Laboratory research and evaluation of geopolymer cement working fluid system

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Abstract. The Portland cement production process has some problems such as high energy consumption and high CO_2 emissions, and the Portland cement has defects such as high brittleness, poor toughness, and poor corrosion resistance. In comparison, geopolymer has the characteristics of wide source of raw materials, energy saving and environmental protection in the production process, good mechanical properties and durability. This paper studies the geopolymer cement working fluid system which can meet to cement site construction. The precursor gel material was formed with the following combinations sinking beads : fly ash : slag = 5 : 3 : 2, and the slow-release activator (Na_2SO_4& $Ca(OH)_2$) was developed, which can achieve good compressive strength performance and controllable thickening time. The working fluid with a density of 1.90g / cm^3 was evaluated. By adding organic phosphate retarder, the thickening time can be adjusted, the compressive strength is more than 14 MPa, the transit time of static gel strength is 12 min, and no channeling occurs when the gas channeling pressure is 300psi (2.1MPa). It has good anti-channeling performance. The elastic modulus after adding fiber is 6.2GPa. The performance of the system meets the requirements of cementing engineering technology. The geopolymer cement working fluid is an ideal cement material.

Keywords : geopolymer ; cementing working fluid; cement material; anti-channeling.

1. Introduction

The geopolymer is an inorganic polymer with a three-dimensional network structure composed of silicon-oxygen tetrahedron and aluminum-oxygen tetrahedron structural units, from amorphous to semi-crystalline non-metallic materials. The structural formula is as follows: $Mn\{-(SiO_2)z-AlO_2\}n\cdot wH_2O$(M represents metal cations, such as Na, K, Ca, etc.; n is the degree of polymerization ; z is the Si/Al molar ratio ; w is the number of bound water)[1,2]. The silicon and aluminum in the aluminosilicate material are dissolved after contact with the alkali solution to form oligomers which undergo condensation reaction to form a three-dimensional skeleton[3,4].

Compared with the large amount of CO_2 emitted during the production of Portland cement (producing 1 ton of cement emits 0.8 tons of CO_2), the production process of geopolymers is more environmentally friendly[5,6]. The raw materials of geopolymers have a wide range of sources, such as fly ash, slag, silica fume, coconut shell ash, red mud and metakaolin[7,8].Meanwhile, Portland cement itself has some defects. In the process of perforation and hydraulic fracturing, cement sheath failure often occurs due to its poor elastic toughness and high brittleness[9]. Its compressive strength will decline at temperatures above 110 °C, especially in deep wells and geothermal wells and wells with thermal loads (such as steam injection wells), and its mechanical performance are not ideal[10,11,12]. At the same time, CCUS (Carbon Capture, Utilization and Storage) technology is the key technology for China to achieve Dual Carbon Goals, which has high requirements for the corrosion resistance of oil well cement in injection wells or abandoned wells and the integrity of the cement sheath in the upper formation of the storage area[13,14]. However, in a CO_2-rich environment, the mechanical properties of Portland cement deteriorate due to carbonation and the formation of unfavorable precipitates ($Ca(OH)_2$), resulting in CO_2 leakage[15,16].

Geopolymers have been widely used in construction and other fields due to wide sources, low carbon and environmental protection in the production process, and excellent mechanical strength and durability[17]. EcoShield™ Geopolymer Cement-free System was first developed by Schlumberger and related applications have been carried out in the Middle East, but there has been no relevant report in China. The related research of geopolymer cement work fluid system should be carried out.

2. Experiment

2.1 Geopolymer Gel Material

Low calcium fly ash (FA), sinking beads (SB) and slag (GGBS) were selected as geopolymer gel materials. The composition of sinking beads is similar to that of fly ash (Fig.1), which is rich in silica dioxide and aluminum oxide. Through particle size analysis (Fig.2), the particle size of fly ash is D50 = 16.14μm, the particle size of precipitated beads is D50 = 1.32μm, and the particle size of slag is D50 = 9.13μm.

Under the premise of a certain amount of slag, the influence of the ratio of SB and FA on the strength of geopolymer was studied (Table 2). With the increase of the amount of SB, the strength increases gradually. When the amount of SB is 80 %, the strength can reach 16MPa (the amount of activator NaOH is 6 %). When the amount of SB is 80 %, the mixability is not good. Finally, the ratio of the precursor is determined to be SB: FA : GGBS = 5 : 3 : 2.

Table 1. XRF test results

Sample	Oxide component content /Wt%							
	SiO_2	Al_2O_3	CaO	K_2O	Na_2O	MgO	SO_3	Fe_2O_3
FA	50.79	32.12	3.64	2.58	0.89	0.77	1.44	5.78
SB	52.92	19.09	11.19	2.92	2.65	1.87	0.22	6.02
GGBS	30.36	17.26	38.86	0.34	0.45	8.41	2.57	0.37

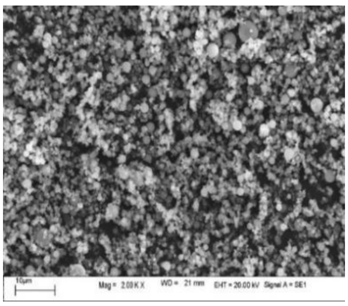


Fig. 1 Microstructure of sinking beads

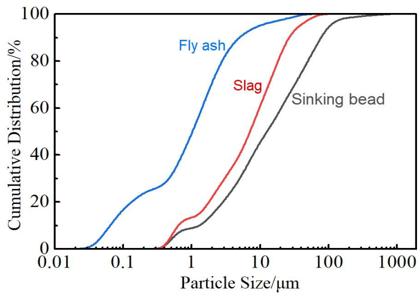


Fig.2 Particle size distribution

Table 2. Geopolymer formulations

Formula	SB/%	FA/%	GGBS/%	NaOH/%	Retarder/%	Compressive stress(24h)/MPa
SB2FA6	20	60	20			6.8
SB3FA5	30	50	20			11.1
SB4FA4	40	40	20	6	2	13.9
SB5FA3	50	30	20			14.2
SB8FA0	80	-	20			16.0

2.2 Activator

2.2.1 Existing questions

Alkali excitation method is a common excitation polymerization method for geopolymers. Commonly used alkali activators include alkaline solutions such as NaOH, KOH, and Na_2SiO_3.

Among them, NaOH and water glass(Na_2SiO_3) are the most commonly used alkali activators.

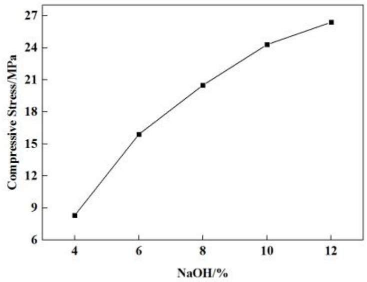


Fig.3 Effect of NaOH content on the compressive strength

Table 3. Effect of the retarder on thickening time(NaOH 6%)

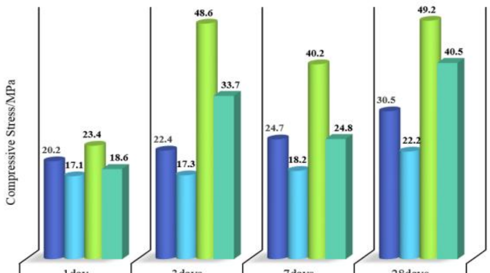
Retarder%	Thickening time(40Bc)/min	Thickening time(100Bc)/min
2.4	14.1	24
3.4	17	27
4.4	34.1	43.6
5.4	52.8	62.6

In this paper, the effect of different content of NaOH on the compressive strength of geopolymer is investigated(Table.3). With the increase of NaOH content, the compressive strength increases gradually. When the content of NaOH is 12 %, the strength can reach 26 MPa. However, when NaOH as the activator is directly added, the reaction is severe. In a short period of time, the system becomes thicker and harder. It is difficult to control the thickening time by common retarders of oil well cement, which can not meet the requirements of cementing construction. Therefore, the idea of developing slow-release activator is put forward, from the regulation of the retarder on the dissolution and hydration of cementitious materials to the regulation of the retarder on the release rate of alkali activator.

2.2.2 Slow-release activator

Aiming at the problem that the thickening time of geopolymer is difficult to control, the preferred principles by using slow-release activator are as follow. The product after reaction is NaOH ,and at least one reactant is difficult to dissolve ,and if the reactant is soluble, its alkalinity is weaker. Four kinds of sodium salts such as Na_2SO_4, Na_2CO_3, NaF and $Na_2C_2O_4$ were selected to combine with $Ca(OH)_2$(CH) to form four kinds of slow-release activators.

The compressive strength with different activator types at 70 °C was evaluated (Fig.4). Compared with the strength of the geopolymer excited by NaOH, the strength of the geopolymer with NaF and CH as activators with the same equivalent NaOH content is the highest, which can reach 24.7MPa after 1day of curing and close to 50MPa after 28day of curing. The strength of the geopolymer with Na_2SO_4 and CH is the lowest, but its compressive strength(1day) is 17.1MPa, which meets the needs of cementing technology.



	1day	3days	7days	28days
Sodium carbonate	20.2	22.4	24.7	30.5
Sodium sulfate	17.1	17.3	18.2	22.2
Sodium fluoride	23.4	48.6	40.2	49.2
Sodium oxalate	18.6	33.7	24.8	40.5

Fig.4 Effect of different types of activators on compressive strength

From the perspective of compressive strength, it can be seen that when the activator is NaF & CH, the compressive strength of the system is the highest. However, in the actual mixing process, it is found that the three types of activator combinations of NaF& CH,Na_2CO_3&CH, and $Na_2C_2O_4$&CH have different degrees of difficulty in mixing(Table .4), which cannot meet the requirements of on-site construction for pumpability and mixability. Therefore, the type of activator is selected as Na_2SO_4 & CH.

Table 4. Effect of activator type on fluidity and mixing time

Activator	Fluidity/cm	Mixing time/s
Na_2CO_3&CH	18	80
Na_2SO_4 &CH	20	40
NaF& CH	16	70
$Na_2C_2O_4$&CH	16	75

2.2.3 Hydration products and microstructure

The hydration products and microstructure of geopolymer activated by the activator Na_2SO_4 & CH were analyzed. XRD analysis showed that the geopolymer was mainly amorphous gel, with some mullite and quartz (possibly in raw materials). Combined with SEM, it can be seen that the reaction becomes more and more thorough with the extension of curing time.

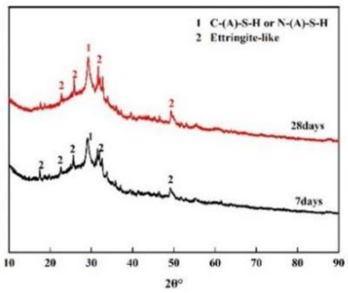


Fig.5 XRD

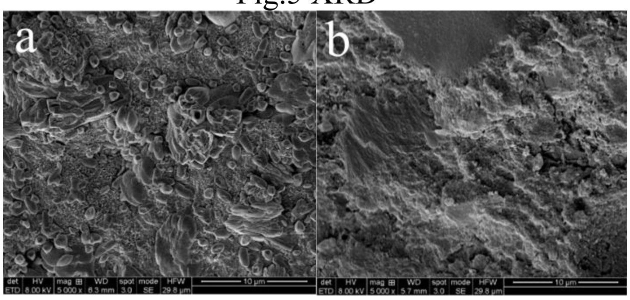


Fig.6 SEM（a.7days　b.28days）

2.3 Performance Evaluation

The most commonly used cement slurry density in cementing engineering is 1.90 g/cm^3. This paper takes 1.90 g/cm^3 geopolymer cement working fluid as an example to carry out relevant performance evaluation.

2.3.1 Fluid loss

Table 5. Evaluation of fluid loss agent

Type	Dosage/%	Fluid loss /mL	Remark
PVA	1	-	Thickening is obvious, loss of fluidity
AMPS1	5	47（7.5min）	

	8	104	
	10	64	
AMPS2	8	49（7.5min）	
AMSP2	6	110	Thickening

Table 6. Evaluation of water loss

Micro silicon/%	Barite/mesh	AMPS1 %	Fluid loss/ml
0	200-300	8	120
6	200-300	8	109
10	200-300	8	78
0	100-200	8	80
6	100-200	8	42
10	100-200	8	30
6	100-200	4	110
10	100-200	4	90
10	100-200	6	48

Several kinds of fluid loss control agents commonly used in the domestic market were selected. PVA is a polyvinyl alcohol fluid loss control agent, and the rest are AMPS fluid loss control agents(Table 5). The experimental results show that the water loss of geopolymer cement fluid cannot be controlled within 50 mL. Adding a large amount of fluid loss agent is beneficial to reduce the water loss of the system, but at the same time increases the cost of use. Therefore, it can not be considered only from the perspective of increasing the amount of fluid loss control agent. The particle size distribution of various materials in the system should be fully considered to control the fluid loss. It can be seen from Table 6 that by adding a certain amount of micro-silicon to the system and optimizing the barite with appropriate particle size (100-200 mesh), the filter cake can be dense, and the fluid loss performance of the system can be achieved within 50 ml.

2.3.2 Thickening time and compressive strength

The self-developed retarder organic phosphate BH-R102L was selected to control the thickening time of the geopolymer system. The experimental temperature was 70°C. The thickening time without retarder was 89min. After adding 2g BH-R102L, the thickening time was extended to 225 min and the compressive strength was 16.0 MPa(curing time 24hours), which met the requirements of field construction.

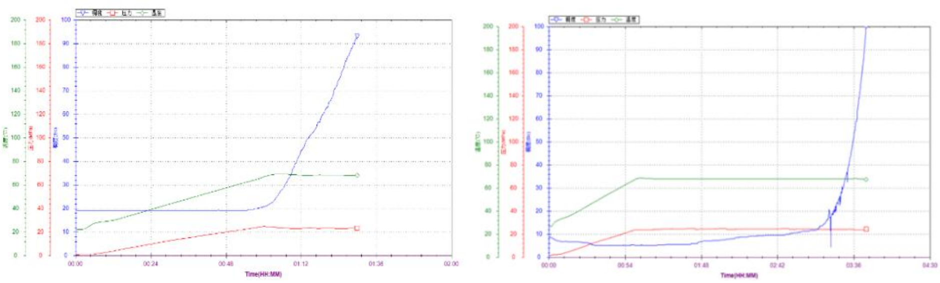


Fig.7 Effect of retarder on thickening time（Left. 0g Right. 2g）

2.3.3 Anti-channeling performance

According to the industry standard of SY/T 5504.5-2022 ' Evaluation method for well cement additives- Part5:Gas block cement additive ', the anti-channeling performance of geopolymer cement fluid system was evaluated. The static gel strength transition time was 12 min and no gas channeling occurred when the gas injection pressure was 300psi (2.1MPa), indicating that the system had good anti-channeling ability.

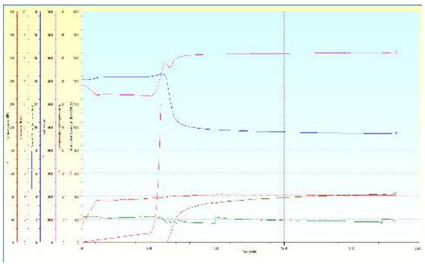


Fig. 9 Static gel strength test

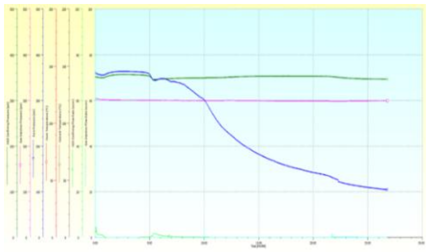


Fig.10 Gas channeling pressure test

2.3.4 Elastic modulus

The elastic modulus of the system was investigated. It can be seen from the triaxial experiment that the compressive strength of the system was 22.73 MPa and the elastic modulus was 7.1 GPa after curing 30 days in the temperature 80℃ when the fiber was not added. After adding the mineral fiber, the compressive strength of the system was 19.04 MPa and the elastic modulus was 6.2 GPa. The fiber can improve the elastic toughness of the system.

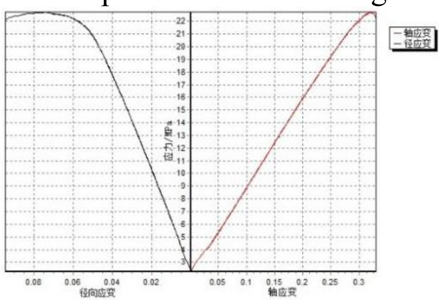


Fig.11 Elastic modulus (adding 0.5 % fiber)

3. Summary

(1) A geopolymer gel material suitable for cementing construction was developed, which has good strength characteristics.

(2) The slow-release activator Na_2SO_4&$Ca(OH)_2$ was developed by using retarder to control the release rate of alkali activator, and the thickening time of the system could be controlled.

(3) The thickening time of geopolymer cement fluid with density of 1.90g/cm^3 is adjustable by using self-developed organic phosphate retarder. The compressive strength is greater than 14MPa. The static gel strength transition time was 12 min and no gas channeling occurred when the gas injection pressure was 300psi (2.1MPa) indicating that the system had good anti-channeling performance. Elastic modulus is 6.2GPa after fiber modification.

(4) It is suggested that the development of additives such as fluid loss agent and drag reducing agent for geopolymer should be carried out, and the long-term durability evaluation should be carried out to provide more technical data for field application.

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