Study on the Oil Well Cement-Based Composites to Prevent Corrosion by Carbon Dioxide and Hydrogen Sulfide at High Temperature

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Abstract: Complex wells with high temperature and the presence of carbon dioxide and hydrogen sulfide acid gas require the use of high-temperature and high-density anti-corrosion cement slurry for cementing operations, and conventional cement slurry does not have the advantages of high density, high-temperature resistance, or corrosion resistance. In order to avoid the severe corrosion of cement slurry by carbon dioxide and hydrogen sulfide at high temperatures, solid phase particles with different particle sizes are combined with polymer materials to form a dense, high-density, high-temperature- and corrosion-resistant cement slurry. In this paper, we consider the use of manganese ore powder weighting agent, composite high-temperature stabilizer, inorganic preservative slag and organic preservative resin to improve the corrosion resistance of cement slurry, design a high-density cement slurry that is resistant to high temperature and carbon dioxide and hydrogen sulfide corrosion, and evaluate the performances of the cement slurry at 180 °C. The results show that the manganese ore powder weighting agent effectively improves the density of the cement slurry. Using composite silica fume with different particle sizes as a high-temperature stabilizer can ensure the rheology of the cement slurry and improve the ability of the cement sample to resist high-temperature damage. The use of slag and resin as preservatives can effectively reduce the corrosion degree in cement slurry. The high-temperature corrosion-resistant cement slurry systems with different densities designed using these materials exhibit good rheological properties, with water loss of less than 50 mL and a thickening time of more than four hours. The compressive strength decreased by less than 5.8% after 28 days at high temperatures. After being corroded by hydrogen sulfide and carbon dioxide (total pressure 30 MPa, 16.7% hydrogen sulfide and 6.7% carbon dioxide) under high temperature (180 °C) for 30 days, the corrosion depth of the cement sample was less than 2 mm, the reduction of compressive strength was low, and the corrosion resistance was strong. These research results can be used for cementing operations of high-temperature oil and gas wells containing hydrogen sulfide and dioxide.

Keywords: high temperature; corrosion; hydrogen sulfide; carbon dioxide; oil well cement

1. Introduction

With the continuous development of oil and gas, there are more and more high-temperature and high-pressure oil and gas wells. The high temperature at the bottom of oil and gas wells makes cementing operations difficult, and the sealing quality of the cement sheath cannot be guaranteed. In particular, there are a lot of acid gases in the humid environment, which react easily with the cement slurry. If the cement sample is corroded, the structure of the cement slurry will be damaged, causing fluid channeling, and reducing the production and service life of oil and gas wells [1–3]. On the one hand, the cement
slurry needs to be resistant to high temperature. On the other hand, for some oil and gas wells with high temperature, high pressure and acid gas, the design of cement slurry is very difficult [4,5]. This is because conventional oil well cement-based composites are prone to a decline in strength at high temperatures and accelerated corrosion reaction. At present, the common corrosive gases in oil and gas wells are hydrogen sulfide and carbon dioxide, which form sulfuric acid and carbonic acid when combined with formation water [3,6]. As the conventional oil well cement is Portland cement, its hydrated products mainly include calcium hydroxide, hydrated calcium silicate, etc. The cement sample is alkaline, and the acid gas dissolves in water and has strong corrosivity to it, so it has high requirements in terms of the corrosion resistance of the oil well cement-based composites. There have been some studies on the corrosion of cement-based composites by a single acid gas [7–10]. However, due to the synergistic corrosion of carbon dioxide and hydrogen sulfide dissolved in water, the synergistic corrosion of carbon dioxide and hydrogen sulfide will damage the hydration products (mainly calcium hydroxide and calcium silicate) of the cement sample, destroy the structure, increase the pore volume, cause the strength to decrease, and make the cement slurry unable to effectively support the formation and casing pipe [11–13]. The research of O.A. Omosebi [14] showed that under high temperature, the acid gas exerts a high degree of corrosion on the cement sheath and causes serious corrosion damage. Therefore, it is necessary to design a high-density-resistant high-temperature anti-corrosion cement slurry for cementing operations in high-temperature formations containing carbon dioxide and hydrogen sulfide.

In order to ensure the sealing integrity of the cement sheath, the type of additives in cement slurry is relatively fixed. For the design of high-temperature and high-density anti-corrosion cement slurry, dispersant, retarder, fluid loss reducer, and other conventional additives have been studied in high-temperature cement slurry and can be used directly [15–18]. However, the weighting agents, high-temperature stabilizers and anti-corrosion materials need to be specially designed, mainly because the content of these materials is very large, which has a great impact on the performances of cement samples; in particular there has been little research performed to date on materials that can improve corrosion resistance to carbon dioxide and hydrogen sulfide at high temperature. A. Abdulmalek et al. [19] and A. Ahmed et al. [20] studied the use of barite and iron ore powder in the design of high-density cement slurry. The density of the cement slurry designed with these weighting materials reached 2.4 kg/m³, making them suitable for cementing operations in high-pressure formations. The research of J.K. Qin et al. [21], B.L.D. Costa et al. [22], and H.J. Liu et al. [23] showed that silica fume can be used as a high-temperature stabilizer of oil well cement to improve the performance of cement samples under high temperature. In order to ensure the quality of cementing cement sheath in acidic gas environments, B. Yuan et al. [24], Z.G. Peng et al. [25], and M.X. Bai et al. [26] studied the corrosion resistance of modified cement with the addition of the corrosion-resistant additive CRA in an H₂S-CO₂ environment. The research results showed that cement with polymer preservatives has excellent acid corrosion resistance due to its film-forming and filling effects, reducing permeability and alkalinity. The results of these studies can serve as a reference for the design of high-temperature and high-density carbon-dioxide-emitting and hydrogen-sulfide-corrosive cement slurry. However, these materials cannot be used simultaneously in high-temperature, high-density, hydrogen sulfide and carbon dioxide environments, so these key materials need to be further developed.

To meet the particular requirements of high-temperature and high-density anti-corrosion cement slurry, in this paper, high-temperature-resistant solid materials are designed with various particle sizes to improve the high-temperature stability of cement slurry, adjust the density of cement slurry, and improve the anti-corrosion performance of cement slurry. At the same time, polymer liquid materials and solid materials are combined to synergize and improve the performance of cement slurry through different mechanisms of action. In this paper, the influence of manganese ore powder weighting agent in the performance of cement slurry was studied under high temperature and high pressure to construct high-density cement
slurry. In view of the fact that the high-temperature environment makes the cement prone to failure and instability, a high-temperature stabilizer is studied to improve the mechanical property stability of the cement sample under high temperatures. Inorganic and organic anti-corrosion materials are studied and used together to improve the corrosion resistance of cement slurry. Based on the admixture materials studied, a high-temperature, high-density and anti-corrosion cement slurry system was designed, and its performance was evaluated. The research results provide technical support for the cementing of high-temperature and high-pressure oil and gas wells containing carbon dioxide and hydrogen sulfide.

2. Experimental Section

2.1. Experimental Materials

Class G oil well cement is used as the primary material of the cement slurry, and the chemical composition of the oil well cement is shown in Table 1. In this study, fluid loss reducer, dispersant and retarder are used to adjust the performance of cement slurry. The fluid loss reducer is a 2-Acrylamido-2-methylpropane sulfonic acid (AMPS)-type water-soluble polymer that can reduce the permeability of filter cakes of oil well cement slurry. In this study, it is mainly used to reduce the water loss of the cement slurry. The dispersant is an aldehyde ketone condensation polymer that is mainly used to reduce the water loss of cement slurry by adjusting the surface charge of the cement particles to obtain cement slurry with appropriate rheological properties. The retarder consists of polymers with carboxylic and sulfonic acid groups that regulate the setting time of cement slurry through adsorption, chelation, dispersion, and wetting. It is mainly used to regulate the thickening time of cement slurry. The manganese ore powder, silicon powder and slag were purchased from the market. The main component of manganese ore powder is manganese tetroxide, with a particle size of less than 6 microns. It is mainly used to adjust the density of cement slurry. The main component of silicon powder is silicon dioxide, and the particle sizes used in this study are mainly 100 and 300 mesh. Silicon powder is mainly used to improve the high-temperature resistance of oil well cement slurry. The main components of the silicon powder are calcium oxide, silicon dioxide, and aluminum trioxide, with a particle size of less than 30 µm. It is mainly used to improve the corrosion resistance of oil well cement slurry. The polymer resin was obtained from the laboratory, and is a bisphenol A type epoxy resin, which is mainly used as an organic preservative to improve the corrosion resistance of cement paste.

Table 1. Chemical composition of oil well cement.

<table>
<thead>
<tr>
<th>Component</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>Na₂O + K₂</th>
<th>Others</th>
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<tr>
<td>Content (%)</td>
<td>64.2</td>
<td>22.5</td>
<td>4.4</td>
<td>4.1</td>
<td>1.6</td>
<td>0.38</td>
<td>2.82</td>
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</table>

2.2. Experimental Methods

2.2.1. Preparation of Cement Slurry

Depending on the proportions in the cement slurry composition, cement and other solid materials (silica fume, weighting agent, slag) were mixed to form dry mixed ash, water and liquid admixture materials (fluid loss reducer, retarder, dispersant, resin), via wet mixing to form mixed solution; dry mixed ash and the mixed solution were placed in a constant-speed mixer (TG-3060A, Shenyang Taige Petroleum Instrument Equipment Co., Ltd., Shenyang, China), and stirred evenly at 4000 r/min. When the cement slurry was mixed, its evenness was observed, bubbles were eliminated, and the uniformly mixed cement slurry was taken as the sample. The composition of cement slurries with high density is shown in Table 2.
Table 2. Composition of high-density cement slurries. Unit: wt.%.  

<table>
<thead>
<tr>
<th>Density (kg/m³)</th>
<th>Cement</th>
<th>Water</th>
<th>Fluid Loss Reducer</th>
<th>Retarder</th>
<th>Dispersant</th>
<th>Silica Fume</th>
<th>Weighting Agent</th>
<th>Slag</th>
<th>Resin</th>
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<tr>
<td>2.0</td>
<td>100</td>
<td>41</td>
<td>7</td>
<td>2.5</td>
<td>2</td>
<td>35</td>
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<tr>
<td>2.1</td>
<td>100</td>
<td>42</td>
<td>7</td>
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<td>3</td>
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<td>32</td>
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<tr>
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<td>100</td>
<td>45</td>
<td>6</td>
<td>2</td>
<td>4.5</td>
<td>35</td>
<td>79</td>
<td>16</td>
<td>10</td>
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</tbody>
</table>

2.2.2. Construction Performance Tests

The performance testing of the cement slurry was carried out in accordance with the provisions of the Chinese standard GB/T 19139-2012 “Test method for oil well cement”. The specific test steps were as follows:

(1) Density test

After the preparation of the cement slurry is completed, the cement slurry is poured into the sample cup of the densimeter, and pushing the cup cover downward into the cup mouth. After the excess cement slurry in the system has been cleaned, it is placed on a balanced rack to test the density of the cement slurry. The density of the cement slurry is tested with a densimeter (YM-3, Qingdao Haitongda Special Instrument Co., Ltd., Shandong, China) under normal temperature and pressure.

(2) Thickening time test

Before the experiment, the sample cup was installed and prepared. After completion of the preparation of the cement slurry sample, the cement slurry is poured into the sample cup, which is sealed. The test cup containing the sample is placed into the thickener. After the kettle is filled with hydrocarbon oil, a temperature sensor is inserted, and the kettle is sealed. The specified temperature and pressure are set on the instrument and the test is started. The thickening time is evaluated with a high-temperature and high-pressure thickener (TG-8040DA, Shenyang Taige Petroleum Instrument Equipment Co., Ltd., Shenyang, China). The temperature and pressure are set to 180 °C and 60 MPa, respectively. When the consistency of the cement slurry reaches 100 Bc, the time is recorded as the thickening time.

(3) Water loss test

The temperature of the high-temperature and high-pressure water loss meter is set to the specified temperature, the tested cement slurry is poured into a water loss test cup, the water loss of the cement slurry is tested under a pressure of 6.9 MPa, the filtration loss is recorded for 30 min, and the water loss is calculated. The water loss of the cement slurry is evaluated using a high-temperature and high-pressure water loss instrument (TG-71, Shenyang Taige Petroleum Instrument Equipment Co., Ltd., Shenyang, China).

(4) Rheological test

During the rheological properties test, the prepared cement slurry is placed in a constant-temperature mixer and cured for 20 min to simulate the flow of cement slurry in the well. Subsequently, the sample is poured into a test cup, and the rheological properties of the cement slurry are tested using a six-speed rheometer (ZNN-D6, Qingdao Chuangmeng Instrument Co., Ltd., Shandong, China). The rheology of the cement slurry is analyzed by evaluating the readings of a six-speed rotational viscometer at different rotational speeds (600 r/min, 300 r/min, 200 r/min, 100 r/min, 6 r/min, 3 r/min).

2.2.3. Compressive Strength Test

After the cement slurry has been prepared, the cement slurry is poured into a sample mold with a compressive strength standard, and the mold containing the cement slurry is cured in a high-temperature and high-pressure curing kettle (TG-7370D, Shenyang Taige Petroleum Instrument Equipment Co., Ltd., Shenyang, China) at 180 °C for a specified time. Subsequently, the cement stone mold is taken out and the mold is removed to obtain a 50.8 mm cube sample. When it was necessary to evaluate the mechanical properties of corroded cement stones, the compressive strength test was performed after the cement
samples are corroded according to the corrosion testing process. The universal mechanical testing machine (HY-20080, Shanghai Hengyi Precision Instrument Co., Ltd., Shanghai, China) is used to evaluate the compressive strength of the cement sample. Compressive strength is the maximum stress of the cement slurry in the process of compression failure. The loading rate during compression is 1.2 kN/s. The sample used is a cube with a side length of 50.8 mm. Three cement stones are tested in each group, and the average value is calculated as the experimental result.

2.2.4. Corrosion Depth Test

The prepared cement slurries are poured into a cylindrical mold with a diameter of 25 mm and a height of 25 mm, and they are placed in a pressurized curing kettle at a temperature of 180 °C and a pressure of 21 MPa for 72 h and then demolded to form an uncorroded cement sample. The cement sample is placed in a high-temperature and high-pressure corrosion tester (TL-3, Jingzhou Tallin Machinery Co., Ltd., Jingzhou, China) made of Hastelloy alloy that is resistant to acid gas corrosion, and its appearance is shown in Figure 1. The total pressure of the corrosion test is 30 MPa, in which the partial pressures of H₂S, CO₂ and N₂ are 4 MPa, 2 MPa and 24 MPa, respectively. After reaching the specified corrosion time, the cement samples are taken out to obtain corroded cement samples.

Figure 1. Photo of high-temperature and high-pressure corrosion tester.

In order to test the corrosion degree of the cement sample, the corrosion depth is taken as the evaluation standard. Due to the alkalinity of the cement sample formed during the hydration of oil well cement, it will turn red or purplish red when encountering phenolphthalein. After the cement stone has been corroded, this alkalinity disappears, causing the corroded area to encounter phenolphthalein without discoloration. Therefore, based on this principle, it is possible to test the corrosion degree of cement stone. After the cement stone has been corroded, the cement sample is cut and the corrosion area is demarcated on the basis of the turning red characteristic of phenolphthalein meeting alkali. The four boundary thickness values of the sample that do not turn red are measured with a vernier caliper, and the average value is taken as the corrosion depth of the cement sample. A schematic diagram of the test is shown in Figure 2.
2.2.5. Micromorphology Test

The prepared cement sample was crushed, and the smooth part in the middle was taken as the sample. The hydration of the sample is terminated by soaking in alcohol for 24 h. Then, the samples are dried in an oven at 60 °C for 24 h, and the microscopic morphologies of the cement samples are observed using a scanning electron microscope (SU8010, Hitachi, Tokyo, Japan).

3. Design of High-Temperature-Resistant High-Density Anti-Corrosion Cement Slurry

3.1. Some Considerations for the Design of Cement Slurry

Since many studies have been performed on high-temperature retarders, fluid loss reducers and dispersants, this paper mainly focuses on the weighting agents, high-temperature stabilizers and preservatives with high content in cement slurry. The high-temperature retarder, high-temperature fluid loss reducer and high-temperature dispersant used were purchased from the market. The high-temperature retarder mainly consists of a multi-polymer, which can form a chelate with calcium ions on the surface of cement particles, preferentially adsorb onto the surface of hydration products, slow down their hydration speed, and show a high-temperature retarding effect. The high-temperature fluid loss reducer mainly consists of an AMPS terpolymer. It increases the viscosity of cement slurry and enhances its filtration resistance when dissolved in water. At the same time, it can be adsorbed on cement particles to form a cohesive state with viscoelasticity, block the pores of the filter cake, improve the compactness of the filter cake, and reduce the water loss of the cement slurry. The dispersant can improve the dispersion of cement particles in cement slurry and improve the rheology of the cement slurry. These additives are added according to the requirements of the experiment to ensure that the cement slurry has good performance.

In the CO₂/H₂S mixed gas environment, CO₂ dissolves in water to form an acid-soluble solution of H₂CO₃, and the cement slurry is corrodes under the action of carbonic acid to form CaCO₃ crystals [27–30]. At the same time, calcium-silicate-hydrate(CSH) also reacts with carbonic acid to form calcium carbonate. With the continuous action of CO₂ in the aqueous solution, calcium carbonate is transformed into water-soluble calcium bicarbonate, which continues to consume calcium hydroxide inside the cement sample, leading to the degradation of the compressive strength, the increase in the permeability, and an impact on the performance of the cement sample. The reaction process between carbon dioxide and hydration products in an aqueous solution is shown in Formulas (1)–(5) [31,32]. When H₂S is dissolved in water, it forms H₂SO₄, which reacts with calcium hydroxide and CSH in the hydration products to generate expansive CaSO₄·2H₂O. The internal stress generated by the expansion causes the internal generation of the cement sample to be listed, further aggravating the corrosion. At the same time, tricalcium aluminate and tetra calcium ferroaluminate in the cement slurry also react with sulfate in the aqueous solution, producing expansive ettringite, destroying the internal structure of the cement sample. The reaction process between carbon dioxide and hydration products in an aqueous solution is shown in Formulas (6)–(12) [33,34].
CO$_2$+H$_2$O $\rightarrow$ H$_2$CO$_3$ $\rightarrow$ H$^+$+HCO$_3^-$  \hspace{1cm} (1)

Ca(OH)$_2$+H$^+$+HCO$_3^-$ $\rightarrow$ CaCO$_3$+2H$_2$O  \hspace{1cm} (2)

CSH + H$^+$+HCO$_3^-$ $\rightarrow$ CaCO$_3$+SiO$_2$+H$_2$O  \hspace{1cm} (3)

CO$_2$+H$_2$O + CaCO$_3$ $\rightarrow$ Ca(HCO$_3$)$_2$  \hspace{1cm} (4)

Ca(HCO$_3$)$_2$ + Ca(OH)$_2$ $\rightarrow$ 2CaCO$_3$+2H$_2$O  \hspace{1cm} (5)

H$_2$S $\rightarrow$ 2H$^+$+S$^{2-}$  \hspace{1cm} (6)

H$^+$+OH$^-$ $\rightarrow$ H$_2$O  \hspace{1cm} (7)

Ca(OH)$_2$+H$_2$S $\rightarrow$ CaS + 2H$_2$O \hspace{1cm} (8)

CSH + H$_2$S + H$_2$O $\rightarrow$ CaSO$_4$·2H$_2$O + C$_{(m)}$S$_{(n)}$H$_{(x)}$ \hspace{1cm} (9)

CSH + H$_2$S+ $\rightarrow$ SiO$_2$+CaS + H$_2$O \hspace{1cm} (10)

3CaO·Al$_2$O$_3$·6H$_2$O + 3Ca$^{2+}$+3SO$_4^{2-}$ $\rightarrow$ 3CaO·Al$_2$O$_3$·3CaSO$_4$+6H$_2$O \hspace{1cm} (11)

4CaOAl$_2$O$_3$·Fe$_2$O$_3$·3H$_2$O + 3Ca$^{2+}$+3SO$_4^{2-}$+29H$_2$O $\rightarrow$ 3CaO·Al$_2$O$_3$·3CaSO$_4$·32H$_2$O + 2Fe$^{3+}$+6OH$^-$ \hspace{1cm} (12)

In an environment of high-temperature CO$_2$/H$_2$S mixed gas, the corrosion process of the cement sample is more complex, seriously affecting the compressive strength, permeability and other properties of the cement sample. The main reason for the corrosion of cement is the reaction of hydration products and acid fluids. In view of the corrosion damage, the corrosion resistance of cement can be improved by reducing the alkali substances and improving the compactness of cement slurry to prevent acidic liquid from flowing into the cement sample and forming an acid-resistant cement structure. We consider combining a variety of mineral admixtures with organic substances to add cement, giving full play to their respective advantages and the synergistic effect of their combination, so as to maximize the corrosion resistance of the cement slurry. At the same time, the preservative used needs to allows for high-temperature resistance.

3.2. High-Temperature-Resistant Manganese Ore Powder Weighting Agent

High-temperature oil and gas wells are usually characterized by high pressure, which requires high-density cement slurry in order to perform cementing operations. When the density of the cement slurry is low, oil, gas and water channeling, and even blowout accidents, can easily be caused. At the same time, higher-density cement slurry can also improve displacement efficiency. The commonly used method for increasing the density of cement slurry is to add weighting agent materials [35,36]. A manganese ore powder with high-temperature resistance and a regular shape is selected as the weighting material for the high-temperature anti-corrosion cement slurry. Its main component is Mn$_3$O$_4$, which is considered to be one of the weighting materials for oil and gas well-working fluid that offers the best performance at present. The microscopic morphology of manganese ore powder is shown in Figure 3. In order to evaluate the performance of manganese ore
powder, different amounts of manganese ore powder were added to the cement slurry to study the impact of manganese ore powder addition in the performance of the cement slurry at 180 °C. The results are shown in Figure 4.

Figure 3. Particle size distribution of manganese ore powder.

Figure 4. Effect of manganese ore powder in the performance of cement slurry.

Figure 3 shows the micromorphology of the manganese ore powder. The regular particle shape of manganese ore powder is spherical, which helps manganese ore powder to be embedded into the pores of the cement slurry. At the same time, the particle size of manganese ore powder is very small. Mineral materials with small particle size usually have a particular activity, and can improve the compactness and microstructure of cement sample, which is beneficial in the design of high-density anti-corrosion cement slurry. The performances of cement slurries formed using different contents of manganese ore powder are shown in Figure 4. Considering that the cement slurry requires better anti-corrosion performance under high-temperature and acid gas environments, manganese ore powder can effectively improve the density of cement slurry, and the prepared high-density cement slurry possesses high compressive strength. The main reason for this is that the manganese ore powder with small particle size forms a closely packed structure inside the cement sample, which improves the density of the cement slurry and prevents the acidic fluid from entering the cement sample to cause corrosion. This is the advantage of using manganese ore powder over other weighting agents.
3.3. Multi-Particle High-Temperature Stabilizer

The strength of oil well cement decreases after curing for a long time at temperatures higher than 110 °C. One study found that adding 35%~40% silica fume could effectively ameliorate the reduction in the high-temperature strength of the cement sample [37]. Currently, the high-temperature stabilizer used to resist the strength deterioration of cement sample is usually 100 mesh (150 µm) silica fume. Due to its large particle size, the stability of high-temperature cement slurry may worsen when designed. Smaller silica fume is more easily suspended in the cement slurry and filled into the cement sample, improving the compactness of the cement sample. However, smaller silica fume has a more significant impact on the rheology of the cement slurry. In order to study high-temperature stabilizers with good performance, 100 mesh and 300 mesh (48 µm) of composite silicon powder are considered. On the one hand, the pore structure of the cement sample is improved through the combination of different particle sizes. On the other hand, the influence of materials with small particle sizes on the rheology of cement slurry is decreased. By analyzing the influence of different silica fume additions on the performance of the cement slurry, the performance and effect of silica fume can be evaluated.

Table 3 shows the influence of the proportion of silica fume with different meshes on the rheology and stability of the cement slurry. Meanwhile, the influence of silica fume particle size on the permeability and the high-temperature stability of the composite silica fume are evaluated. With increasing content of 300 mesh silica fume, the rheological test reading of the cement slurry increases. When the proportion of 100 mesh silica fume is less than 30%, the rheology cannot be tested at 300 r/min, which indicates that the rheology is very poor. Moreover, when the content of 300 silica fume is greater than 50%, there is no free liquid in the cement slurry, which indicates an improvement in the stability of the cement slurry. Figure 5a shows the influence of the proportion of silica fume on permeability. The smaller the particle size of the silica fume, the lower the permeability of the cement slurry, improving the corrosion resistance of cement sample. The difference between the permeability of 75% 300 mesh silica fume and that of 100% 300 mesh silica fume is slight. Comprehensively considering the influence of composite silica fume on the performance of the cement slurry, a ratio of 100 mesh: 300 mesh silica fume equal to 25:75 is determined to be the best proportion. The effect of composite silicon powder on high-temperature strength stability is shown in Figure 5b. The compressive strength of the cement sample increases throughout curing for three days. When the curing time is greater than three days under high temperature, the strength of the cement slurry fluctuates, but the range of change is small. This shows that the composite silica fume is helpful for improving the high-temperature stability of cement sample.

3.4. High-Temperature-Resistant Preservative Mixed with Organic and Inorganic Materials

The corrosion degree of the cement samples is easily aggravated under high temperature, which makes designing anti-corrosion materials more difficult. In order to design high-temperature-resistant anti-corrosion cement slurry, we consider the addition of organic preservatives and inorganic preservatives to the cement slurry to improve the corrosion resistance in different ways. Inorganic preservatives can be used to reduce the corrosion degree of the cement samples by acid gas, mainly by reducing the content of Portland cement in unit volume and improving the compactness of the cement sample. Organic preservatives mainly form a polymer structure in the cement slurry, organizing acid gas to come into contact with the hydration products, thus reducing the permeability and corrosion degree of the cement slurry [38]. In this study, slag was selected as an inorganic preservative and resin as an organic preservative. Preservatives of different quality were added to the cement slurry to evaluate the degree of corrosion of the cement slurry containing the preservatives at 180 °C. The evaluation results of slag and resin are shown in Figures 6 and 7, respectively.
Figure 5. Performances of mixed silica fume cement slurry: (a) Permeability; (b) Compressive strength.

Figure 6. Effect of slag on cement slurry performance.

Figure 7. Effect of polymer resin on cement slurry performance.
Table 3. Effect of composite silica fume on the rheology and free liquid of cement slurry.

<table>
<thead>
<tr>
<th>100 Mesh:300 Mesh</th>
<th>300 r/min</th>
<th>200 r/min</th>
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<td>0:100</td>
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</tbody>
</table>

As a cementitious material to improve the performance of cement slurry, slag can be added in large amounts to the cement slurry, and is helpful in improving the performance of cement slurry at normal temperatures [39–41]. An inorganic preservative is considered in order to improve the high-temperature corrosion resistance of the cement slurry. The influence of the slag on the performance of the cement sample is shown in Figure 6. When the content is lower than 20%, the strength of the slag cement sample increases to a certain extent, thus improving the performance of the cement slurry. At the same time, the addition of slag effectively improves the corrosion resistance, and the corrosion depth of cement sample with 20% slag addition is 60.4% lower than that of pure cement slurry. The hydration products of slag contain almost no Ca(OH)₂. The main impact on the corrosion resistance of the cement sample is that slag can reduce the alkali content and improve the structure of the cement sample. The cement with the addition of slag has a strong anti-corrosion effect.

In addition to inorganic anti-corrosion materials, organic polymer anti-corrosion materials are also employed to form a synergistic effect, improving the corrosion resistance. The resin is demonstrated to improve the elasticity and toughness of cement slurry. It has the same effect as latex, while having less foaming than latex. Figure 7 shows the influence of the addition of resin on the mechanical properties and corrosion resistance of the cement sample. With the addition of resin, the compressive strength continues to degrade. The corrosion depth of the cement sample with 8% resin dosage is only 1.9 mm, which is obviously lower than that of the pure cement sample. The resin polymer particles form a film with high adhesion between the cement slurry and the aggregate. Some polymers with reactive groups can form an interpenetrating network structure and improve the adhesion between particles. A covering film is formed inside the cement sample, which prevents corrosive gases from invading the cement sample, protecting the structure from corrosion damage, and enhancing the corrosion resistance of the cement sample.

4. Evaluation of High-Temperature-Resistant High-Density Anti-Corrosion Cement Slurry

4.1. Construction Performances

Through the study of high-temperature resistant additives, the types and dosage of additives were determined, and a high-temperature-resistant high-density anti-corrosion cement slurry system was constructed. The composition of the cement slurry is shown in Table 2. The performances of the cement slurry are shown in Table 4 and Figure 8.

It can be seen from Table 4 and Figure 8 that the designed high-density anti-corrosion cement slurries have good rheology, thickening time is more than four hours, and water loss is less than 50 mL. All properties meet the requirements of cementing operations, ensuring the construction quality of the cement slurry.

Table 4. Rheology of cement slurries with different densities.

<table>
<thead>
<tr>
<th>Density (kg/m³)</th>
<th>300 r/min</th>
<th>200 r/min</th>
<th>100 r/min</th>
<th>6 r/min</th>
<th>3 r/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>223</td>
<td>160</td>
<td>87</td>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td>2.1</td>
<td>243</td>
<td>178</td>
<td>93</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>2.2</td>
<td>277</td>
<td>197</td>
<td>105</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>2.3</td>
<td>253</td>
<td>189</td>
<td>110</td>
<td>9</td>
<td>6</td>
</tr>
</tbody>
</table>
When hydrated and cured, cement can increase its mechanical properties over time; (Thickening time and water loss of cement slurries with different densities. (b) Water loss.

4.2. Compressive Strength at High Temperature

For cement slurry used in high-temperature environments, construction performance is closely related to construction quality, and the stability of the mechanical properties of the cement sample under high temperature is closely related to the long-term cementing quality. If the high-temperature mechanical properties are poor, the cement slurry will not be able to effectively seal the oil, gas and water, which may result in the abandonment of oil and gas wells. For oil and gas wells containing carbon dioxide and hydrogen sulfide, in particular, sealing failure can further lead to acid gas channeling, threatening the safety of oil and gas wells. By evaluating the compressive strength of cement paste cured at high temperatures for different times and analyzing the changes in compressive strength, it is possible to study the stability of the mechanical properties of cement paste at high temperatures. The stability of cement slurry at high temperature is shown in Figure 9.

![Figure 8](image)

**Figure 8.** Thickening time and water loss of cement slurries with different densities. (a) Thickening time; (b) Water loss.

![Figure 9](image)

**Figure 9.** Compressive strength of high-temperature-resistant and high-density anti-corrosion cement slurry.
It can be seen from Figure 9 that the compressive strength of the cement sample increases for curing times of up to three days and declines after three days of curing, but this decline is slight. This is mainly due to the influence of high temperature on the hydration products of oil well cement, and the high-temperature stabilizer is able to ameliorate the decrease in the strength of the cement sample. When the density of the cement slurry is higher, the compressive strength of the cement sample decreases for curing times of less than three days, but the compressive strength is less affected by temperature during long-term curing. After 28 days of curing, the compressive strength of cement sample decreases by less than 5.8% compared with the maximum strength of the cement sample. It can be considered that, through the design of the cement slurry, the high-density cement slurry has stable mechanical properties at high temperature. When the cement paste does not contain a high-temperature stabilizer of silica fume, and when it is subjected to temperatures higher than 110 °C, the painting product C₃S₂H₃ of the cement paste no longer remains stable, and will be transformed into a hydration product of lower-strength hydrated dicalcium silicate. At higher temperature, the crystallization degree of the hydration products of the cement slurry are limited, and the dehydration of the crystals further weakens the compressive strength of the cement paste. When adding a silicon powder stabilizer to the cement slurry, the silicon powder can react with the hydration products formed by the cement to obtain tobermorite and xonotlite with a C/S ratio close to 1, which changes the chemical composition of the cement paste and improves its strength, thereby preventing the decline in the strength of the cement paste.

4.3. Corrosion Performance

To evaluate the resistance of different high-density cement slurries to carbon dioxide and hydrogen sulfide, the corrosion performance of cement samples subjected to different lengths of time at high temperature was evaluated. Figure 10 shows the appearance of the corrosion depth of the cement slurry after being corroded for 30 days. As more manganese ore powder is added to the cement slurry, the cement slurry becomes reddish brown. When the cement slurry encounters phenolphthalein after being corroded, the color of the cement slurry becomes deeper. The corrosion depth of the cement sample can be measured from the corrosion morphology. Figure 11 shows the corrosion degree of the cement slurries under high temperature. With the increase in density, due to the increase in spherical manganese ore powder weighting agent and the decrease in alkaline Portland cement slurry, the corrosion depth of the cement slurry decreases, which is related to the density of the cement slurry. With increasing corrosion time, the corrosion depth increases. However, the growth range of the corrosion depth after 7 days is far greater than that after 30 days. This is mainly because the early stage of the corrosion mainly occurs on the surface of the cement slurry, and the acid gas can penetrate easily. With the extension of the corrosion time, the penetration depth of the acid gas increases, reducing the corrosion rate. The corrosion depth of cement slurries with different densities after being corroded for 30 days is less than 2 mm. Figure 12 shows the change in compressive strength of high-density cement slurry following different corrosion times. As the cement slurry is corroded under high temperature, the compressive strength of the cement slurry degrades. During the early stage of corrosion, the compressive strength of cement slurry decreases rapidly, which is related to the degree of corrosion. The compressive strength of the cement slurry with a density of 2.0 kg/m³ decreases the most after being corroded. When the cement slurry is corroded for 30 days, the compressive strength of 2.0 kg/m³ cement slurry decreases by 16.6% compared with that of non-corroded cement sample. This is the result of combining the decrease in strength of the cement sample under high temperature with the influence of corrosion on compressive strength. The designed high-density cement slurry has excellent corrosion resistance. The cement stone was corroded to a low degree, helping it to maintain good sealing quality in the well.
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Figure 10. Corroded appearance of cement sample.

Figure 11. Corrosion depth of high-density anti-corrosion cement slurry.

Figure 12. Compressive strength of cement samples with different corrosion times.
4.4. Micromorphology

In order to better analyze the anti-corrosion performance of the high-temperature and high-density cement slurry system, SEM was used to observe the microscopic morphology of the highest- and lowest-density cement slurry with and without a corrosion layer. As can be observed in Figures 13 and 14, there is no obvious crack defect in the cement slurry before corrosion, and the filling of ultra-fine weighted granular materials can be observed in the high-density cement slurry. The manganese ore powder weighting agent inside the cement slurry can still be observed after corrosion, but the structure of the cement slurry becomes obviously less dense than before corrosion. The internal pores of the cement sample increase, and the complete bonding structure of the cement stone is damaged. This is mainly due to the influence of corrosion on the hydration products of cement slurry, resulting in changes in the structure of the cement slurry and defects in the microstructure of cement slurry, which is not conducive to maintaining its integrity. The internal structure of the cement slurry with less corrosion is dense, and the performance of the cement sample is better.

![Figure 13. Morphology of 2.0 kg/m³ cement sample: (a) non-corroded; (b) corroded.](image1)

![Figure 14. Morphology of 2.3 kg/m³ cement sample: (a) non-corroded; (b) corroded.](image2)

5. Conclusions

1. The manganese ore powder weighting agent is spherical in shape, which can not only effectively improve the density of cement slurry, but also has little effect on the compressive strength. The high-temperature stabilizer is determined to be a mixture of silica fume with different particle sizes, and the performance of the high-temperature stabilizer is better when the proportion of 100 mesh: 300 mesh is equal to 25:75.

2. The designed slag and resin can effectively reduce the corrosion depth of cement slurry. Mixing inorganic material slag and organic polymer resin as the preservative of cement slurry can reduce the corrosion degree of cement slurry.

3. The rheology, water loss and thickening time of the designed high-temperature-resistant high-density anti-corrosion cement slurry are excellent, the water loss is
less than 50mL, and the thickening time is greater than four hours. The compressive strength of different high-density cement slurries is stable under high temperatures.

(4) After being corroded by hydrogen sulfide and carbon dioxide at high temperature, the designed oil well cement-based composite has low corrosion depth and strong corrosion resistance. The corrosion resistance of the cement slurry is effectively guaranteed by using manganese ore powder, multi-particle silicon powder, slag, and resin preservatives.

**Author Contributions:** Conceptualization, R.C. and F.Y.; Data curation, C.T., M.W. and F.Y.; Formal analysis, M.W. and R.C.; Investigation, C.T., M.W., R.C. and F.Y.; Methodology, C.T. and M.W.; Project administration, F.Y.; Supervision, R.C.; Validation, C.T.; Writing—original draft, C.T.; Writing—review and editing, M.W., R.C. and F.Y. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by Sinopec Key Laboratory of Cementing and Completion (grant number 35800000-22-ZC0607-0004).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data is contained within the article.

**Conflicts of Interest:** The authors declare no conflict of interest.

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