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RESEARCH ARTICLE

Methanol Treatment for Permeability Restoration in Oil Shale after Water-Induced Permeability Damage

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Abstract

This article presents core-flooding experiments on a Bazhenov Formation core sample designed to evaluate whether post-water methanol treatment can restore permeability. At reservoir conditions (110 °C, 23.5 MPa), the core was first water-flooded and then subjected to oil injection into the water-saturated rock, which caused severe, progressive permeability loss. NMR T1-T2 mapping captured fluid redistribution and the growth of bound/high-viscosity components. Gas chromatography indicated C36+-rich precipitates. A subsequent methanol flush stabilized the pressure drop and restored ∼87% of the pre-damage water permeability. These findings elucidate a water-oil-rock interaction pathway for rapid colmatation in Bazhenov shale and demonstrate an effective methanol-based protocol for permeability restoration.

Keywords: oil shale, waterflooding, methanol, chemical EOR.

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1 Introduction

Ultra-tight organic-rich shales such as the Bazhenov Formation (Western Siberia) present both petrophysical and geochemical challenges during multiphase flow. Water-rock interaction can lower conductivity through clay and kerogen swelling, wettability alteration, and fines transport [1, 2]. Beyond classical water blocking, organic-rich rocks introduce an additional risk pathway, oil-water contact can promote formation of water-in-oil emulsions stabilized by surface-active asphaltenes/resins and deposition of heavy components, which constrict pore throats and cause a permeability decrease [3].

Detecting these mechanisms in situ requires fluid-typing tools with sensitivity to viscosity/bound-state changes. Low-field nuclear magnetic resonance (NMR) relaxometry – particularly 2D T1–T2 mapping – has emerged as a robust laboratory method to partition bound vs. mobile fluids and to distinguish aqueous and hydrocarbon

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components in source rocks and tight reservoirs. Applications in shale show that T1–T2 signatures can recover porosity, movable/bound fractions, and fluid distributions relevant to flow impairment [4].

Mitigation strategies include aromatic solvent washes for asphaltenes and mutual-solvent or alcohol treatments to dehydrate, break emulsions, and reduce water blocks or condensate damage near the wellbore. While aromatics (e.g., xylene/toluene) are effective for heavy-organic dissolution, operationally simpler alcohols are frequently used to mobilize trapped water, destabilize emulsions, and aid cleanup. Methanol in particular is inexpensive, water-miscible, and field-proven for blockage removal in core-flood experiments [5]. However, the sequence of single-phase water flow followed by permeability collapse during oil injection into the Bazhenov Formation rock matrix has previously been considered non-restorable, owing to the irreversible transformation of the organic-rich clay [2].

In this study, we address this gap through reservoir-condition experiments on a Bazhenov core sample. The work combines steady-state core flooding with NMR T1–T2 mapping and chemical analyses to evaluate methanol as a rapid and effective agent for permeability recovery after water and oil flooding.

2 Methodology

2.1 Rock and fluids

A single cylindrical core sample from the Bazhenov Formation was solvent-extracted to constant mass (95 °C) before testing. Gas-porosimetry and permeability screening indicated $\phi \approx 10.3\%$ and absolute $k \approx 0.0056$ mD post-extraction. CT verified no macro-defects. The synthetic formation brine contained 13.86 g/L total salinity (dominant NaCl), and the viscosity at reservoir conditions (110 °C, 23.5 MPa) was taken as 0.264 mPa*s for permeability calculations. Degassed, dehydrated oil from the same oil field as the core sample had $\mu = 1.024$ mPa*s and $\rho = 0.767$ g/cm^3 at reservoir conditions. All fluids were vacuumed before use.

2.2 Core-flood conditions and sequence

Tests were run 110 °C and 23.5 MPa pore pressure. The sequence (Figure 1) was as follows:

1. Vacuuming the dry sample.
2. Water injection until steady flow was reached.
3. Cooling down, weighing the sample, NMR.
4. Resuming water flow.
5. Oil injection into the water-saturated core at 0.12 mL/h, then 0.54 mL/h, then reset to 0.12 mL/h.
6. Cooling down, weighing, NMR.
7. Flipping the core (180°), resuming oil injection.
8. Methanol flush at 0.36 then 0.72 mL/h.
9. NMR and CT.

Pressure drop monitoring was performed in situ during every injection stage. Material balance checks were conducted during quasi-steady segments.

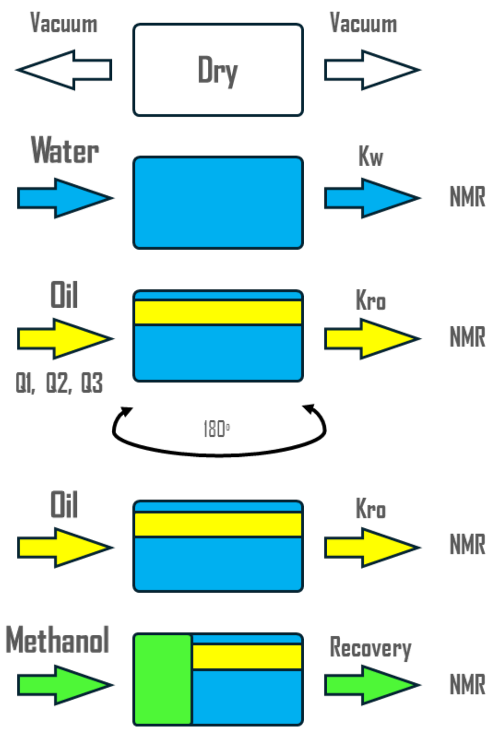

Figure 1. Simplified experimental scheme.

2.3 NMR acquisition and interpretation

A Geospec 2-53 (2 MHz) relaxometer measured T2 (CPMG, TE = 0.1 ms; SNR $\geq$ 100) and 2D T1–T2 maps (SNR $\geq$ 50). A T2 cutoff of 1 ms separated "bound" from "mobile" fluid. Pore-size distributions were inferred using a surface relaxivity of 10 μm/s appropriate for shale. Calibration used vendor saline references. Spectra were processed in GIT Systems v7.5.1.

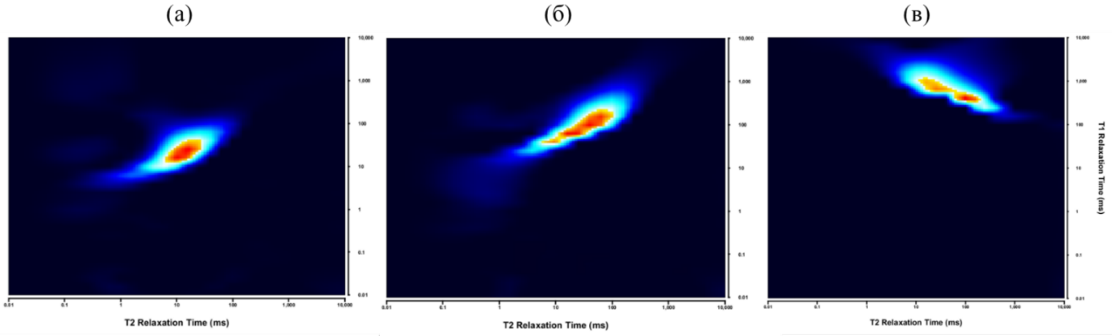

Figure 2. T1–T2 map for (left) 100% water saturated sample, (mid) after oil filtration and (right) the result of their subtraction.

3 Results

3.1 Water flow stage, stable permeability

Initial water flow yielded $k_w \approx 0.00125$ mD, rising to ≈ 0.00195 mD after cleaning superficial rust from an end-face. Mass balance showed closure within ±0.05 g across all tested segments. Water flow remained stable over ~25 PV (pore volume) with no progressive decline. NMR confirmed total liquid of ~2.60 mL in the water-saturated state (porosity by NMR $\approx$ 12-12.4%), with mobile fluid dominating above the 1 ms cutoff. The indicated pore volume resided primarily in ~0.01–2 μm equivalent pores.

3.2 Oil injection stage

Injecting oil into water-saturated rock at 0.12 mL/h produced an initial pressure rise, then a brief plateau corresponding to $k_o \approx 0.00095$ mD. Upon stepping to 0.54 mL/h for ~25 PV, differential pressure accelerated to the 10 MPa limit, implying $k_o \approx 0.00033$ mD. After reducing back to 0.12 mL/h, pressure again climbed to the 10 MPa limit, with $k_o \approx 0.00005$ mD by back-calculation 100 times lower than the absolute permeability. Mass balance on produced fluid was consistent (e.g., 6.72 g out vs. 6.64 g injected during a constant-pressure segment). NMR showed two main changes after oil injection (Figure 2): growth of "bound-like" signal (T2 $<$ 1 ms) from ~0.55 to ~0.65 mL, and an increase in total liquid signal from ~2.60 to ~3.14 mL concentrated in the meso-/macro-pore regime ($\approx$0.3-10 μm). T1/T2 contrast placed added signal predominantly in the high-viscosity hydrocarbon region of the map. Weighing corroborated mass gain of the core despite water displacement, and Karl Fischer titration of produced fluids indicated residual water saturation $\approx$ 52 vol%.

Solids recovered from core ends resembled bituminous matter. Gas chromatography showed ~97.9% in C36+ fraction (potentially with water), consistent with asphaltenes/resins and heavy components, colmatanting the porous space of the sample.

After flipping the core, oil injection again showed a near-linear growth of pressure with PV, indicating continuing colmatation. NMR spectra before/after the reverse run were nearly indistinguishable, suggesting negligible further displacement and a "locked-in" damage state.

3.3 Methanol flush: rapid recovery and partial de-sorption

Methanol injection resulted in stable pressure ($\pm$0.1 MPa over $\approx$1 PV) at ~0.56 MPa Δp, corresponding to $k \approx 0.00173$ mD. Relative to the pre-oil water-flow value ($\approx$0.00195 mD), this was equivalent to ~87% recovery. Displacement coefficients were calculated as ~85% for water and ~106% for oil, both consistent with near-complete removal of mobile phases. Post-methanol NMR indicated porosity $\approx$ 13.5% and total liquid of ~2.83 mL, with a reduction in the sub-0.02 μm "bound" region, consistent with partial removal of high-viscosity hydrocarbons. CT imaging revealed no macro-scale structural damage or fracturing attributable to any stage.

Table 1 and Figure 3 present data on the variations in core sample permeabilities observed during the test.

Table 1. End-of-stage permeabilities.

Stage	K, mD
Water (initial)	0.00195
Oil @ 0.12 mL/h	~0.00095
Oil @ 0.54 mL/h	~0.00033
Oil (0.12 mL/h)	~0.00005
Methanol	**~0.00173 (87% of Kw)**

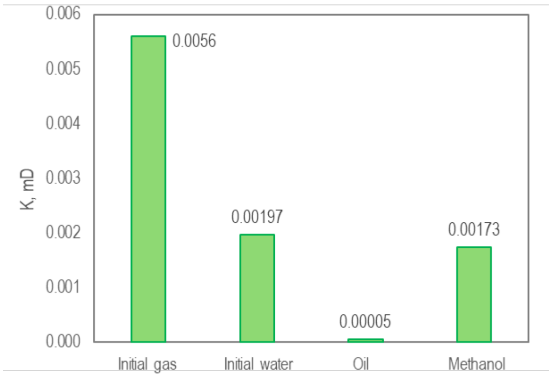

Figure 3. Comparison of permeability observed throughout the experiment.

4 Discussion

The experimental sequence reveals a consistent damage pathway: single-phase water flow did not induce progressive permeability loss (stable ΔP and k over ∼25 PV, NMR indicating a typical bound/mobile partition for this core sample), whereas subsequent oil injection into the water-saturated matrix resulted in monotonic pressure drop increase, stepwise decline in oil permeability, measurable growth of the core mass, increase of the bound and viscous hydrocarbons inside the sample after filtration. Taken together, these observations point to pore-scale colmatation governed by in-situ generation and deposition of heavy hydrocarbon material and stabilized water-in-oil emulsions [6], rather than classical water blocking, clay swelling, fines migration, or simple two-phase relative-permeability effects. This interpretation is consistent with reports that asphaltene/resin precipitation and interfacial film formation drive wettability alteration and severe permeability impairment, and that asphaltenes can stabilize water-in-oil emulsions in porous media [7]. Low-field NMR, especially T1-T2 mapping, is well suited to registering the associated shift toward high-viscosity hydrocarbon signatures and reduced mobility, supporting our mechanistic attribution.

A reasonable chemical route for the observed damage might also involve mild oxidative or catalytic transformation of hydrocarbon fractions during oil injection in a brine-saturated organic-rich matrix. Even with careful vacuuming before the test, trace oxygen cannot be ruled out. Iron-bearing phases (e.g. pyrite) can accelerate redox reactions, condensation of asphaltenic species at elevated temperature, producing heavier, less soluble fractions that adsorb to mineral and kerogen surfaces and constrict pore throats. Iron minerals enhance asphaltene precipitation and emulsion stability, and pyrite oxidation proceeds rapidly under wet, oxygenated conditions [8]. These trends compatible with our observations. In parallel, the low-salinity brine (13.86 g/L) and several PV oil amount may have promoted wettability shifts and interfacial film strengthening, further stabilizing viscous organic layers and emulsions. Such salinity-dependent wettability and IFT effects are well documented for tight rocks and EOR systems [9].

The methanol treatment rapidly stabilized pressure drop, and restored ∼87% of the pre-damage water permeability while reducing the short-T2 signal, indicating partial desorption and solubilization of adsorbed heavy organics and breakup of trapped emulsions without macro-structural alteration on CT. This response agrees with studies for other types of reservoirs showing that alcohols (methanol, isopropanol) mitigate aqueous-phase trapping and water blockage near the wellbore, enhance cleanup of condensate banking and improve relative permeability-effects attributed to their water miscibility and IFT reduction [10]. Although aromatic solvents (e.g. toluene) are potent asphaltene solvents, methanol offers operational simplicity and strong dehydration and emulsion-breaking capability under core-flood conditions, making it a practical first-line breaker in ultra-tight rocks.

These findings carry two operational implications for Bazhenov-type organic-rich shales. First, single-phase brine or oil can filtrate the matrix without significant time-dependent loss of permeability, but oil injection into brine-saturated pores at reservoir pT parameters can rapidly create organic deposits that collapse permeability by several orders of magnitude. Hence, controlling water-oil contact during stimulation and early production is essential. Second, alcohol-based "breaker", e.g. methanol can reverse a large part of the damage even for such complex kerogen-bearing types of shales. Field formulations may blend alcohols with co-solvents or ketones to balance solvency and economic constraints, and should be paired with corrosion control to limit iron-mediated catalysis. More broadly, process designs that reduce or avoid damaging via water-oil interactions, for example, continuous gas flooding in ultra-tight shale [11] have demonstrated high oil recovery without significant asphaltene precipitation or permeability loss, underscoring the value of water-lean strategies where feasible.

The main limitations of this study are the use of a single core. Heterogeneity in mineralogy and kerogen content, as well as oil composition could shift reaction kinetics and thresholds for emulsion formation or deposition. Nonetheless, the presented observations provide a reproducible diagnostic workflow to study water-, oil- and solvent-driven effects and to quantify the extent of physical and chemical processes in ultra-tight organic-rich shales.

5 Conclusion

This study evaluates methanol treatment for restoring permeability in Bazhenov-type shale after water-induced damage. At reservoir conditions, single-phase water flow did not cause progressive loss, whereas subsequent oil injection into a water-saturated matrix produced severe, cumulative permeability damage. NMR T1-T2 mapping and mass and chemical analyses indicated pore-scale colmatation by viscous hydrocarbon phases and C36+ precipitates, rather than classical water blocking or clay swelling. A methanol flush rapidly stabilized pressure and restored ~87% of pre-damage water permeability, consistent with partial dissolution and desorption of deposited organics and emulsion breakup. These results support methanol as an effective first-line "breaker" for kerogen-rich shales. Future work should probe compositional sensitivities (iron, dissolved oxygen, salinity), compare alcohol with aromatic and ketone blends and incorporate dynamic T1-T2 during flow.

Data Availability Statement

Data will be made available on request.

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Conflicts of Interest

The authors declare no conflicts of interest.

Ethical Approval and Consent to Participate

Not applicable.

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