Journal of Petroleum
Science and Technology

A Study on the Mechanism of Urea-assisted Steam Flooding in Heavy Oil Reservoirs

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ABSTRACT

The Biqian-10 block, located in Henan Oilfield of Sinopic, contains many thin and interbedded reservoirs, which have been operated by cyclic steam stimulation for 20 years or more. Therefore, it is a challenge to implement the conventional steam flooding. In order to improve the recovery of steam flooding, urea was used to assist steam flooding. Urea can decompose into CO_2 and NH_3, which are beneficial to enhance oil recovery (EOR). For the sake of exactly quantifying the mechanism of urea assisted steam flooding (UASF), the UASF model was built according to the experimental results. The simulation results show that CO_2 is the key point for EOR, and its pressurization function is more effective than the decrease in oil viscosity by dissolving CO_2. The emulsification of crude oil for NH_3 is weak in interfacial tension tests; thus the effect of emulsification can be ignored in the simulation. The UASF can improve the recovery by about 17.4%, which is 6.8% higher than steam flooding.

Keywords: heavy oil, urea assisted steam flooding, CO_2, mechanism, EOR

INTRODUCTION

Gas-assisted steam flooding has become an effective technology to further EOR after steam flooding [1-4], but it is limited by the gas source. Therefore, gas-assisted steam flooding [5, 6] has not seen a large scale promotion. In order to further enhance the effect of steam flooding, the gas can be generated by chemical agents, which can effectively solve the problem of the gas source and gas generation can also be controlled by a chemical reaction generation rate.

Urea assists steam flooding through the decomposition of urea in the formation of CO_2 and NH_3 to achieve indirect gas-assisted steam flooding. The mechanisms of UASF are the reduction in the viscosity of heavy oil by CO_2 and the emulsification of the heavy oil in theory through NH_3. Meanwhile, the gas can increase the steam spread range, which can further improve heavy oil recovery. In order to describe the mechanism of urea-assisted steam flooding, a real

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Article history
Received: March 7, 2014
Received in revised form: April 12, 2014
Accepted: July 08, 2014
Available online: July 26, 2015

Journal of Petroleum Science and Technology **2015**, 5(2), 36-44 http://jpst.ripi.ir

reservoir model from Biqian 10 reservoir in the Henan oilfield of Sinopec was adopted for reservoir simulations using an advanced thermal simulator.

Urea-assisted Steam Flooding Model

In UASF modeling, in addition to conventional heavy oil viscosity-temperature model (Table 1) and relative permeability-temperature model (Figure 1), the main researches were on urea decomposition model, CO_2 dissolved in oil model, and NH_3 emulsifying oil model.

Table 1: Oil viscosity at different temperatures used in the simulator

Temperature (°C)	Oil viscosity (mPa·s)		
	calculated value	experimental value	Error (%)
30	51949	50720	2.4
50	6166	6505	5.2
70	1219	1190	2.4
90	348	350	0.57
130	60	--	--
150	32	--	--
170	19.4	--	--
200	10.7	--	--
250	5.4	--	--
300	3.4	--	--

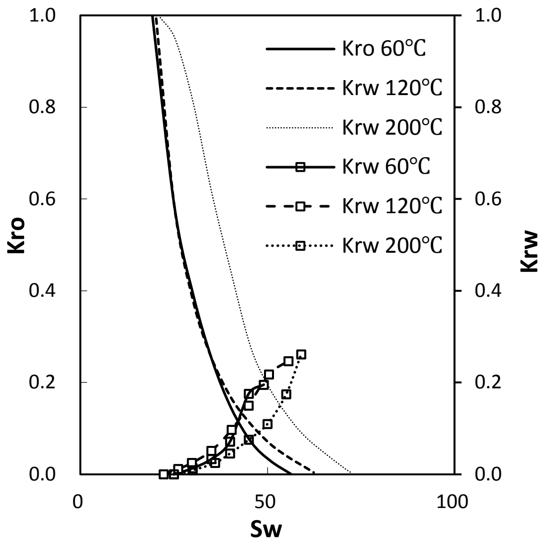

Figure 1: Variations of oil-water relative permeability used in the simulator

Urea Decomposition Model

The decomposition rate of urea is the key factor in controlling the reaction time and the volume of the decomposition gases of CO_2 and NH_3. A high temperature high pressure reactor was employed to simulate the urea decomposition reaction, and the experiment diagram is shown in Figure 2. The experimental conditions and results are shown in Table 2 and Table 3.

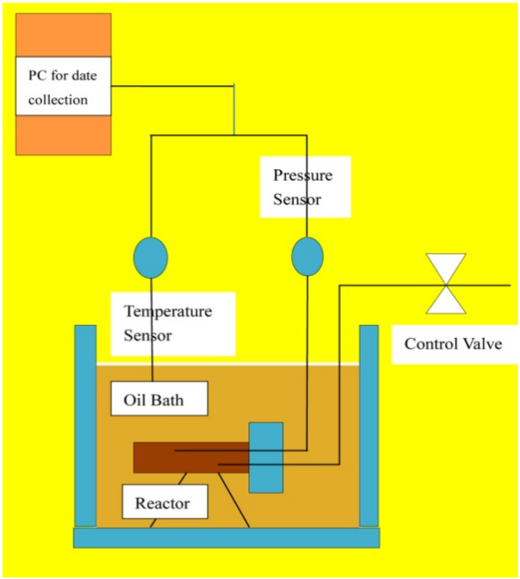

Figure 2: A schematic of urea decomposition reactor

Table 2: Experimental results of urea solution decomposition at different temperatures

Temperature (°C)	Pressure before reaction (MPa)	Pressure after reaction (MPa)	Pressure changes (MPa)	Reaction time(hr)	Decomposition rate ×10^3 (mol/(l.s))
50	0	0	0	0	0
80	0	0.07	0.07	0.37	0.054
110	0.07	0.3	0.23	0.52	0.116
150	0.3	2.95	2.65	1.87	0.357
180	2.95	3.08	0.13	0.6	0.033

It can be summarized that with increasing temperature, the pressure in the reactor was gradually increased in varying degrees. The reactor pressure was essentially unchanged at low temperatures (50 -80°C), which indicated that no substantial decomposition of urea happened and the reaction rate was low. When the temperature was raised to 110°C, the reactor pressure rose to 0.3 MPa and the reaction rate gradually increased. When the temperature was increased to 150°C, the pressure in the reactor was rapidly increased, and the decomposition rate reached 0.357×10^{-3} mol/(l.s), which was 3 times as much as the one obtained at 110°C. When the temperature reached 180 °C, the pressure remained essentially unchanged, indicating that urea decomposition was basically completed at 150°C.

Table 3: Experimental results of urea solution decomposition at different pressures

Temperature (°C)	Pressure before reaction (MPa)	Pressure after reaction (MPa)	Pressure changes (MPa)	Reaction time (hr)	Decomposition rate ×10^3 (mol/(l.s))
150	0	3.04	3.04	0.869	0.829
150	4	7.01	3.01	1.92	0.332
150	14	16.4	2.4	4.86	0.117

For gas generating reactions, the pressure changed with the time to reach equilibrium. At atmospheric pressure, the pressure reached balance after 0.869 hr, and the decomposition rate was 0.829×10^{-3}mol/(l.s). When the pressure rose to 4 MPa (the shallow reservoir pressure), the reaction time was extended to 2 hrs after the pressure reached an equilibrium, and the decomposition rate was reduced to 0.332×10^{-3} mol/(l.s). When the system pressure increased to 14 MPa (the deep reservoir pressure), the average rate of the decomposition was reduced to 0.117×10^{-3} mol/(l.s). Therefore, increasing the reservoir pressure raised the urea decomposition reaction rate, which was not conducive to the rapid decomposition of the urea.

The decomposition of urea belongs to the zero order reaction, because the concentration of urea does not affect the decomposition reaction [8]. Based on the above experimental results, the urea decomposition kinetic parameters used in the thermal simulator were calculated by the Arrhenius equation (Equation 1). The activation energy is 9.83 KJ/mol, and the pre-exponential factor is 1×107 l/(s.kPa).

$$\frac{dp_x}{dt} = k_0 \exp\left(-\frac{E}{RT}\right) \tag{1}$$

where, p_{x} is a gas partial pressure; *t* is the time and k_0 represents pre-exponential factor; *E* is the activation energy and *R* stands for the molar gas constant equal to 8.314; *T is* the model temperature.

Model of CO$_2$ Dissolved in Oil

CO$_2$ is easily dissolved in oil and reduces viscosity. The widely used equation describing CO$_2$ solubility in heavy oil was proposed by Chung [9] (Equation 2).

$$R_s = \frac{1}{\left[a_1 \gamma^{a_2} T^{a_7} + a_3 T^{a_4} \exp\left(-a_5 P + {}^{a_6}\!/_{P}\right)\right]} \tag{2}$$

where, *R$_s$* is the CO$_2$ solubility in heavy oil and *Y* is the severe of oil; *P* stands for the pressure and *T* represents the temperature; a_1, a_2, a_3, a_4, a_5, a_6, and a_7 are constants equal to 0.4934×10^{-2}, 4.0928, 0.571×10^{-6}, 1.6428, 0.6763×10^{-3}, 781.334, and -0.2499 respectively.

The CO$_2$ solubility in heavy oil at different temperatures and pressures was calculated by Chung equation. Table 4 shows the calculated data (CD) and the experimental date (ED) used in the thermal simulator. The CO$_2$ solubility in heavy oil was test by PVT equipment.

The calculated average error in Table 4 is less than 16.67%, which complies with the requirement of engineering computing requirements. Therefore, the CO$_2$ solubility in the thermal simulator can be calculated by Chung formula.

Table 4: Comparison of the experimental and calculated data on CO_2 solubility in heavy oil at different pressures and temperatures

Parameter	Solubility [ml(gas)/100ml(liquid)]														
Pressure (MPa)	40 °C			60 °C			80 °C			100 °C			120 °C		
	CD	ED	Error (%)	CD	ED	Error (%)	CD	ED	Error (%)	CD	ED	Error (%)	CD	ED	Error (%)
3	27	28	3.7	20	21	5	11	10	9.09	8	7	12.5	6	7	16.67
10	85	87	2.3	65	71	9.23	59	55	6.78	49	52	6.12	38	41	7.89
15	104	110	5.77	85	89	4.71	77	76	1.3	69	72	4.35	62	61	1.61
20	116	119	2.59	97	102	5.15	93	94	1.08	89	91	2.25	81	84	3.7

Model of NH_3 Emulsifying Oil

NH_3 solubility in water is high, which is easy to generate weak alkali ammonium hydroxide (NH_3-H_2O). In theory, ammonium hydroxide reacts with the active ingredient in oil by saponification reactions to form a surfactant. The reaction is given by Equation 3:

$$\text{RCOOH+NH}_4\text{OH} \longrightarrow \text{RCOONH}_4\text{+H}_2\text{O} \qquad (3)$$

The generated surfactant can reduce the oil-water interfacial tension to achieve emulsification, and this mechanism can improve the oil displacement efficiency. The interfacial tension between ammonium hydroxide and oil at different concentrations was tested by tension apparatus of TX-500, but the emulsifying effect was not obvious. The experimental results showed that the interfacial tension was between 50×10^{-3} N/m and 58×10^{-3} N/m. Also, King used capillary force method to calculate the interfacial tension between NH_3 and pure water and showed that the interfacial tension decreased from 72.55×10^{-3} N/m to 22×10^{-3} N/m, i.e. a drop of 69% [10]. Therefore, NH_3 can reduce the interface tension between NH_3 and water, but it is not able to reduce the tension between NH_3 and heavy oil, because ammonium hydroxide is a weak alkaline, and the acids in heavy oil belong to weak acids; thus both react a lesser extent [11]. In conventional alkaline flooding, NaOH is the most important component, while ammonium hydroxide is rarely used for its weak alkaline; NaOH can reduce the interfacial tension to values between 0.1×10^{-3} N/m and 0.01×10^{-3} N/m [12]. Furthermore, the accumulation and diffusion of surface is a dynamic process at the interface. If the concentration of surfactant cannot reach critical micelle concentration (CMC), its effect on reducing interfacial tension is not obvious.

Therefore, the role of NH_3 in decreasing the interfacial tension cannot be considered in the numerical simulation.

Mechanism of Urea-assisted Steam Flooding in Reservoir

Reservoir Geology and Production History

Biqian 10 block is a shallow layer of ultra-heavy oil and the basic reservoir parameters are as follows: reservoir depth is 294.6 m; dip is 12 º; the effective thickness is 9.4 m; the porosity is 34%; the permeability is 2.28 D; the original oil saturation is 75%; the original reservoir pressure is 2.9 MPa; the temperature is 30.3°C; dead oil viscosity under reservoir temperature is 50719.6 mPa.s, and the density is 966.8 kg/m^3.

This block has been operating with the CCS process since 1989. Up to now, the recovery has reached 22%, with an average period of 8.1 cycles per single well, and the reservoir pressure has decreased to 1.2 MPa. Especially, the CCS process has reached the economic limit.

Based on the reservoir parameters, four inverted nine-spot well patterns were established as shown in Figure 3.The well spacing is 70 m×100 m, in which there are four injection wells and 21 production wells. The grid of fine geological model is 45×55×9. Moreover, the results of matching the CCS production history of 20 years are shown in Figure 4.

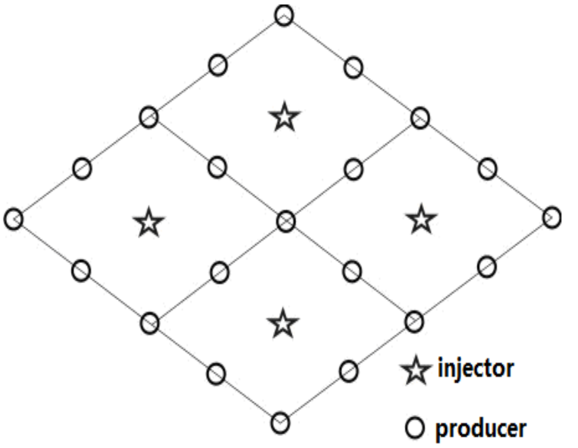

Figure 3: A schematic of 4 inverted nine-spot well patterns

Based on matching the CCS production history of 20 years, steam flooding (SF) and UASF for 30 cycles were compared. The structure of one cycle is shown in Figure 5 and the calculated results are summarized in Table 5. The steam injection pressure was 5.5 MPa and the steam temperature was 200°C. The steam quality was 70%.

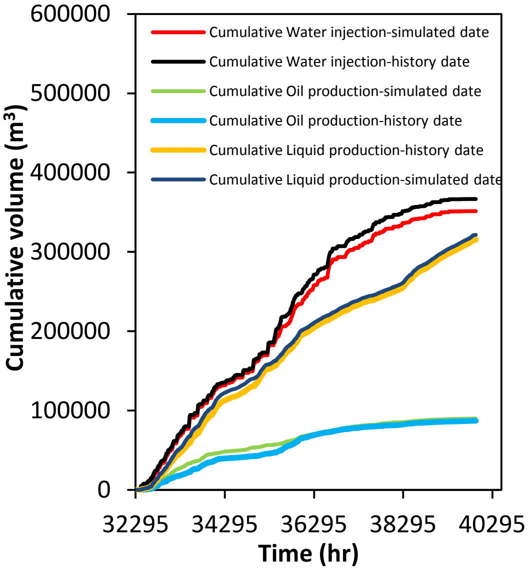

Figure 4: Results of history matching

Table 5: Development results for UASF and SF in 30 cycles

Driving mode	Cumulative cycle	Rate of steam flooding (m^3/d)	Weight of urea in one cycle (t)	The cumulative oil steam ratio (m^3/m^3)	Recovery (%)
Steam flooding	30	80	0	0.14	10.6
Urea-assisted steam flooding	30	80	30	0.24	17.4

Enhancing the Formation Pressure

The decomposition of urea can produce large amount of decomposition gas; reaction of 1 ton urea with 0.3 ton water can generate 373 m^3 CO_2 and 746 m^3 NH_3, which can significantly increase the volume of production. Figure 6 is the average pressure of steam flooding and urea-assisted steam flooding.

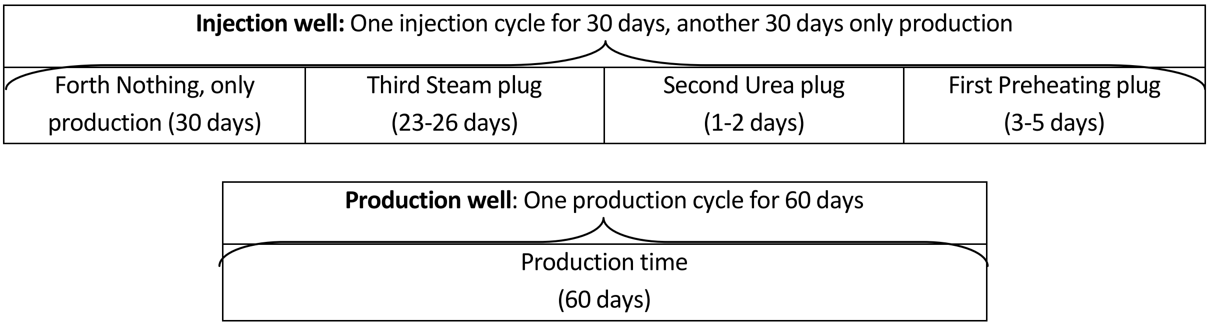

Figure 5: A scheme of single-cycle injection and production for UASF

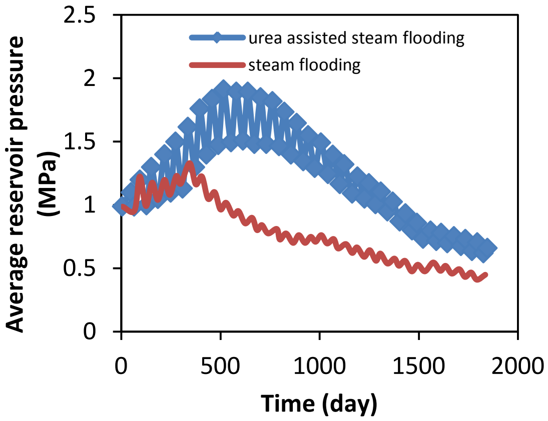

Figure 6: Variations of average pressure of SF and UASF

The reservoir pressure rose to 1.3 MPa by steam flooding, but the pressure declined to 0.5 MPa after steam channeling. UASF boosted the reservoir pressure to 1.9 MPa and the pressure decreased slower than steam flooding after steam channeling. Moreover, the intermittent injection created the jagged form of pressure.

Furthermore, as the reservoir pressure increases, the CO_2 solubility in oil will be enhanced, which can reduce the viscosity of heavy oil. In addition, the increased pressure is beneficial to maintain the steam dryness.

Reducing the Viscosity of Heavy Oil

The viscosity-reducing rate is an important indicator for enhanced heavy oil recovery. The viscosity-reduction rate reached 30% or more in the simulation as tabulated in Table 6.

Expanding Steam Sweep Volume

Figure 7 is the oil saturation field after matching history. Figure 8 displays the oil saturation field for steam flooding and urea-assisted steam flooding after 30 cycles. The red dot positions are the injection well in Figures 7 and 8.

Steam flooding can spread the scope and improve the oil production, but due to the small steam viscosity, high water-oil mobility ratio (which makes it easy to form steam channeling), it results in a lower heat utilization rate.

The gas generated by adding urea to steam flooding can rapidly enhance reservoir pressure and oil production rate.

Table 6: Variation of oil viscosity between injector and producer after UASF

Distance from injector (m)	Mole fraction of CO_2 in heavy oil (%)	Original oil viscosity (mPa·s)	Oil viscosity after UASF (mPa·s)	Viscosity-reducing rate (%)
10	57.57	77.2	11	85.7
30	3.19	741	516	30.4
40	0.1	1129	1114	1.3
50	0	786	786	0

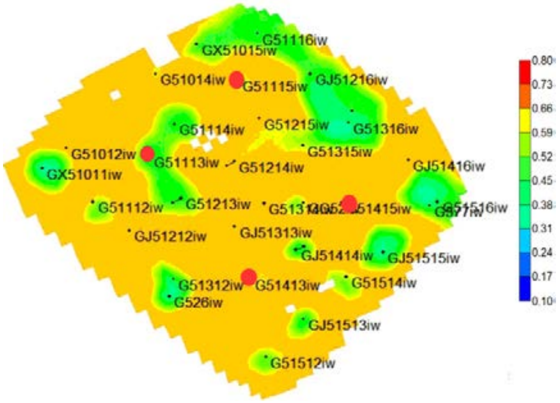

Figure 7: Distribution of oil saturation in the end stage of steam stimulation

The Constitution of EOR by UASF

In order to analysis the contribution of CO_2 and NH_3 to the oil recovery, the gas after the decomposition of urea was selected as the injection fluid; the proportion of CO_2 to NH_3 was 373 m^3 to 746 m^3 for 1 ton of urea. For the sake of the contribution of CO_2 in the viscosity reduction and raised pressure mechanisms, a smaller solubility of N_2 was selected as a counterpoint in the simulation. In order to remove the impact of the intermittent injection on pressure, the mode of single-cycle injection and production was changed as shown in Figure 9. Table 7 and Figure 10 report the results of EOR using different approaches.

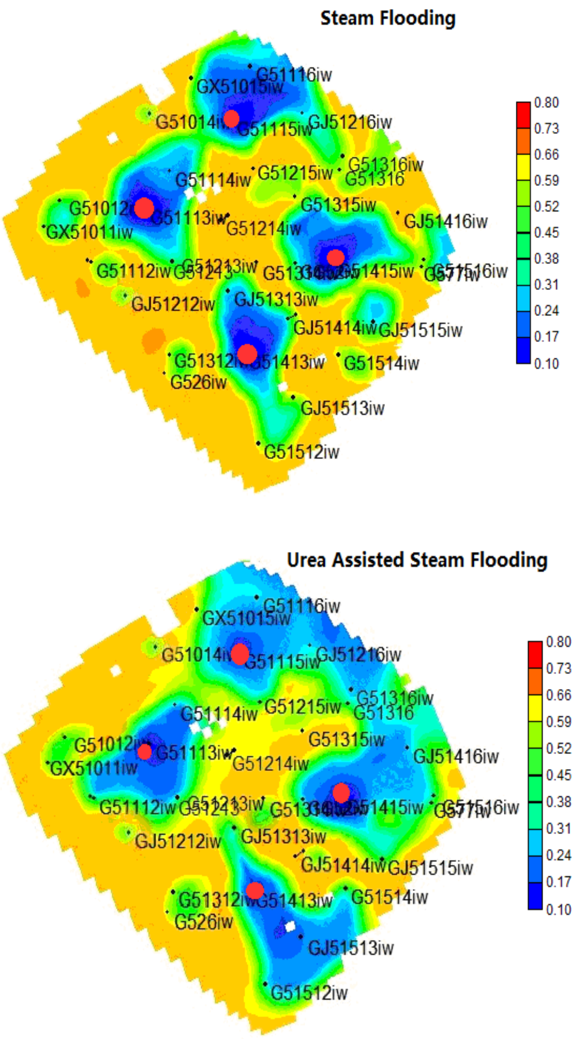

Figure 8: Distribution of oil saturation in 30th cycle after steam flooding (left) and UASF (right)

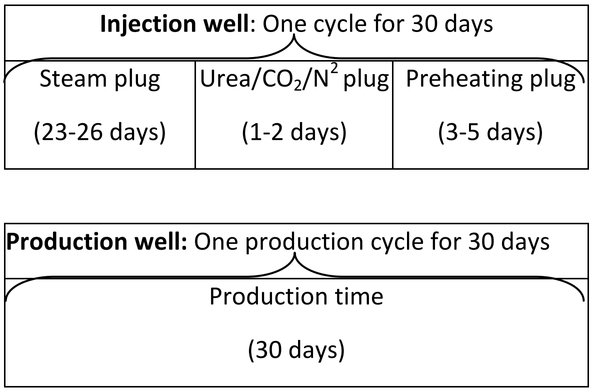

Figure 9: A scheme of a single-cycle injection

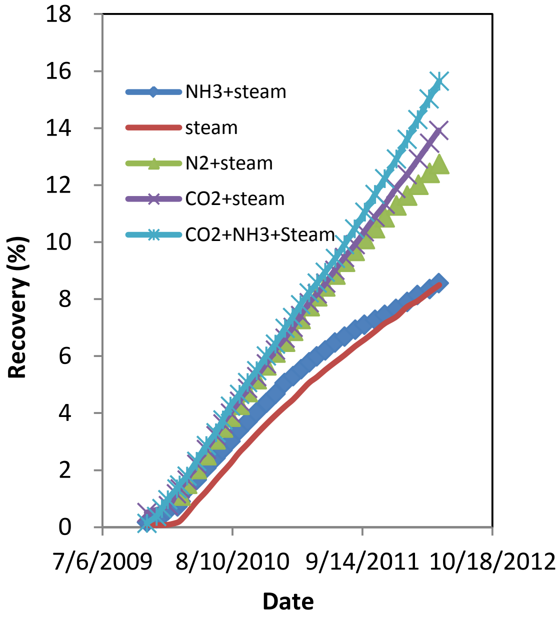

Figure 10: Variations of EOR using different approaches

Table 7: Results of EOR using different approaches

Injection mode	Rate of steam flooding (m^3/d)	Volume of gas in one cycle (m^3/day)		Cumulative volume of steam (m^3/day)	Cumulative volume of gas (m^3/day)		Cumulative volume of oil production (m^3/day)	EOR (%)	Growth based on steam flooding (%)
		CO$_2$	NH$_3$		CO$_2$	NH$_3$			
Steam flooding	[80	0	0	70879	0	0	6442	8.77	0
N$_2$ assisted steam flooding	80	11200	0	70879	335995	0	9605	13.07	4.3
CO$_2$-assisted steam flooding	80	11200	0	70879	335995	0	10568	14.39	5.62
NH$_3$-assisted steam flooding	80	0	22400	70879		671990	6479	8.88	0.11
CO$_2$-and NH$_3$-assisted steam flooding	80	11200	22400	70879	335995	671990	11877	16.17	7.4

Simulation results showed thatNH$_3$ and CO$_2$ were beneficial to enhance steam flooding recovery. The final recovery of steam flooding was similar with NH$_3$-assisted steam flooding, but the production rate of NH$_3$-assisted steam flooding was faster than steam flooding at early stages, which was due to the pressurization of NH$_3$. However, the impact of enhanced pressure on recovery was limited for NH$_3$ owing to its high solubility in water.

The recovery of CO$_2$-assisted steam flooding reached 14.39%, which was 5.62% higher than steam flooding. Therefore, CO$_2$ was the key point to enhance heavy oil recovery.

However, the recovery of CO$_2$-assisted steam flooding was only 1.32% higher than that of N$_2$-assisted steam flooding, which demonstrated that the dissolution of CO$_2$ in heavy oil, and thereby viscosity reduction thereof, was not the most important factor in oil recovery. Furthermore, the pressurization mechanism was a major parameter for CO$_2$ to enhance heavy oil recovery in immiscible flooding.

Meanwhile, the recovery of CO$_2$- and NH$_3$-assisted steam flooding reached 16.17%, which was 7.4% higher than that of steam flooding.

CONCLUSIONS

1- Based on the urea decomposition experiments, CO$_2$ was dissolved in oil and NH$_3$ emulsified oil; the urea-assisted steam flooding model was built by an advanced thermal simulator. Urea-assisted steam flooding model included urea decomposition model, CO$_2$ dissolved in oil model, NH$_3$ emulsifying oil model, and other conventional thermal models such as heavy oil viscosity-temperature model and relative permeability-temperature model. The results of urea-assisted steam flooding model was close to the experiment data.

2- CO$_2$ was the key factor in EOR and its pressurization function was more effective than the decrease in oil viscosity by the dissolution of CO$_2$. However, the NH$_3$-emulsified oil was weak in interfacial tension tests, and thus the effect of emulsification could also be ignored in the simulation.

3- Urea-assisted steam flooding outperforms conventional steam flooding after high stimulation cycles, and this technology has a fine adaptability for heavy oil reservoirs.

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