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A novel self-generating nitrogen foamed cement: The preparation, evaluation and field application

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ABSTRACT

Insufficient top of cement due to lost circulation is an urgent and worldwide technical challenge for oil and gas well cementing. Foamed cement (FC), especially the nitrogen FC, is a promising technology to prevent cement loss occurring in formations with low pressure, naturally occurring fractures or high permeability. However, the existing technology for nitrogen FC is either mechanically complicated or chemically low efficiency. This paper introduces a chemically self-generating nitrogen foamed cement (SNFC) with high performance to meet the requirements of oil and gas well cementing. Based on chemical thermodynamics and electrochemistry, a new nitrogen gas generating reactant (NGR) with high gas generation efficiency has been developed. The mixture of four surfactants with optimized mass ratio is used as the foam-stabilizer. The nitrogen FC is prepared by the injecting and mixing method in a closed vessel. Extensive laboratory tests were conducted to evaluate the properties of this SNFC, such as fluidity, free water, API fluid loss, thickening time, density and compressive strength. Experimental results indicate that the density of SNFC slurries can be adjusted from 1.25 to 1.60 g/cm^3, and the SNFC stone has high compressive strength and low gas permeability. This kind of nitrogen FC has been successfully applied in cementing low-pressure formations.

1. Introduction

Well cementing is an essential part of almost all well completion plans (Velayati et al., 2015). However, lost circulation and insufficient top of cement during well cementing are one of the worldwide and urgent technical challenges, especially across the formations with low pressure, naturally occurring fractures or high permeability (Vidick et al., 1988). In order to prevent and mitigate lost circulation, Huang et al. (2014) invented a new type of downhole device. In other ways, some kinds of cement have been improved and developed, such as low-density cement, fiber cement, thixotropic cement and cross-linked cement (Wang et al., 2015). But fiber cement, thixotropic cement and cross-linked cement need high pumping pressure which may fracture formations, and their preparations in the field are arduous as well.

Foamed cement (FC) is a dominant kind of low-density cement, which is achieved by mechanically or chemically mixing gas into the conventional cement slurry. FC has become popular worldwide in the field of construction, especially used as insulation and cavity filling (Amran et al., 2015). From the aspect of well cementing, FC has excellent performances for lost circulation prevention in low-pressure formations, relieving surface casing channeling in deepwater and improving the cement sheath isolation (Bikmukhametov et al., 2014; Guillot and Le Bastard, 2012; Ahmed et al., 2008). Compared with other cement slurries, FC has the following advantageous characteristics (Taiwo and Ogbonna, 2011; Olowolagba and Brenneis, 2010):

(1) Low density, which leads to low hydrostatic fluid column pressures of slurries avoiding the lost circulation in low-pressure formations;
(2) High compressive strength and low cost, which can provide lighter density slurry capable of achieving compressive strength equivalent to that of the conventional slurry;

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(3) Compressibility, which can appropriately compensate volume reduction caused by lost circulation or cement hydration through foam expansion;
(4) Prevention of gas migration and water influx, the complex three-phase interface interaction and high viscosity are helpful to stop the gas and water flow among the formations and cement columns;
(5) Good compressive strength and ductility, which can effectively avoid the cement sheath fracture caused by hydraulic and thermal stresses and extend the production time of oil well;
(6) Improved mud displacement, the good rheologies (high viscosities and yield points) show improved displacement of drilling fluids by foamed cement;
(7) Elasticity and thixotropy, which impart flexibility to the cement sheath enabling it to achieve a good bond between the formations and casings.

Because of the above benefits, FC is used more and more widely in oil and gas well cementing, especially for the low-pressure and lost circulation formations, steam injection wells, geothermal wells, and deepwater/ultra-deepwater wells (Taiwo and Ogbonna, 2011; Sugama et al., 2005). Nitrogen FC is a safe and economic choice for well cementing. In recent decades, most petroleum service companies have adopted mechanical methods to prepare the nitrogen FC for the cementing work in lost circulation formation and deepwater. But mechanical preparation requires a series of equipment, complicated processes and designs, and automatic controlling systems, which results in high cost and low efficiency. Moreover, there are difficulties in the maintenance and logistic supply especially in desolate areas. On the other hand, FC can also be prepared by chemical method through adding nitrogen gas generating reactant (NGR) and foam-stabilizer. Compared to mechanical method, the nitrogen FC prepared by chemical method has the advantages of simple operation and low cost, because adding the NGR and foam stabilizer into the slurry does not require extra equipment and complicated process. Qu et al. (2000) developed a nitrogen FC by chemical method, but it still needs improvements for the low gas generation efficiency and limited reduction in the density.

So far, the nitrogen FC prepared by chemical method has not been fully understood and needs further study. The selection of NGR depends on the rule of thumb, and the gas generating efficiency is relatively low. Therefore, the quality of the nitrogen FC is still not satisfactory. This paper would firstly investigate the reaction mechanism of nitrogen gas generation, and introduce NGR with high gas generation efficiency as well as high-efficient foam-stabilizer (HFS) for cement slurry. Then, based on these FC key additives, a new self-generating nitrogen foamed cement (SNFC) has been prepared. Based on extensive laboratory tests, the density and microstructure variation law of SNFC slurry with temperature/pressure has been revealed, which was verified through field applications.

2. Study on new nitrogen gas generating reactant

2.1. Reaction mechanism of nitrogen gas generation

Nitrogen element belongs to VA group, whose oxidation number can be positive (+5, +4, +3, +2, +1), zero, or negative (−1, −2, −3). Essentially, the reaction of nitrogen gas generation is a redox, which causes oxidation number of nitrogen to be reduced from positive to zero, or to be raised from negative to zero.

According to the chemical thermodynamics theory, one reaction is feasible only when its reduction of Gibbs free energy ($\Delta_r G_m$) is less than 0, which may occur in practice. If one redox reaction is defined as below:

$$aA_{oxi} + bB_{red} \rightarrow a'A_{red} + b'B_{oxi} \tag{1}$$

Its $\Delta_r G_m$ can be calculated as:

$$\Delta_r G_m = \Delta_r G_m^{\Phi} + RT\ln\frac{\alpha_{A_{red}}^{a'} \cdot \alpha_{B_{oxi}}^{b'}}{\alpha_{A_{oxi}}^{a} \cdot \alpha_{B_{red}}^{b}} \tag{2}$$

where, $\Delta_r G_m^{\Phi}$ is the Gibbs free energy under standard temperature and pressure, R=8.314 J K^{-1}·mol^{-1}, T [K] is the temperature, and α is the chemical activity. The electron transfer for any redox reaction can be converted to a reversible cell through appropriate methods. The reduction of Gibbs free energy is equal to external electrical work under isothermal and isobaric condition, that is:

$$\Delta_r G_m = -W_{elec} = -nFE = RT\ln\frac{\alpha_{A_{red}}^{a'} \cdot \alpha_{B_{oxi}}^{b'}}{\alpha_{A_{oxi}}^{a} \cdot \alpha_{B_{red}}^{b}} - nF\left(\phi_{A_{oxi/red},+}^{\Phi} - \phi_{B_{oxi/red},-}^{\Phi}\right) \tag{3}$$

where, n [mol] is the amount of reversible cell's output charge, E [V] is the electromotive force of the reversible cell, F = 96500 C mol^{-1} is the Faraday constant. $\phi_{A_{oxi/red},+}^{\Phi}$ and $\phi_{B_{oxi/red},-}^{\Phi}$ are the standard electrode potentials of reversible cell's anode and cathode, respectively. For a strong electrolyte D whose chemical formula is $M_{\nu_+}N_{\nu_-}$, its chemical activity can be calculated based on Debye-Huckel theory:

$$\alpha_D = 10^{-A\nu|z_+ \cdot z_-|\left(\frac{1}{2}\sum_i m_i z_i^2\right)^{\frac{1}{2}}} \cdot \left(\frac{m_D}{m^{\Phi}}\right)^{\nu} \cdot \left(\nu_+^{\nu_+} \cdot \nu_-^{\nu_-}\right) \tag{4}$$

where, m^{Φ} [mol·kg^{-1}] is the molality under standard state, m_D is the molality, z_+ and z_- are the valences of cations and anions, respectively. And A is a constant, $\nu = \nu_+ + \nu_-$.

Therefore, the $\Delta_r G_m$ of nitrogen gas generation reaction can be obtained through Eqs. (2)–(4). If $\Delta_r G_m$>0, the reaction will not happen spontaneously to generate nitrogen gas, while if $\Delta_r G_m$<0, the reaction may be spontaneous. If one reaction is spontaneous, based on the thermodynamics theory, its $\Delta_r G_m$ can be reduced by changing reactants or their concentrations or adding catalyzer. All these methods can accelerate the gas generation rate, which helps to meet the requirements of the nitrogen FC prepared by chemical reaction.

2.2. Development of nitrogen gas generating reactant

Generally, ammonium chloride reacts with sodium nitrite to generate nitrogen gas:

$$NH_4Cl + NaNO_2 \rightleftarrows N_2\uparrow + NaCl + 2H_2O, \Delta_r H_m^{\Phi} = -332.58KJ\cdot mol^{-1} \tag{5}$$

For this reaction, accompanied with the generation of nitrogen gas, a large amount of heat is released, which has been used in autogenetic heat fracturing fluid, thermochemistry flooding and other fields of petroleum engineering. According to Eq. (3), the reduction of Gibbs free energy of Eq. (5) can be derived:

$$\Delta_r G_m = -nFE = RT\ln\frac{\alpha_{NO_2^-}^2 \cdot \alpha_{H^+}^{16}}{\alpha_{NH_4^+}^2} - 6F\left(\varphi_{NO_2^-/N_2}^{\Phi} - \varphi_{N_2/NH_4^+}^{\Phi}\right) \tag{6}$$

According to Eq. (6), when the α_{H^+} in the solution increases (i.e.,