Research and application of supramolecular gel plugging agent in abnormal pressure reservoir

B Baletabieke¹, Y X Gu¹, T Zhou¹, D X Duan², J T Liu¹, X J Kong², F Qian², W J Li¹, Z Zhong¹, Y Xiang¹, N Jing² and J Y Li¹

¹ CNPC Engineering Technology R&D Company Limited, Beijing, 102206, China
² China National Oil and Gas Exploration and Development Corporation, Beijing, 100034, China

Email: guyixindr@cnpc.com.cn

Abstract. The Aktobe project is the largest oil and gas producing area of PetroChina in Central Asia. However, after years of exploitation, the pressure of the reservoir has dropped, making it difficult to increase the production of a single well. Both the Kenkyak block and North Troyes block of the project have induced fractured leakage, and frequent leakage affects safe and efficient drilling and completion operations and production. Therefore, the research on leakage prevention and control technology is very necessary. This article focuses on the characteristics of the cracks in the high-pressure area of the Kenkyak block and the cracks in the low-pressure area of the North Troyes block. Aiming at the fracture characteristics of the high-pressure zone in the Kenkyak block and the low-pressure zone in North Troyes block, and taking advantage of the synergistic effect of supramolecules, a supramolecular plugging-while-drilling agent was developed based on the deformable fiber composite gel. It forms a strong adhesion plugging layer on the inner wall of the leakage channel through the strong adhesion force, and it achieves a good plugging effect. The 300-500mD sand disc bearing pressure could reach 700psi when adding 3% agent, and the bearing pressure of 3-5D permeability sand disc could reach above 450psi. A supramolecular static plugging agent was also developed based on the dilatant gel. It is rich in strong shear reversible gel with supramolecular structure, which guarantees its pumpability and plugging performance. The effective rate of one-time plugging is over 80%, and the viscosity is greatly reduced after the gel is broken for 72hr, which benefits the reservoir protection.

1. Introduction
Central Asia is the strategic core area of the “Silk Road Economic Belt” and the main overseas carbonate oil and gas cooperation area of PetroChina (CNPC). The Aktobe block is the largest oil and gas production area in Central Asia, with a cumulative production of more than 400 million tons of oil and gas equivalent. In recent years, the oil and gas production has reached nearly 10 million tons, accounting for about 40% of the total output of Central Asia.

After more than 20 years of exploitation in Aktobe Oilfield, the reservoir pressure has depleted. The pressure funnels have been produced at the high-pressure reservoirs of the Permian and Carboniferous in the Kenkyak block, and the formation pressure coefficient decreased from 1.84-1.88 to 1.3-1.5. Reservoir pressures in the Jeannarjoer block and North Troyes block have been in deficit (the pressure coefficient is about 0.6). As a result, individual-well producing rate has declined significantly. Moreover, since slim holes are often completed with open holes, it is very difficult to increase production by modifying the size of the pipe string [1]. In addition, the carbonate reservoir in Aktobe block has
complex types (porous reservoirs/fracture-porous reservoirs) and strong heterogeneity. A large amount of water injection causes uneven formation pressure distribution. The formation pressure of the Lower Permian under the salt layer is close to the leakage pressure, which is very easy to cause leakage and gas kick. There is a weathering crust on the top of the Carboniferous, the formation pressure is low. It is difficult to determine the depth and thickness of the formation, and leakage occurs frequently [1].

Regarding the mentioned difficult problems, a novel pressure-bearing plugging technology was created to meet the demands of plugging different types of lost circulation layers. It solves the technical problems that the plugging agent is not easy to stay in the leaking layer; the plugging agent is easy to be diluted by water; the plugging agent is difficult to stay and accumulate near the entrance of the leaking layer and the plugging agent is difficult to block the missing channel etc. It provides strong support for the efficient and safe drilling of carbonate reservoirs in Central Asia.

2. Analysis of leakage characteristics, leakage causes and leakage mechanism in the target block

After analysing the drilling complexities of leaking in the Aktobe project (table 1), the main reasons for the leaking are categorized as geological and human factors. Geological factors: Permian terrigenous deposits alternately appear in mudstone, sandstone, thin-bedded siltstone and tight sandstone, which are prone to leakage. The Lower Permian under the salt is a high-pressure oil and gas reservoir with a narrow safety density window which induced leakage easily. The Carboniferous is a carbonate reservoir with well-developed fractures and pressure deficits. Due to the high and low pressure developed in the same layer, fracture-type leakage is prone to occur. Human Factors: The equivalent circulating density may increase due to swabbing effect when running the intermediate casing. Because of the diverse types of Carboniferous reservoirs (porous and fracture-porous reservoirs), the hydraulic pressure of the drilling fluid column is higher than the pore or fracture-pore formation pressure, the drilling fluid may enter the leaky layer under the loss of pressure difference, and the lost circulation occur.

| Well No. | Lost Well Section (m) | Plugging method | Reason for loss |
|---------|----------------------|-----------------|----------------|
| 1#      | 3865.5               | Forced cementing | Lower the technical casing and circulate the leakage formation |
| 2#      | 2810                 | After 2780m plugging slurry is invalid, 650m cement squeezes successfully to plug the leak | Air intrusion, leakage occurs in the throttle circulation, and the leakage occurs in the upper layer of 1st section |
| 3#      | 403                  | Successfully stop the leak after hitting the plugging slurry | Surface leakage |

In conclusion, the Permian and Carboniferous reservoirs under the salt layers in the Kenkyak block have a pressure funnel due to long-term development, which makes it difficult to divide the strata and is prone to leakage. The leakage mechanism is the decrease of reservoir pressure, which causes high and low pressure to appear in the same well section. High-density drilling fluid can balance the high-pressure formation, but at the same time causes the low-pressure formation to be fractured due to excessive pressure difference, causing induced fractured leakage. Leakage causes the level of drilling fluid in the wellbore to drop, and the reduced drilling fluid pressure is not heavy enough to balance the high-pressure formation. The formation fluid may enter the wellbore, causing blowout and leakage in the same layer. The reservoir pressure coefficient of the North Troyes block has dropped to 0.60. The water-based drilling fluid systems are currently used, which is easy to lose. The leakage mechanism is that the reservoir pressure coefficient is too low. The bottom hole pressure of the conventional water-based
drilling fluid system is inevitably higher than the bottom hole pressure, the pressure difference increases, and the drilling fluid enters the reservoir channel or the fracturing formation under the pressure difference and then induced crack leakage.

3. Development of Supramolecular Plugging While-Drilling Agent / Static Plugging Agent

Supramolecular chemistry is the chemistry that studies the complex, orderly and specific functional system formed by two or more chemical species through weak interactions (or secondary bonds) between molecules [2-4]. Supramolecular has the characteristics of synergy, which can overcome the shortcomings of weak interaction between molecules and form a strong force with a certain direction and selectivity [5]. As a result, the research has formed the novel technologies of supramolecular plugging while drilling agent and supramolecular static plugging agent. Compared with conventional plugging technology, supramolecular technology uses weak gels, particles, etc. to achieve plugging while drilling, and does not need to be strictly matched with the leaking holes [6] (Figure 1, Figure 2).

![Figure 1](image1.png)

**Figure 1.** Previous technology: Inert material bridging, filling, etc. to achieve plugging while drilling, requiring strict matching with leak-off holes.

![Figure 2](image2.png)

**Figure 2.** Supramolecular technology: weak gels, particles, etc. realize plugging while drilling, and do not need to be strictly matched with leak-off holes.

3.1. Development of Supramolecular-While-Drilling Plugging Agent

3.1.1. Synthesis and Characterization of Supramolecular-While-Drilling Plugging Agent. Aiming at the crack characteristics of the Permian high-pressure zone in the Kenyak block, a supramolecular plugging while drilling agent was developed which based on deformable fiber composite gel. It is a deformable polymer/fiber composite gel rich in strong adhesion groups. The synthesis method and steps are: Weigh a certain amount of ethylene glycol 2-methacrylate in a flask, stir for 20 minutes, add 0.05% crosslinking agent (N,N-methylene bisacrylamide) and 1% hydroxyethyl cellulose, and stir for 20 minutes. Protect with nitrogen for 20 minutes, add 0.2% initiator (ammonium persulfate), heat to 50°C and keep for 10hr, get a transparent gel. After cooling, vacuum dry at 60°C for 24hr, dry and crush to obtain supramolecular plugging-while-drilling agent particles. Supramolecular- plugging while-drilling agent can form a strong adhesion plugging layer on the inner wall of the leakage channel through its strong adhesion force, so as to achieve the plugging effect, as shown in Figure 3.

Infrared spectroscopy shows that the characteristic peak is blue-shifted (absorption wavelength becomes shorter), indicating that there are a large number of non-covalent bonds in the molecule, and
supramolecular association structures are formed between molecules. TEM found that the supramolecular plugging-while-drilling agent formed a large number of three-dimensional network structures in water, indicating that the association occurred between molecules and the supramolecular structure was formed by non-covalent bonds (Figure 4) [7].

Figure 3. The principle of supramolecular-while-drilling plugging agent.

Figure 4. Infrared comparison before and after synthesis of supramolecular-while-drilling plugging agent.

3.1.2. Evaluation of plugging effect of supramolecular-while-drilling plugging agent. Supramolecular plugging-while-drilling agent has a good plugging effect. The bearing pressures of 300-500mD could reach above 700psi when adding 3% agents (Figure 5) and bearing pressure of 3-5D permeability sand discs could reach above 450psi (Figure 6). The filter cake is dense and has strong adhesion (Figure 7), which is better than other MWD (Measurement While Drilling) plugging agent products.

Figure 5. Evaluation of sand disc plugging with Supramolecular-while-drilling plugging agent (300-500mD sand disc).

Figure 6. Evaluation of sand disc plugging with Supramolecular-while-drilling plugging agent (3-5D sand disc).

Figure 7. Supramolecular-while-drilling plugging agent filter cake (a) and Strong adhesion ability (b).
3.1.3. Performance Evaluation of Supramolecular Plugging-While-Drilling Agent in Polymer Drilling Fluid System. Supramolecular Plugging-While-Drilling Agent has a good plugging effect in polymer drilling fluid systems. After aging at 120°C, the cumulative loss of the system is less than 10ml, and the bearing pressure is above 4.1MPa, which is better than similar products (bearing pressure is above 3MPa). The rheological properties of the supramolecular plugging -while-drilling agent in the base slurry are shown in Table 2, and the pressure-bearing plugging test results are shown in Figure 8.

Table 2. The rheological properties of the supramolecular-while-drilling plugging agent in the base slurry.

| No. | Project                                      | AV/mPa·s | PV/mPa·s |
|-----|----------------------------------------------|----------|----------|
| 1   | Base slurry                                 | 41       | 34       |
| 2   | System+3% Plugging agent                    | 43       | 38       |
|     | (Carb250:Carb40:Carb10=1:1:1)               |          |          |
| 3   | System+3% Plugging agent                    | 46       | 39       |
|     | (Carb250:Carb40:BLN1=1:1:1)                |          |          |
| 4   | System+3% Plugging agent                    | 45       | 39       |
|     | (Carb250:Carb40:G-seal=1:1:1)              |          |          |
| 5   | System+3% Plugging agent                    | 44       | 40       |
|     | (Carb250:Carb40:MC-seal(M)= 1:1:1)         |          |          |
| 6   | (Carb250:Carb40:Supramolecular Plugging agent CMG=1:1:1) | 42       | 35       |

Figure 8. Supramolecular-while-drilling plugging agent under pressure plugging experiment.

3.2. Development of Supramolecular gel static plugging agent

3.2.1. Synthesis and characterization of supramolecular gel static plugging agent. In view of the fracture characteristics of the low-pressure zone in the North Troyes block, a static plugging agent was developed based on the dilatant gel to form a supramolecular gel static plugging system. Because the system has a strong shear reversible gel with a supramolecular structure, it guarantees pumpability and plugging properties through supramolecular crosslinking [8], thereby ensuring the plugging effect, and the one-time sealing is over 80%. In addition, after 72hr of gel breaking, the viscosity of the plugging agent dropped significantly, which helped protect the reservoir, as shown in Figure 9.

The synthetic method and the steps of the supramolecular gel static plugging agent are as follows: An acryloxy cationic monomer and long-chain halide are selected for quaternization reaction to obtain hydrophobic monomer. 1.3g of cationic monomer are dissolved in acetone, and 0.7g of long-chain halide
are added dropwise at 10°C, reaction at room temperature in the dark for more than 24hr, filtered, washed, and dried to obtain a hydrophobic monomer. Using hydrophobic monomers and acrylamide, hydrophobic supramolecular polymers through free radical polymerization is synthesized involving following steps (Figure 10). The synthesis steps are as follows: Weigh 27.7g of acrylamide solution and 150ml of distilled water, add 0.3g of hydrophobic monomer and 0.9g of sodium lauryl sulfate, stir and mix well, pour into a 250ml three-necked flask, and pass nitrogen for protection for 30 minutes. After heating at 50°C, 0.09g of azobisisobutyronitrile was added, and the reaction was carried out for 4hr to obtain a viscous polymer. After cooling, 5g of NaOH aqueous solution was added. Then heated to 80°C and reacted for 5hr, cooled, dried, and pulverized to obtain a white powder, which is a supramolecular gel static plugging agent.

**Figure 9.** The principle of supramolecular static plugging agent.

**Figure 10.** The sample of supramolecular static plugging agent (1 Low concentration; 3 High concentration; 2 Shaking 30s at low concentration; 4 Shaking 30s at high concentration).

3.2.2. **Morphology characterization of supramolecular static plugging agent.** SEM and TEM could find that the supramolecular gel static plugging agent has formed a large number of honeycomb-like supramolecular gel structure (Figure 11), which has strong gel strength and could seal the lost formation efficiently.

**Figure 11.** (a) Supramolecular gel static plugging agent SEM test; (b) Supramolecular gel static plugging agent TEM test.

3.2.3. **Adhesion and tensile strength test of supramolecular static plugging agent.** Supramolecular static plugging agent has good adhesion and stretch resistance. As the polymer concentration increases, its adhesion strength increases from 1.4MPa to 4.7MPa, while the adhesion strength of polyacrylamide gel A523 is only 0.8MPa. In addition, the tensile strength of supramolecular gel is 160KPa, which is much greater than guar gum, polyvinyl alcohol gel and polyacrylamide gel (Figure 12, Figure 13).
3.2.4. Displacement pressure test of supramolecular static plugging agent. By testing the displacement pressure of the supramolecular static plugging agent in the hollow core, the retention capacity and bearing pressure of the fracture leakage layer were studied. Supramolecular static plugging agent could seal 2mm hollow radius cores, and the displacement pressure could reach 11.2MPa, which ensured effective retention and plugging in the pores.

3.2.5. Supramolecular gel static agent plugging performance and the drainage pressure test. The supramolecular gel static plugging agent could effectively seal the malignant loss formation. At a temperature of 120° C, it could seal a bed of 10mm steel balls, with bearing pressure of more than 6MPa (Figure 14), and the discharge pressure of more than 4MPa (Figure 15). It has good anti-spitting ability which is greater than that of conventional inert plugging materials (the bearing pressure of conventional plugging materials is 4MPa) [9].

4. Conclusions
A novel supramolecular plugging-while-drilling agent was developed based on the deformable fiber composite gel. It achieves the plugging effect through forming a strong adhesion plugging layer on the inner wall of the leakage channel. The experiment results showed it could seal 3-5D permeability sand disc with bearing pressure over 700psi after adding 3% agent. It also capable for sealing 300-500mD sand disc with bearing pressure above 450psi.

The supramolecular static plugging agent based on dilatant gels could ensure pumpability and plugging properties through cross-linking effect. A supramolecular gel structure is formed in the leakage channel, which can bear a pressure of more than 6 MPa at 120° C. While protecting the reservoir, it also guarantees the plugging effect. The effective rate of one-time sealing is over 80%.
References

[1] Wang G, Fan H H, Feng J, Li W J, Ye Y, Kong X J, Li Y Y, Liu J T, Liu C C and Yang H J. 2020. Performance and application of high-strength water-swellable material for reducing lost circulation under high temperature. *J. Pet. Sci. Eng.* 189(3): 79-85

[2] Zheng B, Hou Y L, Gao L Y and Zhang M M. 2019. Luminescent Metallo-Supramolecular Polymers. *CHINESE J CHEM.* 37(8): 124-129

[3] Jiang G C, He Y B, Huang X B, Deng Z Q and Qin Y. 2016. A high-density organoclay-free oil base drilling fluid based on supramolecular chemistry. *PETROL EXPLOR DEV.* 43(1): 43-51

[4] Parthasarathi D. 2019. Designing Supramolecular Gelators: Challenges, Frustrations, and Hopes. *Gels.* 5(1): 76-83

[5] Wei P X. 2020. Study on lost circulation prevention and plugging technology in drilling engineering. *Chem. mgt.* (16): 190-191

[6] Rashid F, Hussein D, Lawrence J A and Ahmed Z. 2021. Fluid flow and permeability analysis of tight gas carbonate reservoir rocks using fractures and dynamic data. *J Nat Gas Sci Eng.* (90): 33-42

[7] Cao C, Zhou F J, Cheng L S, Liu S, Lu W P and Wang Q. 2021. A comprehensive method for acid diversion performance evaluation in strongly heterogeneous carbonate reservoirs stimulation using CT. *J. Pet. Sci. Eng.* (13): 203-209

[8] Tan Q G, Kang Y Li, You L J, Xu C Y, Zhang X W and Xie Z C. 2021. Stress-sensitivity mechanisms and its controlling factors of saline-lacustrine fractured tight carbonate reservoir. *J Nat Gas Sci Eng.* (3) 88-91

[9] Li C P, Yang S C, Wen Z, Pan Y, Zeng F Z, Zhao C L and Hany M A A. 2020. The research of new type gel plugging agent for deep well. *Energy Sources.* (4):67-75