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Preparation and Properties of Epoxy Resin Emulsion Cement

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Considering the fact that traditional cementing stone lacks toughness., post-production operations in oil wells often cause various forms of stress to cause cementing rings to produce micro-cracks or microcracks that are difficult to repair, which may affect cementing quality and long-term low durability. In response to the above problems, taking the cement slurry system as a starting point, a new type of epoxy resin emulsion modified slurry was prepared. The effects of resin emulsion at 0~ 20% dosage on the performance of cement slurry and its mechanical properties were studied and analyzed . The results show that when the content of resin emulsion is less than 15%, the bulk density of cement slurry is 1.88±0.04g/cm3 and the rheological properties of the slurry at 20~80℃ are satisfied. Under the same temperature and pressure (80 ℃, 35MPa), the initial consistency can be controlled within 28Bc. The thickening time is 20~ 70% longer than pure cement, and the filtration loss of cement slurry can be obviously improved. Meanwhile, with the increase of the mixing ratio, the impact strength of the resin emulsion cement stone is increased by 15%, the elastic modulus is decreased by about 47.9%, and the toughness of cement stone is obviously improved.

1. Introduction

In the process of oil field production and development, cementing operation is one of the most important links. It is of great significance to maintain the whole operation process of the target oil well from production to scrap. It is of great significance to improve production safety, oil and gas well life and oil field development benefit. In the past, most oil field workers thought that the cement slurry could be effectively pumped into the air without causing a safety accident, and the well logging could meet the requirements. However, in fact, even if the compressive strength meets the requirements of the cement stone, with the increasing number of years of exploitation and the increasing of the mining intensity,the annular pressure and channeling still exists in the later period of production [1-4]. As a kind of brittle material,there are many defects, such as low tensile strength, poor resistance to rupture and low impact strength. Therefore, in the design of cement slurry, we should not only consider the compressive strength of the cement stone, but also consider the long lasting durability of the cement ring, which means that it is necessary to make a certain toughness and modification for the conventional cementing [5-7].

In this regard, this paper focuses on the introduction of a maturer epoxy resin used in the field of construction and mechanical engineering in the modification and toughness of cement[8] [9], so as to solve a series of problems caused by the failure of cementing stone. One of the most important technologies is to introduce resin materials which can be well compatible and dispersed in cement. From the point of view of material, through effective material design, the internal structure frame of the oil well cement stone can be changed, the brittleness of the oil well cement stone can be improved and the deformation capacity of the cement ring can be promoted[10]. Based on the above reasons, this paper, under the premise of meeting the related industry standards, focuses on improving the engineering performance of cementing stone, blending the resin into emulsion to achieve better compatibility with the oil well cement, so as to improve the defects of insufficient toughness and durability, which will help to improve the cement ring length. The material technology of well

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construction quality provides some basic guidance for the application of epoxy resin in the field of well cementing in oil and gas wells and the research of depth mining.

2. Experimental materials

2.1 Experimental materials

G grade oil well cement of Three Gorges brand, self-made epoxy resin emulsion (bisphenol A epoxy resin E-51, PEG-200, OP-10, catalyst, modified amine curing agent) whose solid content is 60%, defoaming agent (two methyl silicone emulsion FG-2B), water loss agent (CG88L), active diluent 660A, water.

2.2 Experimental instrument

ZNN-D6B type electric six speed viscometer, YM-3 type liquid density meter, TG-71 type high temperature and high pressure water loss meter, TG-3060A type constant speed agitator, XJJY-50 type impact tester, DFC-0710B pressurization thickener, M221C universal testing machine, and 8 hole constant temperature water bath maintenance box.

2.3 Preparation of epoxy resin emulsion cement slurry

Considering that epoxy resin is an oily material, it is necessary to emulsify epoxy resin first in order to further strengthen the mixing effect between the epoxy resin and the cement paste, and to reduce the internal hole in the cement stone after curing. On the basis of the selection of a large number of emulsifiers and the optimization of the dosage, a set of resin emulsion combinations with good compatibility and high temperature resistance are selected, and the specific formula and addition amount are show in Table 1.

Table 1 Composition of the preferred resin emulsion slurry

Emulsion formula (solid content 60%)	Oil well cement /g	water /g
6.25%E-51+2.5%PEG-200+0.125%TEOA+0.75%OP-10+6%w+0.075% Defoamer +1.25% Modified amine curing agent +0.5%660A	400	176

First, the epoxy resin E-51 with active diluent 660A was injected into the three port flask of 500ml at a certain proportion and heated in a constant temperature water bath at 80 C. After the reactants were mixed evenly, the TEOA was slowly added into it. After reacting for 30 minutes, OP-10 was added. Then it was transferred to the oven at 110 C to continue to react to 2 to 3 hours. On this basis, the waterborne epoxy resin emulsion was obtained by adding modified a mine curing agent and deionized water. According to the basic requirements of G oil well cement, cement slurry was prepared by 0.44 water cement ratio, and the epoxy resin emulsion with different mass fraction was mixed with cement slurry into mixing cup, and the preparation of epoxy resin emulsion slurry was completed at low speed in agitator with 1min.

2.4 Performance evaluation

The related experiments involved in this experiment aim to test the related properties of cement slurry based on the SY/T 5546-92 "test method of oil well cement application performance", GB 10238-2005 "oil well cement" and GB/T 19139-2005 "oil well cement test method".

3. Results and discussion

3.1 Effect of epoxy resin emulsion on the density of cement slurry

The density of oil well cement slurry is very important for pump injection, balance formation pressure and cementing design. Therefore, it is necessary to study the effect of epoxy resin emulsion on the density of cement slurry. Here, 0%, 5%, 10%, 15% and 20% of epoxy resin emulsion are respectively added into the cement slurry to determine the density change of cement paste. The results are shown in Table 2.

Table 2 Effect of Epoxy Emulsion on Density of Cement Slurry

Resin content %	0	5	10	15	20
Density g/cm3	1.93	1.92	1.88	1.84	1.82

According to the table, the density of cement paste decreases as the amount of resin emulsion increases. This is because the density of epoxy resin used in this experiment is much less than that of pure water slurry in 1.1~1.34 g/cm3 (room temperature). When the ratio of addition is less than 10%, the effect of on the density of cement slurry is less. When the resin content is more than 10%, the effect is greater. In order to increase the bulk density, improving the dosage of resin curing agent, or adding the weighting agent to adjust it can be taken into consideration.

3.2 Rheological properties of epoxy resin emulsion cement slurry system

3.2.1 Influence of epoxy resin emulsion content on rheological properties of cement slurry system
The rheological property of the oil well cement slurry directly determines the flow state of cement slurry under the annular space. It is also the core of the design of the cement slurry formula and the necessary prerequisite for the safety construction. For this reason, the rheological properties of the cement slurry must be ensured first before other performance evaluation work is carried out. When the temperature is constant to 20 C°, the rheological properties of the resin emulsion are measured respectively. The results are shown in Table 3.

Table 3 epoxy resin content of cement paste rheological test

Resin emulsion dosage /%	Φ600/Φ300	Φ200/Φ100	Φ6/Φ3
0%	—/203	194/138	28/23
5%	—/235	172/106	22/15
10%	—/243	186/151	20/14
15%	—/252	203/165	21/14
20%	—/296	226/135	19/11

It can be seen from the above table that the system of resin emulsion toughness cement slurry has a good rheological property, and the readings are less than 300 when Φ equals 300 , and the resin cement slurry can meet the corresponding technical indexes.

3.2.2 Effect of epoxy resin emulsion on rheological properties of cement slurry at variable temperatures
On the basis of the amount (15%) of the unified resin emulsion, adjusting the temperature respectively at 20, 40, 60, and 80 centigrade in the constant temperature curing box, the curing samples were taken out after heating up for 5 minutes, and the rheological properties were tested under the variable temperature adjustment. The experimental results were shown as shown in Table 4.

Table 4 Testing of rheological properties of 15% resin emulsion slurry at variable temperature

test temperature /℃	Φ600/Φ300	Φ200/Φ100	Φ6/Φ3
20	—/252	194/118	14/9
40	—/247	195/111	15/8
60	—/250	192/113	17/11
80	—/254	196/114	19/14

The test results show that the adjustment of temperature has little effect on the rheological behavior of cement slurry, and the value of 300 is less than 300, which meets the requirements of cementing operation.

3.3 Effect of epoxy resin emulsion on filtration loss of cement slurry API

The API loss of oil well cement slurry (high temperature and high pressure water loss) is also an important indicator for evaluating slurry performance. The size of filtration determines the stability of cement slurry, and then affects the inter-layer sealing ability of cement paste.
Considering that the API filter loss of the oil well cement slurry is usually very large, generally more than 1000ml, the filter loss after the resin emulsion is mixed can't be obviously compared. So it is necessary to add the equal amount of filtration loss agent into the cement slurry to make a comparison judgment.
The experimental conditions are 70 C°, 6.9MPa, and the addition of blank samples and resin emulsion with 5% filter loss agents. The water to cement ratio is maintained at 0.44. There are no other additive agents (the

addition of other additives in the routine use of oil well cement can also play a certain role in decreasing the filtration loss). The experimental results are shown in Table 5:

Table 5 Effect of Epoxy Resin Dosage on Filtration Loss of Cement Paste API

Resin content %	0	5	10	15	20
API water loss amount (70℃/ml)	144	124	103	88	65
HTHP Filtration loss (100℃/ml)	186	159	144	119	98

It can be seen from the table that the addition of modified resin emulsion can significantly improve the filtration loss of oil well cement, and with the increase of dosage, the effect of reducing water loss is more obvious. With the increase of the emulsion content, the floc particle structure in the original cement solution is dismantled, the dispersivity of the cement particles is enhanced, the moisture is released, the size distribution of the solid particles becomes more suitable, the time of forming dense filter cake is shorter, and the permeability of the filter cake is also lower [11].

3.4 Effect of epoxy resin emulsion on the thickening of cement slurry

Although the rheological properties of slurry thickening stage can meet the requirements of pumping construction, the pumping ability is completely lost after thickening. Therefore, controlling the thickening time of cement slurry is also one of the key points to ensure the normal operation of cementing operations. In order to investigate the effect of the mixing of resin emulsion on the thickening time of cement slurry, a comparison experiment was carried out between cement slurry without any additives and resin emulsion cement slurry with a 15% dosage ratio (adding / or not 660A) under the same working condition. The test was under the condition of 80 C°, 35MPa, and the corresponding experimental results were shown in Figure 1.

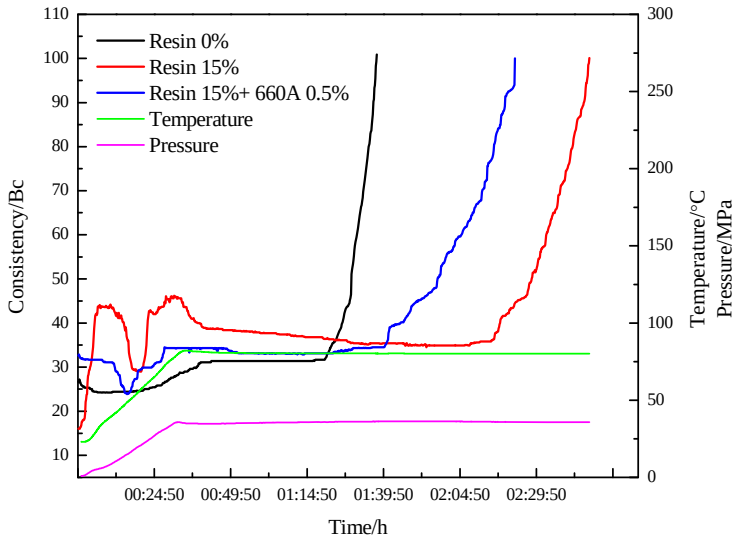

Figure 1 Tthickening curve

It can be seen from the diagram that the initial consistency of cement slurry is about 27Bc, and the thickening time is about one hour and forty minutes. When the cement slurry is mixed with resin emulsion, the initial consistency is about 35Bc, and the thickening time is about two hours and fifty minutes. It is also known that by adjusting the initial consistency of the active diluent 660A (0%~0.5%) to control the initial consistency around 28Bc (the addition of other auxiliaries can also reduce the initial consistency), the thickening time of the resin emulsion slurry can be extended by 20%~70% comparing with that of the blank sample, which ensures that the slurry has more sufficient pump delivery time. The reason is that the addition of resin emulsion can be deposited on the surface of unhydrated cement particles, reducing the hydration rate of cement at the early stage of hydration, delaying the process of hydration, and postponing the thickening time.

3.5 Mechanical properties of resin emulsion cement slurry

In order to investigate the improvement of the toughness of the cement slurry with the addition of the resin emulsion, different formulations have been cured for 24 hours under the condition of a constant temperature (80C°) and constant pressure water bath. The corresponding mechanical properties at room temperature are evaluated at room temperature. In order to ensure the reliability of the data, the results of each experiment are 3 or more test samples. The test is shown in Table 6.

Table 6 Performance of optimized resin emulsion slurry

Sample type	Maximum deformation mm	Impact strength kj/m^2	Compressive strength MPa	Elastic Modulus MPa
Spoil 0%	0.57	1.58	39.14	30368.9
Spoil 5%	0.68	1.65	22.80	23529.7
Spoil 10%	1.02	1.73	17.29	16780.9
Spoil 15%	0.41	1.45	15.72	15754.8
Spoil 20%	0.34	1.36	13.63	13046.0

According to the experimental data, it is known that when the content of the resin emulsion is less than 15%, with the increase of the content, the compressive strength decreases obviously at first, then gradually becomes stable. As the measured compressive strength is greater than 14MPa, it still meets the requirements of the cementing operation. The test of modulus of elasticity also presents a reduction situation, in which the reduction of pure cement sample is at most about 47.9%. In the impact strength test, with the increase of the amount of mixing, it will increase slightly, and the maximum increase is about 15%. When the dosage is more than 15%, the impact strength decreases. This shows that when the resin emulsion is used as cementing slurry to toughen the admixture, the toughness of the cement slurry system is greatly improved on the premise of meeting the requirements of the cementing operation.

3.6 Corrosion resistance of resin emulsion with resin emulsion

Waterborne high content epoxy resin emulsion is a material with strong chemical resistance and plays a great role in corrosion resistance of cementing. In this section, the corrosion resistance of cement concrete with high content of waterborne epoxy resin emulsion to the medium is investigated, and the test sample with good mechanical properties and 15% epoxy resin emulsion content is investigated.

In the acid and alkali resistance test of epoxy cementing materials, a certain quality of 15% resin was added into 10% sulfuric acid solution and 10% NaOH solution on the basis of a certain period of maintenance. The curing age was set as 28 days. Then the corrosion was observed and the mass loss was dried to calculate the mass loss, and the mechanical properties were measured again.The results of the experiment are as follows:

Table 7 Effect of different media on Corrosion of resin modified cement paste

Sample type	Maximum deformation mm	Impact strength kj/m2	Compressive strength MPa	Modulus of elasticity MPa
Addition0%	0.57	1.58	39.14	30368.9
Addition 5%	0.68	1.65	22.80	23529.7
Addition 10%	1.02	1.73	17.29	16780.9
Addition 15%	0.41	1.45	15.72	15754.8
Addition 20%	0.34	1.36	13.63	13046.0

It can be seen from the table that the oil well cement stone with resin emulsion is lower than the pure cement stone in the decline rate of compressive strength and the loss of mass in the immersion environment of nearly one month. This shows that the cement containing epoxy resin has better corrosion resistance to acid and alkali, and has a certain effect on improving the corrosion resistance of conventional oil well cement.

4. Conclusions

By comparing the performance of resin emulsion modified cement paste with the original cement slurry, the following conclusions can be drawn:**(1)** in the rheological properties test, the rheological behavior of cement slurry system is less affected by the amount of resin emulsion and temperature, which is consistent with the requirements of cementing operation. In terms of density, the density of the oil well cement slurry in the 10% resin emulsion is less than that of the pure cement slurry, and the density of the cement paste will continue to increase, and the density is reduced obviously. At this time, the density of the curing agent can be increased by adding the dosage of the curing agent or adding the weighting agent. **(2)** in the aspect of thickening performance, because the resin emulsion is added to postpone the hydration of cement, the thickening time of the resin emulsion cement slurry is about one hour longer than that of the pure cement, and the thickening time of the resin emulsion cement slurry can be longer than that of the blank sample by adjusting the 660A addition (0%~0.5%) of the active diluent to make the initial consistency less than 30Bc. The addition of resin emulsion can effectively improve the filtration loss at variable temperatures. **(3)** as for mechanical properties, when the ratio of the content of resin emulsion is less than 15%, the compressive strength meets the requirements of cementing construction. With the increase of the ratio of dosage, the modulus of elasticity decreases significantly while the impact strength increases and the toughness is better.**(4)**In terms of corrosion evaluation, the acid corrosion resistance of cement mixed with resin emulsion can be improved.
In conclusion, introducing resin emulsion into cementing can improve the cementing quality and improve the durability. It shows a good application prospect and provides a new view and reference for the development of oil field cementing operation.

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