

Article

Application Research of TA-LDHs Intercalated Retarder Modified Ultra-Fine Cement in Casing Damage Remediation of CCUS Injection-Production Wells

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Abstract

For casing damage phenomena including casing corrosion, rupture, and seal failure that frequently occur in carbon capture, utilization, and storage (CCUS) injection-production wells under long-term gas injection and pressure fluctuations, combined with the characteristics of ultra-fine cement slurry such as concentrated hydration heat release and vulnerability to acidic environment corrosion, this study synthesized tartaric acid-intercalated Mg-Al layered double hydroxides (TA-LDHs) through ion-exchange reaction as a functional retarder, and focused on screening the water–cement ratio as well as the dosages of fluid loss additive and dispersant suitable for CCUS working conditions. The results demonstrate that at a water–cement ratio of 0.7 with 1.5% fluid loss additive TSJ-1, 0.4% dispersant FSJ-1, and 0.2% TA-LDHs retarder, the cement slurry presents excellent rheological properties, a short thickening transition time, and remarkable resistance to acidic environment erosion. Plugging performance evaluations reveal that under simulated formation water conditions, the system maintains a breakthrough pressure gradient above $90.5 \text{ MPa} \cdot \text{m}^{-1}$ and a plugging efficiency of more than 99%, and after 30 days of curing, its compressive strength reaches 29 MPa while the plugging efficiency is improved to 99.37%. Furthermore, after exposure to CO_2 -saturated simulated formation brine at 80°C and 20 MPa for 30 days, the TA-LDHs-modified cement exhibited a compressive strength of 27.0 MPa and a strength retention of 93.1%, while its permeability increased by only 23.1%. In comparison, the compressive strength retention of the control cement was 80.8%, and its permeability increased by 138.5%. These results indicate that the TA-LDHs-modified ultra-fine cement possesses favorable plugging performance and improved resistance to CO_2 -induced degradation, showing potential for casing damage remediation in CCUS wells.



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Keywords: CCUS; casing damage remediation; ultra-fine cement; lost circulation material

1. Introduction

With the advancement of the “dual carbon” strategy, carbon capture, utilization, and storage (CCUS) technology have become key paths to achieve the carbon neutrality goal. During the operation of CCUS injection-production wells, due to long-term injection of high-pressure CO_2 and frequent pressure fluctuations, wellbore casings face severe challenges. The acidic environment formed by the dissolution of CO_2 in formation water can easily

lead to corrosion and debonding of the cement sheath, which in turn causes casing damage phenomena such as casing rupture, deformation, and seal failure [1–4]. Once the wellbore seal integrity is lost, it will result in CO₂ leakage, posing serious environmental risks.

As a commonly used lost circulation material, ultra-fine cement has the advantages of high strength and low permeability; however, its hydration reaction rate is fast, and hydration heat is concentrated. In scenarios such as CCUS wells that require extremely high long-term sealing performance, they are prone to microcracks, and ordinary cement stone cannot resist the long-term erosion of acidic fluids.

In 2018, there were more than 2400 casing-damaged wells in Changqing Oilfield, including over 2000 oil production wells and more than 400 water injection wells [5]. Casing damage in oil and water wells has become a difficult problem plaguing the global oil and gas development industry. To ensure the continuous development and production of oilfields, it is necessary to promptly and effectively plug and reinforce damaged casings after casing damage occurs. In 2019, Han Guangming et al. [6] developed a micro-expansive plugging slurry, which has better plugging strength and temperature resistance compared with ordinary cement slurry. Application in 25 casing-damaged wells showed that the success rate of this technology was over 96%. In 2020, Li Xiumei et al. [7] added a nitrogen expansive agent to the ultra-fine cement slurry, which not only reduced the permeability of the cement stone but also improved the interface bonding strength and extended the service life, with a 100% on-site construction success rate. In 2022, Xue Fenglong [8] constructed an ultra-fine tough cement slurry with ultra-fine cement as the main component. After using this system for plugging construction in a well in the Jiaoshi Work Area, the formation water absorption and leakage were significantly reduced, the pressure-bearing capacity of the leakage point was greatly improved, and the plugging effect was remarkable.

Ultra-fine cement is obtained by deep processing of ordinary Grade G oil well cement, with good rheological properties and stability. Its strength is 70% to 90% higher than that of conventional cement. Because of its small particle size, it can better penetrate into the microcracks and pores of the formation, and at the same time enhance the skeleton stress of the formation rock to achieve the plugging effect [9]. Due to the fast hydration rate of ultra-fine cement, to ensure construction safety, it is necessary to ensure that the ultra-fine cement slurry has good rheological properties and controllable thickening time; therefore, it is necessary to add a retarder to the ultra-fine cement slurry system [10–12]. For this reason, this study aims to develop a new type of plugging system suitable for CCUS working conditions. By introducing the TA-LDHs intercalated retarder, it not only regulates the hydration process of ultra-fine cement but also uses the “barrier effect” of its layered structure to improve the corrosion resistance and impermeability of the material. In this study, the dosage of each admixture was optimized, and the plugging performance of the developed system was evaluated under different salinities, curing times, and injection volumes. In addition, the durability of the optimized cement system was investigated in CO₂-saturated simulated formation brine under elevated temperature and pressure by monitoring the changes in compressive strength, permeability, mass, carbonation depth, and microstructure.

2. Experimental

2.1. Materials and Instruments

The raw materials and chemical reagents used in this study are listed in Table 1. Ultra-fine Portland cement was used as the main cementitious material, while JSJ-1 fluid loss additive and FSJ-1 dispersant were used to regulate the filtration loss and dispersion behavior of the cement slurry. Other analytical-grade reagents, including tartaric acid,

magnesium nitrate hexahydrate, sodium hydroxide, and ethylene glycol, were used for slurry preparation and chemical regulation.

Table 1. Materials.

No.	Material	Grade	Supplier
1	Ultra-fine portland cement	Industrial grade	Sichuan Jiahua Cement Co., Ltd., Leshan, China
2	JSJ-1 fluid loss additive	Industrial grade	Henan Weihui Chemical Co., Ltd., Weihui, China
3	FSJ-1 dispersant	Industrial grade	Chengdu Chuanfeng Chemical Engineering Co., Ltd., Chengdu, China
4	Tartaric acid	Analytical grade	Chengdu Kelon Chemicals Co., Ltd., Chengdu, China
5	Magnesium nitrate hexahydrate	Analytical grade	Chengdu Kelon Chemicals Co., Ltd.
6	Sodium hydroxide	Analytical grade	Chengdu Kelon Chemicals Co., Ltd.
7	Ethylene glycol	Analytical grade	Chengdu Kelon Chemicals Co., Ltd.

The main instruments used for sample preparation, performance evaluation, and microstructural characterization are summarized in Table 2. The magnetic stirring water bath and constant-temperature water bath were used for slurry preparation and curing, whereas the scanning electron microscope, infrared spectrometer, and X-ray diffractometer were used to characterize the microstructure and chemical composition of the cement-based samples.

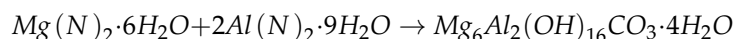
Table 2. Instruments.

No.	Model	Instrument	Manufacturer
1	HH-6	Single-row digital display constant temperature magnetic stirring water bath	Jintan Baita Hengbao Glass Instrument Department, Changzhou, China
2	KYKY-EM6900	Scanning electron microscope	Beijing Zhongke Keyi Co., Ltd., Beijing, China
3	WQF520	Infrared spectrometer	Beijing Rayleigh Analytical Instrument Co., Ltd., Beijing, China
4	DX-2700	X-ray diffractometer	Dandong Haoyuan Instrument Co., Ltd., Dandong, China
5	OWC-1080B	Constant temperature water bath	Shenyang Petroleum Instrument Research Institute Co., Ltd., Shenyang, China
6	NYL-300	Pressure testing machine	Wuxi Building Materials Instrument Machinery Co., Ltd., Wuxi, China
7	DFC-0710B	Pressurized consistometer	Shenyang Jinouke Petroleum Instrument Technology Development Co., Ltd., Shenyang, China
8	TST101A-1B	Electric heating forced-air drying oven	Chengdu Test Instrument Co., Ltd., Chengdu, China

2.2. Synthesis of TA-LDHs Intercalated Retarder

First, the magnesium–aluminum layered double hydroxide precursor was prepared by the co-precipitation method [13]. Magnesium nitrate hexahydrate and aluminum nitrate nonahydrate were weighed according to a molar ratio of Mg to Al of 3:1 and added to deionized water to prepare a 200 mL mixed salt solution. Sodium hydroxide and sodium

carbonate were weighed according to a molar ratio of 4:1 and added to deionized water to prepare a 200 mL alkali solution. The prepared mixed salt solution and alkali solution were simultaneously added dropwise into a three-necked flask; the reaction temperature was maintained at 75 °C; the dropping rate of the alkali solution was kept at one drop every two seconds; and the pH of the solution was maintained between 9 and 10. After reflux crystallization at 75 °C for 5 h, the mixture was filtered by suction and washed with water three times, then dried at 80 °C for 20 h to obtain carbonate-intercalated magnesium–aluminum layered double hydroxides (Mg/Al-CO₃-LDHs), which were used as the precursor for later use. The reaction equation is as follows:



Based on previous experimental work, the optimal conditions for the preparation of tartaric acid-intercalated layered double hydroxides have been determined, and the preparation method is as follows: The tartaric acid-intercalated layered double hydroxide retarder (TA-LDHs) was prepared by the ion exchange method. Tartaric acid was dissolved in ethylene glycol solution and added to a three-necked flask, and the pH was adjusted to about 4.5 with 0.1 mol/L NaOH solution. Then, the precursor was weighed according to a molar ratio of tartaric acid to the layered double hydroxide precursor of 2:1 and added to the three-necked flask. The pH of the solution was measured and maintained at 4.5 with 0.1 mol/L NaOH. After crystallization in an oil bath at 150 °C for 5 h, the mixture was naturally cooled, filtered by suction, washed with deionized water until the pH of the filtrate was neutral, and the filter cake was vacuum-dried at 80 °C for 12 h to obtain tartaric acid-intercalated magnesium–aluminum layered double hydroxides (Mg/Al-TA-LDHs), denoted as TA-LDHs. After tartaric acid is intercalated into magnesium–aluminum layered double hydroxides through an ion exchange reaction, the schematic diagram of the increased interlayer spacing of layered double hydroxides is shown in Figure 1. The yellow bidirectional arrows indicate the migration and diffusion of interlayer species during the ion-exchange process.

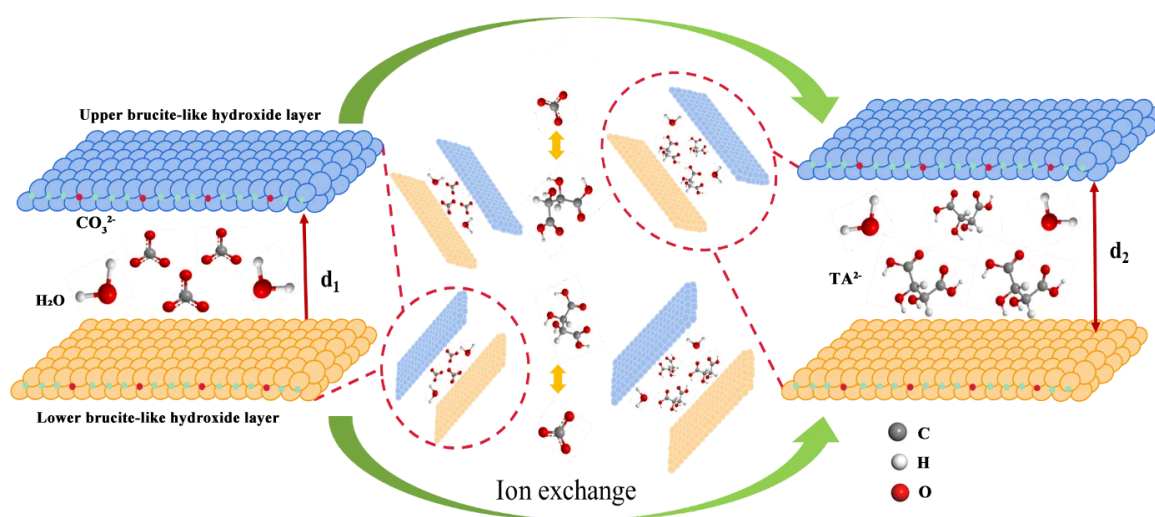


Figure 1. Schematic diagram of the ion exchange reaction between tartaric acid and layered double hydroxides.

2.3. Instrumental Characterization Procedures for the TA-LDHs Intercalated Retarder

Fourier transform infrared spectroscopy, X-ray diffraction, and scanning electron microscopy were carried out on the magnesium–aluminum layered double hydroxide precursor and the tartaric acid-intercalated layered double hydroxide retarder prepared

in the previous section, respectively. The test results were analyzed to determine whether the ion-exchange reaction occurred, whether the intercalation was satisfactory, and to characterize the structure of the retarder.

2.4. Optimization of Admixture Dosage for Ultra-Fine Cement Plugging System

2.4.1. Determination of the Optimum Water–Cement Ratio

The optimum water–cement ratio for the ultra-fine cement plugging system was selected based on the water segregation rate, fluidity, density, and setting time of the cement slurry at 80 °C. For water segregation measurement, 100 mL of cement slurry was taken, and the amount of water segregation within 2 h was recorded. The setting time was measured at 80 °C using a modified procedure based on GB/T 1346-2011 [14].

2.4.2. Static Sedimentation Test

Fresh cement slurry was poured into a 100 mL graduated cylinder immediately after mixing, and the initial slurry height was recorded as H_0 . The cylinder was sealed and maintained statically at 80 °C for 2 h. After standing, the height of the visibly stratified upper zone was recorded as H_s , and the sedimentation height ratio was calculated as follows:

$$S_h = \frac{H_s}{H_0} \times 100\% \quad (1)$$

where S_h is the sedimentation height ratio, H_s is the height of the stratified upper zone after 2 h of standing, and H_0 is the initial height of the slurry.

In addition, the slurry was carefully sampled from the upper and lower sections of the graduated cylinder after static standing. The densities of the top and bottom slurry layers were measured, and the bottom–top density difference was calculated as follows:

$$\Delta\rho = \rho_{\text{bottom}} - \rho_{\text{top}} \quad (2)$$

where ρ_{bottom} and ρ_{top} represent the densities of the bottom and top slurry layers, respectively. The sedimentation height ratio and bottom–top density difference were used as auxiliary indicators to evaluate the vertical concentration gradient and particle sedimentation tendency of the slurry.

2.4.3. Determination of the Optimum Fluid Loss Additive Dosage

The static fluid loss of the cement slurry was tested in accordance with GB/T 19139-2012 [15] using a high-temperature, high-pressure fluid loss apparatus at 80 °C for 30 min.

Fluid loss was selected as the primary optimization parameter because excessive filtrate loss directly changes the effective water-to-cement ratio of ultra-fine cement slurry during placement. In casing-damage remediation, the slurry must enter narrow cracks and porous leakage channels before setting. If the liquid phase is rapidly filtered into the surrounding formation, the slurry near the leakage zone becomes locally dehydrated, which can cause premature thickening, reduced injectability, nonuniform cement distribution, and incomplete filling of microcracks. Conversely, insufficient fluid-loss control may leave behind a porous and heterogeneous cement matrix after curing, weakening the sealing capacity under subsequent CO₂-rich brine exposure.

Therefore, the dosage of the fluid loss additive was optimized at the beginning of the formulation design to ensure that the slurry retained sufficient water during pumping and placement. The selected dosage should reduce filtration loss effectively while avoiding unnecessary additive addition, which may increase slurry viscosity or interfere with cement hydration. In this study, the fluid loss additive dosage was screened before the dispersant

and retarder dosage so that the subsequent optimization steps were conducted on a slurry system with acceptable water retention and basic stability.

2.4.4. Determination of the Optimum Dispersant Dosage

An aldehyde–ketone condensate, FSJ-1, was selected as the dispersant for the ultra-fine cement plugging system. The optimum dosage of the dispersant was determined by investigating the effect of different dispersant contents on the fluidity of the ultra-fine cement slurry [16].

Fluidity was selected as the key starting parameter for dispersant optimization because the ultra-fine cement system is intended to penetrate small casing defects, microfractures, and pore throats. Ultra-fine cement has a large specific surface area and strong particle–particle interaction; therefore, without sufficient dispersion, cement particles tend to flocculate, leading to high apparent viscosity, poor pumpability, and limited penetration depth. Improving dispersion reduces interparticle aggregation and helps the slurry maintain a more uniform particle suspension, which is essential for forming a continuous plugging body inside leakage channels.

However, dispersant dosage cannot be increased without limitation. Excessive dispersion may destabilize the cement suspension, promote particle settling, increase free water, or delay early structure formation. These effects are unfavorable for a plugging material because the slurry must not only flow into the damaged zone but also remain spatially stable after placement. Therefore, the dispersant dosage was optimized by using slurry fluidity as the main evaluation index, while considering the need to avoid over-dispersion and sedimentation. This approach provides a balance between injectability and suspension stability.

2.4.5. Determination of the Optimum TA-LDHs Retarder Dosage

The optimal dosage of the retarder was comprehensively selected by investigating the effects of the retarder on the fluidity, density, rheological properties, thickening time, and compressive strength of the cement slurry.

These properties were selected because the retarder affects both the construction performance and the hardened performance of the ultra-fine cement system. For CCUS casing-damage remediation, the slurry must have a controllable thickening time to ensure safe pumping and sufficient placement time at elevated temperature. Ultra-fine cement hydrates rapidly, and its hydration heat release is relatively concentrated; therefore, without appropriate retardation, the slurry may lose pumpability before reaching the target leakage zone. Thickening time was therefore used as the most direct indicator of whether the retarder can provide an adequate operational window.

At the same time, retarder optimization cannot be based only on thickening time. Fluidity and rheological properties determine whether the slurry can be injected into narrow defects under practical pressure conditions. Density reflects the uniformity and stability of the slurry system and helps identify possible dilution, segregation, or excessive additive effects. Compressive strength was also included because excessive retardation may inhibit hydration and reduce early or final strength, which would compromise the mechanical integrity of the plugging body. Therefore, the TA-LDHs dosage was optimized through a multi-parameter evaluation rather than a single-index method. The selected dosage should provide sufficient retardation while maintaining injectability, slurry stability, and strength development after curing.

2.4.6. Comparative Evaluation of Different Retarders

To compare the retarding performance of TA-LDHs with that of conventional small-molecule retarders, four ultra-fine cement slurry systems were prepared: a control system

without a retarder, a system containing 0.2% tartaric acid, a system containing 0.2% sodium citrate, and a system containing 0.2% TA-LDHs. The retarder dosage was calculated based on the mass of cement. For all systems, the water-to-cement ratio was maintained at 0.7, while the dosages of the JSJ-1 fluid-loss additive and FSJ-1 dispersant were fixed at 1.5% and 0.4%, respectively.

The fluidity, thickening time, and thickening transition time of each slurry were measured at 80 °C. The thickening transition time was defined as the time required for the slurry consistency to increase from 40 Bc to 100 Bc. In addition, cement specimens were cured at 80 °C for 1, 3, and 7 days, and their compressive strengths were measured to evaluate the effect of different retarders on strength development. At least three parallel specimens were tested for each curing age, and the results were expressed as the mean value $\pm$ standard deviation.

2.5. Plugging Performance Evaluation

In this paper, evaluation experiments were carried out on the plugging performance of the ultra-fine cement plugging system under different salinities, curing times, and injection volumes. The flow experimental apparatus is shown in Figure 2.

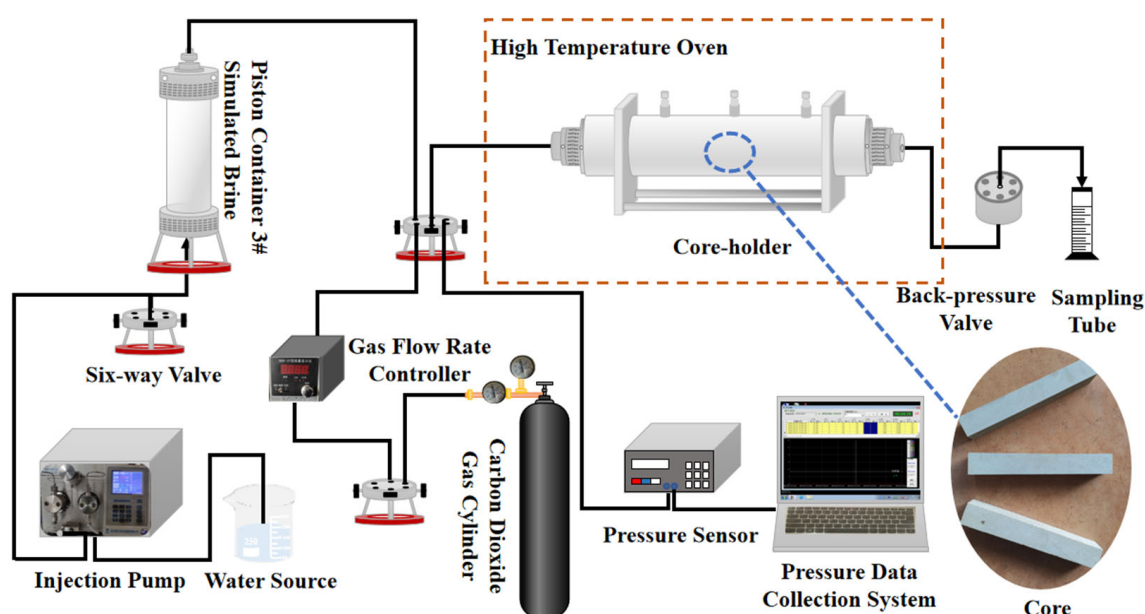


Figure 2. Schematic diagram of the flow experimental apparatus.

The relevant calculation formulas are as follows:

The calculation formula for breakthrough pressure gradient P_m is shown in the formula:

$$P_m = \frac{P_{\max}}{L} \quad (3)$$

where P_m —breakthrough pressure gradient, $\text{MPa} \cdot \text{m}^{-1}$; P_w —maximum pressure at the outlet when the first drop of water is produced during water flooding, MPa; L —length of the porous medium, m.

The calculation formula for permeability K of the sand-packed tube is as follows:

$$K = \frac{Q\mu L}{A\Delta P} \quad (4)$$

where Q —displacement fluid flow rate, cm^3/s ; μ —viscosity of the displacement fluid, $\text{mPa}\cdot\text{s}$; L —length of the sand-packed tube, cm ; A —cross-sectional area of the sand-packed tube, cm^2 ; ΔP —pressure difference between two ends of the sand-packed tube, MPa .

The calculation formula for pore volume PV of the sand-packed tube is as follows:

$$PV = \frac{m_1 - m_2}{\rho} \quad (5)$$

where m_1 —mass of the sand-packed tube after fluid injection, g ; m_2 —mass of the dry sand-packed tube, g ; ρ —density of the fluid, g/cm^3 .

The calculation formula for plugging efficiency E is as follows:

$$E = \left(1 - \frac{K_2}{K_1}\right) \quad (6)$$

where K_1 —permeability before cement injection, μm^2 ; K_2 —permeability after cement injection, μm^2 .

2.6. High-Pressure CO_2 Exposure Test

Two cement systems were prepared for comparison: the control ultra-fine cement system without TA-LDHs and the optimized system containing 0.2% TA-LDHs. The remaining components and the water-to-cement ratio were kept unchanged. The specimens were initially cured at 80°C for 7 days and subsequently exposed to CO_2 -saturated simulated formation brine with a salinity of $65,680 \text{ mg}\cdot\text{L}^{-1}$ in a high-pressure corrosion reactor.

The exposure temperature and CO_2 pressure were maintained at 80°C and 20 MPa, respectively. Specimens were retrieved after 7, 14, and 30 days of exposure. The compressive strength, water-phase permeability, mass change, and carbonation depth were measured. At least three parallel specimens were tested for each condition, and the results were expressed as the mean value $\pm$ standard deviation.

To quantitatively evaluate the mechanical-property retention and permeability evolution of the cement specimens after exposure to high-pressure CO_2 -saturated brine, the compressive strength retention ratio and permeability change ratio were calculated. The compressive strength retention ratio reflects the ability of the cement specimen to maintain its mechanical integrity after CO_2 exposure and was calculated as follows:

$$R_s = \frac{f_{c,t}}{f_{c,0}} \times 100\% \quad (7)$$

where R_s is the compressive strength retention ratio, %; $f_{c,0}$ is the compressive strength before exposure, MPa ; and $f_{c,t}$ is the compressive strength after an exposure duration of (t), MPa .

The permeability change ratio was used to characterize the variation in the pore connectivity and sealing performance of the cement specimen after CO_2 exposure and was calculated as follows:

$$\Delta K = \frac{K_t - K_0}{K_0} \times 100\% \quad (8)$$

where ΔK is the permeability change ratio, %; K_0 is the permeability before exposure; and K_t is the permeability after an exposure duration of (t). A positive value of ΔK indicates an increase in permeability and deterioration of the sealing performance, whereas a negative value indicates a decrease in permeability, which may be associated with pore filling or densification of the cement matrix.

3. Results and Discussion

3.1. Structural Characterization of TA-LDHs Intercalated Retarder

3.1.1. X-Ray Diffraction Test

As shown in Figure 3, the Mg–Al–CO₃-LDHs precursor prepared by the co-precipitation method exhibited a stable baseline and sharp characteristic reflections indexed to the (003), (006), (009), and (110) planes, confirming the formation of a well-crystallized layered double hydroxide structure. After ion exchange with tartaric acid, the basal reflection corresponding to the (003) plane shifted markedly from $2\theta = 11.68^\circ$ to $2\theta = 7.48^\circ$, indicating a pronounced expansion of the interlayer gallery. Based on Bragg's law, the basal spacing of the Mg–Al–CO₃-LDHs precursor was calculated to be approximately 0.757 nm, whereas that of the TA-LDHs product increased to approximately 1.181 nm. Thus, the basal spacing increased by about 0.424 nm, corresponding to a relative expansion of approximately 56.0%.

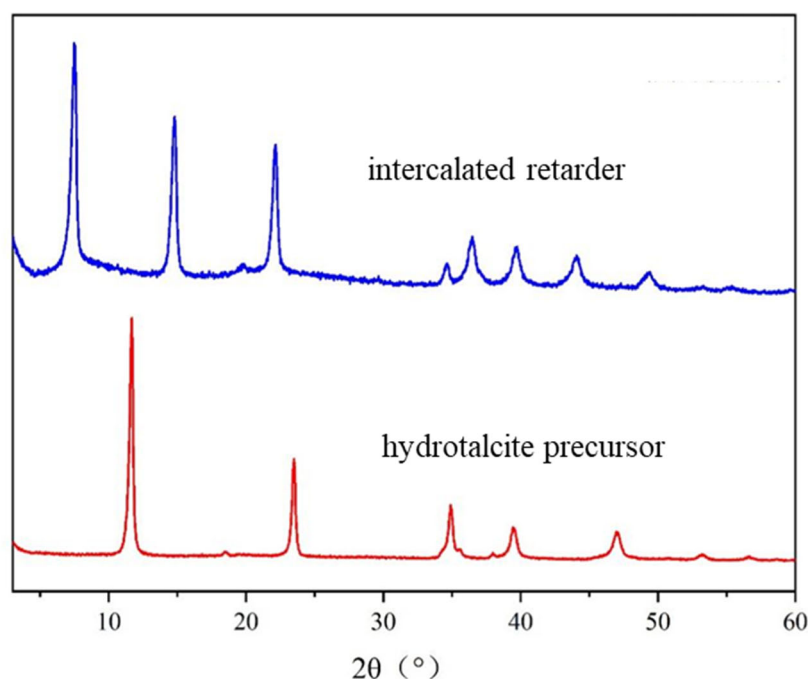


Figure 3. XRD patterns of hydrotalcite precursor and intercalated retarder.

Considering that the thickness of a brucite-like LDH host layer is approximately 0.48 nm, the interlayer gallery height increased from about 0.28 nm for Mg–Al–CO₃-LDHs to about 0.70 nm for TA-LDHs. This increase is consistent with the introduction of larger tartarate species into the interlayer region, further confirming the successful intercalation of tartarate anions.

To further evaluate the ion-exchange degree semi-quantitatively, the apparent XRD intercalation degree was estimated from the integrated peak areas of the residual carbonate-type (003) reflection near 11.68° and the tartarate-intercalated (003) reflection near 7.48° after baseline correction and peak fitting. The dominant low-angle (003) reflection at 7.48° , together with the marked weakening or disappearance of the original carbonate-type basal reflection, indicates that tartarate intercalation was largely achieved. However, because XRD peak intensity can be influenced by crystallinity, preferred orientation, and particle size, the calculated intercalation degree should be regarded as an apparent semi-quantitative value. Therefore, the presence of a small amount of residual carbonate or partially exchanged LDH cannot be completely excluded solely based on the XRD results [17–19].

3.1.2. TGA and ICP Analysis

To further verify the ion-exchange process and the structural stability of the LDH host layers, thermogravimetric analysis (TGA) and inductively coupled plasma analysis (ICP) were performed for CO₃-LDH and TA-LDHs. As shown in Figure 4, for CO₃-LDH, the mass loss below approximately 150 °C is mainly attributed to the removal of physically adsorbed water and interlayer water, while the subsequent mass loss at higher temperatures is associated with dehydroxylation of the LDH layers and decomposition of interlayer carbonate species. In contrast, TA-LDHs showed a more pronounced mass loss over the temperature range of approximately 150–600 °C, which can be attributed to the decomposition of intercalated tartarate species together with the dehydroxylation of the LDH host layers. The final residual mass of CO₃-LDH at 800 °C was approximately 21–22%, whereas that of TA-LDHs was only approximately 3–4%. Therefore, the additional mass loss of TA-LDHs relative to CO₃-LDH was approximately 18 wt.%, indicating that a considerable amount of organic tartarate species had been introduced into the LDH interlayer galleries after ion exchange.

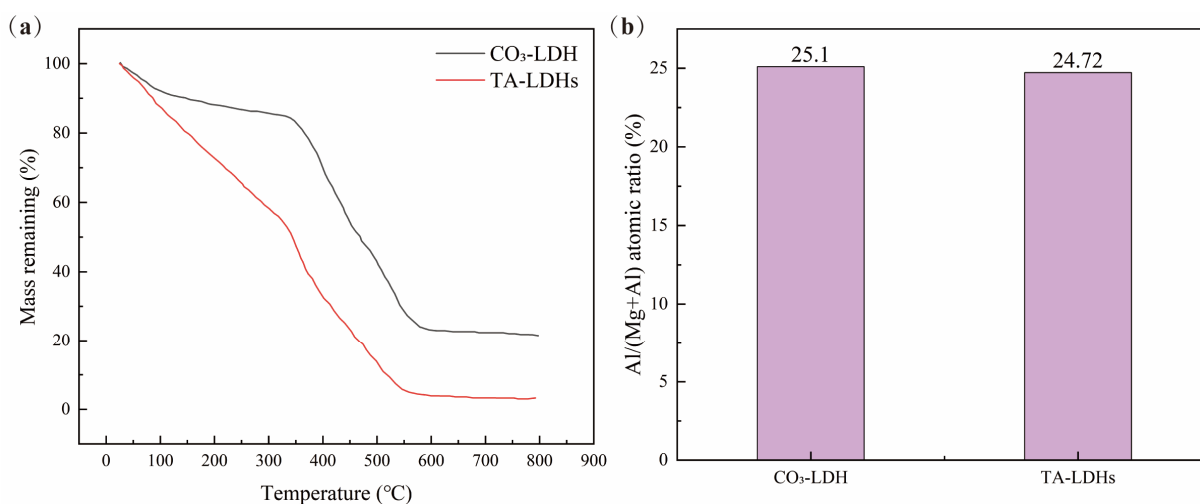


Figure 4. (a) TGA curves of CO₃-LDH and TA-LDHs; (b) ICP-derived Al/(Mg + Al) atomic ratios of CO₃-LDH and TA-LDHs.

Combined with the XRD-derived basal spacing expansion, the additional organic-related mass loss observed in the TGA curves, and the nearly unchanged Mg-Al elemental ratio, these results collectively demonstrate the successful intercalation of tartarate species into the LDH interlayer galleries.

3.1.3. Fourier Transform Infrared Spectroscopy Test

As shown in Figure 5, in the infrared spectrum of Mg/Al-CO₃-LDH, the broad absorption peak near 3500 cm^{−1} is the OH vibration band of physically adsorbed water or crystal water and the stretching vibration absorption peak of M-OH, the absorption peak near 1360 cm^{−1} is the symmetric vibration absorption peak of carbonate ions, the Mg-O-Al stretching vibration peak of the hydrotalcite layer appears at around 750 cm^{−1}, and the bending vibration peak of Mg-OH-Al appears at 680 cm^{−1}, indicating that the Mg-Al hydrotalcite precursor has been successfully prepared by the coprecipitation method [20,21]. By observing the infrared spectrum of Mg/Al-TA-LDH, it can be found that the CO₃^{2−} absorption peak at 1360 cm^{−1} disappears, the antisymmetric and symmetric absorption peaks of carboxylate groups appear near 1600 cm^{−1} and 1400 cm^{−1}, the in-plane bending vibration absorption peak of O-H appears at 1000 cm^{−1}, and the stretching vibration peak of C-H bond appears at 2900 cm^{−1}, which shows that the ion-exchange reaction has

occurred between the hydrotalcite precursor and tartaric acid, and tartaric acid has been successfully inserted into the interlayer of the hydrotalcite precursor and interacted with the hydrotalcite layer through ionic bonds.

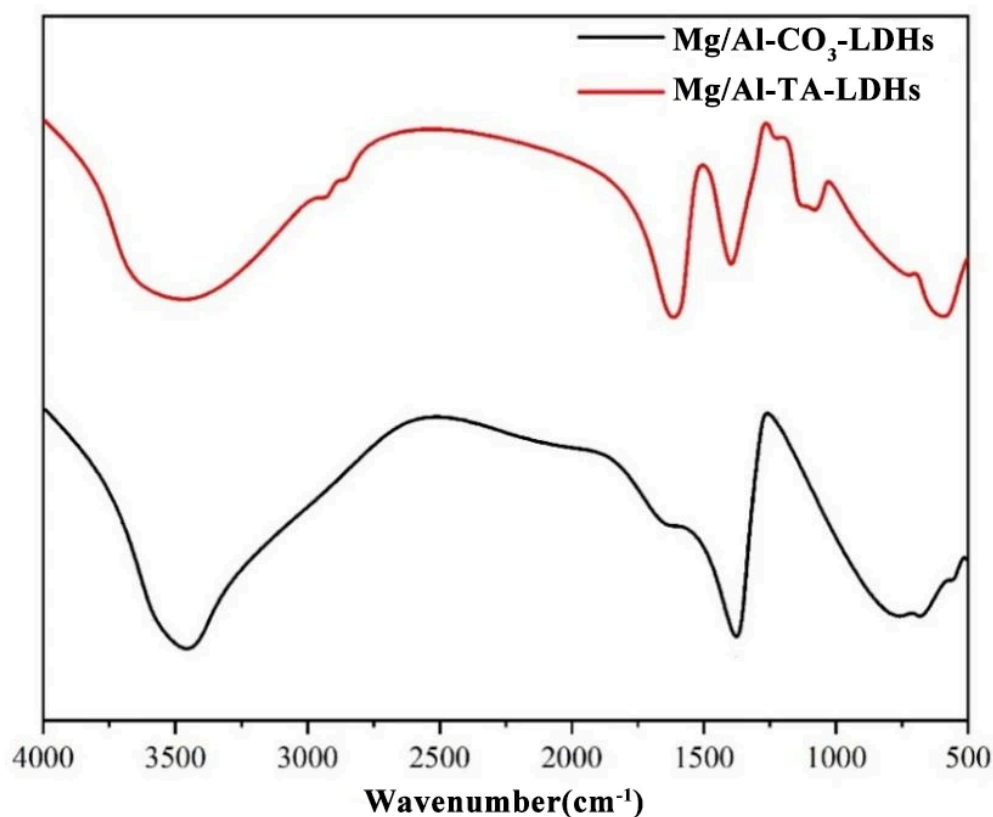


Figure 5. FT-IR Spectra of hydrotalcite precursor and intercalated product.

3.1.4. Scanning Electron Microscopy Test

As shown in Figure 6, the micromorphology of the prepared hydrotalcite precursor does not change significantly after the ion-exchange reaction. In comparison, the lamellar structure of the TA-LDHs sample is more obvious, and the layers are stacked one after another in sequence, showing a relatively large sheet structure. The hydrotalcite precursor also has a lamellar structure with clear boundaries, but the sheets vary in size and are stacked disorderly with wrapping between layers, and some structures appear as small agglomerates. It can be inferred that the exchange of tartrate ions with carbonate ions leads to a more orderly arrangement between the hydrotalcite layers.

3.2. Optimization of Ultra-Fine Cement Plugging System

3.2.1. Optimum Water–Cement Ratio

As shown in Table 3, increasing the water-to-cement ratio from 0.5 to 0.8 gradually improved the slurry fluidity and prolonged both the initial and final setting times. This can be attributed to the dilution effect of additional water, which reduces the frequency of particle collision and delays the formation of a continuous cement hydration network. However, when the water-to-cement ratio was further increased to 0.9 and 1.0, the initial and final setting times decreased instead of continuing to increase.

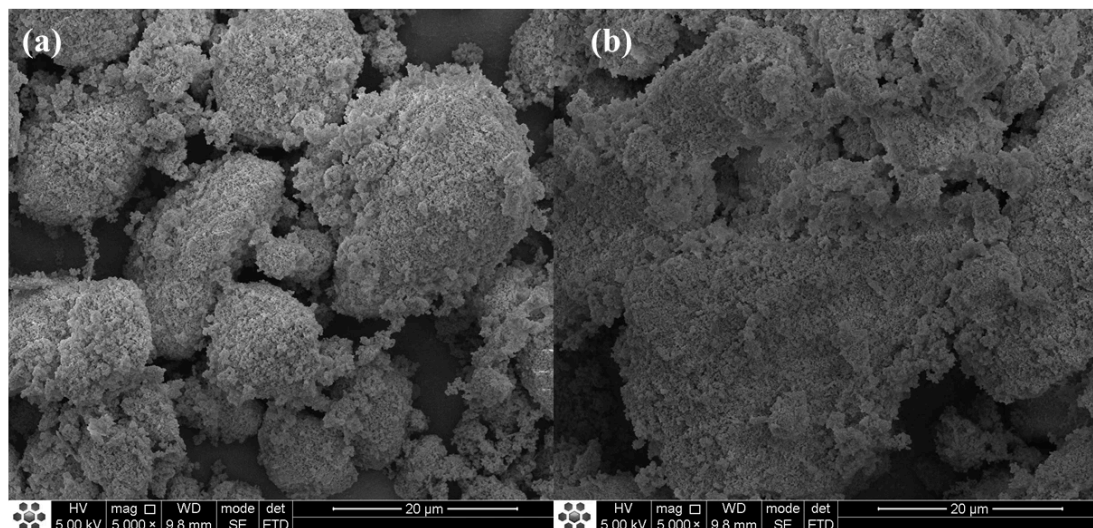


Figure 6. Micromorphology images of hydrotalcite precursor and intercalated product: (a) hydrotalcite precursor, (b) intercalated product.

Table 3. Effect of different water–cement ratios on the basic properties of ultra-fine cement slurry.

Water–Cement Ratio	0.5	0.6	0.7	0.8	0.9	1.0
free water content/mL	0	0	0	0	0	1
fluidity/cm	18.5	24.0	27.0	28.0	29.0	30.0
density/g·cm ^{−3}	1.82	1.74	1.68	1.56	1.40	1.35
initial setting time/min	102	110	123	152	145	135
final setting time/min	125	140	165	189	183	173

It should be noted that the free water contents at water-to-cement ratios of 0.8 and 0.9 were both 0 mL, indicating that no obvious macroscopic bleeding occurred within the 2 h observation period. Therefore, the shortened setting time at high water-to-cement ratios should not be simply attributed to free water separation. To further clarify this phenomenon, static sedimentation tests were conducted. As shown in Figure 7, the sedimentation height ratio remained below 1.5% when the water-to-cement ratio was not higher than 0.8, suggesting good suspension stability. When the water-to-cement ratio increased to 0.9, although no free water was observed, the sedimentation height ratio increased sharply to approximately 4.8%. At a water-to-cement ratio of 1.0, the sedimentation height ratio further increased to approximately 8.6%, indicating obvious slurry instability.

The density distribution results further confirmed the formation of a vertical concentration gradient. With increasing water-to-cement ratio, the density of the top slurry layer decreased continuously, whereas the bottom layer maintained a relatively higher density. The bottom–top density difference increased markedly from a low level at water-to-cement ratios of 0.5–0.8 to approximately 0.12 g·cm^{−3} at a water-to-cement ratio of 0.9 and further to approximately 0.18 g·cm^{−3} at a water-to-cement ratio of 1.0. These results demonstrate that excessive water addition weakened the suspension stability of the ultra-fine cement slurry and promoted particle sedimentation and solid-phase enrichment in the lower part of the slurry, even in the absence of obvious free water.

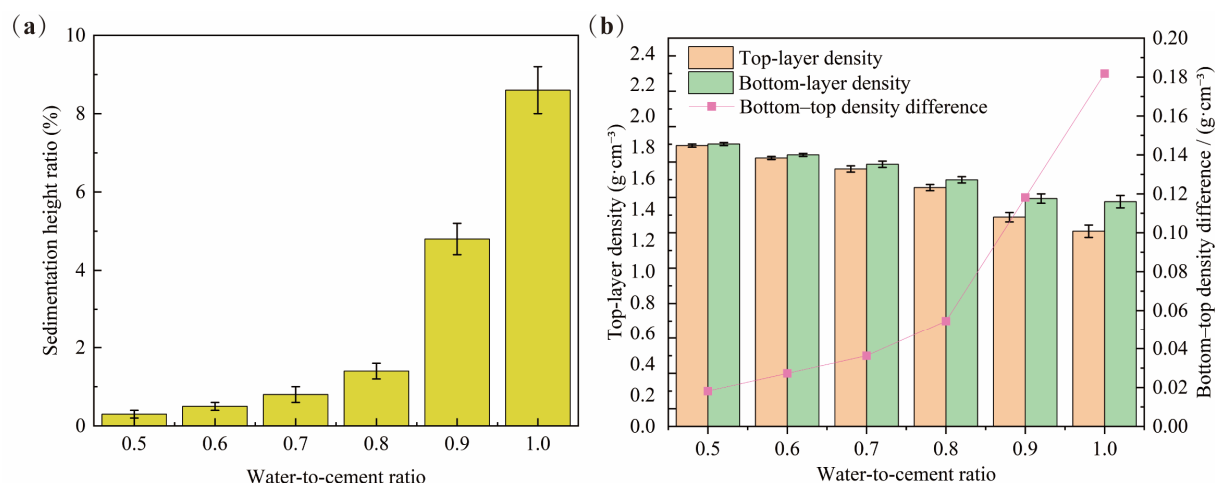


Figure 7. (a) Sedimentation height ratios of ultra-fine cement slurry with different water-to-cement ratios after standing for 2 h at 80 °C; (b) Top-layer density, bottom-layer density, and bottom-top density difference of ultra-fine cement slurry with different water-to-cement ratios after standing for 2 h at 80 °C.

The local enrichment of cement particles in the lower section increased the effective solid concentration and accelerated the formation of a particle-contact network and hydration structure. Therefore, when the water-to-cement ratio exceeded 0.8, the apparent initial and final setting times became shorter. Considering the combined results of free water content, fluidity, density, setting time, sedimentation height ratio, and vertical density difference, a water-to-cement ratio of 0.7 was selected as the optimal value for the ultra-fine cement plugging system [22].

To further support the stability evaluation of the ultra-fine cement slurry, the zeta potential of cement particles at different water-to-cement ratios was introduced as an auxiliary indicator. The results showed that the absolute value of the zeta potential increased from 16.8 mV to 31.2 mV when the water-to-cement ratio increased from 0.5 to 0.8, indicating enhanced electrostatic repulsion among cement particles and improved dispersion stability. This trend is consistent with the increase in slurry fluidity and the delayed setting behavior observed in Figure 8. However, when the water-to-cement ratio further increased to 0.9 and 1.0, the absolute value of the zeta potential decreased to 23.4 mV and 18.7 mV, respectively. This decrease suggests weakened suspension stability, which may be attributed to the excessive dilution of the slurry, reduced solid-phase interaction, and increased tendency of particle sedimentation. Therefore, although a high water-to-cement ratio improves apparent fluidity, excessive water addition may cause segregation and instability. Based on the combined results of free water content, fluidity, density, setting time, and zeta potential, a water-to-cement ratio of 0.7 was selected as a balanced starting formulation for the ultra-fine cement plugging system.

3.2.2. Optimization of Fluid Loss Additive Dosage

The dosage of the fluid loss additive (JSJ-1) is defined as the mass fraction relative to the ultra-fine cement content, expressed as weight percent of cement (bwoc, %). All additive concentrations reported in this study refer to mass percentage based on the dry mass of ultra-fine Portland cement. The effect of fluid loss additive dosage on filtration loss was evaluated using a high-temperature, high-pressure fluid loss test at 80 °C according to GB/T 19139-2012. As can be seen from Figure 9, the fluid loss of ultra-fine cement slurry decreases with the increase in fluid loss additive dosage. When the fluid loss additive dosage is less than 1.5%, the fluid loss reduction effect on cement slurry is significant.

Especially when the fluid loss additive dosage is in the range of 0.5% to 1.2%, the fluid loss of ultra-fine cement slurry can be greatly reduced. When the fluid loss additive dosage is greater than 1.5%, the fluid loss is lower than 50 mL, and further increasing the fluid loss additive dosage does not lead to much additional improvement in fluid loss. Therefore, this paper selects 1.5% as the fluid loss additive dosage for the ultra-fine cement plugging system.

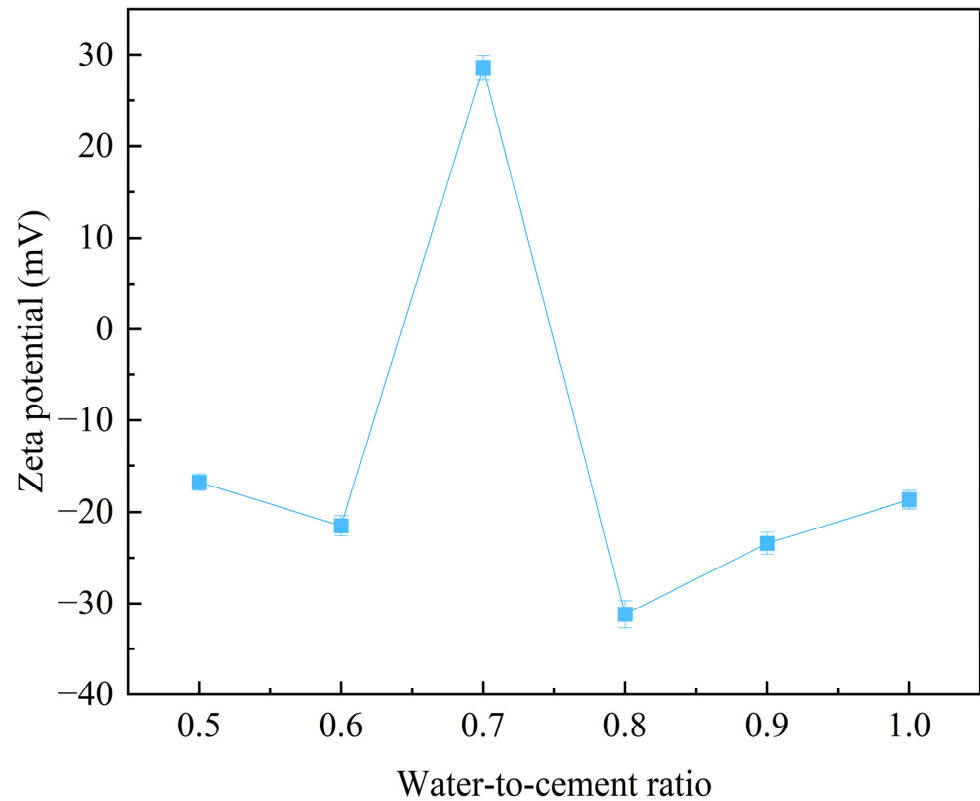


Figure 8. Zeta potential values of ultra-fine cement suspensions with different water-to-cement ratios.

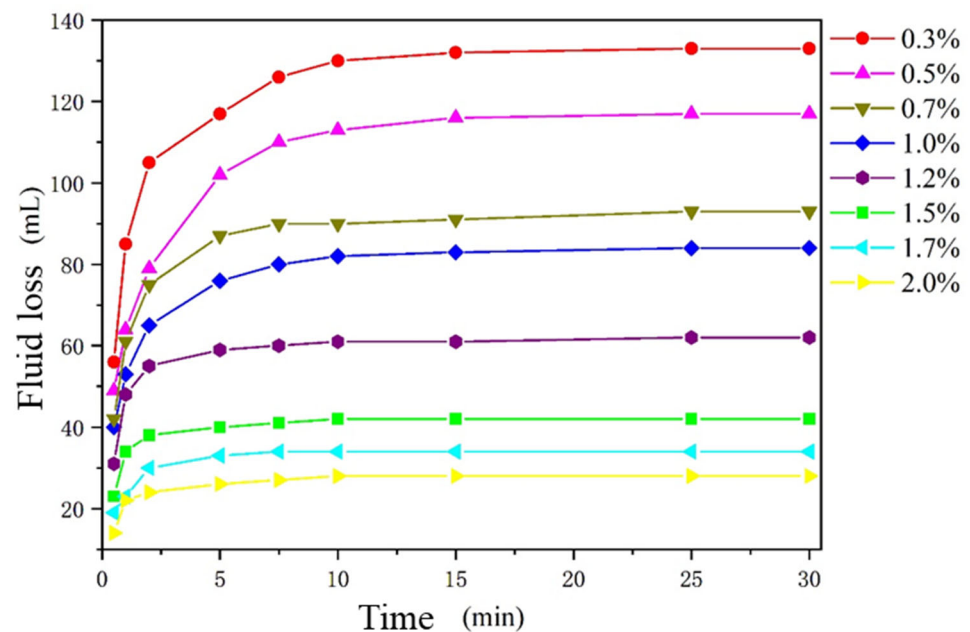


Figure 9. Variation of fluid loss of ultra-fine cement slurry at different fluid loss additive dosages and times.

3.2.3. Optimization of Dispersant Dosage

Dispersant carries negative charges opposite to cement particles and can adsorb onto cement particles. In contrast, hydrated CaSiO_3 carries positive charges identical to cement particles and thus repels the particles. Cement particles are separated from one another under the influence of electric charges. However, excessive dispersion can damage the cement microstructure, resulting in cement particle settling or increased free water. As shown in Figure 10, the fluidity of the ultra-fine cement slurry changes only slightly when the dispersant dosage exceeds 0.4%. Therefore, 0.4% is selected as the optimum dispersant dosage for the ultra-fine cement plugging system.

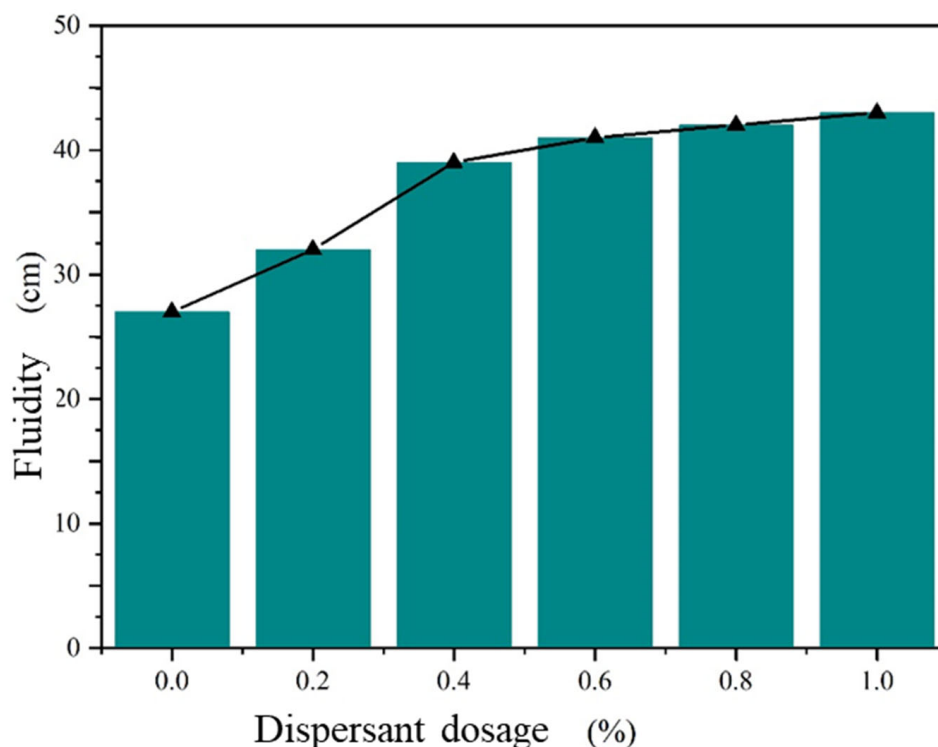


Figure 10. Variation of fluidity of ultra-fine cement slurry at different dispersant dosages.

3.2.4. Optimization of TA-LDHs Retarder Dosage

As can be seen from Figure 11a, the addition of the retarder has little effect on the fluidity and density of the ultra-fine cement slurry. When the retarder dosage increases to 0.2%, the fluidity of the ultra-fine cement slurry rises slightly. As a nanomaterial with a layered structure, hydrotalcite exhibits good dispersibility and can improve the fluidity of the ultra-fine cement slurry. The calculated results in Table 4 show that the addition of the retarder increases the rheological index of the cement slurry and reduces the consistency coefficient, enhancing the fluidity and dispersibility of the cement slurry and resulting in good overall stability of the ultra-fine cement paste. It can be seen from Figure 11b that the addition of the TA-LDHs retarder significantly prolongs the thickening time of the ultra-fine cement plugging system. As the dosage of the TA-LDHs retarder increases from 0 to 0.3%, the thickening time of the cement slurry system is extended from 158 min to 387 min, indicating that the TA-LDHs retarder exerts an excellent retarding effect on the ultra-fine cement slurry at a low dosage, and the thickening time shows a linear relationship with the increase of the retarder dosage [22,23]. The thickening curve at a retarder dosage of 0.2% runs smoothly without channeling, stepwise thickening, flash set, or other abnormal phenomena, and features a short overall transition time with an

obvious right-angle characteristic. As shown in Figure 11c, the compressive strength of the ultra-fine cement stone varies with the TA-LDHs retarder dosage, and the influence differs among curing ages. The 1 d compressive strength remains at a relatively low level and only fluctuates slightly with increasing retarder dosage, indicating that the early-age strength is not severely weakened by TA-LDHs. Therefore, the variation in 1 d strength should not be overinterpreted as a clear “decrease–increase–decrease” trend. For the 3 d and 7 d curing ages, the compressive strength generally increases first and then decreases with increasing retarder dosage. When the TA-LDHs dosage is 0.2%, the 3 d and 7 d compressive strengths reach relatively high values of approximately 24 MPa and 29 MPa, respectively. This improvement may be attributed to the good dispersibility and layered structure of TA-LDHs, which can improve the uniformity of cement particles and facilitate the formation of a denser hydration product network at an appropriate dosage. However, when the dosage increases to 0.3–0.4%, excessive retardation may inhibit the hydration reaction, reduce the formation rate of hydration products, and weaken the development of the hardened structure, resulting in a decline in compressive strength. Considering the fluidity, thickening time, and compressive strength results together, 0.2% TA-LDHs is selected as the optimal retarder dosage. In addition, the error bars in Figure 11c indicate the standard deviation of at least three parallel specimens, which helps reduce the uncertainty caused by experimental fluctuation.

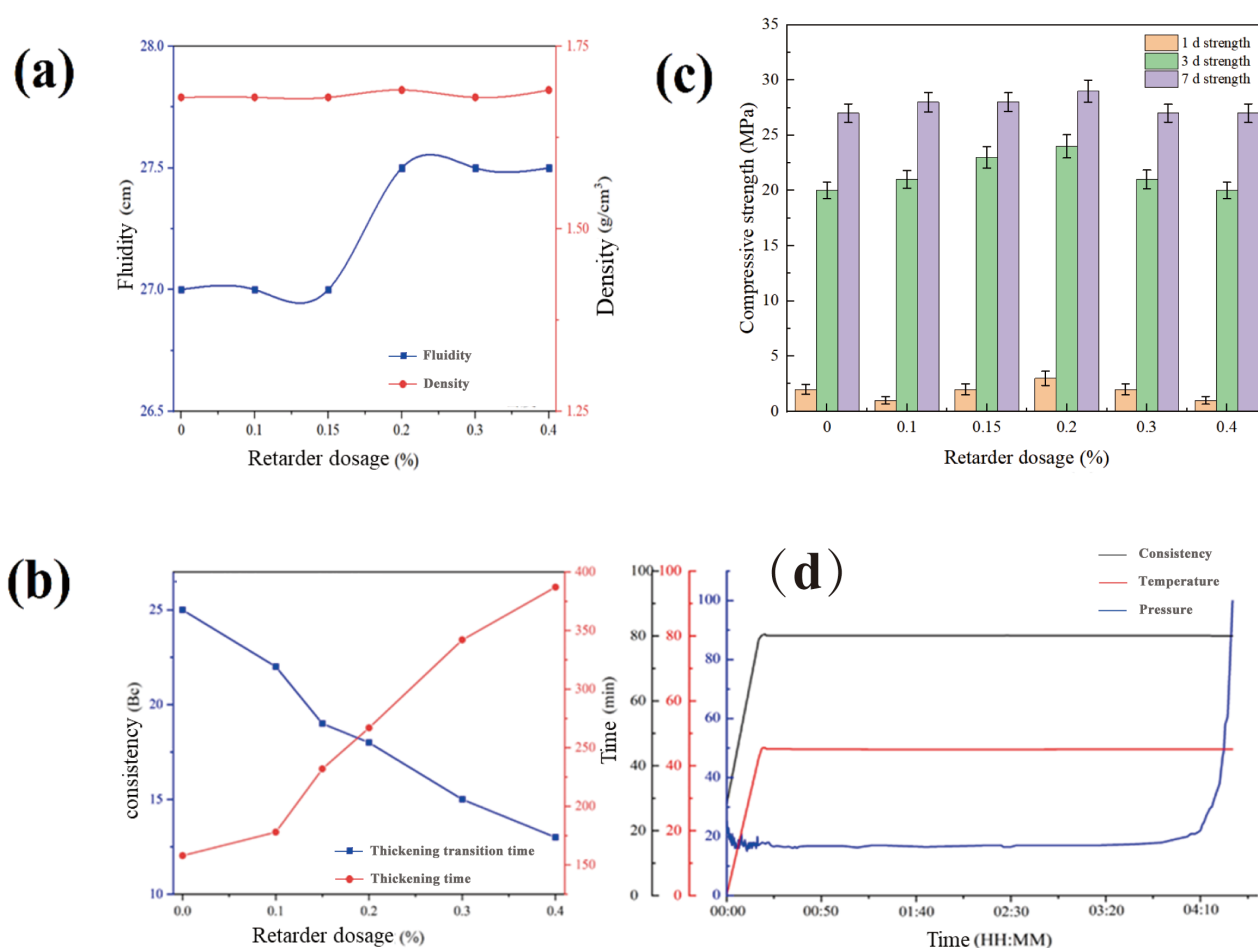


Figure 11. Variation of ultra-fine cement slurry properties at different retarder dosages: (a) fluidity and density, (b) consistency development and thickening time evolution, (c) compressive strength at different curing ages (1 d, 3 d, 7 d), and (d) consistency–time thickening curves.

Table 4. Effect of retarder dosage on flow properties of ultra-fine cement slurry.

Retarder Dosage/%	Φ300	Φ200	Φ100	n	K/Pa·S ⁿ
0	88	61	50	0.514	1.823
0.1	96	69	52	0.557	1.521
0.15	98	62	51	0.593	1.240
0.2	94	58	47	0.630	0.945
0.3	95	60	46	0.659	0.797
0.4	92	56	44	0.670	0.720

3.3. Comparative Evaluation with Conventional Retarders

3.3.1. Retarding and Thickening Behavior

As shown in Figure 12a, the incorporation of the three retarders produced only a limited effect on the fluidity of the ultra-fine cement slurry. The fluidity of the control slurry was 27.0 cm, while the addition of tartaric acid, sodium citrate, and TA-LDHs increased the fluidity to 28.6, 28.3, and 28.0 cm, respectively. The slight increase in fluidity may be associated with the adsorption of the retarders on the surfaces of cement particles, which reduced particle agglomeration and improved slurry dispersion. Overall, all four systems maintained favorable flowability, indicating that the addition of the retarders did not adversely affect the pumpability of the cement slurry.

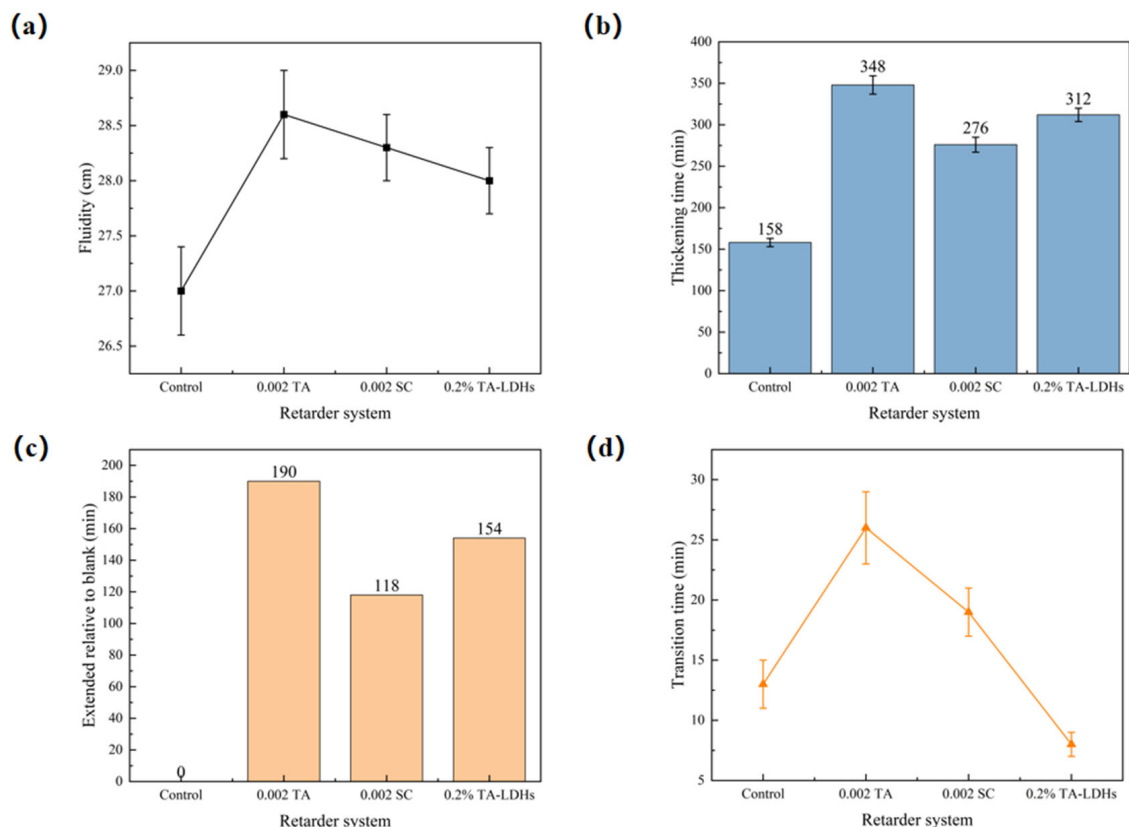


Figure 12. Comparison of the flow and thickening properties of ultra-fine cement slurries containing different retarders at 80 °C: (a) fluidity, (b) thickening time, (c) increase in thickening time relative to the control slurry, and (d) thickening transition time. Error bars represent the standard deviation of parallel measurements.

The thickening results are shown in Figure 12b. The control slurry exhibited a thickening time of 158 min. At the same dosage, tartaric acid produced the strongest retarding

effect, extending the thickening time to 348 min. The thickening times of the sodium-citrate- and TA-LDHs-containing slurries were 276 and 312 min, respectively. Compared with the control slurry, tartaric acid, sodium citrate, and TA-LDHs prolonged the thickening time by 190, 118, and 154 min, respectively (Figure 12c). These results indicate that free tartaric acid provided the highest direct retarding efficiency, followed by TA-LDHs and sodium citrate.

However, the thickening transition behavior differed considerably among the four systems. As shown in Figure 12d, the transition time of the control slurry was approximately 13 min. The addition of tartaric acid and sodium citrate increased the transition time to 26 and 19 min, respectively, indicating a relatively gradual consistency increase. In contrast, the TA-LDHs-containing slurry exhibited the shortest transition time of approximately 8 min, which was 38.5% shorter than that of the control slurry and 69.2% shorter than that of the tartaric-acid-containing slurry. The short transition period suggests that the TA-LDHs-modified slurry maintained a low consistency during the pumpable stage and subsequently developed consistency rapidly, displaying a more pronounced right-angle thickening characteristic.

The prolonged transition time observed for free tartaric acid may be attributed to its rapid dissolution and immediate interaction with calcium ions and reactive cement surfaces, which broadly suppress the hydration reactions. By contrast, the intercalated structure of TA-LDHs may regulate the availability of tartrate species and reduce excessive early-stage retardation. Although TA-LDHs did not produce the longest thickening time, they provided a more favorable balance among slurry fluidity, sufficient pumpability, and rapid consistency development after the end of the pumpable period. This behavior is beneficial for reducing the risk of prolonged transition and fluid migration during field cementing operations.

3.3.2. Compressive Strength Development

The effect of different retarder systems on the fluidity and compressive strength development of the cementitious matrix is shown in Figure 13. As presented in Figure 13a, the initial fluidity of the control sample was approximately 27.0 cm. After the addition of different retarder systems, the fluidity increased to different degrees. In particular, the incorporation of 0.002 TA resulted in the highest fluidity, reaching approximately 28.6 cm, while the 0.002 SC and 0.2% TA-LDHs systems also exhibited improved fluidity compared with the control sample. This indicates that the introduced retarder systems were able to improve the dispersion and workability of the fresh paste to some extent.

The compressive strength results in Figure 13b further demonstrate that the different retarder systems had distinct effects on early-age and later-age strength development. At 1 day, the free TA and SC systems showed lower compressive strength than the control sample, suggesting that the direct addition of small-molecule retarders may delay early hydration and suppress the formation of early hydration products. This effect was particularly evident for the TA-containing system. In contrast, the TA-LDHs system exhibited a slightly higher 1-day compressive strength than the control sample, indicating that the immobilization or controlled release of TA within the LDHs structure may reduce the excessive retardation effect at the early hydration stage.

With increasing curing age, the strength of all samples gradually increased. At 3 days, the TA-LDHs sample showed the highest compressive strength among all tested systems, exceeding both the control sample and the systems containing free TA or SC. A similar trend was observed at 7 days, where the TA-LDHs sample maintained the highest compressive strength, reaching approximately 29 MPa. This result suggests that the TA-LDHs system not only avoids severe early-age strength loss but also contributes to later strength development. The improved performance may be attributed to the regulated release of the retarding

species and the possible nucleation or filler effect of the LDHs particles, which could promote a more uniform hydration process and denser microstructure.

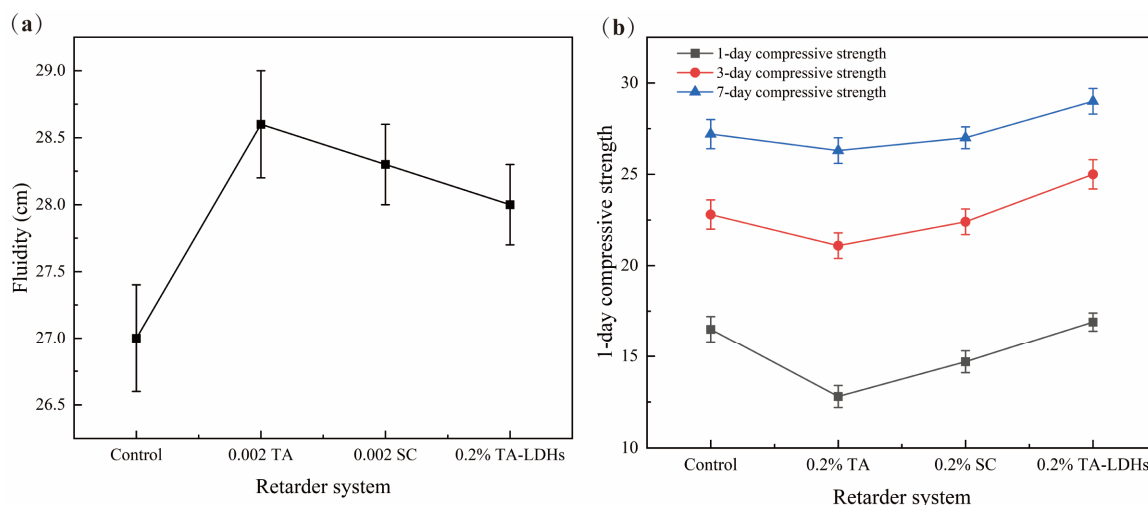


Figure 13. Effects of different retarder systems on the fresh and hardened properties of the cementitious matrix: (a) fluidity and (b) compressive strength development at 1, 3, and 7 days. Error bars represent standard deviations.

However, it should be noted that the present comparison is mainly limited to the control sample and selected laboratory-designed retarder systems. Although free TA and SC were used as reference systems, the proposed TA-LDHs formulation was not systematically compared with commercially available retarding admixtures, such as industrial tartaric acid- or citric acid-based retarders. Therefore, the current results can demonstrate the potential advantage of the TA-LDHs system under the selected experimental conditions, but they are not sufficient to conclude that this formulation outperforms commercial retarder products. Further comparative studies using commercial retarders under equivalent dosage, workability, and curing conditions are still needed to evaluate the practical applicability and competitiveness of the proposed system.

3.4. Evaluation of Plugging Performance of Ultra-Fine Cement Plugging System

3.4.1. The Influence of Mineralization Degree on the Plugging Performance of the Ultra-Fine Cement Plugging System

It can be seen from the data in Table 5 that with the increase of mineralization degree, the breakthrough pressure gradient and plugging rate of the ultra-fine cement plugging system fluctuate within a small range, with little change. The results show that the mineralization degree has little impact on the plugging performance of the ultra-fine cement plugging system, and it has good salt resistance. Moreover, when the mineralization degree is $65,680 \text{ mg} \cdot \text{L}^{-1}$, the ultra-fine cement plugging system can still maintain the breakthrough pressure gradient above $90.5 \text{ MPa} \cdot \text{m}^{-1}$ and the plugging rate above 99%.

3.4.2. The Influence of Different Curing Times on the Plugging Performance of the Ultra-Fine Cement Plugging System

As shown in Table 6, the plugging rate and breakthrough pressure gradient of the ultra-fine cement plugging system increase with the extension of its curing time. When the curing days increase to a certain extent, the plugging system has a relatively high plugging rate and breakthrough pressure gradient, and at this time, the plugging performance of the plugging agent changes slightly with the increase in curing days. When the curing time is

30 days, the breakthrough pressure gradient of the plugging agent reaches the maximum value of $92.03 \text{ MPa} \cdot \text{m}^{-1}$, and the plugging rate also reaches the maximum value of 99.37%.

Table 5. Effect of salinity on plugging performance of ultra-fine cement plugging system.

Salinity/ $\text{mg} \cdot \text{L}^{-1}$	Pre-Injection Permeability/mD	Post-Injection Permeability/mD	Plugging Rate/%	Breakthrough Pressure Gradient/ $\text{MPa} \cdot \text{m}^{-1}$
0	1485.67	13.07	99.12	91.70
10,000	1498.34	13.56	99.09	91.68
20,000	1509.55	15.85	98.95	91.37
30,000	1488.28	13.25	99.11	91.60
40,000	1492.45	14.63	99.02	90.74
50,000	1512.39	15.43	98.98	91.12
65,680	1486.63	14.12	99.03	90.89

Table 6. Effect of different curing times on plugging performance of ultra-fine cement plugging system.

Curing Time/d	Pre-Injection Permeability/mD	Post-Injection Permeability /mD	Plugging Rate/%	Breakthrough Pressure Gradient/ $\text{MPa} \cdot \text{m}^{-1}$
1	1509.31	323.29	78.58	40.75
3	1512.02	186.89	87.64	72.89
7	1485.67	13.07	99.12	91.70
15	1494.58	10.76	99.28	91.91
30	1497.64	9.44	99.37	92.03

3.4.3. The Influence of Different Injection Volumes on the Plugging Performance of the Ultra-Fine Cement Plugging System

As shown in Table 7, the plugging rate and breakthrough pressure gradient of the plugging agent system increase gradually with the increase in injection volume. When the injection volume reaches 0.8 PV, the plugging agent shows favorable plugging performance, with the plugging rate above 90% and the breakthrough pressure gradient higher than $70 \text{ MPa} \cdot \text{m}^{-1}$. When the injection volume is 1 PV, the breakthrough pressure gradient rises to $91.70 \text{ MPa} \cdot \text{m}^{-1}$ and the plugging rate increases to 99.12%.

Table 7. Effect of different injection volumes on plugging performance of ultra-fine cement plugging system.

Injection Volume/PV	Pre-Injection Permeability/mD	Post-Injection Permeability /mD	Plugging Rate/%	Breakthrough Pressure Gradient/ $\text{MPa} \cdot \text{m}^{-1}$
0.1	1497.78	664.27	55.65	21.57
0.3	1505.50	462.48	69.28	33.96
0.5	1496.83	218.69	85.39	59.65
0.8	1512.32	114.18	92.45	73.84
1.0	1485.67	13.07	99.12	91.70

3.5. Resistance to High-Pressure CO_2 -Saturated Brine

3.5.1. Compressive Strength and Strength Retention Rate

As shown in Figure 14a, the compressive strengths of both cement systems initially increased and then decreased with increasing CO_2 exposure time. Before exposure, the

compressive strengths of the control and TA-LDHs-modified cement specimens were 27.6 and 29.0 MPa, respectively. After 7 days of exposure, their compressive strengths increased slightly to 28.4 and 30.2 MPa, corresponding to strength retention ratios of 102.9% and 104.1%, respectively (Figure 14b). The slight increase during the early exposure stage may be attributed to continued cement hydration and the precipitation of carbonate products within the pores, which temporarily densified the cement matrix.

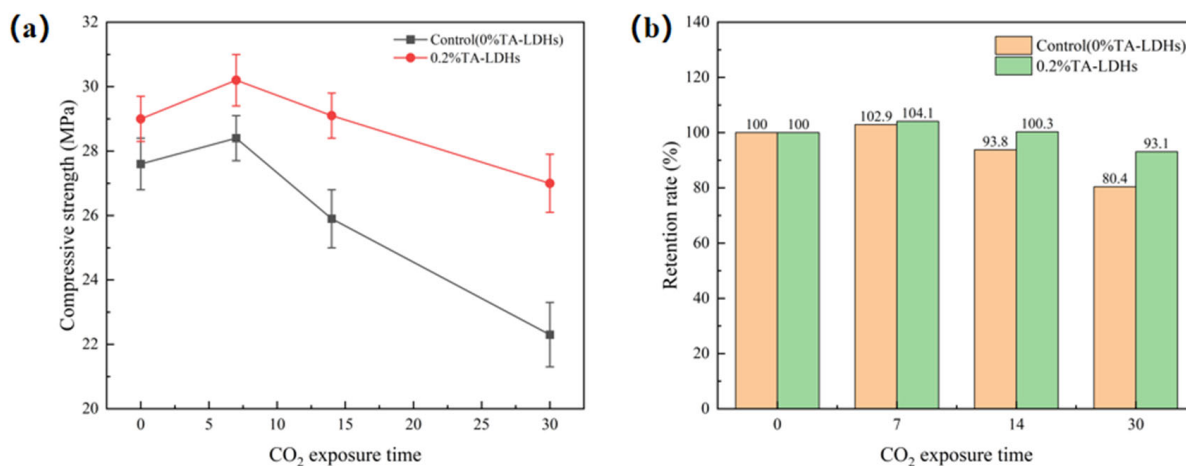


Figure 14. Evolution of the mechanical properties of the control and TA-LDHs-modified ultra-fine cement specimens during exposure to CO₂-saturated formation brine at 80 °C and 20 MPa: (a) compressive strength and (b) compressive strength retention ratio. Error bars represent the standard deviation of three parallel specimens.

With prolonged exposure, the compressive strength of the control specimen decreased markedly. After 14 and 30 days, its compressive strength decreased to 25.9 and 22.3 MPa, corresponding to retention ratios of 93.8% and 80.8%, respectively. In comparison, the TA-LDHs-modified specimen maintained compressive strengths of 29.1 and 27.0 MPa after 14 and 30 days of exposure, with corresponding retention ratios of 100.3% and 93.1%. After 30 days, the compressive strength of the TA-LDHs-modified specimen was 21.1% higher than that of the control specimen.

The progressive strength loss of the control cement at prolonged exposure times may be associated with the dissolution of calcium-bearing phases, decalcification of calcium silicate hydrate, and the resulting deterioration of the cement microstructure. The smaller strength reduction observed for the TA-LDHs-modified cement indicates that the incorporation of TA-LDHs mitigated CO₂-induced mechanical degradation. This improvement may be related to the filling and barrier effects of the layered particles, together with their regulation of cement hydration and pore-structure development.

3.5.2. Water-Phase Permeability

As shown in Figure 15a, the initial water permeabilities of the control and TA-LDHs-modified cement specimens were ($5.2 \times 10^{-18} \text{ m}^2$) and ($3.9 \times 10^{-18} \text{ m}^2$), respectively. The lower initial permeability of the TA-LDHs-modified specimen indicates that the incorporation of TA-LDHs contributed to the formation of a denser cement matrix and reduced the connectivity of transport pathways.

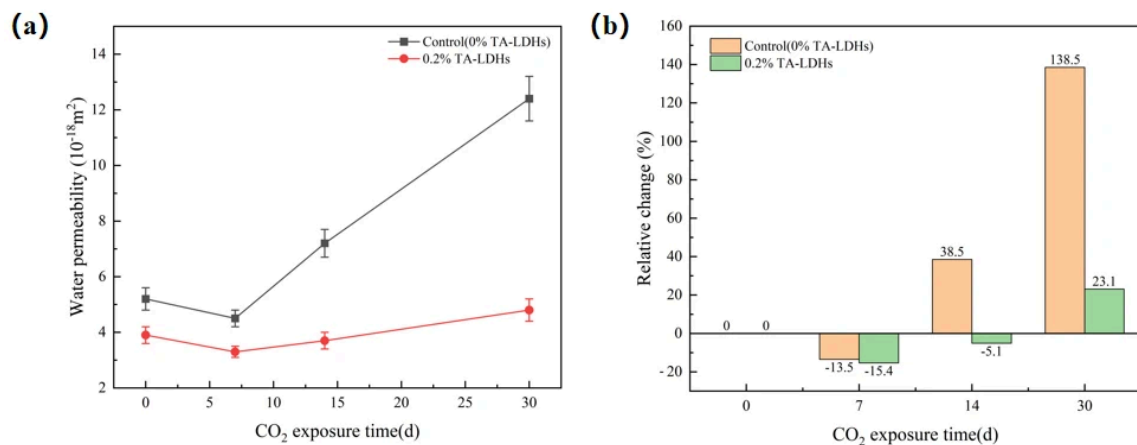


Figure 15. Evolution of the transport properties of the control and TA-LDHs-modified ultra-fine cement specimens during exposure to CO₂-saturated formation brine at 80 °C and 20 MPa: (a) water permeability and (b) relative permeability change. Error bars represent the standard deviation of three parallel specimens.

During the first 7 days of CO₂ exposure, the water permeability of both specimens decreased slightly. The permeability of the control specimen decreased to ($4.5 \times 10^{-18} \text{ m}^2$), corresponding to a relative change of -13.5% , whereas that of the TA-LDHs-modified specimen decreased to ($3.3 \times 10^{-18} \text{ m}^2$), corresponding to a relative change of -15.4% (Figure 15b). This initial reduction may be attributed to continued hydration and the precipitation of carbonate products within the capillary pores, which temporarily blocked fluid-flow channels and improved the compactness of the cement matrix.

With prolonged CO₂ exposure, the permeability of the control specimen increased markedly. After 14 days, its permeability increased to ($7.2 \times 10^{-18} \text{ m}^2$), representing an increase of 38.5% relative to the initial value. After 30 days, the permeability further increased to ($12.4 \times 10^{-18} \text{ m}^2$), corresponding to a relative increase of 138.5% . This pronounced increase indicates the progressive development of connected pores and microcracks, which may be associated with the dissolution of calcium-bearing phases and the decalcification of calcium silicate hydrate under prolonged CO₂ exposure.

In contrast, the permeability of the TA-LDHs-modified specimen remained relatively stable throughout the exposure period. After 14 days, its permeability was ($3.7 \times 10^{-18} \text{ m}^2$), which was still 5.1% lower than its initial value. Even after 30 days, the permeability increased only to ($4.8 \times 10^{-18} \text{ m}^2$), corresponding to a relative increase of 23.1% . At this stage, the permeability of the TA-LDHs-modified specimen was approximately 61.3% lower than that of the control specimen.

These results demonstrate that TA-LDHs substantially suppressed the permeability deterioration induced by prolonged CO₂ exposure and helped preserve the sealing performance of the ultra-fine cement. The improved permeability stability may be associated with the physical filling and barrier effects of the layered TA-LDHs particles, as well as their ability to promote a more compact and less connected pore structure. Nevertheless, further microstructural characterization is required to clarify the specific degradation-mitigation mechanism.

3.5.3. Mass Change and Carbonation Depth

The mass change and carbonation depth of the cement specimens were further investigated to evaluate their physical deterioration during exposure to CO₂-saturated brine. As shown in Figure 16a, both cement systems exhibited a slight mass increase during the initial exposure period. After 7 days, the mass changes of the control and TA-LDHs-modified

specimens were 0.41% and 0.32%, respectively. The initial mass gain may be attributed to continued cement hydration, fluid absorption, and the precipitation of carbonate products within the pore structure.

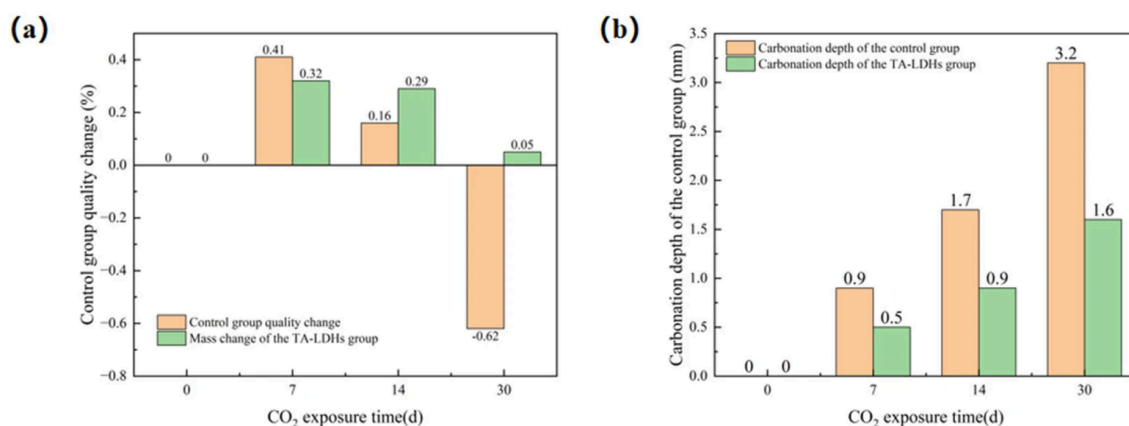


Figure 16. Physical deterioration of the control and TA-LDHs-modified ultra-fine cement specimens during exposure to CO₂-saturated formation brine at 80 °C and 20 MPa: (a) relative mass change and (b) carbonation depth.

After 14 days of exposure, the mass gain of the control specimen decreased to 0.16%, whereas that of the TA-LDHs-modified specimen remained at 0.29%. With further extension of the exposure time to 30 days, the control specimen exhibited a mass loss of 0.62%. This transition from mass gain to mass loss indicates that the dissolution and leaching of calcium-bearing phases gradually became dominant over the pore-filling effect of carbonate precipitation. In contrast, the TA-LDHs-modified specimen retained a slight mass increase of 0.05% after 30 days, suggesting that the incorporation of TA-LDHs effectively mitigated material dissolution and mass loss under prolonged CO₂ exposure.

As shown in Figure 16b, the carbonation depth increased progressively with exposure time for both cement systems. For the control specimen, the carbonation depth increased from 0.9 mm after 7 days to 1.7 mm after 14 days and reached 3.2 mm after 30 days. By comparison, the carbonation depths of the TA-LDHs-modified specimen were only 0.5, 0.9, and 1.6 mm at the corresponding exposure times. Thus, compared with the control specimen, the incorporation of TA-LDHs reduced the carbonation depth by approximately 44.4%, 47.1%, and 50.0% after 7, 14, and 30 days, respectively.

The lower carbonation depth and smaller mass loss of the TA-LDHs-modified cement are consistent with its improved compressive-strength retention and permeability stability. These results indicate that TA-LDHs hindered the inward transport of CO₂-bearing fluids and delayed the progression of the degradation front. This behavior may be associated with the filling and barrier effects of the layered particles and the formation of a denser, less connected pore structure. However, the detailed protection mechanism should be further verified through phase-composition and microstructural analyses.

4. Conclusions

In this study, tartaric acid-intercalated Mg-Al layered double hydroxides (TA-LDHs) were synthesized and introduced into an ultra-fine cement system as a functional retarder for casing-damage remediation in CCUS injection-production wells. Structural characterization confirmed the successful intercalation of tartarate species into the LDH interlayer galleries, indicating that TA-LDHs could regulate cement hydration while contributing to the compactness of the hardened matrix.

The optimized slurry formulation was determined as a water-to-cement ratio of 0.7, 1.5% fluid-loss additive, 0.4% dispersant, and 0.2% TA-LDHs. This system exhibited good fluidity, controllable thickening behavior, and satisfactory strength development. Plugging tests showed that the optimized cement system maintained a breakthrough pressure gradient above $90.5 \text{ MPa} \cdot \text{m}^{-1}$ and a plugging efficiency higher than 99%. After 30 days of curing, the compressive strength reached 29 MPa, and the plugging efficiency increased to 99.37%.

After exposure to CO_2 -saturated formation brine at 80°C and 20 MPa for 30 days, the TA-LDHs-modified cement retained a compressive strength of 27.0 MPa, corresponding to a strength retention ratio of 93.1%, while its permeability increased by only 23.1%. These results were superior to those of the control cement, demonstrating that TA-LDHs improved the resistance of ultra-fine cement to CO_2 -induced degradation. Overall, the TA-LDHs-modified ultra-fine cement system shows strong potential for restoring wellbore sealing integrity in CCUS casing-damage remediation.

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Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: Authors Zhengrong Ye, Peiran Liu, Xiang Zhou, Xiang Liu, and Ran Yi were employed by the company CNPC Research Institute of Petroleum Exploration & Development. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationship that could be construed as a potential conflict of interest.

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