Advances of Researches on Improving the Stability of Foams by Nanoparticles

G Wang, K L Wang and C J Lu

Key Laboratory of Enhanced Oil Recovery of Ministry Education, Northeast Petroleum University, Daqing, 99 university street, China
E-mail: wg_0459@163.com

Abstract. Recently, nano-tech made a change of traditional oil-gas exploration. Considering that foam fluid had a poor stability, investigators proposed to add nanoparticles to stabilize the foam fluid system. This paper described the mechanism of particles to improve the stability of the foam fluid in detail; and emphasized the synergistic effect between nanoparticles and surfactants and its effect on the foaming and foam stability of dispersions; and reviewed the latest applications of foam fluid that was stabilized by nanoparticle in enhancing oil-gas recovery, in which there are analysis that showed that the nanoparticles not only greatly increase the stability of the foam fluid, but also improve the efficiency of foam fluid; and lastly, forecasted the development of nanotechnology in petroleum areas.

1. Introduction

In recent years, among all the researches on enhancing oil recovery efficiency, the foam flooding has attracted more and more attention because of its unique seepage and oil displacement performance[1-5]. On the one hand, the apparent viscosity of foam is larger, which means that it can significantly improve the oil-water mobility ratio, and greatly enhances the macroscopic swept volume; on the other hand, due to the decrease of interfacial tension, the residual oil saturation can be reduced and the microcosmic oil displacement efficiency can be improved [6]. But at the same time, foam fluids also face some challenges technically and economically, such as the source of gas, the cost of compression, and the adsorption of surfactants on rocks, and the biggest one, the stability of foam fluid. Foam fluid is a thermodynamically unstable system [7-10]. Under the reservoir conditions, the surfactant will pyrolyze at high temperature and high pressure, while the ionic surfactant will precipitate at high salinity, and the foam fluid will defoam when encounter in-place oil [11-13]. In order to get a more stable foam system, the leading way at present is to add polyacrylamide and other foam stabilizer, but the macromolecular foam stabilizers will always cause additional damage to the strata, and their prices is expensive, and they are easy to break down at high temperatures. Therefore, based on the shortcomings mentioned above, we need to find a new alternative to stabilize the foam, and to further expand the scope of application of foam fluid.

As early as the beginning of the twentieth century, Ramsden found that colloidal size solid particles could be used to stabilize immiscible phases [14]. Pickering and other researchers further explored this phenomenon, they researched the function mechanism granular emulsifier, and found that particles can be adsorbed to the surface of gas and liquid and stabilize the foam [15]. Foams whose particle is stabilized have not received widespread attention and application in the past for a long period of time, and the reasons are that, firstly, the conventional surfactant foaming agent can basically adapt to the general foaming problem; secondly, the research and application of particle foaming agents require the...
cooperation of the preparation of ultrafine particles and surface modification technology. With the deepening of foam research and the improvement of the preparation of ultrafine particles and the surface modification technology, as a nano-sized particle that possesses special physical and chemical properties, nanoparticle has great application prospects and advantages in stabilizing foam. In this paper, the mechanism of nanoparticles stabilizing foams is introduced in detail, and the application of foam stabilized by nanoparticle in enhancing oil recovery is reviewed, and the future research direction and application prospect are discussed.

2. Mechanism of nanoparticles stabilizing foam

The mechanism of particle stabilizing emulsion is that nanoparticles or micronparticles accumulate at the gas-water interface and form a dense wrap, effectively preventing the dispersed phase droplets from coalescing or merging due to electrostatic attraction, interfacial energy change, spatial structure and other factors. Unlike conventional surfactant foaming agents, the particles form a particulate solid layer on the gas-water surface and the surfactant is formed typical dissolved molecular agglomerate on the gas / water surface.

When the particle-wrapped droplets infinitely close to each other, the state of thin layer of particles in the interface, can be mainly divided into the following two ways [16]:

1) Single-layer arrangement of bridged particles (cf. fig. 1). The particles are arranged in the interface with only one single layer. At this time, the particles are wetted by the two kind of liquid phases, but most of the particles are still immersed in the continuous aqueous phase. Compared with the double-layer arrangement of particles, the stability of the single-layer structure depends mainly on the influence of the spatial resistance, preventing the particles from leaving the bridge layer.

2) The particles are tightly warped and arranged in a stratified layer at the gas-water interface (cf. fig. 2). In this case, the particles prevent droplet coalescence as a physical barrier, and enhance the stability of the aqueous film between the droplets and the continuous phase, which depends on the capillary pressure and interfacial rheological properties among all the particles. The location of the particles in the droplet interface depends on the wettability of the particles themselves.

![Fig.1. Schematic of the hexagonally packed single layer of spherical particles, stabilizing the thin liquid film between two large droplets [17].](image1)

![Fig.2. Schematic of the closely packed double layer of spherical particles, stabilizing the thin liquid film between two large droplets(Ho=1.633R) [17].](image2)
Particle foaming agent is characterized by its greater adsorption energy at the gas-water interface, in other words, its adsorption heat is greater. Thus, the adsorption at the interface can be considered irreversible to adsorb or achieving a balance of adsorption, that is to say, the stability of the particle-stabilized foam is better, and once the foam is formed, it is not easy to be demulsified, and the conventional surfactant foaming agent may desorbs from the interface after a while, leading to foam collapse.

3. Foam flooding under nanoparticles stabilization to enhanced oil recovery

Although stabilizing foam with nanoparticles is not an emerging technology, it is still in the indoor research stage in oil industry areas and most of the research directions are to improve the oil-gas recovery efficiency. Since the foam has a high viscosity in the stratum, it is possible to avoid the phenomenon of "viscous fingering", and blocking water but not oil, it thus is particularly suitable for heterogeneous stratum. Foam flooding can improve both the sweep efficiency and displacement efficiency, which makes it a promising method to enhance recovery efficiency [18]. But the stability of the foam has always been a challenge to hinder the foam from further application, but indoor experiments have shown that nanoparticles can solve this problem, and now there are some regions that are conditional enough to provide support for small-scale experiments, so that they can provide guidance for future field applications.

CO₂ foam flooding can effectively control the mobility of CO₂, which can solve the problems of common viscous fingering phenomenon of CO₂, and decreasing of sweep efficiency due to low density upward along the stratum. Without using surfactant, Worthen, et al. [19] stabilized the foam at 1200 ~ 3000psi (1psi = 6.895 kPa) with supercritical CO₂ fluid and 50% silanized coating of partially hydrophobic SiO₂ nanoparticles, from which the CO₂ foam can maintain transparent and stable for 23 hours, which can be effectively used for CO₂ foam flooding.

Yu, et al. [20,21] injected SiO₂ nanoparticles dispersion and supercritical CO₂ together into a sandstone core in 2013, from which there's CO₂ foam produced. This experiment measured the mobility of foam and retention of particles, and came to the conclusion of that the nanoparticle-stabilized CO₂ foam can improve the recovery efficiency of sandstone after water flooding, meanwhile, the permeability of the core is almost constant, which indicated that nanoparticles do not clog the stratum and can migrate in the pores. Moreover, San, et al. [22] studied the effects of different mineralization degree on nanoparticles-stabilized CO₂ foam. It was found that, under a certain consistency, NaCl and CaCl₂ promoted the foaming, foam stabilizing and mobility controlling, but the polyvalent ions have an inhibitory effect on the stability of CO₂ foam.

Throughout the researches above, it is concluded that, nanoparticles can not only stabilize the CO₂ foam well, but also increase the viscosity of the CO₂ foam to control the mobility in the reservoir conditions.

Compared to CO₂, the properties of N₂ are more stable. It will not corrode the ground equipment and down-hole string, and it is of low density, low hydrostatic head, so it's suitable for shallow depth of oil-gas reservoirs. In order to solve the instability of N₂ foam, Sun, et al. [23] injected partly hydrophobic SiO₂ and anionic surfactant SDS into the micro-model and sandstone filling model to flood oil, in order to evaluate the stability of the foam and the efficiency of oil-gas recovery, and the results showed that SiO₂ / SDS foam are more thermally stable than SDS foam and it has a good quality of oil flooding for homogeneous or heterogeneous strata.

Singh, et al. [24] observed nanoparticles exist in the Plateau boundary of foam under fluorescence microscope, so it effectively delay the foam of bleeding and coarsening. After water flooding, the particles that produced by the injection of SiO₂ nanoparticles and surfactants co-produced foam, can increase the recovery efficiency by about 10%.

In order to further saving costs, Eftekhari, et al. [25] injected coal by-products of nano-scale fly ash particles and anionic surface-active AOS together into the porous medium, the study of N₂ foam foaming and foam. It was found that the addition of nano-fly ash resulted in better foam foaming, more oil flooded, and better stability in the presence of oil than the foam produced by AOS alone.
In addition to conventional N₂ foam flooding, N₂ vapor foam flooding technology is an effective method for improving oil recovery when it is for heavy oil reservoirs with high gravity and high viscosity. In order to overcome the foam stability and a large number of additive losses and other issues, Khajehpour, et al. [26] in the reservoir conditions, the preferred concentration of SiO₂ nanoparticles and the type of surfactant, and the co-generation of the foam used for core flooding experiments. Studies have shown that the addition of nanoparticles can better reduce the flow and control the vapor foam.

Regardless of CO₂ foam or N₂ foam, indoor experiments have shown that foam foaming, foam stabilization; flow control effect and enhanced oil recovery efficiency can be effectively improved after adding nanoparticles. How to combine nanoparticles and oilfield chemical technology, and further applied to the scene, is a step must be taken. In addition, extraction in the field of oil and gas from the conventional oil and gas to unconventional oil and gas across in China, and the stability of nanoparticles in the application of unconventional oil and gas resources, the nanoparticles in the formation of the flow and retention will be low porosity and low permeability. It is a question that must be solved and answered.

4. Problems and prospects of stabilizing foam by nanoparticles

While low oil prices have led to a significant reduction in R&D spending by some oil giants, many colleges and universities are currently working on nanotechnology in oil and gas exploration, where nanoparticle stabilization is one of the most popular research directions. As for the nanoparticles-stabilized foam becoming practical, I think that the facing challenges and prospects of future research are of the following aspects.

(1) The mechanism and influencing factors of nanoparticles stabilizing foams need further study. For example, after the addition of nanoparticles, the interaction between the interface changes in the law is not perfect. In addition, some scholars have concluded that the addition of nonionic surfactants can also be synergistic with the nanoparticles, indicating that in addition to electrostatic adsorption to change the surface wetting of particles, there are other stable foam mechanisms [27]. Only when these problems are solved, the concentration of nanoparticles and surfactants can be optimized, which will be different performance of the foam applied to different areas of oil and gas exploitation.

(2) Some of the laboratory materials used in the study is partially hydrophobic nanoparticles that must be obtained by surface modification, which further increases the cost. But the current downturn in energy prices needs to further reduce the cost of nanotechnology. Optimize the concentration of nanoparticles and consider the use of hydrophilic nanoparticles and surfactants together to stabilize the foam is the idea of response.

(3) At present, the application of nanoparticles-stable foam in oil and gas exploration is still only in the laboratory experimental stage. With regard to the seepage of the foam in the formation of nanoparticles-stabilization, the retention of the nanoparticles in the pores, the relative numerical simulation of the settling of the proppant in the nanoparticles foam fracturing fluid is rare, and the small tests on the site are almost none. However, the combination of experimental data and simulation results, applied to the field of the test is necessary to be carried out. This can also provide a basis for solving the potential damage of the nanoparticles to the formation.

5. Conclusion

Nanoparticles-stable foam can solve many long-standing problems in traditional oil and gas exploration methods. Whether the global research hotspots of shale gas and the national "thirteenth five" plan to vigorously promote the development of coalbed methane, nanoparticles stable foam has a wide range of prospects. In the near future, nanotechnology will write a new chapter in oil and gas exploration.

References

[1] Yuan X, Wang K and Chen J 2010 Acta. Petro. Sin. 01 87-90
[2] Lee S and Kam S I 2013 *EOR. Field. Case. Stu.* **12** 23-63
[3] Li H, Hou J and Li W 2014 *Petro. Ge. Reco. Effic.* **04** 93-96
[4] Pang Z, Liu H and Zhu L 2015 *J. Petro. Sci. Eng.* **128** 184-193
[5] Sheng J J 2013 *EOR. Field. Case. Stu.* **14** 251
[6] Bayat A E, Rajaei K and Junin R 2016 *Colloid. Surface. A.* **511** 222-231
[7] Da C, Xue Z and Worthen A J 2016 *Viscosity and stability of dry CO₂ foams for improved oil recovery*(SPE Improved Oil Recovery Conference) p 11
[8] Gu S, Li W and Luo W 2016 *Chem. Tech. Fuels. Oil.* **52** 386-395
[9] Carpenter C 2016 *J. Petrol. Technol.* **68** 87-88
[10] Yang W, Wang T and Fan Z 2017 *Energ. Fuel.* **31** 4721-4730
[11] Farajzadeh R, Andrianov A and Krastev R 2012 *Adv Colloid.Interface.* **183** 1-13
[12] Andrianov A, Farajzadeh R and Mahmoodi M 2012 *Ind. Eng. Chem. Res.* **51** 2214-2226
[13] Li R F, Yan W and Liu S 2010 *SPE. J.* **15** 928-942
[14] Ramsden W 1903 *Proc. R. Soc. London.* **72** 156
[15] Pickering S U 1907 *J.Chem. Sci.* **91** 2001
[16] Dickinson E 2010 *Curr. Opin. Colloid. In.* **15** 40-49
[17] Kaptay G 2006 *Colloid. Surface. A.* **282** 387-401
[18] Li Zhaoimin 2010 *Application of foams in oil and gas production*(Beijing: Petroleum Industry Press) p 246
[19] Worthen A, Bagaria H and Chen Y 2012 *Nanoparticle stabilized carbon dioxide in water foams for enhanced oil recovery* (SPE Improved Oil Recovery Symposium) p 1-7
[20] Yu J, Mo D and Liu N 2013 *The application of nanoparticle-stabilized CO₂ foam for oil recovery* (SPE International Symposium on Oilfield Chemistry) p 1-9
[21] Yu J, Khalil M and Liu N 2014 *Fuel* **126** 104-108
[22] San J, Wang S and Yu J 2016 *Nanoparticle stabilized CO₂ foam: effect of different ions* (SPE Improved Oil Recovery Conference) p 1-12
[23] Sun Q, Li Z and Li S 2014 *Energ. Fuel.* **28** 2384-2394
[24] Singh R 2015 *Energ. Fuel.* **29** 467-479
[25] Eftekhari A, Krastev R and Farajzadeh R 2015 *Ind. Eng. Chem. Res.* **54** 12482-12491
[26] Khajehpour M, Etminan S R and Goldman J 2016 *Nanoparticles as foam stabilizer for steam-foam process* (SPE EOR Conference at Oil and Gas West Asia) p1-14
[27] Zhang S, Sun D and Dong X 2008 *Colloid. Surface. A.* **32** 41-8