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Research Article

Experimental Study of Enhancing Oil Recovery with Weak Base Alkaline/Surfactant/Polymer

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Na_2CO_3 was used together with surfactant and polymer to form the Alkaline/Surfactant/Polymer (ASP) flooding system. Interfacial tension (IFT) and emulsification of Dagang oil and chemical solutions were studied in the paper. The experiment results show that the ASP system can form super-low interfacial tension with crude oil and emulsified phase. The stability of the emulsion is enhanced by the Na_2CO_3, surfactant, and the soap generated at oil/water contact. Six core flooding experiments are conducted in order to investigate the influence of Na_2CO_3 concentration on oil recovery. The results show the maximum oil recovery can be obtained with 0.3 wt% surfactant, 0.6 wt% Na_2CO_3, and 2000 mg/L polymer. In a heterogeneous reservoir, the ASP flooding could not enhance the oil recovery by reducing IFT until it reaches the critical viscosity, which indicates expanding the sweep volume is the premise for reducing IFT to enhance oil recovery. Reducing or removing the alkali from ASP system to achieve high viscosity will reduce oil recovery because of the declination of oil displacement efficiency. Weak base ASP alkali can ensure that the whole system with sufficient viscosity can start the medium and low permeability layers and enhance oil recovery even if the IFT only reaches 10^{-2} mN/m.

1. Introduction

Rand found that the Alkaline/Surfactant/Polymer could effectively enhance oil recovery [1]. It was the earliest study on ASP flooding. After that, ASP flooding has been reported and applied widely around the world [2–4]. The field test conducted in Daqing oil field revealed the oil recovery of ASP flooding is 20% higher than water flooding [5]. ASP flooding was considered as an effective method to enhance oil recovery by reducing the IFT and mobility ration of oil and water [6, 7]. In a specific ASP system, the alkali will react with the acid in oil and then generates soap which will reduce the IFT [8–10]. The surfactant also reduces the IFT to ultra-low (10^{-3} mN/m) in order to improve the mobility of residual oil. Polymer increased the water phase apparent viscosity to reduce the mobility ratio of oil and water, finally expanding the sweep volume [11].

IFT of oil and water cannot reach ultra-low by just relying on alkali, so it is very necessary to add surfactant in the system. The alkali in ASP system plays the following roles: (1) the alkali reacts with the acid in oil generating natural surfactant; then the surfactant cooperates with the added surfactant which can reduce the IFT of water and oil significantly, (2) the alkali makes the solution with high PH which will reduce the adsorption of surfactant and thus reduces the cost of combination flooding, (3) the alkali acts as a sacrificial agent to protect the added surfactant from reacting with the two or three valences' metal ions in the formation, and (4) the alkali makes the oil emulsify regularly during the ASP flooding, and the residual oil disperses to oil drops [12]. The more the emulsified oil drops are generated, the higher the oil recovery gets. Johnson and Sheng [13, 14] once summarized the roles of alkali played in enhanced oil recovery (EOR) into four mechanisms, which was emulsion carrying, emulsion trapping, wettability reversal, and emulsion coalescence. Sheng [14] also considered emulsification is the most important mechanism for EOR. Once the residual oil contacts with the alkali in different conditions, different types of emulsions will be formed [15]; for example, the O/W type emulsion has lower viscosity which makes it easier to flow through the rock throat, hence improving the displacement efficiency; the W/O type emulsion has higher viscosity which makes it easier to block the water channel, making part of the displacement fluid circumvent to unswept area, hence expanding the sweep volume. In other words, the formation of emulsion is conductive to the recovery of residual oil [16]. Pei et al. [17, 18] and Dong et al. [18] studied the alkali flooding mechanism through microscopic model, which implied that alkali permeated into the oil phase to form emulsion was important for EOR.

As there is a lack of surfactant with good properties, the method of enhancing interfacial activity also relies mainly on adding alkaline, but the added alkali may reduce the apparent viscosity of the ASP system and cause the mineral rock to scale, therefore, leading to incompatibility between decreasing IFT and increasing apparent viscosity [19]. Because the IFT and the viscosity are restricted mutually, there should be an optimum concentration of base to get the maximum oil recovery. The current ASP system mostly contains strong alkalis with high concentrations, which leads to the dispersion and migration of formation clay, the reduction of formation permeability, the complexity of construction process, and scaling in formation and wellbore [20–22]. Strong alkali can largely decrease the viscoelasticity of polymer and thereby reduce the oil recovery. The strong alkali also causes unsatisfactory mobility and results in viscous fingering which would greatly reduce the sweep volume. These disadvantages in strong alkali seriously restrict the development of ASP flooding. Replacing the strong alkali with the weak alkali (Na_2CO_3) is proposed in this paper to overcome the side effects of strong alkali. The study on weak base ASP system would benefit both the pilot test and industrial application.

In this paper, strong alkali is replaced by Na_2CO_3. We wanted to determine the impact of Na_2CO_3 on IFT and explore the impacts of Na_2CO_3 on ASP rheological characteristics and oil emulsification. A series of core flooding experiments are conducted to evaluate the EOR ability of the Na_2CO_3/Surfactant/Polymer system.

2. Experiment

2.1. Experiment Materials. The crude oil and formation water are from Dagang oil field; high speed centrifuge is used to remove the sediments in formation water and crude oil. The physical property of Dagang crude oil is shown in Table 1. The composition of formation water is shown in Table 2.

The physical displacement model used in the experiment is a two-dimensional man-made core with vertical heterogeneity and positive rhythm, and its dimension is 30 cm × 4.5 cm × 4.5 cm (Figure 1). The model is cemented by quartz sand and epoxy resin, and it contains high, medium, and low permeability layers, with a permeability of 2000 mD, 900 mD, and 300 mD, respectively, in order to simulate the main oil layers of Dagang oilfield.

Table 1: Property of Dagang crude oil (at 53°C).

Parameter	Value
Viscosity	26.4 mPa·s
Density	0.8649 g/cm^3
Total acid number	1.273 mg KOH/g oil

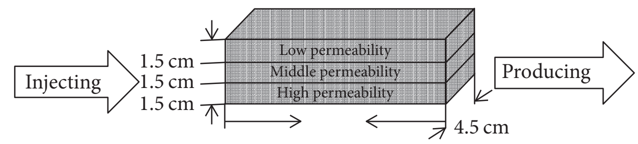


Figure 1: Three layers of heterogeneous core used in the experiment.

The alkali used in the experiment is Na_2CO_3, and the surfactant is mersolates with 240~340 sulfonated segment. And the polymer used is HPAM with a molecular weight of 2×10^6.

2.2. Experiment Content

2.2.1. IFT Measurement. IFT is measured by TX500 at 1000 r/min after 120 min under 53°C. The influences of Na_2CO_3 concentration and surfactant concentration on IFT are studied in the experiment.

2.2.2. Emulsification Test. The emulsion is prepared by the chemical and crude oil stirring at the rate of 1500 r/min for 1 minute at 53°C. The volume ratio of oil and water is 3 : 7. The micro morphology of emulsion is observed by the ZEISS SteREO Discovery.V20 microscope. In the emulsion stability experiment, put the emulsion into the glass tube; the oil and water will separate from each other because of the density difference. The water separating proportion is defined as the ratio of the separated water volume and the original water volume after separating 2 hours and it is used to evaluate the stability of emulsion; the reciprocal of stability constant of Turbiscan Lab Expert (Formulaction Inc.) is used to evaluate the stability of emulsion at the reservoir temperature. The bigger the TSI^{-1} is, the more stable the emulsion is.

2.2.3. Rheology Experiment. The rheological characteristics of ASP solution with different Na_2CO_3 concentrations are measured by HAAK RS-150H rheometer. The ASP loss modulus is measured in the experiment, as well. The experiments are conducted at a constant temperature of 53°C.

2.2.4. Core Flooding Experiment. A series of core experiments are conducted to determine the influence of Na_2CO_3 on oil recovery. The flow chart is shown in Figure 2.

The core holder is 30 cm long, which holds the core with external pressure that is 1-2 MPa more than the inlet pressure. Other equipment includes a high pressure middle vessel, an automatic metering plunger pump, a thermotank, a pressure acquisition system, and a constant flow pump. The pressures

Table 2: Composition of formation brine.

Ion	$K^+ + Na^+$	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}
Concentration, mg/L	2043	36	39	1337	10	3126	135

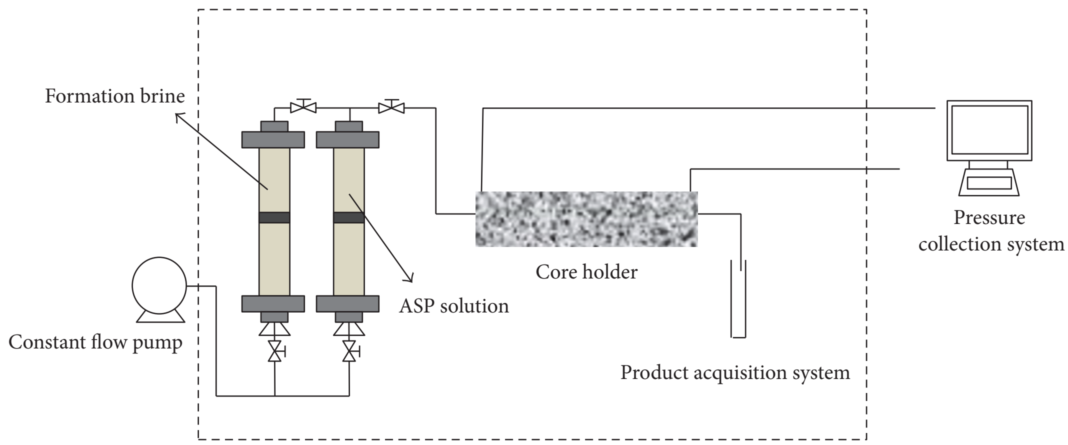


Figure 2: Schematic of the experimental apparatus.

are recorded by the pressure acquisition system and the output liquid is collected to calculate the recovery.

The experiment steps are as follows:

(1) Measure the dry weight, length, and diameter of the core; the permeability is measured by the N_2.

(2) Vacuum the core, saturate it with brine water, weigh the wet weight, and calculate the porosity. Then, saturate the core with oil and calculate the original oil saturation. Keep the core aging for 24 hours at the experiment temperature.

(3) 2 PV fresh water was injected following with 0.8 PV ASP solution, and then another 2 PV of fresh water was injected. The injection rate of all the above experiments is 0.3 cc/min. Measure the produced liquid volume and the injection pressure, and calculate the oil recovery. The output oil was measured; water and pressure were recorded till the water cut of the output liquid is 98%.

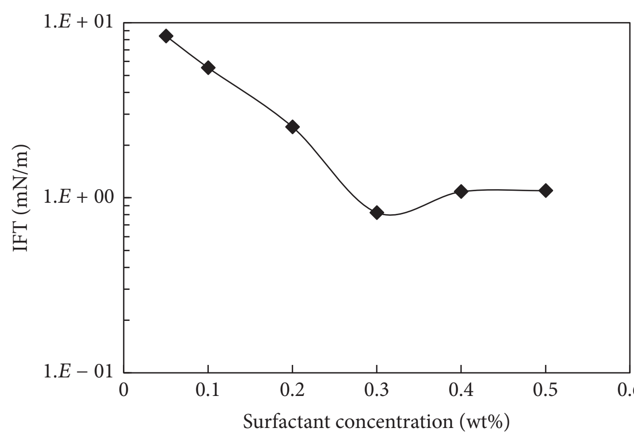


Figure 3: IFT between surfactant solution and oil with different surfactant concentrations.

3. Results and Discussion

3.1. IFT Behavior of ASP Solution and Oil. IFT is an important parameter to evaluate the properties of the flooding system. IFT usually needs to be reduced to 10^{-3} mN/m in homogeneous core in order to enhance oil recovery. A series of experiments are conducted to appraise the capability of Na_2CO_3/Surfactant/Polymer to reduce IFT. Since polymer has little impact on IFT, the following experiments mainly study the influence of Na_2CO_3 and surfactant on IFT with the polymer whose concentration is 2000 mg/L.

Figure 3 shows the IFT of oil and surfactant-polymer solution varies with the surfactant concentration which is in the range of 0.05~0.5 wt%. It shows that the IFT decreases sharply from 8.4 mN/m to 0.82 mN/m when the surfactant concentration increases from 0.05 wt% to 0.3 wt% because the absorbed surfactant molecules on the oil-water interfaces increase along with the increasing of surfactant concentration. When the concentration of surfactant is 0.3 wt%, the absorption of surfactant molecules is saturated on water-oil contact surface; hence IFT reaches the minimum value of 0.82 mN/m. IFT will increase slowly with the raising of surfactant concentration. The result indicates that it is hard to reach ultra-low IFT by just relying on surfactant. Taking IFT and economic factors into account, the concentration of surfactant used in the following experiments is 0.3 wt%.

In order to study the impact of Na_2CO_3 concentration on reducing IFT, several experiments (shown in Figure 4) are carried out to measure the IFT of the Na_2CO_3-polymer solution and the oil. The result indicates that, in certain surfactant concentration, the IFT will decrease from 16.5 mN/m to 1.13 mN/m if the Na_2CO_3 concentration increases from 0.05 wt% to 1.2 wt%. Due to the hydrolysis of Na_2CO_3 into OH-, the produced OH- will react with the petroleum acid HA in the crude oil to produce oil soap NaA, and the NaA acts as a surfactant. Concentration of A^- increases with the

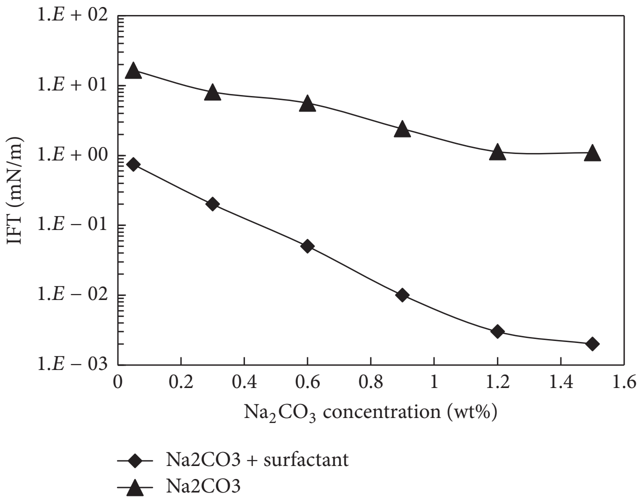


Figure 4: IFT between chemical solution and oil with different Na_2CO_3 concentrations. The surfactant concentration is 0.065 wt%.

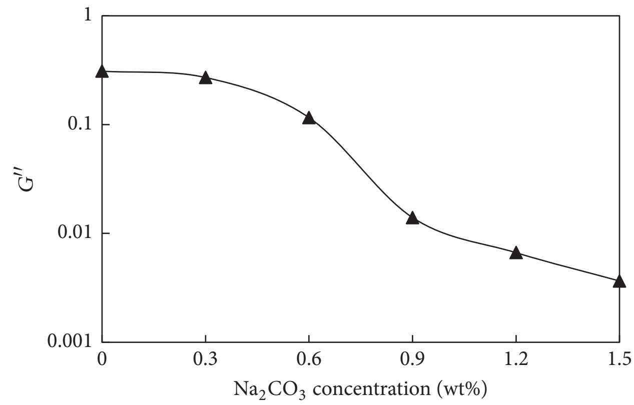


Figure 5: Relationship of G″ and Na_2CO_3 concentration. The surfactant concentration is 0.3 wt% and polymer concentration is 2000 mg/L.

concentration of Na_2CO_3 increasing. Therefore the IFT will decrease because of the arrangement of A^- in the interface. However the IFT would not decrease any more when the concentration of HA reaches critical concentration of 1.2 wt% because the concentration of HA is limited in the crude oil. Figure 3 demonstrates the impact of surfactant on IFT is much greater than Na_2CO_3, which means the surfactant is the main factor to influence IFT.

Several experiments are conducted to measure the IFT of ASP and crude oil for studying the synergistic reaction between Na_2CO_3 and surfactant, and the results are shown in Figure 4. Comparing the IFT of surfactant-polymer and oil with the IFT of Na_2CO_3-polymer and oil, the IFT of Na_2CO_3/Surfactant/Polymer and oil can reduce to 3.11×10^{-3} mN/m. This synergistic reaction of Na_2CO_3 and surfactant illustrates the Na_2CO_3 can promote the ability of surfactant in reducing IFT. The main factors to influence the synergistic reaction are the cooperative adsorption among surfactant, Na_2CO_3, and produced soap molecules. When the Na_2CO_3 cooperates with the surfactant, the surfactant molecules and the produced soap could simultaneously be absorbed on oil-water interface. In addition, the three ions have different diameters, and the diameter of Na^+ is the smallest, so it is easier to absorb between large molecules. The surfactant molecules will arrange more orderly and tightly; accordingly, the IFT will decrease significantly.

3.2. Rheological Characteristics. The loss modulus of ASP solution with certain surfactant and polymer concentration is measured in the experiments. The loss modulus only reduces slightly when the concentration of Na_2CO_3 increases from 0 to 0.6%, as shown Figure 5, because the increment of the ionic strength is little. Moreover, the low concentration of Na_2CO_3 is a benefit for the hydrolysis of polymer. If the Na_2CO_3 concentration in ASP solution is greater than 0.6%, the loss modulus would decrease significantly, because the charge strength increases with the increasing of Na_2CO_3 concentration as stated in many articles, the reaction viscosity of loss modulus. The trend of loss modulus curve illustrates the viscosity of ASP solution will decrease with the increasing of Na_2CO_3 concentration. The effect of Na_2CO_3 on loss modulus reflects the viscosity of ASP is dynamic changing. It is assumed that the more expansive the molecular chain, the greater the viscosity of the polymer, according to the theory of molecular motion. At low Na_2CO_3 concentration, the polyacrylamide molecular chain is in a stretch state due to the repulsive force produced by carboxylic acid with electronegativity. With the increasing of Na_2CO_3 concentration, the ionic strength grows. The electric double layer of polymer chain is compressed, and the negative charge is shielded. The shielding effect of charges weakens the repulsive force between polyacrylamide molecular chains, making the hydrodynamic radius of polyacrylamide molecular chains decrease, and the molecular chains curl up. Ultimately, the viscosity of ASP solution will decrease due to the increasing of Na_2CO_3 concentration. In addition, broken polyacrylamide molecular chain caused the viscosity of ASP solution to decrease at high Na_2CO_3 concentration.

3.3. The Emulsification Behavior of ASP Solution and Oil. Emulsification is a very common phenomenon in ASP flooding; it is an important mechanism of enhancing oil recovery [23, 24]. We conduct several experiments to evaluate the efficiency of chemical agent in emulsifying crude oil. The method used is described in Section 2.2.2. The emulsion is prepared by crude oil and different chemical solutions.

The relationship between the emulsion stability and Na_2CO_3 concentration is shown in Figure 6. The emulsion is made by the ASP solution with the condition of 0.3 wt% surfactant and 2000 mg/L polymer and the crude oil. TSI^{-1} increases when the concentration of Na_2CO_3 increases from 0.3 wt% to 0.6 wt%, as shown in Figure 6, which indicates that the added Na_2CO_3 will strengthen the stability of the emulsion. The IFT curve and the TSI^{-1} curve show a similar trend, which states that Na_2CO_3 causes both the IFT and the water separating rate to decline significantly. There exists a specific phenomenon in the formation of emulsion; the lower

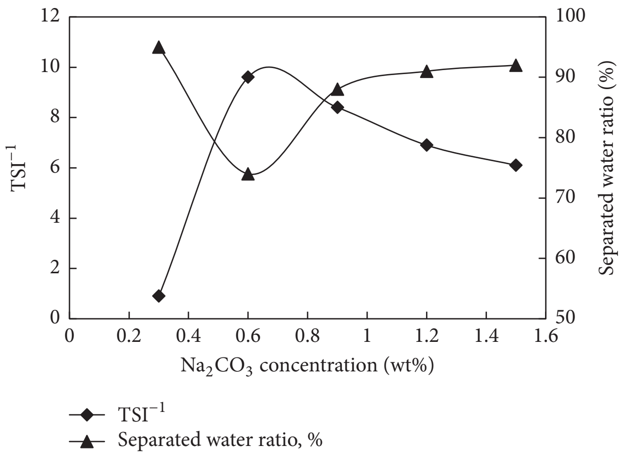


Figure 6: Relationship of TSI^{-1} and separated water ratio when Na_2CO_3 concentration varies. The surfactant concentration is 0.3 wt% and polymer concentration is 2000 mg/L.

the IFT is the easier it is to form the emulsion. But with the concentration of Na_2CO_3 further increasing, the TSI^{-1} declines, while the water separating rate increases. According to Strokes theory, the oil drop rising velocity is proportional to the droplet diameter and density difference of water and oil but is inversely proportional to the viscosity of water phase. The viscosity of ASP solution declines while the Na_2CO_3 concentration increases directly causing the coalescence velocity of oil drop increase for the sake of viscosity declination of ASP solution, destroying the stability of emulsion; besides, the electric double layer around the oil drops would be compressed when the mass fraction is high, reducing the negative charge density and interfacial viscosity in oil drop surface. That is why the high mass fraction of Na_2CO_3 will make the emulsion stability decrease.

Figure 7 is a micrograph of emulsion formed by three kinds of ASP solution and crude oil. The three systems all form O/W emulsion with crude oil and the produced emulsion in Figure 7(c) is much greater than Figures 7(a) and 7(b). It shows that the IFT is much lower in Figure 7(c) which indicates low IFT plays important role in the formation of emulsion. This conclusion is consistent with the above phenomenon.

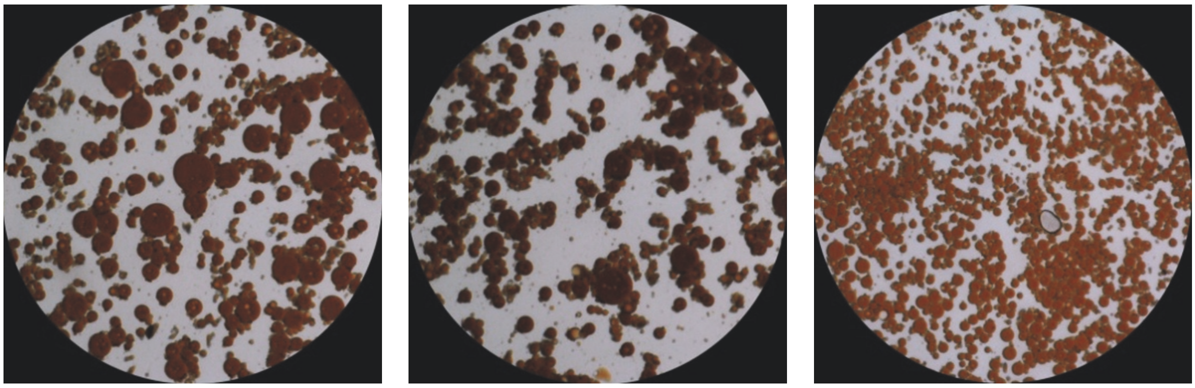
3.4. Core Flooding Experiment. Six heterogeneous core flooding experiments are carried out to study the impact that Na_2CO_3 concentration in Na_2CO_3/Surfactant/Polymer flooding system has on enhancing oil recovery. The Na_2CO_3 concentration is 0 wt%, 0.3 wt%, 0.6 wt%, 0.9 wt%, 1.2 wt%, and 1.5 wt%, separately. The polymer and surfactant concentrations are 2000 mg/L and 0.3 wt%, separately. The experiment procedures are described in Section 2.2.4. After water flooding, 0.8 PV chemical solution slug is injected. The EOR is adopted to evaluate the effect of Na_2CO_3 concentration on oil recovery. As shown in Figure 8, the concentration of Na_2CO_3 has great influence on EOR; when the concentration of Na_2CO_3 increases from 0 to 0.6 wt%, the IFT decreases from 10^0 mN/m to 10^{-2} mN/m, and the EOR increases rapidly from 18.74% to 23.4% (shown in Figure 8(a)). The result shows that adding Na_2CO_3 in surfactant-polymer solution can significantly improve the recovery; it mainly attributes to the synergistic effect to decrease IFT of Na_2CO_3 and surfactant.

Also the Na_2CO_3 has little impact on the polymer viscosity in this concentration range (the polymer viscosity declines from 57.45 mPa·s to 50.36 mPa·s, as in Figure 8(b)); in other words, the absorption of surfactant, Na_2CO_3, and produced soap molecules on the oil-water contact could reduce the IFT to a very low level and make the emulsion easy to form. From the macro and micro morphology of the produced liquid in different displacement stage in Figure 9, the injected chemical agent forms O/w emulsion. It illustrates the extra oil is produced in a form of O/W emulsion during ASP flooding; the emulsion mechanism is crucial for enhancing oil recovery in ASP flooding. However, with the increasing of Na_2CO_3 concentration, from 0.6 wt% to 1.5 wt%, the IFT decreases from 10^{-2} mN/m to 10^{-3} mN/m, and the EOR curve shows a download trend. This suggests high concentration Na_2CO_3 would lower the viscosity of ASP system and results in poor displacement efficiency in heterogeneous reservoir of this low viscosity system, though it could produce ultra-low IFT. Taking the 1.5 wt% Na_2CO_3 system as an example, though IFT is ultra-low (shown in Figure 8), the viscosity of the system is too low to start the medium or low permeability layers, and the oil recovery is the smallest. The 0~0.3 wt% Na_2CO_3 system is of high viscosity, which could start the medium and low permeability layers but the high IFT reduces the oil recovery of the swept layer. In the 0.6 wt% Na_2CO_3 system, however, with proper viscosity and IFT, the oil recovery is greater. It implied that expanding the sweep efficiency is the precondition of the effective action of IFT during ASP flooding. So reducing or cancelling the alkali (the Na_2CO_3 concentration is 0–0.3 wt%) in the system in order to achieve high viscosity would lower the oil displacement efficiency and ultimately decrease the recovery. Viscosity of ASP is big enough with low alkali, so the medium and low permeability layer can be swept effectively. Even if the IFT just reaches 10^{-2} mN/m, oil recovery can be improved. Consequently, for heterogeneous formations, excessive alkali should not be added to get ultra-low IFT, though the alkali is a benefit in improving displacement efficiency.

4. Conclusions

(1) Surfactant is the main factor in ASP that affects IFT. Na_2CO_3 reacts with the organic acid in oil and produces surfactant and decreases IFT to 10^{-3} mN/m through cooperating with the added surfactant. Na_2CO_3 also makes the oil emulsified and dispersed effectively, and because of the synergistic effect of alkali and surfactant the stability of the emulsion is enhanced.

(2) The viscosity of ASP declines significantly with the increasing of alkali concentration. Expanding the sweep efficiency is the precondition of the effective action of IFT during ASP flooding. But reducing or removing the alkali in ASP system in order to achieve higher viscosity would lead to low displacement efficiency and decrease oil recovery.



(a) (b) (c)

Figure 7: Micrographs of emulsions with different chemical agent: (a) 0.3 wt% surfactant + 2000 mg/L polymer; (b) 0.8 wt% Na_2CO_3 + 2000 mg/L polymer; (c) 0.3 wt% surfactant + 0.6 wt% Na_2CO_3 + 2000 mg/L polymer.

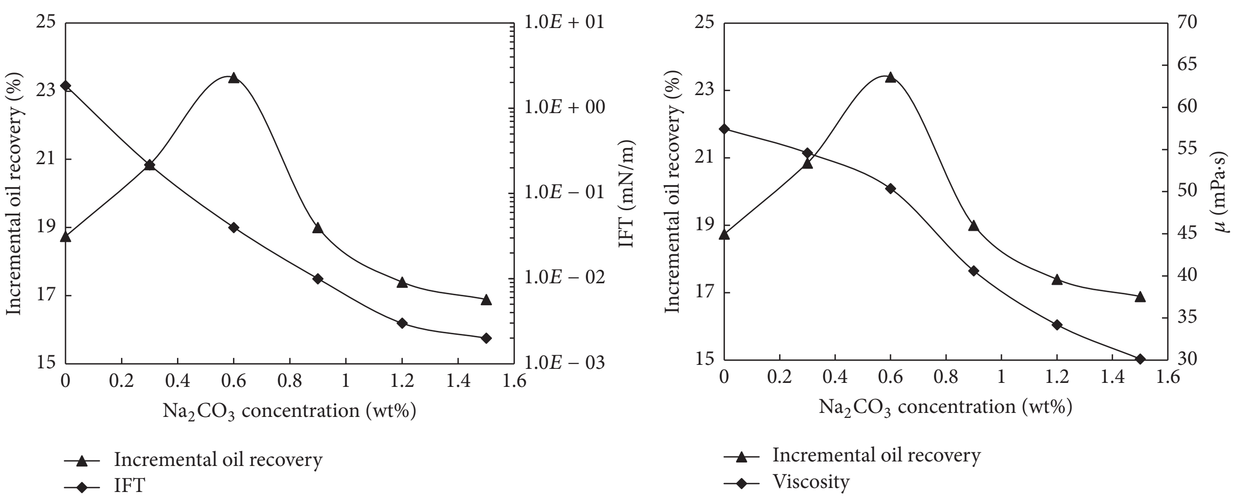
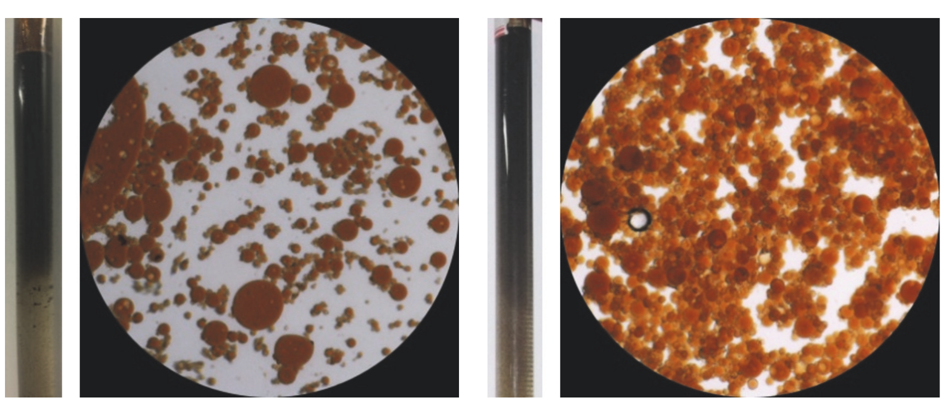


Figure 8: (a) Relationship between incremental oil recovery and IFT when Na_2CO_3 concentration varies. (b) Relationship between incremental oil recovery and viscosity when Na_2CO_3 concentration varies. The surfactant concentration is 0.3 wt% and polymer concentration is 2000 mg/L.



(a) (b)

Figure 9: Micrographs of produced fluids in different production periods when chemical solution was injected: (a) in the earlier production period; (b) in the later production period.

(3) ASP solution has proper viscosity with 0.6 wt% Na_2CO_3, and the medium and low permeability layers are swept; though the IFT only reaches 10^{-2} mN/m, the oil recovery is improved. So the impact of both IFT and viscosity on oil recovery is considered when ASP flooding is applied in heterogeneous reservoirs.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

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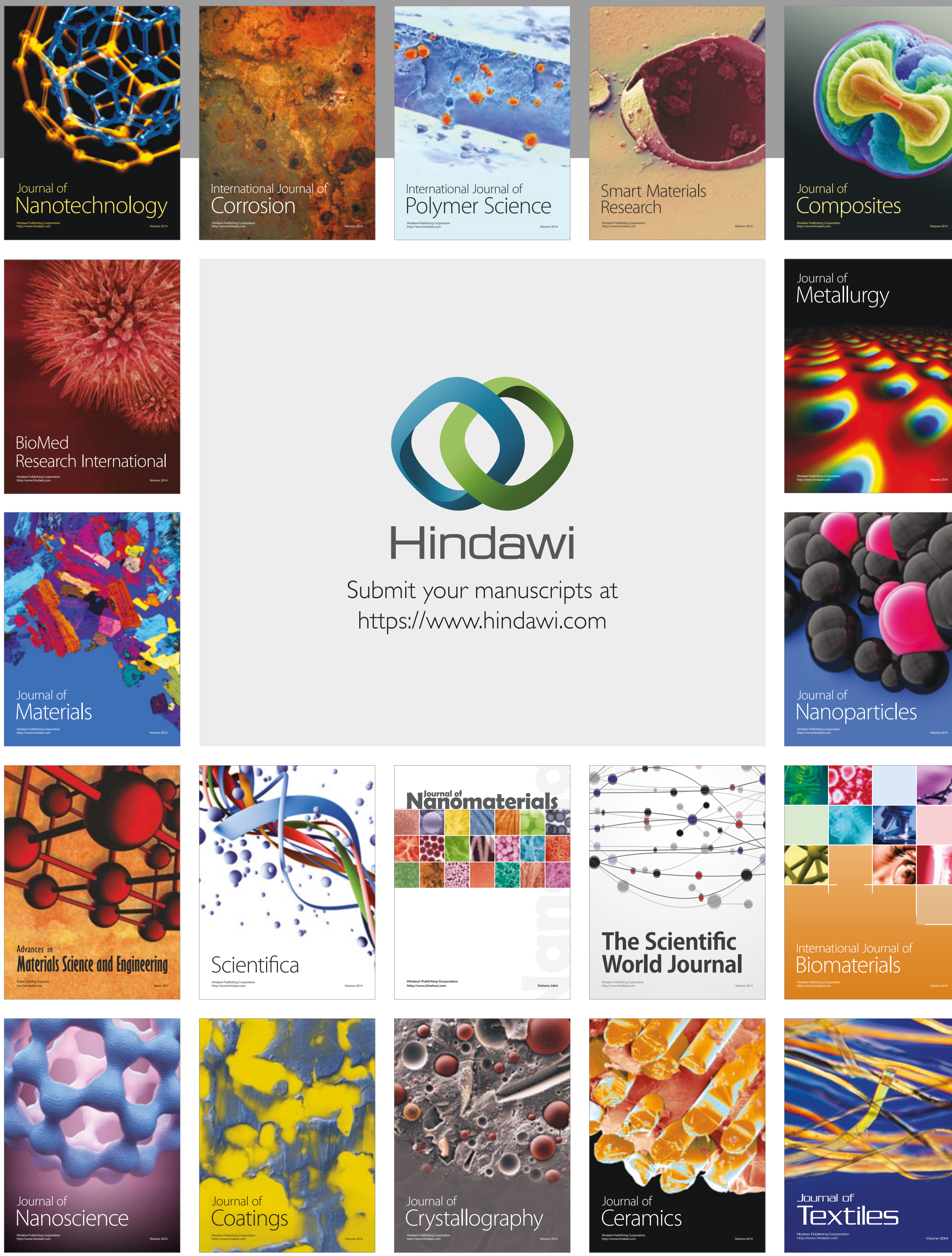
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