Research Progress on the Application of Synergistic Effects of Alkali and Surfactants in Oil-Solid Separation

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Abstract: The use of alkali and surfactant synergistic promotion for oil-solid separation has recently received a lot of attention. In the process of oil-solid separation, the function of surfactants is the key for improving the effect. A common method of oil-solid separation is to rely on the wetting, emulsification and solubilization of surfactants, but in practice the result of single surfactant is not good enough. According to some researches, adding alkali and alkali inorganic-salt to surfactant solution can increasing its activity, reducing interfacial tension between oil and water, increasing ionic strength in solution and promote oil-solid separation with the help of electrostatic repulsion. So delving into the mechanism by which surfactants influence oil - solid separation under alkaline conditions holds pivotal significance for enhancing the efficacy of oil displacement. This article takes chemical flooding as the main research direction and introduces application and mechanism of alkali and surfactant in chemical flooding. Experiments have shown that, The interfacial tension can be as low as 10^{-4} when the temperature is 53℃, the petroleum sulfonate is 0.4%, and the mass ratio of NaOH to Na_2CO_3 is 1:2. The mechanism of activation, solubilization and synergy of alkali or alkali inorganic-salt provides a feasible direction for improving oil-solid separation's effect. It is of great significance for the efficient treatment of oily sludge in oil and gas fields.

1. Introduction

After the periods of primary oil recovery and secondary oil recovery, some oil fields have entered the high water stage, the efficiency of water flooding has gradually reduced, and chemical flooding has gradually begun to be widely used[1]. However, capillary retention is common in the process of water flooding. The retained oil is distributed in the pore throat and pore wall in the form of oil droplets and oil film. In order to wash out this part of the retained crude oil effectively, further enhanced oil recovery and improving the oil-solid separation efficiency between oil and rock have been a key problem to be solved urgently. As an important enhanced oil recovery technology, surfactant flooding can improve oil-solid separation and enhancing oil recovery effectively.

The effects on the oil-solid interface mainly include surface wetting and adsorption. Since the force of solid surface molecules on liquid molecules is greater than the force between liquid molecules, liquid molecules will concentrate towards the liquid-solid interface when the two phases contact, forming an interface layer[2]. The first step of oil-solid separation is to destroy the interface layer, which is always the key in the process of oil extraction and treatment. At present, surfactant flooding is widely used in chemical flooding.

2. The synergistic mechanism of alkali and surfactant

During the displacement of the remaining oil in the rock formation, the key is the separation of the oil components from the solid surface of the rock. From the perspective of interface change, the process of separating oil components from the solid surface is the process of replacing the oil-solid interface with the oil-water interface and the solid-water interface. In oil production, The solid is mainly malmstone or carbonate rock. The rock surface is usually negatively charged, which has a certain adsorption effect on polar components such as colloid and asphaltene in crude oil. The oil molecules adsorbed on the solid surface by van der Waals force and spread out to form an oil-solid interface layer, which not only makes the solid surface become oil-wet, but also forms a more rigid double-layer interface film, which increases the difficulty of oil-solid separation[3].

2.1 The mechanism of alkali

Alkali water flooding is to add alkaline substances (such as sodium hydroxide, sodium carbonate, sodium bicarbonate, sodium silicate, etc.) to the water phase of displacement, and use the characteristics of alkaline

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substances to make the residual oil film free from the oil-wet rock surface to achieve the purpose of oil displacement. Some scholars have proposed that the mechanism of alkali flooding to enhance oil recovery is mainly emulsification carrying and wetting reversal[4]. In the process of chemical flooding, when the alkali is in full contact with the crude oil, Organic acids such as naphthenic acid, fatty acid and carboxylic acid in oil can react with alkali to form natural surface active substances such as carboxylic acid. These surface substances adsorbed to the two-phase interface can reduce the interfacial tension, especially the side chain aliphatic acid components will show stronger interfacial activity after the neutralization reaction[5].The non-acid oxygen-containing compounds in oil can cooperate with surfactants to emulsify and play a role in the emulsifying process of crude oil[6]. The addition of alkali and alkaline substances can change the charge properties of the rock surface, increase the charge density of the oil-solid interface, form a relatively stable water film on the rock surface, enhance the hydrophilicity of the rock surface, and facilitate the displacement of the oil film, thus improving the oil-solid separation efficiency[7].

2.2 The mechanism of surfactant

In the oil field, Surfactants are often used as an effective oil displacement agent to enhance oil recovery and control water rate.

There are different types of surfactants: ionic, non-ionic and amphoteric. The hydrophilic polar component is called the head, and the oil-philic nonpolar part which is a hydrocarbon chain is known as the chain of the surfactant.[11]Surfactants are amphiphilic molecules with both hydrophilic groups and oil-philic groups. By reducing the interfacial tension to make the residual oil into a mobile oil and changing the wettability of the rock surface, the surfactant can remove the oil phase from the surface of the solid particles and stabilize it in the aqueous solution, increasing the dispersion of oil in water. From a macroscopic point of view, the surfactant can reduce the interfacial tension, so that the oil film on the rock surface is easy to emulsify and disperse into the water phase, and no longer adsorbed on the rock surface. From a microscopic point of view, since the concentration of surfactant increases to a certain extent, the surfactant molecules will begin to aggregate into micelles in the system, and the concentration at this time is called the critical micelle concentration (CMC). When the surfactant concentration is less than CMC, the surfactant molecules are diffused in the oil -solid two-phase system, and the polar groups adsorbed on the oil surface repel each other from the negatively charged solid surface, resulting in the separation of oil and solid. When the surfactant concentration is greater than CMC, the surfactant molecules will aggregate into micelles with oil - philic group inward and hydrophilic group outward[8]. Micelles can adsorb oil that is insoluble in water and wrap it inside to promote oil-solid separation, which is solubilization. The difficulty of oil-solid separation can be characterized by adhesion work, as shown in formula (1).

$$W_a = \gamma_{ow}(1+\cos\theta) \quad (1)$$

The amount of adhesion work depends on the interfacial tension between oil and water and the contact angle of the oil droplets on the solid surface. By using the method of molecular dynamics simulation, Ding Feng simulated the values of the interfacial tension and contact angle of oil and water by using Young's equation. The results show that the addition of surfactants can reduce the interfacial tension of oil and water, the contact angle, the adhesion work of solid surface, and promote the stripping of crude oil from the solid surface[9]. At the same time, the decrease of the contact angle of the oil droplets on the solid surface proves that the wettability of the rock surface changes from oil-wet to water-wet after the addition of the surfactant solution, which is more conducive to the separation of oil from the solid surface. The interaction between surfactant solution and formation crude oil has been evaluated by means of absorbance test, small angle neutron scattering and transmission electron microscopy. The results show that surfactants can improve oil recovery by solubilizing part of crude oil and in situ emulsifying oil carrying[10].

2.3 The synergistic mechanism of alkali and surfactant

The surface active substance produced by the reaction of alkaline water alone with trace acid in the ground is limited, and it is difficult to reach the ultra-low degree of oil-water interfacial tension. However, it is difficult to achieve the oil displacement effect by adding a small amount of surfactants to the single surfactant flooding. So the common application of alkali and surfactant is gradually popular[12].

Some scholars believe that the synergistic effect of alkali and surfactant is conducive to the spontaneous emulsification of oil components[13]. The base reacts with the organic acid groups in the oil, form a natural surface active substance and can emulsify the remaining oil in the formation into emulsion droplets. After alkali is added to the surfactant solution, the surface activity in the original solution is increased, so that the remaining oil in the formation can be better dislodged. By comparing the change of adhesion between heavy oil and calcium carbonate particles at different pH of surfactant solutions, which can be found that the adhesion between oil and solid decreases with the increase of pH of solution. Because after the pH value rises, the OH^- in the solution increases, which compresses the double electric layer formed by charge adsorption at the oil-solid interface[14]. It is easier to overcome the electrostatic repulsion with the charged solid surface, adsorb on the solid surface, and separate the oil molecules from the solid surface. Studies have shown that in the combination of NaOH and surfactant, with the increase of NaOH concentration, the movement rate of surfactant molecules is accelerated, the emulsification time of oil adsorbed on the solid surface is shortened, and the emulsification ability of surfactant solution is enhanced[15]. However, in the compound system of alkali and surfactant, the concentration of alkali is not the higher the better. When the alkali in the system reaches a certain concentration, almost all the organic acids in the oil react with the alkali and ionize, and the negative charge density on the surface of the oil is the highest[16]. The electrostatic repulsion between the oil and the solid surface is the largest, and it is not easy to recoalesce and adsorption.

3. The application of alkali and surfactant in chemical flooding

3.1 The application of alkali flooding

Alkali flooding, as an early EOR technology, has played a role in the field of primary extraction. Table 1 shows the experimental conditions of heavy oil recovery by single alkali flooding in Liaohe Oilfield, Daqing Oilfield Oil production plant and Jiangsu oilfield. Among them, part of the effect of oil-solid separation is characterized by the interfacial tension, the lower the interfacial tension, the better the oil displacement effect. The interfacial tension was measured as $10^{-2}mN \cdot m^{-1}$ at pH=11 and temperature 30℃ by KOH in Liaohe oilfield[17].1g·L^{-1}NaOH was used in the experiment in Daqing oilfield. Under the experimental condition of 60℃, the calculated recovery rate was 56.9%. The interfacial tension measured by NaOH and Na_2CO_3 at room temperature in Jiangsu oilfield is 0.77 mN·m^{-1} and 0.03 mN·m^{-1} respectively.

As can be seen from Table 1, alkaline water flooding can achieve certain results in the treatment of heavy oil with high acid value, and the most critical factor in the play of alkali effect is the acid value of raw oil.

Generally, the acid value is greater than 0.5mg/g of crude oil, the effect of alkali play better[12]. But alkali and alkaline inorganic salt will react with the mineral composition of the reservoir rock to precipitate, increase the seepage resistance or increase the mechanical wear of oil production, so it is not widely used at present.

Table 1. The application of alkali and alkaline inorganic salt in chemical flooding

	concentration	temperature	Oil-solid separation effect
KOH	pH=11	30℃	ITF<$10^{-2}mN \cdot m^{-1}$
NaOH	1g·L^{-1}	60℃	Recovery efficiency 56.9%
	0.75%	Room temperature	ITF=0.77mN·m^{-1}
Na_2CO_3	1.5%	Room temperature	ITF=0.03mN·m^{-1}

3.2 The application of alkali and surfactant flooding

In the process of chemical flooding, the treatment effect of a single alkaline substance is relatively general, so it is not widely used in practice. The current research direction is gradually developing towards the direction of the combination of alkali and surfactant. Surfactant as a chemical flooding agent can reduce the interfacial tension of oil and water, so that the residual oil in the formation emulsifies to form microemulsion or micelles, which is not easy to adhere to the rock surface, enhances the flow of crude oil, and makes a large amount of residual oil in the blind end of the reservoir flow out with the water phase[18]. Some scholars have proved through contact angle experiments that the compound ratio of 0.1%NaOH and 0.1%RS-1 surfactant 0.2%RS-1 surfactant alone can better weaken the lipophilicity of formation rock surface and enhance its hydrophilicity[19]. In Table 2, the effects of different formulations of alkali and surfactant on oil-solid separation are compared in terms of interfacial tension, adhesion and oil displacement

Table 2. The application of alkali and surfactant in chemical flooding

	surfactant	surfactant concentration	alkali concentration	temperature	Oil-solid separation effect
NaOH	Rhamnolipid	0.5‰	pH= 10.5	45℃	The adhesion reaches 0.1
	sophorolipid	500 mg·L^{-1}	pH= 8.5	45℃	Contact Angle 45.9°
	B-100	10g·L^{-1}	10g/L	45℃	Oil displacement rate increased by 20%
	ORS-41	0.3%	0.3%	45℃	Oil displacement rate increased by13.5%~ 16%
	Petroleum sulfonate	0.4%	1%	53℃	Oil displacement rate increased by 20.6%

As can be seen from Table 2, the presence of alkali can play a synergistic role in the oil-solid separation of surfactants, resulting in ultra-low interfacial tension in the composite system. The combination of NaOH and sulfonate surfactants, anionic surfactants and biosurfactants has a good effect on oil-solid separation, and can increase the oil displacement rate by about 13%-20% compared with water flooding. But the compound pairing of alkali and surfactant has great damage to the formation, which is easy to cause formation scaling, block the pore throat, block the channel of oil displacement, and lead to the decline of oil displacement efficiency[20]. At the same time, if the alkali concentration is too high, the ionic strength of the system will increase, and then compress the double electron layer around the oil droplet, so that the size of the oil droplet will increase and coalescence phenomenon will occur, which is not conducive to the production of residual oil in the pores[21].

3.3 The application of Alkaline inorganic salt and surfactant flooding

In order to reduce the adverse effects of strong alkali on environment and equipment, alkaline inorganic salts were used to replace strong alkali NaOH and KOH, and alkaline inorganic salts and surfactants were formed, which achieved ideal results in chemical flooding.

The combination of alkaline inorganic salts and surfactants forms a weak base complex system, and the surfactants used in this system are usually sulfonates. studies have shown that the combination of lipid peptides, sulfonates and Na_2CO_3 can reduce the interfacial tension of oil and water to 10^{-4} orders of magnitude. Na_2CO_3 not only plays a role in generating oleic acid soap and reducing interfacial tension, but also plays a role in shielding electrostatic repulsion between polar head groups of anionic surfactant molecules to promote their interfacial activity[22]. Experiments have shown that when Na_2CO_3 is mixed with 0.5%OP-10 and 0.5% petroleum sulfonate, the emulsification rate of oil components increases first and then decreases with the mass fraction of Na_2CO_3[23]. When the concentration of Na_2CO_3 is 0.4%, the emulsification rate is the highest, which promotes the emulsification of crude oil while reducing the interfacial tension, and improves the oil-solid separation efficiency[24].Table 3 investigates several alkaline inorganic salts and surfactants compound formula experiments, in order of interfacial tension to characterize the effect of oil-solid separation[25].

Table 3. The application of alkali and alkaline inorganic salt in chemical flooding

	surfactant	surfactant concentration	alkaline concentration	temperature	Oil-solid separation effect
Na_2SiO_3	Petroleum sulfonate	0.1%	3.8wt%	45℃	ITF=6×10^{-2}mN·m^{-1}
Na_2CO_3	Petroleum sulfonate	0.1%	1.5wt%	45℃	ITF=8×10^{-2}mN·m^{-1}
	heavy alkylbenzene sulfonate	0.2%	1%	45℃	ITF=10^{-3}mN·m^{-1}
Na_2CO_3+NaOH	Petroleum sulfonate	0.4%	m(Na_2CO_3): m(NaOH)=2:1	53℃	ITF=10^{-4}mN·m^{-1}

As can be seen from Table 3, the terpolymer flooding prepared with weak bases such as Na_2SiO_3 and Na_2CO_3 and sulfonate surfactants can also meet the requirements of ultra-low interfacial tension, and the treatment effect of oil-solid separation is good. The interfacial tension of Na_2CO_3 combined with a strong base is lower than that of a single weak base, and the oil-solid separation effect is better.

4. Conclusion

Due to their own characteristics, alkali and alkaline inorganic salts can react with acids in crude oil to form surfactant, reduce the interfacial tension of oil solid surface and promote the separation of oil solid. Surfactants can change the wettability, adsorb on the solid phase interface, increase the solubility of emulsification, and reduce the interfacial tension. The combination of alkaline substance and surfactant can not only reduce the critical micelle concentration, but also increase the salinity and ionic strength of the solution, improve the adsorption of surfactant molecules on the oil-solid interface, and cooperate with surfactants to separate oil and solid.

The alkaline inorganic salt can play a good synergistic effect on the surfactant in oil-solid separation, and get a good effect. The combination of 1%Na_2CO_3 and 0.2% heavy alkyl benzene sulfonate can make the interfacial tension as low as 10^{-3} orders of magnitude. In the field of chemical oil flooding, it is a feasible development direction to study the effect of alkali and alkaline inorganic salts on oil flooding and the synergistic promotion of surfactants and provides an important idea for other oil-solid separation researches.

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