Preventing sour gas kicks during workover of natural gas wells from deep carbonate reservoirs with anti-hydrogen sulfide fuzzy-ball kill fluid

Zhenfeng Yan1,2 | Chinedu J. Okere3 | Xinghang Zeng4 | Zhonghui Yao5 | Guandong Su3 | Maozong Gan3 | Yarong Fu6 | Xiujuan Tao3,7 | Lihui Zheng1,3

1College of Petroleum Engineering, National Engineering Laboratory of Oil and Gas Well Drilling Technology, Yangtze University, Wuhan, China
2CNPC Bohai Drilling Engineering Company Limited, Tianjin, China
3State Key Laboratory of Petroleum Resources and Engineering, College of Petroleum Engineering, China University of Petroleum (Beijing), Beijing, China
4SINOPEC Research Institute of Petroleum Engineering, Beijing, China
5Department of Engineering Supervision, PetroChina Changqing Oilfield Company, Xi’an, Shaanxi, China
6PetroChina Huabei Oilfield Company, Renqiu, China
7Key Laboratory of Auxiliary Chemistry and Technology of Chemical Industry, College of Chemical and Chemistry, Shaanxi University of Science and Technology, Xi’an, China

Correspondence
Xiujuan Tao, Key Laboratory of Auxiliary Chemistry and Technology of Chemical Industry, College of Chemical and Chemistry, Shaanxi University of Science and Technology, Xi’an 710021, China.
Email: taoxiujuan@sust.edu.cn

Lihui Zheng, College of Petroleum Engineering, State Key Laboratory of Petroleum Resources and Engineering, China University of Petroleum (Beijing), Beijing 102249, China.
Email: zhenglihui@cup.edu.cn

Funding information
Education Department of Shaanxi Province, Grant/Award Number: 20JK0542; China Scholarship Council, Grant/Award Number: 2019ZFY020452; Ministry of Science and Technology of the People’s Republic of China, Grant/Award Number: 2016ZX05066

Abstract
Workover of natural gas wells in deep carbonate gas reservoirs (DCRs) is facing multiple challenges such as fluid leakage, high temperature, and hydrogen sulfide (H2S) gas kick. Hence, well-killing fluids with satisfactory plugging ability, high-temperature tolerance, and anti-H2S ability are necessary. In this study, we developed a multifunctional anti-hydrogen sulfide fuzzy-ball kill fluid (AFKF) for preventing sour gas kicks in DCRs. The performance of the AFKF was optimized and analyzed via experiments and verified through a case study application. The results showed that the fuzzy-ball structures in the AFKFs demonstrated good stability under extreme H2S aging. The rate of change of certain critical rheological parameters such as apparent viscosity, dynamic plastic ratio, and density of AFKFs before and after hot rolling were no more than 5%. After plugging the fractures with the AFKFs at temperatures between 110°C and 150°C, the inlet driving pressure of the fractures increased from 20.73°C to 21.07 MPa, and no fluid loss was observed at the core outlet after a secondary displacement of formation water. The permeability recovery rate was greater than 90%. Application of AFKF in well DW-2 showed that the shut-in pressure rose to 24.6 MPa with no trace of...
H₂S gas at the wellhead after 4 days. The investigation of the H₂S mitigation mechanisms revealed that the plugging of the seepage channels by AFKFs forms interconnected bonds that improve the mechanical properties of the reservoir. Additionally, AFKFs absorb H₂S gases by protonation and dissociation reactions which convert the hazardous gas into an aqueous solution of sulfide ions (S²⁻). The proposed AFKF has proven to be effective means of mitigating H₂S in DCRs, and minimize the negative impacts of environmental polution, health risks, and equipment corrosion.

KEYWORDS
anti-hydrogen sulfide, deep carbonate reservoirs, formation damage, fuzzy-ball fluids, plugging ability, well-killing fluids

1 | INTRODUCTION

To meet the ever-increasing global natural gas demands, more deep carbonate reservoirs (DCRs) that are characterized by fractures, caves, and vugs are increasingly exploited.¹,² For example, in China, the onshore Puguang gas field, Taizhong gas field, Shunbei gas field, and offshore Bozhong gas field are famous gas fields belonging to Paleozoic carbonate gas reservoirs. Natural gas resources in DCRs are usually buried in deep formation that contains high acid gas such as hydrogen sulfide (H₂S).³ However, the constant action of acid gas under a high-temperature condition could lead to the wearing and tearing of the casings and the propagation of cracks in the cement sheath.⁴ In addition, high H₂S leakage during gas production also leads to adverse environmental, health, and safety issues that limit the field development processes.⁵–¹⁰ In this situation, experts could either abandon the well or execute a special well workover operation.¹¹

Workover operations in DCRs are usually challenging coupled with the potential emission of toxic H₂S gases that endanger the successful completion of the operation. Further, other associated problems such as high formation temperature that leads to equipment failure, reservoir damage, and environmental pollution are prone to occur.¹²,¹³ After long-term production cycles, three possible transformations occur in DCRs. First, the pressure gradient significantly declines. Then more interconnected fractures with complex networks are generated. Finally, the reservoir becomes strongly heterogeneous. These changes will make the workover operation a high-risk project (due to the serious leakage of formation and working fluids) that will negatively impact the project cost and outcome. Hence, it is important to develop a well-killing fluid with satisfactory plugging ability, high-temperature tolerance and stability, low degree of formation damage, and excellent H₂S absorption ability to complement the workover process of DCRs.

Previously, water-based well-killing fluids (WBKFs) were used to balance the formation pressure and inhibit fluid flow from the seepage channels based on cost advantages.¹⁴ However, because of the existence of multiple seepage channels in DCRs, a large amount of water leakage occurs and the plugging structure could not be formed. Hence, the balance between the pressure of the WBKF and the formation pressure will be difficult to control due to their weak plugging abilities, which could affect productivity, and possibly sour gas kick or blowout. To overcome the shortcomings of the WBKFs, oil-based, invert emulsion, and other hydrocarbon-based well-killing fluids were introduced. Although these kill-fluid systems showed good plugging ability, high-temperature tolerance, and stability, however, they are cost-ineffective, with negative environmental impact, and few reports have shown their good anti-H₂S abilities. Afterward, hydrogel-based kill fluids were developed to solve the problems of H₂S kicks during the workover operations in DCRs. The gel system is formed by crosslinking which creates a barrier within the seepage channels thereby isolating the connection between the wellbore and formation. But gels are prone to structural shrinkage under high-temperature conditions that will generate spaces within the plugging structure and seepage channel which may lead to the leakage of hazardous H₂S gases.¹⁵–²¹

Several fields and laboratory studies on the application of fuzzy-ball fluids have demonstrated its efficacy in providing high plugging strength at different reservoir conditions.²² Furthermore, the fuzzy-ball fluids are characterized by a dynamic plugging structure with self-matching and deformation ability, and vesicles of varying effective diameter that enables the formulation of a high plugging structure in different seepage channels. To date, conventional fuzzy-ball kill fluid (CFKF) has been successfully applied during
workover operations in tight sandstone reservoirs. Even so, field experiences indicate that the CFKF could not simultaneously solve the H₂S kick and low formation pressure challenges in DCRs. Therefore, it is necessary to develop a multifunctional fuzzy-ball kill fluid that will simultaneously solve the multiple challenges encountered during workover operation in DCRs. Such fluid will play a vital role in overcoming the environmental, health, and safety challenges encountered during several oil and gas field operations.

In this study, a multifunctional anti-hydrogen sulfide fuzzy-ball kill fluid (AFKF) was developed to overcome the aforementioned challenges in DCRs. Dry desulfurizing agents were optimized and added to the CFKFs to enhance their H₂S absorption ability. Laboratory experiments were systematically performed to optimize and evaluate the plugging ability, desulfurizing ability, thermostability, permeability recovery rate, and degree of formation damage of the AFKF. Furthermore, the application of the AFKF was verified through a reported case study application and the analysis of its well-killing mechanisms.

2 | EXPERIMENTAL DESIGN

Samples of the CFKF were prepared in the laboratory following the established procedures and guidelines prescribed in previous research (Appendix B1). Then desulfurizing agents were added to modify its rheological property and enhance its H₂S absorption ability. To optimize, analyze and improve its performance in reservoir conditions, four sets of experiments were conducted. At first, fluid sample optimization experiments were carried out to select an optimal desulfurizing agent. Second, stability evaluation experiments were done to ascertain the stability of the optimized samples under extreme conditions. Third, a plugging evaluation test was performed to ascertain its plugging ability under normal and extreme conditions. Finally, a formation damage evaluation experiment was conducted to determine its degree of formation damage and permeability recovery rate.

2.1 | Fluid sample optimization experiments

Fluid sample optimization experiments such as Iodometric titration and TURBISCAN-based experiments were conducted to select the best combination of a desulfurizing agent with stable particle size and compatibility. Detailed experimental procedures are provided in the following subsections.

2.1.1 | Optimization of desulfurizing agents: Iodometric titration

Nine simulated samples of AFKFs were prepared by adding 1 wt% each of nine different dry desulfurizing agents into a CFKF (Table B2). Their desulfurizing ability was measured according to the experimental flow chart described in Figure 1. H₂S from a gas cylinder was continuously injected into these samples for 60 min. The concentration of the absorbed sulfide ion (S²⁻) in the kill fluid for different samples of the formulated AFKFs was measured by iodometric titration. Then four fluid samples (fluid samples 6, 7, 8, and 9) with the highest concentration of S²⁻ were selected (Table SB2).

2.1.2 | Optimization of particle size and stability analysis: TURBISCAN-based experiment

The static stability of a mixture of fluids is usually characterized using the light scattering technique that is based on the operating principles of the Turbiscan LAB (Figure C1). Through a synchronous optical sensor, the...
Turbiscan measures the backscattered light as a function of the distance along the axis of the tube and time. To optimize the particle size and analyze the stability of the selected AFKFs (i.e., Fluid samples 6, 7, 8, and 9), a Turbiscan experiment was performed. The experimental procedures include (1) Pouring 20 ml of the AFKFs into the Turbiscan glass cell to a height of 40 mm (see Figure SC1b). (2) Place the glass cell into the Turbiscan stability analyzer. (3) Switch on the multi-user interface, fill in the necessary information describing the samples, set the scanning time to 30 min (for each sample), and click the “Start scanning” button. (4) After scanning, remove the scanned sample and insert it into the storage station. (5) Record the results of the backscattering (BS) and transmission (T) curves, the foam size, and its distribution rule before and after aging of the fluid samples.

The Turbiscan stability index (TSI) is used to estimate the stability of samples and their formulations. To determine the TSI for any sample, a specific height is selected, then every scan of measurement is compared to the preceding height, and the result is divided by the total selected height. The mathematical expression of the TSI is shown in Equation (1).

\[
\text{Turbiscan stability index (TSI)} = \sum \frac{\sum_{i} [\text{Scan}_{i}(h) - \text{Scan}_{i-1}(h)]}{H}
\]  

In Equation (1), \( h \) and \( H \) represent the selected height and the total height of the sample, respectively. Therefore, the smaller the TSI value the higher the stability of the sample. It is important to note that, at the end of the Turbiscan stability analysis, one of the four samples which demonstrates the highest stability is selected as the best choice for field-scale design and application.

### 2.2 | Stability evaluation experiments

Two sets of experiments were performed to evaluate the stability of the AFKFs under simulated conditions. First, the rheological properties of the fluid were observed at high temperatures and \( H_2S \) corrosive environment. Then the temperature protective ability of the formulation was observed at different densities. The mixture was stirred at 8000 r/min for 30 min and rolled for 16 h at different temperatures. Then the densities and other rheological parameters were recorded.

#### 2.2.1 | Evaluating the rheological properties of the AFKFs

A high temperature and \( H_2S \) corrosion testing kettle were used to age the AFKFs at a temperature of 130°C and pressure of 8.36 MPa (\( H_2S \) partial pressure is 2.65 MPa, carbon dioxide partial pressure is 2 MPa) for 48 h. Rheological properties (such as apparent and plastic viscosity, dynamic shear force pH value) of the AFKFs before and after aging were recorded. It is noteworthy that the maximum experimental temperature was set at 130°C due to the allowable operating temperature limit of the corrosion testing kettle.

#### 2.2.2 | Thermostability evaluation

To meet the high-temperature demand of carbonate reservoirs, a high-temperature protective agent was added to the AFKFs. Then the temperature protective ability of the formulation was observed at different densities. The mixture was stirred at 8000 r/min for 30 min and rolled for 16 h at different temperatures. Then the densities and other rheological parameters were recorded.

### 2.3 | Plugging evaluation experiments

Different seepage channels such as natural fractures and acid corroded fractures with varying permeability and width exist in DCRs. Hence, the plugging performance of AFKFs is evaluated using unfractured cores of varying permeabilities to simulate natural fracture channels and artificially fractured cores of different widths as acid-etched fracture channels. In addition, its plugging ability under high temperatures and pressures was observed.

#### 2.3.1 | Plugging performance evaluation experiment in unfractured core samples of different permeability

In this experiment, three artificial carbonate core samples #1, #2, and #3 with permeability 23.42, 143.5, and 623.2 mD, respectively, were used (Figure SC2b). The unfractured artificial carbonate samples were manufactured by injecting quartz sand and cement at the laboratory temperature into a sand-packed tube. Then both ends of the cores were covered with a smooth material and the annulus was effectively packed. The product was allowed to be set and dried before extraction. The plugging performance evaluation experiment was performed at a temperature of 130°C, confining pressure of 60 MPa, and back pressure of 0.8 MPa. The cores were initially saturated with simulated formation water. Then AFKFs was intermittently injected. Again, the samples were displaced by simulated formation water as secondary displacement. The plugging pressure at each displacement stage and the volume...
of fluid loss at the outlet of the core holder were recorded.

2.3.2 | Plugging performance evaluation experiment of core samples with different fracture width

Herein, three artificially fractured carbonate core samples #4, #5, and #6 with fracture widths of 1, 2, and 3 mm respectively, were used (Figure SC2a). To mimic a naturally fractured rock, the unfractured artificial carbonate samples were divided into halves using the fracture-generating device. Two copper wires with a thickness similar to the width of the intended fracture were placed parallel between the two halves. Then the cores were wrapped using a heat-shrink tubing and finally dried in an oven for future use (Figure SC2c). With a similar experimental condition as in Section 2.3.1, the cores were initially displaced with simulated formation water and then with the AFKF. Finally, nitrogen gas was used during the secondary displacement process. The plugging pressure at each displacement stage and fluid loss were recorded.

2.3.3 | Plugging performance evaluation experiment under simulated high temperature and pressure conditions

The pressure bearing capacity of the AFKF in fractures at different temperatures was observed. Carbonate core of diameter and length of 5 and 7.5 cm, respectively, was cleaned and dried in a vacuum dryer for 4 h, then the core was inserted into the core holder. Core leakage was observed by gradually increasing the driving pressure of the displacement pump, keeping the back pressure and confining pressure constant at 2 MPa. With no observed core leakage, the inlet driving pressure was increased by 0.5 MPa at a specific interval. Then AFKF was injected into the core through the displacement pump under different driving pressures and temperatures. With no leakage observed, the inlet driving pressure was increased by 0.2 MPa at a specific temperature and time. After a core leakage was observed, the pump flow rate was increased and the inlet driving pressure was recorded. The experiment was performed for 0–48 h at five different temperatures (within 110–150°C) and the time-dependent variation of the pressure bearing capacity of AFKF in fractures at different temperatures was observed.

2.4 | Formation damage evaluation experiment

In this experiment, artificial carbonate core samples were used, CFKF was used as displacement fluids. Core samples were treated with the AFKF for 2h. The displacement sequence of the core flooding test was carried out following the procedures in Section 2.3.1. The permeability before and after damage by the AFKF was recorded and the condition of the core samples before and after the damage was observed and reported under the three treatment remarks (no treatment, cyclic treatment, and gel breaking treatment). Then the permeability damage and recovery rates were calculated using Equations (2) and (3), respectively:

\[
\text{Permeability damage rate (\%) = } \frac{|K_{BD} - K_{AD}|}{K_{BD}} \times 100 \tag{2}
\]

\[
\text{Permeability recovery rate (\%) = } \left( \frac{K_{AD}}{K_{BD}} \right) \times 100 \tag{3}
\]

where \(K_{BD}\) and \(K_{AD}\) represent the permeability before and after damage by AFKF, respectively.

3 | CASE STUDY APPLICATION

To validate the performance of the formulated AFKF and verify the results of the experiments described in Section 2, a field report on the application of AFKF in a DCR is illustrated in this section.

3.1 | Background, historical operations, and challenges

Puguang sour gas field is located in Xuanhan-Daxian block, northeastern Sichuan Basin is the largest gas discovery in the Paleozoic marine strata in China, with proven gas reserves above 9 trillion cubic feet.26 Well DW-2 is a high \(H_2S\) DCR located in the Puguang gas field with about 18% \(H_2S\). It was drilled to a depth of 5060 m with an average reservoir porosity and permeability of 8.84% and 3.37 mD, respectively, the temperature of the production interval was 111.19°C. The formation pressure was 42.44 MPa with a pressure coefficient of 0.88. After two successful acidizing operations, the fracture half-length became 28.3 m. A field survey in 2016 led to the discovery of several technical and environmental challenges in Well DW-2. The report revealed that the well was undergoing
multiple challenges including high H₂S concentration, low-pressure gradient, severe gas leakage, and formation damage. To control the well, reduce the wellhead pressure, and safely shut in the well for workover operations, field operators attempted using a less dense kill fluid (active water) to kill the well on four different occasions. However, this could not solve the problem as the wellhead pressure increased rapidly after each killing operation at the rate of 30, 12, 5, and 1.8 MPa/d. In this regard, an AFKF was recommended.

3.2 | Design and application mode

Based on the formation pressure gradient of well DW-2 and a factor of safety of 0.05–0.07, the density of the AFKF was designed in the range of 0.93–0.95 g/cm³. According to the internal volume of the tubing and the casing volume under the tubing shoe, a 33 m³ CFKF was injected into the formation to plug the seepage channels. Then 115 m³ AFKF with an apparent viscosity of 50 mPa s and a yield point-plastic ratio of 0.8 Pa/mPa s was prepared. The stability of the AFKF was verified in the laboratory for 180 days. Because the completion string uses a permanent packer and cannot be circulated, the AFKF was directly injected from the tubing, and the oil pressure before the well-kill operation was 30.95 MPa.

4 | RESULTS AND DISCUSSION

4.1 | Experimental results and analysis

4.1.1 | Fluid sample optimization experiments

Based on the results of the TURBISCAN experiment in Section 2.1.2, the transmission and BS profile along with the height of the cell for AFKF samples 6, 7, 8, and 9, after aging is presented in Figure 2.

For all samples of the AFKF, the transmission profiles moved upwards over the whole length of samples, as depicted in Figure 2A–D. Implying that coalescence was the main destabilization phenomenon and particle accumulation was formed during the analysis. The transmission intensity was relatively lower in the middle of the samples; however, the peak values were visible at the top and bottom of the samples, which indicates the presence of creaming and sedimentation, respectively. Since the transmission intensity of different heights varies uniformly over time, and the rate of

![Figure 2](A–D) Transmission and backscattering profiles of samples of AFKF with different desulfurizing agents. AFKF, anti-hydrogen sulfide fuzzy-ball kill fluid
change of different heights was almost the same, the AFKF formed a homogeneous system. Further, the BS values of the four samples were close to the baseline during the entire analysis time, indicating that the AFKFs were relatively homogeneous and stable after aging. So, the BS values present two variations at the top and the bottom of the samples. Between these two zones, the sedimentation and creaming for each scan are homogeneous and present a constant value of the percentage of BS. In the middle of the cell, BS greatly increased in samples 6, 7, and 9 and slightly increased in sample 8. This indicates that samples 6, 7, and 9 show some relatively low degree of stability due to the coalescence of the particles, while sample 8 shows a tendency of better stability with larger particle size. The trends obtained for the three samples (i.e., samples 6, 7, and 9) are qualitatively similar and it is possible to assume that they are characterized by the same destabilizing phenomena. To further verify the physical stability of these samples, the destabilization kinetics graph is shown in Figure 3.

The results of the TSI profiles in Figure 3 were coherent with their transmission profiles. Samples 6, 7, and 9 showed a significant variation of the slope after specific intervals, corresponding with the first coalescence phase. This slope change could be attributed to the gelification process due to the interaction of particles. After the gelification process, sample 6 had the highest TSI value and thus it is the least stable. Samples 9 and 7 showed stability higher than sample 6, whereas sample 8 offered excellent stability. Therefore, sample 8 is the recommended choice of combination of desulfurizing agent (methyl diethanolamine) and the CFKF. To further evaluate the quality of the particles of the selected desulfurizing agent, and the overall sustainability of the preferred AFKF under extreme H₂S aging, stability evaluation experiments in Section 2.2 were performed. A detailed analysis is presented in the next section.

4.1.2 | Stability evaluation experiments

According to the results of the experiment in Section 2.2.1, the rheological property of the AFKF before and after H₂S aging is shown in Figure 4.

After aging the rheological properties of the AFKF were almost the same, and there was no obvious variation in density and apparent viscosity before and after aging (Figure 4). This indicated that its rheological properties were independent of aging under the constant action of H₂S. One possible explanation for the above results is that both the microstructure and the rheological properties of AFKFs are governed by their chemical composition. Specifically, different chemical components form different microstructures, and the morphology and distribution of the rheological properties of AFKFs are dependent on its chemical compositions. It is evident that the pH value significantly decreased after aging. This is because of the dissolution of the added acid gas (i.e., H₂S) which forms hydrogen ions that lowers the overall pH and alkalinity of the fluid. The slight decline in the dynamic shear force after aging was due to the microstructural changes of the AFKF during the aging time that causes a resistance to the shearing flow of the fluid. As shown in Figure 4, the plastic viscosity increased during the aging time due to the flocculation process.
process that results in high viscosities. After aging, only a few changes occurred in the overall rheological property of the AFKF, which is an indication of its stability under extreme H$_2$S aging.

DCRs are characterized by high reservoir temperatures which could affect the stability of working fluids under such conditions. Hence, the relatively high stability of the AFKF under extreme H$_2$S conditions does not completely justify its application in carbonate wells. Therefore, it is necessary to further investigate the temperature protective effect on the stability of AFKFs.

For this purpose, the thermostability test in Section 2.2.2 was performed and the results are presented in Figure 5.

The percentage change in density before and after hot rolling at 110°C, 120°C, and 130°C was less than 5% and changes in other rheological parameters such as apparent viscosity and the dynamic plastic ratio were also minimal (Figure 5). This implies that the AFKF can simultaneously exhibit excellent rheological properties and a high-temperature protective effect. Combining the results of the experiments in Section 2.2, it is verified that the rheological properties of the AFKF are relatively stable under extreme H$_2$S and temperature conditions.

A key characteristic of an effective killing fluid is its ability to plug the seepage channels that allow the leakage of formation fluids and potential hazardous fluids. Therefore, it is important to evaluate the plugging ability of the AFKFs. In this regard, the plugging experiment was conducted.

4.1.3 | Plugging evaluation experiments

Based on the results of the experiment in Section 2.3.1, the blocking ability of AFKF in simulating natural fractures is summarized in Table 1.

The injected AFKF initially blocked the fractures of the core samples at a maximum plugging pressure of
30 MPa, as indicated in Table 1. After secondary displacement, no fluid loss was observed at the core outlet, confirming that the plugging of the natural fractures by the AFKF was effective. These results were consistent with the findings of previous scholars. They explained that the microstructure of the fuzzy ball fluids consists of flexible flosses. These flosses aggregate to form intermolecular bonded structures with varying diameters that generate high-blocking structures.

In addition, the fuzzy balls are hydrophilic fluids with a strong affinity to the formation of water thereby providing a long-term water plugging ability. However, to better understand the plugging ability of AFKFs in induced fractures (such as the acid-etched fractures), the experiment described in Section 2.3.2 was performed, and the result is presented in Figure 6. The results of Figure 6 show that there was no fluid leakage for cores #4 and #5 with fracture widths of 1 and 2 mm, respectively. However, a fluid loss of 8.5 ml was observed for core #6 with a fracture width of 3 mm. To effectively plug large fractures, the vesicles of CFKFs must form a plane binary tree structure, which is usually time-consuming. Also, a high volume of the AFKF will be required to effectively block large fractures. The breakthrough pressure of the gas was between 2.5 and 3.2 MPa, implying that the recovery effect of fractured cores is better than unfractured cores, and the larger the fracture size, the easier the permeability recovery. In both unfractured and fractured experiments, AFKF has demonstrated an excellent plugging effect with a high-pressure bearing capacity of about 30 MPa.

The plugging ability of the AFKF under a high-temperature environment is yet to be explored. Therefore, the pressure bearing capacity of the AFKF in fractures at different temperatures was observed following the experimental guidelines in Section 2.3.3. The result is shown in Figure 7.

It can be seen from Figure 7 that after plugging the fracture at the temperature range of 110–150°C, the inlet driving pressure of the fracture increased from 20.73 to 21.07 MPa. This indicates that the AFKF provided a good pressure-bearing capacity. After 48 h of continuous injection of 1% H2S gas, the inlet pressure gradually declined from 19.85 to 20.31 MPa, and the percentage decrease was 3.61%–4.85%. This shows that considering the self-degradation effect of CFKFs, the percentage decrease was small. Therefore, the pressure bearing capacity of the AFKF was generally stable. Furthermore, a regression model explaining the quantitative relationship between inlet driving pressure and time for each temperature is

| Parameters                              | Core #1 | Core #2 | Core #3 |
|-----------------------------------------|---------|---------|---------|
| Forming water stability pressure (MPa)  | 1.8     | 0.2     | 0.15    |
| Maximum plugging pressure of AFKF (MPa) | 30      | 30      | 30      |
| Maximum plugging pressure of formation water (MPa) | 30      | 30      | 30      |
| Fluid loss at core outlet (ml)          | 0       | 0       | 0       |

Abbreviation: AFKF, anti-hydrogen sulfide fuzzy-ball kill fluid.

**FIGURE 6** Plugging results of fractured core samples with different fracture widths
established. The linear equations for the temperatures in Figure 7 are shown in Equations (4–8).

\[
\Delta P = -0.0158t + 20.990 \quad (4)
\]
\[
\Delta P = -0.0171t + 20.899 \quad (5)
\]
\[
\Delta P = -0.0180t + 20.649 \quad (6)
\]
\[
\Delta P = -0.0201t + 20.761 \quad (7)
\]
\[
\Delta P = -0.0206t + 20.924 \quad (8)
\]

where \( \Delta P \) is the inlet driving pressure (MPa) and \( t \) is the simulation time (h).

From Equations (4–8), the distribution of the R-squared \( (R^2) \) value is within 0.898–0.992, indicating that over 89% of the observed variation can be explained by the model’s inputs. For instance, in a well with a critical pressure bearing capacity of 14 MPa, substituting into Equations (4–8), the optimum time of achieving effective plugging structure becomes 442, 403, 369, 336, and 336 h for 110°C, 120°C, 130°C, 140°C, and 150°C, respectively. This implies that in high temperature and \( H_2S \) conditions, considering the self-degradation effect of the AFKFs, it will take about 14–18 days. Furthermore, the results of the plugging experiments suggest that the AFKF can effectively plug flow channels with high plugging pressure under complex reservoir conditions. The pumping of foreign fluids into a formation often leads to significant formation damage. However, the degree of formation damage caused by the AFKFs is still unknown; hence, the following sections address this issue.

4.1.4 | Formation damage evaluation experiment

The results of the formation damage experiment in Section 2.4 are shown in Table 2.

Combining the specification in Table SB3 and the result of Table 2, it can be seen that the highest degree of formation damage induced by the AFKF is moderate. Furthermore, AFKF resulted in weak damage on samples 1 and 2 and a medium to weak damage on sample 3. In addition, the strength of the temporary plugging was high and stable at 35 MPa. These results are attributed to the damage-control mechanism of the AFKF. A temporary plugging structure (i.e., filter cake) is formed in the seepage channels thereby protecting the reservoir from solid and fluid invasions. The desulfurizing agent (MDEA) shows high compatibility with the reservoir by overcoming potential formation damage due to rock-fluid interactions. For the untreated sample, the permeability recovery rate was greater than 60%, exceeding 85% for the brine treated sample, and above 90% for the gel breaking treated sample, implying that the natural degradation of the AFKF does not cause significant permeability damage. Therefore, the AFKF results in minimum formation damage to carbonate reservoirs by providing a good reservoir protection effect.

The experimental results demonstrated in this study have proven that the desulfurizing agent (MDEA) is compatible with the AFKF and DCR systems. The stability of the AFKF was high under \( H_2S \) exposure with excellent temperature resistance and plugging abilities. However, it is worthwhile to further validate these findings with field results.
4.2 Field application results and analysis

During the well-killing operation, the minimum oil pressure, pump pressure, and displacement were 1.76 MPa, 2.9 MPa, and 0.15–0.8 m³/min, respectively. At the early stage of the AFKF injection process, the oil pressure significantly declined, and during the mid and later stages, the overall decline in oil pressure gradually dropped. At the end of the operation, oil pressure dropped to zero and the cumulative volume of the injected AFKF was 98 m³ with a good pump efficiency. After successful killing and workover operations, a pressure buildup test was conducted in well DW-2. The test report showing the increase in bottom hole pressure after 10 days of the shut-in period is presented in Figure 8.

As Figure 8 indicates, the mechanisms of the well-killing and pressure buildup processes are explained in the following stages.

Stage 1: The first 5 h after AFKF injection (on the 8th of April), the shut-in pressure was 0 MPa. At this stage, the injected AFKF provided a plugging and absorption effect. Hence, the gas was trapped in the downhole hole thereby preventing further flow of gas to the wellhead.

Stage 2: Within the next 10 h, the shut-in pressure gradually increased to about 6.5 MPa. Significant fluid loss (at an average fluid loss of 0.02 m³/h) occurred as the AFKF mixed with the wellbore fluids and some untrapped gases flowed to the surface to contribute to the wellhead pressure.

Stage 3: In the subsequent 15 h, the shut-in pressure was stable. Because there was a balanced mixture of the AFKF and wellbore fluid as almost no untrapped gas is left. Thus, no gas flowed to the wellhead.

Stage 4: An irregular increase in the pressure occurred for 10 h. This was due to the pressure difference, as the wellhead pressure dropped, trapped fluid tended to flow to the surface.

Stage 5: For 50 h, the average pressure recovery rate significantly increased by 0.5 MPa/h. The wellbore fluids flowed into the seepage channels plugging and some of the flow channels were effectively plugged by the AFKF.

Step 6: By 12th April, the pressure gradually increased to 24.6 MPa with no trace of H₂S gas at the wellhead. After 4 days, AFKF effectively blocked all the seepage channels initially occupied by trapped gases and reservoir fluids and the pressure recovery rate was constant. In addition, when the reservoir flow channels are blocked by a plugging technology, a rapid rise in bottom hole pressure due to increased formation pressure is experienced, which will eventually lead to a corresponding increase in the wellhead pressure. Therefore, at high temperatures and extreme sulfur environments, AFKF could provide long-term prevention of H₂S pollution. Also, AFKF maintained very high stability.

| Core number | Diameter (cm) | Length (cm) | Plugging strength (MPa) | Permeability before damage (mD) | Permeability after damage (mD) | Permeability damage rate (%) | Permeability recovery rate (%) | Remarks |
|-------------|---------------|-------------|-------------------------|---------------------------------|-----------------------------|-----------------------------|-----------------------------|--------|
| 1           | 2.52          | 5.52        | 35                      | 169.56                          | 103.48                      | 38.97                       | 61.03                       | No treatment |
| 2           | 2.51          | 5.36        | 35                      | 174.22                          | 102.11                      | 12.69                       | 87.31                       | Gel breaking treatment |
| 3           | 2.51          | 5.51        | 35                      | 177.57                          | 162.26                      | 8.62                        | 91.38                       | Gel breaking treatment |

Table 2 Results of formation damage evaluation experiment of the AFKF

Abbreviation: AFKF, anti-hydrogen sulfide fuzzy-ball kill fluid.
under high reservoir conditions and effectively killed the well.

Combining the results of the experiments and field report, it has been confirmed that AFKF has high plugging and pressure bearing capacity, effectively absorbs H₂S, maintains a stable plugging system under high temperature, and does not cause significant damage to the reservoir. However, an explanation of its mitigation mechanisms will further validate the findings of this study.

4.3 Mechanisms of H₂S mitigation by AFKFs in carbonate wells

A CFKF mainly comprises of two distinct parts, namely the fuzz (outer layer), and the vesicle structures (which constitute the inner core). Studies have shown that the vesicle structure of CFKFs is compatible with formation water, polymers, and other displacement systems that make it suitable for workover operations. 30,31 For carbonate reservoirs with a high degree of heterogeneity, a large portion of the vesicles easily migrates into the high permeable zones. 22 The two main mechanisms of mitigating H₂S by AFKFs (identified from experimental and field analysis) are plugging and chemical absorption. These mechanisms will be analyzed separately.

Since formation fluids often leak into the wellbore or subsurface through certain seepage channels such as fractures, pore throats, loss of circulation paths, and so on. These leakages are prevented through the blocking of the seepage channels. Concerning the diameter of the vesicles and the width of the seepage channels, there are three plugging mechanisms of the AFKFs. (1) When the diameter of the vesicle is larger than the width of the flow channel, an impermeable gel barrier with high strength is formed on the surface of the channel, blocking the flow of formation fluids and H₂S gas (Figure SB2c). (2) When the diameter of the vesicles is approximately equal to the width of channels, they will be absorbed into the flow channel, thereby plugging the channels as shown in (Figure SB2b). (3) When the diameter of the vesicle is smaller than the width of channels, the vesicles will aggregate and form the shape of a “plane binary tree,” resulting in a large-scale blocking structure (Figure SB2a). Hence, the AFKF plugs the seepage channels and prevents the migration of H₂S and formation fluids to the wellhead. However, in the field, the width of the flow channels varies significantly. Therefore, the three above-mentioned mechanisms of plugging by AFKFs always occur simultaneously. Further, when an AFKF is pumped into a carbonate reservoir, it plugs the seepage channels and provides stability to the wellbore through a pressure-bearing seal to maintain the stability of the wellbore and the flow channels. 31 AFKFs accumulate in the void spaces of the seepage channels through the fluidity and deformability of the vesicles. Then it binds the fine particles in the fractures to form an effective plugging structure comprising of polymer vesicles as the pressure-bearing center and polyanionic cellulose chains as connectors. The AFKF successfully blocked the seepage zones and transformed the structure of the reservoir from a discontinuous to a continuous phase. The AFKFs form interconnected molecular bonds and adhere to the surface of the fracture, thereby influencing the reservoir rock properties by improving the Poisson’s ratio, cohesive force, formation strength, and reducing the brittleness.
index of the fracture, which enhances the well-killing operation.

Several scholars have reported amines as a widely used dry desulfurizing agent because they are both highly soluble in water and can absorb acid gases. Additionally, they possess one hydroxyl and amino group in their chemical structure which enables the removal of H$_2$S by chemical absorption process. Different types of amines such as Monoethanolamide (MEA), Diethanolamine (DEA), and MDEA can be used in chemical absorption. The MDEA (a tertiary amine solution) is the most preferred absorption solvent for removing H$_2$S gas today because of its high H$_2$S selectivity and absorption capacity, low corrosivity and regeneration energy, and minimal hot degradation. AFKFs are composed of MDEA as desulfurizing agent (Table SB2). Therefore, when the AFKF is injected and mixed with existing formation fluids and H$_2$S in the reservoir, the MDEA enhances the desulfurization of H$_2$S in the seepage channels via its H$_2$S absorption and selective ability, thereby preventing the accumulation and migration of H$_2$S to the wellhead (Figure 9). Hence, this will eventually mitigate the hazardous effects of H$_2$S on health, safety, environment, and improve the well-killing operation.

The desulfurization of H$_2$S by MDEA occurs through a chemical absorption process that involves an exothermic reaction that takes advantage of the reactions between absorbed substance (H$_2$S) and solvent (MDEA) to form a solution of sulfide (S$^{2-}$). In this regard, chemical absorption reactions occur in two stages, namely:

First, the protonation reaction of MDEA involves an instantaneous reaction between H$_2$S gas and MDEA through a direct proton transfer to form a tertiary (3°) ammonium ion and an unstable disulfide ion as shown in the equation below.

$$R_1R_2R_3N + H_2S \leftrightarrow R_1R_2R_3NH^+ + HS^- \quad (9)$$

And the dissociation reaction of the disulfide ion in Equation (9) through the ionization of the unstable disulfide ion in the formation of water to form a stable sulfide ion (Equation 10).

$$HS^- + H_2O \leftrightarrow S^{2-} + H_3O^+ \quad (10)$$

As Equations (9) and (10) indicate, the MDEA not only offers kinetic selectivity toward H$_2$S but also favors the forward equilibrium reaction towards the absorption of H$_2$S. Therefore, due to its excellent plugging and chemical absorption abilities, high degree of stability, temperature resistance ability, minimal formation damage, and improved rock modulus of elasticity and strength, the AFKFs can effectively control H$_2$S exposure under multi-challenging reservoir conditions for successful well-killing operation.

5 | CONCLUSIONS

This study proposes a novel AFKF for preventing H$_2$S gas kick in sour gas wells under extreme reservoir conditions. Its performance was optimized and analyzed through laboratory tests and verified by a case study application. Further, the discussed mechanisms provided a reliable basis for understanding the effectiveness of the AFKFs in well control operations. The following are the main conclusions of this study:
1. Based on compatibility, efficiency, and particle size stability, the methyl diethanolamine (MDEA) was selected as the best choice of desulfurizing agent for solving complex well control challenges in gas wells. The AFKFs could serve as a multifunctional killing fluid that can be used in developing DCRs, geothermal resources, and other related well types.

2. The experimental results further revealed that the AFKFs provided a long-term resistance to H2S exposure with stable performance (such as a high degree of stability under high H2S conditions, good temperature resistance, pressure bearing capacity, and excellent plugging ability), and negligible degree of formation damage.

3. The outcome from the field application revealed that after 4 days, the pressure of well DW-2 recovered to 24.6 MPa, confirming that AFKFs can effectively provide a stable plugging effect at high temperature and H2S conditions, preventing potential sour gas kick, and improving the well control technology.

4. Through the plugging mechanism, AFKFs form interconnected molecular bonds that influence the properties of the reservoir rock by improving the Poisson’s ratio, cohesive force, formation strength, and reducing the brittleness index of the fracture, which will eventually enhance the well-killing operation.

5. AFKFs effectively absorb H2S gas by protonation and dissociation reactions which transform the hazardous gas into an aqueous solution of sulfide ion, thereby mitigating possible health, safety, and environmental challenges during well-killing operations.

Due to the high amount of fluid loss in the case study well, a large volume of the AFKFs was required to successfully perform the well control operation. Therefore, it is recommended to design a more economical AFKF in future research that will reduce the high volumetric consumption rate during field applications.

ACKNOWLEDGMENTS
The authors wish to thank the Ministry of Science and Technology of the People’s Republic of China (Grant no. 2016ZX05066) and the Research Fund of Education Department of Shaanxi Provincial Government (Grant no. 20JK0542) for their financial support. Chinedu J. Okere appreciates the scholarship granted by the China Scholarship Council (Grant no. 2019ZFY020452).

ORCID
Chinedu J. Okere © https://orcid.org/0000-0001-5730-7490

REFERENCES
1. Ahmad T, Zhang D. A critical review of comparative global historical energy consumption and future demand: the story told so far. Energy Rep. 2020;6:1973-1991. doi:10.1016/j.egyr.2020.07.020

2. Amani M, Almodaris M. Safe practices in drilling and completion of sour gas wells. J Pet Environ Biotechnol. 2016;7:293. doi:10.4172/2157-7463.1000293

3. Cordes EE, Jones DOB, Schlacher TA, et al. Environmental impacts of the deep-water oil and gas industry: a review to guide management strategies. Front Environ Sci. 2016;4:58. doi:10.3389/fenvs.2016.00058

4. Zhang Z, Zheng Y, Hou D, Zhang H, Li Y, Zhang L. The influence of hydrogen sulfide on internal pressure strength of carbon steel production casing in the gas well. J Pet Eng. 2020;191:107113.

5. Boch R, Leis A, Haslinger E, et al. Scale-fragment formation impairing geothermal energy production: interacting H2S corrosion and CaCO3 crystal growth. Geotherm Energy. 2017;5:4. doi:10.1186/s40517-017-0062-3

6. Ma X, Zheng G, Liang M, et al. Occurrence and origin of H2S from volcanic reservoirs in Niudong area of the Santanghu Basin, NW China. Geofluids. 2019;2019:1279658. doi:10.1155/2019/1279658

7. Onerhime A, Kveps A, Elie D. Addressing safety challenges of operating in sour gas fields: a case study from the Middle East. Paper presented at the SPE Middle East Health, Safety, Environment & Sustainable Development Conference and Exhibition, Doha, Qatar; 2014. doi:10.2118/170393-MS

8. Zhu G, Liu X, Yang H, et al. Genesis and distribution of hydrogen sulfide in deep heavy oil of the Halahatang area in the Tarim Basin, China. J Nat Gas Geosci. 2017;2(1):57-71. doi:10.1155/jnggs.2017.03.004

9. Zhu G, Zhang S, Liang Y. The controlling factors and distribution prediction of H2S formation in marine carbonate gas reservoir, China. Chin Sci Bull. 2007;52:150-163. doi:10.1007/s11434-007-6022-8

10. Chen J, Yang S, Yang D, et al. Influence of pore structure and solid bitumen on the development of deep carbonate gas reservoirs: a case study of the Longwangmiao Reservoir in Gaoshit – Longnusi Area, Sichuan Basin, SW China. Energies. 2020;13(15):3825. doi:10.3390/en13153825

11. Alessandro G, Joao BV. Hydrogen sulfide biochemistry and interplay with other gaseous mediators in mammalian physiology. Oxid Med Cell Longevity. 2018;2018:6290931. doi:10.1155/2018/6290931

12. Abdelgawad KZ, Mahmoud MA, Elkatatny SM. Stimulation of high temperature carbonate reservoirs using seawater and GLDA chelating agents: reaction kinetics comparative study. Paper presented at the SPE Kuwait Oil & Gas Show and Conference, Kuwait City, Kuwait; 2017. doi:10.2118/187558-MS

13. Ahmad M, Mohamed IN, Youssi FZ, et al. HPHT sour gas production-case study. Paper presented at the Abu Dhabi International Petroleum Exhibition & Conference, Abu Dhabi, UAE; 2017. doi:10.2118/188782-MS

14. Karpov AIA, Vakhrushev SA, Siddikov MR, Zdolnik SE, Kuzmin AM. Well control and management: killing fluids for oil fields of JSOC Bashneft. Paper presented at the SPE
15. Alabdullatif ZA, Al-Yami AS, Wagle VB, Bubshait AS, Al-Safran AM. Development of new kill fluids with minimum sagging problems for high pressure Jilh formation in Saudi Arabia. Society of Petroleum Engineers; 2014. doi:10.2118/171683-MS

16. Bondarenko AV, Islamov SR, Ignatyev KV, Mardashov DV. Laboratory investigation of polymer compositions for well killing in fractured reservoirs. *Perm J Pet Min Eng*. 2020;20(1):37-48. doi:10.15593/2224-9923/2020.1.4

17. Fan H, Deng S, Ren W, Duan X, Cui C, Yang J. A new calculation method of dynamic kill fluid density variation during deep water drilling. *Math Probl Eng*. 2017;2017:9642917. doi:10.1155/2017/9642917

18. Mardashov DV, Rogachev MK, Zeigman YV, Mukhametshin VV. Well killing technology before workover operation in complicated conditions. *Energies*. 2021;14(3):654. doi:10.3390/en14030654

19. Miao H, Mingbiao X, Jun L, Gonghui L. A new two-phase model to simulate sour gas kicks in MPD operations with water based mud. *J Pet Sci Eng*. 2017;159:331-343. doi:10.1016/j.jpetrol.2017.09.024

20. Yin H, Liu P, Li Q, Wang G, Gao D. A new approach to risk control of gas kick in high-pressure sour gas wells. *J Nat Gas Sci Eng*. 2015;26:142-148. doi:10.1016/j.jngse.2015.06.014

21. Ying X, Yuan X, Yadong Z, Ziyi F. Study of gel plug for temporary blocking and well-killing technology in low-pressure, leakage-prone gas well. *Soc Pet Eng*. 2020;36:234-244. doi:10.2118/204213-PA

22. He J, Okere CJ, Su G, et al. Formation damage mitigation mechanism for coalbed methane wells via refracturing with fuzzy-ball fluid as temporary blocking agents. *J Nat Gas Sci Eng*. 2021;90. doi:10.1016/j.jngse.2021.103956

23. Zheng L, Kong L, Cao Y, Wang H, Han Z, He X. The mechanism for fuzzy-ball working fluids for controlling & killing lost circulation. *Chin Sci Bull*. 2010;55:4074-4082. doi:10.1007/s11434-010-3202-8

24. Ren Y, Zheng J, Xu Z, Zhang Y, Zheng J. Application of Turbiscan LAB to study the influence of lignite on the static stability of PCLWS. *Fuel*. 2018;214:446-456. doi:10.1016/j.fuel.2017.08.026

25. Okere CJ, Su G, Zheng L, Cai Y, Li Z, Liu H. Experimental, algorithmic, and theoretical analyses for selecting an optimal laboratory method to evaluate working fluid damage in coal bed methane reservoirs. *Fuel*. 2020;282:118513. doi:10.1016/j.fuel.2020.118513

26. Ma Y, Zhang S, Guo T, Zhu G, Cai X, Li M. Petroleum geology of the Puguang sour gas field in the Sichuan Basin, SW China. *Mar Pet Geol*. 2008;25:357-370.

27. Guo J, Gou B, Qin N, et al. An innovative concept on deep carbonate reservoir stimulation: three-dimensional acid fracturing technology. *Nat Gas Ind B*. 2020;7(5):484-497. doi:10.1016/j.ngib.2020.09.006

28. Zheng LH, Kong L, Cao Y, Wang H, Han Z. A new fuzzy ball working fluid for plugging lost circulation paths in depleted reservoirs. *Pet Sci Technol*. 2012;30(24):2517-2530. doi:10.1080/10916461003792286

29. Wang C, Liu H, Wang X, Zheng L. High blocking capacity of fuzzy-ball fluid to further enhance oil recovery after polymer flooding in heterogeneous sandstone reservoirs. *ACS Omega*. 2021;6(49):34035-34043. doi:10.1021/acs.omega.1c05427

30. Zheng L, Kong L, Cao Y, Wang H, Han Z, He X. The mechanism for fuzzy-ball working fluids for controlling & killing lost circulation. *Chin Sci Bull*. 2010;55:4074-4082. doi:10.1007/s11434-010-3202-8

31. Zheng L, Su G, Zhong-hui L, et al. The wellbore instability control mechanism of fuzzy ball drilling fluids for coal bed methane wells via bonding formation. *J Nat Gas Sci Eng*. 2018;56(107-120):2018-2120.

32. Joo-Youp L, Tim CK, Jeffery YY. Potential flue gas impurities in carbon dioxide streams separated from coal-fired power plants. *J Air Waste Manage Assoc*. 2009;59(6):725-732. doi:10.3155/1047-3289.59.6.725

33. Shoukat U, Pinto DD, Knuutila HK. Study of various aqueous and non-aqueous amine blends for hydrogen sulfide removal from natural gas. *Processes*. 2019;7(3):160. doi:10.3390/pr7030160

34. Siefers AM. *A Novel and Cost-Effective Hydrogen Sulfide Removal Technology Using Tire Derived Rubber Particles*. Graduate Theses and Dissertations. 2010:11281. https://lib.dr.iastate.edu/etd/11281

35. Mandal BP, Biswas AK, Bandypadhyay SS. Selective absorption of H2S from gas streams containing H2S and CO2 into aqueous solutions of N-methyldiethanolamine and 2-amino-2-methyl-1-propanol. *Sep Purif Technol*. 2004;35(3):191-202. doi:10.1016/S1383-5866(03)00139-4

**SUPPORTING INFORMATION**

Additional supporting information can be found online in the Supporting Information section at the end of this article.

---

**How to cite this article:** Yan Z, Okere CJ, Zeng X, et al. Preventing sour gas kicks during workover of natural gas wells from deep carbonate reservoirs with anti-hydrogen sulfide fuzzy-ball kill fluid. *Energy Sci Eng*. 2022;10:2674-2688. doi:10.1002/ese3.1158