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RESEARCH PAPER

A nano-particle foam unloading agent applied in unloading liquid of deep gas well

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Abstract: To solve the problem of unloading liquid of deep gas well with high gas temperature and salinity, high concentrations of H_2S gas and condensate oil, a nanoparticle foam unloading agent was developed and evaluated, and the field test was carried out. The liquid phase foam unloading agent was prepared by blending high temperature resistant anionic surfactant, high salinity and H_2S resistant zwitterionic surfactant and the condensate oil resistant fluorocarbon surfactant. The nanoparticle foam unloading agent was developed by introducing silane coupling agent modified nano silica spheres into the liquid phase foam unloading agent as the solid foam stabilizer. The property of nanoparticle foam unloading agent was studied through lab experiment, and the results show that: the agent has temperature resistance as high as 150 °C, salinity resistance up to 250 g/L, H_2S resistance up to 0.04%, condensate oil resistance up to 30%, which proves high foaming ability and foam stabilizing ability. The optical microscope and zeta potential results show that: the mechanism of enhancing the property of liquid phase foam unloading agent by nanoparticles lies in the fact that the nanoparticles can adsorb onto the gas-water interface to form a solid particle film, and it has the best foam stabilizing effect at the modified nano-silica sphere concentration of about 0.002%. The field test results show that: the agent has steady performance, meets the site construction requirements, and can improve the water drainage – gas recovery efficiency in gas well and reduce the cost.

Key words: deep gas well; nano-particle; nano silica sphere; foam unloading agent; unloading liquid in gas well

Introduction

With advantages of simple operation, quick effect and low cost, foam dewatering gas recovery process has become the first choice in unloading liquid in gas well domestically and abroad, and accounts for about 40% of dewatering gas recovery treatment in China. Foam dewatering gas recovery is to inject foam unloading agent which can produce a large number of low density aqueous foam into a well with insufficient liquid carrying ability from the well head to the well bottom, to enable the accumulated liquid carried by the current from the well bottom to the ground, so as to achieve stable and higher yield, and longer flowing period of the gas well. Appropriate foam unloading agent is the key to the success of foam dewatering gas recovery process. At present, domestic existing foam unloading agents are generally suitable for formations with temperature below 90 °C, salinity of less than 100 g/L, condensate oil content of less than 10%, and no H_2S gas. As the formation temperature, salinity, H_2S concentration and condensate oil content increase, the foaming and foam stabilizing ability of foam unloading agents decline significantly, and even without foaming at all[1], which seriously block the application of foam dewatering gas recovery process in high temperature gas wells. Therefore, the foam unloading agent suitable for high temperature gas wells with liquid loading problem needs to be developed.

As foam system is a thermodynamically unstable system[2–3], improving foam stability is the key to the development of foam unloading agent. The ways improving foam stability now mainly include: (1) mixing different types of surfactants to maximize Margangoni effect and thus strengthen the repair ability of surface film[4]; (2) adding some polymers to increase the system viscosity to reduce foam drainage rate[5]. However, these methods have some deficiencies: foam unloading agents prepared by mixing modified surfactants work fairly well, but they are expensive; polymers will degrade thermally under high temperature and produce residual organic matter particles which can cause formation damage to certain extent. As a new science and technology which analyzes and manipulates matter in nanometer scale, nanotechnology has already been widely applied in food, ma-

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terial and energy industries[6–7], but there is no literature reporting about application in dewatering gas recovery to date.

In this study, a nanoparticle foam unloading agent with good foaming and foam stabilizing ability under high temperature, high salinity, high content of condensate oil and H_2S gas has been developed by adding modified silica nanosphere into the liquid foam unloading agent as solid foam stabilizer, and the influence of concentration, temperature, salinity, concentration of H_2S and condensate oil on the performance of the foam agent has been studied too.

1. Development of foam unloading agent

The following factors should be considered when choosing surfactants: (1) in the aspect of high temperature resistance, the surfactant with sulfonic group with high resistance to high temperature should be introduced; (2) in the aspect of resistance to salinity and H_2S gas, the zwitterionic surfactant containing both cationic and anionic group should be selected, because its solubility is less restricted by electrolyte and pH range of the solution; (3) in terms of resistance to condensate oil, a fluorocarbon surfactant which can significantly lower the surface tension and thus reduce the total surface energy of the system should be added, so as to enhance the foam stabilizing ability. Suitable surfactants were selected based on the above principles, and orthogonal experiment was carried out to find out the best mix proportion, and the compounded system obtained is used as the liquid foam unloading agent.

The modified silica nanosphere with a contact angle of 65°–85°, diameter of less than 100 nm was introduced into the liquid foam unloading agent as solid foam stabilizer, which could have synergistic effect with the surfactants and form a dense particle film at the gas-liquid interface to prevent bubble coalescence and disproportionation[8–9]. The preparation process of modified silica nanosphere is as follows: firstly, the silica nanosphere of desired size were synthesized by Stöber hydrolysis method; then, the silica sphere solution with abundant hydroxyl were grafting modified by silane coupling agent.

Fig. 1 shows the variations of initial foaming volume and half life period (the time of foam height decreasing to half of its initial height) when different concentrations of modified silica nanospheres are added to concentration of 0.1% of the liquid foam unloading agent. The data was measured by the high temperature and pressure foam evaluation instrument at 130 °C, 1 MPa and the salinity of 200 g/L. It can be seen from Fig. 1 that: the initial foam volume and half life period of the foam unloading agent with nanoparticles are much higher than those of the foam unloading agent without nanoparticles, which proves the selected nanoparticle has strong foam stabilizing ability; with the increase of nanoparticle concentration, the initial foam volume and half life period increase at first and reduce later, which proves that the concentration of the nanoparticle is not the higher, the better, and has an optimal value.

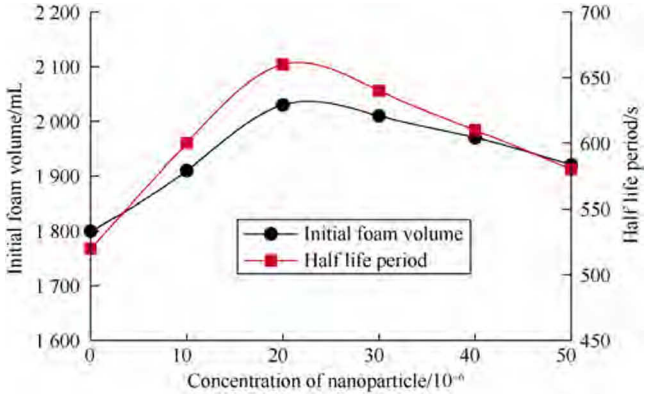

Fig. 1. Variation of initial foam volume and half life period when adding different concentrations of modified silica nanospheres to liquid foam unloading agent with concentration of 0.1%.

Based on the analysis results of Fig. 1, a new nanoparticle foam unloading agent CYS–E was prepared by mixing the liquid foam unloading agent and modified silica nanospheres at the ratio of 50:1.

2. Property evaluation

2.1. Introduction of experiment

2.1.1. Reagent and instrument

The main experimental reagents include: Tetraethylorthosilicate (TEOS), silane coupling agent A, ammonium hydroxide (NH_4OH), and ethanol. They were purchased from the Beijing chemical plant and were of analytical grade.

The main experimental instruments include: high temperature and high pressure foam performance evaluation device designed by ourselves, Optical Microscope Axioplan-40 (Zeiss, Germany), and Nano ZS particle size analyzer from ZetaSizer Nano Series, and Zeta potential instrument made by British Malvern Instruments.

2.1.2. Foam evaluation method

For foam evaluation at more than 90 °C, Ross-Miles method can only reflect whether the molecular structure has changed, but can't show the foaming, foam decaying situations of foam fluid under high temperature. In this study, the foam performance was evaluated by the high temperature and high pressure foam performance evaluation device designed by ourselves, which could simulate and analyze the foam performance at formation pressure of 10 MPa and 200 °C. The initial foam volume and half life period were recorded to reflect the foaming and foam stabilizing ability respectively, the experiment test fluid volume was 200 ml.

2.2. Comparison of nanoparticle foam unloading agent with ordinary liquid foam unloading agent

Pouring method was used to foam the ordinary liquid foam unloading agent and nanoparticle foam unloading agent at the concentrations of 0.1%, 0.2%, 0.3%, 0.4% and 0.5%, and the variation of foam after a certain time was observed. Fig. 2 shows that, the foam formed by ordinary liquid foam unloading

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