

Critical Trapping Numbers and Capillary Desaturation in Mixed-to-Oil-Wet Carbonates under High-Temperature, High-Salinity Surfactant Flooding

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* Manuscript under review at *Geoenergy Science and Engineering* (Elsevier).

Abstract

This study reports capillary desaturation curves (CDCs) for three crude-oil-aged carbonate systems with expected mixed-to-oil-wet behavior—two Middle East reservoir core plugs (RC1, RC2) and an Indiana Limestone outcrop analogue (IL)—at 100 °C and 243,028 ppm TDS connate-water salinity. Prior to tertiary injection, each core was centrifuge-conditioned to establish a less end-effect-biased residual-oil baseline (S_{orw}) for CDC construction. We quantify the critical trapping number ($N_{t,crit}$) and the desaturation response using a multi-rate flooding protocol. Each experiment comprised a synthetic seawater pre-flush (43,373 ppm TDS), followed by a near-optimal surfactant flood formulated in seawater. The surfactant blend (Guerbet alkoxy carboxylate (GAC) and internal olefin sulfonate (IOS)) yields an ultra-low interfacial tension $\sigma_{os}(100\text{ °C}) = 3.07 \times 10^{-3}$ mN/m. In reservoir core plug RC1 ($k_{w,Sorw} = 2.24$ mD), surfactant flooding reduced oil saturation from $S_{orw} = 40\%$ to $S_{orc} = 7.2\%$, yielding $N_{t,crit} = 2.23 \times 10^{-3}$. In reservoir core plug RC2 ($k_{w,Sorw} = 4.86$ mD), surfactant flooding reduced oil saturation from $S_{orw} = 17.04\%$ to $S_{orc} = 9.96\%$, yielding $N_{t,crit} = 1.72 \times 10^{-3}$. In the Indiana Limestone outcrop ($k_{w,Sorw} = 74.93$ mD), oil saturation decreased from $S_{orw} = 16.5\%$ to $S_{orc} = 9.5\%$, yielding $N_{t,crit} = 8.47 \times 10^{-4}$. These measured mobilization thresholds are substantially higher than a classical water-wet sandstone baseline ($\sim 10^{-5}$) for all three tested carbonates. Under the adopted field-rate scaling, ultra-low IFT at $u = 1$ ft/day gives $N_t \approx 2.09 \times 10^{-3}$ for RC1 and $N_t \approx 1.68 \times 10^{-3}$ for RC2, both slightly below their own onsets, providing limited margin for deeper desaturation. For the tested low-permeability reservoir carbonates, viscosity enhancement remains a screening variable for higher trapping-number targets, subject to injectivity, polymer propagation, retention, and fracture-pressure constraints. These results provide carbonate-specific CDC and $N_{t,crit}$ benchmarks for screening surfactant flooding in mature HTHS carbonate reservoirs, where direct transfer of water-wet correlations may underrepresent the mobilizing force required.

Keywords

Surfactant flooding; Capillary desaturation curve; Trapping number; Mixed-wet carbonate; HTHS chemical EOR; Centrifuge conditioning; Mature carbonate reservoirs

1. Introduction

Trapped oil mobilization in carbonates is governed by capillary forces, which retain oil in pores, and viscous and gravitational forces. The capillary number N_c quantifies the dimensionless ratio of viscous to capillary forces [1,2]. In surfactant enhanced oil recovery (EOR), residual-oil mobilization is commonly evaluated from capillary desaturation behavior, in which IFT reduction increases the applied mobilizing force when the desaturation threshold is exceeded [3,4]. To account for gravitational contributions, the Bond number N_b defines the ratio of buoyancy to capillary forces. Following Pope et al. [12] (originally developed for gas-condensate systems but applicable to oil-water displacement under the same dimensionless-number framework), the total trapping number N_t vectorially combines N_c and N_b to represent the total mobilizing force. Reliable carbonate-specific mobilization thresholds are therefore relevant to mature-reservoir recovery efficiency and sustainable hydrocarbon production.

Capillary trapping and desaturation depend strongly on wetting state and pore architecture. In classical, strongly water-wet systems, residual oil is predominantly trapped as discontinuous ganglia within larger pore bodies via snap-off and bypassing mechanisms at pore constrictions [18,20]. Mobilization of these isolated ganglia typically begins over a narrow threshold near $N_{t,crit} = 1 \times 10^{-5} - 2 \times 10^{-5}$ [2]. This water-wet paradigm does not transfer directly to non-water-wet carbonates. Mixed-to-oil-wet carbonate surfaces can retain oil in smaller pores, micro-porosity, and continuous wetting films on the rock matrix [5]. Displacement therefore requires overcoming higher capillary resistance associated with film drainage [6].

As wettability departs from strongly water-wet conditions, the capillary desaturation curve (CDC) can shift to higher mobilizing forces. Masalmeh [5] and Humphry et al. [6] showed that mobilization thresholds in non-water-wet rocks can increase by orders of magnitude,

placing $N_{t,crit}$ within the 10^{-4} to 10^{-2} range depending on rock type, wettability, and experimental protocol. At standard reservoir Darcy velocities (e.g., $u = 1$ ft/day), generating these mobilizing forces through viscous pressure gradients alone may be operationally constrained. Direct transfer of water-wet sandstone CDC correlations to mixed-wet carbonate systems can, therefore, underrepresent the mobilizing force required for tertiary recovery.

Critical gaps remain in published N_t -based desaturation scaling. First, executing the extended multi-rate protocols required to establish CDCs under severe HTHS conditions is experimentally challenging due to surfactant degradation, divalent-ion precipitation, and phase-behavior instability over the extended laboratory timeframes required to reach steady-state [7,8].

Second, historical CDC datasets frequently define S_{orw} using waterflood endpoints obtained at low laboratory pressure gradients. As demonstrated by Masalmeh [5], low-rate waterfloods in mixed-to-oil-wet rocks can terminate at an apparent remaining oil saturation rather than a lower residual-oil baseline. This apparent saturation may be inflated by capillary end effects at the outlet boundary and by very low oil relative permeability (k_{ro}) near residual conditions. If this remaining saturation is used as the CDC baseline, the resulting critical trapping number may be biased downward and chemical-EOR screening forecasts may become optimistic. High-speed centrifuge conditioning provides a mechanical route to reduce this boundary artifact by imposing a more controlled outflow condition [9]; it was therefore used here to condition the plugs to the reference S_{orw} before tertiary injection.

Third, rigorously conditioned CDC datasets for aged or mixed-wet rocks under HTHS conditions remain limited compared with classical strongly water-wet sandstone datasets and recent carbonate surfactant-EOR studies have continued to emphasize permeability dependence, wettability alteration, adsorption, and recovery response rather than directly measured trapping-number thresholds [24–26]. Consequently, reservoir models and chemical-EOR screening workflows may default to published water-wet desaturation correlations (e.g., [2]) when evaluating mobilization in carbonates. This transfer is not generally conservative for mixed-wet systems because the mobilization threshold depends on wettability, pore architecture, residual-oil baseline definition, and the velocity convention used in the dimensionless number.

To address these gaps, this study reports centrifuge-conditioned CDCs and $N_{t,crit}$ values for two low-permeability reservoir carbonate plugs (RC1, RC2) and a higher-permeability Indiana Limestone outcrop analogue (IL) at 100 °C. We used a Guerbet alkoxy carboxylate (GAC) and internal olefin sulfonate (IOS) blend (SF1) with $\sigma_{os}(100\text{ °C}) = 3.07 \times 10^{-3}$ mN/m, extrapolated from spinning-drop measurements up to 90 °C. Each plug was centrifuge-conditioned to establish the reference S_{orw} prior to chemical injection, and a stepwise, multi-rate flooding protocol was then applied at ultra-low IFT. The objective is to isolate the N_t -controlled desaturation response from macroscopic end-effect bias and to evaluate how the measured thresholds affect surfactant-EOR screening at field-representative Darcy velocities.

2. Methodology

2.1. Materials.

Aqueous Phase Composition. We synthesized aqueous phases by dissolving analytical-grade salts—sodium chloride (NaCl), calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), sodium sulfate (Na_2SO_4), and sodium bicarbonate (NaHCO_3)—into deionized water (resistivity $\geq 18.2\text{ M}\Omega \cdot \text{cm}$). We used two brine compositions:

- Seawater (SW): The injection base fluid and solvent for the surfactant slug. Total Dissolved Solids (TDS) was fixed at 43,373 ppm, replicating the field injection source.
- Formation Water (FW): Synthesized with 243,028 ppm TDS and high divalent ion content to simulate connate water saturation.

The ionic compositions and physical properties of both brines are summarized in Table 1. These formulations were used throughout the coreflood program.

Table 1. Properties and Ionic Composition of Synthetic Formation Water (FW) and Injection Seawater (SW)

Ion	FW	SW	Property	FW	SW
Na ⁺	66,130	13,662	Total dissolved solids (ppm)	243,028	43,373
Ca ²⁺	23,246	539	Hardness (ppm as CaCO ₃)	26,520	2,122
Mg ²⁺	2,674	1,583	Viscosity (cP)	1.57	1.02
K ⁺	—	498	Density (g/cm ³)	1.17	1.04
Cl ⁻	150,675	27,092			
SO ₄ ²⁻	230	0			
HCO ₃ ⁻	—	0			
Br ⁻	—	0			
I ⁻	—	0			
TDS (ppm)	243,028	43,373			

Note: Density and viscosity values are reported at ambient conditions (25 °C, 1 atm).

Reservoir Crude Oil. We used stock-tank crude oil from the target Middle Eastern carbonate reservoir. The crude underwent a conditioning protocol: mechanical centrifugation to remove basic sediments and water, filtration through a 0.5-micron inline filter to eliminate suspended asphaltene aggregates, and vacuum-degassing. Rheological characterization established a dead oil viscosity of 1.25 cP at 100 °C.

Surfactant Formulation. We used Formulation SF1 to maintain aqueous compatibility and interfacial activity under the HTHS conditions evaluated here. The primary surfactant was a sodium Guerbet alkoxy carboxylate (C24–35PO–30EO–COONa) at 0.5 wt% active matter basis. Internal olefin sulfonates (IOS 15–18 and IOS 20–24 sodium salt) were used as co-surfactants to broaden the Winsor Type III microemulsion window [10]. An ethoxylated phenol co-solvent (0.5 wt% active basis) was included to reduce interfacial rigidity, suppress macroemulsions, and accelerate equilibration kinetics [11]. All reported concentrations are normalized to active matter content.

Porous Media Characterization. We selected three carbonate plugs spanning a wide permeability range to compare CDC response under identical chemistry and temperature. The cores were used as contrasting end-members for this screening study: two low-permeability reservoir carbonate plugs ($k_{w,Sorw} = 2.24$ and 4.86 mD) recovered from different wells and stratigraphic intervals, and a higher-permeability Indiana Limestone outcrop analogue (~75 mD effective water permeability at S_{orw}).

- Reservoir Carbonate 1 (RC1): A reservoir carbonate core plug from a low-permeability interval ($k_{w,Sorw} = 2.24$ mD, $\phi = 0.22$)
- Reservoir Carbonate 2 (RC2): A second reservoir carbonate core plug from a different well and stratigraphic interval ($k_{w,Sorw} = 4.86$ mD, $\phi = 0.273$)
- Outcrop Carbonate (IL): A moderate-to-high-permeability Indiana Limestone outcrop ($k_{w,Sorw} = 74.93$ mD, $\phi = 0.18$)

Prior to dynamic testing, the plugs underwent petrophysical preparation. The samples were trimmed, cleaned to remove residual fluids, and oven-dried to establish baseline porosity. Following vacuum saturation with formation water (FW), the absolute brine permeability, k_b , was measured. Primary drainage was then conducted using the filtered reservoir crude oil to establish the initial water saturation S_{wi} . To promote a representative aged carbonate wetting state, the plugs were submerged in crude oil within pressurized aging cells and thermally aged at 100 °C for three weeks. The wetting state was inferred from the aging protocol and displacement-response interpretation, not independently quantified by Amott, USBM, or contact-angle measurements. Core dimensions and petrophysical properties are listed in Table 2.

Table 2. Core Dimensions and Petrophysical Properties

Core ID	Length (cm)	Diameter (cm)	PV (cm ³)	k_b (mD)	$k_{w,Sorw}$ (mD)	ϕ (frac.)	S_{wi} (frac.)	S_{orw} (frac.)
RC1	5.13	3.75	12.11	10.07	2.24	0.22	0.23	0.40
RC2	4.95	3.83	14.97	8.54	4.86	0.273	0.104	0.170
IL	4.99	3.80	9.58	97.58	74.93	0.18	0.31	0.165

2.2. Experimental Procedures. Dynamic displacement experiments used a HPHT coreflood system, a confining pressure of 1200 psi and back pressure of 200 psi, temperature control at 100 °C, differential pressure monitoring, and back-pressure regulation.

2.3. Residual Oil Conditioning and Centrifuge Data Interpretation.

To establish a residual-oil baseline less affected by capillary end effects, each plug was conditioned using a multispeed centrifuge prior to the tertiary sequence [5]. At each rotational speed, fluid production was monitored until an equilibrium plateau was reached. The S_{orw} values reported prior to chemical injection are therefore treated as centrifuge-conditioned reference baselines for CDC construction, not as universal residual saturations independent of protocol and rock type.

Dynamic Desaturation via Stepwise Coreflooding and Trapping Number Formulation. Following centrifuge conditioning to the reference S_{orw} , we used a dynamic coreflooding protocol to evaluate desaturation under controlled increases in mobilizing force. We quantify the total mobilizing force using the trapping number (N_t), which vectorially combines the capillary number (N_c) and Bond number (N_b) [12]. In this study, u denotes Darcy (superficial) velocity and $v = u/\phi$ denotes interstitial velocity. The viscous component is evaluated on an interstitial-velocity basis, so that $N_c = v\mu/\sigma = u\mu/(\phi\sigma)$. This convention is used consistently for the laboratory and field-rate scaling calculations; benchmark comparisons are converted to the same basis before interpretation.

$$N_c = \frac{v \cdot \mu}{\sigma} = \frac{u \cdot \mu}{\phi \cdot \sigma} \quad (1)$$

where v is the interstitial velocity, u is the Darcy (superficial) velocity, μ is the viscosity of the displacing aqueous phase, σ is the interfacial tension, and ϕ is the porosity. At 100 °C, μ is 0.40 cP for both seawater and the SF1-in-seawater solution; the surfactant formulation did not measurably change the aqueous baseline viscosity. By defining μ as the aqueous displacing-phase viscosity, the applied viscous force is referenced to a defined fluid property rather than to the complex, shear-dependent microemulsion viscosities that may form in situ.

$$v = \frac{u}{\phi} \quad (2)$$

The Bond number N_b defines the ratio of buoyancy to capillary forces and is calculated using Eq. (3):

$$N_b = \frac{\Delta\rho \cdot g \cdot k_{w,Sorw}}{\phi \cdot \sigma} \quad (3)$$

where $\Delta\rho$ is the density difference between the aqueous and oleic phases (200 kg/m³), g is gravitational acceleration (9.81 m/s²), $k_{w,Sorw}$ is the effective permeability to water at residual oil saturation, and ϕ is the porosity.

For the baseline N_c and N_b calculations, the wettability term ($\cos \theta$) is omitted (effectively set to unity) to isolate the applied mechanical viscous and buoyancy forces from rock-fluid interaction terms. The N_b formulation (Eq. (3)) follows the Masalmeh [5] definition ($N_b = k_{w,Sorw}\Delta\rho g / \phi\sigma \cos \theta$), which places the buoyancy term on the same interstitial basis as the viscous term in Eq. (1), so that the two combine consistently in Eq. (5). It differs by a factor of $1/\phi$ from the Pope et al. [12] convention, which omits porosity from the denominator. Incorporating in situ contact angle can be necessary when the objective is to represent the apparent capillary resistance of mixed-to-oil-wet systems. The simplified formulation adopted here should therefore be interpreted as a defined mechanical baseline rather than a complete wettability-dependent trapping criterion. The trapping number N_t vectorially combines these forces using Eq. (4):

$$N_t = \sqrt{N_c^2 + 2 N_c N_b \sin \alpha + N_b^2} \quad (4)$$

For the horizontal displacement configuration used in this study ($\alpha = 0^\circ$), N_t reduces to Eq. (5):

$$N_t = \sqrt{N_c^2 + N_b^2} \quad (5)$$

To map the capillary desaturation curve, we applied a stepwise injection protocol that incrementally escalated the applied N_t on a single sample. Each rate step was maintained for at least 1.5 pore volumes and continued until both differential pressure and effluent fractional flow approached stable values. Because the onset criterion depends on measurable oil production, $N_{t,crit}$ is reported operationally as the highest tested trapping number before measurable desaturation.

The protocol advanced through the following defined stages:

- **Baseline Conditioning:** Prior to surfactant injection, each core was flooded with seawater to establish the injection salinity and confirm a stable reference residual-oil baseline. Seawater was injected over a sequence of flow rates, after which the rate was

returned to 0.25 cm³/min before surfactant injection. No incremental oil was produced at this reference rate, supporting use of the centrifuge-conditioned baseline for the tertiary desaturation sequence.

- **Surfactant Injection:** The IFT of formulation SF1 is $\sigma_{os} \approx 3.07 \times 10^{-3}$ mN/m. Once the oil cut ceased at the lowest reference rate, the injection flow rate was increased to $Q = 0.075, 0.25, 0.5, 1, 2, 6, 8,$ and 12 cm³/min. Each rate plateau was maintained for a minimum of 1.5 pore volumes, and the rate was increased only after the differential pressure (ΔP) and effluent fractional flow approached stable values.
- **Salinity-Gradient Post-Flush:** Following the maximum applied viscous pressure-gradient step, a seawater chase and a subsequent 50% diluted-salinity brine ($Q = 0.25$ cm³/min) were injected. Because this step was executed at low flow rate, it was used to probe whether phase-behavior changes could mobilize additional oil without increasing mechanical forcing. The interpretation is therefore limited to a phase-behavior-related response consistent with a shift from near-optimum Winsor Type III conditions toward under-optimum Winsor Type I conditions [13,14].

Uncertainty in the trapping-number estimates is dominated by the adopted oil–surfactant IFT. The oil–surfactant IFT, σ_{os} , was measured by spinning-drop tensiometry up to 90 °C and extrapolated to 100 °C using a power-law regression ($R^2 = 0.994$); the independent Huh-derived estimate, $\sigma_{Huh} = 3.32 \times 10^{-3}$ mN/m, differs by ~8% from the extrapolated $\sigma_{os}(100\text{ °C}) = 3.07 \times 10^{-3}$ mN/m. Because N_t is inversely proportional to σ , a $\pm 20\%$ uncertainty in σ propagates to a $\pm 20\%$ uncertainty in $N_{t,crit}$; for Core RC1 this gives a propagated range of approximately $(1.78\text{--}2.68) \times 10^{-3}$, for Core RC2 approximately $(1.38\text{--}2.07) \times 10^{-3}$, and for Core IL approximately $(6.78 \times 10^{-4} - 1.02 \times 10^{-3})$. Separately, the operational definition of $N_{t,crit}$ places an empirical bracket between the highest tested trapping number before measurable desaturation and the next rate step at which oil was produced; this empirical bracket spans 2.23×10^{-3} to 4.47×10^{-3} for Core RC1, 1.72×10^{-3} to 3.45×10^{-3} for Core RC2, and 8.47×10^{-4} to 2.69×10^{-3} for Core IL.

3. Results and Discussion

3.1. Phase Behavior and Interfacial Tension Validation. Formulation SF1 was characterized under HTHS conditions to confirm aqueous stability and Winsor Type III microemulsion formation near the injection salinity (43,373 ppm TDS). Salinity scans at 100 °C demonstrated a Type I to Type III to Type II phase transition. The aqueous stability limit extended to 70,000 ppm, establishing a margin above the injection salinity. At the optimal salinity ($S^* = 45,000$ ppm), the formulation exhibited an optimal solubilization ratio (R^*) of 9.5 cm³/cm³. A summary of SF1 fluid properties and phase behavior at 100 °C is listed in Table 3.

Table 3. Summary of SF1 Fluid Properties and Phase Behavior at 100 °C

Parameter	Value	Unit
Optimal salinity (S^*)	45,000	ppm TDS
Solubilization ratio (R^*)	9.5	cm ³ /cm ³
Calculated IFT, Chun–Huh (σ_{Huh})	3.32×10^{-3}	mN/m
Spinning drop IFT (σ_{os})	3.07×10^{-3}	mN/m
Baseline, pendant drop (σ_{ow})	24.3	mN/m
Aqueous stability limit	70,000	ppm TDS
Aqueous slug viscosity (μ)	0.40	cP
Microemulsion type	Winsor III	—

Baseline oil–seawater interfacial tension at 100 °C was measured by pendant-drop tensiometry and was 24.3 mN/m. Fig. 1 defines the phase-behavior boundary condition used for SF1. Fig. 1a presents solubilization ratios (V_o/V_s and V_w/V_s) versus salinity, showing a Winsor I to III to II transition. The optimum salinity ($S^* = 45,000$ ppm) and optimum solubilization ratio ($R^* = 9.5$ cm³/cm³) are close to the injection seawater salinity (43,373 ppm). Fig. 1b shows the interfacial tension (σ_{os}) between the crude oil and the SF1 formulation as a function of temperature, measured by spinning-drop tensiometry.

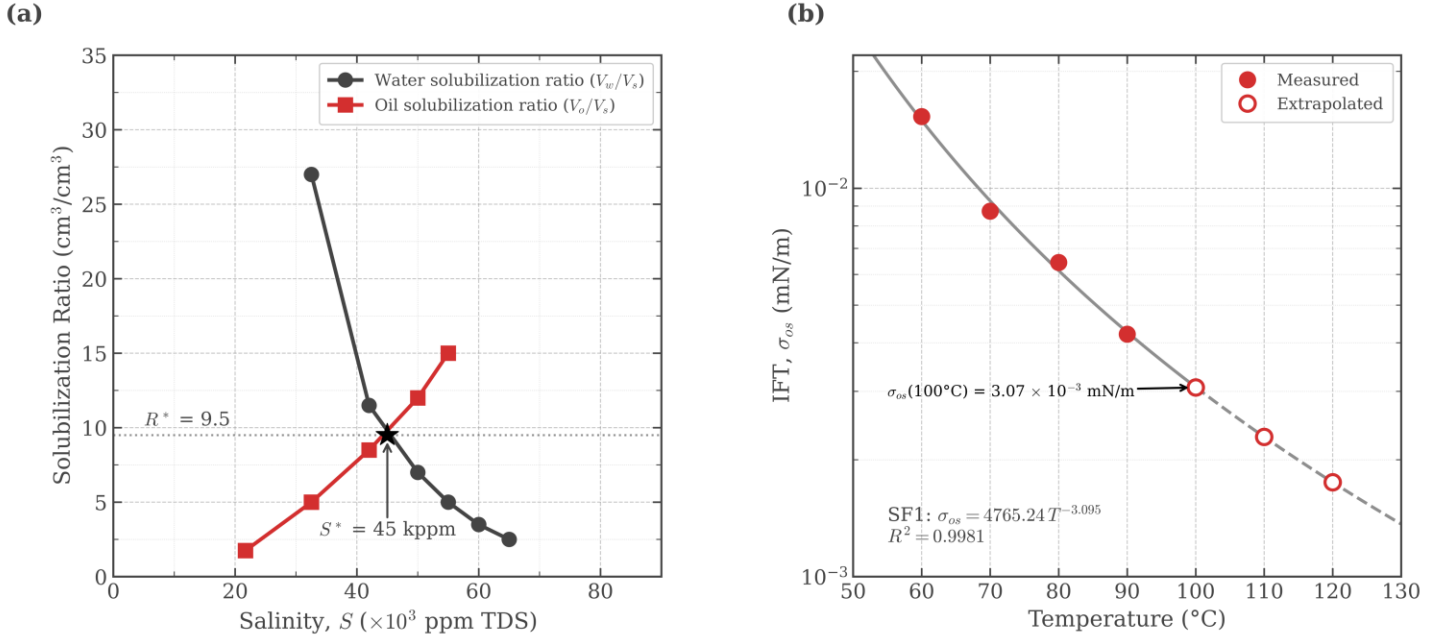


Fig. 1. SF1 phase behavior and oil-surfactant IFT. Panels show (a) solubilization ratios versus salinity and (b) spinning-drop IFT versus temperature.

Measurements were acquired up to 90 °C. The observed temperature trend is consistent with the reported behavior of Guerbet alkoxy carboxylate (GAC) systems, where increasing temperature can shift the formulation toward optimum phase behavior and reduce IFT at fixed salinity and composition [15]. The GAC headgroup is designed for elevated-temperature stability. Therefore, the observed IFT decrease is interpreted as interfacial re-partitioning rather than surfactant loss under the tested conditions. This contrasts with sulfate systems, where hydrolysis can degrade the surfactant and offset IFT reduction [7].

Due to the temperature limit of the available equipment, σ_{os} was extrapolated to 100 °C, 105 °C, and 120 °C using a power-law regression ($R^2 = 0.994$). This gives $\sigma_{os}(100^\circ\text{C}) = 3.07 \times 10^{-3}$ mN/m for trapping-number calculations. The extrapolation assumes that the same phase environment persists from 90 °C to 100 °C. Surfactant IFT does not necessarily decline monotonically if increasing temperature moves the system across a phase-inversion boundary; such transitions typically yield a V-shaped or U-shaped IFT trajectory rather than a continuous decline [16]. Prior aqueous stability screening showed that the SF1 formulation remained thermally stable and physically homogeneous for at least 21 days at 120 °C. This stability result supports the plausibility of the extrapolated boundary condition, while the uncertainty associated with the above-90 °C extrapolation is treated in Section 2.3. Because N_t is inversely proportional to σ , uncertainty in $\sigma_{os}(100^\circ\text{C})$ transfers directly into the calculated trapping numbers.

The Huh equation [17], defined in Eq. (6), provides an independent estimate of interfacial tension from the solubilization ratio at optimum conditions.

$$\sigma = \frac{C}{(R^*)^2} \quad (6)$$

We applied a scaling constant of $C = 0.3$ mN/m, which is the characteristic value for typical crude oil-surfactant-brine systems [8]. Using $C = 0.3$ mN/m and $R^* = 9.5$ cm³/cm³ gives $\sigma_{\text{Huh}} = 3.32 \times 10^{-3}$ mN/m. This analytical estimate agrees within 8% of the extrapolated spinning-drop value ($\sigma_{os} = 3.07 \times 10^{-3}$ mN/m at 100 °C). The agreement supports the plausibility of the adopted ultra-low-IFT boundary condition, but it should not be interpreted as independent verification of the temperature extrapolation above the measured range.

3.2. Centrifuge-Conditioned Residual-Oil Baseline. To reduce capillary end-effect bias in the residual-oil baseline, each plug was conditioned using a multispeed centrifuge prior to the tertiary sequence ($S_{\text{orw}} = 40\%$ for Core RC1; 17.04% for Core RC2; 16.5% for Core IL).

3.3. Dynamic Viscous Desaturation Response. Following centrifuge conditioning, the coreflooding experiments progressively increased the trapping number to identify the onset of measurable residual-oil mobilization.

We computed N_t from capillary and buoyancy contributions [12]. For the horizontal configuration ($\alpha = 0^\circ$), N_t reduces to Eq. (5). We computed N_c using the interstitial-velocity convention defined above ($v = u/\phi$), with $\mu = 0.40$ cP, $\phi = 0.22$, and $\sigma_{os}(100^\circ\text{C}) = 3.07 \times 10^{-3}$ mN/m for Core RC1. To evaluate mobilization potential under reservoir-rate conditions, the calculation is shown for a standard field Darcy (superficial) velocity of $u = 1$ ft/day (3.53×10^{-6} m/s) for Core RC1:

- Darcy velocity (u): 3.53×10^{-6} m/s (1 ft/day)
- Interstitial velocity ($v = u/\phi$, Eq. (2)): 1.60×10^{-5} m/s (~ 4.54 ft/day)
- Viscosity (μ): 0.40 cP (4.0×10^{-4} Pa·s)
- Interfacial tension (σ_{os}): 3.07×10^{-3} mN/m (3.07×10^{-6} N/m)
- $N_c = \frac{v\mu}{\sigma} = \frac{(1.60 \times 10^{-5})(4.0 \times 10^{-4})}{(3.07 \times 10^{-6})} = 2.09 \times 10^{-3}$
- $N_b = 6.42 \times 10^{-6}$
- $N_t = \sqrt{N_c^2 + N_b^2} = 2.09 \times 10^{-3}$

This calculation shows that at $u = 1$ ft/day, the applied trapping number for Core RC1 ($N_t \approx 2.09 \times 10^{-3}$) is slightly below the measured onset for this low-permeability reservoir rock ($N_{t,crit} = 2.23 \times 10^{-3}$). The same field-rate scaling gives $N_t \approx 1.68 \times 10^{-3}$ for Core RC2, against its measured onset of $N_{t,crit} = 1.72 \times 10^{-3}$. Consequently, the multi-rate laboratory protocol increased the injection rate up to 12 cm³/min ($u = 51.3$ ft/day, $N_t = 1.07 \times 10^{-1}$) to map the complete desaturation trajectory. These elevated N_t steps are laboratory diagnostic endpoints used to define the CDC, not field-gradient targets.

Fig. 2 presents oil saturation as a function of the applied total trapping number for Cores RC1, RC2, and IL. The baseline seawater pre-flush generated no incremental oil, supporting the stability of the centrifuge-conditioned reference S_{orw} .

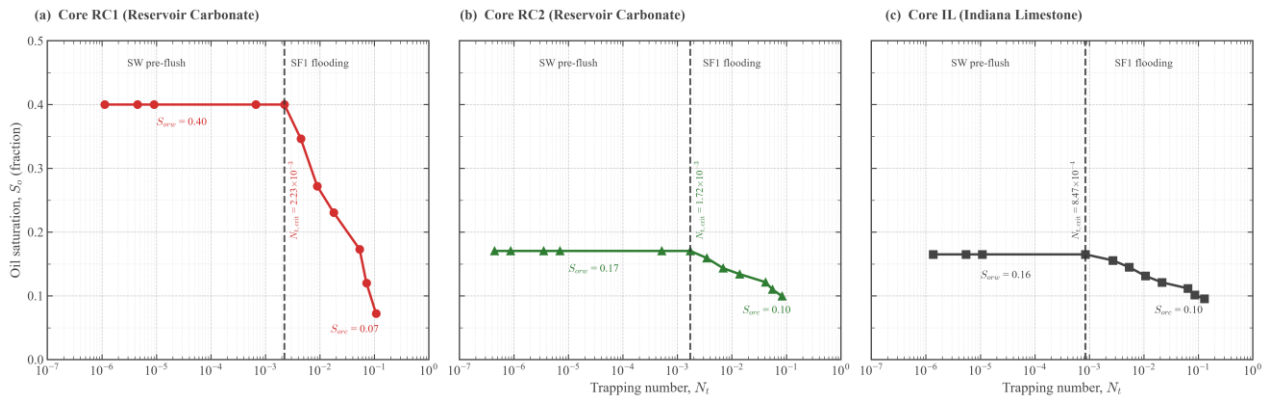


Fig. 2. Oil saturation versus trapping number at 100 °C. Panels show (a) Core RC1, (b) Core RC2, and (c) Core IL, with seawater pre-flush endpoints, SF1 rate-escalation desaturation, and the measured $N_{t,crit}$ for each core.

During SF1 surfactant injection ($\sigma_{os} = 3.07 \times 10^{-3}$ mN/m), the three cores exhibited distinct mobilization thresholds. For Core RC1, the initial ultra-low-IFT injection sequence yielded no measurable desaturation up to $N_t = 2.23 \times 10^{-3}$ ($Q = 0.25$ cm³/min), and oil was mobilized at $N_t = 4.47 \times 10^{-3}$. The reported critical trapping number is therefore $N_{t,crit} = 2.23 \times 10^{-3}$. Beyond this threshold, desaturation proceeded sharply, reaching $S_{orc} = 7.2\%$ (81.95% of S_{orw} mobilized) at the maximum laboratory viscous limit ($N_t = 1.07 \times 10^{-1}$).

Core RC2, a second reservoir carbonate plug recovered from a different well and stratigraphic interval, yielded no measurable desaturation up to $N_t = 1.72 \times 10^{-3}$ ($Q = 0.25$ cm³/min), and oil was mobilized at $N_t = 3.45 \times 10^{-3}$. The reported critical trapping number is therefore $N_{t,crit} = 1.72 \times 10^{-3}$. Desaturation proceeded from $S_{orw} = 17.04\%$ to $S_{orc} = 9.96\%$ (41.55% of S_{orw} mobilized) at the maximum applied trapping number for this plug ($N_t = 8.28 \times 10^{-2}$). This threshold is a factor of 1.3 lower than Core RC1 ($N_{t,crit} = 2.23 \times 10^{-3}$), despite the two reservoir plugs differing in permeability by a factor of 2.2 ($k_{w,Sorw} = 4.86$ mD versus 2.24 mD); the reservoir-carbonate mobilization threshold is therefore reported as a measured range rather than a single point.

The higher-permeability outcrop analogue (Core IL) exhibited an earlier onset. No measurable desaturation was observed up to $N_t = 8.47 \times 10^{-4}$, defining $N_{t,crit} = 8.47 \times 10^{-4}$. Because Core IL initiated from a much lower S_{orw} of 16.5%, the incremental tertiary recovery was more limited, reaching a terminal S_{orc} of 9.5% (42.22% of S_{orw} mobilized) at the maximum trapping number.

3.4. Water-Wet Sandstone Benchmark as a Screening-Risk Reference. To evaluate the design risk of transferring water-wet CDC criteria to aged carbonate systems, the measured CDCs were benchmarked against a classical water-wet sandstone reference. Fig. 3 presents normalized CDCs (S_o/S_{orw} versus N_t) for both carbonate plugs and the Chatzis and Morrow [2] reference curve. In strongly water-wet media, residual oil is commonly trapped as discontinuous ganglia in larger pores through snap-off at pore constrictions [18,19], with mobilization over a relatively narrow threshold.

The sandstone reference in Fig. 3 uses values tabulated by Chatzis and Morrow [2] for 16 consolidated water-wet sandstones. To place their data on the same basis, their capillary number, $N_{c,2}$, was converted to the trapping-number definition used here. Chatzis and Morrow define $N_{c,2}$ using brine permeability (k_w) and the imposed pressure gradient: $N_{c,2} = k_w \Delta P / (L\sigma)$. Substituting Darcy's law for the aqueous

phase, $u = k_{rw}w/\mu \times \Delta P/L$, gives $\Delta P/L = u\mu/(k_{rw}w)$ and therefore $N_{c,2} = u\mu/(\sigma k_{rw})$. The present trapping number uses the interstitial-velocity convention, $N_t = u\mu/(\phi\sigma)$ (Eq. (7)). Dividing N_t by $N_{c,2}$ gives $N_t = N_{c,2} \times (k_{rw}/\phi)$ (Eq. (8)). For Berea BL-2, which anchors the Chatzis dataset, k_{rw} at S_{orw} is 0.202 and ϕ is 0.225, giving a multiplier of ~ 0.9 . This conversion is used only to place the onset comparison on a consistent basis; on an N_t axis spanning several orders of magnitude, $\log_{10}(0.9) = -0.046$ is visually negligible.

$$N_t = \frac{u\mu}{\phi\sigma} \quad (7)$$

$$N_t = N_{c,2} \times \left(\frac{k_{rw}}{\phi}\right) \quad (8)$$

The overlay shows that all three tested carbonate systems require substantially higher mobilizing forces than the selected water-wet sandstone baseline. The 16 water-wet sandstones have a mean mobilization onset of $(1.9 \pm 0.6) \times 10^{-5}$. Core RC1 ($N_{t,crit} = 2.23 \times 10^{-3}$) is $\sim 117\times$ higher (2.07 log orders), Core RC2 ($N_{t,crit} = 1.72 \times 10^{-3}$) is $\sim 91\times$ higher (1.96 log orders), and Core IL ($N_{t,crit} = 8.47 \times 10^{-4}$) is $\sim 45\times$ higher (1.65 log orders). All three thresholds exceed the +1 standard-deviation upper bound (2.5×10^{-5}). This comparison supports carbonate-specific CDC thresholds in screening calculations and cautions against direct transfer of water-wet sandstone criteria to aged or mixed-wet carbonates. Consistent with Humphry et al. [6], the magnitude of the shift is attributed primarily to wettability rather than sandstone-carbonate lithology contrast.

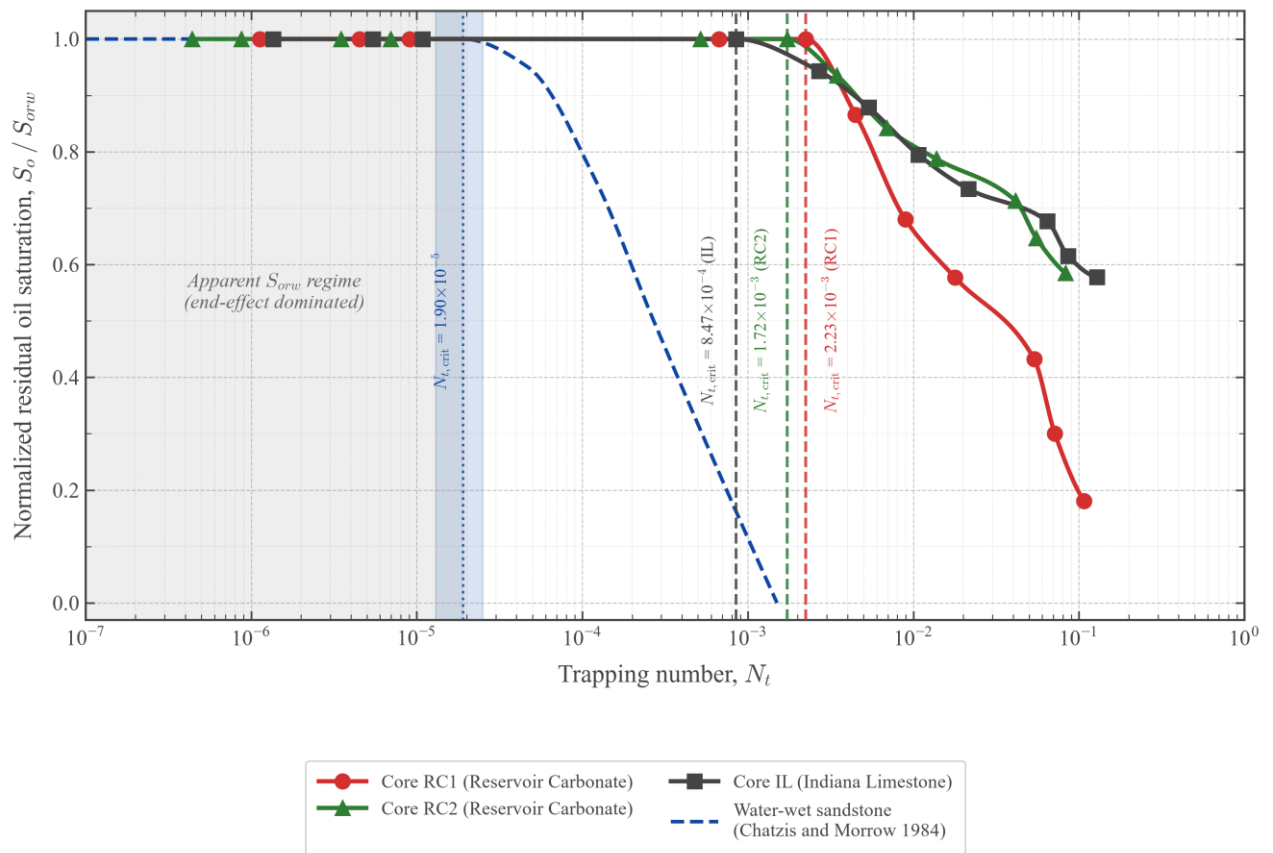


Fig. 3. Normalized CDCs for Cores RC1, RC2, and IL and the water-wet sandstone reference [2]. Curves are plotted as S_o/S_{orw} versus N_t under $\sigma_{os} = 3.07 \times 10^{-3}$ mN/m.

3.5. CDC Slope and Trapping Behavior. The rightward CDC shift is consistent with stronger capillary retention in the tested aged carbonate systems. In strongly water-wet sandstone systems, residual oil commonly occurs as disconnected ganglia in larger pores, and mobilization can occur over a relatively narrow interval once the critical threshold is exceeded [18,20].

In the tested aged carbonate plugs, delayed onset and more gradual desaturation are consistent with oil retained on rough carbonate surfaces, in microporosity, and in wetting films [5]. Because no pore-scale imaging was acquired, this interpretation is a mechanistic explanation consistent with the observed CDCs rather than direct evidence of pore-scale configuration.

The CDC slope provides qualitative diagnostic information about trapping behavior. Core RC1 shows a sharper transition immediately after $N_{t,crit}$, suggesting that a larger fraction of tertiary movable oil enters the mobilization window over a narrow N_t range. Cores RC2

and IL both show a more gradual response over more than one order of magnitude in N_t , consistent with a broader distribution of accessible pore-scale trapping environments and macro-pore/micro-pore partitioning in complex carbonates [21]. Water-wet step-function CDC models can therefore overpredict the onset and efficiency of chemical mobilization when applied directly to the tested carbonate systems.

The mobilized fraction is consistent with a dependence on the residual-oil baseline rather than on reservoir-versus-outcrop provenance. Core RC2 initiated from $S_{orw} = 17.04\%$, close to the Core IL value of 16.5% , and reached $E_{D,SF1} = 41.55\%$ against 42.22% for Core IL; Core RC1, initiating from $S_{orw} = 40\%$, reached 81.95% . Both the mobilized fraction and the post-onset slope therefore group Core RC2 with the outcrop analogue rather than with the other reservoir plug.

3.6. Salinity-Gradient Post-Flush Response. Fig. 4 summarizes normalized endpoint oil saturations (S_o/S_{orw}) across the primary experimental stages. After the maximum viscous pressure-gradient plateau ($Q = 12 \text{ cm}^3/\text{min}$), a 50% diluted-salinity brine at $Q = 0.25 \text{ cm}^3/\text{min}$ reduced S_o in Core RC1 from 7.2% to 5.8% and in Core RC2 from 9.96% to 9.37% , whereas Core IL remained at 9.5% . This low-rate post-flush tested whether additional oil could be mobilized through salinity-driven phase behavior rather than increased mechanical forcing.

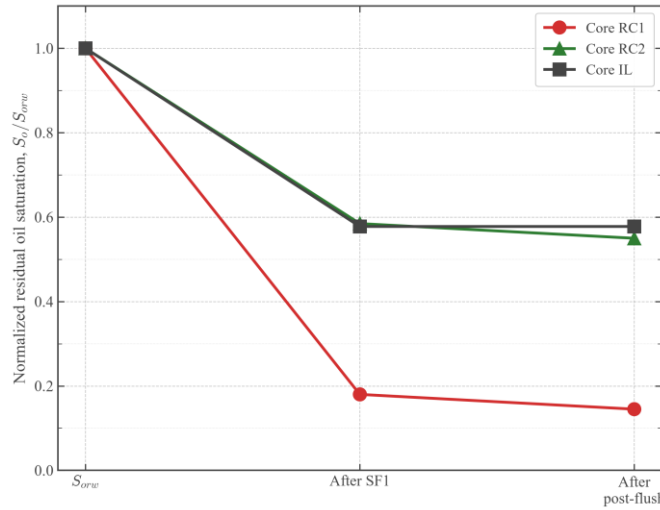


Fig. 4. Normalized endpoint oil saturations by experimental stage for Cores RC1, RC2, and IL. Endpoints separate SF1 viscous desaturation from the low-rate salinity-gradient post-flush.

Because the late-stage mobilization in Core RC1 occurred at a low flow rate, the response is consistent with a phase-behavior contribution rather than increased viscous stress. The same low-rate response was reproduced in Core RC2: both reservoir plugs shed 3.5% of S_{orw} on the salinity-gradient post-flush (Core RC1, 7.2% to 5.8% ; Core RC2, 9.96% to 9.37%). Dilution can shift the local phase environment from optimum Winsor Type III toward an under-optimum water-soluble Winsor Type I state [13,14]. Similar engineered-brine/surfactant carbonate experiments show that brine composition, wettability alteration, Winsor III microemulsion behavior, and IFT reduction can act jointly during tertiary recovery [22].

This shift provides a plausible basis for resolubilization of trapped microemulsion or reduced interfacial-film stability, but the present data do not uniquely identify the mechanism. The absence of additional response in Core IL may reflect poorer access to remaining oil, different pore-scale trapping, or measurement-resolution limits.

Table 4 summarizes the measured petrophysical parameters, endpoint saturations, and microscopic displacement efficiencies for the three corefloods.

Table 4. Summary of CDC Coreflooding Experiments

Parameter	Core RC1 (Reservoir)	Core RC2 (Reservoir)	Core IL (Outcrop)
Absolute permeability k_b	10.07 mD	8.54 mD	97.58 mD
Effective permeability at S_{orw} ($k_{w,Sorw}$)	2.24 mD	4.86 mD	74.93 mD
Porosity (ϕ)	0.22	0.273	0.18
Residual oil saturation after waterflood (S_{orw})	40%	17.04%	16.5%
Critical trapping number ($N_{t,crit}$)	2.23×10^{-3}	1.72×10^{-3}	8.47×10^{-4}
Final oil saturation after SF1 (S_{orc})	7.2%	9.96%	9.5%
Final oil saturation after post-flush ($S_{o,post}$)	5.8%	9.37%	9.5%
Microscopic displacement efficiency after SF1 (ED,SF1)	81.95%	41.55%	42.22%
Microscopic displacement efficiency after post-flush ($E_{D,post}$)	85.48%	45.01%	42.22%

3.7. Field-Rate Scaling and Viscosity Constraints. Translating the laboratory diagnostic limits into field-rate screening exposes the chemical-EOR challenge in the tested low-permeability reservoir carbonates. To evaluate feasibility, we assess the mobilizing force at a representative field Darcy velocity of $u = 1$ ft/day. Applying the aqueous viscosity ($\mu = 0.40$ cP) and the extrapolated ultra-low IFT of formulation SF1 ($\sigma_{os}(100\text{ }^\circ\text{C}) = 3.07 \times 10^{-3}$ mN/m) for Core RC1 ($\phi = 0.22$) gives $N_t \approx 2.09 \times 10^{-3}$. This value is slightly below the measured Core RC1 onset ($N_{t,crit} = 2.23 \times 10^{-3}$), indicating that ultra-low IFT alone provides limited margin for initiating desaturation in the low-permeability reservoir plug under the adopted scaling. The same scaling for Core RC2 ($\phi = 0.273$) gives $N_t \approx 1.68 \times 10^{-3}$, against its measured onset of $N_{t,crit} = 1.72 \times 10^{-3}$ (0.98 $\times$ onset). For Core IL, the measured threshold is lower ($N_{t,crit} = 8.47 \times 10^{-4}$), so the same field-rate scaling would exceed the IL onset threshold; however, IL is an outcrop analogue and should not be generalized as a reservoir prediction.

The near-unity ratios reported above for Cores RC1 (0.94 $\times$ onset) and RC2 (0.98 $\times$ onset) are not independent corroboration. The desaturation onset for both reservoir plugs fell on the same rate step ($Q = 0.25$ cm³/min), which for plugs of these dimensions corresponds to $u = 1.03$ – 1.07 ft/day, so the ratios reflect the placement of the rate ladder relative to the field reference velocity. Because the operational bracket extends to the next rate step, a factor of two in rate, the resolved onset for both reservoir plugs lies between roughly 1 and 2 ft/day equivalent Darcy velocity at the tested IFT.

Fig. 5 translates the Core RC1 CDC into viscosity scaling at field Darcy velocities. Only a modest viscosity increase would be required to cross the Core RC1 onset threshold at $u = 1$ ft/day under the adopted calculation. The same scaling gives $\mu \approx 0.41$ cP for Core RC2 at $u = 1$ ft/day to reach its own onset threshold. Higher viscosities, on the order of ~ 2 cP and above, correspond to deeper desaturation targets near $N_t \approx 10^{-2}$ rather than onset alone. Under the HTHS conditions evaluated here (100 $^\circ\text{C}$ and 243,028 ppm TDS), polymer selection and propagation would require HTHS-stable chemistries, such as acrylamido tertiary butyl sulfonate (ATBS)-based synthetic polymers, rather than conventional hydrolyzed polyacrylamide (HPAM). Literature values indicate that achieving in situ viscosities of approximately 2 cP may require active polymer concentrations of 1,500–2,000 ppm, while reaching approximately 10 cP may require 3,500–4,000 ppm [23]. These values are used as viscosity screening targets; polymer rheology, retention, degradation, and propagation were not directly measured in this study.

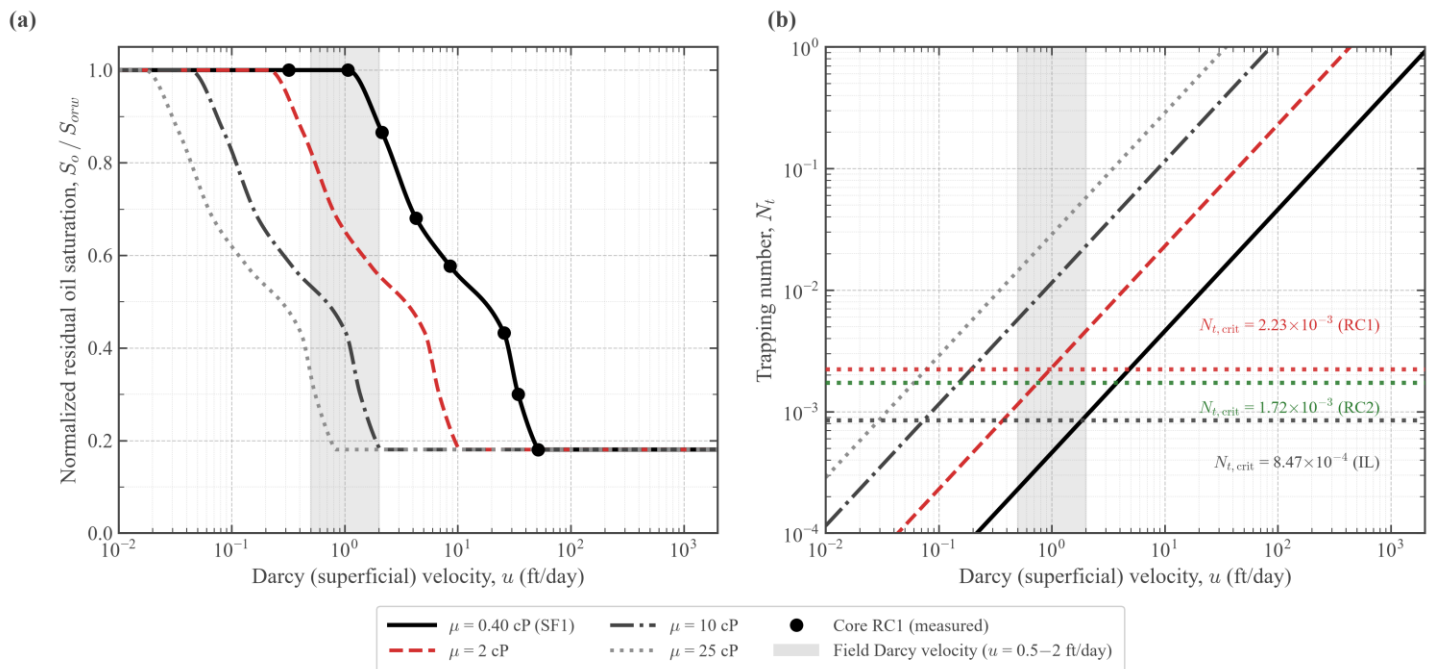


Fig. 5. Velocity–viscosity sensitivity for Core RC1 under ultra-low IFT. Panels show (a) S_o/S_{orw} versus Darcy velocity for Core RC1 and (b) N_t versus Darcy velocity for Cores RC1, RC2, and IL; the shaded band indicates 0.5–2 ft/day.

Translating this viscosity requirement into field execution requires pressure-gradient and injectivity analysis. In low-permeability lithologies such as Core RC1 ($k_{w,Sorw} \approx 2.24$ mD), viscous polymer injection may be constrained by injectivity, mechanical degradation, filtration or face-plugging, and formation fracture-pressure limits. These constraints make the viscosity-injectivity trade-off a screening decision point for mature low-permeability carbonate fields, rather than a post hoc implementation detail. The present experiments do not directly measure these limits; therefore, the field implication is restricted to the identification of a likely implementation constraint.

In higher-permeability intervals—represented here only by the outcrop analogue (Core IL, $k_{w,Sorw} \approx 75$ mD)—viscosity enhancement would increase the calculated trapping number more readily at the same Darcy velocity. However, this does not establish that polymer solutions can be propagated without exceeding formation parting pressure or incurring unacceptable retention. The economic and technical viability of high-concentration polymer slugs depends on injectivity, polymer retention, shear stability, salinity tolerance, and adsorption on carbonate surfaces, all of which require separate evaluation before field design.

3.8. Cross-Core Comparison of Measured Thresholds. Fig. 6 places the three measured $N_{t,crit}$ values against $k_{w,Sorw}$ (panel a) and the three measured $E_{D,SF1}$ values against S_{orw} (panel b). Across the three plugs, $k_{w,Sorw}$ varies by a factor of 33 (2.24 to 74.93 mD) while $N_{t,crit}$ varies by a factor of 2.6 (2.23×10^{-3} to 8.47×10^{-4}). The direction, higher permeability corresponding to lower onset, is consistent across the dataset, but the magnitude is small relative to the 45- to 117-fold shift from the water-wet sandstone mean onset shown as the shaded reference band. Error bars carry the $\pm 20\%$ IFT-propagated uncertainty defined in Section 2.3. N_o trend line is fitted to the three points.

Panel (b) plots $E_{D,SF1}$ against S_{orw} for the same three plugs. Core RC2 ($S_{orw} = 17.04\%$, $E_{D,SF1} = 41.55\%$) and Core IL ($S_{orw} = 16.5\%$, $E_{D,SF1} = 42.22\%$) fall close together, while Core RC1 ($S_{orw} = 40\%$, $E_{D,SF1} = 81.95\%$) is separated along both axes, consistent with the mobilized-fraction dependence on the residual-oil baseline described in Section 3.5. Taken together, the three measured $N_{t,crit}$ values (2.23×10^{-3} , 1.72×10^{-3} , and 8.47×10^{-4}) place the reservoir-carbonate threshold within a measured range of 1.72×10^{-3} to 2.23×10^{-3} rather than at a single value, with all three plugs 45 to 117 times the water-wet sandstone mean onset. With $n = 3$ plugs, neither the permeability dependence in panel (a) nor the baseline dependence in panel (b) is established as a general correlation.

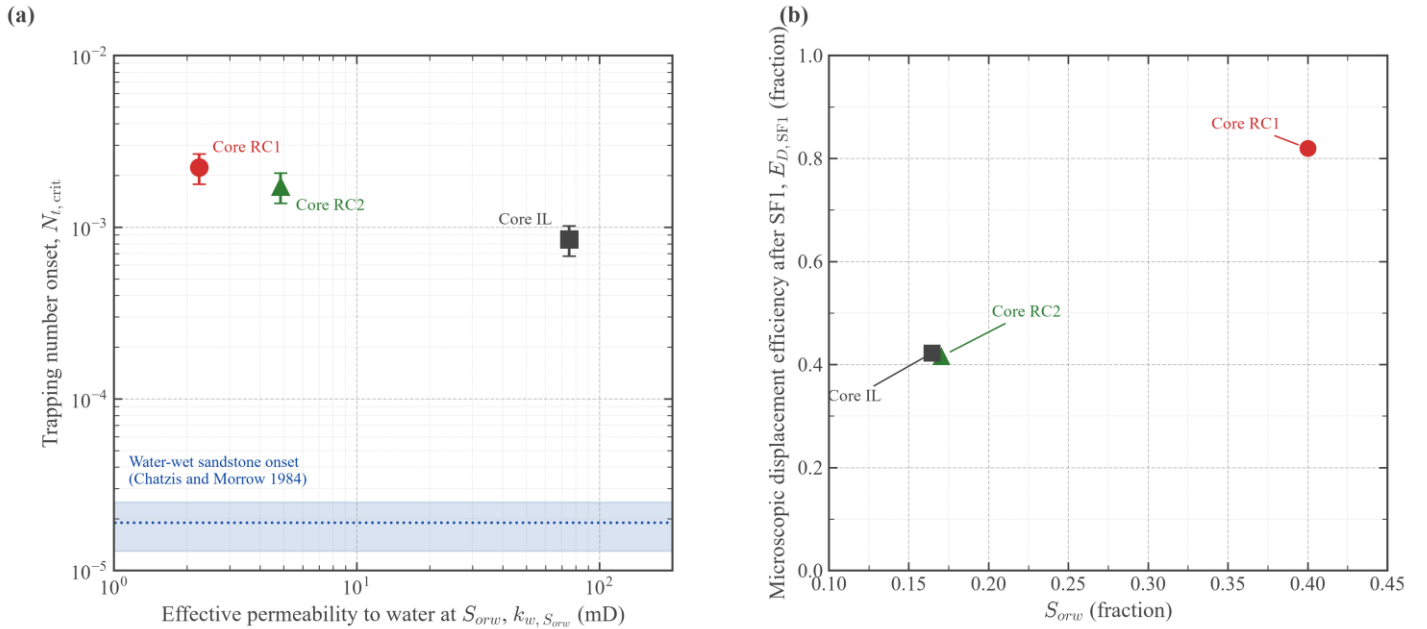


Fig. 6. Cross-core comparison of measured desaturation thresholds. (a) Critical trapping number ($N_{t,crit}$) versus effective water permeability at S_{orw} ($k_{w,S_{orw}}$) for Cores RC1, RC2, and IL, with the water-wet sandstone reference band, $(1.9 \pm 0.6) \times 10^{-5}$ [2], and $\pm 20\%$ IFT-propagated error bars on each point; no trend line is fitted. (b) Microscopic displacement efficiency after SF1 ($E_{D,SF1}$) versus residual oil saturation after waterflood (S_{orw}) for the same three cores.

These results should be read within the experimental limits of the study. The dataset comprises two reservoir plugs (Core RC1, Core RC2) and one outcrop analogue (Core IL), the wetting state is inferred rather than independently quantified as stated in Section 2.1, and the oil–surfactant IFT used in N_t calculations is extrapolated above 90 °C with uncertainty quantified in Section 2.3. In addition, $N_{t,crit}$ is an operational bracket defined by the highest tested trapping number before measurable desaturation and the next rate step that produced oil, rather than a continuously resolved onset.

4. Summary and Conclusions

Experimental characterization of capillary desaturation curves (CDCs) for two crude-oil-aged reservoir carbonate plugs (Core RC1, Core RC2) and an Indiana Limestone outcrop analogue (Core IL) at 100 °C under seawater injection (43,373 ppm TDS) supports the following conclusions:

- **Residual-Oil Baseline Definition:** Centrifuge conditioning established S_{orw} baselines of 40% for Core RC1, 17.04% for Core RC2, and 16.5% for Core IL; these reference values are protocol- and rock-dependent rather than universal residual saturations.
- **Measured Carbonate Trapping Thresholds:** The measured critical trapping numbers were $N_{t,crit} = 2.23 \times 10^{-3}$ for Core RC1, 1.72×10^{-3} for Core RC2, and 8.47×10^{-4} for Core IL; all three exceed the selected water-wet sandstone reference, indicating larger mobilizing-force requirements in the tested aged carbonate plugs.
- **Sandstone Benchmark and CDC Response:** Cores RC1, RC2, and IL showed 117×, 91×, and 45× higher mobilization thresholds, respectively, than the selected sandstone onset; because only two reservoir plugs and one outcrop analogue were tested, CDC slope differences remain sample-bounded.
- **Field-Rate Scaling and Screening Implication:** At $u = 1$ ft/day, the ultra-low-IFT formulation gives $N_t \approx 2.09 \times 10^{-3}$ (Core RC1) and 1.68×10^{-3} (Core RC2), both slightly below their own onsets, which the rate ladder resolves to between roughly 1 and 2 ft/day; viscosity enhancement can provide additional margin toward deeper desaturation targets (e.g., $N_t \approx 10^{-2}$ at ~ 2 cP), but injectivity, polymer propagation, retention, salinity tolerance, and fracture-pressure constraints bound screening for mature HTHS carbonate reservoirs.

Nomenclature

Symbols

C	Huh constant, mN/m
E_D	Microscopic displacement efficiency, fraction

g	Gravitational acceleration, m/s ²
k_b	Absolute (brine) permeability, mD
k_{rw}	Relative permeability to water, fraction
$k_{w,Sorw}$	Effective permeability to water at residual oil saturation, mD
L	Core plug length, cm
N_b	Bond number, dimensionless
N_c	Capillary number, dimensionless
$N_{c,2}$	Chatzis capillary number definition, dimensionless
N_t	Trapping number, dimensionless
$N_{t,crit}$	Critical trapping number, dimensionless
Q	Volumetric flow rate, cm ³ /min
R^*	Optimal solubilization ratio, cm ³ /cm ³
S^*	Optimal salinity, ppm TDS
S_o	Oil saturation, fraction
S_{orc}	Residual oil saturation after chemical flood, fraction
S_{orw}	Residual oil saturation after waterflood, fraction
S_{wi}	Initial water saturation, fraction
u	Darcy (superficial) velocity, ft/day
v	Interstitial velocity, ft/day
v_{crit}	Critical interstitial velocity, ft/day
V_o	Oil volume in middle phase, cm ³
V_s	Surfactant volume, cm ³
V_w	Water volume in middle phase, cm ³

Greek letters

α	Dip angle, degrees
$\Delta\rho$	Density difference between phases, kg/m ³
ΔP	Differential pressure, psi or Pa
ϕ	Porosity, fraction
μ	Aqueous displacing-phase viscosity, cP
σ_{Huh}	IFT derived from Huh relation, mN/m
σ_{ow}	Oil-water interfacial tension, mN/m
σ_{os}	Oil-surfactant interfacial tension, mN/m
θ	Contact angle, degrees

Abbreviations

ATBS	Acrylamido tertiary butyl sulfonate
CDC	Capillary Desaturation Curve
EOR	Enhanced Oil Recovery

FW	Formation Water
GAC	Guerbet Alkoxy Carboxylate surfactant
HPAM	Hydrolyzed polyacrylamide
HPHT	High Pressure, High Temperature
HTHS	High Temperature, High Salinity
IFT	Interfacial Tension
IL	Indiana Limestone outcrop core plug
IOS	Internal Olefin Sulfonate surfactant
PV	Pore Volume
RC1	Reservoir Carbonate core plug 1
RC2	Reservoir Carbonate core plug 2
SF1	Surfactant Formulation 1
SW	Seawater
TDS	Total Dissolved Solids

CRediT authorship contribution statement

Imad A. Adel: Conceptualization, Methodology, Data curation, Formal analysis, Investigation, Software, Visualization, Writing – original draft, Writing – review & editing. **Alvaro Hernandez Morales:** Conceptualization, Investigation, Writing – review & editing. **Mohamed Efara:** Conceptualization, Investigation. **Emad W. Al-Shalabi:** Investigation, Project administration, Supervision, Writing – review & editing. **Ali AlSumaiti:** Conceptualization, Project administration, Supervision. **Shehadeh Masalmeh:** Conceptualization, Formal analysis, Investigation, Project administration, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability Statement

Data supporting the findings of this study are available from the corresponding author upon reasonable request.

Acknowledgments

This research was funded by Khalifa University of Science and Technology through the ADNOC Grant Call under Project ID: KU-EXT-ADNOC-2022-8434000317. This research was supported by the Research and Innovation Center on CO₂ and Hydrogen, Khalifa University of Science and Technology (KU-RICH).

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