Construction and Building Materials 104 (2016) 72–84

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

The application of coated superabsorbent polymer in well cement for plugging the microcrack

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HIGHLIGHTS

- SAP has adverse effects on the pumpability, strength and integrity of cement.
- Gypsum–chitosan–gypsum coated SAP is used in well cement to plug the microcrack.
- Percolation theory is taken to calculate the dosage of coated SAP.
- Results show that successful plugging of microcrack is achieved.

ARTICLE INFO

Article history:
Received 4 August 2015
Received in revised form 5 November 2015
Accepted 9 December 2015
Available online 11 December 2015

Keywords:
Well cement
Coated SAP
Percolation theory
Plugging microcrack

ABSTRACT

The research objectives are designed to realize the application of superabsorbent polymer (SAP) in well cement to plug microcrack. Gypsum–chitosan–gypsum coated SAP is proposed. Percolation theory is used to research plugging microcrack mechanism. According to the exact analytical solution of square plane percolation threshold, dosage threshold of coated SAP microspheres is calculated as 28.40%, which can deliver the plugging of microcrack. The method of manufacturing quantitative microcrack is established, and self-designed instrument is employed to test plugging performance. The results show the ability of plugging microcrack when the dosage of coated SAP microsphere is higher than the threshold.

1. Introduction

Cement has been used in wells which are drilled for the production of oil and gas [1,2], the capture and storage of carbon dioxide [3,4] and the exploitation of geothermal energy [5] for many years. Cement slurry is pumped into the annular space between the casing and formation to form cement sheath [6]. Cement sheath has the function of supporting casing and zonal isolation with the latter as the main function. Zonal isolation can prevent cross flow between layers, avoid pollution and ensure the safety of energy production. However, a large number of wells lose the zonal isolation, which is caused by the integrity failure of the cement sheath, i.e. cement sheath cracks [7,8]. Due to the brittleness of cement, many well operations could lead to integrity failure. For example, in CO_2 storage well and steam injection well [4,9], during the process of injection, the pressure under the well fluctuates, which can exert extra stress on cement sheath. At present, cement squeeze of workover operation is commonly used to solve the integrity failure of cement sheath; however this technology has high risk and cost [10].

Superabsorbent polymers (SAP) have been used in cement for many functions [11–15]. A self-healing oil well cement system including cement, water and SAP has been proposed by Sylvaine and co-workers [16]. When the cement sheath cracks, the water from the reservoir or the formation invades into cement along the crack section; consequently the SAP swells in contact with water, which can plug the crack. This cement slurry might prevent formation fluids from entering the water table and polluting drinking water, or prevent water from passing into the well instead of oil and gas. Since SAP is highly reactive with water, if the concentration added to the blend is too much, the slurry may typically have a too high viscosity for pumping in favorable conditions; but if the dosage is too small, the plugging may not be effective. Therefore, avoiding the above mentioned two issues is the key problem. Encapsulation has numerous applications to immobilize, isolate,

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http://dx.doi.org/10.1016/j.conbuildmat.2015.12.058
0950-0618/

protect and control the rate of transfer of many substances like acids, drugs, nutrients, perfumes and phase change materials [17,18]. It also should have the ability to control the initial water absorption rate of SAP. Coating could prevent SAP from contacting with cement slurry. Therefore, the influence of coated SAP on cement slurry property would be reduced to a minimum.

Coating performance mainly depends on the coating material. In this paper, chitosan and gypsum are used to coat the SAP microspheres. Microscopic plugging mechanism is analyzed. The percolation analysis of microcrack plane flow is carried out based on the percolation theory. The distribution model of SAP microspheres in cement matrix is established. The method of manufacturing quantitative microcrack is developed by using the chisel and transparent plastic tube. Finally, the self-designed instrument is taken to evaluate the self-plugging performance of microcrack.

2. Experimental

2.1. Materials

Glacial acetic acid (Analytical Reagent), α-calcium sulfate hemihydrate (D_{50} = 15 μm, Chemical Pure), glutaraldehyde (Analytical Reagent, 25%), xylene (Chemical Pure), Span-80 (Analytical Reagent) and $CaCO_3$ (Analytical Reagent) were provided by Sinopharm Chemical Reagent Co., Ltd. Class G oil well cement was used in the experiments. The typical mineral composition and physical properties of class G oil well cement are given in Table 1. Typical chemical composition is given in Table 2. Chitosans (150–200 kDa and 90–92% deacetylation degree) used in this study were commercial products from Naijin industry (Shanghai, China). The MW and deacetylation degree were supplied by the manufacturer.

Data obtained in previous study indicated that SAP with lower density of anionic groups has no negative effect on the compressive strength of the mortar [19]. Polyacrylamide superabsorbent polymers of which the synthesis technology is simple doesn't have anionic functional groups. However, the water absorption amount of polyacrylamide superabsorbent polymers in cement slurry filtrate is easily affected by temperature. The pH of cement slurry filtrate (W/C = 0.44) was tested at 75 °C, and the result was 12.88. In alkaline circumstance and high temperature, amide group is able to hydrolyze, which will influence the properties of polyacrylamide superabsorbent polymers sharply. Therefore, poly acrylamide/bentonite/N, N-dimethyl acrylamide superabsorbent polymer microsphere which is stable in cement slurry with high temperature were prepared by inverse suspension polymerization. The particle size range of microsphere is about 80–100 μm, which is determined by using sieve.

S1 mixture which contains SAP is used to test the effects of SAP on the performances of cement. The dosage of SAP is 1.0% by weight of cement, which was proposed by Snoeck et al. to decrease the permeability of microcrack in cement matrix [11,20]. The dosage of water and superplasticizer is 0.44 (water–cement ratio) and 0.5% (by weight of cement) respectively, which is commonly used to prepare cement slurry. S2 mixture is plain slurry. The mixture proportions of S1 and S2 are given in Table 3.

2.2. Method

2.2.1. The testing of basic properties of oil well cement

(1) Manufacturing process

Cement slurry was mixed based on API Spec. 10B-3-2004. After being prepared, the basic properties were tested as follows.

(2) Thickening time

Thickening time tests are designed to determine the length of time which slurry remains in a pumpable fluid state. The pumpability or consistency of the slurry is measured in Bearden units (BC), a dimensionless quantity with no direct conversion factor to more common units of viscosity such as the poise. The end of a thickening time test is defined when the cement slurry reaches a consistency of 100 BC; however, 70 BC is generally considered to be the maximum pumpable consistency.

Table 1
Phase composition and physical properties of class G oil well cement.

C_3S (wt%)	C_2S (wt%)	C_3AC (wt%)	C_3AF (wt%)	Specific density (kg/L)	Specific surface area (m^2/kg)
53.7	30.46	2.8	8.0	3.17	332

Table 2
The main chemical composition of class G oil well cement.

SiO_2 (wt%)	Al_2O_3 (wt%)	Fe_2O_3 (wt%)	CaO (wt%)	SO_3 (wt%)	MgO (wt%)	K_2O (wt%)	Loss on ignition (wt %)
22.70	3.39	4.81	65.60	1.21	0.90	0.37	0.49

Table 3
Mix proportions of cement slurry.

Slurry[a]	S/C (%)	D/C (%)	De/C (%)	W/C
S1	1.0	0.5	0.5	0.44
S2	0	0.5	0.5	0.44

[a] C, S, D, De and W are, respectively, the weight of cement, uncoated SAP, dispersant (sulfonated ketone/aldehyde polycondensates), defoamer and water.

There is a rotating cup with a fixed blade in consistometer. The cup driven by the motor is counter clockwise rotation at the speed of 150 r/min. The cement slurry in cup gives the blade a certain resistance which is proportional to the consistency of cement slurry. This resistance torque and potentiometer spring torque are in balance. Therefore, the consistency signal can be imported to the recorder through the potentiometer. Considering the temperature conditions in downhole, in this research, the consistency was tested at 75 °C and 0.1 MPa.

(3) Compressive strength

Cement slurry was placed into compressive-strength moulds (50 mm × 50 mm × 50 mm). Considering the temperature circumstance in downhole, the device and moulds were put into high temperature curing chamber, and cement slurries were cured for different time periods at 75 °C, which is chosen to simulate the downhole temperature. After curing, the set cement cubes were removed from the moulds, placed in hydraulic compression test equipment and loaded to failure. The compressive strength was recorded as the maximum compressive stress.

(4) Cement slurry stability

The purpose of this test is to determine the static stability of the cement slurry, and to determine if the cement slurry experiences particle sedimentation. The slurry is poured into a sedimentation tube. The sedimentation tube should have an inner diameter of 25 mm plus or minus 5 mm. The most common tube length is approximately 200 mm. The inside of the tube, and all joints, should be lightly greased to ensure that it is leak-tight and so that the set cement can be removed without damage. After curing the slurry at 75 °C for 24 h, the tube is cooled down to room temperature and the set cement is removed. The cement sample is immersed and kept in water as much as possible to prevent it from drying out. The length of the set cement specimen should be measured. The specimen is marked approximately 20 mm from bottom and top sides of the sample. The middle section, between the marks, is divided into roughly equal pieces with 5 segments. The sections must be kept in the same order. The sections are immersed and kept in water until each is weighed. The density of every section is tested by using drainage method.

(5) The integrity evaluation of cement stone

The cement slurry was cured at 75 °C for 4 days. During being cured, the slurry did not any contact with water. Then, the hardened cement is immersed for 24 h with the temperature of 75 °C. Observation is carried out to track the changes in the cement matrix and if it would destroy.

2.2.2. X-ray diffraction

XRD analyses were conducted in the State Key Laboratory of Heavy Oil Research using a PANalytical X′Pert MPD X-ray diffractometer. The data acquisition was carried out within the range of well-known cement minerals 2°–70° at a grade of 0.02° increments with Cu K_α radiation.

2.2.3. Elastic modulus and Poisson ratio

The relationship between elastic parameters of solid and velocity of ultrasonic propagation in solid are given by:

$$V_P = \sqrt{\frac{E}{\rho}\frac{1-v}{(1+v)(1-2v)}} \tag{1}$$

and

$$v = \frac{V_P^2/2 - V_S^2}{V_P^2 - V_S^2} \tag{2}$$