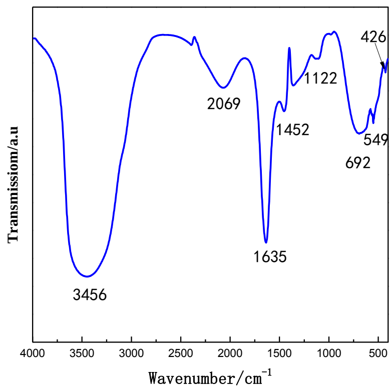


Figure 1. FT-IR spectrum of the suspended solids in the oil-water phase

The chemical compositions and characteristics in the solid phase

According to the procedure shown in the Scheme 2, the composition of the silt was analyzed. The silt including 19.3% of water and 76.65% of the organics (mainly polymers and crude oil), and the rest of ingredients are for scale-like mud. The scale-like mud contains large amounts of $CaSO_4$, SiO_2, Fe_2O_3, Fe_3O_4, $Fe(OH)_3$, a small amount of $MgCO_3$, and a trace amount of $Ca(OH)_2$, $Mg(OH)_2$. Wherein, the iron oxides, along with a certain amount of anorthite and small amounts of other substances are produced by considerable etching.

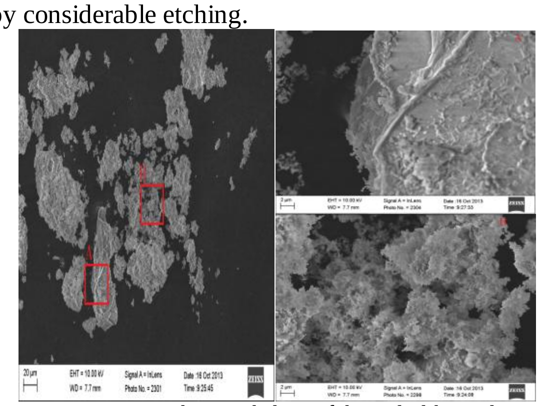


Figure 2. The morphology of the scale-like mud

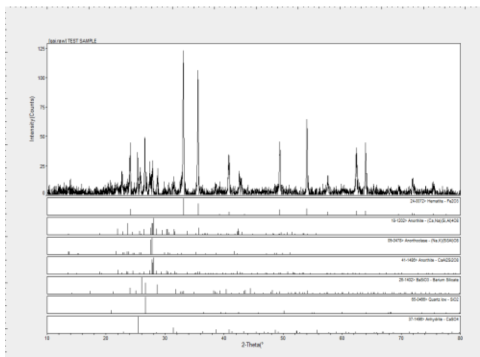


Figure 3. XRD of the scale-like mud

The scale-like mud was analyzed by SEM and XRD, shown in Figure 2 and Figure 3, respectively. They look like blocks, with strips of polyacrylamide chain macromolecules (A) or some chunks combined with twiggy-mer (B). Besides, mineral composition and crystallographic structure of the scale-like mud can be observed. The crystalline phase of the scale-like mud is mainly iron(Fe_2O_3), a certain amount of anorthite and minor amounts of other substances.

Comparing with the lithology data provided by scene, the solid phase from high concentrations of polymer flooding is composed of 90% water and organics,while the remaining is inorganic. There must be no montmorillonite in inorganic and high iron content in the silt,which described that solid phase material containing corrosion products, maybe, from sandstone cementation of siderite (pyrite) or the minerals in the stratum. To sum up, the solid phase from high concentrations of polymer flooding is primarily outgoing organics, small amounts of corrosion products, aluminosilicate and carbonate scale, etc.

There are many factors affecting the solid phase from high concentrations of polymer flooding, including self-contained polyacrylamide, the wax crystals in crude oil, the silt, temperature, the combined effect of the bacteria and the time. The corrosion products, carbonate scale, and aluminosilicate are packaged in polyacrylamide, forming micelles that are difficult to separate. The wax crystals will precipitate accumulate on the wall, easy to form a three-dimensional network structure, and then surrounding a part of contaminants to form gel particles adhered to the inner wall of the pipe and the borehole.

The viscosity-temperature characteristics of produced fluid

Generally, the viscosity of the produced fluid from different produced wells is less than 10 mPa·s, the lowest is the Well 11-1803, reaching 1.1 mPa·s and the highest is the Well 9-PS2131, reaching 8.5 mPa·s. The viscosity of water at 25℃ is 0.893 mPa·s, and the viscosity of the water flooding is between 0.8-3.5 mPa·s, thus, polymer is an important factor in viscosity of the produced fluid. The overall trend is that, viscosity is proportional to polymer concentration, inversely proportional to temperature as well.

The viscosity of the produced fluid decreases with increasing temperature. Elevated temperature, HPAM degrades from macromolecules, so the viscosity decreases. At 30℃, the viscosity of the produced fluid from twenty wells reduced by an average 9.39%. While, when the temperature reaches 60℃, the viscosity reduced by an average 44.81%. The above description that temperature can reduce the viscosity of the produced fluid effectively.

The average viscosity of both water flooding and polymer flooding at various temperatures is calculated to draw viscosity-temperature curve. As we can seen, at 30℃, the average viscosity of water flooding is up to 1.36 mPa·s, polymer flooding is 3.72 mPa·s, simultaneously. When the temperature reaches 60℃, the average viscosity of water flooding just attains 0.64 mPa·s, polymer flooding attains 2.01 mPa·s. The viscosity of both water flooding and polymer flooding is decreased with increasing temperature, but polymer flooding decline greater than water flooding.

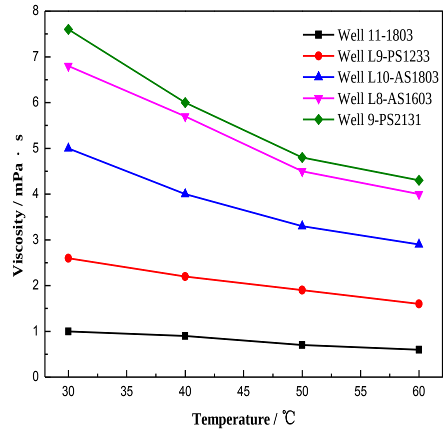


Figure 4. Viscosity-temperature curve. The polymer concentration of these five produced wells as follows: Well 11-1803, 72 mg/L; Well L9-PS1233, 473 mg/L; Well L10-AS1803, 557 mg/L; Well L8-AS1603, 1222 mg/L; Well 9-PS2131, 1032 mg/L.

The viscosity of water flooding[29] is between 1.2-1.55 mPa·s, and the viscosity of polymer flooding is between 2.6-6.5 mPa·s. The viscosity of polymer flooding is significantly higher than water flooding at the same temperature, which illustrates that the presence of the polymer directly affects the viscosity of the produced fluid, so the viscosity of produced fluid increases.

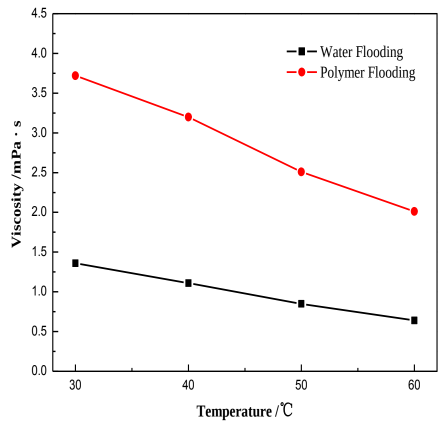


Figure 5. Viscosity-temperature curve for both water flooding and polymer flooding

CONCLUSION

This paper systematically analyzes the chemical compositions of produced liquids from the high concentrated polymer flooding by modern analytical devices. Comparing with the lithology data provided by scene, the solid phase sources of produced fluid can be identified.

(1) The viscosity of produced liquids from polymer flooding depends on polymer content. The higher the polymer concentration it grows, the greater the viscosity will be. However, due to the different shear rate and external environmental factors, there will be an anomaly.

(2) Viscosity is inversely proportional to temperature. Elevated temperature, HPAM degrades from macromolecules, so the viscosity as well as the emulsification decreases.

(3) Neutral polymer doesn' t affect the pH of the produced liquids. However, PH has a direct impact on the dissociation degree of carboxyl of hydrolyzed polyacrylamide, thereby affecting the extension of the molecule in solution.

(4) Produced fluids weakly alkaline, with high salinity and Cl^-, HCO^{3-} concentration. Ca^{2+}, Mg^{2+}, CO_3^{2-} can weaken the intermolecular forces by influencing suspended solids content, thus, applied force directly acts on the molecular chain, which makes the viscosity decreases. Therefore, the high salinity of the produced fluid is not conducive to the use of reinjection.

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