

Original Paper

Laboratory evaluation of an inorganic gel for conformance control in high-temperature gas reservoirs



Tao Song^{a,b,c}, Man-Tian Li^{a,b,c}, Ying-Ting Zhu^{a,b,c}, Song Zhang^{a,b,c}, Fa-Lin Wei^{a,b,c,*},
Bin Ding^{a,b,c}

^a State Key Laboratory of Enhanced Oil & Gas Recovery, Beijing, 100083, China

^b Research Institute of Petroleum Exploration & Development (RIPE), CNPC, Beijing, 100083, China

^c Key Laboratory of Oilfield Chemicals, CNPC, Beijing, 100083, China

ARTICLE INFO

Article history:

Received 10 April 2026

Received in revised form

1 June 2026

Accepted 2 June 2026

Available online 8 June 2026

Edited by Yan-Hua Sun

Keywords:

Water shutoff

High-temperature gas reservoir

Polyaluminium chloride

Water invasion

ABSTRACT

Water invasion is a widely encountered challenge in deep fractured gas reservoirs. Gel treatment is an effective method for controlling excessive water production, yet existing gel systems cannot fully meet the requirements of long-term, large-volume injection in terms of cost, injectivity, gelation time control, and stability. In this study, a high-temperature, high-salinity-tolerant inorganic gel system based on polyaluminum chloride (PAC) was developed, and the factors influencing gelation time and gel strength were systematically evaluated. The injectivity and plugging performance of the PAC gel were also investigated using sandpack and fracture models. Results indicate that the addition of methyl lactate effectively delays gelation at high temperatures, allowing gelation time at 150 °C to be controlled from a few hours to several days. The PAC gelant can be easily injected into the rock matrix with an injection pressure gradient below 1.2 MPa/m, achieves over 99% plugging efficiency for 1.2 mm open fractures, and delivers a water breakthrough pressure gradient of 2.6 MPa/m. A 50-m long-tube dynamic gelation test further confirmed that the PAC system can gel in open fractures under dynamic conditions, with gelation time effectively regulated at high temperatures. The PAC gel exhibits excellent thermal stability at high temperatures, with only slight syneresis observed at 150 °C over a 200-d stability test. Overall, the PAC inorganic gel system developed in this study addresses the key bottlenecks of traditional gels applied in high-temperature, high-salinity fractured gas reservoirs, provides a low-cost, high-performance solution for water invasion control in gas reservoirs, and lays a solid laboratory foundation for subsequent field pilot tests and large-scale industrial application.

© 2026 The Authors. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co. Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Most deep, bottom- or edge-water-drive fractured-gas reservoirs face severe water invasion issues, and the formation water can preferentially flow through these high-permeability zones, causing early water breakthrough and a dramatic loss in gas production (Amani et al., 2022; Hearn, 2010; Roozshenas et al., 2021; Zhao et al., 2024a, 2024b). Gel treatments, which have been widely applied in oil reservoirs, can also be used to address water production issues in gas reservoirs after detailed modifications to the

gelant composition and placement design (Bai et al., 2015; Pu et al., 2019, 2024; Smith, 2023; Tugan, 2020).

In our previous work, we reported a pilot test using organic polymer gels to plug the inter-well fractures or high-permeability zones in the Tarim Basin (Song et al., 2025). The aim of this job is to evaluate the feasibility of placing gels in structural low position to delay water invasion to gas wells located in structural high positions, as these wells are connected by lots of tiny fractures and high-permeability matrix. The result is quite invigorating, and the inter-well water invasion was reduced by over 40% after injecting 1875 m³ of gel. Therefore, based on the previous work we decided to increase the gel volume and switch from organic gel to inorganic polymer gels with significantly improved thermal stability at high temperatures. To be more precise, the temperature and salinity of next well we plan to treat is extremely high (150 °C, 200,000 mg/L). Even though several organic polymer gels were reported to

* Corresponding author.

E-mail address: weifalin@petrochina.com.cn (F.-L. Wei).

Peer review under the responsibility of China University of Petroleum (Beijing).

have excellent thermal stability and controllable gelation time, it is still impossible to place large volumes of such gelant considering the high chemical cost (Song et al., 2023, 2024; Zhu et al., 2017).

Therefore, we focus on inorganic polymer gels with acceptable cost, gelation time, thermal stability, and high injectivity. Several inorganic gels have been developed and applied during steam flooding, including silicate, AlCl_3 , and other metal ions that could form gel aggregates after hydrolysis (Chen et al., 2022, 2024; Karadkar et al., 2023).

The enzyme-induced calcium carbonate precipitation (EICP) method utilized urease enzyme to hydrolyze urea, producing bicarbonate ions that react with Ca^{2+} to precipitate CaCO_3 (Ahenkorah et al., 2021; Larsen et al., 2006). This technique offers controlled, in situ consolidation with adjustable kinetics at low to medium temperatures. The precipitation time is highly temperature-dependent, typically requiring less than 12 h at temperatures over 50 °C. The maximum application temperature is generally below 80 °C due to the biological activity limitations of the enzymes.

Aluminum chloride/urea (AlCl_3 -urea) system, also designated as the GALCA/GALKA system, was first developed and systematically investigated by Altunina and co-workers from the Institute of Petroleum Chemistry, Russian Academy of Sciences, in the 1990s (Altunina et al., 1995). This system was originally engineered to address conformance control challenges in high-temperature sandstone reservoirs, where conventional organic polymer gels often suffer from thermal degradation and long-term stability issues.

The core working mechanism of the AlCl_3 -urea system relies on thermally triggered in situ gelation, driven by sequential hydrolysis reactions occurring under reservoir temperature conditions. Under surface conditions, the system is formulated as a low-viscosity aqueous solution with an initial pH of 2.5–3.5. It primarily consists of aluminum chloride, urea, and minor functional additives, allowing for easy injection into the reservoir using standard oilfield equipment without premature viscosity buildup. Once placed in the target formation, the hydrolysis of urea was initiated, elevating the solution pH. When the pH reaches the narrow critical window of 3.8–4.2, rapid hydrolysis and polycondensation of aluminum ions occur, leading to instantaneous formation of a three-dimensional coagulated aluminum hydroxide gel (Altunina and Kuvshinov, 2007). AlCl_3 -urea system has been extensively validated in pilot tests and commercial field applications across multiple oil fields globally. The earliest and most extensive field implementations were conducted in Upper Jurassic high-temperature reservoirs (340–400 K, 67–127 °C) of West Siberia, including the Nivagalskoye, Las-Eganskoye, Pokamassovskoye, and Ershovoye oil fields. In these applications, 24–50 m³ of gel-forming solution was injected per well, with a designed gelation time of 3–14 d (Altunina and Kuvshinov, 2008). Field results demonstrated that the system effectively modified the water injection profile, reduced production well water cut by 10%–50%, and achieved incremental oil production of nearly 40–60 tons per ton of injected gel-forming system. Following success in West Siberia, the system was successfully applied in the White Tiger offshore oil field in Vietnam, withstanding formation temperatures up to 170 °C. In the Usinskoye oil field in Russia's Komi Republic, the commercial GALKA was applied in steam injection wells, withstanding temperatures up to 300–320 °C, reducing water cut by 3%–45% and increasing oil production by an average of 23% across 29 production wells (Altunina et al., 2011). In addition, this gel system has been applied to control water production in the Tunu gas reservoirs, achieving relatively good results in reducing the volume of water invasion (Chaabouni et al., 2007; Cheneviere et al., 2005). However, the gas production rate of several wells also

dropped significantly. These field applications have proven the technical and economic feasibility of the AlCl_3 -urea system in specific high-temperature reservoir conditions, establishing it as a classic inorganic gel system for water shutoff and profile control.

However, despite its successful applications, the inherent limitations and application defects of the traditional AlCl_3 -urea system have severely restricted its widespread promotion and adaptation to complex reservoir conditions, especially in high-temperature, high-salinity, and strongly heterogeneous reservoirs. The gelation is excessively strong temperature and pH dependent. The gelation process is governed by two consecutive reactions: urea hydrolysis acts as the rate-limiting step at 70–100 °C. Above 100 °C, aluminum hydroxide coagulation becomes the rate-controlling step. This strong temperature dependency creates fatal operational risks: in high-temperature deep reservoirs, the system is prone to premature gelation in the wellbore or near-wellbore zone. Besides, the system has an extremely narrow pH window for gelation initiation, coupled with poor anti-interference ability against complex formation environments. Uniform bulk gelation can only be achieved within the narrow pH range of 3.8–4.2, and multiple factors in actual reservoir conditions severely disrupt the system's pH evolution. On one hand, massive dilution by formation water reduces the effective concentration of aluminum salt and urea, and alters the acid-base environment via formation water buffering. On the other hand, the strongly acidic initial solution reacts with carbonate cements and clay minerals in the reservoir, consuming H^+ in the system and causing abnormal pH fluctuations, which ultimately lead to uncontrolled gelation time, discontinuous gel structure, or even complete gelation failure. Furthermore, the strongly acidic AlCl_3 solution causes severe corrosion to downhole metal pipes and equipment, greatly increasing anti-corrosion costs in field construction. These inherent defects of the traditional AlCl_3 -urea system make it difficult to meet water shutoff and profile control requirements under complex reservoir conditions.

Polyaluminum chloride (PAC), with its pre-polymerized aluminum-oxygen polynuclear structure, wider gelation pH range, milder acid-base properties, and excellent dilution resistance and salt tolerance, has emerged as the most promising core material to replace traditional AlCl_3 (Altunina et al., 1995; Herring et al., 1984). Developed as an alternative to traditional coagulants like aluminum sulfate, it emerged from advancements in water treatment chemistry (Shen and Dempsey, 1998). PAC is primarily used in water purification (drinking water and wastewater treatment) to remove suspended solids, colloids, and organic matter.

PAC is cheaper than some commonly used organic polymers such as acrylamide-based polymers and polysaccharide. Owing to the low viscosity, excellent thermal stability, and injectivity, PAC gels have been widely applied to control the conformance problems in steam flooding projects, and the concentration could reach up to 20% (Chen et al., 2024). PAC is often combined with urea to accelerate the gelation at low to medium temperatures. While at high temperature, even PAC alone could gel readily within several hours (He et al., 2017). Therefore, we must extend the gelation time of PAC to assure a relatively wide safety window during the field execution. Another problem that needs to be solved is that the low viscosity of PAC solution after being placed in the fracture could be diluted and flushed out by the formation water readily. Viscous pre and tail polymer slugs are needed to prevent the PAC solution from diluting and filtration.

In this work, we systematically evaluate the gelation behavior of PAC with different components and additives. We also explore approaches to delaying the gelation of polyaluminum chloride at high temperatures. In addition, the injectivity and plugging performance of PAC is evaluated using sandstone cores, sand packs,

and open fractures. Last, we evaluate the dynamic gelation behavior of PAC at high temperatures using a long-tube model.

2. Experimental section

2.1. Materials

Polyaluminium chloride with basicities of 35% and 75% was purchased from Gongyi Water Purification Company. Methyl formate, ethyl acetate, methyl lactate, ethyl lactate, and urea were obtained from Sigma. Polymers were kindly donated by SNF Floerger and Shandong Polymer Biochemicals Co., Ltd.

2.2. Gelation behavior

The gelation time was defined as the time when the gelant solution transformed into a non-flowable gel plug. Gel code method was used to evaluate the gel strength, as shown in Table 1 (Sydansk, 1988). A typical gelation test procedure is shown as follows: First, dissolve 8%–15% of PAC, along with a retarder or an accelerator, in tap water. Transfer the gelant solution into tubes and age them in a high-temperature oven. The tubes were checked periodically to determine the gelation time.

2.3. Thermal stability

A high-temperature and high-pressure resistant glass tube and a stainless steel container were used during the long-term thermal stability test. The gelant was transferred to the container after sparging with argon for 20 min. Gel strength and dehydration ratio were recorded throughout the test.

2.4. Core flooding experiment

2.4.1. Injectivity test

This work aims to develop a mature gel formulation for the upcoming pilot test. The target well has experienced severe sand production, and the bottom intake interval has been clogged by sand. Therefore, a critical property to evaluate is injectivity. The gelant should not form a gel cake at the core inlet and the injection pressure should remain stable throughout the large-volume injectivity test. Berea sandstone cores with water permeability ranging from 20 to 900 mD were used during the test. The injection rate varied from 1 to 10 mL/min.

2.4.2. Static plugging test

The fracture model was used to evaluate the plugging performance of the PAC gel, as shown in Fig. 1. The preparation procedure for the fracture model is detailed in our previous publications (Song et al., 2022a, 2022b). A typical plugging test was conducted as follows: First, a 12% PAC gelant was injected into the fracture at

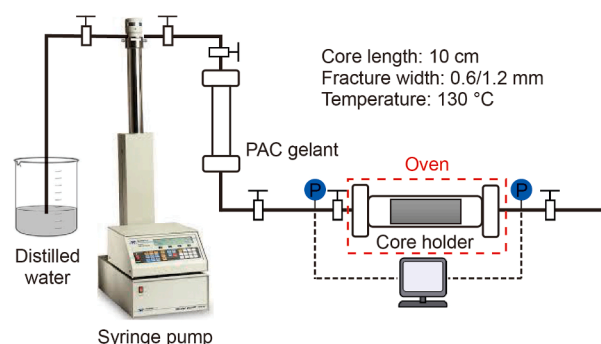


Fig. 1. Static core flooding setup.

an injection rate of 1 mL/min. A total of 10 pore volumes (PV) of gelant was injected to ensure the fracture was completely filled. Next, the core holder was sealed and aged at 130 °C for 2 d to allow the gel to fully cure. After curing, a 2% KCl solution was injected at an injection rate of 1 mL/min to determine the water breakthrough pressure. Following water breakthrough, the flow rate was increased to 1, 3, and 5 mL/min to assess whether the gel could be easily flushed out of the fracture.

2.4.3. Dynamic plugging test

A 50-m-long stainless steel tube with an inner diameter of 2 mm was used to evaluate the dynamic gelation behavior of PAC at 130 °C, as shown in Fig. 2. A backup pressure gauge was installed at the tube outlet to prevent water evaporation. The gelant injection rate was 0.0545 mL/min (25 m/d), and the injection pressure was monitored throughout the injection process.

3. Results and discussion

3.1. Effect of basicity and temperature on gelation time

The gelation behavior of PAC is highly sensitive to pH and basicity. A high pH can accelerate the gelation process and sometimes cause the direct formation of $\text{Al}(\text{OH})_3$ precipitate. A further increase in pH can dissolve the $\text{Al}(\text{OH})_3$ precipitate. Basicity is defined as the ratio of OH^- to Al^{3+} ions and one of the most important parameters of PAC.

In the case of low-basicity PAC, the solution contains positively charged PAC oligomers. The gelation process involves two main steps. First, PAC oligomers form long-chain polymers through hydrolysis and hydroxyl bonding. Then these long-chain polymers transform into a bulk gel through further reaction. In contrast, for

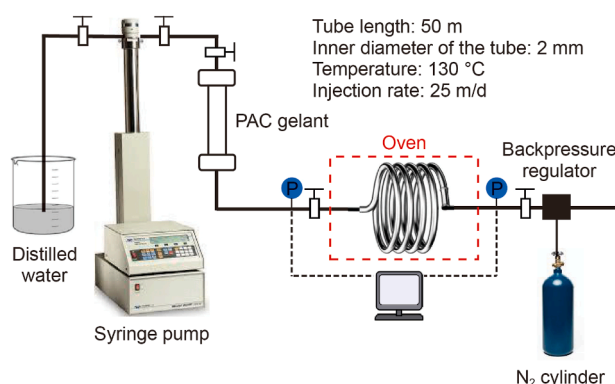


Fig. 2. Dynamic core flooding setup.

Table 1
Gel code method.

Strength code	Description
A	No detectable gel formed
B	Highly flowing gel
C	Flowing gel
D	Moderately flowing gel
E	Barely flowing gel
F	Highly deformable nonflowing gel
G	Moderately deformable nonflowing gel
H	Slightly deformable nonflowing gel
I	Rigid gel



Fig. 3. Gelant appearance of low-basidity PAC at 150 °C.

the high-basidity PAC, the gelation occurs relatively faster because PAC chains are relatively larger compared with those in low-basidity PAC. Theoretically, at high temperatures, retarders are required to delay the gelation rate of high-basidity PAC, while accelerators are needed for the low-basidity PAC.

We prepared PAC solutions at different concentrations with tap water to evaluate gelation behavior at 100–150 °C. The PAC concentrations range from 5% to 15%. The initial pH values of the low- and high-basidity PAC were 3.22 and 4.13, respectively. It should be noted that the low-basidity PAC failed to form a gel at 130–150 °C during the two-week gelation test, as shown in Fig. 3. This failure is attributed to the initially low pH, which prevented PAC hydrolysis under acidic conditions. Previous studies have proven that the PAC hydrolysis is extremely slow when the solution pH is below 3.5, necessitating the use of accelerator for the low-basidity PAC (Zhao et al., 2009). Furthermore, the solution pH decreases during hydrolysis, which further prevents the formation of PAC aggregates, causing the reaction to halt during the induction period.

For high-basidity PAC, gelation occurs readily at high temperatures, and the gelation time increases with concentration, as shown in Table 2. The gelation times of 15% PAC at 100, 130, and 150 °C were 36, 33, and 16 h, respectively. At 130 °C, the gelation times of 7%, 12%, and 15% PAC were 22, 28, and 36 h, respectively. This behavior is attributed to the increasing repulsion between the highly positive charges on PAC aggregates as the PAC concentration increases, preventing the further aggregation (Chen et al., 2009).

Table 2

PAC gelation time at different temperatures.

PAC basicity	PAC concentration, %	Gelation time at different temperatures, h		
		100 °C	130 °C	150 °C
Low basicity	7	–	–	–
Low basicity	12	–	–	–
Low basicity	15	–	–	–
High basicity	7	22	10	2
High basicity	12	28	10	2
High basicity	15	36	12	3



Fig. 4. Gelation behavior of PAC/urea and PAC/NaHCO₃ mixtures.

However, it should be noted that the 7% PAC gel is too weak and brittle to meet field requirements. Therefore, we further studied the gel behavior of 12% and 15% PAC gels.

3.2. Effects of accelerator and retarder on gelation time

As mentioned above, low-basidity PAC failed to gel at high temperatures, therefore, accelerators such as urea were added to trigger gelation at medium to high temperatures. It should be noted that the gelant did not gel when the urea concentration was 4.5%, but gelled within 2 h at 130 °C, when the urea concentration increases from 4.6% to 5.0%. The hydrolysis of urea gradually increases the pH, facilitating the hydrolysis of PAC. However, the gelation of low-basidity PAC is very sensitive to pH changes and difficult to control. Additionally, the addition of NaHCO₃ and NaOH can cause direct precipitation of Al(OH)₃, as shown in Fig. 4. Furthermore, the low-basidity PAC/urea system has poor thermal stability at high temperatures, with severe syneresis observed after 17 h of aging at 130 °C, as shown in Fig. 5. Therefore, based on the gelation tests, low-basidity PAC is not recommended for conformance control in high-temperature reservoirs.

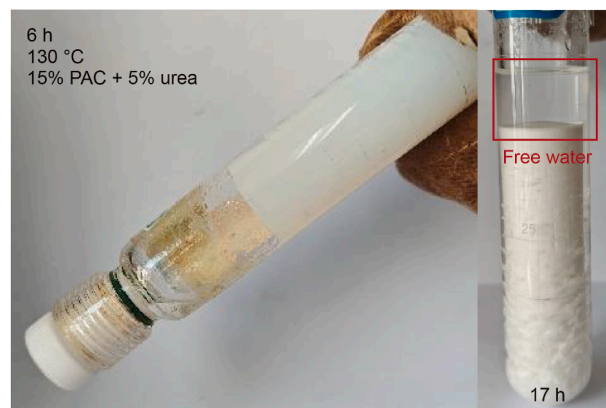


Fig. 5. Low-basidity PAC gel suffers from severe syneresis at high temperature.

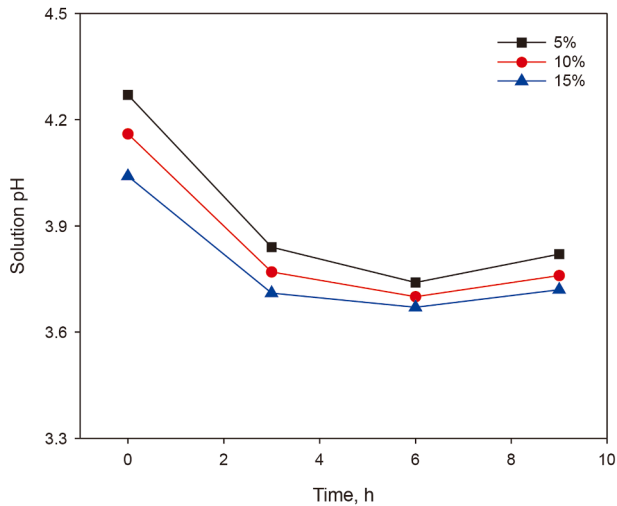


Fig. 6. pH changes during the gelation process.



Fig. 7. Effect of pH on the gelation behavior of 12% PAC at 130 °C.

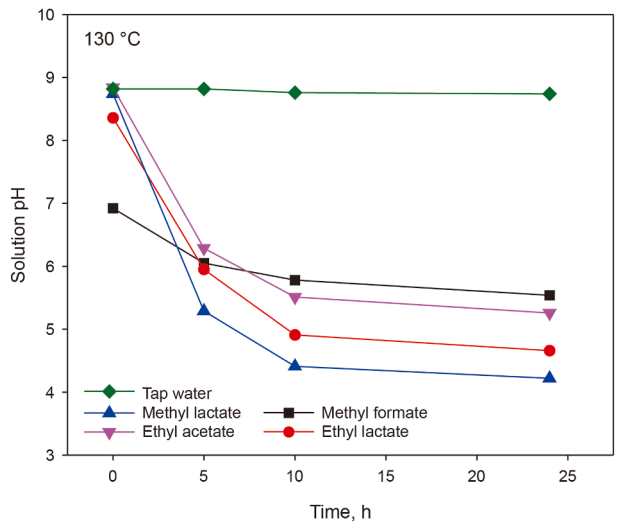


Fig. 8. Solution pH changes over time.

Table 3
PAC gelation time of high-basicity PAC/methyl lactate under different temperatures.

Temperature, °C	PAC concentration, %	Gelation time at different methyl lactate concentrations, h		
		0	0.1%	0.2%
130	12	10	24	36
	15	12	28	44
150	12	2	6	9
	15	3	14	18

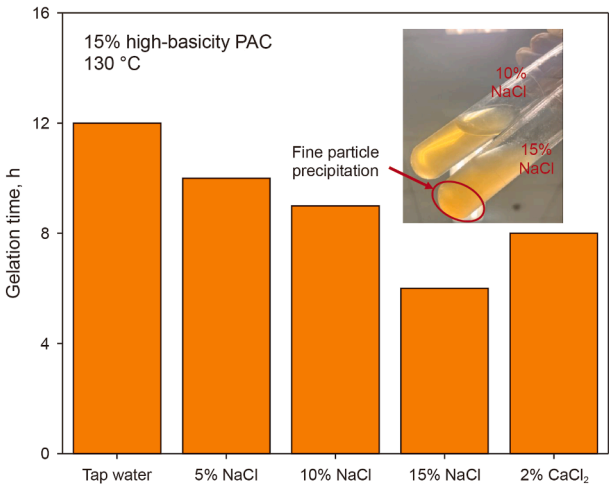


Fig. 9. Effect of salinity on the gelation time of high-basicity PAC.

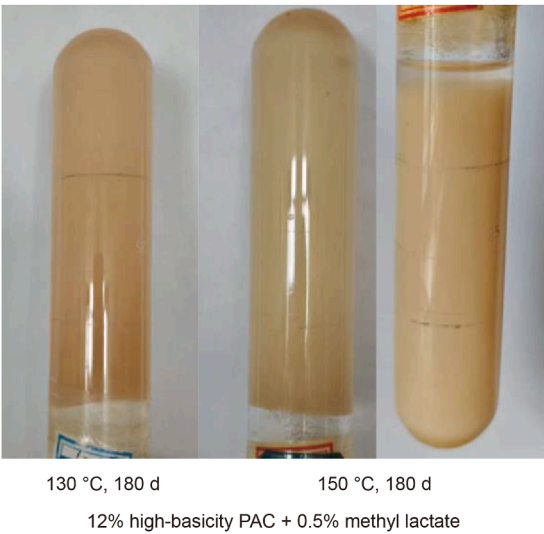


Fig. 10. Long-term thermal stability of high-basicity PAC at 130 and 150 °C.

Fig. 6 shows the pH changes during the gelation process of high-basicity PAC, where the pH gradually decreases from 4.1 to below 3.5 as gelation progresses. The gelation of high-basicity PAC occurs relatively fast at high temperature (150 °C); however, large-volume injections can last several days. Therefore, we aim to delay

the gelation time by adjusting the solution pH. Based on the gelation mechanism, one possible approach to delay gelation is to lower the solution pH. This is because the gelation reaction is reversible, and the forward reaction rate and extent can be slowed by adding products, especially H^+ . However, it is important to note that the pH cannot be directly altered by adding strong acids such as HCl or HNO_3 . Similar to low-basidity PAC, high-basidity PAC does

not gel when the solution pH is below 3.5. As shown in Fig. 7, even a few drops of these strong acids are sufficient to prevent gelation, making it extremely difficult to control the amount of strong acid added during field applications. Therefore, we aim for a gradual decrease in solution pH, where the hydrolysis of PAC is hindered but not completely stopped. Esters can generate H^+ during hydrolysis at high temperatures at a relatively slow rate, and their

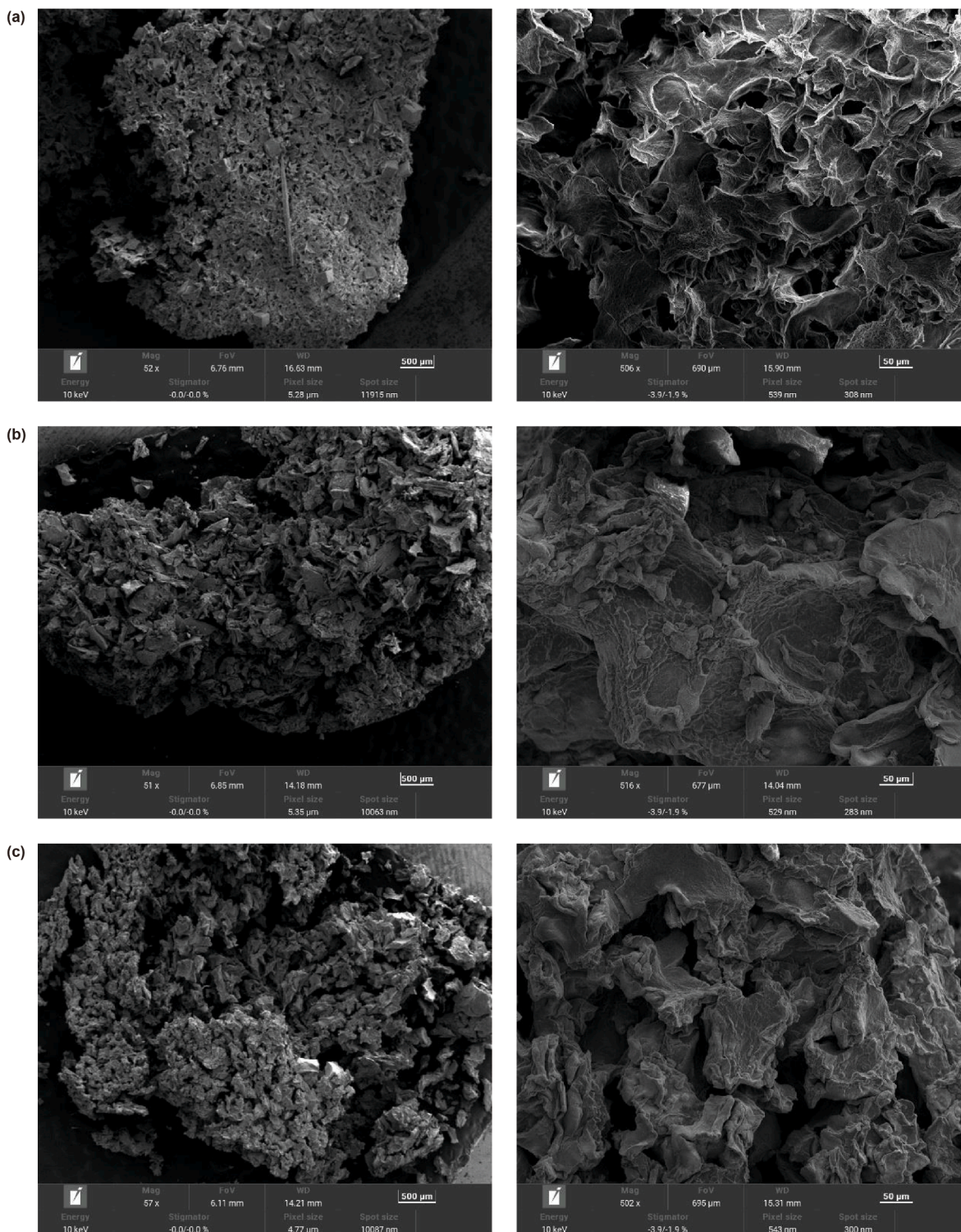


Fig. 11. SEM images of 7% (a), 12% (b), and 15% (c) PAC gels.

hydrolysis products are less potent than HCl or HNO₃, which would delay rather than prevent gelation.

Fig. 8 shows the pH changes of ester solutions over time. Methyl lactate is more effective than other esters in lowering the solution pH. To be more precise, it can reduce the solution pH to 4–5 after 10 h of aging at 130 °C.

Table 3 summarizes the gelation behavior of PAC/methyl lactate at 130 and 150 °C. The gelation time could be extended to over 70 h at 130 °C with 0.2% methyl lactate. In addition, at 150 °C, the gelation time could be further delayed from 2–3 to 6–18 h by adding 0.1%–0.2% methyl lactate. The laboratory experiment demonstrated that adding an ester to the PAC solution is an effective method to delay gelation time at high temperatures.

3.3. Effect of salinity on gelation time and thermal stability

In this section, we evaluated the effects of salinity on gelation behavior, gel strength, and long-term thermal stability at 130 °C. Fig. 9 shows that salinity negatively affects gelation time, which decreased from 12 to 6 h as the NaCl concentration increased from 0 to 15%. In addition, divalent cations have a more pronounced impact on gelation time. The gelation times in 15% NaCl and 2% CaCl₂ solutions were 6 and 8 h, respectively. It should be noted that gel strength increased with increasing salinity. PAC dissolved readily in 0–12% NaCl solutions but could not completely dissolve when the NaCl concentration exceeded 13%. Some extremely fine particles were found at the bottom of the beaker, which could not be dissolved even after vigorous stirring. However, these gelants could still form gels at high temperatures. Fig. 10 shows the long-term thermal stability of PAC gels at high temperatures, with the gel color gradually changing from orange to light orange. PAC exhibited excellent thermal and phase stability at 130 °C, with only a trace amount of free water observed on top of the gel. At 150 °C, syneresis occurred with water loss of less than 5%, yet the gel maintained good structural integrity.

3.4. SEM analysis

We studied the microstructure of PAC gels at various concentrations, ranging from 7% to 15%, as shown in Fig. 11. A notable difference among different samples is that the network integrity gradually decreases as the PAC concentration increases. The 7% PAC gel exhibits a relatively dense network structure, whereas the 12% and 15% PAC gels appear more like amorphous particles, lacking a distinct network structure.

3.5. TGA analysis

At the temperature of 0–100 °C, all samples exhibit rapid weight loss, primarily due to the evaporation of physically adsorbed water and weakly bound surface water, as shown in Fig. 12. The dry powders (represented by hollow symbols) and gels (solid symbols) show similar initial trends. Thermogravimetric (TG) analysis characterizes the thermal decomposition behavior of the initial dry powders and PAC gels, with black curves representing high-basidity PAC formulations and red curves indicating their low-basidity counterparts. As the temperature advances to 100–300 °C, the rate of weight loss diminishes, corresponding to the dehydration of coordinated water molecules and the condensation of surface hydroxyl groups. Within this mid-temperature range, high-basidity PAC specimens retain a higher residual mass compared to low-basidity samples. This trend results from the dense, hydroxyl-enriched structural architecture of high-basidity PAC, which contains less labile water and undergoes more gradual dehydroxylation kinetics (Hartman et al., 2005; Zhang

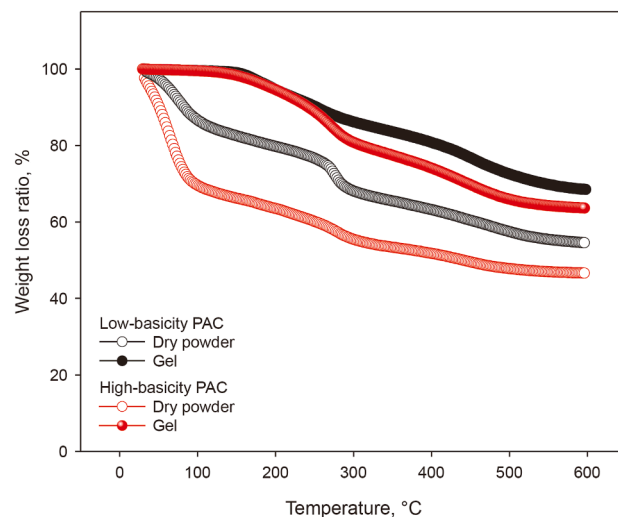


Fig. 12. TG curves of dry powders and PAC gels with low and high basicities.

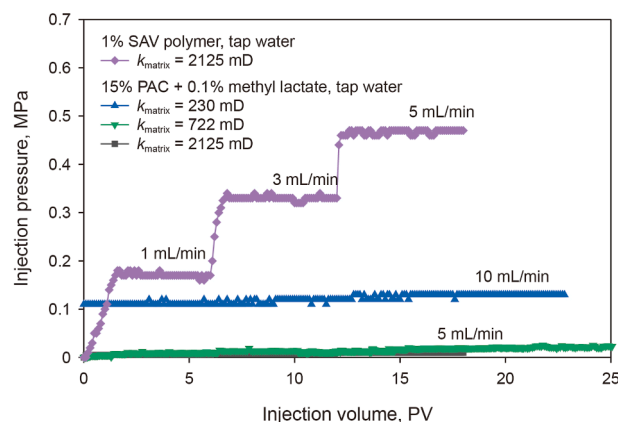


Fig. 13. Injectivity of PAC in cores with different permeability at 80 °C (core length: 10 cm; k_{matrix} is the permeability of rock matrix).

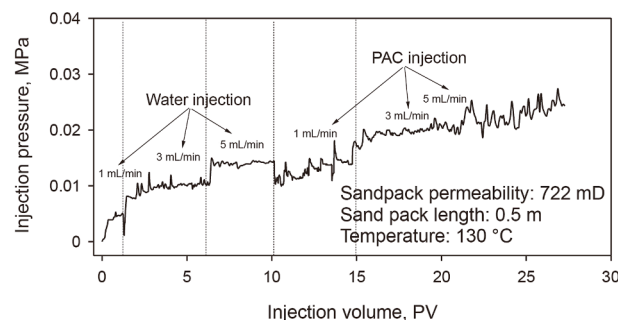


Fig. 14. Injectivity of PAC in a 722-mD sandpack at 130 °C.

et al., 2018). In the high-temperature range (300–600 °C), a sustained, gradual weight loss occurs, corresponding to the decomposition of residual hydroxyl groups and the structural transformation of amorphous aluminum oxyhydroxide phases into crystalline forms (Bishay et al., 2011).

Importantly, the thermal decomposition behavior observed via thermogravimetric analysis (TGA) provides fundamental mechanistic insights into the hydrothermal stability of PAC gels under

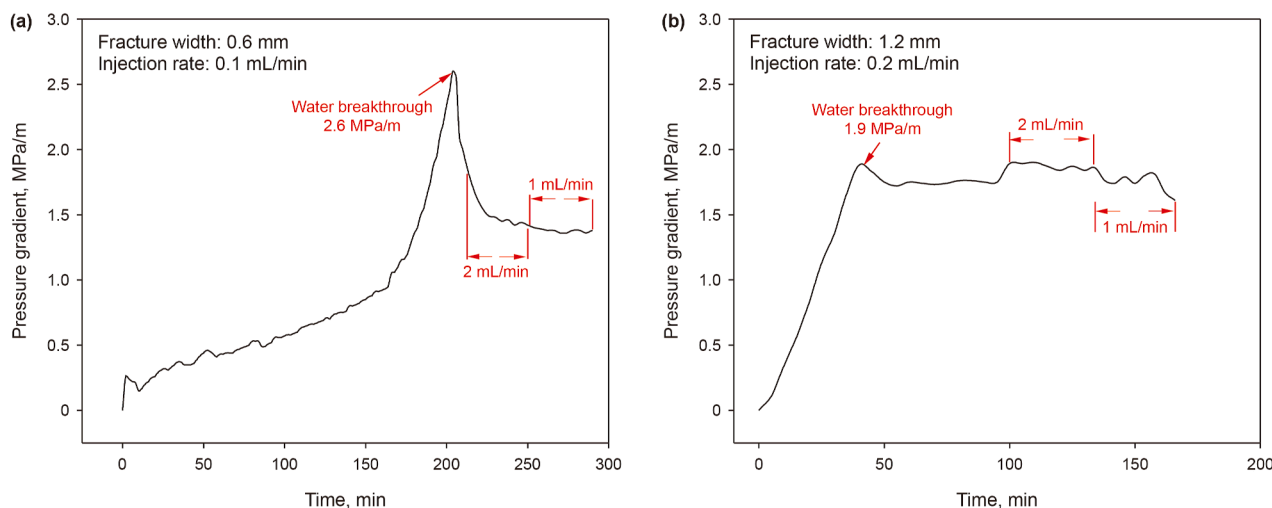


Fig. 15. Plugging test results for fracture widths of 0.6 (a) and 1.2 (b) mm.

reservoir conditions (Zhang et al., 2019). While TGA measures thermal degradation under programmed heating in air, the underlying structural transformation mechanisms directly correspond to those occurring during long-term hydrothermal aging at constant high temperatures in aqueous environments. The gradual dehydroxylation and condensation reactions of Al–O–hydroxyl groups observed in the 100–300 °C range in TGA represent the primary structural degradation pathways of PAC gels under hydrothermal conditions. High-basicity PAC specimens exhibited slower dehydroxylation kinetics and higher residual mass retention in this temperature range due to their intrinsically more condensed Al–O network architecture with fewer labile hydroxyl groups. This inherent structural stability explains why high-basicity PAC gels maintained superior mechanical strength and plugging performance after prolonged hydrothermal aging at high temperatures, whereas low-basicity PAC gels underwent more rapid structural breakdown and performance deterioration. Thus, TGA not only characterizes the thermal decomposition profile of PAC materials but also serves as a rapid predictive tool for evaluating their long-term hydrothermal stability in oilfield applications.

3.6. Injectivity test

The objective of this study is to develop a PAC gel system that can be effectively injected into fractured, high-temperature, and high-salinity sandstone gas reservoirs experiencing severe sand production. Therefore, we systematically investigated the injectivity of PAC in cores with varying permeability. Fig. 13 shows the injection pressure of PAC and SAV polymer in matrix samples of different permeability at 80 °C. PAC was easily placed within the rock matrix, with an injection pressure gradient of below 1.2 MPa/m in all cores. Moreover, under the same conditions, the injection pressure gradient of PAC was significantly lower than that of SAV polymer used in previous pilot tests. Fig. 14 shows the injectivity of PAC in a high-permeability sandpack at 130 °C. PAC was readily injected into the high-permeability sandpack, with an injection pressure gradient below 0.06 MPa/m at an injection rate of 5 mL/min.

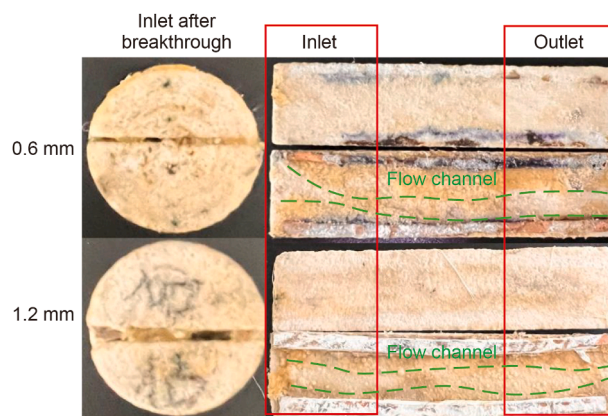


Fig. 16. Gel distribution in fractures after water breakthrough.

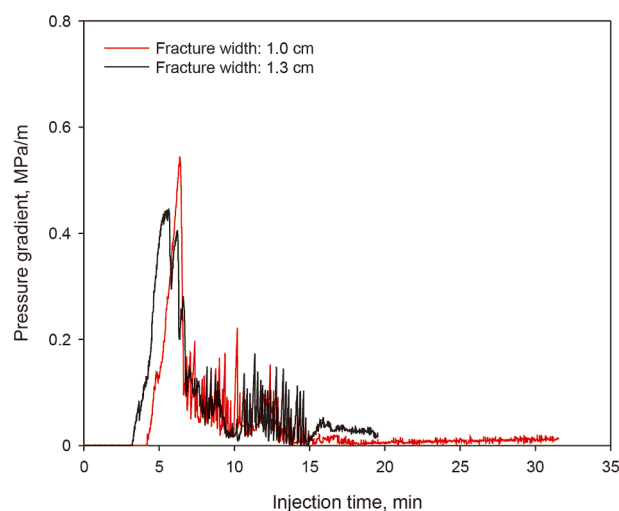


Fig. 17. Water breakthrough pressure gradients in large-opening fractures with widths of 1.0 and 1.3 cm.

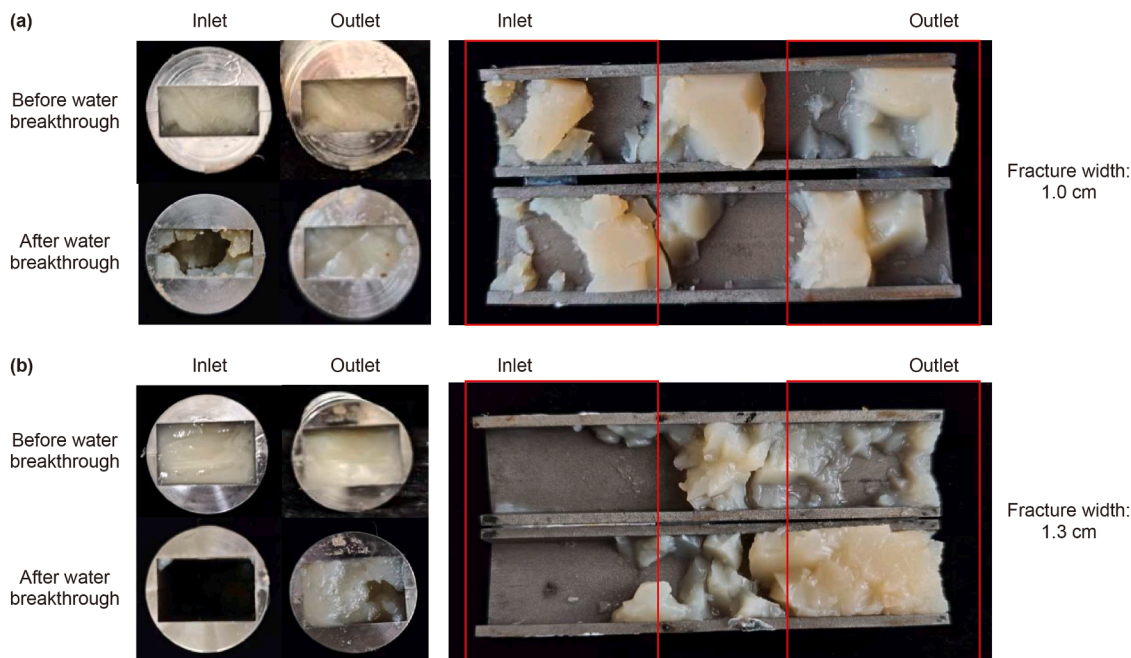


Fig. 18. Gel distribution in fractures after water breakthrough for fracture widths of 1.0 (a) and 1.3 (b) cm.

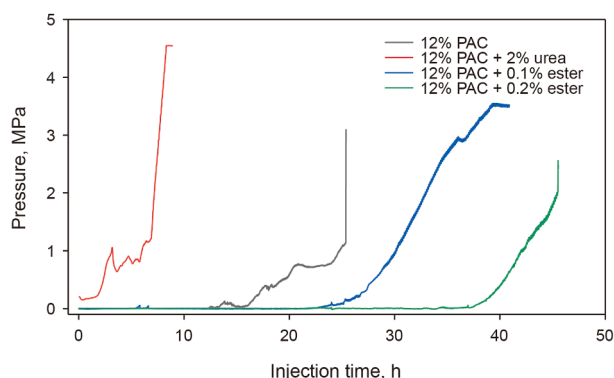


Fig. 19. Dynamic gelation behavior of PAC gels in a long tube at 130 °C.

3.7. Plugging test

Figs. 15 and 16 show the water breakthrough pressure tests for 0.6 and 1.2 mm fracture samples. The water breakthrough pressure gradients for 0.6 and 1.2 mm fracture samples were 2.6 and 1.9 MPa/m, respectively. It should be noted that even after water breakthrough, the post-injection pressure remains relatively high, with a stable water injection pressure gradient exceeding 1.5 MPa/m.

Figs. 17 and 18 show the water breakthrough tests conducted on large-opening fractures with widths of 1.0 and 1.3 cm, respectively. The water breakthrough pressure gradients for the 1.0 and 1.3 cm fractures were both below 0.6 MPa/m. Additionally, the post-water injection pressure gradients were lower than those observed in the previous millimeter-sized fracture models. After the experiments, a substantial volume of PAC gel was observed within the fractures. In the 1.0 cm fracture model, the PAC gel did not advance to the outlet; while for the 1.3 cm fracture model, the gel cake was displaced away from the inlet and gradually accumulated near the outlet.

Fig. 19 shows the dynamic gelation behavior of PAC gels within a stainless-steel tube with an inner diameter of 2 mm. The

dynamic gelation time was defined as the moment when the injection pressure increased sharply. At 130 °C, the dynamic gelation times for 12% PAC, 12% PAC + 2% urea, 12% PAC + 0.1% ester, and 12% PAC + 0.2% ester were 4, 12, 26, and 38 h, respectively. It is important to note that, unlike most organic polymer gel systems, the dynamic gelation of PAC gel is similar to its static gelation time (He et al., 2017; Zhang et al., 2014). The dynamic gelation test confirmed that adding ester could delay instead of preventing the gelation.

4. Further discussion

In this study, we successfully delayed the gelation rate of PAC by adding esters, providing a new strategy to control unwanted water production. However, this gel system has several limitations. First, a relatively high concentration of PAC is required to ensure long-term thermal and phase stability, and optimal concentration increases with reservoir temperature and salinity. Additionally, the gelation of PAC is strongly pH-dependent, even though the initial gelant pH can be controlled by adding weak or strong acid. During large-volume, long-term injection, however, formation water and reservoir rock can act as potent buffers, causing fluctuations in pH and gelant composition. In this work, we extended gelation time by adding ester. It should be noted that adding ester is an effective method to delay gelation in fractures or void spaces, but when dealing with permeable rock, chromatographic separation cannot be ignored, as the adsorption capacities of formation rock to PAC and ester differ. Gelation is insensitive to PAC concentration but highly sensitive to ester concentration; thus even a slight variation in ester concentration can significantly affect gelation time. In addition, due to the differences in molecular size and polarity between PAC and ester, they do not migrate at the same pace through the rock matrix.

To address the challenge of chromatographic separation in porous media during field operations, several strategies can be employed. First, pre-flush the formation rock with an ester solution at 1.2–1.5 times the concentration of the main gelant slug to saturate the adsorption sites. This approach significantly reduces

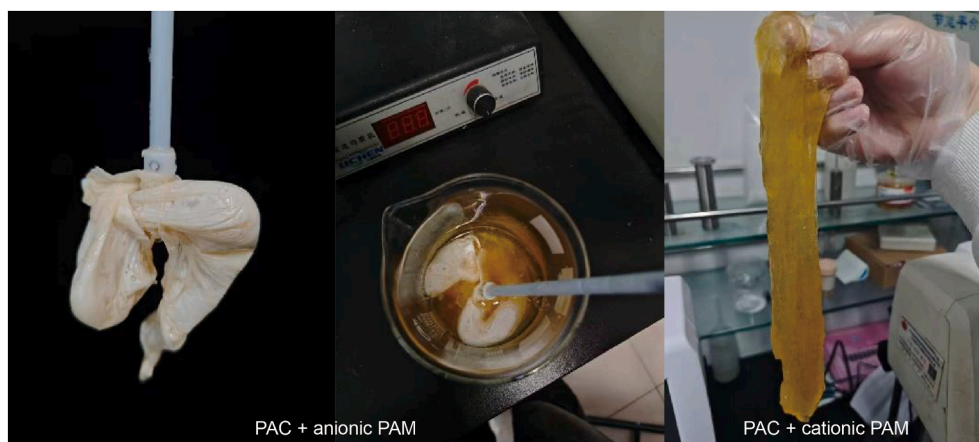


Fig. 20. PAC and polymer mixture.

the adsorption of ester from the subsequent main gelant slug. Second, for in-depth profile control, a concentration gradient slug design can be adopted. In this design, the front 20%–30% of the main gelant slug contains 50%–60% higher ester concentration than the designed average, while the rear 20%–30% contains 10%–15% lower ester concentration. The specific concentrations can be calculated based on the water invasion volume of the treated strata. This gradient design compensates for the faster migration of ester molecules, ensuring that the entire gelant slug maintains a relatively uniform ratio during treatment. Finally, increasing the injection rate within the formation fracture pressure limit can reduce the residence time of the gelant in the porous media, thereby limiting the extent of chromatographic separation.

Finally, in real scenarios of fracture shutoff in a high-temperature gas reservoir, the gelant slug should have a relatively high viscosity. This is because if the initial viscosity of gelant is too low, the gelant could be flushed out from the target zones readily and cannot form a continuous gel plug in the fractures, as the energy of adjacent aquifer is potent. For example, in our previous pilot research, PEI and SAV-333 was deployed as the main component, the viscosity of initial gelant at 130 °C under the shear rate of 7.34 s^{-1} was around 33 mPa·s, which is relatively high compared with formation water. However, the viscosity of PAC solution is lower than 3 mPa·s at 130 °C under the shear rate of 7.34 s^{-1} . Two methods could be deployed to improve the plugging capacity, including tackifying the PAC solution or injecting viscous polymer solution before and after PAC injection. Tackifying the PAC solution requires a high concentration of polymer, and the polymer should be compatible with PAC at high temperatures. This is quite challenging, because most commercially available polymers are anionic and non-ionic PAM which could be chelated by PAC readily at ambient temperatures. Theoretically, cationic polymer should be compatible with PAC, but they are quite expensive, and a relatively high concentration of cationic polymer is needed to increase the viscosity of PAC solution. We evaluated the compatibility of several commercially available polymer with PAC and found cationic polymer is a good choice to be used as the pre and tail slug during PAC injection. PAC could gel the polymer solution gradually, instead of forming precipitation, as shown in Fig. 20.

To improve the anti-scouring ability of the low-viscosity PAC solution, a multi-slug combination injection process is proposed as the primary field solution. First, a weak and mobile PEI-based organic gel slug is placed before PAC injection. The front polymer gel slug not only increases the viscosity of the displacement front to reduce viscous fingering but also forms a viscous buffer zone

that prevents the subsequent low-viscosity gelant from being rapidly flushed by formation water. After PAC placement, a large volume of viscous cationic polymer solution is injected as a tail slug, which can gradually gel with PAC and prevent the backflow of PAC gelant.

5. Conclusions

Targeting the technical requirements of water shutoff in fractured gas reservoirs with ultra-high temperature (150 °C) and high salinity (200,000 mg/L), this study systematically evaluated the gelation behavior, key influencing factors, thermal stability, injectivity, and plugging performance of PAC-based inorganic gel. The main conclusions are drawn as follows:

- (1) Basicity is the dominant parameter governing the high-temperature gelation capacity of PAC. Low-basicity PAC (initial pH 3.22) suffers from severely inhibited hydrolysis at 130–150 °C, and fails to form effective gels within the 14-d test period. In contrast, high-basicity PAC (initial pH 4.13) undergoes rapid hydrolysis and polycondensation at high temperatures, resulting in the formation of a three-dimensional network gel. The gelation time increases with rising PAC concentration. A gel formed by 7% PAC has insufficient strength and high brittleness, whereas high-basicity PAC at 12%–15% mass concentration forms high-strength gels that meet field construction requirements.
- (2) Methyl lactate serves as a high-efficiency retarder to achieve precise regulation of PAC gelation time at high temperatures. It slowly releases H^+ via high-temperature hydrolysis, delaying rather than completely blocking the hydrolysis and polycondensation of PAC. This addresses the industry pain points of strong acid-based pH regulation, which tends to cause complete gelation failure and is difficult to dose accurately in the field. With 0.2% mass concentration of methyl lactate, the gelation time of 15% PAC system is extended from 12 to 44 h at 130 °C, and from 3 to 30 h at 150 °C, fully meeting the safe construction window requirements for large-volume field injection.
- (3) The high-basicity PAC gel system has excellent thermal stability and salt resistance. Thermogravimetric analysis (TGA) confirms that high-basicity PAC possesses a denser pre-polymerized Al–O polynuclear structure, resulting in superior thermal stability in the 300–600 °C range and significantly lower total mass loss compared to low-basicity

PAC. Scanning electron microscopy (SEM) results reveal that 7% PAC forms a dense three-dimensional network structure, whereas 12%–15% PAC gel presents an amorphous particle aggregate morphology that provides sufficient structural strength. After aging at 130 °C for 180 d, the gel contains only trace amount of free water and maintains excellent structural integrity; slight syneresis occurs at 150 °C, but the gel retains a stable structure. The system can be completely dissolved and form stable gels at NaCl mass fractions up to 12%, with gel strength slightly increasing with rising salinity, enabling adaptation to high-salinity formation conditions.

- (4) The PAC gel system exhibits outstanding injectivity and fracture plugging performance. The system has an ultra-low initial viscosity, with an injection pressure gradient below 1.2 MPa/m in sandstone cores of varying permeabilities, significantly outperforming traditional organic polymer gels in injectivity. In 0.6 and 1.2 mm wide fractures, the gel achieves water breakthrough pressure gradients of 2.6 and 1.9 MPa/m, respectively, and maintains a stable injection pressure gradient above 1.5 MPa/m after water breakthrough, providing long-term effective fracture plugging. The 50-m long-tube dynamic gelation test confirms that methyl lactate retains excellent regulation performance on dynamic gelation, and the system has good consistency between static and dynamic gelation time, allowing accurate prediction of field gelation behavior via laboratory static tests.
- (5) The PAC-methyl lactate inorganic gel system developed in this study effectively overcomes the inherent limitations of the traditional AlCl_3 -urea system, including its strong temperature sensitivity during gelation, narrow pH gelation window, severe corrosion of downhole tubing and equipment, and poor adaptability to formation conditions. Meanwhile, its raw material cost is 3 times lower than that of organic polymer gels, demonstrating promising potential for field applications in conformance control and water shutoff in high-temperature, high-salinity fractured gas reservoirs. To address the potential chromatographic separation effect in porous media and the risk of gelant being washed out by formation water due to low initial viscosity, future studies will focus on the compatibility and tackification of PAC with cationic polymers, as well as the evaluation of long-distance migration and gelation behavior at the core scale, aiming to improve the deep profile control performance of the system.

CRedit authorship contribution statement

Tao Song: Writing – review & editing, Writing – original draft, Visualization, Investigation, Formal analysis, Data curation, Conceptualization. **Man-Tian Li:** Methodology, Investigation. **Ying-Ting Zhu:** Investigation, Formal analysis, Data curation. **Song Zhang:** Software, Resources. **Fa-Lin Wei:** Visualization, Validation, Supervision. **Bin Ding:** Writing – review & editing, Visualization, Funding acquisition, Formal analysis.

Acknowledgments

This work was supported by the National Science and Technology Major Project for Novel Oil and Gas Exploration and Development (2025ZD1406402).

References

- Ahenkorah, I., Rahman, M.M., Karim, M.R., et al., 2021. Enzyme induced calcium carbonate precipitation and its engineering application: A systematic review and meta-analysis. *Constr. Build. Mater.* 308, 125000. <https://doi.org/10.1016/j.conbuildmat.2021.125000>.
- Altunina, L.K., Kuvshinov, V.A., 2007. Physicochemical methods for enhancing oil recovery from oil fields. *Russ. Chem. Rev.* 76 (10), 971. <https://doi.org/10.1070/RC2007v076n10ABEH003723>.
- Altunina, L., Kuvshinov, V., 2008. Improved oil recovery of high-viscosity oil pools with physicochemical methods and thermal-steam treatments. *Oil Gas Sci. Technol. – Rev. IFP* 63 (1), 37–48. <https://doi.org/10.2516/ogst:2007075>.
- Altunina, L., Bokserman, A., Kuvshinov, V., et al., 1995. Inorganic gels for enhanced oil recovery at high temperature. *Geol. Soc. Lond. Spec. Publ.* 84 (1), 219–223. <https://doi.org/10.1144/GSL.SP.1995.084.01.22>.
- Altunina, L., Kuvshinov, V., Ursegov, S., et al., 2011. Synergism of physicochemical and thermal methods intended to improve oil recovery from high-viscosity oil pools. In: IOR 2011–16th European Symposium on Improved Oil Recovery. <https://doi.org/10.3997/2214-4609.201404753>.
- Amani, P., Rudolph, V., Hurter, S., Firouzi, M., 2022. Sustainable dewatering of unconventional gas wells using engineered multiphase flow dynamics. *Fuel* 324, 124675. <https://doi.org/10.1016/j.fuel.2022.124675>.
- Bai, B., Zhou, J., Yin, M., 2015. A comprehensive review of polyacrylamide polymer gels for conformance control. *Petrol. Explor. Dev.* 42 (4), 525–532. [https://doi.org/10.1016/S1876-3804\(15\)30045-8](https://doi.org/10.1016/S1876-3804(15)30045-8).
- Bishay, I., Abd-El-Messieh, S., Mansour, S., 2011. Electrical, mechanical and thermal properties of polyvinyl chloride composites filled with aluminum powder. *Mater. Des.* 32 (1), 62–68. <https://doi.org/10.1016/j.matdes.2010.06.035>.
- Chaabouni, H., Enkababian, P., Chan, K.S., et al., 2007. Successful innovative water-shutoff operations in low-permeability gas wells. In: SPE Middle East Oil and Gas Show and Conference. <https://doi.org/10.2118/105262-MS>.
- Chen, L., Zhang, Z., Zeng, H., et al., 2024. Preparation and performance of high-temperature-resistant, degradable inorganic gel for steam applications. *SPE J.* 29 (8), 4266–4281. <https://doi.org/10.2118/219775-PA>.
- Chen, X.Q., Xie, L., Cao, M., et al., 2022. Synthesis and primary investigation of a novel inorganic gel based on calcium oxalate oligomers. *J. Mater. Sci.* 57 (2), 1036–1043. <https://doi.org/10.1007/s10853-021-06705-4>.
- Chen, Z., Luan, Z., Jia, Z., Li, X., 2009. Study on the hydrolysis/precipitation behavior of Keggin Al_{13} and Al_{30} polymers in polyaluminum solutions. *J. Environ. Manag.* 90 (8), 2831–2840. <https://doi.org/10.1016/j.jenvman.2009.04.001>.
- Cheneviere, P., Falxa, P., Alfenore, J., et al., 2005. Chemical water shutoff interventions in the Tunu gas field: Optimisation of the treatment fluids, well interventions, and operational challenges. In: SPE European Formation Damage Conference and Exhibition. <https://doi.org/10.2118/95010-MS>.
- Hartman, M., Trnka, O., Šolcova, O., 2005. Thermal decomposition of aluminum chloride hexahydrate. *Ind. Eng. Chem. Res.* 44 (17), 6591–6598. <https://doi.org/10.1021/ie058005y>.
- He, H., Wang, Y., Qi, Z., et al., 2017. Gelation performance and feasibility study of an environmental friendly improved inorganic aluminum gel for conformance control under harsh reservoir conditions. *J. Energy Resour. Technol.* 139 (1), 012911. <https://doi.org/10.1115/1.4035512>.
- Hearn, W., 2010. Gas well deliquification. In: Abu Dhabi International Petroleum Exhibition and Conference. <https://doi.org/10.2118/138672-MS>.
- Herring, G.D., Milloway, J.T., Wilson, W.N., 1984. Selective gas shut-off using sodium silicate in the prudhoe Bay field, AK. In: SPE Formation Damage Control Symposium. <https://doi.org/10.2118/12473-MS>.
- Karadkar, P., Almohsin, A., Bataweel, M., et al., 2023. In-situ pore plugging using nanosilica-based fluid system for gas shutoff to maximize oil production. *SPE Prod. Oper.* 38 (1), 104–112. <https://doi.org/10.2118/197578-PA>.
- Larsen, T., Lioliou, M., Josang, L.O., et al., 2006. Quasinatural consolidation of poorly consolidated oilfield reservoirs. In: SPE International Oilfield Scale Symposium. <https://doi.org/10.2118/100598-MS>.
- Pu, J., Bai, B., Schuman, T., 2019. A recrosslinkable preformed particle gel for conformance control in heterogeneous reservoirs containing linear-flow features. *SPE J.* 24 (4), 1714–1725. <https://doi.org/10.2118/191697-PA>.
- Pu, J., Luo, M.L., Wang, K., et al., 2024. Fabrication and release mechanism study of a nanocapsule breaker for controlling degradation rate of insoluble residue in slickwater at moderate-temperature reservoirs. *SPE J.* 29 (2), 973–984. <https://doi.org/10.2118/217981-PA>.
- Rooszhenas, A.A., Hematpur, H., Abdollahi, R., et al., 2021. Water production problem in gas reservoirs: Concepts, challenges, and practical solutions. *Math. Probl Eng.* 2021 (1), 9075560. <https://doi.org/10.1155/2021/9075560>.
- Shen, Y.-H., Dempsey, B.A., 1998. Synthesis and speciation of polyaluminum chloride for water treatment. *Environ. Int.* 24 (8), 899–910. [https://doi.org/10.1016/S0160-4120\(98\)00073-7](https://doi.org/10.1016/S0160-4120(98)00073-7).
- Smith, D., 2023. Flood management: Solving conformance or sweep efficiency problems: Part 1. *J. Pet. Technol.* 75 (4), 44–48. <https://doi.org/10.2118/0423-0044-JPT>.
- Song, T., Ahdaya, M., Zhao, S., et al., 2022a. Evaluation of a novel recrosslinkable hyperbranched preformed particle gel for the conformance control of high-

- temperature reservoirs with fractures. *SPE J.* 27 (6), 3598–3610. <https://doi.org/10.2118/209451-PA>.
- Song, T., Zhai, Z., Liu, J., et al., 2022b. Laboratory evaluation of a novel self-healable polymer gel for CO₂ leakage remediation during CO₂ storage and CO₂ flooding. *Chem. Eng. J.* 444, 136635. <https://doi.org/10.1016/j.cej.2022.136635>.
- Song, T., Bai, B., Eriyagama, Y., et al., 2023. Lysine crosslinked polyacrylamide—A novel green polymer gel for preferential flow control. *ACS Appl. Mater. Interfaces* 15 (3), 4419–4429. <https://doi.org/10.1021/acsami.2c17390>.
- Song, T., Tian, X., Bai, B., et al., 2024. Laboratory evaluation of high-temperature resistant lysine-based polymer gel systems for leakage control. *Geoenergy Sci. Eng.* 234, 212685. <https://doi.org/10.1016/j.geoen.2024.212685>.
- Song, T., Wu, H., Liu, P., et al., 2025. Water shutoff with polymer gels in a high-temperature gas reservoir in China: A success story. *Energies* 18 (24), 6554. <https://doi.org/10.3390/en18246554>.
- Sydansk, R.D., 1988. A new conformance-improvement-treatment chromium(III) gel technology. In: *SPE Enhanced Oil Recovery Symposium*. <https://doi.org/10.2118/17329-MS>.
- Tugan, M.F., 2020. Deliquification techniques for conventional and unconventional gas wells: Review, field cases and lessons learned for mitigation of liquid loading. *J. Nat. Gas Sci. Eng.* 83, 103568. <https://doi.org/10.1016/j.jngse.2020.103568>.
- Zhang, J., He, H., Wang, Y., et al., 2014. Gelation performance and microstructure study of chromium gel and phenolic resin gel in bulk and porous media. *J. Energy Resour. Technol.* 136 (4), 042910. <https://doi.org/10.1115/1.4027570>.
- Zhang, X., Han, M., Fuseni, A., et al., 2019. An approach to evaluate polyacrylamide-type polymers' long-term stability under high temperature and high salinity environment. *J. Pet. Sci. Eng.* 180, 518–525. <https://doi.org/10.1016/j.petrol.2019.04.092>.
- Zhang, Z., Jing, R., He, S., et al., 2018. Coagulation of low temperature and low turbidity water: Adjusting basicity of polyaluminum chloride (PAC) and using chitosan as coagulant aid. *Sep. Purif. Technol.* 206, 131–139. <https://doi.org/10.1016/j.seppur.2018.05.051>.
- Zhao, H., Liu, H., Qu, J., 2009. Effect of pH on the aluminum salts hydrolysis during coagulation process: Formation and decomposition of polymeric aluminum species. *J. Colloid Interface Sci.* 330 (1), 105–112. <https://doi.org/10.1016/j.jcis.2008.10.020>.
- Zhao, Y., Wen, X., Liu, Y., et al., 2024a. Innovative zoning control techniques for optimizing a megaton-scale CCUS-EOR project with large-pore-volume CO₂ flooding. *Energy Fuels* 38 (4), 2910–2928. <https://doi.org/10.1021/acs.energyfuels.3c04913>.
- Zhao, Y., Wen, X., Rui, Z., et al., 2024b. A novel dual-network CO₂-responsive particle gel for mitigating CO₂ channeling and leakage in hydrocarbon recovery and carbon storage. *Chem. Eng. J.* 498, 155187. <https://doi.org/10.1016/j.cej.2024.155187>.
- Zhu, D., Bai, B., Hou, J., 2017. Polymer gel systems for water management in high-temperature petroleum reservoirs: A chemical review. *Energy Fuels* 31 (12), 13063–13087. <https://doi.org/10.1021/acs.energyfuels.7b02897>.