



# A research into recyclable foam fluid for petroleum exploration and development



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## ABSTRACT

Since foam liquid has been applied widely in the oil and gas field exploration and development, as in drilling, downhole operation and enhanced oil recovery, for its low density, low filtration, low damage, high viscosity and high carrying capacity, an in-depth study is necessary to make it more economical, more efficient and more environmentally friendly. Through theoretical analysis and a large number of tests, this research selected AOS-CoAO from the anionic surfactant and zwitterionic surfactant compound system as foaming agent for recyclable foam, with Xanthan gum as foam stabilizer for it can greatly improve foam stability, and with acid-base system of calcium oxide and sulfuric acid as regulator for it almost does not affect the activity of foam. It has been shown that the recyclable foam under question has good salt resistance, desirable foamability and stability either in sea water or in oil field wastewater, and high temperature resistance – its performance keeps mostly unchanged under 302 F. Having been recycled for 10 times, it still has foam height of over 150 mm and foam half-life period of over 200 min. When the concentration of crude oil is lower than 20%, the foamability and stability are desirable; when the concentration is greater than 20%, the foamability and stability drop significantly.

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## 1. Introduction

In the early 1940s, foam fluid, which features low density, began to be applied in drilling and stimulation operations, though it showed poor foamability and stability at that time (Behrens, 1963; Bernard and Holm, 1964; Somerton, 1943). Under normal pressure, the lowest density of foam is 0.103–0.104 g/cm<sup>3</sup>; in other words, foam can be used as a type of drilling fluid to achieve underbalanced drilling in the low/ultra-low pressure formation (Bentsen, 1976; Essary and Rogers, 1976; Hall and Roberts, 1984). It can help solve such problems as lost circulation and formation damage in the low/ultra-low pressure formation.

Up to end of the 20th century, micro-foam (Colloidal Gas Aphrons, CGA) with high stability had been developed (Frederick et al., 2003; Ivan et al., 2002; Sebba, 1987). Under ambient temperature and pressure conditions, more than 92% of the micro-foams is 10–100 μm in size; owing to the point contact pattern between

foams, stability was greatly improved; meanwhile, micro-foam can be recycled under a solid control system. Foam quality is adjustable within the range of 0.2–0.6 and its density is 0.6–0.95 g/cm<sup>3</sup>.

Foam stability (apparent viscosity) increases with increased foaming agent (or foam stabilizer) concentration and foam quality, and decreases with increased temperature (Amitabha et al., 2000; Martins et al., 2000; Sani et al., 2001). Though a small number of foaming agents work properly in the presence of 30% of oil, most of foaming agents are inefficient in concentrations higher than 20%.

Foam fluid has high shear force and viscosity (Harris and Heath, 1996). Under the low velocity, foam fluid can carry more cuttings than air, water, or even normal drilling fluids. It exhibits good cuttings-carrying performance in horizontal wells (Chen, 2005; Ozbayoglu, 2002). Therefore, it is a kind of ideal working fluid for the underbalanced drilling horizontal wells or horizontal wells sand-washing, its properties also enables it to be widely used in formation fracturing and enhanced oil recovery (EOR) (Frik, 1995; Kitsios et al., 1994).

For the sake of economy and efficiency in the process of exploration and exploitation, recyclable foam has become the main development orientation. Just as its name suggests, recyclable foam can be reused, which not only greatly reduces the cost, but also can effectively avoid environmental problems.

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## 2. The development of recyclable foam fluid

### 2.1. Selection of optimal foaming agent

In consideration of the actual needs in drilling operation, the foam is expected to be defoamable when it returns to ground. To achieve the purposes of cuttings separation and recyclability, the foaming agent should meet three requirements:

- (1) Foamability is sensitive to pH, or rather, it can be controlled by varied pH.
- (2) Having been defoamed, it must assume the phase of liquid and may also be water-insoluble, so that it can be separated for recyclable use.
- (3) It should be alkaline. Otherwise, downhole tools are in danger of being damaged.

Cationic surfactant has cationic hydrophilic groups, and the main types of cationic surfactants are amine salt ( $\text{RNH}_2 \cdot \text{HX}$ ) and quaternary ammonium salt ( $\text{RN} + (\text{CH}_3)_3 \times$ ) (James, 1990; John and Edward, 1994). Amine salt is weak alkaline salt, sensitive to pH; under acidic conditions, its nitrogen atom is positively charged when combined with hydrogen ions, indicating that cationic surfactant is able to foam; under alkaline conditions, cationic surfactant and foaming property should be lost – that is to say, amine salt is foamable only under acidic. The main difference between amine salt and quaternary ammonium salt is that the latter is strong alkali – strong alkaline nitrogen atoms show the electropositive under both acid conditions and alkali conditions. Therefore, quaternary ammonium salts are not sensitive to the pH and cannot be used alone as foaming agent to be recycled.

Anionic surfactant has anionic hydrophilic groups, and can be divided into carboxylates ( $-\text{COONa}$ ) and sulfonates ( $-\text{SO}_3\text{Na}$ ) according to the structure of the hydrophilic groups (Vollhardt and Schore, 2009). Under alkaline conditions, carboxylic groups are negatively charged and have foaming ability; carboxylic groups are not charged and have no foaming ability under acidic conditions, therefore carboxylates are sensitive to the pH and can be used alone as foaming agent to be recycled. Either under the acid or under the alkaline condition, sulfonates show anionic nature and have foaming properties.

Zwitterionic surfactant contains both anionic hydrophilic groups and cationic hydrophilic groups in the same molecule (Peresupkin and Menger, 1999; Seredyuk and Alami, 2002), and their major feature is that they not only receive proton, some of zwitterionic surfactants can even give a proton. Zwitterionic surfactant has surface activity under both acidic and alkaline conditions, but the surface activity does not change with the variation of pH. Therefore, the zwitterionic surfactant alone does not meet the requirements.

The above analysis of pH effect on the surface activity of anionic and zwitterionic surfactant shows that mixtures of species of both types can achieve recyclable use with pH changed. The theory of recyclable use of foaming agent is: under alkaline conditions, and with a compound of zwitterionic and anionic surfactant, the whole system has foaming ability – whether the zwitterionic surfactant is in the form of salt or anionic – because the entire system maintains anionic nature. Under acidic conditions, zwitterionic surfactant shows the character of positive ion, while anionic surfactant exhibits the property of anionic. The system loses surface activity and foaming ability when anionic and cationic charges are neutralized. When pH is adjusted back to alkaline, the foaming ability of the system is restored and, finally, by the adjusting of pH, a cycle of “foaming → defoaming → foaming → ...” can be achieved.

This research selected three sulfonate anionic surfactant, namely, sodium alcohol ether sulphate (AES), alpha olefin sulfonate

(AOS) and disodium ether sulfosuccinate (MES) and six zwitterionic surfactant, namely, dodecyl carboxyl betaine (BS), cocoamidopropyl betaine (CAB), N-laurylaminoacetic acid (DG), dodecyl amphoteric imidazoline (BMIZ), lauryl amine oxide (LOA) and cocoamine oxide (CoAO) to formulate foaming agents.

Anionic surfactants and zwitterionic surfactants are mixed in a 1:1 M ratio. Solutions were prepared with 0.5 wt.% surfactants in fresh water or sea water (14,440 mg/L  $\text{Na}^+$ ; 400 mg/L  $\text{K}^+$ ; 450 mg/L  $\text{Ca}^{2+}$ ; 1300 mg/L  $\text{Mg}^{2+}$ ; 14,950 mg/L  $\text{Cl}^-$ ; 1610 mg/L  $\text{SO}_4^{2-}$ ; 90 mg/L  $\text{HCO}_3^-$ ; others: 80 mg/L; total degree of mineralization 33,320 mg/L). Ross–Miles method (Rosen and Solash, 1969) was used to measure foam height and half-life period of each system at ambient pressure conditions and 140 F. The results are shown in Table 1.

Eight compounded systems with desirable foaming ability AOS-CoAO, AES-CoAO, AOS-LOA, AES-LOA, AOS-CAB and AOS-BS were selected to separately prepare solutions with sea water, at the concentration of 0.5% and the related properties were evaluated.

Fig. 1 shows that foaming ability of AOS-CoAO is the highest under alkaline conditions, and it is the lowest under acidic conditions. Fig. 2 and Fig. 3 show that in the same cycle index, AOS-CoAO has the largest foam height and longest half-life period; as the cycle index increases, foam height and half-life period of AOS-CoAO can still maintain at a high level.

Under normal conditions, and with higher apparent viscosity, the foam has good stability (Chen et al., 2007). We test foam apparent viscosity was tested with rotational viscometer. Fig. 4 shows that apparent viscosity of AOS-CoAO is highest under alkaline conditions, which means that foaming agent of AOS-CoAO is the best.

The conductivity rate is the ratio of foam fluid conductivity and foam conductivity (Varley et al., 2004). Fig. 5 presents relationship between time and conductivity rate of each system, and results show that conductivity rate of AOS-CoAO drops most slowly with the increasing of test time. It also indicates that the foaming agent of AOS-CoAO boasts the best stability. According to analysis above, we selected AOS-CoAO system as the recyclable foaming agent.

### 2.2. Concentration of foaming agent

To determine the concentration of a foaming agent (AOS-CoAO), we need to evaluate the relationship between concentration and foam performance.

Fig. 6 shows that foam height and the half-life period of AOS-CoAO increase as concentration of the foaming agent increases in

**Table 1**  
Foaming ability of each system (pH = 10).

Name	Fresh water		Sea water	
	Foam height (mm)	Half-life period (min)	Foam height (mm)	Half-life period (min)
AOS-CoAO	229	274	224	268
AES-CoAO	222	248	218	242
AOS-LOA	211	258	208	240
AES-LOA	198	226	189	218
AOS-CAB	186	262	178	254
AES-CAB	178	246	167	212
AOS-BS	178	246	175	236
AES-BS	167	232	158	208
MES-CAB	157	210	151	198
AES-DG	156	224	150	200
MES-CoAO	149	124	146	136
MES-BS	149	186	141	172
MES-LOA	138	124	131	110
AOS-DG	136	198	129	184
AES-BMIZ	134	188	128	180
AOS-BMIZ	127	180	120	172
MES-DG	126	168	120	160
MES-BMIZ	111	142	104	130

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