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Evaluation the performance of sodium metaborate as a novel alkali in alkali/surfactant/polymer flooding

Fuzhen Chen [a,*], Hanqiao Jiang [a], Xiaohu Bai [b], Wei Zheng [c]

[a] MOE Key Laboratory of Petroleum Engineering and College of Petroleum Engineering, China University of Petroleum Beijing, Beijing 102249, China
[b] Ultra-Low Permeability Reservoir Research Center, Changqing Oilfield Company, CNPC, Xi'an 710000, Shanxi, China
[c] CNOOC Research Institute, Beijing 100027, China

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ABSTRACT

Sodium metaborate, a novel alkali, is introduced into alkali/surfactant/polymer (ASP) flooding to solve the negative effects caused by conventional alkalis. Sodium metaborate can reduce the adsorption loss of the surfactant as well as the interfacial tension (IFT). Weak alkali sodium metaborate causes less viscosity reduction compared with strong alkalis. Scale precipitation study shows that sodium metaborate can be effective to avoid the scale precipitation damage. Study results indicate that sodium metaborate result in the highest oil recovery of 56% compared with sodium carbonate and sodium hydroxide, and at the same time avoid the problems caused by conventional alkalis.

1. Introduction

Laboratory and field pilot studies have shown that the crosslinked polymer can effectively enhance oil recovery and the alkali/polymer technology can recover more oil than alkali or polymer solution alone [1,2]. Research report done by Frank et al. in 1987 indicated that oil recovery can be improved by using a combination of alkali, surfactant and polymer [3]. This is the early investigation of alkali/surfactant/polymer (ASP) flood. After that, the ASP technology for improving sweep efficiency and mobilization of residual oil has been amply reported around the world with high percentage of success [4,5]. ASP flooding has been proved to be effective in enhanced oil recovery through reduction of IFT and mobility ratio between oil and water phases. The ASP flood mechanisms have been studied by Nasr-El-Din et al. and they indicated that the residual oil was recovered by two mechanisms: low IFT and wettability reversal [6]. The combined effects of alkali/surfactant/polymer on physical chemical properties were studied by Nedjhioui et al. [7]. In ASP agent system, alkali is intended to react with the acids in the crude oil to generate in situ soaps to reduce IFT and to overcome the surfactant depletion due to adsorption. The surfactant is responsible for reducing the IFT between oil and water phases to attain ultralow IFT that promotes the mobilization of trapped oil drops. The role of the polymer is to increase the viscosity, hence reduce the mobility ratio, which in turn results in greater volumetric sweep efficiency [8].

Several mechanisms have been studied to explain the role of alkali in ASP flooding, including reduced surfactant adsorption, low IFT, wettability reversal, emulsification, and entrapment [9]. The presence of organic acids in the crude oil is an important criterion for these mechanisms. These acidic components react with the alkali to produce petroleum surfactants which enhances oil recovery by one or more of the mechanisms above mentioned. According to current research results, alkali is mainly used to reduce surfactant adsorption. Then the chemical cost will be reduced because alkali is normally much cheaper than surfactant. In acidic crude oil, alkali will also convert the petroleum acids into in situ soaps, thereby lowering the IFT [10].

Despite the success of ASP in laboratory studies, most oilfield applications were not as successful as anticipated and ASP flooding has not been widely applied as polymer flooding. One reason is that the alkali can decrease the viscosity of ASP solution significantly and reduce the oil recovery because of the incompatibility of alkali with polymer [11]. The other reason is the scale precipitation caused by the reaction between alkali and hard ions (such as Ca^{2+} and Mg^{2+}) in the formation brine [12]. These challenges have been barriers for the wide application of ASP flooding although the alkalis have many positive effects. Hence the selection and optimization of alkali is an important issue for ASP flooding.

Sandstone reservoirs are characterized as water-wet, a favorable condition for the ASP flooding. Most of the ASP flooding studies and applications were focused on sandstone reservoirs.

* Corresponding author. Tel.: +86 13488780191.
E-mail address: chenfuzhen19@gmail.com (F. Chen).

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Nomenclature

ASP	alkali/surfactant/polymer
IFT	interfacial tension
mD	10^{-3} μm^2
wt%	weight percent
PV	pore volume
MPa	10^6 Pa

Thus, in this paper, the performance of sodium metaborate in sandstone reservoir was studied. In this paper, sodium metaborate ($NaB(OH)_4$) was evaluated as a novel alkali. The objectives of this work are: (1) to determine the contribution of sodium metaborate on the reduction of IFT, (2) to examine the effect of sodium metaborate on the rheology of ASP solution, (3) to obtain more insight into mechanisms of how alkali protects surfactant from adsorption, (4) to study the performance of sodium metaborate on scale precipitation with formation brine, and (5) to study the enhanced oil recovery abilities of three kinds of alkalis by core flood tests.

2. Experimental studies

2.1. Material descriptions

Crude oil from the Suizhong offshore oilfield in China was used for this study. Basic sediment and water in the crude oil was removed by high-speed centrifugation. The properties of the Suizhong crude oil, including the total amount of organic acids, are listed in Table 1. Two kinds of synthetic formation brines were used in this study. Their composition and properties are listed in Table 2. Compared with the favorable formation brine, the unfavorable formation brine contains higher amount of divalent cations (such as Ca^{2+} and Mg^{2+}).

Artificial cores were used for core flood test. The cores were made of epoxy resin and silica-sand, which will not react with crude oil and injected fluids. The parameters of the cores were designed according to the rock properties of the Suizhong oilfield. A total 34 cores, of dimensions 20 cm in length and 2.5 cm in diameter were prepared. The porosity was 0.29 and the permeability was 2200 mD.

The alkalis tested in this study were sodium metaborate ($NaB(OH)_4$, a novel alkali), sodium carbonate and sodium hydroxide. Like other alkali metal borates, monomeric borate ion ($B(OH)_4^-$) will strongly hydrolyze to form hydroxide ion and increase the pH of solution. Sodium carbonate and sodium hydroxide are two kinds of conventional alkalis which are usually used in ASP flooding. Sodium alkyl benzene sulfonate (ORS-41) was chosen as the surfactant. A high molecular weight polyacrylamide, with a molecular mass of 11.6 million Daltons, 24.0% hydrolyzed (HPAM), was used as the polymer. Unless specified otherwise, the surfactant and polymer mentioned in the following study are referred to as ORS-41 and HPAM, and their concentrations were constant at 1.05 wt% and 0.16 wt%, respectively.

Table 1
Properties of Suizhong crude oil (at 40 °C).

Parameter	Value
Viscosity	57.1 mPa s
Density	866.5 kg/m^3
Total acid number	0.34 mg KOH/g oil

2.2. Experimental apparatus and procedure

2.2.1. IFT test

IFT between Suizhong crude oil and formation brine was measured by pendant drop method. IFT between ASP solution and Suizhong crude oil was measured using the Spinning Drop Tensiometer model 500 which was made in Texas University. The stable value of IFT was taken after aging for 120 min at 40 °C. The effects of sodium metaborate and surfactant on IFT were studied with the variation of sodium metaborate and surfactant concentrations.

2.2.2. Rheology test

The rheology of ASP solution was tested for different sodium metaborate and polymer concentrations by HAAK RS-150H rhemeter. The loss modulus and viscosity of ASP solution were measured. The temperature was constant at 40 °C during the test process.

2.2.3. Core flood test

The effects of alkalis (sodium metaborate, sodium carbonate and sodium hydroxide) on chemical adsorption, scale precipitation and oil recovery were measured by a series of core flooding tests. The schematic of the core flood setup used in experiments is shown in Fig. 1.

The following steps were applied:

(1) The core was inserted into the core holder. 5.0 PV (pore volume) favorable formation brine and 5.0 PV crude oil were injected into the core for water and oil saturation processes separately. This was allowed to stabilize for 24 h of aging.

Table 2
Composition and properties of formation brines (at 40 °C).

Formation brine type	Composition	Concentration (mg/L)	Properties	Value
Favorable formation brine	Na^+	3916	Viscosity	0.67 mPa s
	K^+	1486	Density	1002 kg/m^3
	Cl^-	6622	pH	8.6
	HCO_3^-	588	Conductivity	10.4 ms/cm
	SO_4^{2-}	570		
	Total dissolved solids	13,182		
Unfavorable formation brine	Na^+	2187	Viscosity	0.65 mPa s
	K^+	187	Density	1005 kg/m^3
	Ca^{2+}	3760	pH	8.7
	Mg^{2+}	464	Conductivity	10.7 ms/cm
	Cl^-	10873		
	HCO_3^-	643		
	SO_4^{2-}	408		
	Total dissolved solids	18,522		

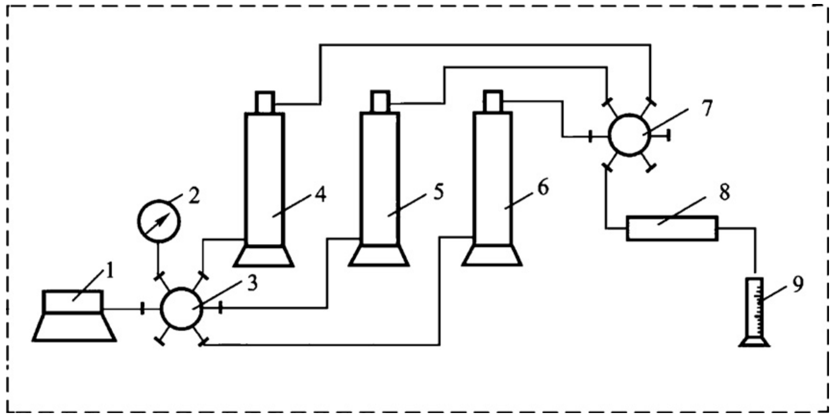

Fig. 1. Equipments used in core flood experiment (1, pump; 2, pressure gauge; 3, valve; 4, formation brine tank; 5, crude oil tank; 6, ASP solution tank; 7, valve; 8, core holder; and 9, measuring cylinder).

(2) For water flood process, favorable formation brine was injected into the core until the injection volume reached 2.0 PV, followed by ASP flood with 1.0 PV ASP solution. Finally, 2.0 PV favorable formation brine was injected as continued water flood.
(3) A constant injection rate of 0.3 ml/min was maintained in the above steps. For the scale precipitation measurement and enhanced oil recovery study sections, the unfavorable formation brine was employed to replace the favorable formation brine. During the experiment process, the effluent chemical components' concentrations, injection pressure data and oil recovery were measured.

3. Results and discussion

3.1. IFT measurements

A series of experiments were conducted to measure the IFT between ASP solution and crude oil. An inverse distance weighting interpolation method was used to deal with the IFT test results [13]. The interpolated results are shown in Fig. 2.

Fig. 2 shows IFT as a function of sodium metaborate and surfactant concentrations. For constant surfactant concentration, the IFT decreased with the increase of sodium metaborate concentration. The acidic components in the crude oil were taken as HA. Sodium metaborate can react with HA and generate special in situ soaps (NaA) which are petroleum surfactants. With the increase of sodium metaborate concentration, the concentration of A^- ions at the oil/water interface will increase. Hence, the IFT will drop due to the arrangement of A^- ions at the interface. However, when the sodium metaborate achieves a critical concentration, more alkali will not contribute to the reduction of the IFT, as the concentration of the HA is limited.

For a constant sodium metaborate concentration, the IFT decreased significantly with the increase of surfactant concentration (see Fig. 2). This was caused by the surfactant arrangement at the oil/water interface [14]. When IFT is less than 0.01 mN/m, it is usually called as Ultra-low IFT, which is one of the primary enhance oil recovery mechanisms of the ASP flood [15]. The ultra-low IFT will be achieved after the surfactant concentration reached 1.05 wt% under sodium metaborate concentration as 0 wt%. With the increase of sodium metaborate concentration, the specific surfactant concentration required to achieve the Ultra-low IFT will decrease (as shown in Fig. 2). This is the synergistic enhancement among sodium metaborate and surfactant. It can also be observed that the surfactant has more affect on IFT compared to sodium metaborate. This indicates that the surfactant is the major factor affecting IFT and sodium metaborate can enhance the performance of the surfactant to reduce the IFT.

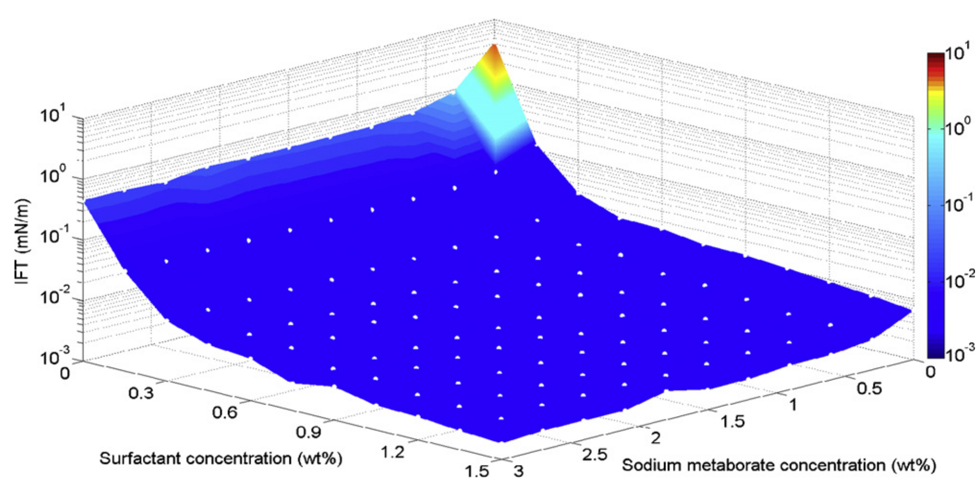

Fig. 2. Effect of sodium metaborate and surfactant on IFT (the white points represent the experimental result data).

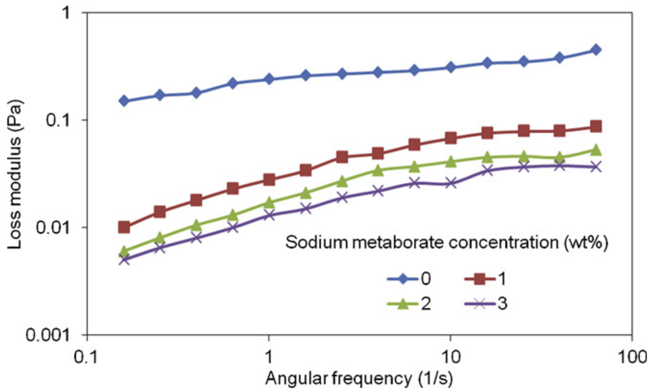

Fig. 3. Loss modulus of ASP solution.

3.2. Rheology study

The loss modulus of ASP solution was measured for constant concentrations of surfactant and polymer. As shown in Fig. 3, the loss modulus dropped significantly after 1 wt% sodium metaborate was added into the solution. The decrease of loss modulus was due to the ion strength increase with the increase of sodium metaborate concentration. When sodium metaborate concentration increased from 1 to 3 wt%, slight decrease of loss modulus can be observed due to the diminished scope of ion strength to increase. As many papers reported, the loss modulus reflects the viscosity [16]. Hence the variation trend of the loss modulus indicated that the viscosity of the ASP solution will decrease with the increase of sodium metaborate concentration.

The effects of sodium metaborate on the loss modulus which reflect the viscosity are dramatic. To examine the effects further, the viscosity of ASP solution was measured under different sodium metaborate and polymer concentrations. According to the molecular dynamics theory, the more the polymer (polyacrylamide) molecular chains are stretched, the higher the solution's viscosity is. Hence at the same sodium metaborate concentration, ASP solution's viscosity increases with the increase of polymer concentration (see Fig. 4). It can also be observed that sodium metaborate has not much effect on viscosity for 0 wt% polymer concentration. However, the drop of viscosity was significant with the increase of sodium metaborate concentration for high polymer concentration. At low sodium metaborate concentration, the polyacrylamide molecular chains are stretched due to the repulsive force among the negative electric charges of the carboxylate groups. With the increase of sodium metaborate concentration, the ionic strength will increase. Hence the electrical double layers of the polyacrylamide molecular chains will compress and the negative electric charges are shielded. Then the repulsive forces within the polyacrylamide molecular chains will decrease due to the charge screening effect. This change reduces the hydraulic radius of polyacrylamide molecular chain and causes it to shrink instead of stretching. Finally, the ASP solution's viscosity will decrease with the increase of sodium metaborate concentration. In addition, polymer molecules weight will diminish at high sodium metaborate concentration and this will drop the ASP solution's viscosity too.

Fig. 5 shows the plot of the ASP solution viscosity measurements versus the alkali concentration when sodium metaborate, sodium carbonate and sodium hydroxide were tested individually as the alkali. As analyzed earlier, polyacrylamide molecular chain will shrink and ASP solution's viscosity will decrease at high pH condition. As a strong alkali, sodium hydroxide solution's pH is higher than the sodium metaborate and sodium carbonate under the same concentration. Hence the viscosity drop of sodium hydroxide was more significant than the other two kinds of alkalis (see Fig. 5). Sodium metaborate is a weak alkali which can keep the pH in low level. Hence it has the least effect on viscosity than sodium carbonate and sodium hydroxide.

In the ASP flooding field pilots of Daqing Oilfield in which sodium hydroxide was used, the polymer concentration was increased from 0.12 wt% to 0.16 wt%, even to 0.23 wt% in some cases to offset the negative effect of sodium hydroxide and ensure that the viscosity of the ASP solution is no less than 20 mPa s, so as to get an incremental oil recovery of 20% [17]. The experimental result is in good agreement with the field pilot result.

3.3. Chemical adsorption study

Chemical adsorption is of interest, as the success of ASP flooding depends on the ratio of surfactant adsorbed on the rock matrix. The surfactant adsorption on the rock matrix cannot decrease the IFT and it will not contribute to the ASP flooding efficiency [18]. To keep the free surfactant at essential concentration under high surfactant adsorption ratio, the surfactant cost will increase. The

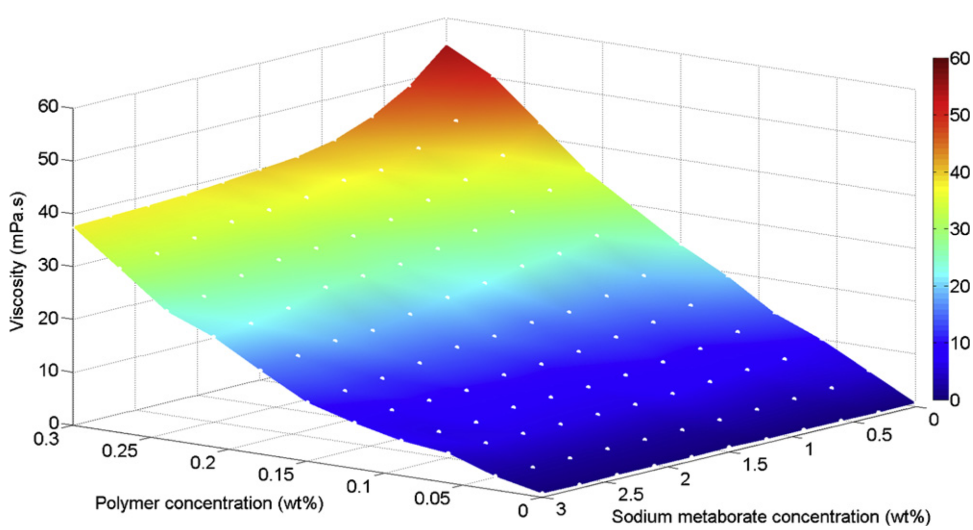

Fig. 4. Effect of sodium metaborate and polymer on the viscosity of ASP solution (the white points represent the experimental result data).

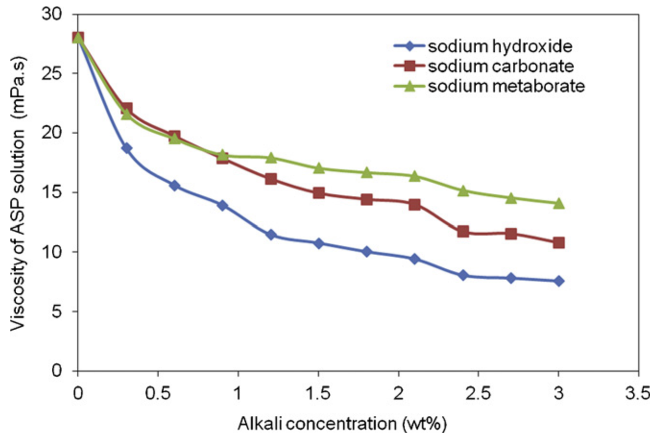

Fig. 5. Effect of alkalis on the viscosity of ASP solution.

main reason of surfactant adsorption is the electrostatic attraction between the charged head-group in the surfactant and the charged minerals on the rock [19,20]. To reduce the surfactant adsorption, repulsion forces between the rock and surfactant should be generated. As sodium alkyl benzene sulfonate was used in this study, which is anionic. Hence, creates a negative potential between the rock and formation brine is needed. This will help in creating repulsive forces which can reduce surfactant adsorption. For this reason, sodium metaborate is added into the ASP solution to increase the solution's pH and create a negatively charged environment to protect surfactant from adsorption.

Figs. 6 and 7 show the effluent concentration of surfactant and sodium metaborate based on a series of core flood tests. The effluent surfactant and sodium metaborate concentrations were normalized by their injected concentration values. As shown in Fig. 6, there is significant increase of effluent surfactant concentration with the increase of injected sodium metaborate concentration. It means that only a small part of surfactant was adsorbed on the rock matrix under high sodium metaborate concentration. Most of the surfactant arranged on the interface between crude oil and ASP solution to decrease IFT and finally flowed out with the liquid produced from the outlet of the core. This indicated that sodium metaborate can protect the surfactant from adsorption. Fig. 7 shows the effluent concentration of sodium metaborate. The loss of sodium metaborate was mainly due to the adsorption on the rock matrix. The reactions of sodium metaborate with the organic acids present in the crude oil caused a relatively small loss [21].

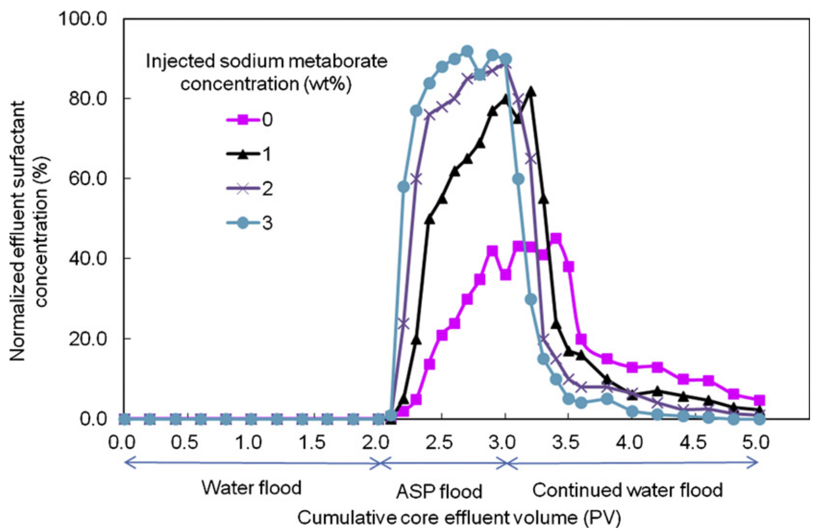

Fig. 6. Surfactant effluent concentration of ASP flooding.

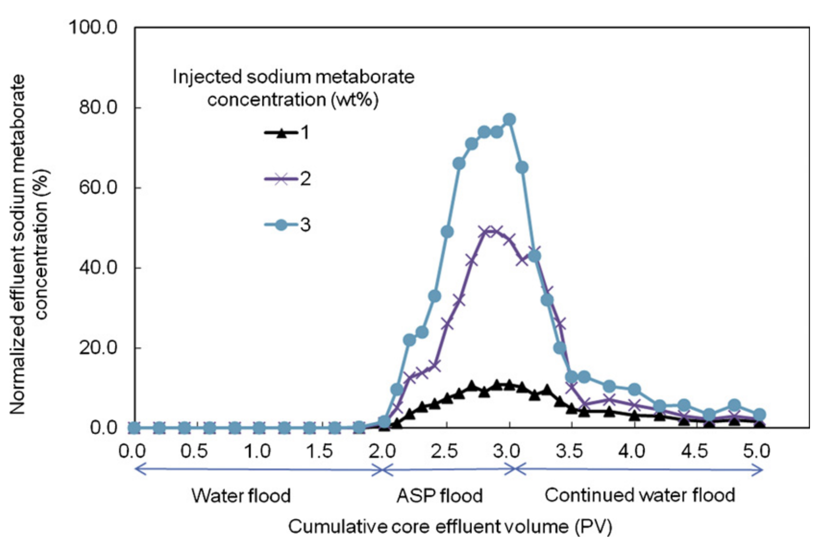

Fig. 7. Sodium metaborate effluent concentration of ASP flooding.

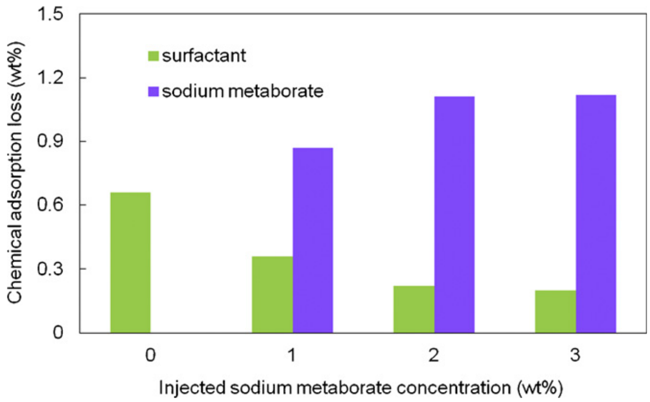

Fig. 8. Chemical adsorption loss of ASP flooding.

Furthermore, petroleum surfactants will be generated by the reactions and they can compensate the adsorption loss of surfactant partly. In the continued water flooding process, the surfactant and sodium metaborate adsorbed on the rock matrix will be desorbed, so their concentration will not be zero at this period (see Figs. 6 and 7).

The adsorption loss of surfactant and sodium metaborate during ASP flood process was shown in Fig. 8. It was calculated by the experimental results shown in Figs. 6 and 7. It can be observed that with the increase of injected sodium metaborate concentration, surfactant adsorption loss decreased and sodium metaborate adsorption loss increased. This means that sodium metaborate can adsorb on the rock matrix prior to the surfactant, and then reduce the adsorption loss of surfactant. A slight variation of chemical adsorption loss can be seen after injecting sodium metaborate concentration higher than 2.0 wt% (see Fig. 8). Fig. 6 also shows that the normalized effluent surfactant concentration remained at its maximum value for a longer period of time after sodium metaborate concentration achieved 2.0 wt%. Hence it can be confirmed that 2.0 wt% is the critical concentration of sodium metaborate in this study which can reduce surfactant adsorption loss to a relatively low level.

3.4. Scale precipitation study

Two series of core flooding tests were conducted to study the impact of reaction between alkali and hard ions in the core samples. Scale precipitations of sodium metaborate, sodium hydroxide and sodium carbonate in unfavorable formation brine were studied in the first series of tests, and their concentrations were constant at 2 wt% during the experiment process. The second series of tests were conducted to study the scale precipitation under different sodium metaborate concentrations and formation brines.

As shown in Fig. 9, the injection pressure has increased significantly from the water flood stage to the ASP flood stage and has dropped sharply from the ASP flood stage to the continued water flood stage. This is mainly caused by the higher viscosity of ASP solution compared to that of water. The injected fluids were the same during the water flood process and the continued water flood process. However, the stable injection pressure of water (which sodium hydroxide and sodium carbonate were employed as alkalis) in the continued water flood process was higher than that in the water flood process (see Fig. 9). This was due to scale precipitation. During ASP flood process, high concentrations of Mg^{2+} and Ca^{2+} in the unfavorable formation brine can interact with sodium hydroxide and sodium carbonate to generate precipitation. Much precipitation will result in plugging the pores in the core and then increases the injection pressure [22]. Hence the difference of injection pressures between the water flood stage and the continued water flood stage reflects the amount of scale precipitation generated in ASP flooding process. During the continued water flood process, it can also be seen that the stable injection pressure, when sodium metaborate was employed as alkali, is almost similar to that in the water flood process. This indicates that there is no scale precipitation during the ASP flood process when sodium metaborate was used.

To examine the effects of sodium metaborate on scale precipitation further, the average injection pressure during the continued water flood process was measured. It can be observed that the average injection pressure has no significant variation between favorable and unfavorable formation brines (see Fig. 10). This indicates that sodium metaborate has high tolerance to Ca^{2+} and Mg^{2+} in the unfavorable formation brine. On the other hand, with the increase of sodium metaborate concentration, the average injection pressure has slight variation. This implies that the scale precipitation would not occur even in high sodium metaborate concentration level. The monomeric form $B(OH)_4^-$ is the most stable form for ASP flooding. It is a classic alkali buffer in detergent formulations. The unfavorable formation brine contains higher amount of Ca^{2+} and Mg^{2+} compared with the favorable formation brine. Calcium and magnesium can sequester the borate, and hinder it from changing into polymeric borate species in

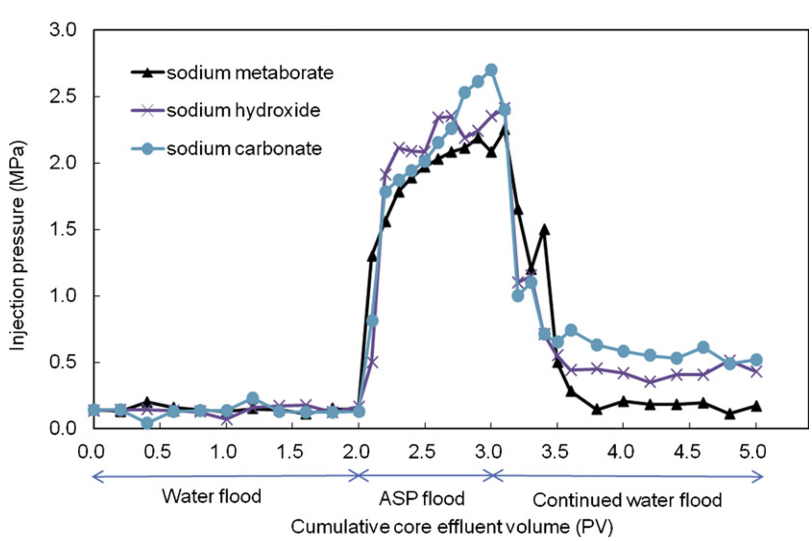

Fig. 9. Effect of alkali types on scale precipitation.

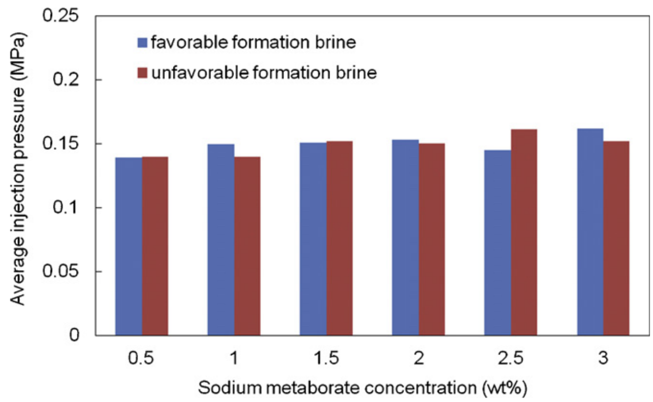

Fig. 10. Effect of sodium metaborate on scale precipitation.

unfavorable formation brine. The experimental results did not indicate any solid $Ca(OH)_2$ or $Mg(OH)_2$ precipitate, which shows the stability of the ionic borate forms sequestered by calcium and magnesium. Sodium metaborate shows a good stability in unfavorable formation brine and supply a wide concentration range for ASP flooding application. Sodium metaborate can tolerate high concentrations of divalent cations, and makes it possible to use ASP flooding in hard formation brine condition.

3.5. The effect of alkali on oil recovery

The effects of sodium metaborate, sodium hydroxide and sodium carbonate on ASP flooding oil recovery were investigated based on a series of core flood tests.

As shown in Fig. 11, the oil recovery first increased with increased alkali concentration. However, the oil recovery dropped after the alkali concentration reached a critical value. As discussed in Section 3.3 earlier, when alkali concentration reaches a critical value, the adsorption of surfactant will achieve a relatively low level. Hence, more alkali will not continuously increase the oil recovery. On the contrary, as the alkali is incompatible with the polymer, the reduction of the viscosity of ASP solution by alkali is more and more significant with the increase of alkali concentration (the details are described in Section 3.2). This will reduce the sweep efficiency, causing the oil recovery to drop (see Fig. 11). It indicates that high alkali concentration does not correspond to high oil recovery. However, the oil recovery can be optimized by maintaining the critical concentration of the alkali.

It can also be observed that the three kinds of alkalis tested in this study have similar performance when their concentration is

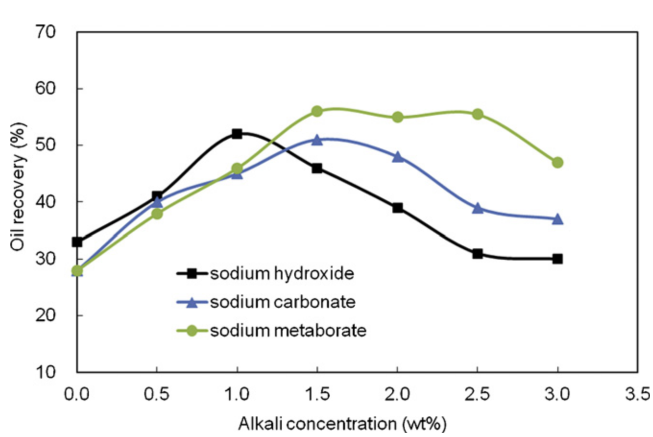

Fig. 11. The influence of alkali on oil recovery.

low (see Fig. 11). If the concentration of sodium hydroxide is higher than 1.0 wt%, the oil recovery drops. This is because sodium hydroxide is a strong alkali which reduces the viscosity of ASP solution significantly at high concentration. For sodium carbonate, the reduction of viscosity and heavy scale precipitation caused the decrease of oil recovery. Sodium metaborate can achieve the highest oil recovery of 56% when its concentration is 1.5 wt% compared with sodium hydroxide and sodium carbonate. This was a result of the minimized reduction of viscosity combined with no scale precipitation damage.

4. Conclusions

(1) In ASP agent system, surfactant is the major factor affecting IFT. Sodium metaborate can react with organic acids in the crude oil to generate petroleum surfactants to reduce the IFT.
(2) The viscosity of ASP solution drops significantly with the increase of alkali concentration. As a weak alkali, sodium metaborate can keep ASP solution's pH at a relatively low level. Hence it causes less reduction of viscosity compared to the strong alkalis.
(3) Experimental results show that the adsorption of surfactant will decrease when sodium metaborate is present. On the one hand, a negatively charged environment can be created on the rock surface by sodium metaborate. On the other hand, sodium metaborate can adsorb on the rock matrix prior to the surfactant. Those two aspects support sodium metaborate to protect the surfactant from adsorption.
(4) Sodium metaborate can avoid the scale precipitation damage caused by conventional alkalis and can be used in the case of high level of divalent cations.
(5) Sodium metaborate can gain the highest oil recovery at a concentration of 1.5 wt% compared with sodium hydroxide and sodium carbonate. This is due to the minimized reduction of viscosity and lack of scale precipitation damage. Sodium metaborate performs with the excellent ability to enhance oil recovery and at the same time minimize the negative effects.

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