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4 **A Novel Self-Generating Nitrogen Foamed Cement: the**

5 **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/cm³, 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.

Key words: Foamed cement; Nitrogen gas generating reactant; Well cementing; Lost circulation; 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 down-hole 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 Bastard, 2012; Ahmed et al., 2008). Compared with other cement slurries, FC has the following advantageous characteristics (Taiwo, 2011; Kolawole et al., 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;

(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, 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:

Its $\Delta_r G_m$ can be calculated as:

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

where, $\Delta_r G_m^\Phi$ is the Gibbs free energy under standard temperature and pressure, $R=8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, 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:

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

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

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

where, m^{Φ} [$\text{mol}\cdot\text{kg}^{-1}$] 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, $\nu = v_+ + v_-$.

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:

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:

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

According to Eq. (6), when the α_{H^+} in the solution increases (i.e., the pH decreases, and the acidity of the solution increases) or the temperature T increases, the value of E will

increase too, i.e., the more negative the $\Delta_r G_m$ is, and the reaction becomes more spontaneous. Otherwise, under the condition of low temperature or high pH (the solution is alkaline), the reaction may not happen spontaneously and no nitrogen gas will be released. The experiment was conducted to confirm the reaction law of NH_4Cl and NaNO_2 . The formulation was: 7 g NH_4Cl (AR) + 5.4 g NaNO_2 (AR) + 50 g H_2O , and the generated gas was collected by water displacement method. The results are shown in Figs. 1 and 2.

Fig. 1. Dependence of temperature and reaction time on nitrogen gas volume

Fig. 2. Dependence of pH and reaction time on nitrogen gas volume

The experimental results indicated that more nitrogen gas is generated with a lower pH. However, the cement slurry is alkaline (pH=12.3) and detrimental for the gas generation. Under the alkaline condition, if NH_4Cl is oxidized to generate nitrogen gas, the electrode reaction can be written as:

According to the Nernst equation of electrode reaction, we can get:

$$\varphi_- = \varphi_{\text{N}_2/\text{NH}_4^+}^\Phi + \frac{RT}{6F} \lg \frac{\alpha_{\text{NH}_4^+}^2 \cdot \alpha_{\text{OH}^-}^8}{(p_{\text{N}_2} / p^\Phi)} \quad (8)$$

Eq. (8) tells us that the electrode potential of the negative pole will increase in an alkaline solution, which results in the increase of $\Delta_r G_m$ for the oxidation reaction of NH_4Cl . This means it becomes much more difficult for the reaction to generate nitrogen gas spontaneously. In order to generate nitrogen gas under the alkaline condition spontaneously, the $\Delta_r G_m$ of Eq. (5) should be reduced and the electrode potential of the positive pole should be increased. The stronger oxidant and reductant can be adopted as positive and negative pole, such as ClO_3^- and $-\text{N}_2\text{H}_4$, respectively. We determined the nitrogen gas volumes generated by the combinations of NH_4Cl - NaNO_2 , NH_4Cl - KClO_3 , and $(-\text{N}_2\text{H}_4)$ - KClO_3 at pH=12.0 and room temperature, respectively. The results are shown in Fig. 3. It is clear that the combination of $(-\text{N}_2\text{H}_4)$ - KClO_3 has a high gas generation rate under the alkaline condition of cement slurry, which can be used for nitrogen FC.

Fig. 3. Curves of nitrogen gas volume generated by different reactants

Based on the above analyses and experiments, a new NGR (including two components: NGR-I is potassium chlorate, and NGR-II is mainly made of hydrazine materials) has been developed, and its physical properties are displayed in Table 1.

Table 1 Physical properties of NGR

Component	Appearance	Density (g/cm ³)	Solubility
NGR-I	Grey fine powder	1.97-2.02	Freely soluble in water
NGR-II	Pale yellow liquid	1.05-1.15	Freely soluble in water

2.3 Performances of nitrogen gas generating reactant

We prepared three sets of cement slurry (containing 9 g NGR-I + 150 g water) with 0 g, 50 g, and 100 g Class-G oil well cement, respectively. Then, we added different dosages of NGR-II into the three sets of slurry, and collected the generated nitrogen gas by water displacement method. Each experiment was repeated three times to get the average volume of generated nitrogen gas. The measurements are shown in Fig. 4.

Fig. 4. Curves of nitrogen gas volume changing with NGR-II dosage in different systems

As can be seen from Fig. 4, in the blank set (no cement, represented by the black line), the nitrogen gas volume increases linearly with the increase of NGR-II, and reaches a plateau of 990 mL when the addition of NGR-II is more than 3.6 mL. In the other two sets, Class-G oil well cement is added to the systems (the red and blue line), the final volumes of generated nitrogen gas are clearly less than that of the blank set. This is because part of the nitrogen gas is trapped in the cement slurry due to its high viscosity. But the volumes of nitrogen gas at the beginning stage are slightly larger than that of the blank set, this is because the heat of cement hydration raises the temperature and accelerates the reaction rate. Experimental results demonstrate that Class-G cement has little effect on NGR reaction. This means NGR is well suitable for the cement alkaline condition. When the nitrogen gas volumes reach the plateau, the mass ratio of NGR-I/NGR-II is about 2.5:1, which is the optimum ratio and results in the maximum gas generation efficiency. Under this condition, the maximum nitrogen gas volume generated by per gram NGR is 78.57 mL.

2.4 Effect of nitrogen gas generating reactant on cement

In order to investigate the effect of NGR on the compressive strength of the cement stone, FC slurries were prepared with the water to cement ratio of 0.44 according to the API

10B-4-2004 “Recommended Practice on Preparation and Testing of Foamed Cement Slurries at Atmospheric Pressure” standards. And different amounts of NGR (mass ratio of NGR-I/NGR-II was 2.5:1) were added into the slurries. Then the cement slurries were cured at 40 °C for 24 h to test their compressive strengths (Fig. 5). The results indicate that the NGR slightly increases the compressive strength, because the potassium chloride salt generated by the NGR reaction promotes cement hydration.

Fig. 5. Compressive strengths of foamed cement stones with different NGR dosages

According to the API 10B-4-2004 standards, the effect of 1.5% NGR on the thickening time of Class-G cement slurry was tested under the condition of 40 °C and atmospheric pressure. The neat slurry with no NGR was used as a blank reference for comparison. The results suggest that NGR does not extend the thickening time of cement slurry (Fig. 6).

Fig. 6. Thickening time of foamed cement slurry with NGR

In order to investigate the ability of NGR to reduce the slurry density, the densities of cement slurries with different NGR dosages were measured. The water to cement ratio was 0.5. The results (Table 2) indicate that the addition of NGR can only slightly reduce the slurry density, although NGR is able to generate a large volume of nitrogen gas. This is because the FC is not stable, and most of the nitrogen gas escapes from the cement slurry. Therefore, besides the NGR, the foam-stabilizer is also needed to maintain a stable FC.

Table 2 Densities of foamed cement slurries with different NGR dosages

Group	Class-G cement (g)	NGR (%)	Water to cement ratio	Density (g/cm ³)
1	500	0	0.5	1.845
2	500	0.5	0.5	1.822
3	500	1.0	0.5	1.815
4	500	1.5	0.5	1.812
5	500	2.0	0.5	1.810

3 Study on the high-efficient foam-stabilizer

3.1 Development of High-efficient foam-stabilizer

Foamed cement slurry is a multi-phase dispersion system that consists of gas, liquid and solid phases (Nelson, 2006). Due to the effect of complicated phase interface, the structure of FC slurry varies with time, which results in the difficulties in predicting its properties. At present, there are mainly three kinds of foam-stabilizers, but they all have some limitations. For example, abietic resin based surfactant has poor capacity of foaming and foam-stabilizing in cement slurry. Anionic surfactant has excellent foaming ability but poor foam-stabilizing ability, while protein-based surfactant has good foam-stabilizing ability but poor foaming ability.

In this study, the abilities of several surfactants to stabilize foam were tested (Table 3) using the Waring-Blender method at room temperature (25 °C). In order to develop a new foam-stabilizer, surfactants with good performances in stabilizing foam were selected, such as CAB, AEO-9, CAO, and hydrolyzed protein AP-1, as basic components for a new foam-stabilizer. The synergism of these four surfactants may result in a high-efficient foam-stabilizer. So we prepared a series of solutions containing different volume ratios of these surfactants, and tested their performances in stabilizing foam. Based on these results, the best ratio of CAB, AEO-9, CAO, and AP-1 was determined and the high-efficient foam-stabilizer (HFS) was developed. HFS comprises the well-mixed CAB, AEO-9, CAO, and AP-1 with the volume ratio of 1.0:0.52:0.75:1.2 and has an excellent performance in stabilizing foam (Table 4).

Table 3 Performances of different surfactants in stabilizing foam

Surfactants	V ₀ (mL)	t _{1/2} (min)	V _{1/2} (mL)
AES	450	30	390
AEO-9	540	34	465
OP-10	530	7	515
LAB	430	5	420
LAO	490	12	450

CAB	520	62	510
CAO	470	78	430
AP-1	405	93	395
AP-2	400	66	335
AP-3	370	80	350

* V_0 = initial volume of the foam, $t_{1/2}$ = foam drainage half-life, $V_{1/2}$ = volume of the foam at $t_{1/2}$ time.

Table 4 Performance of HFS in stabilizing foam

Foam-stabilizer	V_0 (mL)	$t_{1/2}$ (min)	$V_{1/2}$ (mL)
HFS	580	120	565

3.2 Performances of high-efficient foam-stabilizer

In order to investigate the effect of HFS on FC, this study tested the densities of FC slurries with different HFS dosages following the standard API 10B-4-2004 “Recommended Practice on Preparation and Testing of Foamed Cement Slurries at Atmospheric Pressure”. The experimental results are shown in [Table 5](#).

Table 5 Densities of foamed cement slurries with different HFS dosages

Group	Class-G cement (g)	HFS (%)	Water to cement ratio (%)	Density (g/cm ³)	Density falling rate (%)
1	500	0	0.50	1.845	0
2	500	0.10	0.50	1.812	1.79
3	500	0.20	0.50	1.780	3.52
4	500	0.30	0.50	1.736	5.91
5	500	0.40	0.50	1.575	14.63
6	500	0.50	0.50	1.503	18.54
7	500	0.60	0.50	1.480	19.78
8	500	0.70	0.50	1.476	20.00
9	500	0.80	0.50	1.475	20.05

It can be seen from [Table 5](#) that the density of the FC slurry decreases with the increase of HFS. It should be noted that the density decreases slightly when the HFS dosage is less than 0.3% or more than 0.6%, while the density decreases significantly as the HFS increases

from 0.4% to 0.6%. This indicates that the generated nitrogen gas is trapped in the slurry to form stable FC when the slurry has 0.4-0.6% HFS. Therefore, the optimal dosage of HFS in FC is 0.5-0.6%, which can reduce the density of cement slurry by nearly 20%.

To further study the effect of HFS on foam stability, the densities of the FC slurry with the initial density of 1.48 g/cm^3 were measured over time at room temperature (Fig. 7). The FC slurry consisted of Class-G oil well cement, 0.6% HFS and 50% water. The corresponding appearances at different times are shown in Fig. 8. The slurry density increases obviously in the first 10 min due to the foam burst caused by stirring. And then the density increases slowly with time. After being prepared for 70 min, the slurry density increases by 4.93% from 1.48 g/cm^3 to 1.553 g/cm^3 . It can also be observed from Fig. 8 that the FC slurry with HFS has excellent stability. Overall, the experimental results demonstrate that HFS plays a remarkable role in foam stabilization.

Fig. 7. Densities of foamed cement slurry with HFS in different stationary times

Fig. 8. Appearances of foamed cement slurry with HFS in different stationary times

4 Study on self-generating nitrogen foamed cement

4.1 Preparation of SNFC through the injecting and mixing method in a closed vessel

Based on the mechanism of foam stability and the field well cementing work, the nitrogen FC is prepared by the injecting and mixing method in a closed vessel as the following steps:

(1) Open the mixing vessel, and add a certain amount of water, HFS and other liquid additives into it;

(2) Mix the oil well cement powder, NGR-I and other solid additives, and then add them into the vessel within 15 sec at the stirring rate of 4000 rpm;

(3) Close the vessel, and then inject a certain volume of NGR-II into the vessel within 5 sec. After that, stir the slurry at a rate of 12000 rpm for 35 sec. Finally, the slurry with stable foams will completely fill the closed vessel, which is the FC slurry.

The new self-generating nitrogen foamed cement (SNFC) slurry can be prepared through

the injecting and mixing method in a closed vessel. The SNFC slurry consists of water and Class-G oil well cement with the ratio of 0.50-0.53. NGR is used to generate nitrogen gas through chemical reaction, and HFS is used to effectively stabilize the foams. We also use the dispersant USZ (purchased from Henan Weihui Chemical Co., Ltd.), fluid loss reducer NF-L and retarder NF-R (self-made) to adjust the properties of the slurry, such as rheological characteristics, fluid loss and thickening time. After a comprehensive set of experimental tests, the density of the SNFC slurry can be controlled within 1.25-1.60 g/cm³ (Table 6).

Table 6 Components proportion of SNFC

Group	Cement	NGR (%)	HFS (%)	USZ (%)	NF-L (%)	NF-R (%)	Water (%)	Density (g/cm ³)
1	Class-G	1.60	0.6	0.25	2.5	0.35	53	1.25
2	Class-G	1.40	0.6	0.25	2.5	0.35	53	1.30
3	Class-G	1.25	0.55	0.2	2.3	0.35	52	1.40
4	Class-G	1.0	0.5	0.2	2.2	0.4	50	1.50
5	Class-G	0.80	0.5	0.15	2.0	0.4	50	1.60

4.2 Performances of self-generating nitrogen foamed cement slurry

The performances of SNFC slurry, such as the fluidity (the average diameter of a certain volume of cement slurry spreading on the flat table), the free water under room temperature (the volume of water separating out from cement slurry), the API fluid loss at 80 °C (the volume of cement slurry infiltrating into formation/filter under pressures) and the thickening time at 80 °C/35 MPa (the time of the consistency of cement slurry to achieve 100 Bc) were measured according to the API 10B-4-2004 “Recommended Practice on Preparation and Testing of Foamed Cement Slurries at Atmospheric Pressure” standards. Table 7 summarizes these testing results. We also measured the compressive strength and the gas permeability of the SNFC after being cured for 72 h at 40 °C and 80 °C, respectively. The SNFC slurries with different densities were poured into cylindrical curing molds (50.8 mm in diameter × 101.6 mm in height), and then seal the molds to prevent gas escaping and slurry expansion by heating. The sealed molds were placed into an atmospheric-pressure water bath at 40 °C and

80 °C, respectively, and then cured for 72 h to measure the compressive strength and gas permeability. The results are shown in Table 8.

Table 7 Performances of SNFC slurries

Group	Density (g/cm ³)	Fluidity (cm)	Free water (mL)	API fluid loss (mL/30 min)	Thickening time (min)
1	1.25	24	0	47	205
2	1.30	24	0	50	190
3	1.40	24.5	0	43	215
4	1.50	24.5	0	46	239
5	1.60	25	0	42	260

Table 8 Compressive strengths and nitrogen permeabilities of SNFC stones

SNFC density (g/cm ³)		1.25	1.30	1.40	1.50	1.60
At 40 °C for 72 h	Compressive strength (MPa)	16.07	16.92	18.63	24.21	26.64
	Permeability (×10 ⁻³ μm ²)	0.62	0.57	0.38	0.12	0.09
At 80 °C for 72 h	Compressive strength (MPa)	17.90	19.25	21.62	26.63	29.32
	Permeability (×10 ⁻³ μm ²)	0.60	0.55	0.36	0.12	0.08

Tables 7 and 8 manifest that the SNFC slurry has excellent performances, such as favorable fluidity, no free water, low API fluid loss (less than 50 mL/30 min), and proper thickening time at 80 °C/35 MPa (190-260 min), which meet the requirements for oil and gas well cementing. The compressive strengths of cement stones with different densities after being cured for 72 h at 40 °C, 80 °C under atmospheric pressure are all greater than 16 MPa, and the gas permeabilities are all less than 0.65×10⁻³ μm². As the increase of SNFC density, the compressive strength will grow and the permeability will decrease. So we can choose appropriate slurry density to prevent lost circulation in thief formations.

4.3 Density and microstructure variation law of SNFC slurry

It is significant to find out the density variation law of SNFC slurry with pressure and temperature in order to rationally adjust the SNFC slurry density based on the bottom hole temperature and pressure (Kutchko et al., 2015). The SNFC slurry with 1.25 g/cm³ was heated

and pressurized for curing following the method of [De Rozieres and Ferriere \(1991\)](#). The density variation of the SNFC slurry was calculated by the volume change before and after being heated and pressurized. The results ([Table 9](#)) suggest that the density of the SNFC slurry increases significantly with pressure.

Table 9 Density variation of SNFC slurries with 1.25 g/cm³

Temperature and pressure	25 °C/0.1 MPa	40 °C/10 MPa	60 °C/30 MPa
SNFC density (g/cm ³)	1.25	1.443	1.462

The micro morphologies of SNFC slurries with 1.25 g/cm³ cured at 25 °C/atmospheric-pressure, 40 °C/10 MPa, and 60 °C/30 MPa, respectively, are displayed as SEM photographs in [Fig. 9](#). It can be seen from [Fig. 9](#), at the curing condition of 25 °C/atmospheric-pressure, the main diameters of foams in the cement stone are 150-250 μm, and the biggest size is 450 μm. At 40 °C/10 MPa, the main diameters of foams decrease to 50-70 μm. At 60 °C/30 MPa, the diameters of most foams in the cement stone are around 30 μm.

(a) Cured at 25 °C/ atmospheric-pressure

(b) Cured at 40 °C/10 MPa

(c) Cured at 60 °C/30 MPa

Fig. 9. SEM photographs of SNFC slurries with 1.25 g/cm³ cured at different conditions

5 Field Applications

5.1 Field application of SNFC in directional well Yan225-x1

Directional well Yan225-x1 is located in the northwest of Yongan oilfield, Dongying city, China. This oilfield is mainly composed of conglomerate reservoirs. Severe lost circulation often occurs because of the formation anisotropy by the different buried depth and diagenesis.

Directional well Yan225-x1 is a production well with the depth of 2735 m. The bottom-hole temperature is 75 °C, and the oil layer is located between 2200-2675 m. This borehole was drilled to 350 m by $\Phi 346.1$ mm bit and followed by $\Phi 339.7$ mm surface casing, then was drilled to 2735 m by $\Phi 215.9$ mm bit and followed by $\Phi 139.7$ mm production casing. And the cement was required to return to the surface. The SNFC combined with ductile and micro-swelling cement system (Table 10) was applied for cementing to prevent lost circulation. The field monitoring data indicate that the cement returns to surface without lost, and all properties meet the design requirements.

Table 10 Field cementing usage of Yan225-x1

Cement	Density (g/cm ³)	Return depth (m)	Cement column (m)	Slurry volume (m ³)	Cement mass (t)
SNFC	1.50-1.55	Surface	2000	78	80
Ductile and micro-swelling cement	1.82-1.88	2000	725	17	30

5.2 Field application of SNFC in cluster well TS71-2D

Well TS71-2D is a production cluster well for coal-bed methane (CBM), located in Qinshui basin of Shanxi province, China. The drilling depth is 1082 m for No. 3 CBM formation in Taiyuan group of Lower Permian between 1025.24-1031.62 m. This borehole was drilled to 47 m by $\Phi 311.15$ mm bit and followed by $\Phi 244.5$ mm surface casing, then was drilled to 1082 m by $\Phi 215.9$ mm bit and followed by $\Phi 139.7$ mm production casing. And the cement was required to return to above No. 3 CBM formation for 200 m.

Lost circulation occurred with the rate greater than 10 m³/h when drilling to the depth of 182 m, 201 m and 330 m. The loss rate of circulation increased to 40 m³/h at 388 m. And the loss rate was greater than 15 m³/h when drilling to the depth of 518 m, 629 m and 731 m. Several traditional methods were adopted to relieve the lost circulation during drilling, but they failed to maintain a normal circulation before cementing. In order to resolve the problem of serious lost circulation, the SNFC slurry with 1.25 g/cm³ was used for cementing, and received good CBL/VDL logging results as shown in Fig. 10. The results show that the SNFC

returns to 676 m deep with a column length of 390 m. This means that the SNFC returns to above No. 3 CBM formation for 349 m, which meets the cementing design requirements. Besides, the cementing qualification rate reaches 100%, and the qualification rates of the first and the second interfaces reach 97.92%.

(a)

(b)

(c)

Fig. 10. CBL/VDL logs for well TS71-2D

Since July 2013, the $\Phi 339.7$ mm surface casings of thirty-seven wells in low-pressure formations have been cemented using the SNFC slurry. In these wells, the cement returns to surface without lost, which meets the design requirements. Since October 2012, eleven CBM wells have been cemented using the SNFC slurry. Of those 11 wells, CBL/VDL logs showed

excellent bonding quality and indicated that the cement returned to above CBM formations for 276-512 m, i.e., 26-262 m higher than the operator's requirement (250 m).

Conclusions

In order to resolve or relieve the problem of lost circulation and insufficient top of cement during well cementing, this study conducted a series of theoretical analyses and laboratory experiments on the nitrogen foamed cement.

(1) Based on chemical thermodynamics and electrochemistry, the reaction mechanism of nitrogen gas generation has been revealed, and a new nitrogen gas generating reactant (NGR) has been developed. NGR has a high gas generation efficiency of 78.57 mL/g and no adverse effects on the thickening time and compressive strength of oil well cement.

(2) The high-efficient foam-stabilizer (HFS) was prepared by the combination of surfactants CAB, AEO-9, CAO and AP-1. HFS is well suitable for stabilizing foam in cement slurry.

(3) The novel self-generating nitrogen foamed cement (SNFC) has been prepared through the injecting and mixing method in a closed vessel. The density of SNFC slurry can be controlled within 1.25-1.60 g/cm³. And SNFC slurry has excellent performances, such as favorable fluidity, no free water, low API fluid loss (less than 50 mL/30 min), proper thickening time at 80 °C/35 MPa (190-260 min), and high early compressive strength, which fully meet the requirements of oil and gas well cementing.

(4) The density variation law and microstructure characteristics of 1.25 g/cm³ SNFC slurry with temperature/pressure have been revealed through stimulation tests and SEM analyses.

(5) The self-generating nitrogen foamed cement (SNFC) exhibits excellent properties that can effectively solve the lost circulation problems in low-pressure formations and CBM wells. In all cases, the cement returned to designed depth and showed excellent bonding quality, which met the technical requirements.

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