STUDY ON NON-CEMENT BASED ALKALI ACTIVATED MATERIAL FOR OIL AND GAS WELL CEMENTING AT LOW AND MODERATE TEMPERATURE

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ABSTRACT:

Non-cement based alkali-activated material (geopolymer) used for well cementing was studied to solve defects of quick strength decline and poor anticorrosion of well cement stone at heavy oil, low permeability and CO_2-rich reservoirs. Results showed that this cementitious material met the requirement of complex oil and gas reservoir well cementing at low and moderate temperature. The cementitious material using 60 percent of metakaolin and 40 percent of slag as the raw materials was activated by NaOH and waterglass solution. It had density of 1.68 g/cm^3, fluidity of 23.2 cm and free-water content of 0 ml at the liquid/solid ratio of 0.89 ml/g. Special retarder BCH was developed to solve the problem of short thickening time of geopolymer slurry. When the addition of BCH was 5.0%, initial setting time at 80^{o}C was prolonged 18.3 times to that containing no BCH. Its thickening time was 723 min and 108 min under the condition of 21 MPa at 50 ^{o}C and 80 ^{o}C, respectively. Filtrate reducer-LN was used to reduce slurry filtration: the filter loss varied from 294 ml to 240 ml when LN addition increasing from 4.0% to 10.0%. Compressive strength of hardened geopolymer reached 30.6 MPa when cured at 80 ^{o}C for 24 hours. Geopolymer samples could not be penetrated by 7.0 MPa and 15.0 MPa pressure at different during the curing time (7 d, 28 d and 90 d). After curing 3 days, the porosity ratio was 6.27% and almost all pores were smaller than 20 nm in diameter. Compared to common oil well cement stones, this compact geopolymer had higher compressive strength and lower porosity. Moreover, the preparation of geopolymer consumed great amount of slag and did not produce any hazardous gas, such as CO_2, which is beneficial for waste recovery.

Keywords: Complex oil and gas reservoir; Well cementing; Geopolymer; Metakaolin; Alkali-activated material

1. INTRODUCTION

Use of domestic medium and high permeable oil and gas well reservoirs are ceasing while the complex reservoirs, such as the low-permeable, deep and heavy-oil reservoirs, are becoming increasingly important roles in the exploration and development of petroleum. Ordinary oil well cement can not completely meet the demand of long-term efficient seal due to the complexity stratum formation and the difficulty of construction operations of unconventionality reservoirs. Moreover, the cement industry is a typical energy and resource consumption industry. Furthermore, large amounts of dust and the greenhouse emissions caused by oil well cement production will pollute atmosphere seriously [1]. Therefore, it is imperative and important to develop high quality, cheap and environmental friendly cementing material for the use of oil and gas reservoirs.

Geopolymers are a family of materials with excellent performances formed by alkali activation of aluminum and silicon-rich industrial wastes. The production does not necessarily process "two milling and one bake" and uses limestone, therefore significantly saving energy and resources and reducing greenhouse effect and dust emissions [2,3].

Geopolymer solidification process is quite different from cement hydration. The former undergoes the bond dissolution of Al-O-Si, Al-O-Al, Si-O-Si in metakaolin by activator. The low polymerized cluster ions then recombine into new structures, which are different from those of raw materials[4,5]. Geopolymers are attracting increasing attention and their properties have been extensively studied[6~8]. Currently, a few products have been applied in engineering construction[9~11], though little work of its application in the oilfield has been carried out. This report will study the applications of geopolymer in oilfields. The experiment will focus on the mechanical properties and engineering performances, which determine the application of geopolymer in oil and gas well cementing.

2. EXPERIMENTS

2.1 Materials

The MK used for this study was obtained from Suzhou (Jiangsu Province, China) and treated at 900 °C for 6 h before use. Slag was obtained from Nanjing Jiangsu Province, China. The used oil well cement was Grade-G. Chemical composition of kaolin, slag and oil well cement as determined by X-ray Fluorescence (XRF) is given in Table 1. Chemical grade sodium hydroxide and distilled water were mixed into waterglass (with modulus 2.4, Na_2O=12.92 mass%, SiO_2=29.8 mass%) to prepare liquid activator and wait for 24 h prior to use.

Table 1 Chemical compositions of metakaolin, slag and oil well cement/ (mass%)

Element as oxides	Content / %		
	Metakaolin	Slag	Oil well cement
SiO_2	52.20	36.86	23.69
Al_2O_3	44.04	19.84	4.02
CaO	0.31	31.75	64.81
K_2O	0.68	0.53	0.32
Na_2O	0.15	0.37	0.29
Fe_2O_3	0.65	0.80	4.27
MgO	0.27	8.53	1.22

2.2 Specimens and Test Methods

The slurries were prepared and tested in accordance to the American Petroleum Institute (API) procedures[12]. The water/solid ratios of geopolymer and oil well cement slurries were 0.89 and 0.44, respectively. Compressive strength and flexural strength data was obtained from Hualong model WHY-200 machine. The impact energy was tested on Chengde model XJJ-5 machine. The penetrate property of samples cured 3 days at 80 °C was analyzed by HLY-2 testing machine. Pore structure of geopolymer and cement was analyzed by GT-60 Mercury Intrusion Porosimetry (MIP). Micrograph of fracture surface of geopolymer and cement stone was observed by JSM-5900 Scanning Electron Microscopy (SEM). The thicken time was also evaluated.

3. RESULTS AND DISCUSSION

3.1 Basic properties

Oil and gas well cementing is different from ordinary ground engineering technique. It has strict demand on the properties of cementing slurry. The density of geopolymer, 1.68 g/cm^3, is quite lower than oil well cement slurry. It is beneficial to well cementing and the improvement of well recovery ratio of low pressure and easy leaking stratum. Furthermore, low density slurry is beneficial to pumping and the improvement of slurry replacing efficiency. Geopolymer slurry fluidity is good (23.2 cm) and free water content was 0 ml. The slurry properties of geopolymer can meet the demand of oil and gas well cementing.

Net geopolymer slurry had high filtration loss (Table 2). LN-latex additive was used to control the filtration loss of geopolymer slurry. Filtration loss of geopolymer slurry was 240 ml as filter pressure of 7.0 MPa and temperature of 80 °C when LN-latex addition was 10%. LN-latex was emulsification granule and it could be dispersed in slurry homogeneously by high-speed stirring and adding Al^{3+} and Ca^{2+} ions. The liquid was consumed along with alkali activation, thus the granule could contact with each other more frequently. At the same time, filtrate loss rapidly in initial time, it promoted latex to assemble and accelerated the forming of the membrane of latex granule, which could reduce filtration loss.

Table 2 Effect of LN-latex content on filtration loss of geopolymer slurry

LN-latex additive / %	filtration loss (Q_{30}) / ml
0	1053
4	294
6	258
8	251
10	240

Note: filter pressure-7.0 MPa; temperature-80 °C

Thickening time of well cementing material is an important engineering parameter for oil and gas well cementing. The thickening time of geopolymer was quite short and it obstructed the application of geopolymer in oilfield. Retarder BCH was used in this study. When the addition of retarder of BCH was 5.0%, thickening time was 342 min at 80 °C (Table 3). According to thickening curves (Fig 1), geopolymer containing 5.0% BCH was selected for further study.

Table 3 Effect of BCH content on geopolymer setting time (80 °C)

BCH content / %	Setting time / min	
	Initial setting	Final setting
0	18	26
2.0	106	147
4.0	276	329
5.0	329	342
6.0	318	335
8.0	253	296

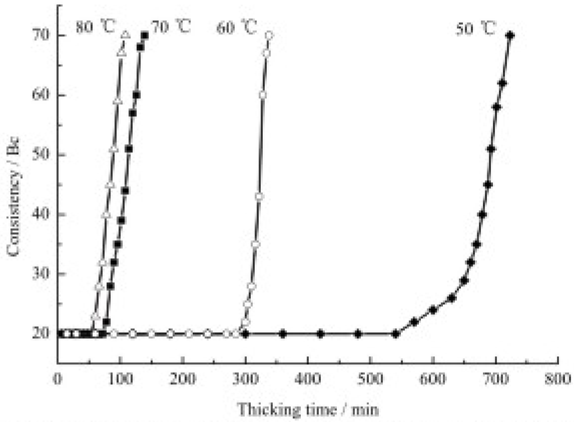

Fig.1 Thickening curves of geopolymer slurry at different temperatures (thicking presure: 21.0 MPa)

3.2 Comparison between geopolymer and oil well cement

(1) Compressive strength

Geopolymer showed higher compressive strength than oil well cement at age of 1 d, 3 d, 7 d and 28 d (Fig.2). Geopolymer had quick initial strength development and the compressive strength of 1 d was 30.6 MPa, 20% higher than oil well cement. The compressive strength of geopolymer increased along with curing time and it increased by 18.30% at 28 d. Due to this increase, the oil and gas well cementing quality can be improved. Metakaolin and slag are silicon and aluminum-rich materials. Long chains of Si-O and Al-O bands will undergo the destruction-polycondensation reaction under strong alkali condition. The fresh formed units of geopolymer bind were bound by covalent bond and electrovalent bond, which are much stronger than hydrogen bond and Vander Waals force, the form in which the products of oil well cement bound to each other.

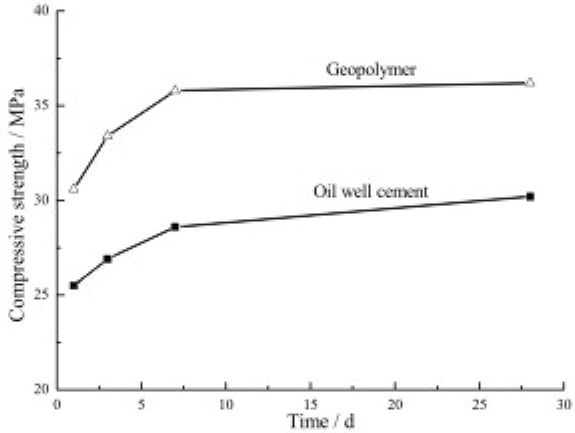

Fig.2 Compressive strength of geopolymer and oil well cement (80 °C)

(2) Permeability

Oil and well cementing quality has close relationship with the permeability of the used well cementing material. High permeability of cementing material will lead poor anticorrosion, the well life-span reduction and crossflow and so on. Oil well cement stone was permeable at 7.0 MPa and 15.0 MPa (permeability coefficient is between 1.02 to1.66 $\times10^{-3}$ μm^2). As the driven pressure increased, the permeability coefficient also increased (Table 4). Geopolymer samples can not be penetrated owing to their high compactness property. The impermeability could enhance exploit quality of oil and gas well cementing.

Table 4 Permeability coefficient k of geopolymer and oil well cement (80 °C)

Sample	*k*（7.0 MPa）/ $\times10^{-3}$ μm^2			*k*（15.0 MPa）/ $\times10^{-3}$ μm^2		
	7 d	28 d	90 d	7 d	28 d	90 d
GEO	0	0	0	0	0	0
OWC	1.06	1.04	1.02	1.66	1.57	1.38

Note: (1) 7.0 MPa and15.0 MPa is driven pressure of water;
(2) GEO is Geopolymer, OWC is Oil well cement.

(3) Pore structure

Fig.3 shows the pore size distribution of geopolymer and oil well cement at 3 d and detailed date are given in Table 5. The porosity ratio of geopolymer was 6.27%, much lower than that of oil well cement. Geopolymer had a pore size distribution between 0 to 100 nm and 55.28% (in volume) pores were smaller than 20 nm. On the other hand, the pore size distribution of cement mainly focused from 20 to 50 nm (44.55% in volume). The metakaolin particles and slag adulterated with each other, which led to the internal pore size reduction and compact degree improvement of final products. This property of geopolymer was beneficial to oil and gas well cementing quality as well as the durability of well under erosive condition (in medium within salt, CO_2, H_2S, etc.).

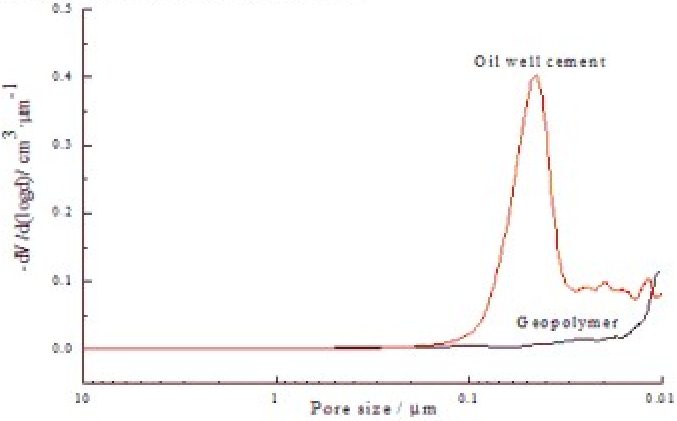

Fig.3 Pore size distribution of geopolymer and cement samples (80 °C × 3 d)

Table 5 Pore size distribution of geopolymer and oil well cement (in volume)

Samples	Porosity / %	Pore size distribution / %			
		＜20 nm	20~50 nm	50~200 nm	＞200 nm
Geopolymer	6.27	55.28	19.33	11.44	13.95
Oil well cement	22.43	18.38	44.55	13.65	13.42

(4) Microstructure

Fig.4 describes the microstructure of geopolymer. The final products of geopolymer were hardened gels, consisting of Si, Al, Ca and O. In the process of geopolymerisation, the intermediate phases from alkali-activation metakaolin and alkali-activation slag could compound with each other, thus forming high compact structure.

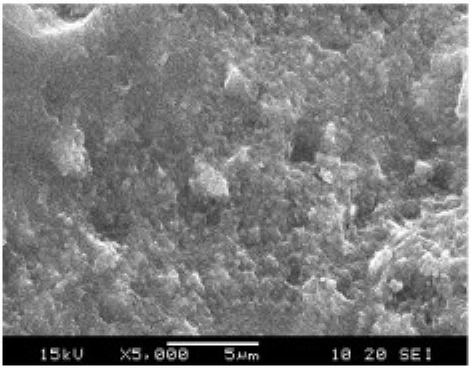

Fig.4 SEM micromorphology of geopolymer fracture surface (80 ^{o}C × 3 d)

4. CONCLUSIONS

A geopolymer was developed by alkali-activated metakaolin and slag. By using LN-latex addition and retarder BCH, the basic engineering properties, including filtration loss, setting time and thickening time, of geopolymer met the demand of oil and gas well cementing application at low and moderate temperature. Compared with common used cement, geopolymer had higher compressive strength and excellent impermeability. The porosity of geopolymer was much lower than cement stone. All of these show the high potential of geopolymer to be used as the new well cementing material.

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