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An NMR Investigation of the Influence of Cation Content in Polymer Ion Retarder on Hydration of Oil Well Cement

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Abstract: Low field pulse nuclear magnetic resonance (LF-NMR) was used to analyze the effects of a polymeric ion retarder and the amount of acryloxyethyl trimethylammonium chloride (DMC) in the retarder on the distribution of T_2, thickening property, and strength of cement paste. The effect of pressure and temperature on the thickening curve was investigated, and the hydration products were analyzed using XRD. The result shows that the wrapped water of the precipitation is the main reaction aqueous phase of cement slurry in the hydration, with short T_2 time and a large relaxation peak area. The retarder weakens the van der Waals force and electrostatic adsorption force between the water and cement particles, reducing the hydration rate of cement particles. An appropriate increase in the cationic content of polymeric ion retarder can improve the early strength of cement slurry.

Keywords: NMR; oil well cement; hydration; retarder

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1. Introduction

In order to improve crude oil production and support economic development, oil exploration and development has begun to expand to deep oil and gas reservoirs. In particular, the discovery of a large number of ultra-deep wells in recent years has brought huge oil reserves and great challenges in cementing operations [1–3]. A tremendous amount of cementing practices have shown that the technical difficulty of the cementing operation in the long well section is that the large temperature difference formed in the long well section causes the top cement slurry to be over retarded, and the key to cause the problem is the retarder. Due to the large temperature difference (>40 °C) between the top and bottom of the well, the cement additives are used across the temperature zone, seriously reducing the use effect of most of the additives and cementing quality [4]. In order to ensure the safe pumping of cement slurry under high temperature conditions, high-temperature retarders are usually introduced into cement slurry. Most of the high-temperature retarders currently cannot adapt to the large temperature difference. When the cement slurry returns from the bottom to the top low-temperature well section, the retarding effect cannot be removed in time, and the strength of the cement slurry develops more slowly at low temperature, which make it difficult to guarantee the quality of the top cementing and ensure the safety of the well [5].

Water involved in the hydration process of the oil well cement can be classified into three types, which are chemically bound water, physically bound water, and free water. The three types of water undergo a dynamic transition during the hydration process. Cement additives can improve the performance of cement slurry and can have a significant impact on the hydration reaction of cement. For example, the retarder can prolong the thickening time and ensure the safe operation of the cement injection process in the deep well with a large temperature difference and long sealing section. Currently, the retarders used in the deep well with large temperature difference and long sealing section are always based on the 2-acrylamide-2-methylpropanesulfonic acid (AMPS). 2-2-Acrylamide-2-methylpropanesulfonic acid (AMPS) is one of the most common copolymerization main monomers, which consists of oil well cement retarders at home and abroad. Its structure is characterized by sulfonic acid groups, amide groups, high charged carbonyl group and the large side chain, which makes AMPS resistant to high temperature and salt, acid and alkali, with excellent thermal stability, adsorption, complexation and hydrolysis stability [6]. Liang et al. [7] synthesized polymer retarder PAIN using AMPS, itaconic acid (IA) and N-vinylpyrrolidone (NVP); regulator isopropanol and redox system are initiators during the synthesis process, and its five-membered pyrrole ring structure makes the cement paste system with PAIN obtain high-temperature stability and a thickening time of 256 min at 110 °C and 234 min at 130 °C. In order to overcome the problems of over-sensitivity, PC-H42L was synthesized by Hu et al. [8] using AMPS and two unsaturated carboxylic acid monomers, and the thickening time was controlled in 4–5 h by adjusting the retarder dosage in the range of 60–210 °C. It has no adverse effect on the stability of cement paste settlement and water loss, and also has good anti-flutter performance. Guo et al. [9] synthesized polymeric retarders under acidic conditions with AMPS and IA at 60 °C. For this kind of retarder, the suitable temperature ranges from 50 °C to 180 °C; it can significantly extend the thickening time of cement slurry, and exert an excellent high-temperature retarding effect. However, with retarders, if not controlled properly, the cementing safety and cementing quality of the low-temperature section of the well cannot be guaranteed [10–12]. Therefore, exploring the influence of retarder on different types of water during cement hydration reaction has important significance for better understanding the hardening mechanism of cement, guiding the optimization of the cementing slurry system and ensuring the safety of the cementing operation [13,14].

With the development of the nuclear magnetic resonance (NMR) technology, NMR has been applied as a non-destructive testing technique to characterize the pore structures of cement-based materials [15,16]. Nuclear magnetic resonance analysis technology can be roughly divided into three parts: magnetic resonance imaging (MRI), nuclear magnetic resonance spectroscopy, and time domain nuclear magnetic resonance (TD-NMR) technology [17–20]. These three parts are commonly referred to as low field nuclear magnetic resonance technology (LF-NMR). LF-NMR mainly uses hydrogen protons as probes to study the mobility of molecules. In the analysis of LF-NMR, the transverse relaxation time T_2 is often used to reflect the movement of molecules by measuring the relaxation time of the molecules to characterize the pore structure changes, swelling and phase transition in the sample [21]. In the cement slurry hydration process, the existence form of the water molecule can be judged by the different relaxation time of the hydrogen atom.

In this paper, low field pulse nuclear magnetic resonance (LF-NMR) was used to analyze the relaxation signal of protons in water molecules to study the mechanism of water and polymeric ion retarders in the cement-hardening process. The process by which a nuclear spin system in a high-energy state transfers energy to a similar magnetic nucleus in a neighboring low-energy state is called spin–spin relaxation, or transverse relaxation [22,23]. This process is only the energy exchange of the spin state of similar magnetic nuclei, and does not cause the change of the total nuclear magnetic energy. Its half-life is expressed in T_2. In particular, the T_2 distribution of cement slurry was analyzed to determine the existing state of water and the retarding mechanism at the early stage of the cement-hardening reaction [24,25]. The T_2 in this paper was acquired with the standard Carr–Purcell–Meiboom–Gill (CPMG) sequence from the built-in software.

This article aims to explore the hardening mechanism of cement slurry and better synthetic conditions of the retarder suitable for a large temperature difference, which has positive significance for building up a kind of cement slurry system suitable for the development of oil and geothermal resources in deep formations.

2. Materials and Methods

2.1. Reagents and Instruments

2-Acryloylamino-2-methyl-1-propanesulfonic acid (AMPS), itaconic acid (IA), methoxy-polyethylene glycols (MG) NaOH, and $K_2S_2O_8$ are all analytical reagents (ARs) and were purchased from Shanghai Jizhi Biochemical Technology Co., Ltd. (Shanghai, China). Methacryloxyethyltrimethyl ammonium chloride (DMC) is an AR from Wuhan Fengtai Weiyuan Technology Co., Ltd. (Wuhan, China). Shengwei G-grade oil well cement was provided by the Scientific Research Institute of Shengli Oilfield cementing center. Defoamers were provided by the Scientific Research Institute of well cementing center of Shengli Oilfield; fluid loss additive was self-made by the laboratory.

The MacroMR movable fluid distribution detection nuclear magnetic resonance imager was purchased from Suzhou Newmark Electronic Technology Co., Ltd. (Suzhou, China). The X'PERT Pro X-ray diffractometer was purchased from Panaco (Amsterdam, the Netherlands). The HT/HP thickener was purchased from Chandler company (Santa Ana, CA, USA). The HTD7370 HT/HP curing kettle was purchased from Qingdao Haitongda Special Instrument Co., Ltd. (Qingdao, China), and the Yaw-300 pressure testing machine was purchased from Jinan Liling Testing Machine Co., Ltd. (Jinan, China).

The cement slurry formula in this paper was as follows: G-grade oil well cement + IADN polymeric ion retarder (0, 0.5%) + fluid loss additive (0.8%) + defoamer (3–5 drops). The water–cement ratio was 0.44, the curing temperature was 85 °C, and the curing duration were 0.5 h, 1 h, 1.5 h, 2 h, 2.5 h, and 3 h, respectively.

2.2. Synthesis of IADN Retarder

A solution of 2 mol% IA, 3 mol% AMPS, 0.1 mol% DMC, and 0.03 mol% MG was first prepared. Then, NaOH was used to adjust the solution pH to 7–9, and 1.5 mol% of $K_2S_2O_8$ was added as the initiator. The mixture was put in a 65 °C water bath under nitrogen atmosphere for 5 h to create a viscous copolymer, which was then precipitated and purified with 100% ethanol, washed with acetone, and dried under vacuum at 40 °C for 1 day to obtain the final product of polymerized ionic retarder (IADN).

We changed the content of DMC from 0.1 mol% to 0 mol%, 0.05 mol%, 0.15 mol%, 0.25 mol%, 0.56 mol%, 0.6 mol%, 1.25 mol% in order to prepare three kinds of solutions. Then, we followed the above steps for the synthesis of IADN with 0%, 1%, 3%, 5%, 10%, 15%, and 20% DMC.

2.3. Analysis Methods

The LF-NMR was applied to measure the relaxation time (T_2) of the cement slurry during the hydration process to obtain the distribution, connectivity, and physical parameters of pores in the cement slurry in the form of a gel [26–28].

The hard pulse CPMG sequence was used to obtain the T_2 value of the cement slurry. The CPMG sequence, which is based on the spin echo pulse sequence, generates a series of 180-degree pulses to obtain the echo pulse sequence of multiple echo signals, and can improve the detection signal's signal-to-noise ratio. The attenuated echo signal reflects the relaxation signal of H^1 in the water; the T_2 distribution was calculated by Laplace transform or Fourier transform of CPMG echo signal of proton H^1. The relative quantities of chemically bound water, physically bound water, and free water in the cement slurry could be determined by computing the area under the T_2 distribution. The peak location and change in peak area of T_2 distribution represent the dynamic transformation of the states of water, providing an analytical method for studying the hydration process and curing mechanism of cement slurry [29].

A MacroMR nuclear magnetic resonance analyzer was employed for the LF-NMR. The permanent magnet's magnetic field intensity was (0.5 $\pm$ 0.08) t, the magnetic field frequency was 21.3 MHz, and the diameter of the probe coil was 60 mm. The number of echoes and the echo length were set to 1000 and 1200 ms, respectively. The T_2 distribution was plotted using the MacroMR moveable fluid moisture distribution detecting nuclear magnetic resonance imager.

The HT/HP thickener Yaw-300 pressure testing machine and X'PERT Pro X-ray diffractometer were used to obtain the thickening time, compressive strength and XRD pattern of the cement slurry. The HTD7370 HT/HP curing kettle was employed for curing the cement slurry.

3. Results and Discussion

3.1. Effect of Retarder on T_2 Distribution of Cement Slurry

As mentioned earlier, the relaxation time (T_2) of the cement slurry was obtained using the MacroMR nuclear magnetic resonance analyzer. Six T_2 distributions with different curing time were obtained for each group, and the results of the slurry samples without and with retarders are shown in Figures 1 and 2.

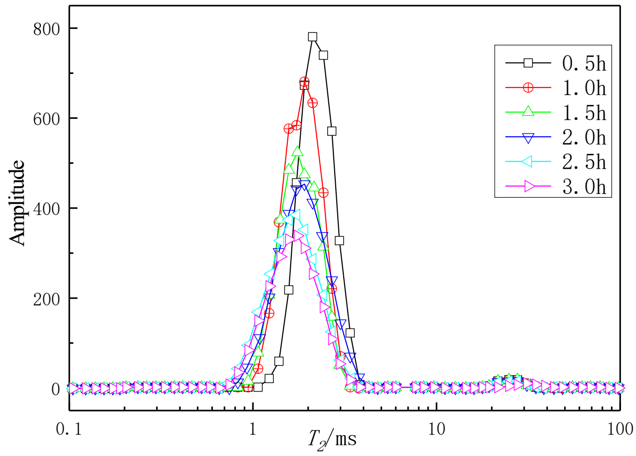

Figure 1. T_2 distribution of blank cement slurry.

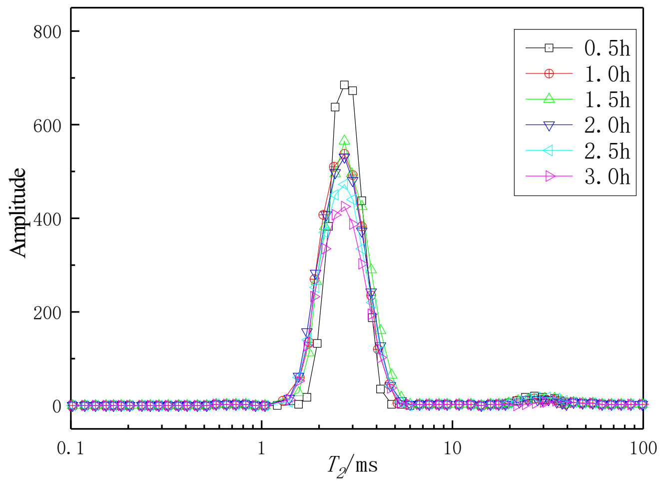

Figure 2. T_2 distribution of cement slurry with the retarder.

The T_2 distributions of the blank cement slurry and the cement slurry with retarder exhibit two distinctive peaks, as shown in Figures 1 and 2. The position of the peaks represents the different states of water in the slurry, namely, the peaks at 2 ms and 30 ms in the figures indicate that the slurry contained two phases of water. Comparing Figures 1 and 2, the peaks generally shifted to the right in the presence of the retarder. The area under the strong peak was significantly larger than that under the weak peak, showing the dominance of the type of the water phase represented by the former. However, as the curing time increased, the peak value of the strong peak rapidly dropped. This suggests that the relative amount of this type of aqueous phase declined rapidly during the hydration process, which was mirrored in the dramatic reduction in the corresponding peak area. The change in the peak (2 ms) area was greatly affected by the hydration reaction. For the peak at 30 ms, the reduction became less significant with the increase in the curing time.

At the early stage of hydration, C_3S and C_2S reacted with water to produce a large amount of hydrated calcium silicate (C-S-H) gel, as well as Ca^{2+}, OH^-, and $H_3SiO_4^-$ ions (Equation (1)). The hydration products then gathered and formed precipitates due to the van der Waals and electrostatic interactions between these ions. The water wrapped in the flocculation has the smaller relaxation time due to the high volume fraction of flocculation, while the free water in the cement slurry has the larger relaxation time. Thus, the peak at 30 ms corresponds to the relaxation signal of the wrapped water gathered in the flocculation, which is consistent with the relevant literature [30–33]:

$$2Ca_3SiO_5 + 8H_2O \rightarrow 6Ca^{2+} + 10OH^- + 2H_3SiO_4^- \quad (1)$$

Comparing Figures 1 and 2, the strong and weak peaks of cement slurry shifted to the right in the presence of the retarder, and the peak area at 30 ms was relatively small. This means that the retarder weakened the van der Waals force and electrostatic force on the water wrapped in the flocculant, reducing the extent of hydration reaction between cement particles and water, resulting in the reduction in the amount of C-S-H gel generated and the initial strength of the cement, and the increase in the hardening time.

3.2. Effect of DMC Content in Retarder on Relaxation Time T_2

As described earlier, the retarder was prepared under three synthesizing conditions with DMC contents of 0%, 10%, and 20%, respectively. The T_2 distributions of the cement slurry after curing for 0.5 h, 5 h, and 12 h are shown in Figures 3–5.

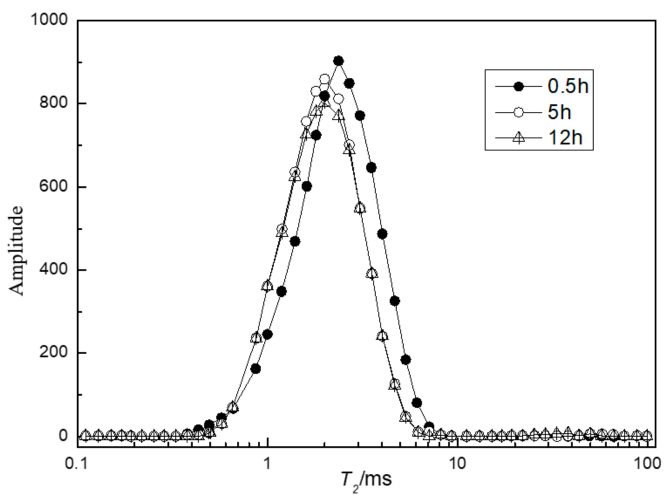

Figure 3. T_2 distribution of cement slurry with DMC content of 0%.

It can be seen from the figures that the T_2 peak of the cement slurry shifted to the left, and the peak value dropped as the curing time increased. Moreover, the peak value of cement slurry containing the DMC cationic retarder was significantly higher in the early hydration stage (within the first 5 h). To investigate the corresponding relationship between T_2 distribution and retarder synthesized with different contents of DMC, the relative content of amorphous water in the hydration products was evaluated using the peak area. The area under the strong peak and the weak peak can respectively indicate the relative amount of water wrapped in the flocculation and free water in the cement slurry. Figure 6 shows the change in the peak area with the cement slurry curing time to demonstrate the effect of different retarders on the hydration process of cement.

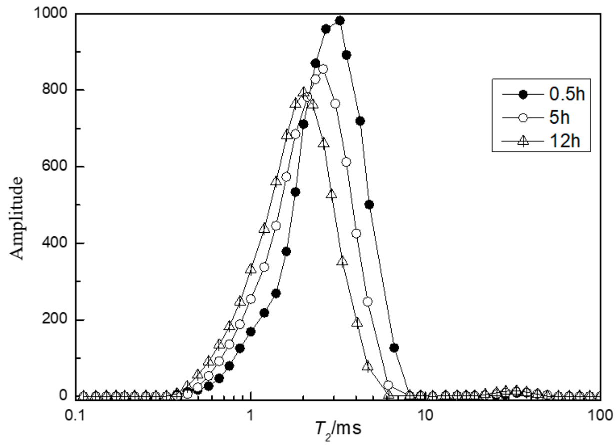

Figure 4. T_2 distribution of cement slurry with DMC content of 10%.

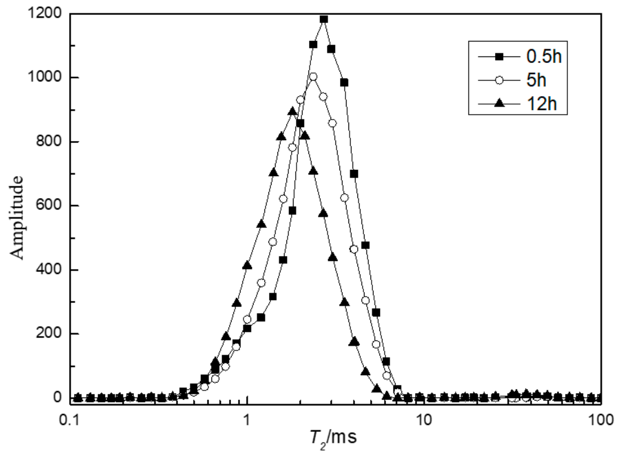

Figure 5. T_2 distribution of cement slurry with DMC content of 20%.

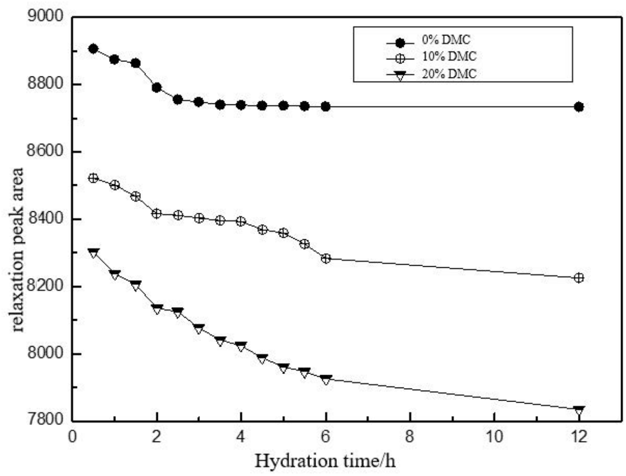

Figure 6. Changes in the relaxation peak area with time.

As shown in Figure 6, the T_2 peak area of cement slurry with retarders synthesized with different DMC dosages showed a relatively sharp decrease at the early stage of hydration (within the first 5 h), indicating that the cement slurry experienced a strong hydration reaction in the first 5 h. The trend then slowed down as the curing time increased. After 5 h, the peak area in the T_2 distribution of cement slurry containing retarder synthesized with 0% DMC essentially remained stable against the curing time. However, for cement slurry samples with retarders synthesized with 10% DMC and 20% DMC, the peak area continued to decrease after 5 h of curing time; the higher the DMC content, the greater the reduction in the peak area. The reduction in the peak area indicated that the water wrapped in the flocculant reacted with the flocculant and formed chemically bound water, promoting the extent of hydration reaction. The result shows that increasing the amount of cationic DMC in the retarder increased the relative percentage of the chemically bound water in the hydration products in the cement slurry. In other words, increasing the amount of DMC can promote hydration. This implies that DMC is conducive to improving the early strength of the cementing slurry in the low-temperature well section in the presence of a large temperature difference, preventing the excessively long retarding of the cement slurry in the low-temperature well section, and reducing the cementation quality of the cement slurry.

3.3. Effect of Cationic Dosage on Thickening Property and Compressive Strength of Cement Slurry

As shown in Figure 7, as the DMC dosage increased from 1% to 10%, the thickening time of cement slurry at 60 °C rose from 245 min to 350 min. The cement slurry was stable without settlement, and the compressive strength reached the maximum. With the further increase in the DMC dosage to 15% or 20%, the thickening time of the cement slurry decreased rapidly. Experimental observation indicates that there was significant stratification in the cement slurry at this DMC concentration, indicating that above the concentration of 10%, DMC will promote the excessive formation of early hydration products, resulting in instability, such as slurry flocculation and stratification and compromised retarding performance. Moreover, the contribution of early hydration products to the strength of the cement paste was not sufficient to offset the decline in cement paste strength caused by slurry settlement stratification, prohibiting the further improvement in strength.

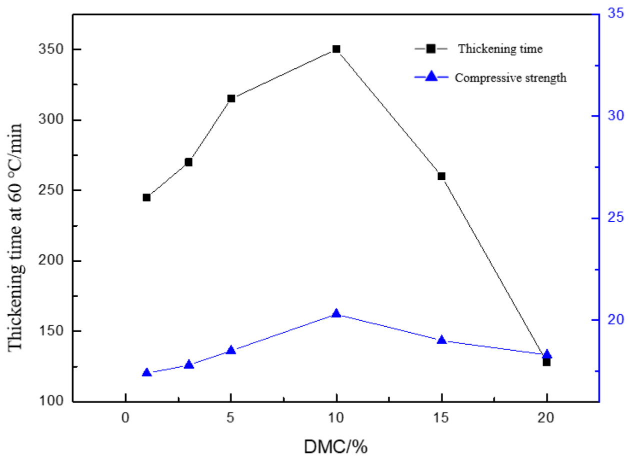

Figure 7. Effect of DMC dosage on the thickening time and compressive strength of cement slurry at 60 °C.

3.4. Effect of Temperature and Pressure on Thickening Performance of Cement Slurry

The thickening time of cement slurry was investigated by varying the experimental temperature and pressure to simulate the process where the temperature and pressure of the cement injection first increased and then decreased, as often encountered in oilfield application.

As illustrated in Figures 8 and 9, not only can polymeric ion retarders assure the thickening performance of cement slurry at the bottom of the well in the high-temperature and high-pressure well section, but they also adapt to the low-temperature and low-pressure section of the upper formation. At about 350 min and 480 min, the consistency of the cement slurry rose rapidly, which means that the right-angle thickening appeared on the distributions, and the slurry had a great thickening property. This can be attributed to DMC contribution to the formation of the early hydrate, which successfully ensured the cementing quality of low-temperature well sections.

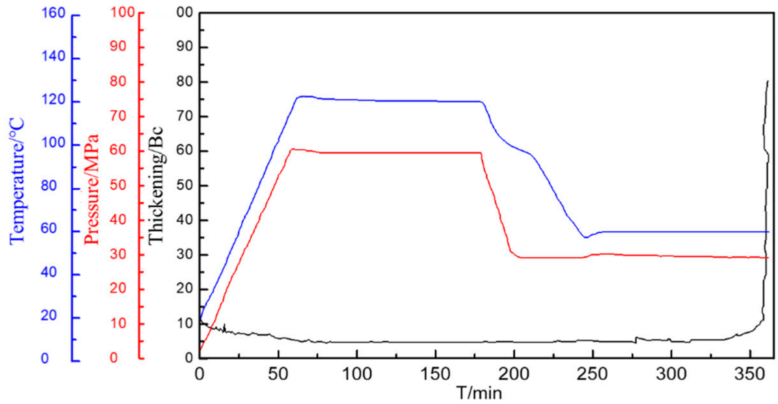

Figure 8. Thickening curve of polymeric ion retarder from 120 °C to 60 °C.

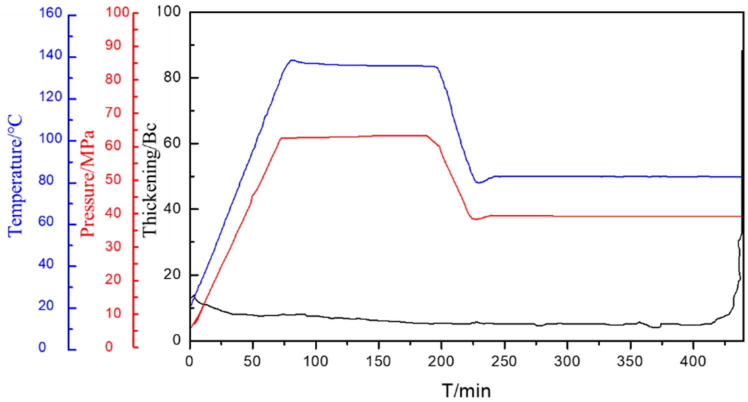

Figure 9. Thickening curve of polymeric ion retarder from 150 °C to 90 °C.

The modified retarder in this paper is mainly used to narrow the gap between the setting time of the cement slurry in the top section of the well with low temperature and the bottom section of the well with high temperature. If the conventional retarder is added, the cement slurry in the low temperature environment will not solidify for 24 h, while the cement slurry in the high temperature environment may solidify in 3–5 h. It can be seen from Figures 8 and 9 that the cement slurry with the polymer ion retarder is simulated to return to the low temperature environment at the upper part of the well from the bottom of the well with high temperature. The thickening time of the cement slurry is 6–7 h, which is equivalent to the thickening time under the high-temperature environment at the bottom of the well. It ensures that the cement slurry of the whole well section maintains a similar hydration rate, while improving the cementing quality.

3.5. XRD Analysis of the Influence of Polymeric Ion Retarder on the Hydration Performance of Cement

The four kinds of cement slurry without retarder and with retarder containing 0% DMC, 10% DMC, and 20% DMC were cured at 90 °C for 24 h, and then the X-ray diffraction analyzer was used to analyze the components of the cement. The results are shown in Figure 10.

As shown in Figure 10, in blank samples and samples containing retarders, the characteristic diffraction peaks of Ca $(OH)_2$, C-S-H, and ettringite (AFT) can be identified in all the XRD patterns, indicating that retarders did not affect the composition of cement hydration products. However, the diffraction peak intensity of the blank sample was the highest in four patterns, followed by the sample with 20% DMC in the retarder. With the decrease in DMC content, the intensity of the characteristic diffraction peaks of $Ca(OH)_2$, C-S-H, and AFT gradually decreased, indicating that the retarder inhibited the formation of a hydration product. What this also indicates is that the introduction of DMC into the retarder could facilitate the formation of $Ca(OH)_2$ crystals and C-S-H gel, promoting the early strength of cement slurry, making it possible to meet the requirement of the strength of the cement slurry during the curing time in low-temperature well sections under the condition of a large temperature difference.

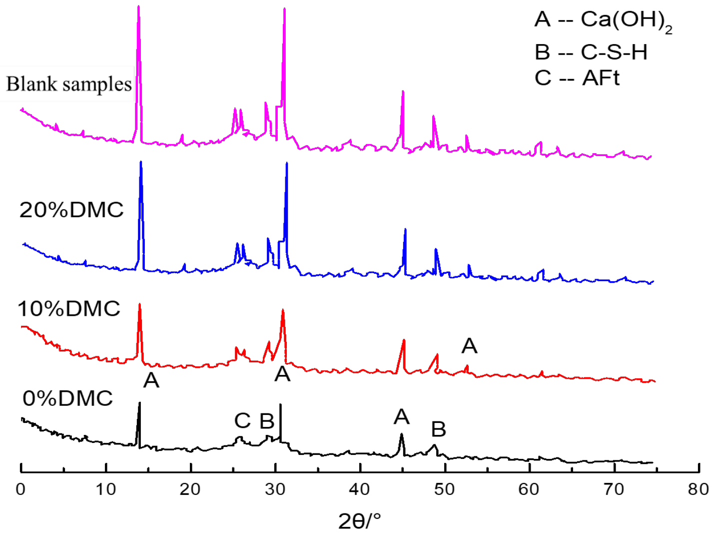

Figure 10. XRD patterns of cured cement with different retarders.

4. Conclusions

1. The water phases in the early hydration stage of cement slurry, wrapped water in precipitate and free water, were characterized using NMR, which shows that the former is the major reaction phase.
2. Compared to the blank cement slurry, the relaxation time T_2 of the cement slurry with a retarder shifted to the right, and the relaxation duration, relaxation peak value, and relaxation area dropped during the hydration process. This indicates that the retarder reduced the van der Waals and electrostatic forces as well as the hydration reaction rate between the wrapped water in the precipitate and the cement particles, resulting in low early cement strength and a longer hardening time.
3. The addition of cationic DMC to the retarder promoted the amount of chemically bound water in the hydration products of the cement slurry, thereby improving the cement slurry's early hydration, reducing the prolonged curing of the cement slurry containing a conventional retarder at lower temperatures, and improving the early strength of the cementing in the upper low-temperature well section with a large temperature difference.
4. XRD analysis results show that introducing cationic DMC into the retarder could promote the formation of $Ca(OH)_2$ crystal and C-S-H gel, enhancing the early strength development of the cement slurry, and ensuring the cement slurry strength in low-temperature well sections.

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Data Availability Statement: The authors confirm that the data supporting the findings of this study are available within the article.

Conflicts of Interest: We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled.

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