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Self-healing Agent Enhanced by Calcium Ions in Cement Slurry to Achieve Self-healing Cement in Adjustment Wells with High Water Cut

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Abstract

With high water cut in adjustment wells, water channeling in cement sheath has been encountered attributable to the failure of zonal isolation, due to downhole stresses and other contributing factors. Self-healing cement (SHC) which is modified by a water-swellable polymer can solve this challenge. The self-healing agent was prepared from an aqueous solution, and the functional monomers were diacetone acrylamide (DAAM) and dimethyl diallyl ammonium chloride (DMDAAC). The results show two outstanding features of the self-healing agent. One feature is pH sensitivity. The water absorption rate of the agent in cement slurry filtrate (pH=12.88) is 12.65 g/g, which is about half of that in water. As a cationic monomer, DMDAAC weakens the stretching of the molecular chain in strong alkaline solutions, resulting in a low absorption rate. The other feature is that calcium ions in cement slurry can increase the absorption rate of the agent in water, which is about 1.5 times the direct absorption rate in water. Furthermore, the self-healing agent helps to reduce water loss of cement slurry. The rheology and thickening time of cement slurry can be adjusted by adding additives to meet the requirements of cementing operation. When the dosage of the self-healing agent is 0.7% by weight of cement, 100 μm microcracks can be healed. The results will help guide future engineering and operations in adjustment wells around the world.

Introduction

The main function of the oil well cement sheath is to provide a sealed annulus and safe channel for the long-term exploitation of oil and gas (Guo et al. 2020; Liu et al. 2021). The destruction of the cement sheath, such as micro-cracks and micro-annulus, can lead to fluid channeling and formation pressure disturbances, and disrupt the normal production of oil and gas. Self-healing cement (SHC) has been developed to solve the fluid channeling problem (Cavanagh et al. 2007; Darbe, Pewitt, and Karcher 2009; Lu et al. 2016; Wang et al. 2019; Hu et al. 2019).

Self-healing microcapsules and oil/water-swellable polymers have been developed in many studies. Epoxy resin is the main component in self-healing microcapsules. Dong et al. used epoxy resin E-51 as the curing agent and urea-formaldehyde resin as the shell (Dong et al. 2017). The healing efficiency of permeability increased to a maximum level of 19.8%. Sodium silicate is another curing agent and produces C-S-H gels to fill microcracks. Miao et al. developed a sodium silicate-based self-healing microcapsule and found that the microcrack depth reduced to 58% after 7-day's curing at 80°C (Mao, Litina, and Al-Tabbaa 2020).

Oil-swellable polymers can absorb oil flowing through the cracks and expand to seal the cracks. Lu et al. synthesized an oil-swellable polymer with an oil absorption rate as high as 7 g/g and developed a new crack self-healing technique (Lu et al. 2016). Wang et al. prepared an oil-absorbent microsphere and solved the compatibility of oil-swellable polymer with cement slurry (Wang, Bu, and Zhao 2017; Wang et al. 2017). Johnson et al. developed a self-healing cement by oil swellable polymer that protected long-term safe exploitation (Johnson et al. 2019). Adjustment wells have high water cuts. Water swellable polymers were prepared to achieve self-healing in adjustment wells. Wang et al. synthesized a pH-sensitive water-swellable polymer that had a low water absorption rate in cement slurry to reduce the effect of the polymer on the pumpability of cement slurry (Wang et al. 2019). However, the hydrolysis of ester groups and the cross-linking of carboxyl groups with Ca^{2+} ions increased the cross-linking density of the polymer, limiting its self-healing capacity at high temperatures.

In this paper, a hydrolysis-resistant monomer dimethyl diallyl ammonium chloride (DMDAAC) was used to prepare a pH-sensitive self-healing agent. It absorbed less water in cement slurry filtrate than that in water. The other monomer is diacetone acrylamide (DAAM). Calcium ions in the cement slurry filtrate can increase the absorption rate of the agent in water. In addition, the effect of the agent on the properties of cement slurry and the self-healing ability was evaluated.

Materials and Method

Materials

High sulfate-resistant (HSR) Class G oil well cement was used in this paper and the chemical composition was SiO_2 (21.93%), Al_2O_3 (3.26%), Fe_2O_3 (5.05%), TiO_2 (0.35), CaO (62.33%), MgO (1.60%), SO_3 (2.55%), K_2O (0.39), Na_2O

(0.23%), MnO (0.10%), P_2O_5 (0.13%), loss on ignition (1.49%). Dispersion, fluid loss additive, and retarder were got from commercial sources. The monomers diacetone acrylamide (DAAM 98%) and dimethyl diallyl ammonium chloride (DMDAAC, 60%), the cross-linking agent methylene-bis-acrylamide (MBA, 99%), and the co-initiator N,N,N',N'-tetramethylethylenediamine (TEMED, 99%) were purchased from Shanghai Macklin Biochemical Co., Ltd., Shanghai, China. Calcium chloride ($CaCl_2$, 99%) Sodium hydroxide (NaOH, 95%), and initiator ammonium persulfate (APS, 98%) were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Distilled water was used throughout the experiments. The molecular structure of the two monomers is shown in Figure 1.

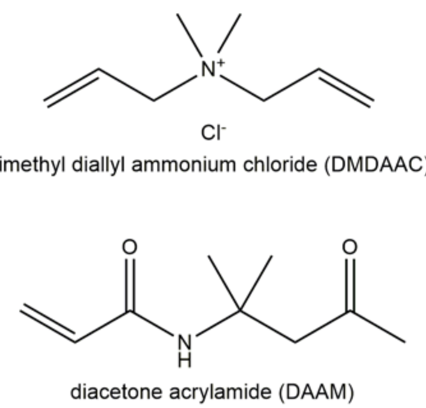

Figure 1 – Molecular structure of the monomers

Synthesis of the self-healing agent

Aqueous solution polymerization was employed to synthesize the self-healing agent in this paper. In the reaction vessel, distilled water, monomers (DAAM and DMDAAC), and cross-linking agent (MBA) were introduced sequentially. The solution was stirred for 10 min until MBA was completely dissolved. Nitrogen was introduced into the solution to eliminate the air. Then the initiator (APS) solution was introduced. 5 min later, a co-initiator (TEMED) was introduced. The solution was stirred for 10 min more and then left to react at 30°C for 8 h. The product was withdrawn from the vessel and dried in a vacuum drying oven at 80 °C for 24 h, and then pulverized and passed through a 50-mesh sieve to obtain the self-healing agent.

Water Absorption Rate

The self-healing agent's absorption rate was calculated as the weight of water absorbed divided by its weight. W_1 denoted the weight of a certain amount of self-healing agent. A nylon bag was used to carry the self-healing agent. The total mass of the self-healing agent and the nylon bag was denoted by W_2. After that, the nylon bag was submerged in the test liquid. The nylon bag was removed at regular intervals, and the water on its surface was absorbed using absorbent paper. W_3 denoted the total mass of the nylon bag and self-healing agent after water absorption. The self-healing agent's absorption rate (G, g/g) was estimated using the Equation below:

$$G=(W_3-W_2)/W_1$$

Properties of cement slurry

Several studies were carried out to improve the cement slurry formulation. The current study focused on optimum cement designs and their attributes. The cement slurries were blended according to API standard, and the composition of control and self-healing cement (SHC) is shown in Table 1.

The properties of cement slurry were carried out according to the API standard, including the rheological property, thickening time, and water loss. A self-made device was used to test the self-healing property, mainly by observing the water flow. The test temperature was set as 90°C.

Table 1 – Cement slurry formulations.

Composition	Control	SHC
Oil well cement, g	600.0	600.0
Water, g	264.0	264.0
Dispersant, g	1.8	3.0
Fluid loss additive, g	9.0	9.0
Retarder, g	1.8	1.8
Self-healing agent, g	0	4.2

Results and Discussion

The effect of monomer ratio on the water absorption rate of the self-healing agent

The monomer mass ratios of DAAM to DMDAAC were set as 1:3, 1:4, 1:5, and 1:6. MBA dosage was 0.3% by weight of the monomers, and the monomer concentration was 60%. Figure 2 shows the absorption rate of the four self-healing agents in water and cement slurry filtrate at 90°C with time. It takes about 180 min for all the self-healing agents to be saturated with water. The final absorption rates of the four self-healing agents are summarized in Table 2. From Table 2, the final absorption rate of the self-healing agents in water and cement slurry filtrate increases with increasing DMDAAC content. Due to the pH sensitivity of the self-healing agent, the absorption rate in water is higher than that in cement slurry filtrate with a pH of up to 12.88.

In addition, when the mass ratio of DAAM to DMDAAC is 1:4 to 1:6, G_{wb}, which is the agent's absorption rate in water after being tested in cement slurry filtrate, is higher than that directly tested in water. G_{wb}/G_{wa} first increases and then decreases as the amount of DMDAAC increases. When the mass ratio of DAAM to DMDAAC is 1:5, G_{wb}/G_{wa} is the highest. It demonstrates that cement slurry filtrate increases the absorption rate of the agent in water, which is beneficial for the cement to achieve self-healing. G_{wb}/G_{CSF} represents the self-healing ability. It first increases and then decreases as the amount of DMDAAC increases. When the mass ratio of DAAM to DMDAAC is 1:5, G_{wb}/G_{CSF} is the highest, 3.03. Therefore, the optimum monomer ratio of DAAM to DMDAAC in the self-healing agent is 1:5.

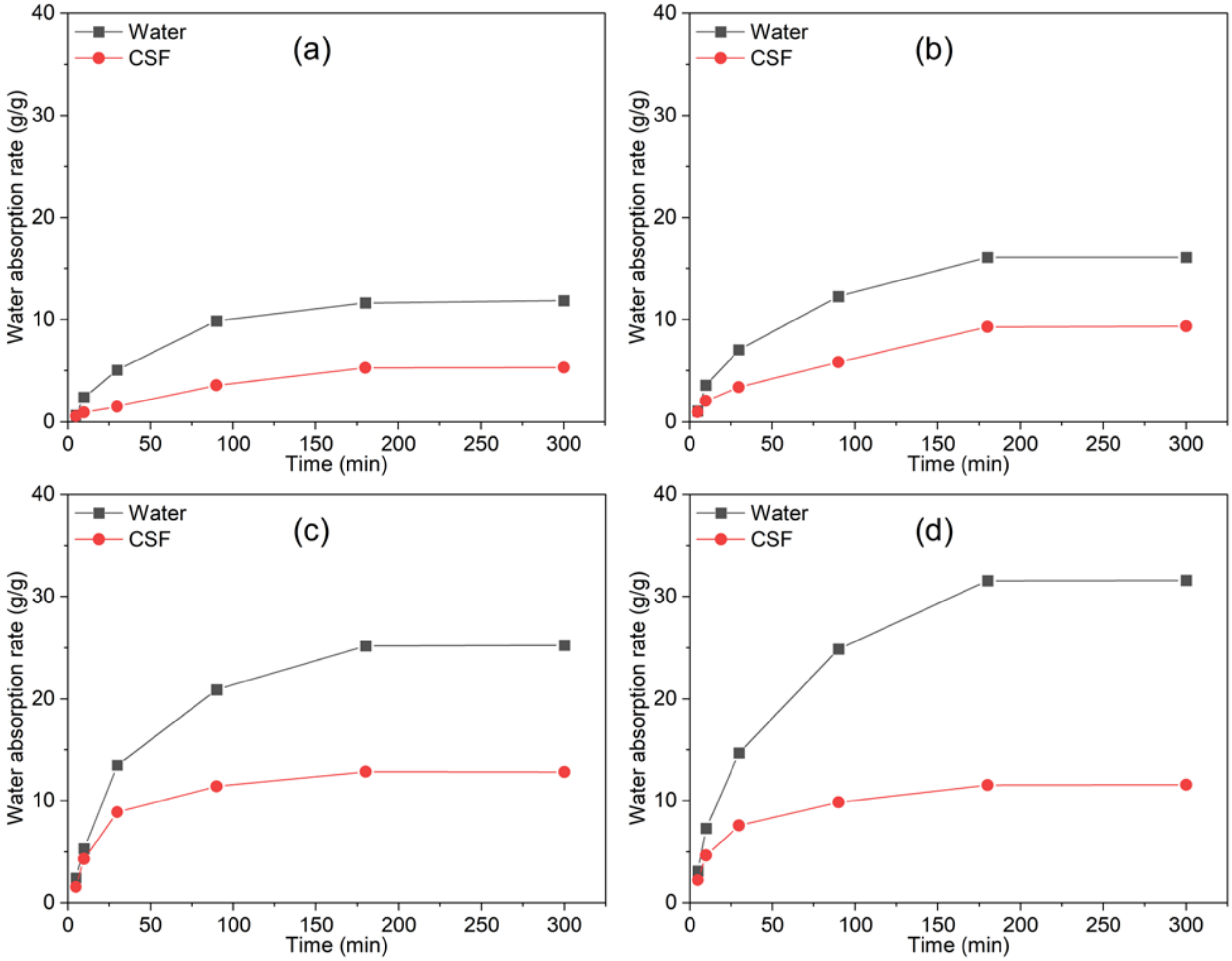

Figure 2 – The absorption rates of the self-healing agent prepared with different mass ratios tested at 90°C in water, and in cement slurry filtrate varied with time; the mass ratios of DAAM to DMDAAC are (a) 1:3, (b) 1:4, (c) 1:5, and (d) 1:6.

Table 2 – Summary of final absorption rates of self-healing agent prepared with different mass ratios tested at 90°C; G_{wa} is the agent's absorption rate in water, G_{CSF} is the agent's absorption rate in cement slurry filtrate, and G_{wb} is the agent's absorption rate in water after tested in cement slurry filtrate.

Mass ratio of DAAM to DMDAAC	G_{wa}	G_{CSF}	G_{wb}	G_{wb}/G_{wa}	G_{wb}/G_{CSF}
1:3	11.87	5.32	9.97	0.84	1.87
1:4	16.09	9.34	18.64	1.16	2.00
1:5	25.25	12.80	38.73	1.53	3.03
1:6	31.57	11.56	32.58	1.03	2.82

The effect of MBA dosage on the water absorption rate of the self-healing agent

The cross-linking agent MBA dosage was set as 0.3%, 0.5%, 0.7%, and 0.9% by weight of the monomers. The monomer ratio of DAAM to DMDAAC in the self-healing agent is 1:5, and the monomer concentration was 60%. Figure 3 shows the absorption rate of the four self-healing agents in water and cement slurry filtrate at 90°C with time. It also takes about 180 min for all the self-healing agents to be saturated with water.

The final absorption rates of the four self-healing agents are summarized in Table 3. From Table 3, the final absorption rate of the self-healing agents in water decreases with increasing MBA dosage. However, the absorption rate of the agents in cement slurry filtrate changes little. This results in a decrease in the pH sensitivity of the agent with the increasing MBA dosage. When the MBA dosage is no more than 0.7%, G_{wb} is higher than G_{wa}, which again demonstrates that cement slurry filtrate increases the absorption rate of the agent in water. G_{wb}/G_{CSF} decreases with the increasing MBA dosage. Therefore, the optimum MBA dosage is 0.3%.

Table 3 – Summary of final absorption rates of self-healing agents prepared with different MBA dosages tested at 90°C.

MBA dosage	G_{wa}	G_{CSF}	G_{wb}	G_{wb}/G_{wa}	G_{wb}/G_{CSF}
0.3%	25.25	12.80	38.73	1.53	3.03
0.5%	24.01	12.40	27.06	1.13	2.18
0.7%	19.58	12.08	21.78	1.11	1.80
0.9%	16.82	11.74	12.08	0.72	1.03

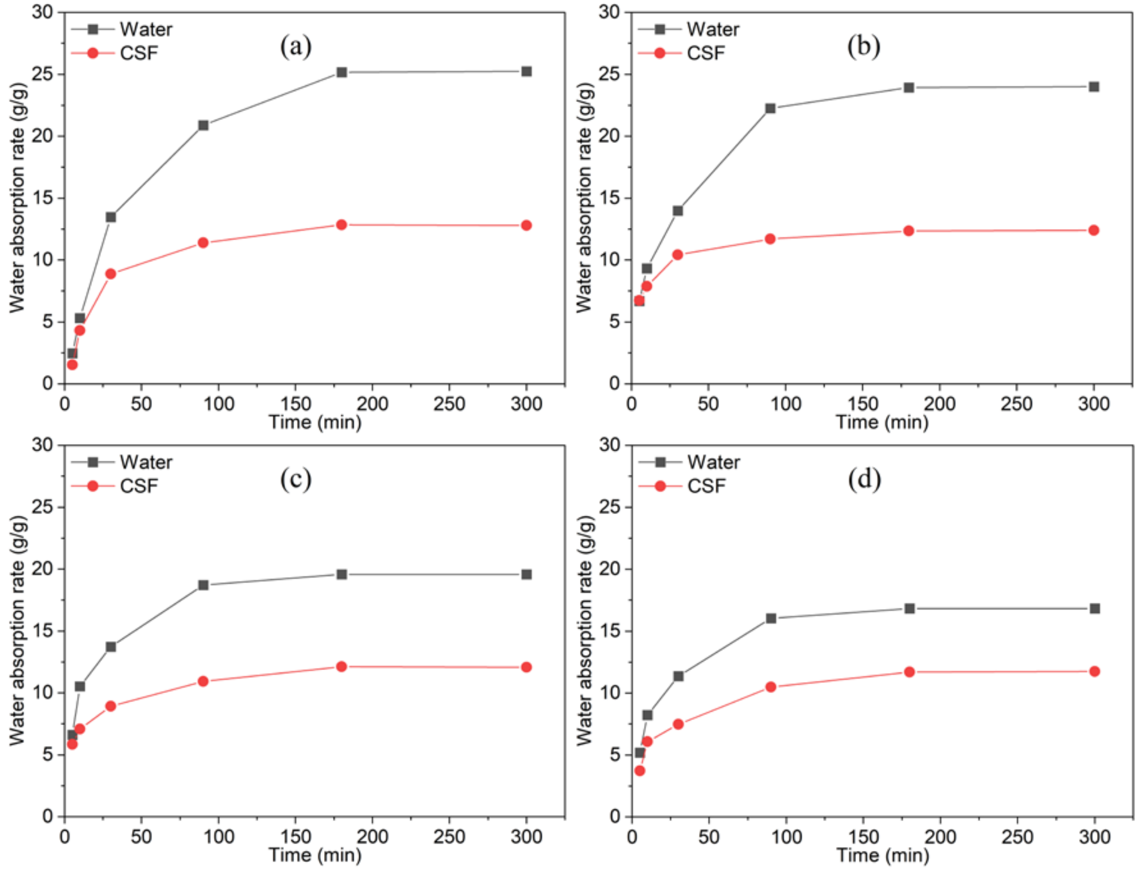

Figure 3 – The absorption rates of the self-healing agent tested at 90°C in water, and in cement slurry filtrate varied with time; the dosages of MBA are (a) 0.3%, (b) 0.5%, (c) 0.7%, and (d) 0.9%.

The water absorption rate of the self-healing agent in different solutions

The self-healing agent with DAAM to DMDAAC ratio of 1:5 and MBA dosage of 0.3% is used for further research. The effect of $CaCl_2$ (0.012 mol/L) and NaOH (pH = 13) solutions on the water absorption rate is conducted to investigate which component in the cement slurry increases the water absorption rate. Figure 4 shows the absorption rates of the agent in different solutions and the secondary absorption rates in the water of the agent after saturated absorption in different solutions. Both cement slurry filtrate and $CaCl_2$ increase the secondary absorption rate of the agent in water (38.73 and 38.38 g/g), which is about 1.5 times the direct absorption rate in water (25.25 g/g). However, NaOH has little effect on the absorption rate in water. Through comparison, it can be found that the calcium ions in the cemnt slurry increase the secondary absorption rate in water.

The effect of the self-healing agent on the properties of cement slurry

Since the self-healing agent absorbs water in the cement slurry, more dispersants are added to self-healing cement (SHC). Dispersants makes the rheology curve of self-healing cement resemble the control, as shown in Figure 5. The rheological pattern of both the control and self-healing cement belongs to the Bingham model. The yield stresses are 13.343 and 14.161 Pa, and the plastic viscosities are 0.127 and 0.138 Pa·s for the control and self-healing cement respectively.

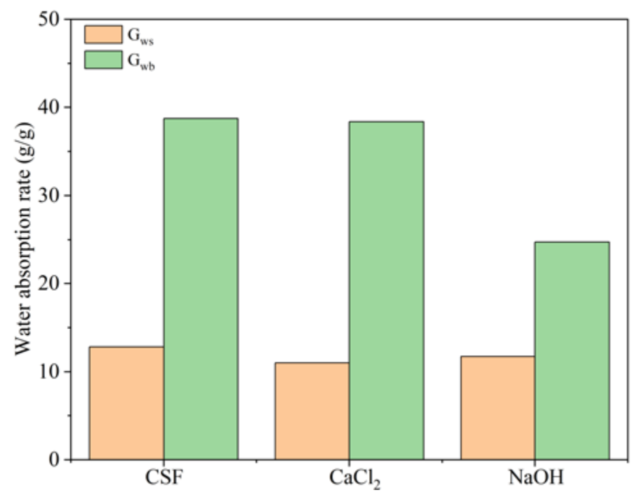

Figure 4 – The absorption rates in different solutions of the self-healing agent (G_{ws}), and the secondary absorption rates in the water of the self-healing agent after saturated absorption in different solutions (G_{wb}).

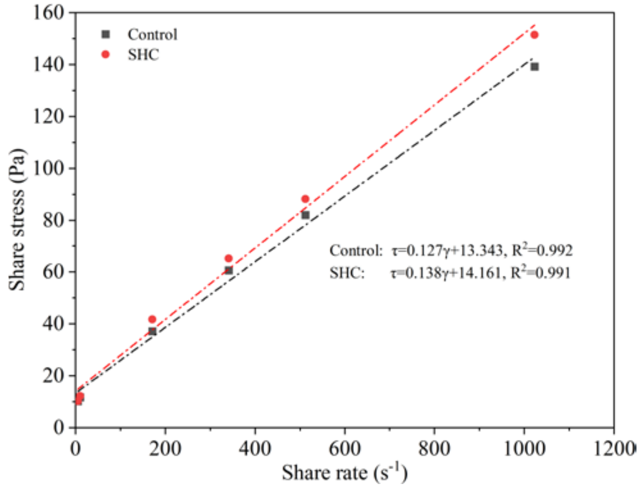

Figure 5 –Rheological curves of the control and self-healing cement.

The thickening curves of the control and self-healing cement at 90°C and atmospheric pressure are shown in Figure 6. The self-healing agent has little effect on the thickening time of cement slurries. The thickening time is 323 and 312 min for the control and self-healing cement respectively. In addition, the water loss of the control at 90°C is 86 mL, while the water loss of the self-healing cement is 48 mL. This demonstrates that the self-healing agent helps reduce the water loss of cement slurry. Self-healing evaluation shows that SHC can stop water flow in micro-cracks up to 100 μm, while the control does not have self-healing properties.

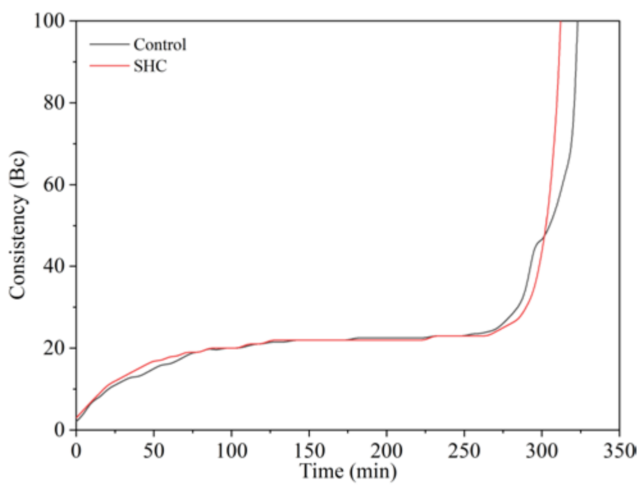

Figure 6 – Thickening curves of the control and self-healing cement at 90°C and atmospheric pressure. Control: 70 Bc, 100 Bc at 320 and 323 min. SHC: 70 Bc, 100 Bc at 308 and 312 min.

Conclusions

A self-healing agent was developed in this paper to achieve self-healing cement in adjustment wells with high water cut. The optimum monomer ratio of DAAM to DMDAAC in the self-healing agent is 1:5, and the optimum MBA dosage is 0.3%. DMDAAC makes the self-healing agent pH sensitive. The water absorption rate of the agent in cement slurry filtrate is about half of that in water. In addition, calcium ions in cement slurry can increase the absorption rate of the agent in water. The absorption rate of the agent in water is significantly increased and is 1.5 times higher after saturated absorption in cement slurry filtrate. The self-healing agent helps reduce water loss of cement slurry. When the dosage of the self-healing agent is 0.7% by weight of cement, 100 μm microcracks can be healed.

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