Study on the Preparation and Anti-CO₂ Corrosion Performance of Soap-Free Latex for Oil Well Cement

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ABSTRACT: To improve the resistance to CO₂ corrosion of oil well cement, soap-free emulsion polymerization was used to prepare a soap-free latex (PSAC) with sodium styrene sulfonate (SSS) and nano-SiO₂ (SSS/SiO₂) as the ionic copolymer emulsifier. The effects of SSS/SiO₂ on the performance, thermal stability, and latex particle morphology of the PSAC were investigated through zeta potential, TGA, and TEM measurements, respectively. The carbonation resistance properties of cement with PSAC were evaluated, and the anticorrosion mechanism of the PSAC cement was determined by SEM, EDS, XRD, and ²⁹Si NMR analyses. The results showed that the PSAC particle size was uniform, the particles were monodispersed, and they had a typical core−shell structure and good heat resistance. The carbonation resistance test results showed that after 60 days of corrosion, the corrosion depth of the cement with 12.0% PSAC content was only 2.16 mm, the permeability was 0.0018 mD, and the decrease in the compressive strength was 6.65%. The porosity in the cement was reduced significantly, and the pore volume (>50 nm) of the cement was reduced by 0.24 times. The PSAC film formation decreased the contact between hydration products and CO₂. In addition, the nano-SiO₂ in the PSAC reacted with Ca(OH)₂ to reduce the free Ca(OH)₂ content in the cement and generate C−S−H gel with a low Ca/Si ratio and high polymerization, which did not react as readily with CO₂.

1. INTRODUCTION

In recent years, the increasing attention has been paid to the corrosion of cement rings by downhole acid gases.¹⁻² There is a large amount of acidic CO₂ gas in marine carbonate reservoirs that corrodes and destroys cement rings in high-temperature, high-pressure, and high-humidity environments, causing the strength of the cement rings to decrease and the permeability to increase.³⁻⁴ The aggravation of the corrosion degree leads to cement mantle separation and induces fluid channeling or other accidents, which substantially shorten the production life of oil and gas wells and cause large economic losses.⁵⁻⁶ Therefore, to form high acid gas contents or wells implementing CO₂ flooding technology, the cement stone must have strong corrosion resistance. The results of previous studies showed that improving the compactness of cement could increase its resistance to a CO₂ attack.⁷⁻⁸ At present, the main method to increase the compactness of cement is to add a component with narrow size, such as silica powder and fly ash; the SiO₂ particles in these materials reduce the porosity of cement by filling pores and participating in the hydration reaction,⁹⁻¹⁰ but this method cannot fundamentally prevent the diffusion of CO₂ and CO₃²⁻ in cement and cause pore size coarsening in the cement stone after corrosion.¹¹⁻¹³ Practical experience and theoretical research have shown that the latex cement slurry system could improve the corrosion resistance of oil well cement through film formation.¹¹,¹² However, most of the latex on the market is styrene−butadiene latex and styrene−acrylic latex, which

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contain large amounts of emulsifiers. Cement stone with residual emulsifiers swell and soften after encountering water, and the strength is greatly weakened, which substantially impacts the sealing effect and corrosion resistance of the cement sheath.\textsuperscript{13,14} Soap-free latex polymerization uses only a trace amount of emulsifier or no emulsifier during the reaction process. Compared to the properties of conventional latex, soap-free latex has the advantages of a high solid content, good stability, and clean latex particles, which has aroused the interest of many researchers.\textsuperscript{15} In recent years, the study of soap-free latex has become a new research direction for oil well cement admixtures. Scholars\textsuperscript{16} have proven that soap-free latex could effectively improve the corrosion resistance of cement, and the film-forming characteristic of soap-free latex could hinder the acid medium contact with cement. There are series of complex chemical reactions in the process of CO\textsubscript{2} corrosion, but the above studies only studied the latex film characteristic and did not consider the chemical reaction of CO\textsubscript{2} corrosion; therefore, this single anticorrosion method indicated that the corrosion inhibition of the cement stone still had substantial room for improvement.

Nanosilica-latex is compounded from organic latex and inorganic nano-SiO\textsubscript{2}. Therefore, the nanosilica-latex has both characteristics of latex and SiO\textsubscript{2} and is also a rapidly developing field in polymer material science in recent years.\textsuperscript{17–21} On the basis of above analyses, in order to further improve the corrosion resistance of oil well cement, this study designed and synthesized soap-free latex (PSAC), which combined the advantages of SiO\textsubscript{2} and latex by using SSS and nano-SiO\textsubscript{2} (SSS/SiO\textsubscript{2}) as ionic copolymer composite emulsifiers and using styrene (St), butyl acrylate (BA), and methyl methacrylate (MMA) as monomers. In terms of the latex performance, nano-SiO\textsubscript{2} could improve the chemical stability and thermal stability of latex. In terms of anticorrosion performance, nano-SiO\textsubscript{2} could react with hydration products and improve the anticorrosion performance of cement in several ways. Then, PSAC was applied to the cement slurry to investigate its influence on the corrosion depth, compressive strength, permeability, and the pore size structure of well-bore cement in a corrosive CO\textsubscript{2} environment and to explore the corrosion prevention mechanism.

2. RESULTS

2.1. The Effects of SSS/SiO\textsubscript{2} on the Properties of the PSAC. The effects of the amount of SSS/SiO\textsubscript{2} on hydrophilicity, the particle size, and zeta potential of the PSAC particles were determined. The results are shown in Table 1.

As shown in Table 1, with the increasing SSS/SiO\textsubscript{2} dose, the average particle size of the polymer microspheres decreased, the absolute value and viscosity of the zeta potential increased, the contact angle of the latex film decreased (as shown in Figure 1),\textsuperscript{22–24} the stability of the latex increased gradually, and the appearance gradually tended to become milky white with blue light (as shown in Figure 2).

![Figure 1. Effect of SSS/SiO\textsubscript{2} on the contact angle of the PSAC.](https://dx.doi.org/10.1021/acsomega.0c02729)

The increase in the SSS/SiO\textsubscript{2} dose caused an increase in the initial nucleation number and monomer polymer number in the water phase, which resulted in a decrease in the polymer microsphere size and an increase in the viscosity. The decrease in the particle size led to an increase in the specific surface area of the particle microspheres and an increase in the number of sulfonic radicals per unit area. The zeta potential and hydrophilicity of the surface of the polymer microspheres were mainly provided by the sulfonic radical group, so the absolute value and viscosity of the zeta potential increased, the contact angle of the surface decreased, and the stability of the latex increased gradually.

2.2. FTIR Analysis of the PSAC. Figure 3 exhibits the FTIR spectra of the core, shell, and core-shell of the PSAC. Some of the major functional group peaks from the PSAC are as follows. All three parts of the spectra exhibited the characteristic stretching vibration peak of the \(\text{SO}_3^−\) group. The peak at 1084 \text{cm}^{-1} is also characteristic of the \(\text{SO}_3^−\) group. The peak at 980 \text{cm}^{-1} is a characteristic flexural vibration absorption peak of \(\text{Si}−\text{OH}\), and the peak at 805 \text{cm}^{-1} is the symmetric stretching vibration peak of \(\text{Si}−\text{O}\) in SiO\textsubscript{2}. The reason for the above phenomena is the presence of SSS and SiO\textsubscript{2} in both the nucleus and shell monomers. Since there was styrene (St) in the nuclear monomer, the characteristic diffraction peak of \(\text{C}−\text{C}\) of the benzene ring in St appeared at 1638 \text{cm}^{-1} in the spectrum of the nuclear part. Similarly, since there was MMA in the shell monomer, the characteristic diffraction peak of \(\text{C}−\text{O}−\text{C}\) in MMA appeared at 1460 \text{cm}^{-1} in the spectrum of the shell part. Furthermore, the vibration absorption band of \(\text{C}−\text{C}−\text{C}−\) (approximately at 1665 \text{cm}^{-1}) was not found in the three spectra, indicating that all the reaction monomers were fully polymerized.

2.3. The Thermal Stability of the PSAC. The TGA and differential thermogravimetric (DTG) curves of the PSAC are shown in Figure 4. The initial thermal decomposition temperature of the PSAC with the 1.0% SSS/SiO\textsubscript{2} composite emulsifier was approximately 224.69 °C, and the total heat loss
was approximately 64% at 350 °C. The initial thermal decomposition temperature of the PSAC with the 2.0% SSS/SiO2 composite emulsifier increased to 237.02 °C, and the total heat weight loss was approximately 60% at 350 °C.

This might be because nano-SiO2 had excellent thermal stability, and its thermal performance was better than that of a small molecular emulsifier. With an increase in the total polymerization, more nano-SiO2 was polymerized in the polymer chains. On the one hand, the heat conduction was hindered during the pyrolysis process and delayed the degradation rate of the latex. On the other hand, nano-SiO2 increased the molecular chain bending, rotating and moving resistances, limited the motion of the polymer segments, and improved the fracture energy; thus, to a certain extent, the thermal decomposition of the molecular chain was hindered, which improved the temperature resistance of the PSAC.

2.4. TEM of the PSAC. Figures 5 and 6 show the TEM images and the particle size distribution of PSAC with a mass fraction of 0.4%.

By comparing Figures 5 and 6, it could be seen that when the amount of emulsifier was 1.0%, latex particles varied in size and were irregular in shape, and the particle size distribution was wide. The median particle size was approximately 254.42 nm, and the average particle size was approximately 480.62 nm. When the amount of emulsifier increased to 2%, the number of fine particles in the latex increased, the latex particle shape was a regular circle, and the particle size distribution narrowed obviously. The median particle size was approximately 220.67 nm, and the average particle size was approximately 408.45 nm. The appearance from above was consistent with that described in Table 1.
The hydrophilicity of the latex particles increased with an increase in the emulsifier dose of SSS/SiO$_2$; the process of latex polymerization was controlled by the mechanism of homogeneous nucleation, and the “secondary nucleation” trend in the whole latex polymerization process increased. Therefore, the latex particle size decreased with increasing the emulsifier dose; moreover, the particle size became concentrated. In addition, the latex had an improved dispersion and stability.

2.5. Evaluation of the CO$_2$ Corrosion Resistance of the PSAC Cement Slurry System. 2.5.1. Carbonation Depth. The cross-sectional and optical microscopy pictures of the blank cement stone and the PSAC cement after 30 days of corrosion are shown in Figure 7, and the corrosion depth of the cement stone after 60 days of CO$_2$ corrosion is shown in Figure 7, and the corrosion depth of the blank cement stone was corroded very obviously, but the corrosion degree of the cement stone with 6 and 12.0% PSAC increased to 4.38 and 2.16 mm, respectively, and the rate of the corrosion depth increased by 32.36 and 72.75% for the cement stone with 6 and 12.0% PSAC, respectively. After 60 days of carbonation corrosion, the corrosion depth of the cement stone was 11.26, and the decreasing rates of the cement stone decreased less obviously than the blank cement stone. With an increase in the latex dose, the compressive strength of the latex cement stones decreased, but the compressive strength of the cement stones decreased, but the compressive strength of the cement stone increased gradually and was higher than that of the blank cement stone. When curing in a saturated CO$_2$ water solution, the compressive strength of the two kinds of cement stones appeared to rise first and then decrease. With the prolonged carbonization time for the first 14 days, the compressive strength of the cement stone increased gradually and was higher than that of the cement stone that underwent normal water bath curing. When the carbonization time was longer than 14 days, the compressive strength of the two cement stones decreased, but the compressive strength of the latex cement stones decreased less obviously than the blank cement stones. With an increase in the latex dose, the decreasing trend of the strength of the cement stone was smaller. After 60 days of carbonation corrosion, the compressive strength degradation rate of the blank cement stone was 11.26, and the decreasing rates of the cement stone with 6 and 12% PSAC were 8.75 and 6.65%, respectively. The above phenomena indicated that the latex cement stone effectively slowed the severe strength deterioration of the cement stone in an acid medium, and the corrosion inhibition of the latex cement stone was better than that of the blank cement stone.

2.5.2. Compressive Strength. The corrosive effect of CO$_2$ on oil well cement is mainly due to the chemical action of CO$_2$ dissolved in pore water and the alkaline hydration products in the cement paste that change the composition and microstructure of the hydration products, which further affect the normal development of the compressive strength of the cement stone. Therefore, the development of the compressive strength of the cement stone after certain corrosion conditions could reflect the corrosion resistance of the cement stone to a certain extent. The development of the compressive strength in the blank cement stone and latex cement stone in different curing environments is shown in Figure 8. The letter A represents the normal water bath curing, and B represents the corrosion resistance of the cement stone to a certain extent.

| Table 2. Carbonation Depth of the Cement Stones (Unit: mm) |
|---------------------------------|---------------------|-------------------|-------------------|
| Corrosion time (d) | Blank cement | Cement with 6.0% PSAC | Cement with 12.0% PSAC |
| 7 | 0.36 | 0.00 | 0.00 |
| 14 | 1.83 | 0.72 | 0.48 |
| 30 | 4.11 | 2.78 | 1.12 |
| 60 | 7.26 | 4.38 | 2.16 |

As shown in Figure 8, under the condition of water bath curing, the compressive strength of the two kinds of cement stone showed a trend of rapid development during the early stage and a steady trend at the later stage, and the compressive strength of the latex cement stone was higher than that of blank cement stone. When curing in a saturated CO$_2$ water solution, the compressive strength of the two kinds of cement stones appeared to rise first and then decrease. With the prolonged carbonization time for the first 14 days, the compressive strength of the cement stone increased gradually and was higher than that of the cement stone that underwent normal water bath curing. When the carbonization time was longer than 14 days, the compressive strength of the two cement stones decreased, but the compressive strength of the latex cement stones decreased less obviously than the blank cement stones. With an increase in the latex dose, the decreasing trend of the strength of the cement stone was smaller. After 60 days of carbonation corrosion, the compressive strength degradation rate of the blank cement stone was 11.26, and the decreasing rates of the cement stone with 6 and 12% PSAC were 8.75 and 6.65%, respectively. The above phenomena indicated that the latex cement stone effectively slowed the severe strength deterioration of the cement stone in an acid medium, and the corrosion inhibition of the latex cement stone was better than that of the blank cement stone.
2.5.3. Porosity. Pores in the cement stone with different sizes provided channels for CO₂ and other corrosive media to penetrate the material. However, studies by Lian et al. indicated that the permeability of corrosive fluids through gel holes is very small, and the permeability of cement paste is mainly determined by transition holes and rough holes. Therefore, to study the effect of the latex on the pore structure in the cement stone, the porosity and pore size distribution in the blank cement stone and latex cement stone after corrosion were investigated.

As shown in Figure 9, the porosity in the uncorroded latex cement stone was significantly lower than that of the blank cement stone, and the initial permeability of the blank cement stone was 12.53%, while the porosity in the cement stones with 6 and 12% PSAC was 9.65 and 8.32%, respectively. With an extended corrosion time, the porosity in the two kinds of cement stones after CO₂ corrosion first decreased and then increased. After 14 days of curing in a corrosive environment, the porosity in the blank cement stone decreased to 11.04%, and the porosity in the cement stone with 6 and 12% PSAC decreased to 8.61 and 7.52%, respectively. After 60 days of corrosion, the porosity in the blank cement stone increased to 14.54%, while the porosity in the cement stone with 6 and 12% PSAC increased to 10.78 and 8.55%, respectively.

The main reason for the above phenomena is that at the early stage of carbonization, calcium hydroxide in pore water in the cement stone and CO₂ reacted to form calcium carbonate precipitates that filled in the pores in the cement stone and decreased the porosity. During the latter stage of carbonization corrosion and the continuous dissolution of CO₂, the reaction between calcium carbonate and CO₂ produced water-soluble calcium bicarbonate, and the continuously dissolved calcium bicarbonate led to an increased porosity in the cement stone. For the latex cement stone, the filling and film formation of the latex particles inhibited the sustained effect of the calcium carbonate and CO₂ to slow the increase in the porosity of the cement. In addition, nano-SiO₂ promoted the hydration of the cement, generated large amounts of Ca(OH)₂ gel, and decreased the porosity inside the cement matrix. After 60 days of corrosion, compared with the initial number of pores, the pores with a size of over 50 nm in the blank cement stone increased by 0.98 times, while those in the 12% latex cement stone decreased by 0.24 times. The number of pores with a size of less than 50 nm increased by 0.68 times.

In conclusion, the porosity and pore size in the blank cement stone after CO₂ corrosion increased. The number of pores larger than 50 nm increased obviously. However, the latex effectively reduced the porosity and pore size in the cement stone, and the proportion of pores smaller than 50 nm increased slightly. Academician Zhongwei Wu suggested that by reducing harmful pores larger than 100 nm or increasing less harmful and harmless pores smaller than 50 nm, the durability and corrosion resistance of the cement-based materials could be improved.

3. DISCUSSION

3.1. Study of the Mechanism of CO₂ Corrosion. The clinker composition and the changes in the type of hydration products in the cement are shown in Table 3.

![Figure 9. Porosity and pore size distribution of the carbonized cement stone.](image)

Table 3. Composition and the Reaction Process of the Cement Clinker

| Clinker composition | Chemical formula of the clinker | Relative content | Hydration products |
|--------------------|-------------------------------|----------------|------------------|
| C₃S                | 3CaO·SiO₂                      | 50−60%         | Ca(OH)₂          |
| C₂S                | 2CaO·SiO₂                      | 20%            | Ca(OH)₂          |
| C₃A                | 3CaO·Al₂O₃                    | 5−15%          | Ca₆Al₆(OH)₁₄.₃SiO₂ |
| C₃S                | 3CaO·Al₂O₃·3SiO₂·3H₂O(Al₂(OH)_₆) |                |                  |
| C₃A                | 3CaO·Al₂O₃·3SiO₂·3H₂O(Al₂(OH)_₆) |                |                  |

Among them, the total proportion of C₃S and C₂S was 80% of the total amount of cement clinker. Therefore, a large amount of calcium hydroxide (Ca(OH)₂) was generated during cement hydration, as shown in Figure 10a. It can also be seen that a mass of Ca(OH)₂ filled in the holes of the cement stone. Carbon dioxide reacted readily with calcium hydroxide to form calcium carbonate (as shown in Figure 10b). During this process, CO₂ reacted with Ca(OH)₂, resulting in an increase in the number of pores and an open structure in the cement. At the same time, the porous structure also provided a channel for the penetration of CO₂, thus accelerating the corrosion process.

In general, the process of corrosion can be expressed by the following reactions:

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \tag{1}
\]

\[
\text{Ca(OH)}_2 + \text{H}^+ + \text{HCO}_3^- \rightarrow \text{CaCO}_3 + 2\text{H}_2\text{O} \tag{2}
\]

\[
\text{C}–\text{S}–\text{H} + \text{H}^+ + \text{HCO}_3^- \rightarrow \text{CaCO}_3 + x\text{SiO}_2\cdot y\text{H}_2\text{O} \tag{3}
\]

\[
\text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3 \rightarrow \text{Ca(HCO}_3)_2 \tag{4}
\]

\[
\text{Ca(HCO}_3)_2 + \text{Ca(OH)}_2 \rightarrow 2\text{CaCO}_3 + 2\text{H}_2\text{O} \tag{5}
\]

In general, the main reasons for the extensive cement corrosion by CO₂ are as follows. First, the porous structure of the cement provided an easy way for the CO₂ to penetrate the cement. Second, the CO₂ reacted with Ca(OH)₂ and C–S–H, resulting in an increase in the number of pores in the cement and an open structure.

At low temperatures, the hydration products in the cement were mainly Ca(OH)₂, ettringite (Aft), and amorphous C–S–
H₂ such as C₂SH₂ and C₆S₂H₃. When the temperature exceeded 110 °C, the hydration products were mainly C₂SH and tobermorite (C₅S₆H₅), and when the temperature rose above 150 °C, xonotlite (C₆S₆H) appeared. Literature reports³¹,³² showed that the standard Gibbs free-energy of the reaction between each hydration product mentioned above and HCO₃⁻ was less than 0, and the standard Gibbs free-energy of the reaction between Ca(OH)₂ and HCO₃⁻ was the smallest, which indicated that CH was most likely to react with CO₂. In other words, Ca(OH)₂ reacted with CO₂ first. In addition, Revertegat et al.³³ pointed out that Ca(OH)₂ could be stable only when the pH value of the solution is greater than 12.23, and C−S−H could be stable when the pH value is greater than 10.40, and the results also proved that Ca(OH)₂ reacts with CO₂ first.

3.2. Proposed Anti-Corrosion Mechanism. Based on the above analysis, we propose approaches to improve the corrosion resistance of cement, as follows:

Since hydration products, such as CH, C−S−H and Aft, could react with CO₂, reducing exposure between the hydration products and CO₂ as much as possible would improve the CO₂ corrosion resistance of cement. Second, as mentioned, Ca(OH)₂ is the first hydration product to react with CO₂;³⁴ therefore, reducing the content of free Ca(OH)₂ in cement slurries or forming C−S−H, which does not react as readily with CO₂, would also improve the CO₂ corrosion resistance of cement.

In addition, the results of a previous study showed that hydration products with low CaO/SiO₂ (Ca/Si) ratios were less likely to react with CO₂ than hydration products with high Ca/Si ratios.³⁶ Therefore, promoting the formation of hydration products with a low Ca/Si ratio would improve the CO₂ corrosion resistance of cement.

3.2.1. SEM Analysis. The SEM images of the blank cement and PSAC latex cement after 30 days of corrosion are shown in Figure 11.

As shown in Figure 11, the surface of the blank cement was rough, and holes and gelatinous hydration products could be clearly observed. However, the surface of the PSAC cement was smooth, and the latex film covered the pore structure and hydration products. Therefore, the film formation due to the PSAC latex could effectively reduce the contact between hydration products and CO₂ and improve the corrosion resistance of cement.

3.2.2. XRD Analysis. The hydration products in the blank cement and PSAC cement before corrosion are shown in Figure 12a, and the hydration products of the two kinds of cement after 30 days of corrosion are shown in Figure 12b. The dose of PSAC in the experiment was 12%.

In Figure 12a, CH, C₂SH₂, and C₆S₂H₃ diffraction peaks appeared in the XRD spectra for the two kinds of cement; however, the SiO₂ diffraction peak appeared in the spectrum for the PSAC cement, and the CH diffraction peak intensity in the PSAC cement was lower because of the reaction between CH and SiO₂. Figure 12b shows that after 30 days of corrosion, obvious CaCO₃ characteristic diffraction peaks appeared in the blank cement, while the characteristic peaks of CH, C₂SH₂, and C₆S₂H₃ decreased significantly, indicating that CH, C₂SH₂, and C₆S₂H₃ were consumed by CO₂. Compared with that of the blank cement, the CaCO₃ diffraction peak also existed in
the PSAC cement, but the content of CH was less and a new hydration product, $\text{C}_2\text{S}_2\text{H}_3$, appeared in the PSAC cement as the result of the participation of SiO$_2$ in the hydration reaction. The above results indicated that the PSAC could reduce the content of free Ca(OH)$_2$ in cement slurries to form additional $\text{C-S-H}$ gel that does not react as readily with CO$_2$. The lower the content of CH is, the greater the content of $\text{C-S-H}$, and the better the corrosion resistance of the cement, which corresponds to previous research results.$^{37,38}$

3.2.3. 29Si NMR Analysis. To further investigate the changes in silicate moieties in the PSAC cement before and after corrosion, $^{29}$Si NMR analysis was conducted. $Q^1$ (δ = −68 to −76 ppm) represents an isolated [SiO$_4$]$^{4-}$ tetrahedron; $Q^2$ (δ = −76 to −82 ppm) indicates the [SiO$_4$]$^{4-}$ tetrahedron in a dimer or at the end of a straight chain in high polymers; and the [SiO$_4$]$^{4-}$ tetrahedron in the middle of the linear chain is indicated by $Q^2$ (δ = −82 to −88 ppm). Since C−S−H structures are chains, the average chain length (&) of the C−S−H chains can be expressed by the formula$^{39}$

$$
&) = 2 \times \frac{I(Q^1) + I(Q^2)}{I(Q^2)}
$$

where $I(Q^1)$ and $I(Q^2)$ are the integral intensities of the signals $Q^1$ and $Q^2$, respectively, and are calculated by the integral percents from the fitted $^{29}$Si NMR spectra. The $^{29}$Si NMR analysis results of the PSAC cement and blank cement are shown in Figure 13. Table 4 shows the test results of the average chain length (&).
Table 4 shows that the quantity of [SiO₄]⁴⁻ tetrahedron in the middle of the linear chain (Q²) and the average chain length (\&) of the PSAC cement were more than those of blank cement regardless of whether the CO₂ corrosion time was 0 d or 30 d, which indicates the higher polymerization degree of the C−S−H chains in the PSAC cement. The amount of isolated [SiO₄]⁴⁻ tetrahedron (Q⁰) in the PSAC cement was less than that in the blank cement, which meant that more C₃S and C₂S were consumed in the PSAC cement.30 The above results showed that there were more highly polymerized C−S−H chains in the PSAC cement, which was due to the involvement of SiO₂ in the PSAC in the hydration reaction.

3.2.4. Ca/Si Ratio Analysis of the Hydration Products. The addition of SiO₂ to cement was conducive to the formation of hydration products with a low Ca/SiO₂ ratio, which had better corrosion resistance than the hydration products with a high Ca/SiO₂ ratio.25 EDS spectra from the blank cement and PSAC cement are shown in Figure 14a,b, respectively.

From Figure 14a, it can be determined that the Ca/Si atomic ratio for the blank cement was 23.07:11.73, which is close to 2:1. Figure 14b revealed that the Ca/Si atomic ratio of the PSAC cement was 25.2:18.81, which is approximately equal to 1.34:1. Since H could not be tested by EDS, the Ca/Si ratio (1.34:1) is close to the chemical formula of C₃S₂H₃ for the PSAC cement, as mentioned in Figure 12b. The above results indicated that the Ca/Si ratio of the hydration products in the PSAC cement was lower, which meant that SiO₂ in the PSAC could promote the formation of hydration products with a low Ca/Si ratio. Combined with the results in Figure 13, it could be seen that the hydration products (C−S−H) in the PSAC cement had a higher degree of polymerization and a lower Ca/Si ratio. More importantly, prior studies reported that a lower Ca/Si ratio promoted higher polymerized C−S−H chains, which corresponds with the above results.41,42

| CO₂ corrosion time (d) | samples | I(Q⁰) (%) | I(Q¹) | I(Q²) | \& |
|------------------------|---------|-----------|-------|-------|-----|
| 0                      | blank cement | 33.25 | 40.23 | 26.52 | 3.32 |
|                        | PSAC cement  | 20.25 | 42.66 | 37.09 | 3.74 |
| 30                     | blank cement | 22.05 | 42.98 | 34.97 | 3.63 |
|                        | PSAC cement  | 17.87 | 41.77 | 40.36 | 3.93 |

4. CONCLUSIONS

In this work, soap-free latex (PSAC) was synthesized, and its basic properties and microstructures were characterized. In addition, the CO₂ corrosion inhibition of PSAC cement was determined by carbonation depth, porosity, and strength experiments, and the corrosion prevention mechanism of the
PSAC latex cement was studied by SEM, XRD, EDS, and \(^{29}\)Si NMR. The following conclusions can be drawn:

1. With an increase in the emulsifier (SSS/SiO\(_2\)), the absolute value of the zeta potential, the hydrophilicity, and the stability of PSAC increased gradually. FTIR spectra shows that the monomers were completely polymerized, and TG analysis indicated that PSAC had excellent heat resistance. The TEM analysis revealed that the latex particles had good microsphere morphology and a typical core–shell structure, and the particle size distribution was narrow.

2. The results of the carbonation depth, compressive strength, and porosity measurements show that PSAC effectively improved the resistance to CO\(_2\) corrosion for the cement.

3. The film formation of the PSAC reduced the initial permeability and porosity in the cement but also reduced the contact between hydration products and CO\(_2\). Thus, the nano-SiO\(_2\) in the PSAC consumed free Ca(OH)\(_2\) and generated an increased number of polymerized C–S–H chains, which did not react as readily with CO\(_2\). EDS proved that the SiO\(_2\) in the PSAC promoted the formation of hydration products with low Ca/Si ratios.

5. EXPERIMENTAL METHODS

5.1. Materials. Styrene (St), methyl methacrylate (MMA), ammonium persulfate (APS), butyl acrylate (BA), sodium hydroxide (NaOH), sodium bicarbonate (NaHCO\(_3\)), sodium p-styrene sulfonate (SSS), silane coupling agent KH-570, nano-SiO\(_2\), and silica fume were purchased from Kelong Chemical Co., Ltd (Chengdu, China). The grade G cement (Sichuan, Jiahua Cement Factory), dispersant SXY, water loss reducer SZ1-2 and defoamer were purchased from Chengdu Chuanfeng Chemical Engineering Co., Ltd (Chengdu, China).

5.2. Preparation of the Soap-Free Latex (PSAC). A certain amount of nano-SiO\(_2\) was activated at 100 °C for 24 h and added to 100 mL ethanol. After ultrasonic dispersion for 30 min, the silane coupling agent KH-570 was added, and then after a process of continuous ultrasonic dispersion, the mixed solution was placed into a 250 mL four-necked flask, and the reaction lasted for 3 h at 60 °C. After the mixture was cooled to room temperature and centrifuged several times, the obtained white powder was put into a vacuum drying oven to room temperature and centrifuged several times, the obtained white powder was put into a vacuum drying oven until it reached a constant mass. The modified nano-SiO\(_2\) was obtained.

Soap-free latex (PSAC) was prepared by seed latex polymerization. Distilled deionized water (45 mL), 0.14 g SSS, 0.28 g modified nano-SiO\(_2\), 7.65 g St, and 2.35 g BA (the mass was 1/3 of the core monomer) were placed into the 250 mL four-necked flask, and APS aqueous solution (5 mL) was added at 90 °C, and then the reaction mixture was incubated at 90 °C for 12 h. The size distribution was narrow.

5.3. Characterization and Evaluation Methods. After demulsification, washing, and drying of the PSAC, the samples were characterized by infrared spectroscopy using a WQF-520 Fourier transform infrared spectrometer, and the thermal stability was investigated utilizing differential thermogravimetry (DTG) and thermogravimetry (TG).

The latex was diluted with deionized water into a mass fraction of 0.4% aqueous solution. The mean particle size and zeta potential were measured. The structure of the latex was characterized by TEM.

The cement slurry with PSAC was prepared according to the standard of API specifications. Various cement slurries with the compositions listed in Table 5 were mixed with water at a liquid–solid ratio of 0.44.

| Table 5. Composition of the Prepared Cement Samples |
|-----------------------------------------------|
| sample | G class oil cement | freshwater | PSAC | SZ1-2 | SXY | defoamer |
| blank cement | 100.0 | 44.0 | 0.0 | 1.0 | 0.3 | 0.05 |
| PSAC cement | 100.0 | 44.0 | 60.0/12.0 | 1.0 | 0.3 | 0.05 |

After three days of constant pressure curing at 90 °C, the cement samples were put into a high-temperature and high-pressure curing autoclave to proceed with the carbonization corrosion test for 7, 14, 30, and 60 days. The curing temperature was 90 °C, and the pressure was 10 MPa (the N\(_2\) pressure was 7.0 MPa and the CO\(_2\) pressure was 3.0 MPa).

The specimens were used to measure the compressive strength, permeability, corrosion depth, pore size distribution, and microstructure of the cement stone. Moreover, after a CO\(_2\) corrosion period of 30 days, scanning electron microscopy was used to observe the surface of the blank cement and PSAC cement, X-ray diffraction was used to analyze the hydration products in the blank cement and PSAC cement, and \(^{29}\)Si solid-state nuclear magnetic resonance was applied to study the chemical environment of the Si element and the structure in the blank cement and PSAC cement.

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Notes
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