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Research Article

Laboratory Research on Annulus Leak Plugging Agent in High Sulfur Gas Field

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Abstract

The leakage of annulus protection fluid in high-sulfur gas wells has seriously affected the safety and stable production of gas wells. For plugging process, an epoxy resin-based plugging agent base with low viscosity and adjustable density of 1.15-1.4 g/cm³ was designed. With a liquid dicyandiamide curing agent, a plugging agent with controllable gel time was obtained. After testing, the plugging agent exhibits strong pressure resistance, excellent bonding performance and good thermal stability, which can be used to solve the problem that the leakage of the annulus protective fluid from the bottom packer of the high-sulfur gas field oil jacket.

Keywords: High-sulfur gas field; Annulus protection fluid; Plugging agent; Epoxy resin; Gel time

Introduction

During the development of high-sulfur gas fields, CO_2, H_2S and other corrosive media may enter the annulus and cause serious corrosion of metal oilpipe and casing due to the tightness of the connection parts such as screws [1,2]. In order to extend the service life of oil pipe and casing, a packer will be used to complete the well, and annulus protection fluid will be added in the annulus [3,4]. After long-term production, part of the annulus protection fluid will leak from the packer and needs to be replenished in time. While the filling of annulus protection fluid can only be carried out through the "pressure relief and filling" circulation mode, which is difficult to construct and cannot fundamentally solve the problem of leakage of the annulus protection fluid.

With the continuous advancement of polymer chemical technology, the proportion of chemical plugging agents [5-9] in oil and gas well loss aids is increasing. Among them, resin plugging agents [10-12] have plenty of advantages such as better compressive strength, tensile strength and shear bond strength, flexible and airtight filling method, adjusted curing time, and long plugging period. Therefore, it has attracted widely attention and has replaced the traditional cement plugging agent becoming the most popular plugging chemical system. In this study, epoxy resin-based annulus leak plugging agent was prepared. The plugging agent can be pumped by a cement truck and can be injected into the oil and sleeve annulus through a multi-functional production auxiliary process to maintain a positive pressure difference so that make the plugging agent settle to the leak point and enter the leaking channel. The plugging agent cross links and solidifies under certain temperature conditions, forming a sealing effect in the leaking channel with good sealing, strong resistance to pressure difference, and stability.

Experimental

Materials and instruments

Materials: Bisphenol F epoxy resin DER-354 (viscosity 2000-3500 mPa•s), industrial grade. Biluent butyl glycidyl ether (BGE), industrial grade.Silicon powder, 5000 mesh. Silane coupling agent KH560, industrial grade. Liquid dicyandiamide curing agent, self-made.

Instruments: Electronic density balance FA1004J.Rotary viscometer NDJ-8S.Electronic universal testing machine, UTM6104. Differential scanning calorimeter DSC204, Germany NETZSCH. Thermogravimetric analyzer TG209, Germany NETZSCH.Field emission scanning electron microscope Quanta250FEG, American FEI.

Preparation and characterization

Preparation of annulus leak plugging agent

An annulus leak plugging agent with low viscosity and adjustable density is obtained by mixing epoxy resin DER-354, diluent GBE, filler silicon micro powder, silane coupling agent KH560, and modified liquid dicyandiamide curing agent according to the formula, and then stirring it evenly.

Viscosity and density measurement

Plugging agent viscosity measurement: Pour the plugging agent into a specific container of a rotary viscometer and control the temperature. Choose a suitable rotor to immerse in the sample, adjust the rotor speed, and measure the viscosity of the system.

Density measurement of plugging agent: Pour the plugging agent into a specific container of an electronic density balance and control the temperature. Ensure that the liquid density test module is submerged by the plugging system and measure the system density.

Gel time measurement

Use the "plate-knife method" to measure the gel time of the plugging agent: First use a dropper to take a small amount of the prepared plugging agent, drop 2~3 drops on the slide, and then place the slide on a hot stage set at 90, 110 and 130°C, and start timing. Use a knife to continuously pick up the solution on the slide until it can form a long and thin filament when the knife is picked up. It is

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considered that the plugging system has gelled, and the current time is the gel time of the plugging agent.**Stability test**

Let the plugging agent naturally settle in the annulus protection fluid, and then stir it vigorously and let it stand for 1h. Then remove the annulus protection fluid and observe the curing effect of the plugging agent at high temperature to test the stability of the plugging agent in the annulus protection fluid

Compression test

The compression performance test samples would be processed according to the requirements of GB/T 2567-2008. The spline was placed on an electronic universal testing machine to conduct a compression test at 2 mm/min along the specimen axis. Take 5 test samples of each group for average.

Bonding test

According to the requirements of GB/T 7124-2008, evenly apply the plugging agent to the designated part of the rigid material of the specified size, bond the two rigid materials together, and use it parallel to the bonding surface and in the direction of the main axis of the sample. The universal electronic testing machine applies tensile force and uses a constant test speed for the test. The failure time is between 60 and 20 s to test the shear stress at the bond.

Thermal stability test

NETZSCHTG 209 thermal weightlessness analyzer was used to determine the thermal stability of the plugging agent in a nitrogen atmosphere. Approximately 10 mg of the cured product of the plugging agent was placed in the sample cell of the thermo gravimetric analyzer, the nitrogen flow rate was 20mL/min, the temperature change range was 50-550, and the heating rate was 10mL/min.

Micro-morphology characterization

After the vacuum-plated treatment of the impact section of the solidified plugging agent, it is placed in a field emission scanning electron microscope to observe the micro-morphology of the section.

Result and Discussion

Viscosity and density of plugging agent

The annulus leak plugging agent needs to be pumped into the annulus, and then sinks to the leakage channel of the bottom packer by gravity. This not only requires the plugging agent to have low viscosity which meets the pumping requirements, but also have a higher density to ensure rapid sinking in the annulus protection fluid (density 1.10 ~ 1.20g/m^3). A plugging agent matrix with low viscosity and adjustable density was obtained by using low initial viscosity bisphenol F epoxy resin DER-354, combining with non-reactive diluent GBE phthalate to reduce the viscosity of the plugging agent, adding silicon fine powder to increase the system density, and adding silane coupling agent KH560 to slow down the filler sedimentation.

Figure 1 is the change of the viscosity and density of the plugging agent under different amounts of solvent. It can be seen that after the amount of diluent is greater than 10%, the viscosity of the system drops below 1000 mPa·s while the dilution effect is no longer obvious when the amount of diluent is greater than 10%. Since the non-reactive diluent has a great influence on the mechanical properties of the cured product, [13] it is determined that the addition amount of the non-reactive diluent is 10%.

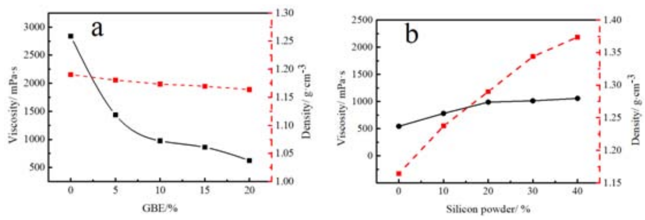

Figure 1: Changes in viscosity and density (a) Different solvent dosage (b) Different filler dosage.

Table 1: Gel time test results.

Curing agent %	10	15	20	25	20 +20% Silicon powder
T/°C					
130	6h	2.5h	1h	0.5h	1h
110	7h	5.5h	3.5h	2.5h	3.5h
90	>10h	>10h	>10h	>10h	>10h

Table 2: Characteristic temperature of TG (Different dosage of curing agent).

Characteristic temperature/°C	10%	15%	20%	25%
$T_{0.1}$	320	329	325	322
$T_{0.5}$	406	407	405	400
T_p	413	412	408	411
T_f	439	443	449	444

Figure 1 shows the changes in viscosity and density of the plugging agent under different filler additions. It can be seen that the addition of silicon powder can significantly increase the density of the system. By controlling the amount of silicon fine powder added, the density of the plugging agent can be adjusted from 1.15 to 1.4 g/cm3 to meet the requirement of natural sinking in the protective liquid.

Gel time of the plugging agent

Gel time generally refers to the time required for the resin to change from a flowing liquid state to a solid gel at a specified temperature. It is the time required for the plugging agent to increase in viscosity and lose fluidity during the curing process [14]. In the plugging process, the plugging agent should be naturally settled to the leaking part by gravity, which requires the plugging system to have an appropriate gel time, not only to ensure the fluidity of the sinking process, but also to solidify quickly when it reaches the leaking part.

Table 1 shows the test results of gel time at 90, 110 and 130°C for different amount of curing agent. It can be seen from the data in the table that with the increase of the amount of curing agent, the gel time is shortened, and the addition of filler has no effect on the gel time. The gelation time of the plugging agent at 90°C is greater than 10 h, indicating that the liquid dicyandiamide curing agent also has a certain latency. By changing the dosage of curing agent at 110°C, the gelling time can be adjusted at 2.5-7h; at 130°C, the gelation time can be adjusted at 0.5-6h.

Stability test of plugging agent

The plugging agent needs to pass through the annulus protection liquid to reach the plugging position and then solidify, so its stability

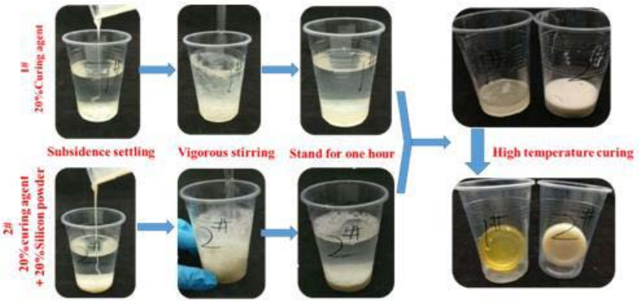

Figure 2: Stability test of annulus leak plugging agent.

Table 3: Characteristic temperature of TG (Different filler dosage).

Characteristic temperature/°C	0%	10%	20%	30%
$T_{0.1}$	325	333	330	327
$T_{0.5}$	405	408	418	429
T_p	408	413	411	406
T_f	449	445	441	448

in the annulus protection liquid must be considered. The stability of the plugging agent in the annulus protection fluid was verified by allowing the plugging agent to settle naturally in the annulus protection fluid, stirring it vigorously, and allowing it to stand for a period of time, and then observing the curing effect of the plugging agent at a high temperature.

As figure 2 shown, the plugging agent can be cured normally after removing the annulus protection fluid, and the gel and curing time have not changed significantly. The addition of filler has no effect on the curing of the plugging agent. It shows that the plugging agent can settle stably in the annulus protection liquid and curing well.

Compressive properties of the plugging agent cured product

The compression resistance represents the ability of the plugging agent to withstand the external high-pressure environment after it enters the leak channel and cross links and solidifies [15]. Figure 3 shows the change of the compressive strength and modulus of the plugging agent under different dosages of curing agent. It can be seen that the compressive strength and modulus are lower when the dosage of the curing agent is 10%, and the compressive strength reaches the maximum value of 113.4MPa when the dosage of the curing agent is 15%. As the dosage of the curing agent continues to increase, the tensile strength is reduced slightly. It may attribute to the curing agent is 10%, the amount of the curing agent is insufficient, and the cross-linking density of the cured product is small, resulting in a small compressive strength and modulus. When the amount of curing agent is greater than 15%, as the amount of curing agent increases, the tensile strength decreases slightly due to the addition of non-reactive solvents during the preparation of the curing agent. As the amount of curing agent increases, the amount of non-reactive solvents in the plugging agent increases. The cross-link density of the cured product is reduced, and the mechanical properties of the cured product are reduced.

Figure 3 shows the effect of filler addition on compression resistance when 15% curing agent is used. It can be seen that the

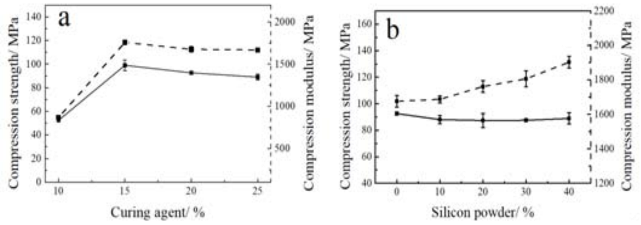

Figure 3: Compression performance test results (a) Different dosage of curing agent (b) Different filler dosage.

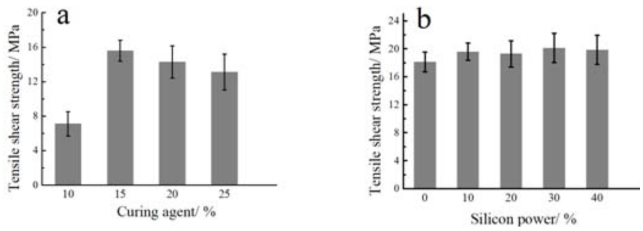

Figure 4: Adhesion performance test results (a) Different dosage of curing agent (b) Different filler dosage.

compressive strength of the plugging agent does not change much with the addition of filler, and the compressive elastic modulus increases with the increase of filler, indicating that the addition of filler increases the rigidity of the cured plugging agent. After adding the filler, the compressive strength of the cured plugging agent is >87MPa.

Adhesive performance of plugging agent

The adhesion ability of the plugging agent to the metal represents its sealing performance in the leakage channel [16]. The change of tensile shear strength of the plugging agent under different dosages of curing agent is shown in Figure 4. It can be seen that the change of the bonding strength with the amount of curing agent and the compression performance with the amount of curing agent have the same trend. When the amount of curing agent is 10%, the amount of curing agent is insufficient, and the adhesion performance of the plugging system is more poor, when the dosage of curing agent is 15%, the maximum tensile shear strength can reach 16MPa, when the dosage of curing agent is 20%, the tensile shear strength decreases slightly (14MPa). This shows that the plugging agent has excellent adhesive performance.

Figure 4 is the test result of the adhesion performance of the plugging agent when the amount of curing agent is 15% and the amount of filler is different. It can be seen that after adding the filler, the plugging agent has better adhesion properties to the metal, and the tensile shear strength can reach more than 18MPa. The addition of the filler will increase the adhesion strength.

Thermal stability of plugging agent

As figure 5 shown, the cured product has a similar thermal decomposition process under different curing agent dosage conditions. It can also be seen from Table 2 that the amount of curing agent has little effect on the thermal decomposition temperature of the cured product. Taking 10% weight loss as the initial decomposition temperature, the decomposition temperature of each system is above

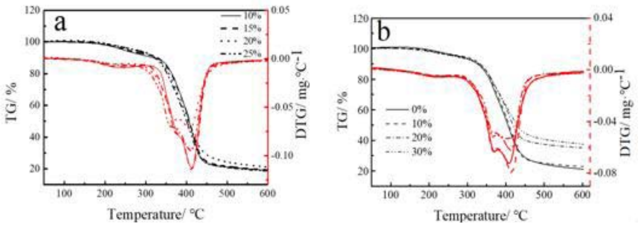

Figure 5: The TG,DTG curve of plugging agent (a) Different dosage of curing agent. (b) Different filler dosage.

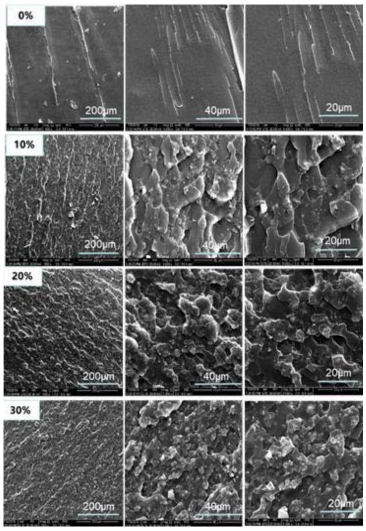

Figure 6: SEM image of plugging agent.

320°C, and the maximum weight loss rate temperature is 400°C the above, which indicate that the cured product has a good heat resistance.

The cured product under the plugging system with different filler additions has a similar thermal decomposition process, as shown in figure 5 and table 3. It is found that the addition of fillers in the plugging system has little effect on the thermal decomposition temperature of the cured product. Taking 10% weight loss as the initial temperature of decomposition, it can be seen that the decomposition temperature of each system is above 320°C.

Micro-morphology of the plugging agent

The pure epoxy resin matrix shows obvious brittle fracture, the impact section is relatively smooth, and the surface roughness is small. After adding the filler, the impact section becomes rough, and it can be seen that the filler is evenly distributed in the resin. The silicon fine powder is added to the resin as inorganic rigid particles. When the external force is applied, a stress concentration effect will occur, which will cause micro-cracks in the epoxy resin matrix around the silicon fine powder and absorb part of the energy applied from the outside. When the filler is added, a silane coupling agent is added, so that a large amount of organic groups are grafted on the surface of the silicon micro powder, which increases the compatibility with the resin matrix and produces a strong interface effect. When the resin matrix is impacted, the particles encapsulated the organic layer will first absorb part of the energy, and at the same time cause cavitations, cracking, and shear bands on the substrate, which play a toughening effect. The addition of a large amount of fillers will increase the number of defects while toughening, which will reduce the mechanical properties. This can also be seen from the test results of mechanical properties.

Conclusion

(1) A plugging agent matrix with a viscosity of <1000mPa•s and an adjustable density of 1.15-1.4g/cm^3 was obtained by using bisphenol F epoxy resin DER-354 with low initial viscosity, combined with diluent and filler.

(2) With the liquid modified dicyandiamide curing agent, the gelation time of the plugging agent can be adjusted by changing the dosage of the curing agent. When it is 110°C, it can be adjusted from 2.5-7h. When it is 130°C, it can be adjusted from 0.5-6h.

(3) The performance of the plugging agent under different dosages of the curing agent and the amount of filler added, the results show that the prepared annulus plugging agent has good compression resistance, adhesion performance and thermal stability. Compressive strength>87MPa; tensile shear strength>14; thermal decomposition temperature above 320°C. It is determined that a high-performance annulus plugging agent that can be used to solve the leakage problem of the annulus bottom packer of the oil jacket in the high-sulfur gas field is obtained.

References

1. Zhang NY, Zhang Z, Rui ZH, Li J, Zhang C, Zhang QS, et al. Comprehensive risk assessment of high sulfur-containing gas well. Journal of Petroleum Science and Engineering. 2018; 170: 888-97.

2. Ding YS, BaiZQ, Han Y, Yi CG. Research Status of Elemental Sulfur Corrosion in High Sulfur Gas Field. Hot Working Technology. 2016; 45:20-3.

3. Yang YK, Zhai JM. Casing program optimization technology for ultra-deep horizontal wellsin the YuanbaGasfield, Sichuan Basin. Natural Gas Industry. 2015; 35:79-84.

4. Zheng LH; Zhang JB; Yang H; Wang HL. Study and Application on New Annular Protecting Fluid Corrosion. Oil Drilling & Production Technology. 2004; 26:13-16.

5. Yuan JS, Cao GS, Chen P, Gao Y. A kind of novel chemical plugging removal technology study for polymer flooding wells. Advanced Materials Research. 2014; 884-885: 7-11.

6. Zhan JY, Liu SH, Liu JH, Zhang FY, Cheng ZW. Development and application of chemical consolidation plugging agent HDL-1. Petroleum Drilling Techniques. 2014; 42: 69-74.

7. Zhang QS. Development and application of low viscosity corrosion-resistant plugging agent. Fault Block Oil & Gas Field. 2020; 27: 258-26.

8. Mao JC, Fan JM, Zhao JZ, Chen SN, Zhang WL, Song ZF. Research and development of chemical temporary plugging technique. Petrochemical Technology. 2019; 48: 76-81.

9. Qin XP, Zheng JP, Li LC, Li CX. Sun GL, Lu HW, et al. Preparation and Performance of an Adsorption Type Gel Plugging Agent as Enhanced Oil Recovery Chemical. Journal of Chemistry. 2015; 1-6.

10. Guo G, Zhou ZP, Li QW. Application of Polymer Resin on Casing Plugging. Oilfield Chemistry. 2019; 36:755-60.

11. Lei XY, Li H, Chen S, Li WT, Qi ZG, Chen DJ. Research on modification of polyvinyl alcohol-urea resin water plugging agent. Applied Chemical Industry. 2014; 207-208, 211.

12. Zhang WC, Xu HM, Huang X, Gao XX, Liu HC, Huang GS, et al. Preparation and Performance Evaluation of n-Butylated phenolic-epoxy Resin Applied in

Gas Field Plugging Agent. Oilfield Chemistry. 2019; 444-9.

13. Geun LJ, Han S-H, Jung T. Mechanical Properties and Curing Characteristic of Epoxy Resin by Diluent Addition. 2019; 31:1317-1324.

14. A. A. Shimkin. Methods for the determination of the gel time of polymer resins and prepregs. Russian Journal of General Chemistry. 2016; 86: 1488-93.

15. Liu JH, Liu SH, Long DQ. Cross-linking film formation and chemical consolidation pressure and leakage stoppage technology in ming 1 well. Petroleum Drilling Technology. 2017; 45: 55-7.

16. Wang C, Hou SL, Qi B. Research and application of self-cementing plugging technology. Drilling Fluid & Completion Fluid. 2016; 33: 64-6.