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ARTICLE TYPE

Synthesis and performances of itaconic acid/ acrylamide/ sodium styrene sulfonate as a self-adapting retarder for oil well cementHongxu Zhang¹, Jia Zhuang^{1*}, Sheng Huang¹, Xiaowei Cheng¹, Qichao Hu², Qipeng Guo³, Jiang Guo¹*Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX*

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A novel self-adapting retarder itaconic acid/ acrylamide/ sodium styrene sulfonate (IA/AM/SSS, hereinafter referred to as PIAS) was synthesized by free-radical, aqueous-solution polymerization and characterized by FTIR and TG. The optimum reaction conditions of polymerization were obtained from orthogonal experiments (L₃³) and subsequent data analysis. According to the evaluation as retarder, the PIAS made it possible to obtain both a long thickening time and a swift compressive strength development for cement slurry, and therefore the applicable range of bottom hole circulation temperature to the cement slurry has been widened to 60-180 °C. Moreover, the working mechanism of self-adapting retarder PIAS was found to rely on changing the spatial structure of molecules to retard the hydration of cement. This paper also expounds that the delayed coagulation of cement slurry attributes to adsorption, chelation and “poisoning” effect of PIAS molecules on the surface of hydrated particles or ions through XRD and SEM analysis.

Introduction

The retarders serve to control the setting time that cement slurry required to be flowable and pumpable for cementing operation.¹ Retarders for the oil well cement commonly include two major categories: low-molecular-weight organic compounds and inorganic salts.² The application of aforementioned retarders were limited because of their defects of poor temperature resistance, sensitivity to dosage and so on. Various polymeric retarders have been employed widely for cementing operation by virtue of their uniformity, stability and repeatability since 1990s. Several typical polymeric retarders are as follows: AMPS[®] (2-acrylamido-2-methylpropanesulfonic acid)/IA (itaconic acid), AMPS[®]/MA (maleic acid), AMPS[®]/SSS (sodium styrene sulfonate)/IA, and AMPS[®]/IA/NVP (*N*-vinyl-2-pyrrolidone),³⁻⁵ etc. However these polymeric retarders still have two main problems, one is the poor thermal stability, and the other is the “super-retardation” of cement slurry caused by polymeric retarders. Many of the polymeric retarders cannot effectively retard the hydration of cement due to their decomposition under high temperature and pressure present in deep wells. For the cementing operation, the cement slurry transforms a workable plastic slurry into a rigid material early and leads to the failure of cementing operation. In long cementing interval of deep well, there is always a large temperature difference between the top and bottom of cement slurry column. The polymeric retarder can cause “super-retardation” of cement slurry in the top of the cement slurry column, that is to say a kind of special phenomenon occurred at a lower temperature and pressure. The “super-retardation” cement slurry will take an unmerciful length of time to develop an acceptable early-age compressive strength, and that cannot meet the engineering requirements of secondary drilling for a deeper

horizon in drilling operation.⁶

In this work presented, a novel self-adapting retarder PIAS was synthesized and it could be applied to the bottom hole circulation temperature (BHCT) from 60 °C to 180 °C. It was found that PIAS had the property of self-regulation by changing the spatial form and structure of molecules under dynamic conditions present in deep wells. An acceptable thickening time and a sufficient early-age compressive strength was achieved during the performances evaluation of cement slurry (or set cement) with PIAS, and the “super-retardation” phenomenon of cement slurry was avoided at a relatively low temperature and pressure. The adaptability of cement slurry was improved and that could meet the engineering requirements of drilling operation for further.

Experimental**Chemicals**

Acrylamide (AM) (KeLong Chemical, China), itaconic acid (IA) (KeLong Chemical, China), sodium styrene sulfonate (SSS) (Zian Chemical Co. Ltd, China), potassium persulfate (KeLong Chemical, China), sodium hypophosphite (KeLong Chemical, China), and sodium hydroxide (KeLong Chemical, China), G33S (an anionic sulfonate polymer has better anti-temperature and anti-salt ability, fluid loss additive ⁷) (CNPC Western Drilling Engineering Co. Ltd, China).

Oil well cement

An API class G high sulfate-resistant (HSR) grade oil well cement (API monogram certification from Jiahua Enterprise Corp. Sichuan, China) equivalent to American Petroleum

Institute (API) Specification 10A was used in all cement slurry and set cement preparation.⁸

Molecular structure design

According to the previous research on functional groups and the retardation mechanism,⁹ a novel polymeric retarder PIAS was designed and developed. From the molecular design, the carboxyl groups were able to act on the hydrated particles and crystal nuclei in the cement slurry to retard the hydration of cement through adsorption and chelation.¹⁰ In order to enhance the temperature resistance of PIAS, the large-volume groups of the phenyl and sulfonate groups were introduced into the molecules by free-radical, aqueous-solution polymerization.¹¹ The amide groups were introduced into PIAS molecules as the variable portion under dynamic conditions present in deep well. In a fairly high temperature and pressure environment, the amide groups were converted into carboxyl via hydrolysis reaction and acted synergistically with other functional groups on reducing the hydration velocity of cement. The carboxyl groups were partially restored to the original state through the reverse reaction of hydrolysis therefore the retardation was weakened at a lower temperature. In one word, the molecular design makes PIAS possess the property of retardation and self-adapting by means of its functional groups and variable molecular structure (or spatial morphology). By the way, the amide groups can improve the salt-resistance of the cement slurry at a fairly low temperature and pressure.¹²

Synthesis of PIAS

In a 250 mL round bottom three-necked flask, some AM and SSS monomers were fully dissolved into distilled water, and the flask was heated to reaction temperature (55, 60, or 65 °C according to the orthogonal experiments). A certain amount of IA was added into a beaker and dispersed with ultrasonic vibration for 120 s, the pH value of the IA solution was adjusted to 6-7 with prepared sodium hydroxide solution (1 mol/L). The polymerization system was purged with nitrogen and then the IA solution and initiator were dropped into the flask slowly. In a constant temperature for 5 h with stirring, the product solution was obtained. The polymerization equation is shown in Fig. 1.

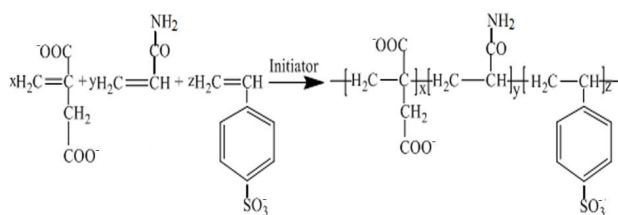


Fig. 1 Copolymerization equation of retarder PIAS.

PIAS was extracted by dropping the product solution into a sufficient amount of acetone and stirring with glass rod, the gelatinous polymer was deposited and gathered up. After drying and crushing, the milky powder of PIAS was obtained. Then the PIAS powder was fully dissolved with distilled water and repeated the aforementioned extraction, drying and crushing of three times, the milky purified PIAS was prepared for characterization and performance evaluation.

Methods

Cement slurry preparation

The cement slurries were prepared according to procedures set in API Specification 10A. The OWC-9360 blade-type blender manufactured by Shenyang institute of aeronautical engineering (Shenyang, China) was employed for mixing the slurries at specific ratio of water-to-cement (W/C) in the thickening time and the early-age compressive strength tests. The PIAS was dissolved in distilled water sufficiently before being mixed with the cement. All additives were present as a portion by weight of cement (% BWOC). In the procedure set of cement slurry preparation, the mixture of cement and powdery additives was added within 15 s to water contained in a blender cup under low speed stirring (4000 rpm) and high speed stirring (12000 rpm) for 35 s.

Determination of the thickening time

The OWC-9380B-type (Shenyang, China) consistometer was employed for the thickening time tests. The cement slurry viscosity was measured in Bearden Units of Consistency (Bc) under high temperature and high pressure through the thickening instrument. In the cementing operation, the value of 70 Bc is generally considered the maximum consistency for cement slurry to pump, and therefore the thickening time was determined by the aforementioned consistometer from the initial consistency (usually < 20 Bc) of cement slurry to 70 Bc or higher.¹³ In the tests, the cement slurry was added into a rotating cylindrical slurry container equipped with a stationary paddle, the consistometer was capable of maintaining the given temperature and pressure oil bath and of rotating the container at a speed of 150 rpm $\pm$ 15 rpm.

Early-age compressive strength analysis

For early-age compressive strength measurements of set cements, the YA-300-type (Beijing, China) electronic hydraulic pressure testing machine was used. The set cement samples were obtained by curing the cement slurry placed in the molds that conformed to the requirements in API Specification 10A "Specification for Cements and Materials for Well Cementing" at specific temperature for 24 and 48 h in atmospheric pressure and water bath. The cube specimens (5.08 cm $\times$ 5.08 cm $\times$ 5.08 cm) of set cements were crushed by the hydraulic pressure testing machine and the value of compressive strength were obtained. For the early-age compressive strength values, the average of three independent samples were taken.

Set cement characterization

The surface and phases composition of set cement samples were analyzed via JSM-7500F scanning electron microscope (20 kV, JEOL, Japan), and PANalytical X'Pert PRO diffractometer using Cu K α radiation (λ = 0.15418 nm) at 40 kV and 30 mA.

Result and discussion

Orthogonal experiments of polymerization

The orthogonal experiments (L3³) (in Table 1) were designed and

arranged to investigate the effects of the molar ratio of monomers (A), the amount of initiator (B), and the reaction temperature (C) on PIAS. The longer thickening time and higher early-age compressive strength showed the better performance of the retarder PIAS.

Table 1 Factors of Orthogonal experiments (L3³)

Levels	1	2	3
A:Molar ratio of monomers	7.7:56.3:14.6	7.7:14.1:19.4	7.7:28.2:4.9
B:Amount of initiator (%)	3	4	5
C:Reaction temperature (□)	55	60	65

Table 2 Orthogonal experiments and results of copolymerization

	Factor			Thickening	Early-age compressive strength
	A	B/%	C/□	Time/min (90□, 40MPa)	Of set cement /MPa (90□, 24h)
1	A ₁	3	55	245	14.4
2	A ₁	5	60	302	—
3	A ₁	4	65	309	—
4	A ₂	4	55	184	20.9
5	A ₂	3	60	187	20.4
6	A ₂	5	65	173	21.4
7	A ₃	5	55	300	—
8	A ₃	3	65	360	—
9	A ₃	4	60	326	—
K ₁	285.3	264.0	243.0		
K ₂	181.3	273.0	283.0		
K ₃	328.7	258.3	280.7		
R	147.4	14.7	37.7		
A ₃		B ₂	C ₂		
K ₁ [*]	4.8	11.6	11.9		
K ₂ [*]	20.9	7.0	6.8		
K ₃ [*]	0	7.1	7.0		
R [*]	16.1	4.5	5.1		
A ₂		B ₁	C ₁		

Note: K₁ (K₁^{*}): average thickening time (early-age compressive strength) of level 1; K₂ (K₂^{*}): average thickening time (early-age compressive strength) of level 2; K₃ (K₃^{*}): average thickening time (early-age compressive strength) of level 3; R (R^{*}): range.

The intuitive analysis and the range analysis were used to get the main influence factor from the orthogonal experiments (in Table 2). By comparing the R (and R^{*}) of three factors, it was found that the impact decreased in the following sequence: the molar ratio of monomers (A) > the reaction temperature (C) > the amount of initiator (B). It is obvious that PIAS has good performance for retarding the hydration of cement slurry when PIAS has a monomer molar ratio of A₁ or A₃. Unfortunately, there was no early-age compressive strength development when set cements contained PIAS with a monomer molar ratio of A₃ in less than 24 h. The optimal polymerization conditions were obtained through the general equilibrium analysis as follows:

A₁B₁C₁, scilicet the molar ratio of monomers IA/AM/SSS, 7.7:56.3:14.6; the reaction temperature, 55 °C; the amount of initiator, 3 wt%; the pH of the reaction solution, 6-7; the reaction time, 5 h and the effects of PIAS on thickening time and early-age compressive strength had been taken into account. In the thickening time and the compressive strength tests, PIAS was present in a proportion of 0.2% and 0.6% BWOC respectively and the mass ratio of W/C was 0.44.

PIAS characterization

The FTIR spectrum of PIAS was recorded on Nicolet 6700 Fourier infrared spectrometer (KBr pellet, in the range of 400-4000 cm⁻¹) and shown in Fig. 2. In the spectrum, the characteristic bands at 3423.07 cm⁻¹ and 3178.23 cm⁻¹ are symmetrical and unsymmetrical stretching vibrations absorption signals corresponding to N-H in amide group of AM, whereas 2933.61 cm⁻¹ is the characteristic absorption range of -CH₂-, and 1676.77 cm⁻¹ is the characteristic absorption band of C=O, the spectrum shows the vibrations absorption signal of benzene ring skeleton in SSS at 1564.78 cm⁻¹, and 1191.46 cm⁻¹ is the characteristic absorption range of C-O in carboxyl group of IA, the characteristic ranges at 1125.09 cm⁻¹, 1046.28 cm⁻¹, 668.81 cm⁻¹ for stretching vibrations are introduced by unsymmetrical and symmetrical of S=O and S-O in sulfonate group of SSS, respectively. From 1630 cm⁻¹ to 1645 cm⁻¹, there are no characteristic absorption ranges corresponded to -CH=CH₂-, means that no monomer residues in the analysis samples. According to the analysis of FTIR spectrum above, we can infer that the target PIAS was obtained.

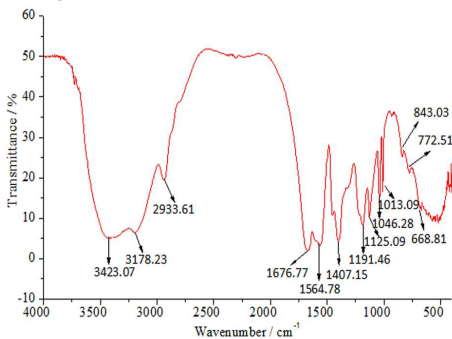


Fig. 2 Copolymerization FTIR spectrum of PIAS.

The chromatograph of gel permeation (GPC, Waters e2695-2414 RI Detector, USA) was employed to test the molecular weight of PIAS. As shown in Fig. 3, the PIAS has a number average molecular weight of 70834 and a weight average molecular weight 149525.

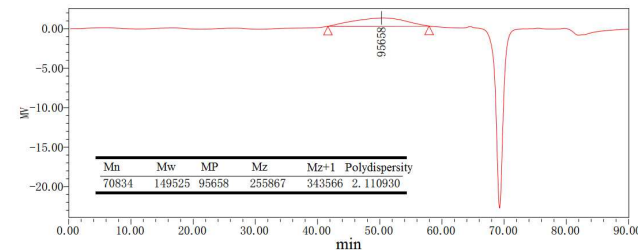


Fig. 3 Gel permeation chromatogram of PIAS

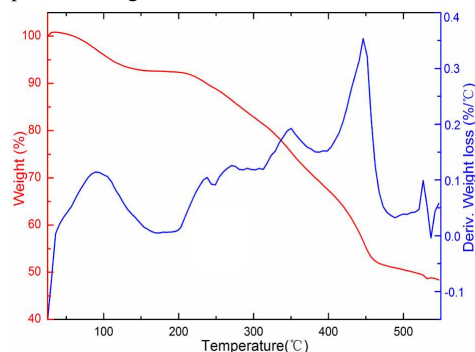
As shown in Fig. 4 , the thermal stability of PIAS was studied with Mettler Toledo thermo gravimetric and simultaneous

Table 3 Effect of PIAS on the basic properties of cement slurry

Cement slurry	Readings on six-speed rotational viscometer(s ⁻¹)						Flow index (n)	Consistency coefficient (K/mPa·s ⁿ)	Plastic viscosity (mPa·s)	Fluid loss (mL)
	600	300	200	100	6	3				
neat	237	145	112	76	11	7	0.71	0.88	92	33
0.2% PIAS	205	124	102	42	6	3	0.73	0.65	81	35

differential thermal combined analyzer of type TGA/SDTA851e from 25 °C to 550 °C with a heating rate of 10 °C/min under nitrogen atmosphere.

From the TG and DTG curve of PIAS (Fig. 4), the weight loss of PIAS sample was divided into two stages. The first stage occurred in the range of 25 °C to 200 °C, and the weight loss of 8.4% was caused by volatilization and decomposition of small molecular impurities in the sample. There existed an obvious weight loss of 40.7% in the second stage from 200 °C to 550 °C, and the decomposition of amide (200-250°C, 3.3%), carboxyl (250-315 °C, 7.5%), sulfonate groups (315-400 °C, 14.3%) and the carbon chain (400-490 °C, 15.6%) in the molecules of PIAS gave rise to the weight loss. The sharp peaks at 100 °C, 230 °C, 270 °C, 350 °C, and 450 °C in the DTG curve show the maximum decomposition rate of water, amide, carboxyl, sulfonate groups and carbon chain respectively.¹⁴ The sample residues of 50.9% attributed to the broken molecular fragments contained benzene ring and the burning residues at the temperature range of tests.¹⁵

**Fig. 4** TG and DTG curves of PIAS.

The amide and carboxyl groups were protected by introducing the phenyl nearby and the intramolecular effect of stereo-hindrance in PIAS molecules. Therefore, the retarder PIAS has an excellent heat resisting property when the temperature below 200 °C according to the analysis above.

Basic parameters of cement slurry with PIAS

The performances of cement slurry have greatly effect on cementing operation. Table 3 shows the basic parameters of cement slurry with PIAS. It can be seen that the PIAS has slightly effect on the rheology of cement slurry. The consistency coefficient of cement slurry with PIAS was decreased from 0.88 mPa·sⁿ to 0.65 mPa·sⁿ, and the plastic viscosity was decreased from 92 mPa·s to 81 mPa·s relative to neat cement slurry. The above data illustrate that the PIAS has a dilution effect on

cement slurry. The fluid loss tests inferred PIAS has slightly effect on filtration property of cement slurry.

Evaluation of thickening time and dosage-sensitive coefficient

The effect of PIAS on hydration of cement was determined by thickening time tests at different conditions. The formulations of cement slurry, test conditions and the results are shown in Table 4. It was found that PIAS could prolong the thickening time of cement slurry by the comparison of between different cement slurry.

Table 4 Effect of PIAS on thickening time of cement slurry

Conditions		Formulation of cement slurry /%, BWOC	Thickening time/min
1	90 □×40 MPa	W/C, 0.44; 1% G33S+0.2% PIAS	244
2	150 □×94.4 MPa	W/C, 0.55; 2%G33S+35%sand+2%PIAS	192
3	180 □×115 MPa	W/C, 0.57; 2%G33S+35%sand+4%PIAS	168
4	180 □×115 MPa	W/C, 0.57; 2%G33S+35%sand+6%PIAS	341

In addition, the dosage-sensitive coefficient has been calculated from Table 4 (Test No.4-5) as follows:

The increasing rate of thickening time:

$$TT_{IR} = \frac{TT_2 - TT_1}{(TT_1 + TT_2)} \times 100\% = \frac{341 - 168}{(168 + 341)/2} \times 100\% = 67.98\%$$

(1)

The increasing rate of dosage:

$$D_{IR} = \frac{D_2 - D_1}{(D_1 + D_2)/2} \times 100\% = \frac{6\% - 3\%}{(3\% + 6\%)/2} \times 100\% = 66.67\%$$

(2)

The dosage-sensitive coefficient:

$$DSC = \frac{TT_{IR}}{D_{IR}} = \frac{67.98\%}{66.67\%} = 1.02$$

(3)

Where

- TT_{IR} is increasing rate of thickening time,
- TT_1 and TT_2 are thickening time at different dosages,
- D_{IR} is increasing rate of dosage,
- D_1 and D_2 are different dosages,
- DSC is the dosage-sensitive coefficient.

The dosage-sensitive coefficient 1.02 was in the range of 0.1-3.0 on the basis of standard API Specification 10A, that meant PIAS

was insensitivity to dosage. It was likely because of the insensitivity to dosage, the anomalous gelatinization phenomenon such as “flash set” and “false set” was avoided when the cement slurry with different dosages of PIAS in thickening time tests. Fig. 5 is the thickening curves of cement slurry with 6% BWOC PIAS at 180 °C, 115 MPa. It was found that the thickening time was up to 341min with a short transition time from 40 Bc to 100 Bc. In Fig. 5, during the gradually increased of temperature and pressure, the consistency of cement slurry was below 22 Bc and the curve was smooth. The stable consistency curve meant the good flowability of cement slurry with PIAS under dynamic conditions present in deep well. Furthermore, the cement slurry maintained a consistency around 25 Bc and lasted over 200 min when the test conditions reached 180 °C, 115 MPa and kept constant. Through the analysis of thickening curves above, it has been apparent that PIAS shows an excellent property of retardation on cement hydration under high temperature and pressure.

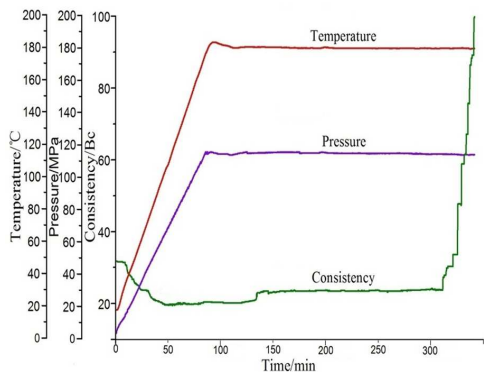


Fig. 5 Thickening curves of cement slurry with 6% BWOC PIAS.

Evaluation of initial and final setting time

In cementing operation, a long initial setting time and a short time interval with final setting time of cement slurry was conducive to construction. The effect of PIAS on initial and final setting time of cement slurry was determined by a Vicat needle under 90 °C, atm. The comparison of initial and final setting time between cement slurries with different retarders were shown in Table 5.

As can be seen from the table, sodium styrene sulfonate, BCR-260L, DRH-200L and PIAS could effectively extend the initial and final setting time of cement slurry. At the same dosage, cement slurry with PIAS of 0.5% BWOC has the longest thickening time (354 min) and shortest time interval between initial and final setting time (35min). This combination of long initial setting time and a short time interval with final setting time showed good engineering performance of PIAS.

The self-adapting of PIAS in cementing operation

In the cementing operation, it is particularly difficult to reconcile two vital requirements, which are not only to sufficiently retard the setting of the cement slurry, but also not to prolong unduly. Therefore, it is crucial that a long thickening time and a swift compressive strength development were obtained synchronously, especially the cement slurry which located at the lower temperature and pressure hole section.

Table 5 Effect of different retarders on cement slurry initial and final

	Neat cement slurry	0.5% Sodium Styrene sulfonate	0.5% BCR-260L	0.5% DRH-200L	0.5% PIAS
Initial setting time/min	110	145	185	200	365
Final setting time/min	205	235	240	285	400
Thickening Time/min	105	154	185	198	354

setting time

Note: 1. Initial and final setting time of different cement slurries were tested by Vicat apparatus under 90 °C, atm; 2. Thickening time of different cement slurries were tested under 90 °C, 40 MPa; 3. BCR-260L, cement retarder, CNPC Offshore Engineering Co., Ltd.(China); 4. DRH-200L, cement retarder, CNPC Drilling Institute (China).

In order to evaluate the self-adapting property of retarder PIAS, a four periods heating-cooling thickening time test of cement slurry with PIAS was implemented and it could simulate the cementing operation from the hole section of 90 °C, 53.3 MPa to 180 °C, 115 MPa. Fig. 6 shows the thickening curves of cement slurry with 4.5% BWOC PIAS. During the test, the temperature and pressure were increased to 180 °C, 115 MPa in the first period (86 min) and remained stable in the second period (20 min). The consistency of cement slurry with PIAS was below 20 Bc and showed good flowability. The cement slurry was cooled to 90 °C and the pressure of the system was dropped to 53.5 MPa in the third period (20 min), the decrease of temperature and pressure caused a delayed, slight increase in consistency. The slightly increased consistency almost had no effect on the flowability of cement slurry. The test lasted for another 186min until the consistency of cement slurry reached 100Bc in the fourth period. According to the analysis of thickening time above, it was found that PIAS showed an excellent property of retardation on cement hydration under dynamic conditions. The long thickening time and good flowability of cement slurry with PIAS ensured the safety of cementing operation.

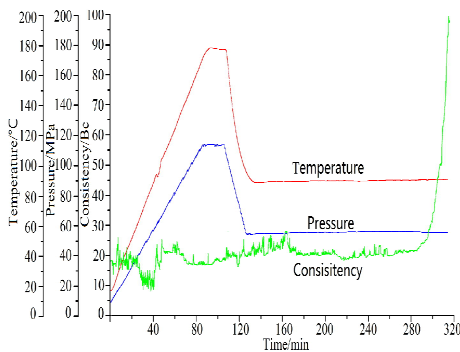


Fig. 6 Heating and cooling thickening time test of cement slurry with PIAS.

From other parallel heating-cooling thickening time tests of cement slurries with PIAS, the cement slurries were removed from the consistometer at the beginning of the fourth period, and the set cement samples were obtained by curing the cement slurries that placed in the cube molds (5.08 cm×5.08 cm×5.08 cm) for 24 h and 48 h under the condition of atmospheric pressure and

water bath. The early-age compressive strength of the aforementioned set cements is shown in Table 6. It can be seen that the early-age compressive strength of set cements with 4.5% BWOC PIAS was 9.82 MPa (24 h) and 12.20 MPa (48 h), which was larger than the criterion of the secondary drilling cement strength 3.5 MPa.^{16, 17} It is obvious that an acceptable thickening time and a very swift compressive strength development were obtained synchronously through the heating-cooling thickening time test and compressive strength tests. The good matching of thickening time and compressive strength was the key advantage of the self-adapting retarder PIAS and the excellent engineering performances of PIAS foreshadow the broad application prospect in drilling operation.

The reversibility of amide hydrolysis in PIAS

The reversibility of amide hydrolysis was the key point of self-adapting, and which was confirmed through EDS analysis of heating-cooling treated PIAS. The 4.5 wt% solution was formed by fully dissolved PIAS into distilled water. In order to simulate the weakly alkaline environment in cement slurry, the pH value of the solution was adjusted to 8-10 with NaOH (1 mol/L). The solution was poured into the PTEE (polytetrafluoroethylene) container of a stainless steel closed reaction kettle, and heated to 180 °C, held for 20 min. The PIAS was extracted by acetone after the PIAS solution was cooled to 90 °C and taken out from the reaction kettle. The heating-cooling treated PIAS powder was obtained by drying and crushing the extracted gelatinous polymer. Fig. 7 shows the contents of the main elements C, N, O, S, Cl and Na in PIAS and heating-cooling treated PIAS powder. It was obvious that the content of N was reduced from 3.46% to 2.03% and O was increased from 9.69% to 11.76% under dynamic conditions of heating and cooling, and other elements almost had the same contents.

Studies have demonstrated that the amide could convert to carboxyl groups and release ammonia by hydrolysis in weakly alkaline environment. The sustained reaction could consume the amide groups in an open system. Because of the high temperature and pressure in the closed system of reaction kettle, the released ammonia could dissolve in the solution and react with the carboxyl groups, and the amide had a palingenesis. The obvious changes in the contents of N and O element gave the best proof to the aforementioned deduction. Through the reverse reaction of hydrolysis, the retardation of PIAS on cement hydration was weakened and the “super-retardation” of cement slurry was avoided, so that the time of waiting on cement was shortened.

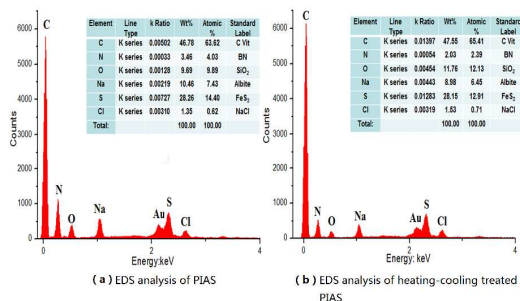


Fig. 7 EDS analysis of PIAS.

Table 6 Effect of PIAS on early compressive strength of set cement in heating-cooling heating-cooling thickening time tests of cement slurries

	Amount of PIAS /% (BWOC)	Early-age Compressive strength/MPa			Average /MPa
		1	2	3	
95□, 0.1MPa (24 h)	4.5	10.06	9.48	9.92	9.82
95□, 0.1MPa (48 h)	4.5	12.06	12.96	11.58	12.20

Phase analysis using XRD

The XRD patterns of set cements are shown in Fig. 8. The phase compositions of the set cements were determined according to the inorganic crystal structure database, portlandite ($\text{Ca}(\text{OH})_2$), (JCPDS 44-1481); calcium silicate hydrate, C-S-H($\square$), ($\text{Ca}_2\text{SiO}_4 \cdot 3\text{H}_2\text{O}$, JCPDS 29-0374),¹⁸ monosulphoaluminate (AFm), (JCPDS 45-0158), ettringite (AFt), (JCPDS 41-1451),¹⁹⁻²¹ which were the phases forming the interlocked grid work of the set cement and producing high mechanical resistance.

The samples of set cements were obtained by curing cement slurry at 90 °C, 24 h. In Fig. 8, the phase compositions of the set cement without PIAS (Fig. 8a) were in accord with that had a dosage of 0.2% BWOC (Fig. 8b) and 1% BWOC (Fig. 8c) PIAS. It is obvious that with the amount of PIAS increased, the diffraction peaks of portlandite were weakened by the comparison of FIG. 8a-c, as opposed to that of AFt and AFm. From the aforementioned analysis, it is reasonable to infer that the precipitation and growth of portlandite crystals are restrained by PIAS, on the contrary, the growth of AFt and AFm are promoted to some extent.

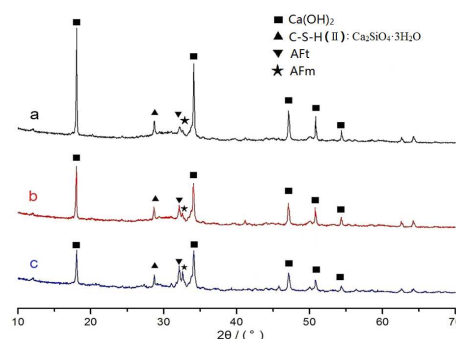


Fig. 8 XRD patterns of set cements curing at 90 °C, 24 h (a: without PIAS; b: with 0.2% BWOC PIAS; c: with 1% BWOC PIAS).

SEM analysis

Fig. 9 shows the SEM images of set cements which were in accord with the samples in XRD analysis. In Fig. 9a, the hexagonal sheet portlandite crystals, the acicular AFt crystals and the irregular lamellar AFm crystals growing on the clinker grains of set cement without PIAS.²² Fig. 9b is the micrograph of set cement with 0.2% BWOC PIAS, and it can be seen that the number of portlandite crystals and AFm crystals are decreased, but the AFt prismatic crystals, on the contrary, have significantly increased in quantity. Fig. 9c is the micrograph of set cement

with 1% BWOC PIAS, and it is apparent that the crystalline form of portlandite crystals become thicker and larger. We can also see the AFt acicular crystals in the areatus distribution between the clearance and surface of lumps. Furthermore, in Fig. 9c, the crystalline forms of AFt and AFm became more regular than that of Fig. 9a and Fig. 9b, which also corroborated XRD analysis conclusions, that is PIAS could enhance the growth of AFt and AFm crystals.

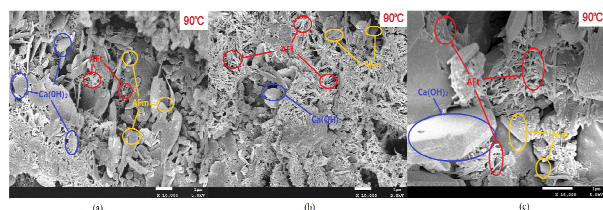


Fig. 9 SEM images of set cement surface and interface at curing conditions of 90 °C, 24 h (a: without PIAS; b: with 0.2% BWOC PIAS; c: with 1% BWOC PIAS).

It is quite obvious that PIAS has a significant effect on crystals shapes of portlandite, AFt, and AFm in set cement. The PIAS might restrain the nucleation rate of portlandite crystals, thereby give rise to the decline in amount of crystals and the morphology changes. At the same time, PIAS can promote the growth and development of AFt and AFm, that's why AFt and AFm crystals have apparent changes in crystalline form and quantity.

Retardation Mechanism of PIAS

The hydration process of cement could be divided into five periods as follows: (□) the pre-induction period; (□) the induction period; (□) the acceleration period; (□) the deceleration period; (□) the stabilization period.²³ Generally speaking, the retarders play a powerful role on extending the induction period (period (□) in Fig. 10) to prolong thickening time of cement slurry.

Many chemical admixtures retard the hydration of cement slurry through mechanisms that are not generally understood. There are four theories that discuss on the mechanism of retardation and summarized as follows: (□) Adsorption theory, it is generally accepted that retardation occurs because retarder adsorbs to: (1) surfaces of the hydrating cement particles, and/or (2) surfaces of hydrates, thereby forming a temporary barrier to further hydration;²⁴ (□) Precipitation theory, the retarder could react with Ca^{2+} and OH^- , therefore the insoluble and impermeable film was formed and coated on the surfaces of hydrating cement particles to retard the hydration;^{25, 26} (□) Nucleation theory, retarder absorbs to the micronucleus of hydrates and hinders its development;²⁷ (□) Complexation theory, The adsorption of retarder on cement particles may take place through a process called chelation where the organic molecules form a complex with the metal ions in cement slurry.²⁸

It is difficult to theorize why PIAS slow the hydration rate of cement slurry because the retardation mechanisms are so poorly understood. Combining the data gained from the XRD analysis and microstructure studies presented in this paper with theories aforementioned in the literature, the following explanation is proposed.

The oil well cement clinker powder can be mixed with water to form a slurry (the so-called cement slurry), and then harden to produce high mechanical resistance through the complex hydration. In the early age of hydration, there was a large number

of hydrated particles formed in the cement slurry (Fig. 11a and Fig. 11a'). The ions (Ca^{2+} and OH^- especially) that produced by hydration could move into free fluid from hydrated layers under the effect of concentration difference. During the hydration of cement slurry, micronuclei of hydrate crystals emerged and grew up in hydrated layers (Fig. 11b).

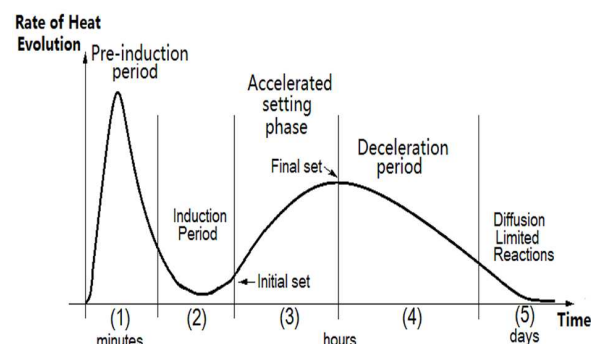


Fig. 10 Heat evolution and process during the hydration of a cement slurry.

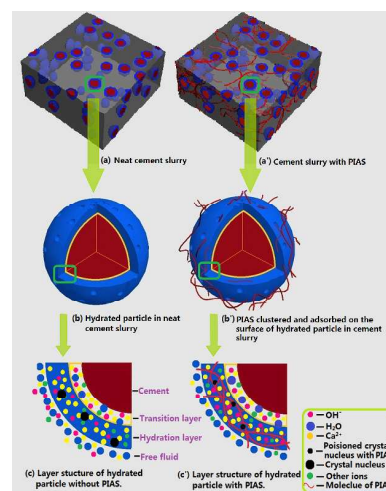


Fig. 11 Modeling of microstructure of hydrated particle and its layer structure in neat cement slurry and cement slurry with PIAS.²⁹

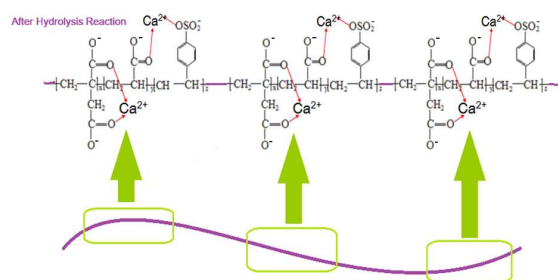


Fig. 12 Schematic diagram of chelating between PIAS molecule and Ca^{2+} ions. Note: The purple curve represents the molecular chain of retarder PIAS.

Hydrophilic groups were abundant in PIAS molecules, such as carboxyl and sulfonate groups. Thereby, PIAS was able to adsorb on the surface of hydrated particles forcefully. Due to the high

specific surface area of hydrated particles, the PIAS molecules were embedded in hydrated layer after they were gathered around the hydrated particles (Fig.11b'), so that the growth and development of the nuclei were hindered because of complex "poisoning effect". From Fig.11c and Fig.11c', it is obvious that the growth of "poisoned" crystal nuclei was restrained by adsorptive action of PIAS. Meanwhile the hydrated layer became dense and had a sharp decline in the specific surface area owing to the participation of PIAS on forming hydrated layers. The permeability of hydrated layer was therefore reduced, and that was not conducive to the exchange of ions (Ca^{2+} , OH^- and H_2O especially) between the free fluid and internal hydrated particles. The nuclei grew on the hydrated layers were "poisoned" by molecules of PIAS through chelation, which was also carried out in the free fluid of cement slurry between PIAS and Ca^{2+} ions (Fig.12). The concentration of Ca^{2+} ions was decreased by forming irregular chelates and the growth of portlandite crystal were impeded. As a result, the thickening time of cement slurry was extended effectively.

Working mechanism of self-adapting retarder PIAS

In the process of cementing operation, cement slurry was injected downwardly through a pipe (sometimes refer to as well casing), and back up to a predetermined height from the annulus between the casing and the borehole wall (Fig.13a).

The PIAS was still able to keep the integrity of molecular structure due to its excellent thermal stability when the cement slurry contained PIAS pumping into the well section of high temperature and pressure. The long molecular chains of PIAS were unfolded as a result of its segments activity which was enhanced by high temperature and pressure of the stratum. The peripheral space of hydrated particles was occupied by unfolded PIAS molecules alternately. Therefore, the crowded peripheral space around hydrated particles was unfavorable for the exchange of H_2O (or other ions) between free fluid and particles in cement slurry (Fig.13b). What's more, a large proportion of amide groups were converted to carboxyl groups by hydrolysis, so that the chelation and "poisoning" effect were intensified in alkaline environment of cement slurry (Fig.14). In such a variety of synergistic action, hydration of cement slurry was delayed.

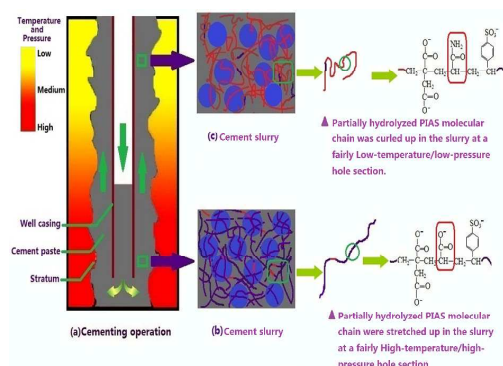


Fig. 13 Schematic diagram of cementing operation and cement slurry with PIAS at different hole section (a: cementing operation; b: unfolded PIAS molecule of partially hydrolyzed in cement slurry under a fairly low temperature and pressure hole section; c: curls of partially hydrolyzed PIAS molecule in cement slurry under a fairly high temperature and pressure hole section).

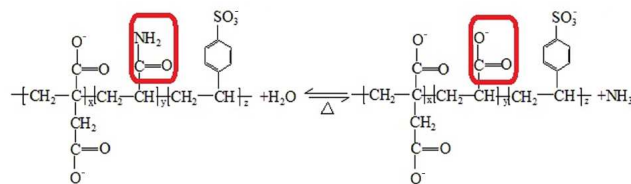


Fig. 14 Hydrolysis reaction equations of PIAS.

By contrast, the chain molecules of PIAS were curled up when cement slurry was pumped back towards predetermined height well section of a lower temperature and pressure, so that a large amount of peripheral space around the particles was released (Fig. 13c). The unobstructed peripheral space around hydrated particles was propitious for the exchange of H_2O (or other ions) between solid particles and free fluid. Through the reverse reaction of hydrolysis, excess carboxyl groups were converted back to its original states in the PIAS molecules, that is to say palingenesis of the amide groups, lead to the great reducing of retarding action caused by carboxyl in the system therefore avoided the "super-retardation" of cement slurry. By the comparison of PIAS state changes in cement slurry at different temperature and pressure, the self-adapting of retarder PIAS was reflected sufficiently. The portlandite cannot directly produce strength to the cement slurry, only after it was translated to calcium silicate hydrate gel by pozzolanic reaction with active minerals.²⁷ The more of portlandite development was restrained or consumed, the more calcium silicate hydrate gel was formed, and the higher the strength of cement. During the hydration of cement slurry, the development of portlandite was restrained by PIAS. PIAS has a significantly positive effect to the growth and development of AFt and AFm crystals which could effectively enhanced the strength of calcium silicate hydrate gel. This is very helpful to the early strength development of cement, therefore avoid the "super-retardation" of cement slurry. That was why the set cement with relatively large dosage of PIAS could still obtain a certain degree of early-age compressive strength at fairly low-temperature/low-pressure well section.

Conclusions

The orthogonal experiments (L_3^3) were designed and arranged to investigate the effects of different factors. Through intuitive analysis and range analysis, the optimum reaction conditions were obtained as follows: the molar ratio of monomers IA/AM/SSS, 7.7:56.3:14.6; the reaction temperature, 55 °C; the amount of initiator, 3 wt%; the pH of the reaction solution, 6~7; the reaction time, 5 h.

Based on FTIR and TGA-SDTA analysis, it was demonstrated that the target polymer was obtained and it had an excellent thermal stability below 200 °C.

Through the performances evaluation of PIAS, it was found that the retarder PIAS applicable to the BHCT of 60-180°C. A long setting time and a very swift compressive strength development for the cement slurry were obtained almost at the same time.

Through the heating-cooling thickening time test and EDS analysis, the self-adapting of retarder was confirmed.

Due to XRD and SEM analysis of the set cements, the retardation mechanism of PIAS was identified to rely on adsorption, chelation and poisoning" effect on hydrated particles, ions or nuclei. Meanwhile, the paper argues that the self-adapting of PIAS is achieved by means of changing the spatial form and structure of molecule under dynamic conditions of cementing operation.

Notes and references

^a School of Materials Science and Engineering, Southwest Petroleum University, Chengdu 610500, PR China. Tel: +86 13550396098; Fax: +86 0288 3033286. Email: zj-656@163.com (J. Zhuang)

^b School of Electrical Engineering and Information, Southwest Petroleum University, Chengdu 610500, China, Chengdu 610000, PR China 35

^c Institute for Frontier for Materials, Deakin University, Locked Bag 2000, Geelong, Victoria 3220, Australia

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