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A study of melamine-based mobility control of condensed water during steam flooding process

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Abstract

The purpose of the research is to propose a novel method of mobility control of condensed water by melamine during steam flooding process. Melamine is working as water permeability modifier in a non-foaming manner to control mobility of condensed water, supported by the theoretic analysis. Wettability alternatation, water residual resistance factor, and oil displacement efficiecy by melamine addition were investigated in the experiments. The contact angle was decreased by 3.6° at 200 °C indicating that the core tends to be more water wet upon addition of melamine. Water residual resistance factor, approximately representing water/oil mobility ratio, increased in response to the temperature elevation and increased pore volume during melamine injection. Water residual resistance factor reached close to 1 after subsequent hot water flood, which indicated that the reduced water permeability by melamine precipitation could be restored. The oil recovery by saturated melamine injection was increasd by 11.7% when temperature dropped from 200 to 160 °C, in comparison with pure water flooding under the same condition. The results verify the feasibility of melamine to enhance oil recovery by controlling mobility of condensed water in a steam flooding process.

Keywords Heavy oil · Melamine · Thermal recovery · Mobility control · Laboratory

Introduction

The most frequently applied EOR method for producing heavy oil is steam flooding (Cai et al. 2013). Steam contains a large amount of heat to reduce the viscosity of heavy oil. The flooding efficiency was increased by mobility control using foam to divert steam into high oil saturated zones (Stoll et al. 1993). In general, there are four ways to control mobility during water or steam flooding process, namely by reducing oil viscosity and relative water permeability, or by increasing water viscosity and relative oil permeability. In a steam flooding reservoir, oil viscosity is dramatically reduced due to heat carried by steam transferring into the reservoir. Relative water permeability and water viscosity are often modified by addition of foaming additives.

Numerous laboratory studies on the applicability of mobility control using foaming additives have been reported (Li et al. 2010, 2017; Nonnekes et al. 2015; Qian et al. 2016; Saleh et al. 2017). In steam flooding process, high-temperature-resistant surfactants are usually introduced for improving oil displacement efficiency. When these surfactants are foamed in situ, they partially seal the highly permeable reservoir zones and possess the ability to increase the viscosity of steam or water thus to enhance oil recovery. Foam flooding with steam injection also has some defects, one of which is the instability of the foam.

In steam flooding reservoirs, steam has experienced heat losses and condensed to water near displacement front where characteristics of hot water flood is exhibited (Hu 2011). Mobility of condensed water has a great impact on the sweeping efficiency of steam and oil recovery can be increased by controlling it. From perspective of reducing water permeability, mobility control can be achieved by applying some kind of additive to plug off part of water flow paths. The additive shall be dissolved in hot water and steam while being injected along with them. They will be gradually precipitating from the saturated solution when temperature drops due to heat losses and energy consumption. In porous

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media, fractional flow of oil and water occurs within their own flow matrix without interfering each other. Water-wet additives preferentially occupy water flow matrix and effectively reduce relative water permeability without affecting the flow of oil. As a result, mobility control of condensed water is achieved and oil recovery is thus enhanced. With heat expansion along with continuous steam (or hot water) injection, precipitated substance is dissolved by the subsequent steam (hot water) and conveyed further to a zone where temperature is low enough for them to precipitate again. This process repeats itself until the additives break through to producer to be recovered to surface. When the injected additives are recovered, water permeability is reinstated. In other words, the reduction of relative water permeability is a temporary and reversible process, which causes no damage to reservoirs.

Little attention has been paid to reducing relative water permeability in a non-foaming manner in the previous studies of steam flooding. This paper is an attempt for mobility control using a non-foaming additive called melamine (MA) in the process of thermal recovery, which may provide EOR techniques with a different perspective.

Theoretical fundamentals

During steam flooding, there is a transition zone between the steam (hot zone) and the oil (cold zone) where the steam condenses to hot water. The transition zone can be regarded as the displacement front of the steam in terms of temperature profile. Ahead of the transition zone is the steam with high temperature while the cold oil with connate water is present behind it. The transition zone is advancing with continuous steam injection to drive the oil forward and our focus is to control it by application of the additive. According to fractional flow theory, either oil or water flows on its own path and does not influence each other. In water-wet rocks, water flows near the rock surface while oil flows through the center of the porous media. The additive is transported to transition zone and precipitates due to the sudden temperature drop. If the additive is hydrophilic it will occupy the water flow paths to reduce the water permeability without impact on the oil permeability, resulting in reduction in water/oil mobility ratio.

Based on Buckley and Leverett (1942), velocity of displacement front can be expressed as:

$$\frac{\mathrm{d}x_f}{\mathrm{d}t} = \frac{q_t}{A\varphi}\left(\frac{f_{wf}}{S_{wf} - S_{wi}}\right), \tag{1}$$

where A is cross-sectional area, φ is porosity, x_f denotes the location of front, f_{wf} is fractional flow to water at front, S

represents water saturation and subscripts {wi,wf} refer to connate water and water at front.

The oil recovery when breakthrough is expressed as:

$$E_R = \frac{\overline{S}_W - S_{Wi}}{1 - S_{Wi}}, \tag{2}$$

where E_R denotes oil recovery and $\overline{S}_W$ is average water saturation.

Fractional flow f_w is the function of temperature T and water saturation S_w

$$f_W(S_W, T) = \frac{1}{1 + \frac{K_{ro}}{K_{rW}}\frac{\mu_W}{\mu_o}}. \tag{3}$$

Because temperature T_1 ahead of front is higher than temperature T_0 behind front, fractional flow at T_1 and T_0 obeys the following relationship:

$$f_W\left(S_W, T_0\right) = f_W^{(0)}\left(S_W\right) > f_W^{(1)}\left(S_W\right) = f_W\left(S_W, T_1\right). \tag{4}$$

The average water saturation can be obtained from fractional flow curves as shown in Fig. 1. The extrapolated tangent intercepting the line $f_w = 1$ represents the average water saturation $\overline{S}_{wT}^{(1)}$. The slope of the tangent to $f_w^{(1)}$ is expressed as:

$$m = \frac{V\phi A}{q_t} = \frac{V\phi}{u}, \tag{5}$$

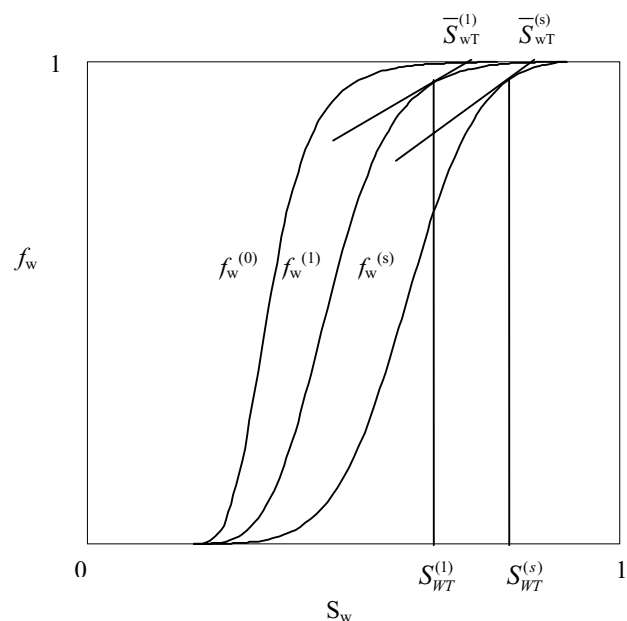where V is velocity of flood-front and u is Darcy velocity.

Fig. 1 Fractional flow curves

In steam flooding process, steam and condensed water is continuously passing the front. C_1 is the concentration of the additive at T_1 and C_0 is the concentration at T_0; the velocity of injected solution v can be obtained by application of the law of conservation of mass:

$$v = \frac{u}{\phi} \frac{\bar{f}_W^{(1)}}{\bar{S}_W^{(1)}}. \tag{6}$$

We assume it takes Δt for the solution to arrive at flood-front, then:

$$v\Delta t = V(t_1 + \Delta t). \tag{7}$$

The following equation is obtained by combination of Eqs. (5), (6), and (7)

$$\Delta t = \frac{t_1}{\dfrac{u}{V\phi}\dfrac{\bar{f}_W^{(1)}}{\bar{S}_W^{(1)}} - 1} = \frac{t_1}{\dfrac{1}{m}\dfrac{\bar{f}_W^{(1)}}{\bar{S}_W^{(1)}} - 1}. \tag{8}$$

Since $m < 1$ and $\bar{f}_W^{(1)} > \bar{S}_W^{(1)}$, $\Delta t > 0$ is proven, which means that the solution can reach flood-front and is saturated at either ahead of the front or behind it due to the temperature drop across the area.

Here residual resistance factor (RRF) is used to present the permeability reduction after hydrophilic additive is involved in the flooding process. The more RRF is, the more permeability is reduced

$$\text{RRF}(S_A) = \frac{K_{rW}(S_W)}{K_{rW}^*(S_W, S_A)} \geq 1. \tag{9}$$

After additive is introduced to the displacement process, mobility ratio and oil recovery can be expressed as:

$$M^s = \frac{K_{rWT}^{(1)}}{RRF(S_A)K_{rWT}^{(0)}} \frac{\mu_{WT}^{(0)}}{\mu_{WT}^{(1)}} = \frac{M}{RRF(S_A)} \tag{10}$$

$$E_R^{(s)} = \frac{\bar{S}_{WT}^{(s)} - S_{Wi}}{1 - S_{Wi}}, \tag{11}$$

where M and E_R denote mobility ratio (water/oil) and oil recovery, respectively. Superscripts $\{s\}$ refer to the parameters after additive is introduced.

Since $S_{WT}^{(s)} > S_{WT}^{(l)}$, $E_R^{(s)} > E_R^{(l)}$ is proven. As is well-known, the displacement front is stable when mobility ratio (invading/displaced) is reduced. From Eqs. (10) and (11), it is concluded that displacement process becomes more stable and oil recovery is enhanced by applying hydrophilic additive.

Experimental

Additive screening and evaluation

According to above-mentioned theory, the ability of the additive for mobility control is associated with solubility sensitive to temperature. The additive shall be highly soluble in water or steam at high temperature while hardly dissolved at low temperatures. This particular property will enable large amount of additives to be transferred to transition zone during steam flooding and precipitate by a temperature drop at the displacement front. The additive shall also remain stable under reservoir conditions and inert to crude oil. Flow path of condensed water in porous rock is occupied by the precipitated additive, resulting in the temporary reduction of relative water permeability. When steam is continuously injected and displacement front propagates, the precipitated additives are dissolved again in the subsequent condensed water or steam and conveyed further until another pressure drop at the mobile displacement front. This process repeats so that mobility of condensed water is controlled.

After reviewing chemicals handbook, MA presents perfect chemical and physical properties as discribed above for mobility control. MA is an organic compound, a trimer of cyanamide with a 1,3,5-triazine skeleton. The chemical and physical properties of MA are listed in Table 1.

MA has very limited solubility in cold water, but high aqueous solubility at high temperature. It is not soluble in crude oil. Experiment was conducted to meaure the aqueous solubility of MA under various temperatures. To measure aqueous solubility of MA at high temperature (above 100 °C), a piston container with a certain volume of distilled water and excessive MA was placed in a thermostatic oven (maximum 350 °C) at predetermined temperature for 24 h. The pressure was also maintained at piston container to acertain water to be aqueous at the temperature. The saturated

Table 1 The chemical and physical properties of MA

Chemical formula	Vapor pressure (Pa, 20 °C)	Density (g/cm^3)	Melting point (°C)	Aqueous solubility (g/L)		Autoignition temperature (°C)
				20 °C	100 °C	
$C_3H_6N_6$	4.7×10^{-8}	1.574	354	3.2	5	> 500

solution was then displaced into a weighing bottle to measure MA mass after water vaporization and aqueous solubility was calculated. The result is presented in Fig. 2. As is shown, aqueous solubility is increased with temperature elevation, reaching 105.62 g/100 cm^3 at 250 °C. In a steam flooding researvoir, large amount of MA can be carried by hot water or steam at high temperature and precipitate when temperature drops across the displacement front.
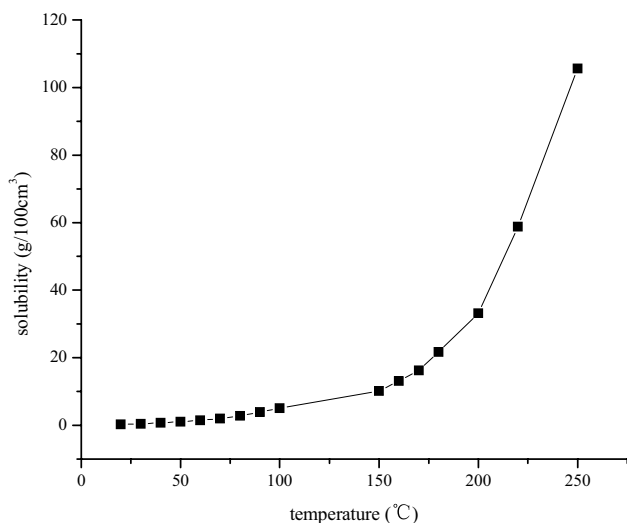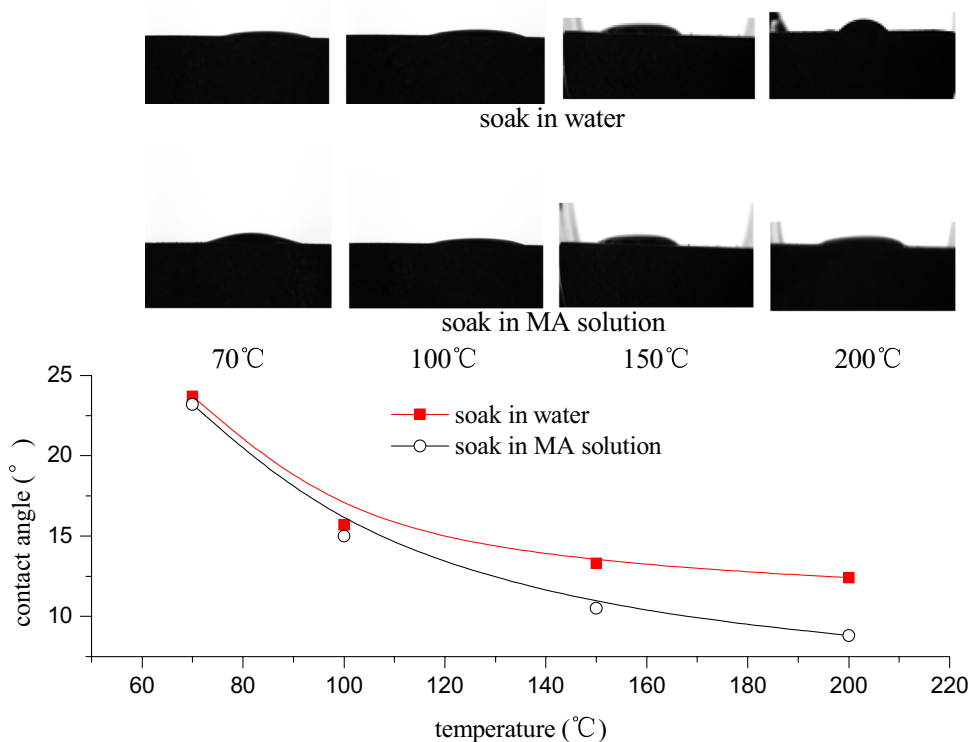
It is of importance to maintain water-wet surface during thermal recovery process. Wettability of two pieces of natrual cores obtained from Block Qi40 of Liaohe Oilfield was evaluated by soaking in distilled water and saturated MA solution individually for 15 days at different temperatures then measuring contact angle using KRUSS device. The piece of core was polished before being soaked. A liquid drop was placed on the surface after soaking, then the photo of the liquid drop was taken for measuring contact angle. The contact angles results are shown in Fig. 3. The curves of contact angles are going down with increasing temperature. When temperature is elevated, resin and asphaltene adsorbed on the rock surface are gradually desorbed. This desorption process leads to an increase in water wettability. At relatively low temperature only small amount of MA was dissolved so that the wetability was not impacted too much. With more MA dissolved at high temperature, contact angle was decreased compared with that of core being soaked in distilled water, e.g., the contact angle was 8.8° soaked in 200 °C MA while 12.4° in distilled water. The core tends to be more water wet upon adding MA into water.

MA precipitation in porous media

Based on Eq. 10, water residual resistance factor (RRF$_w$) can be used to approximately represent the mobility ratio of water/oil, namely demonstrate the ability of MA to plug off porous media. The basic elements in the experiment include

Fig. 2 Solubility of MA at various temperatures

Fig. 3 Contact angles after cores being soaked for 15 days

natural cores, formation water and MA. The natural cores were obtained from Block Qi40 of Liaohe Oilfield in China and the formation water was prepared with a mixture of NaCl (5 wt%) and CaCl$_2$ (2 wt%). MA was analytically pure, which was purchased from Shanghai Chemical Agent Plant.

All experiments were conducted using a modified steam flooding experimental system as shown in Fig. 4. The system is composed of injection pumps, thermostatic oven, core holder, pressure transmitter, back pressure system, confining pressure pump, vacuum systemp, metering system, and so on. The back pressure system can provide 0.2–50 MPa back pressure. The thermostatic oven can privide a maximum of 350 °C temperature and be cooled down by air ventilation for a quick temperature drop. A separator is included in the metering system to allow accruate measurement and all data will be recorded in the PC.

The labrotory procedures are as follows:

1. Measure the cores under dry condition, vacuum for 5 h then saturate with formation water, measure weight and calculate pore volume;
2. Exert confining pressure on cores to maintain 2 MPa differential over outlet pressure;
3. Displace with formation water using constant-flow pump until stable parameters are obtained (0.1 MPa pump pressure and 1 ml/min), five sets of data to be recorded to calculate water permeability;
4. Switch on thermostatic oven to maintain programmed temperatures for 5 h under confining pressure. Displace with saturated MA solution at programmed temperature then cool down to atmosphere temperature for 24 h, calculate water permeability and RRF$_w$.

During experiments the range of temperature was from 150 to 240 °C and injected pore volumes (PV) of MA ranged from 0.5 to 2.0 PV. The results are shown in Fig. 5.

As shown in Fig. 5, RRF$_w$ increased in response to the temperature rise and injected PV during MA injection. The solubility of MA in water increased with temperature elevation and vice versa, resulting in more MA being carried by water to precipitate at displacement front. The more temperature dropped, the more MA precipitated. It is obvious that temperature is one of the key influential factors in the process. The injected PV is also a very important factor. Higher volume of solution entrains more MA to precipitate for sealing off the highly permeable zones.

In general, it is always necessary to estimate the damage to reservoir when injecting additives. In the experiment,
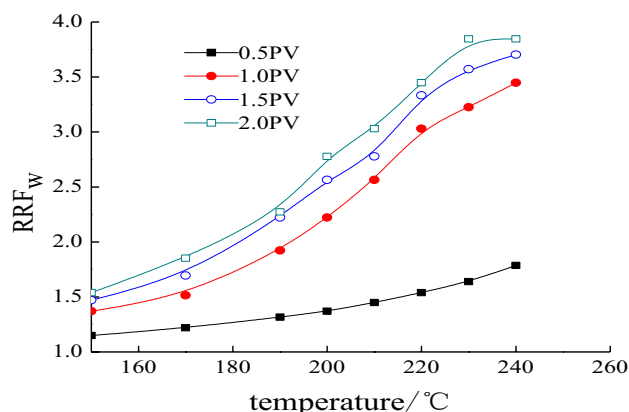
Fig. 5 The relationship between temperature and RRF$_w$ at various PVs
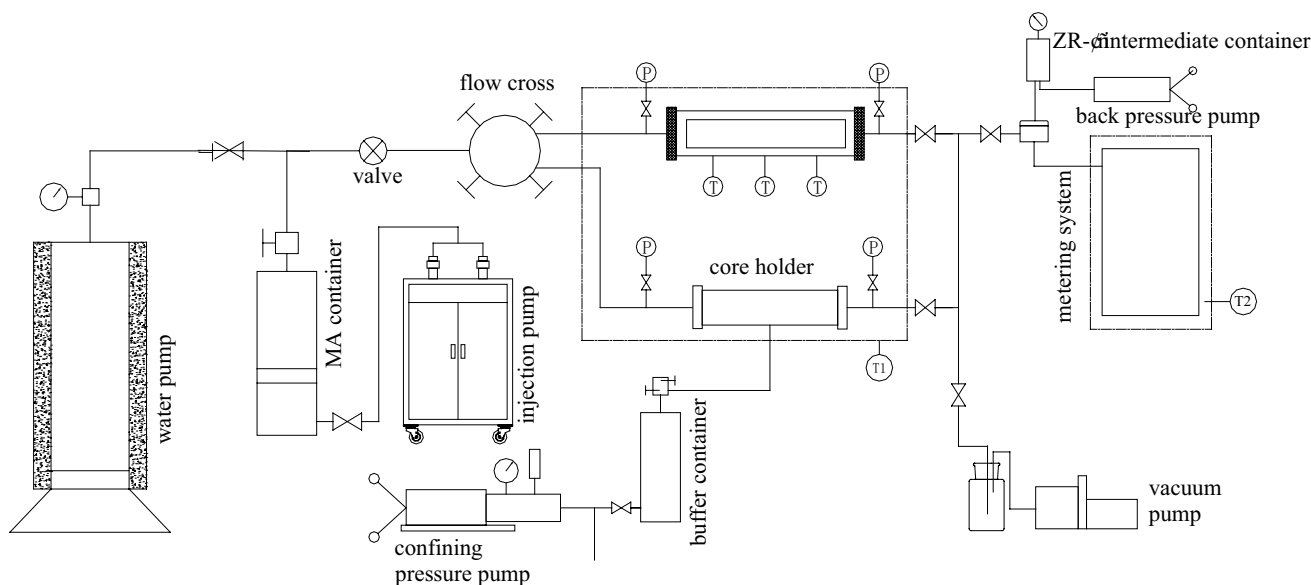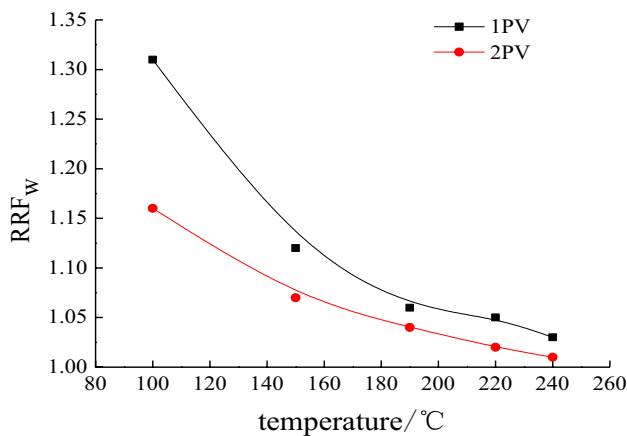
Fig. 4 A full view of the experimental system

two cores with approximately same properties (permeability 0.581 and 0.526 Darcy, respectively) were filled with saturated solution of MA at 170 °C. Then, the permeability was measured after temperature drop. Core#1 was heated to 100 °C and displaced by 1 and 2 PV of 100 °C hot water, respectively. Then the temperature was elevated to 150 °C and 1 and 2 PV of 150 °C hot water was displaced. The experimental procedures were repeated on Core#2 at the temperature ranging from 190 to 240 °C. The effect of temperature on RRF_w is shown in Fig. 6.

Figure 6 shows that RRF_w decreased with temperature rise and increased injected PV. The higher the temperature was, the closer the RRF_w reached 1. Hot water was more likely to dissolve the precipitated MA at high temperature, which led to the recovery of reduced permeability caused by MA precipitation. Injected PV behaved the same way as temperature. All results demonstrated that MA injection temporarily reduced relative water permeability with no damage to reservoir and the reduction of relative water permeability was recoverable under specific conditions.

In addition, the RRF_o was also investigated to evaluate the impact of MA injection on relative oil permeability. In the experiment, four cores were initially saturated with MA solution at 240 °C, then dropped in the controlled manner to 220, 200, 180, and 160 °C, respectively. The result is

shown in Table 2. As is shown, there was only slight reduction in relative oil permeability pre and post MA injection and RRF_o was very close to 1. It is wellknow that introduction of heat to the reservoir rock will change the physical properties of the reservoir during thermal process. However, only neglectable change was observed in terms of relative oil permeability, which means no distirbulance was caused to oil flow by introducing MA solution into the reservoir. MA exibits the ability to control water/oil mobility ratio by increasing RRF_w while exerting neglectable impact on RRF_o, thus oil recovery is enhanced.
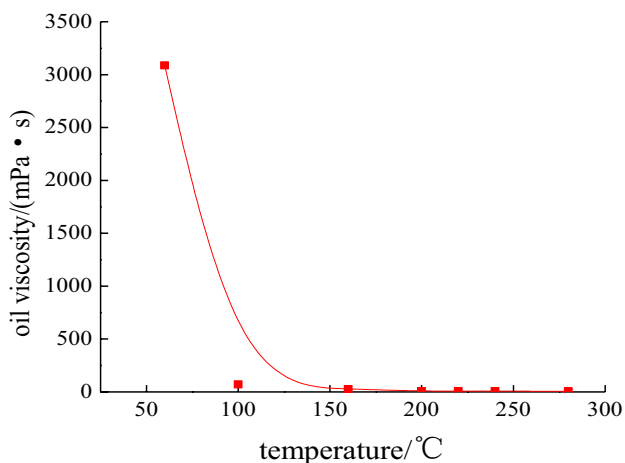
Oil displacement experiment

The 2.5 mm × 10 cm artificial core was made of quartz, potassic feldspar, plagioclase, kaoline, montmorillonite, and chlorite in accordance with the rock constituents of Block Qi40 of Liaohe Oilfield, with porosity range from 24.1 to 26.6%, and the permeability range from 1.51 to 1.57 Darcy. The heavy crude oil was obtained from Block Qi40. The relationship between oil viscosity and temperature is illustrated in Fig. 7. The formation water was prepared with a mixture of NaCl (5 wt%) and $CaCl_2$ (2 wt%).
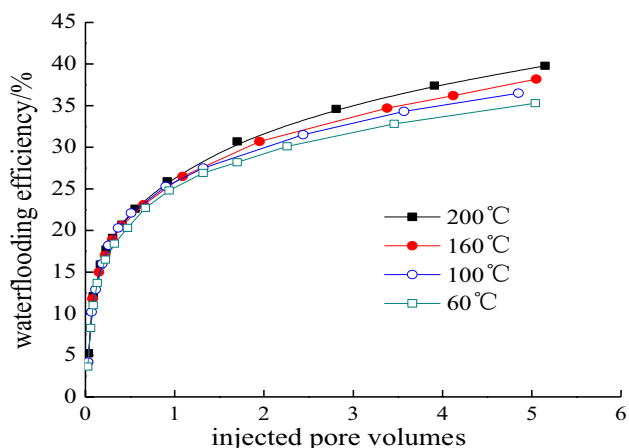
At the displacement front during steamflood, steam conveys the heat to formation fluids and condenses as hot water. Therefore, only hot waterflood was studied in this experiment. The temperature of hot water zones in a steamflood project of Block Qi40 ranged from 60 to 200 °C. The experimental temperature of hot water was determined to be 60, 100, 160 and 200 °C, respectively. The oil displacemet experimental procedures as follows:

1. Establish initial oil/water conditions in the core.
2. Inject hot water or MA solution at required temperature and pressure, and maintain back pressure 0.5–1 MPa over the saturated vapor pressure at the experimental temperatures.
3. When water cut is more than 98% and pressure differential across core is stable, the experiment is deemed to come to an end.

The water flooding efficiency by pure hot water is shown in Fig. 8. After the injection of saturated solution of MA at

Fig. 6 Relationship between temperature and RRF_w with different PVs

Table 2 RRF_o comparison pre and post MA injection with various temperature drops

Core	Porosity (%)	Permeability (D)	Temperature (°C)	Relative oil Permeability pre MA	Relative oil Permeability post MA	RRF_o
3	25.3	1.54	220	0.859	0.851	1.009401
4	26.4	1.50	200	0.802	0.798	1.005013
5	24.1	1.56	180	0.773	0.762	1.014436
6	26.4	1.53	160	0.915	0.901	1.015538

Fig. 7 Relationship curve of viscosity–temperature of crude oil from Block Qi40

Fig. 9 Flooding efficiency comparison with temperature drop from 200 to 160 °C (200 °C pure waterflood as reference)

Fig. 10 Flooding efficiency comparison with temperature drop from 200 to 160 °C (200 °C pure waterflood as reference)
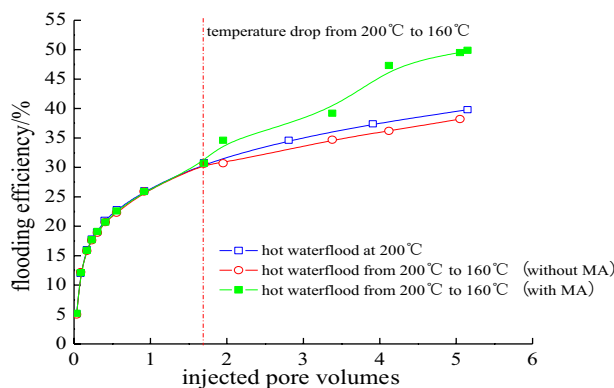

Fig. 8 Water flooding efficiency curve of the oil displacement experiments

200 °C, the temperature was dropped to 160 °C in a controlled manner. The core was then flooded by saturated solution of MA at the temperature of 160 °C. Then the experiment was repeated with the temperature drop from 200 to 60 °C. The results are demonstrated in Figs. 9 and 10.

Figure 8 shows that oil recovery was enhanced in response to the increase of injected water temperature. In hot water zones of a steamflood project, different oil recoveries were obtained when the injected water temperature varied from 60 to 200 °C. The oil recovery by 200 °C hot water increased by 4.5% in comparison with the oil recovery by 60 °C hot water. Only small incremental oil recovery was obtained by elevating water temperature.

When the saturated solution of MA was used instead of hot water at the temperature of 200 °C, as shown in Figs. 9 and 10, the oil recovery by MA injection was not changing obviously at the beginning. Dissolved in hot water, MA
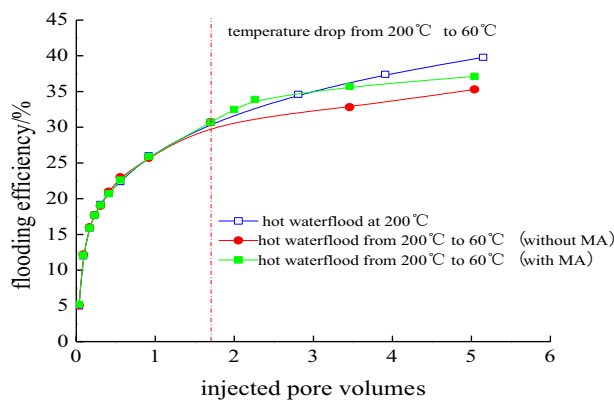
did not function effectively when there was no temperature change. However, when the temperature dropped from 200 to 160 °C to simulate the heat loss at displacement front, the oil recovery was increased by 11.7% in comparison with pure water flooding under the same thermal condition and by 10.1% compared with 200 °C water flooding without temperature change. When the temperature dropped from 200 to 60 °C, the oil recovery was about 37.1%, which fell into the interval between 200 °C hot waterflood (39.8%) and 60 °C hot waterflood (35.3%).

The major reason why MA injection could enhance oil recovery during thermal process was that the precipitation of MA due to heat losses controlled mobility of condensed water by reducing relative water permeability and leaving oil permeability almost unaffected. The injected water was diverted into low permeability zones because its flow resistance in highly permeable zones increased. As a result, oil recovery was enhanced when swept volume was increased.

However, oil viscosity would also increase in the process of temperature drop since it is temperature sensitive. This

would lead to the undesirable increase of water/oil mobility. When temperature dropped from 200 to 160 °C, the limited increase of oil viscosity exerted very little unfavorable effects on water/oil mobility and the reduction of relative water permeability caused by MA precipitation was the dominant factor in this process. So the oil recovery is still greatly enhanced. When big temperature drop was encountered, e.g., from 200 to 60 °C, oil viscosity increased to a relatively large extent, exerting unfavorable effects on water/oil mobility. It explains in Fig. 10 that MA flooding efficiency is only 1.8% higher than hot waterflooding efficiency when temperature dropped from 200 to 60 °C. If huge heat losses occurred in a reservoir resulting in big temperature drop, MA would not behave as good as expected. Under such circumstances more MA precipitation could not compensate the undesired effects caused by oil viscosity increase due to big temperature drop.

Conclusion

A method of melamine-based mobility control method of condensed water during steam flooding process was introduced with the conclusions as follows:

1. Theoretical analysis has been made verifying that addition of MA can enhance oil recovery and RRFw can approximately represent mobility ratio.
2. Aqueous solubility of MA is increased with temperature elevation, reaching 105.62 g/100 cm^3 at 250 °C while 1.49 g/100 cm^3 at 60 °C. This property allows MA to be dissolved at high temperature and precipitate at low temperature. Water wettability was also enhanced by addition of MA.
3. Water residual resistance factor increased in response to the temperature elevation and increased pore volume during MA injection. Water residual resistance factor reached close to 1 after subsequent hot water flood, which indicated that the reduced water permeability by MA precipitatation could be restored.
4. The oil recovery by saturated MA injection was increasd by 11.7% when temperature dropped from 200 to 160 °C, in comparison with pure water flooding under the same condition. When temperature dropped from 200 to 60 °C, MA did not behave better in spite of more precipitation because oil viscosity was increased.
5. It has been verified that addition of MA can control mobility of condensed water during steam flooding process thus to enhance oil recovery.

Compliance with ethical standards

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