

Study on Preparation of Cement Slurry Retarder with High Temperature Resistance for Cementing

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Abstract

With the rapid development of petroleum industry, the exploration and development of oil fields has developed towards medium and deep wells and ultra-deep wells, which brings many new problems to oilfield cementing engineering. To solve the problem of slow development of strength at the top of cement slurry column with large temperature difference in long sealing section of deep and ultra-deep wells, a new polymer retarder with high temperature resistance was developed by free radical aqueous solution polymerization, and its performance was evaluated. The results show that the product has good retarding effect at high temperature, and has good compatibility with most dispersants and fluid loss additives. The prepared cement slurry has the characteristics of high temperature right angle thickening. In the temperature range of 90 ~ 130 °C, the new high-temperature retarder has certain high-temperature filtration reduction performance, and the compressive strength of cement paste mixed with the new high-temperature retarder can meet the basic technical requirements of cementing operation under high-temperature curing. It is of great significance to improve cementing quality, simplify wellbore structure and save drilling cost in long cementing section of deep well.

Keywords

High Temperature Resistance; Cementing; Cement Slurry Retarder.

1. Introduction

Cementing is the construction process of running casing into a well and injecting cement into the annulus between the wellbore and casing. Its function is to reinforce the shaft wall, fix the casing, and seal off the oil, gas and water layers, thus ensuring the smooth progress of the later operation. However, cementing is a one-time project with high cost. Poor cementing quality is generally difficult to remedy, and even leads to the scrapping of the whole oil and gas well, thus causing significant energy and material losses. Therefore, it is very important to ensure the smooth progress of cementing operation and improve the cementing quality, and cement slurry additives for cementing play a very important role in this respect.

There are many kinds of retarders, which can be divided into inorganic retarders and organic retarders according to their chemical composition [1]. Among them, inorganic retarders include phosphate, zinc salt, ferric sulfate, copper sulfate, borate, fluorosilicate, etc. Organic retarder includes lignosulfonic acid and its salt, hydroxycarboxylic acid and its salt, organic phosphonic acid and its salt, sugar and carbohydrate, etc. Literature [2] thinks that the main action mechanism of hydroxycarboxylic acids and their salt retarders is the nucleation poisoning mechanism. Literature [3] A liquid retarder CH20L was prepared from starch by deep oxidation. This kind of retarder is a kind of high temperature resistant retarder, and its maximum service temperature can reach 180 °C. Literature [4] An organic phosphonic acid (salt)

and inorganic phosphoric acid (salt) were compounded according to a certain proportion, and a high temperature resistant retarder with excellent performance was prepared. Literature [5] synthesized an organic phosphonic acid retarder for oil well cement. The performance evaluation results show that the retarder has excellent performance, linearly adjustable thickening time and ideal thickening curve, and the applicable temperature range is 50~170 °C. In the process of cementing in the long cementing section of deep wells, in order to ensure the safety of cementing operation, a large number of retarders need to be added to the cement slurry. However, under the condition of large temperature difference, cement slurry containing polymer retarders is prone to problems such as slow development of strength of cement paste at the top of cement slurry column or over-retarding, which not only affects the cementing quality and prolongs the drilling cycle, but also brings risks to the later drilling and completion operations. Therefore, a new type of retarder with high temperature resistance has been developed, which has the characteristics of high temperature resistance, salt resistance and insensitivity, and can be constructed under extremely harsh environmental conditions without crystallization or crystallization.

2. Mechanism of retarder

Retarders mainly achieve retarding effect by inhibiting hydration speed of cement minerals and coagulation process of cement-hydrogel system [6].

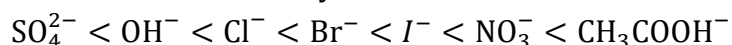
2.1. Mechanism of inorganic salt retarder

Inorganic compounds have a significant impact on cement setting, which is electrolyte salts. When inorganic electrolyte salts are added to cement-water system, cations with different charges are dissociated from the electrolyte in the solution. With the increase of repulsion between cement particles, the fluidity of cement-water system increases, which plays a retarding role [7]. The retarding ability of cations to cement-water system from weak to strong is:



Generally speaking, the displacement ability of cations varies with their electronegativity, ion radius and ion concentration, while the retarding effect of ions with the same valence depends on their ion radius and hydration degree, and the smaller the atomic number, the stronger the retarding effect.

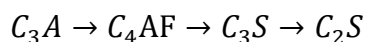
Besides cations, anions also play a certain role in cement setting. With the increase of anion valence, the retarding ability of electrolyte to cement increases correspondingly. Therefore, if the setting time of cement needs to be delayed, high-priced electrolyte salts can be used. The retarding effect of anion on cement-water system is as follows:



2.2. Action mechanism of organic retarder

Generally speaking, most organic retarders have surface activity and play the roles of adsorption, dispersion and wetting. They produce adsorption at the solid-liquid interface and change the surface properties of solid particles. Or a large number of water molecules are adsorbed by hydrophilic groups in molecules to form a thick water film layer, so that the crystals are in contact with each other and shielded, and the structure formation process is changed; Or some functional groups in the molecule and free Ca^{2+} generate insoluble calcium salt, which is adsorbed on the surface of mineral particles, thereby inhibiting the hydration process of cement, slowing down the hydration reaction speed and achieving the retarding effect.

Adsorption theory is usually used to explain the effects of sugar retarders, polyols and their derivatives on hydration of oil well cement. Generally, the order of selective adsorption of organic retarder by cement minerals is as follows:



When the retarder is added into the cement slurry, the hydroxyl group of the retarder selectively adsorbs O^{2-} on the surface of cement mineral particles and hydration products.

At the same time, other hydroxyl groups are associated with water molecules through hydrogen bonds, and in addition, the hydrogen bonds between water molecules form a stable solvated water film on the surface of cement particles, which prevents the direct contact of cement particles and inhibits the hydration speed of aluminate components. While inhibiting the hydration of C_3A , it also inhibits the hydration of silicate components, thus achieving the retarding effect.

3. Preparation of cement slurry retarder

3.1. Testing materials and instruments

Retarder and fluid loss reducer, homemade; Quartz sand with purity of 99% and particle size of 0.1 mm; Micro silicon; Sulfonated acetone formal dispersant DRS-1S; Stabilizer DRK-3S, sodium hydroxide, NaCl, industrial grade. OWC-2000D corrugated mixer, TDA 305 gel permeation chromatograph, chandler 5265u static gel strength analyzer, Chandler 6265U cement stone mechanical strength analyzer.

3.2. Structural design of retarder

The retarder structure is designed from three aspects:

- (1) Introducing sulfonic acid group and polymerized monomer which can form stable cyclic structure, increasing the rigidity of molecular chain and insensitivity to external cation attack, and improving the temperature resistance and salt resistance of polymer molecular main chain.
- (2) Organic substances with polycarboxylic acid groups are introduced to reduce the hydration rate of cement, and at the same time, Ca^{2+} in the liquid phase of cement slurry is complexed to generate slightly soluble precipitates, thus realizing slow setting.
- (3) The introduction of polymerizable cationic monomer with surface activity can form a stable association structure between molecules and within molecules, which makes the polymer have temperature-sensitive scalability, that is, the molecular chain is curled up at low temperature, and some retarding groups are "embedded" in the association structure. With the increase of temperature, the molecular chain gradually expands and disassociates, and the proportion of "exposed" retarding groups gradually increases. And the process is reversible.

3.3. Experimental materials

AMPS, sodium hydroxide, TA, ammonium persulfate, sodium sulfite, sodium chloride, G-grade oil well cement.

3.4. Experimental method

- (1) Accurately weigh AMPS and TA according to the formula, put them into a beaker, add water to dissolve them, and adjust their pH value to the set value with sodium hydroxide of fixed concentration.
- (2) Put the prepared monomer solution in a four-necked bottle equipped with stirrer, thermometer and nitrogen, and add a certain amount of deionized water.
- (3) Heating the reaction device to a set temperature, adding an initiator, and simultaneously introducing nitrogen for protection. React for a certain time to obtain colorless transparent liquid copolymer.

4. Performance evaluation of high temperature retarder

4.1. Salt resistance

When cementing in salt-gypsum strata, the salt substances in the strata will invade the cement slurry. If the salt resistance of additives in cement slurry is poor, it will lead to poor performance of cement slurry, which will affect the cementing quality and even lead to the failure of cementing operation. Therefore, the additive must have good salt resistance.

The salt resistance test results of high-temperature retarder are shown in Table 1. Because the copolymer has certain dispersing effect, 0.5% suspending agent is added in the test to keep the stability of cement slurry.

Table 1. Salt resistance of high temperature retarder

Serial number	High temperature resistant retarder /%	Water quality	Amount of water added	t/min	$t_{transit}/min$
1	0.6	Tap water	328mL	141	8
2	0.6	17% saline	328mL	283	6
3	0.7	Tap water	328mL	154	7
4	0.7	17% saline	0.5(W/C)	266	6

The sulfonate group in itaconic acid copolymer, a new type of high-temperature retarder, not only has good high-temperature resistance but also has good salt resistance, which can inhibit the dispersion of NaCl on copolymer, especially resist the destruction of copolymer structure by Cl^- . When the slurry water contains 18% salt, no retarding and sensitive phenomena are found.

4.2. Coagulation regulating performance

The thickening performance of cement slurry is a key index in cementing operation, which requires not only moderate thickening time, short transition time and "right angle" thickening of cement slurry, but also moderate initial consistency and good thickening alignment of cement slurry, and no "bulging", "core covering" and other phenomena endangering construction safety.

See fig. 1 for the relationship between thickening time of cement slurry with different densities at 120°C and the dosage of new high temperature resistant retarder. The relationship between thickening time and experimental temperature of cement slurries with different densities is shown in Figure 2 when the new high temperature resistant retarder is added at 2%.

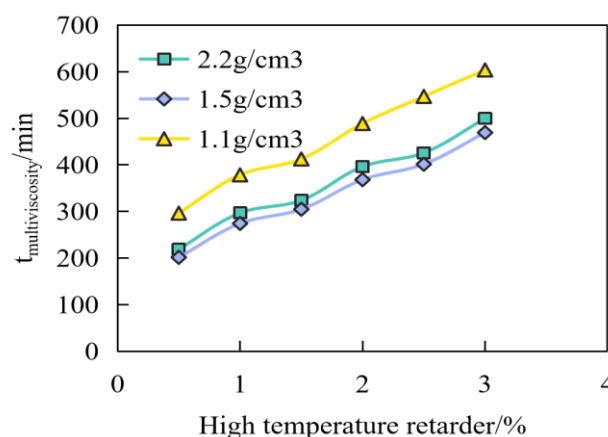


Figure 1. Relationship between thickening time of cement slurry at 120°C and dosage of retarder

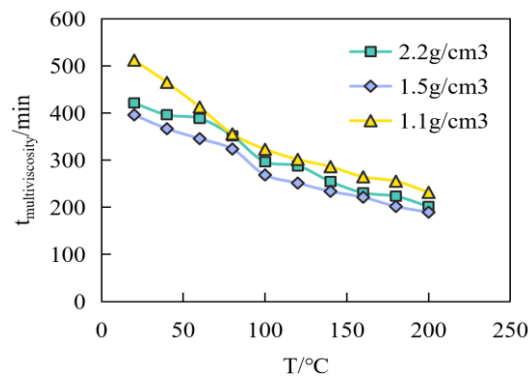


Figure 2. Relationship between thickening time and temperature of cement slurry containing 2% new high temperature resistant retarder

It can be seen from Figure 1 that at the same temperature, the thickening time of cement slurry with different densities is prolonged with the increase of the new high temperature resistant retarder, showing a good linear relationship.

It can be seen from Figure 2 that under the same dosage of retarder, the thickening time of cement slurry is shortened with the increase of temperature, showing a good linear relationship with temperature, which shows that the performance of the new high-temperature resistant retarder is relatively stable, and the thickening time of cement slurry can be effectively controlled by adjusting the dosage of retarder, thus effectively preventing the risks caused by inaccurate thickening time. If thickening time is shorter than expected, cement slurry will be solidified in casing in advance, resulting in major liability accident. However, thickening time is longer than expected, which will easily lead to long-term non-coagulation of cement slurry, resulting in waste of time and money.

4.3. Influence of high temperature resistant retarder on strength of cement paste

Compressive strength of cement paste is an important index to evaluate the performance of cement paste. It has a great influence on cementing quality. Generally, we hope that the addition of retarder will not negatively affect the strength of cement paste. However, the previous research results show that the addition of retarder will hinder the development of cement paste strength more or less. To understand the influence of the new high-temperature resistant retarder on the strength of cement paste, we tested the compressive strength of cement paste with different retarder dosage at 140 °C, 20MPa for 24h, 72h and 168h respectively, and the results are shown in Table 2.

Table 2. Influence of new high temperature retarder on strength of cement paste

Number	Curing temperature °C	Retarder dosage (bwoc) %	Thickening time/min	Compressive strength (MPa)		
				24h	72h	168h
1	140	0.1	/	41.5	44.6	49.5
2	140	1.6	277	28.7	39.8	47.3
3	140	2.1	326	26.1	36.7	45.5
4	140	3.2	417	19.8	30.2	46.9

It can be seen from Table 2 that at the same curing temperature, with the increase of retarder dosage, the compressive strength of cement paste shows a downward trend.

At 24h, compared with pure cement, with the increase of retarder dosage, the strength of cement paste decreased rapidly. When the amount of retarder is 1.6%, the strength of cement paste decreases by 28.7%. When the dosage is 2.1%, the strength of cement paste decreases by

39.21%. When the dosage is 3.2%, the strength of cement paste decreases by 53.89%. This shows that the new high temperature resistant retarder only has a great influence on the early strength of cement paste, but has little influence on the later strength.

The reason may be that the retarding group in the new high temperature resistant retarder is preferentially adsorbed on the C_3S surface, which prevents C_3S from further hydration, thus leading to the slow development of early strength of cement paste. However, it is less adsorbed on C_3S surface and compatible with fluid loss reducer, so retarder has less influence on the later strength of cement paste.

4.4. Compatibility with fluid loss reducer

At 80°C and 90°C, the compatibility test results of itaconic acid copolymer with G301, G302 and G306 fluid loss additives are shown in table 3.

Table 3. Compatibility test of new high temperature retarder and fluid loss

Fluid loss reducer	Dosage %	New high temperature resistant retarder%	$FL_{80^\circ C}$ mL	$FL_{90^\circ C}$ mL
G301	1.3	0	91	125
	1.3	1	93	136
G302	1.3	0	28	22
	1.3	1	21	27
G306	1.3	0	33	29
	1.3	1	37	31

It can be seen from Table 3 that the copolymer has good compatibility with G301, G302 and G306 fluid loss additives, and has no significant influence on their fluid loss reduction ability.

4.5. Fluid loss reduction effect of new high temperature retarder

In order to investigate the influence of new anti-high temperature retarder on the fluid loss of cement slurry, this paper measured the relationship between the content of new anti-high temperature retarder and the fluid loss of cement slurry at high temperature (Figure 3). Experiments show that the new anti-high temperature retarder not only has certain fluid loss performance at high temperature, but also has better effect after being compounded with fluid loss reducer.

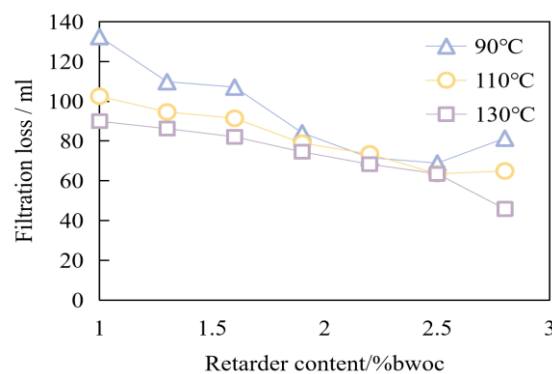


Figure 3. Relationship between dosage of new high temperature resistant retarder and fluid loss of cement slurry at different temperatures

It can be seen from fig. 3 that when the temperature is 90°C and the content of the new high temperature resistant retarder is 1.0%, the filtration loss of cement slurry can reach within 85 ml/7mpa×30min; With the addition of the new high-temperature resistant retarder increased to 2.8%, the fluid loss decreased to 40ml, which was 1830ml lower than that of the pure pulp of 1850ml. When the temperature is 110°C, the dosage of the new high temperature resistant

retarder is between 10% and 28%, and the fluid loss is always controlled within 100ml. Although the fluid loss increased slightly when the temperature rose to 130°C, it still decreased by 95~98% compared with the pure pulp.

The new high-temperature retarder not only has good high-temperature retarding effect, but also has a certain filtration loss reduction effect [8]. The reason may be that the sulfonate group in the molecular chain of the new high-temperature retarder has the characteristics of strong hydration ability and weak attraction to cations, and the spatial network structure formed by the molecular chain of the new high-temperature retarder also traps some free water, so the new high-temperature retarder has a certain filtration loss reduction effect [9].

5. Summary

Through rational molecular structure design, a new type of retarder with high temperature resistance was developed, which has the characteristics of high temperature resistance, salt resistance and insensitivity, and can be constructed under extremely harsh environmental conditions without crystallization or crystallization. Temperature resistance up to 200°C, salt resistance up to saturation; Weak dispersibility at high temperature; There is a good linear relationship between dosage, temperature and thickening time of cement slurry. Under the condition of large temperature difference, the strength of cement paste develops rapidly; The new high temperature resistant retarder cement slurry with different densities has good comprehensive performance, which can meet the cementing requirements of long cementing section with large temperature difference. Low dispersibility, excellent salt resistance and good compatibility with other admixtures, and the retarder has little influence on the later strength of cement paste. The cement slurry system with the retarder as the main agent has good comprehensive performance, can meet the cementing needs of different density systems and different salt concentrations, and has a good application prospect.

References

- [1] Liu Qiang. Study on the Properties and Preparation of a High Temperature Corrosion Resistant Coatings Under Insulation[J]. coating industry, 2019, 049(009):7-13.
- [2] Bi Zongyue, Huang Xiaohui, Ding Wubin, et al. Study on Performance of High Temperature Resistant and Internal Anticorrosion and Thermal Pipeline[J]. welded tube, 2019, 042(008):30-35.
- [3] Jun-jun, Yan X F, Huang W G, et al. High-temperature oxidation behavior of 9Cr-5Si-3Al ferritic heat-resistant steel[J]. International Journal of Minerals Metallurgy and Materials, 2020, v.27; No.191 (09):82-88.
- [4] Tyagunov A G, Baryshev E E, Tyagunov G V, et al. High-Temperature Melt Treatment in the Production of Heat-Resistant Alloys with a High Content of Foundry Wastes[J]. Steel in Translation, 2019, 49(3):163-167.
- [5] Li H, Li L, Zheng S, et al. High Temperature Resistant Separator of PVDF-HFP/DBP/C-TiO₂ for Lithium-Ion Batteries[J]. Materials, 2019, 12(17):2813.
- [6] Zhang Fan, Li Xiaoping, Li Xiaoshen. Development of Preparation Systems with K₂CsSb Photocathodes and Study on the Preparation Process[J]. Chinese Physics Letters, 2019,36(02):8-11.
- [7] Wang Shouxing, Wei Meiling, Zhou Changling, et al. The Optimization of Adhesive Properties of High-temperature Resistant Ceramic Binder[J]. journal of ceramics, 2019, 040(004):440-444.
- [8] Bai Y, Lian Y, Ban C, et al. Facile synthesis of temperature-resistant hydroxylated carbon black/polyacrylamide nanocomposite gel based on chemical crosslinking and its application in oilfield[J]. Journal of Molecular Liquids, 2021, 329(4):115578.
- [9] Wen G, Chen K, Zhang Y, et al. Preparation of alkali-resistant PVDF membranes via immobilization of sodium lauryl sulfate (SDS) on surface[J]. Applied Water Science, 2021, 11(3):1-14.