

Effects of Pore-throat Structure on Reservoir Blockage and Wettability Alteration during CO₂ Injection

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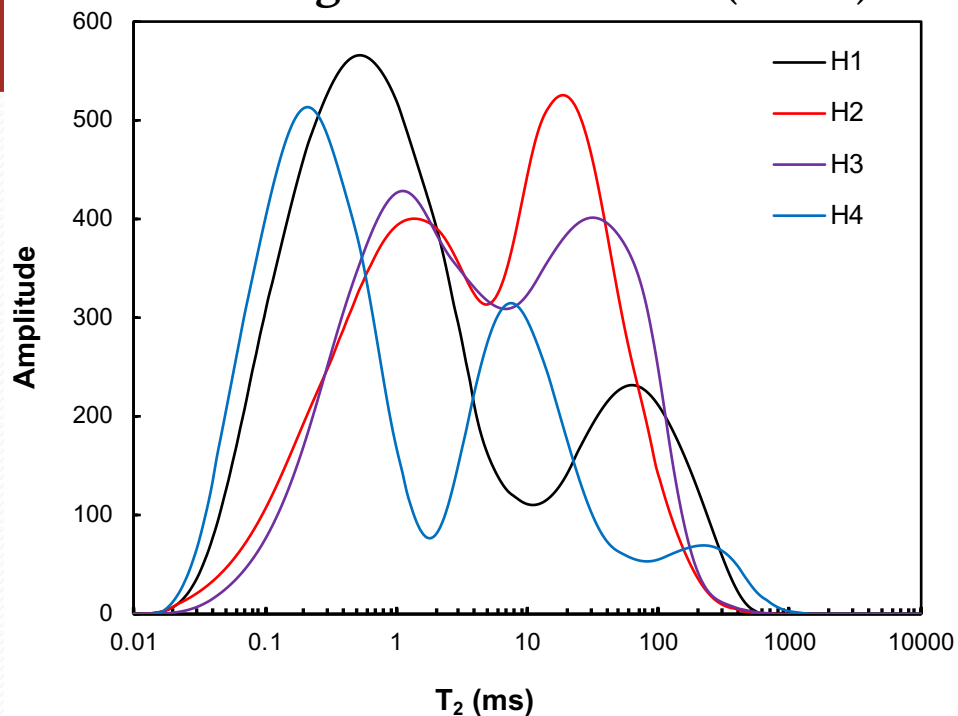
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Pore and throat blockage as well as wettability alteration caused by **asphaltene deposition** are serious problems during injection of CO₂ into subsurface reservoirs for Enhanced Oil Recovery (EOR).

During miscible and immiscible CO₂ flooding, the efficacy and distribution of fluid flow in sandstone reservoirs is controlled by the **pore-throat microstructure** of the rock. Furthermore, CO₂ injection promotes asphaltene precipitation on pore surfaces and in the pore throats, **decreasing the permeability and altering reservoir wettability**.

Miscible and immiscible CO₂ flooding experiments under reservoir conditions (up to 70°C, 18 MPa) have been carried out on four samples with very similar permeabilities but significantly different pore size distributions and pore-throat structures in order to study the effects of pore-throat microstructure on formation damage.

Nuclear Magnetic Resonance (NMR) tests



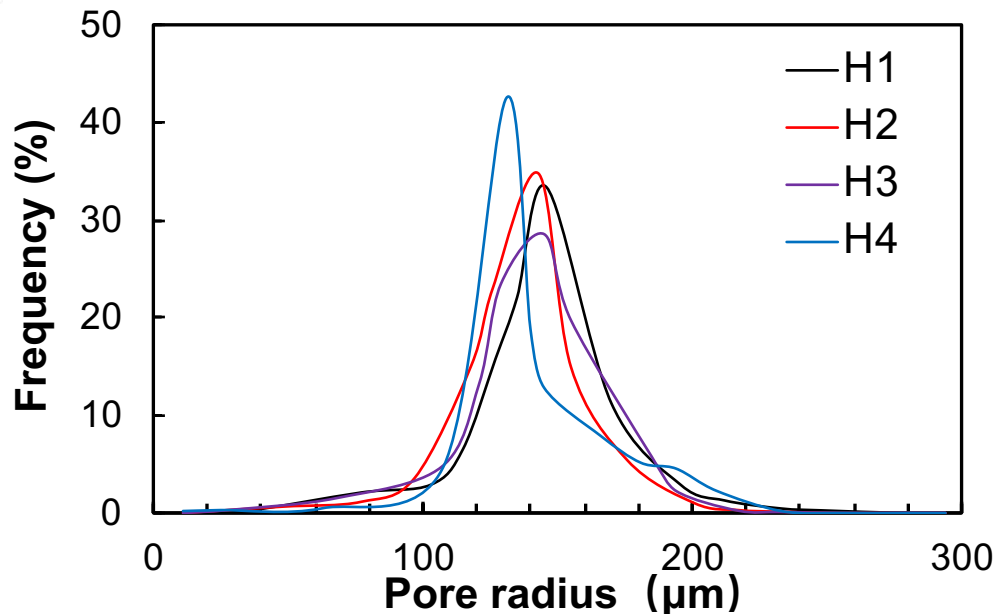
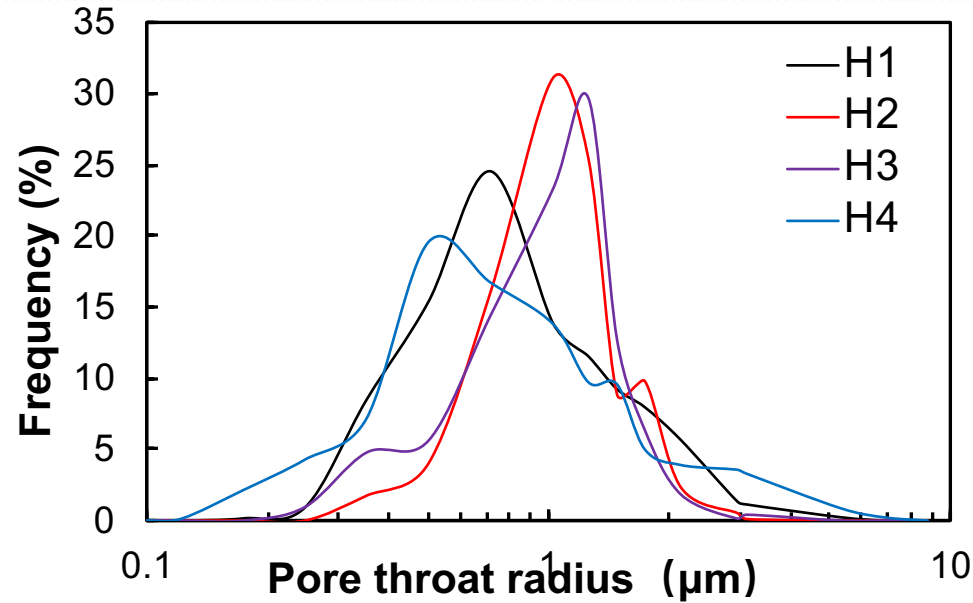
The different or similar amplitudes of the left and right peaks illustrate that the core samples can have rather different or similar fractions of small and large pore-throats. For example, a higher left peak and a lower higher right peak indicates a fraction of greater pore-throats and smaller fraction of larger pore-throats, respectively. Tri-modal distributions imply there may be microcracks present in the core sample .

The shape of T_2 distribution of 19 samples with similar permeability values exhibits 4 typical T_2 distributions of Changqing reservoir rocks by NMR tests. A subset of 4 cores were selected from the 19 cores to represent the 4 typical T_2 distributions.

Core	Length (cm)	Diameter (cm)	Permeability (mD)	Porosity (%)
H1	5.11	2.54	0.713	14.62
H2	5.07	2.54	0.742	14.14
H3	5.09	2.53	0.769	13.62
H4	5.02	2.54	0.734	11.85

Core Pore-throat Microstructure I

The results of constant-rate mercury intrusion (CRMI) tests before experiments

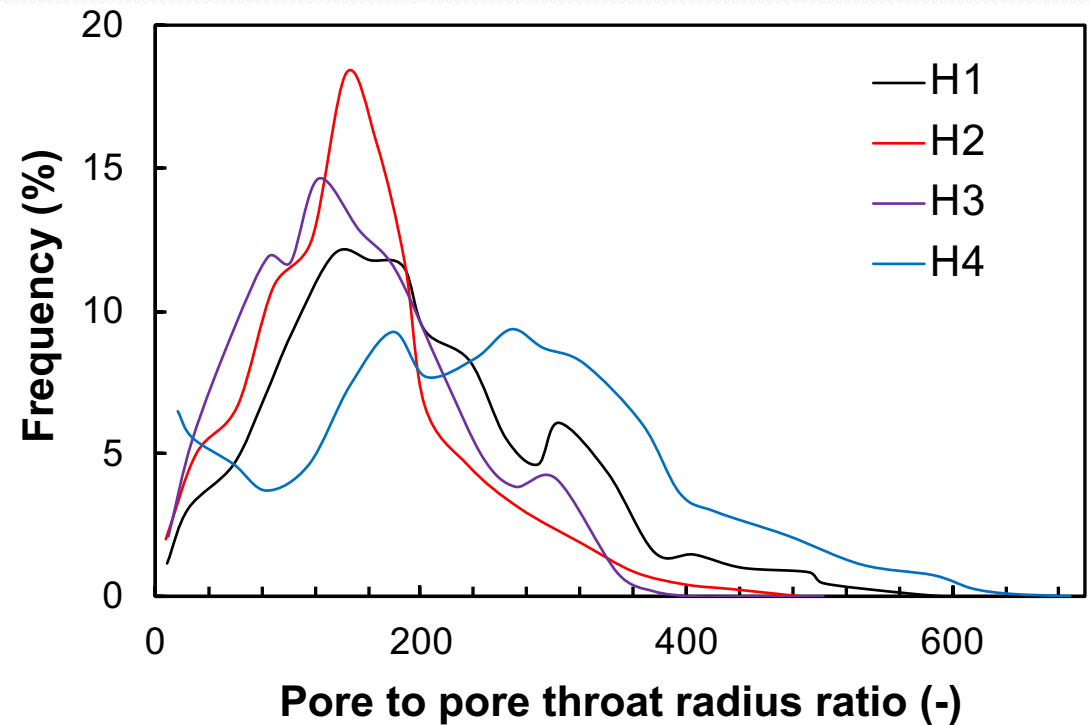


There is no significant difference in the pore distribution of the four cores, but this does not imply that the four cores have the same pore volume. The pore throat distributions of H2 and H3 each have a well-defined peak. H1 and H4 exhibit a single, but much wider peak. This implies that H1 and H4 have a higher proportion of large pore throats, which, if well-connected would provide a high permeability.

Since all four core types have been chosen to have practically the same permeability, it is possible to infer that the pores of H1 and H4 are less well-connected for fluid flow even though their individual pore throats are large.

Core Pore-throat Microstructure II

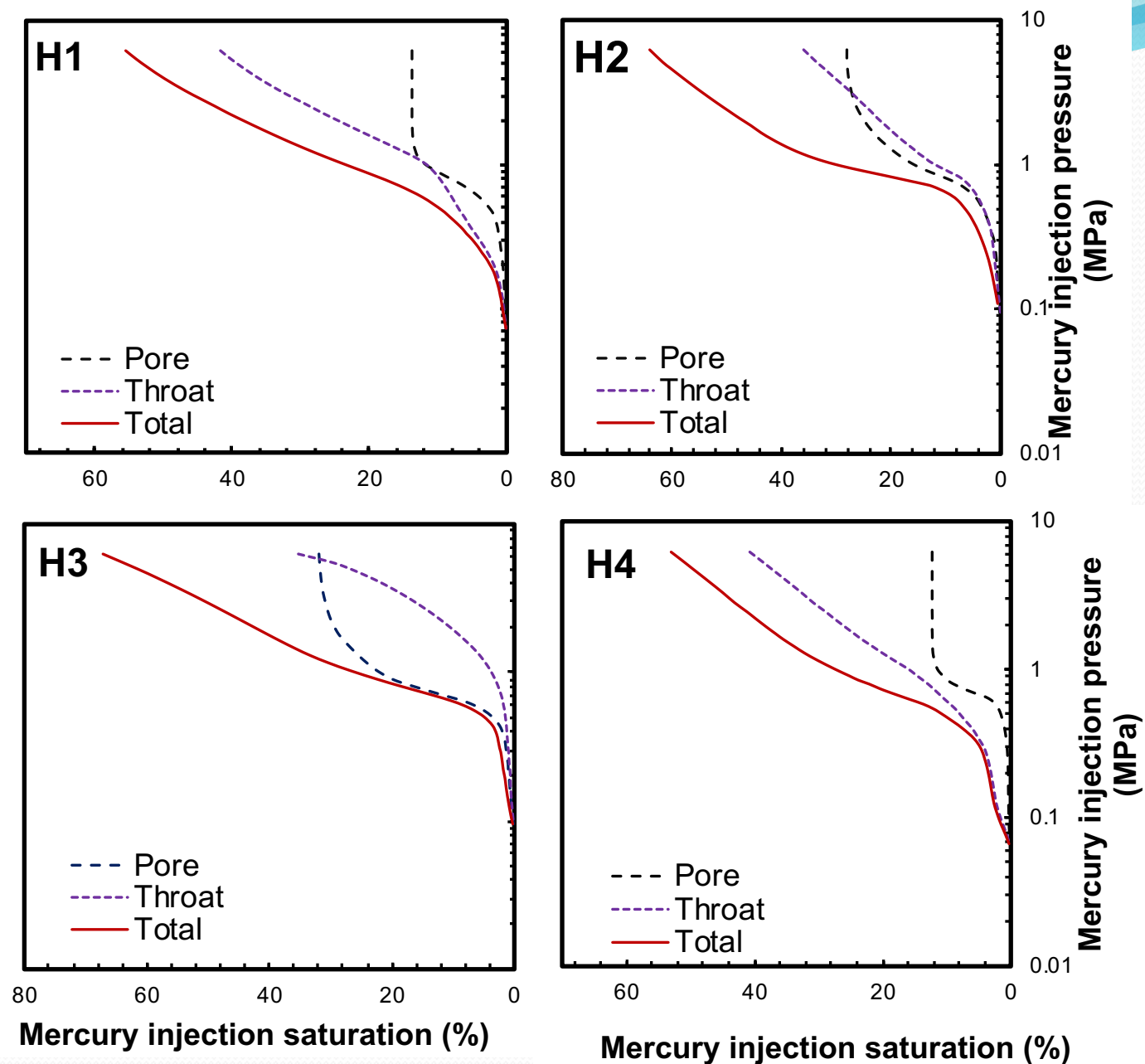
Conversely H2 and H3 have small pore throats in general. Since their permeability is the same as that of H1 and H4, it may be inferred that, though connected by small pore throats the overall connectivity of the pore microstructure is good and pervasive.



In addition, the distributions of pore-throat ratio also imply that H1 and H4 have strong heterogeneity in pore-throat microstructure, and H3 has the best pore-throat microstructure.

Core Pore-throat Microstructure III

For samples H1 and H4, the total intrusion is consistent with pore throat intrusion controlling the increase of pressure. With the increase of pressure, the throat intrusion increases continuously, while the incremental pore body intrusion only occurs over a narrow pressure range, indicating that pore bodies are mainly connected by a small number of relatively large throats. The very narrow pressure range over which intrusion takes place in H4 is an indicator that this sample may contain micro cracks. Samples H2 and H3 belong to the other type, where the total intrusion is controlled by intrusion of the pores, and where the saturation of mercury in both pores and pore throats increases relatively steadily with increases in pressure.

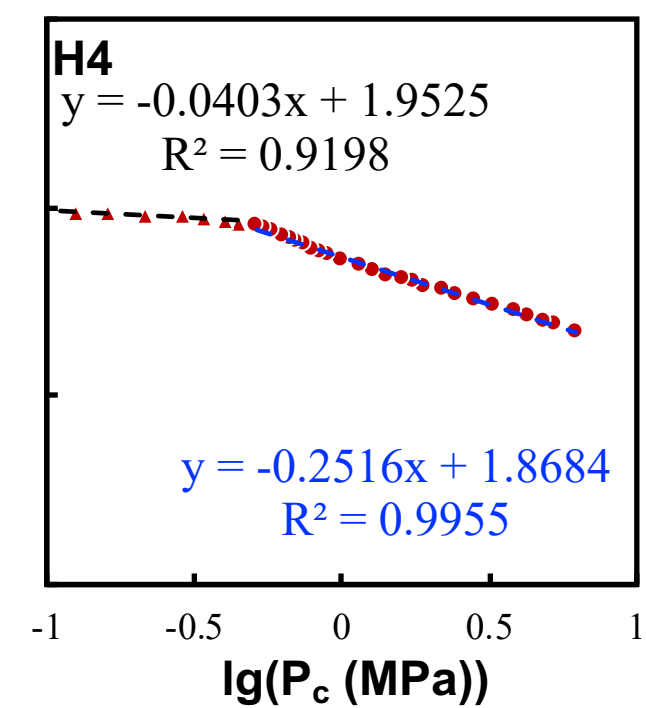
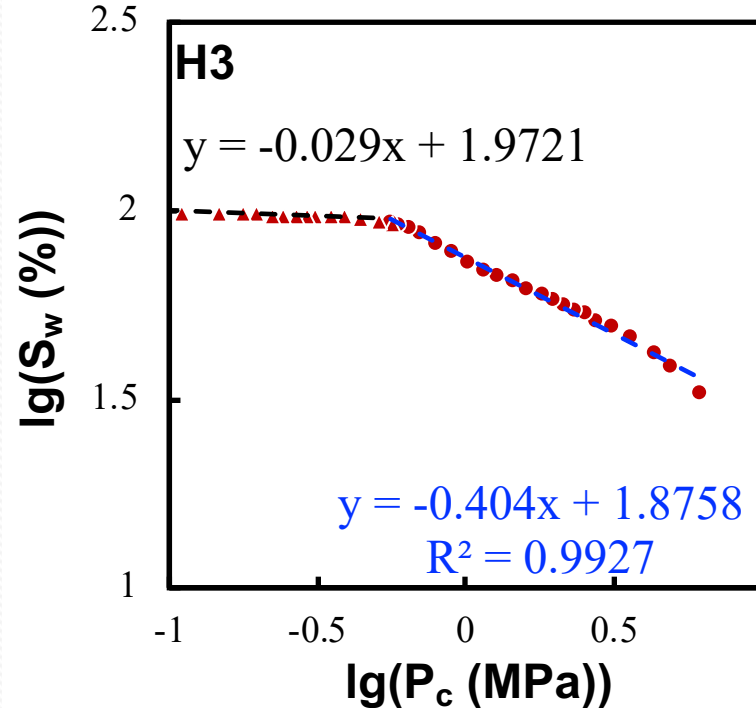
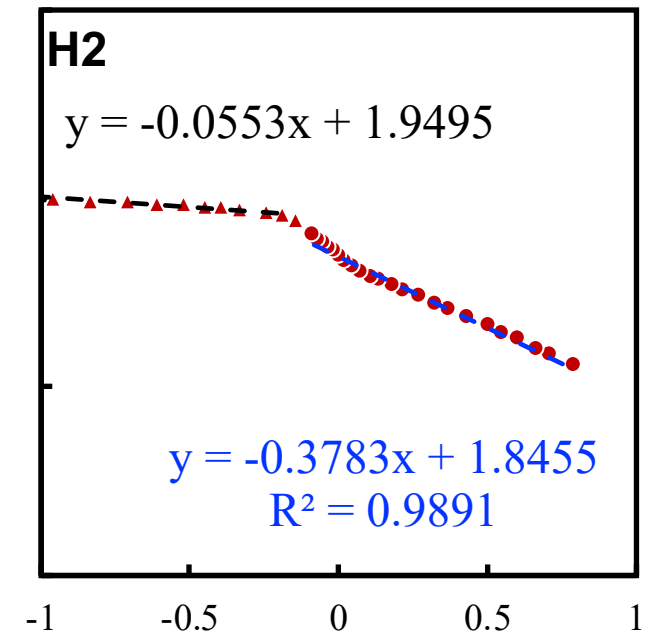
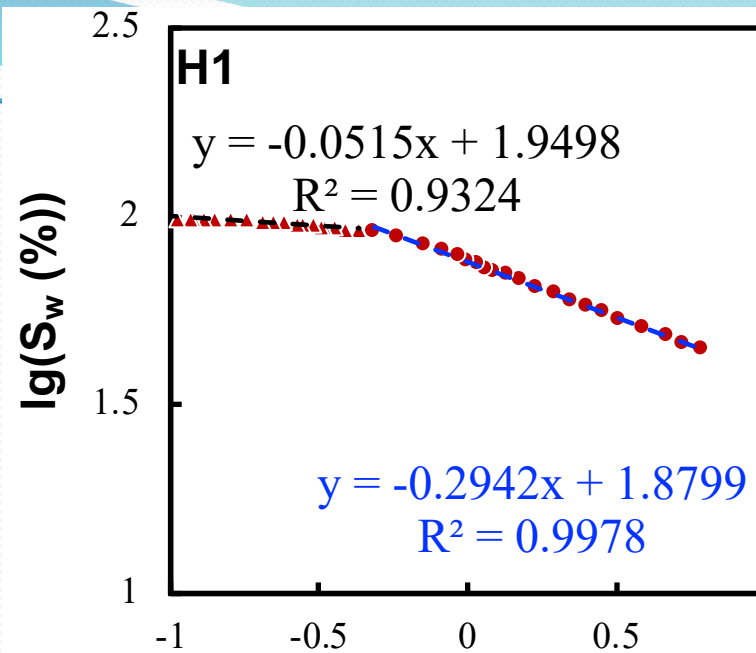


Core Pore-throat Microstructure IV

$$\log S = (D - 3) \log P_c + (3 - D) \log P_{min}$$

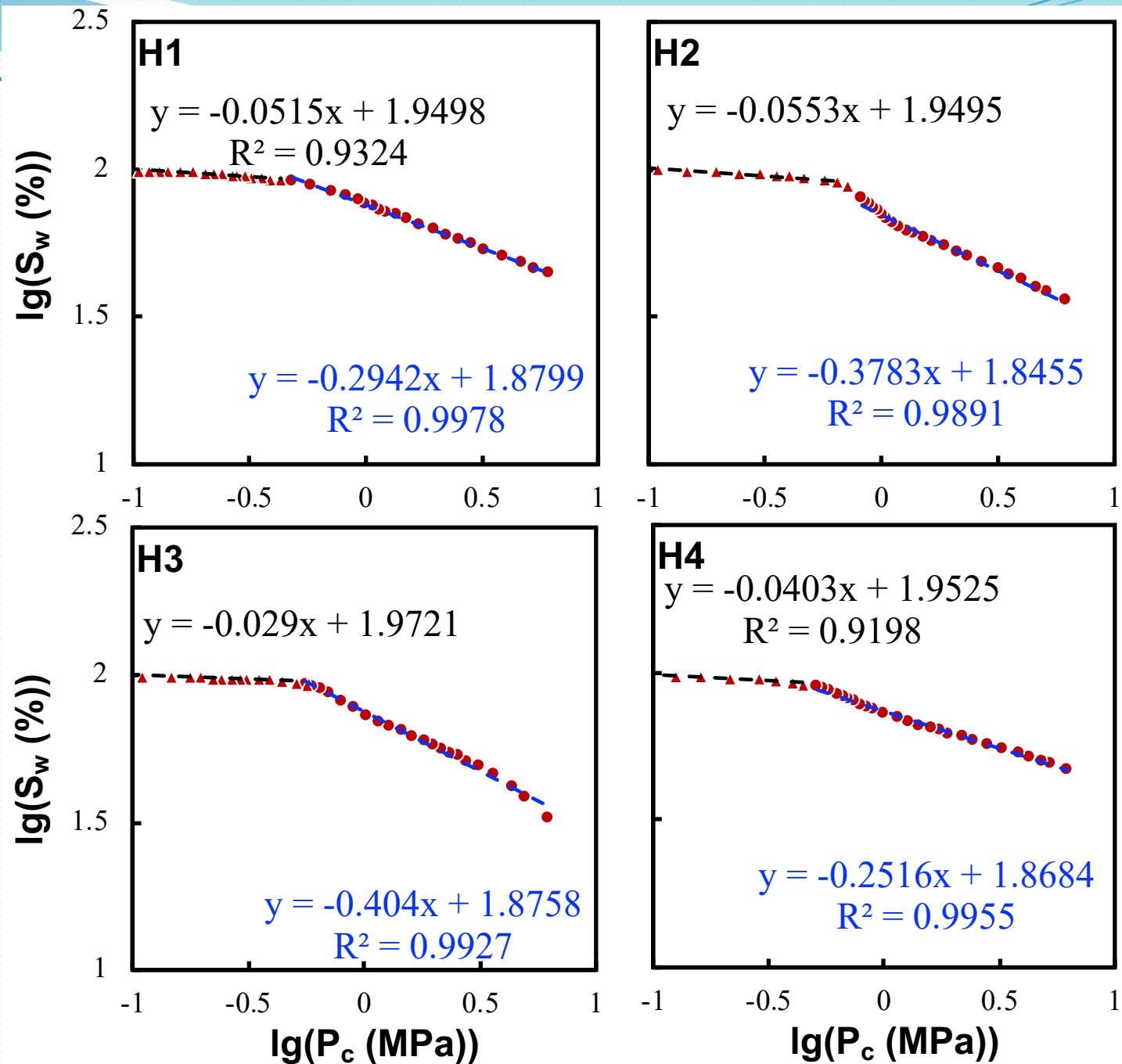
where S (fractional) is the saturation of the wetting phase corresponding to the capillary pressure, P_c (MPa), D is the fractal dimension (unitless), P_{min} is the capillary pressure corresponding to the largest pore-throat (MPa).

The curves of $\log(S_w)$ versus $\log(P_c)$ breaks into two segments, small pores or throats (corresponding to high capillary pressure) tend to have slopes range from -0.25 to -0.41, while large pores were more likely to have slopes close to 0. The fractal dimensions were calculated using the slope of straight part of each curve (above).

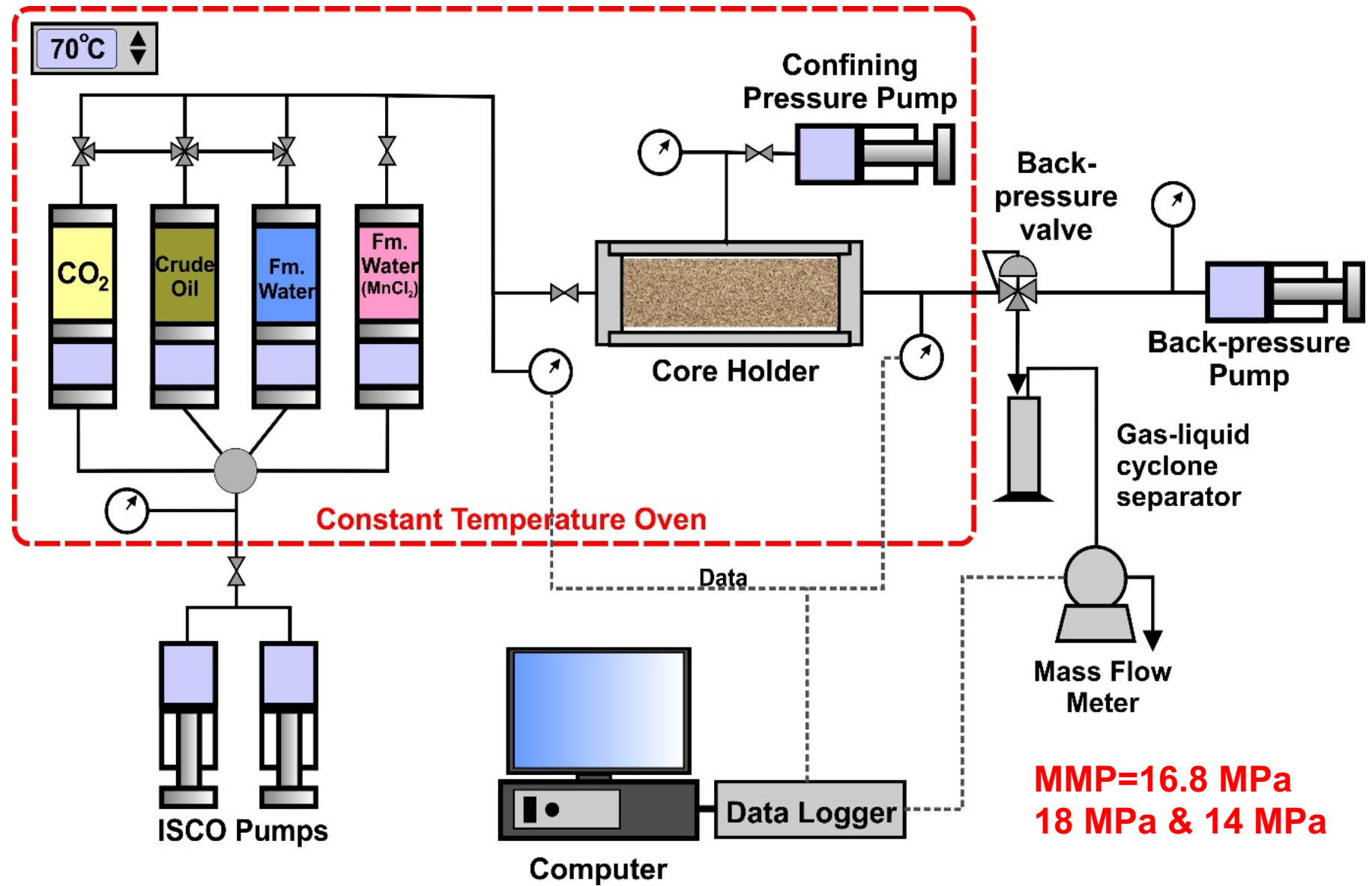


Core Pore-throat Microstructure IV

The fractal dimensions of small pores or throats can be ranked in increasing order: H3 (2.596) < H2 (2.622) < H1 (2.706) < H4 (2.748), however, the fractal dimensions of large pores are less than 3 but very close to 3, this may mean that large pores cannot be effectively evaluated by this fractal analysis method, while fractal dimension is mainly associated with small pores or throats.



Apparatus

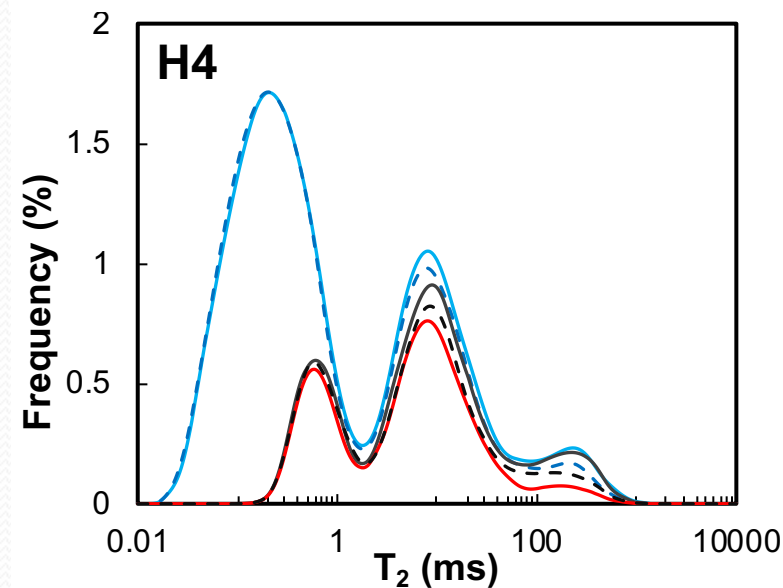
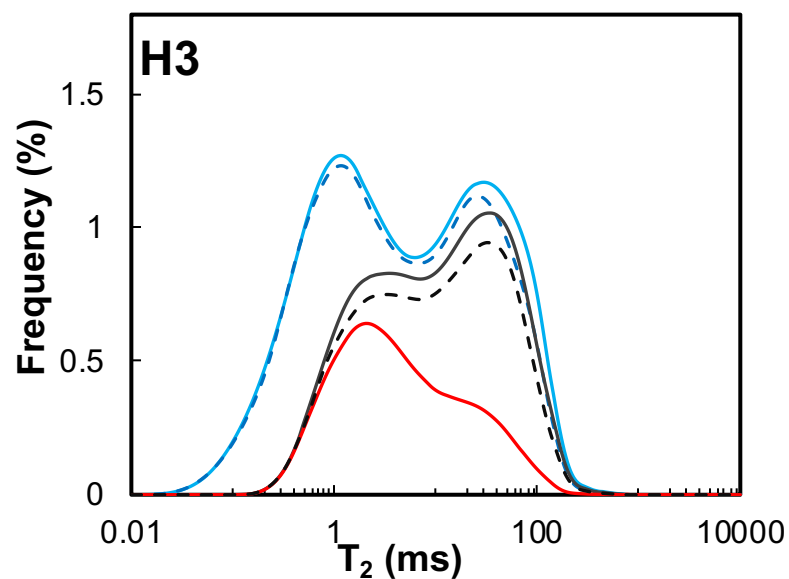
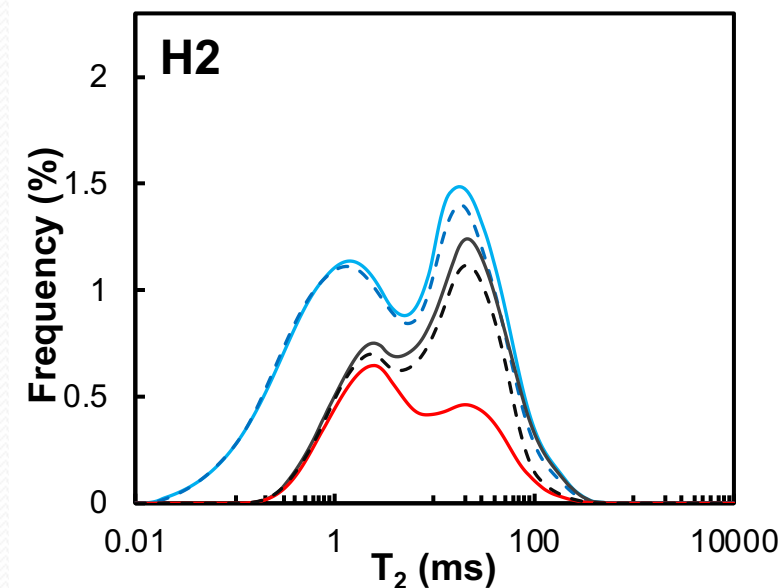
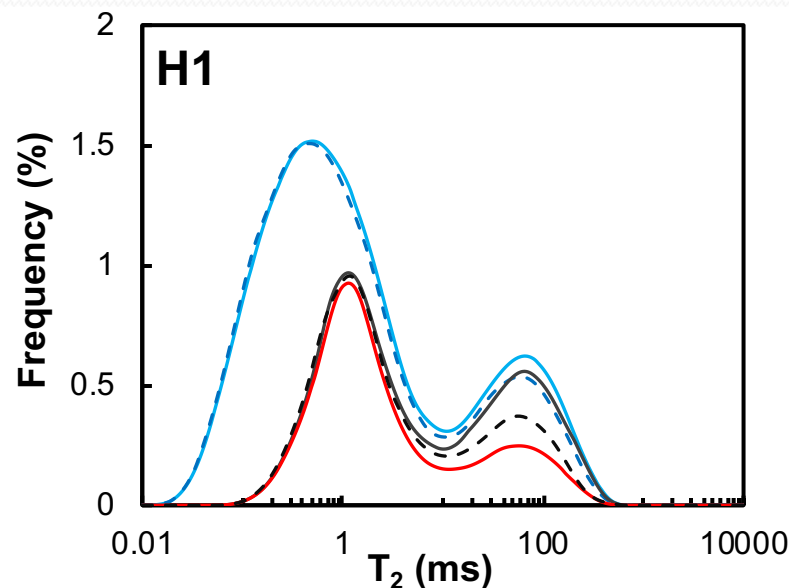


The brine containing Mn²⁺ is used to shield the water signal during NMR tests to obtain the oil distribution in the core

Oil Recovery Factors/Residual Oil Distributions

NMR T_2 spectra of fluid distribution in cores before immiscible flooding, residual oil and fluid re-saturation after **immiscible** flooding.

- initial brine before flooding
- - - re-saturated brine after flooding
- initial oil before flooding
- residual oil after flooding
- - - re-saturated oil after flooding



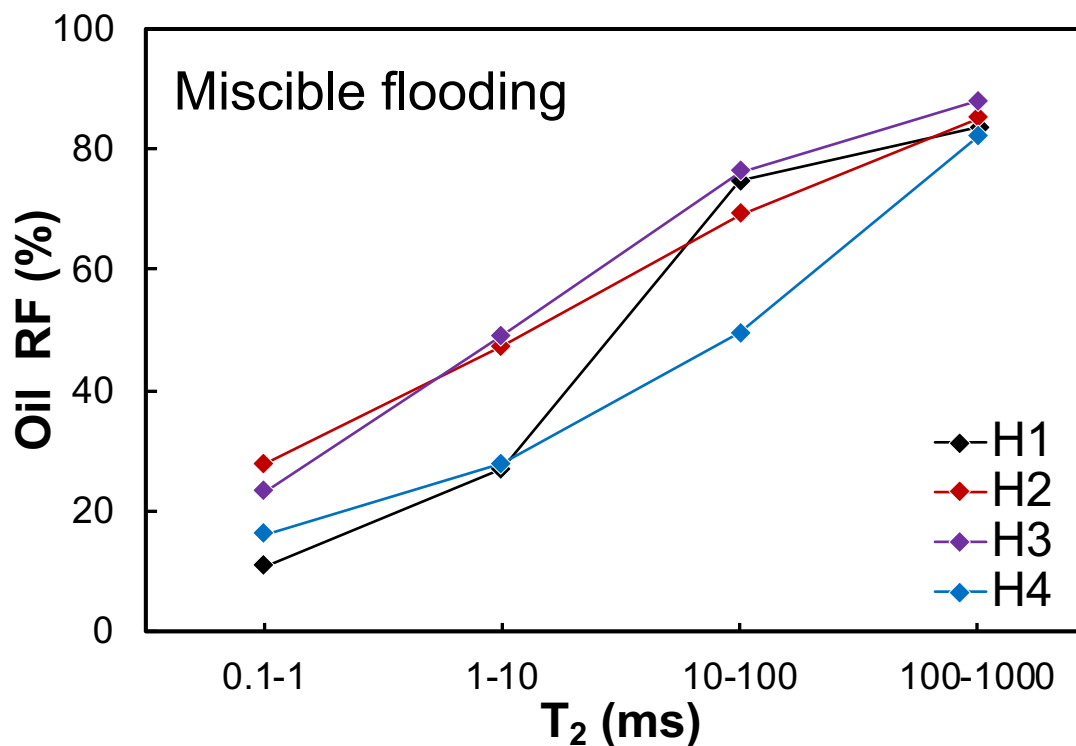
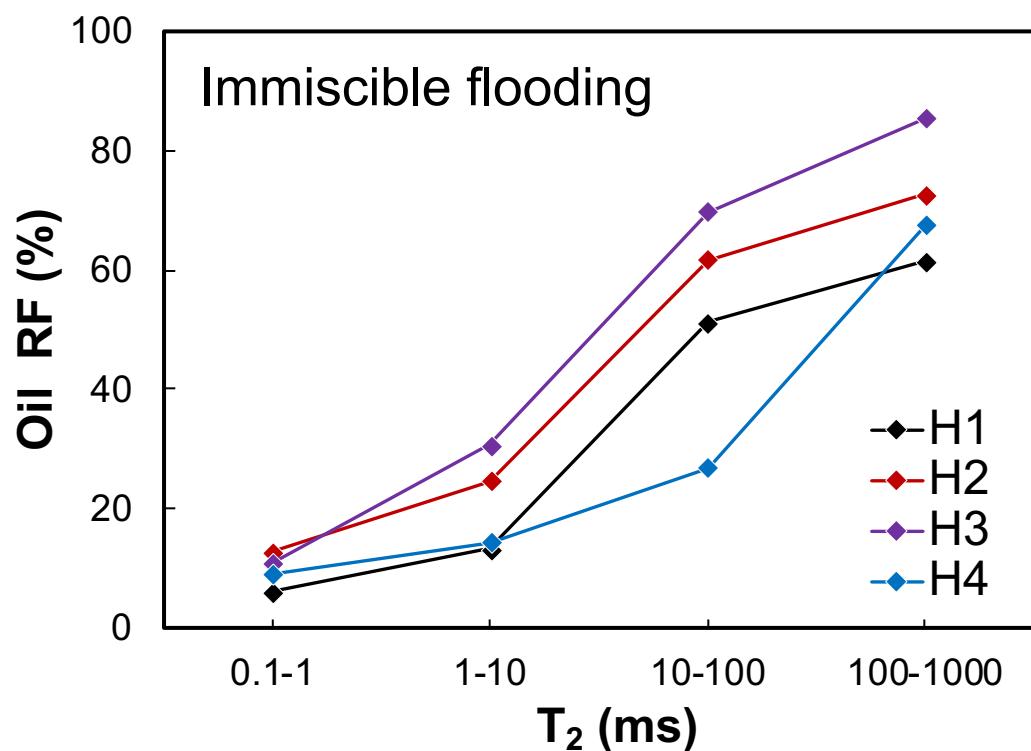
Oil Recovery Factors/Residual Oil Distributions

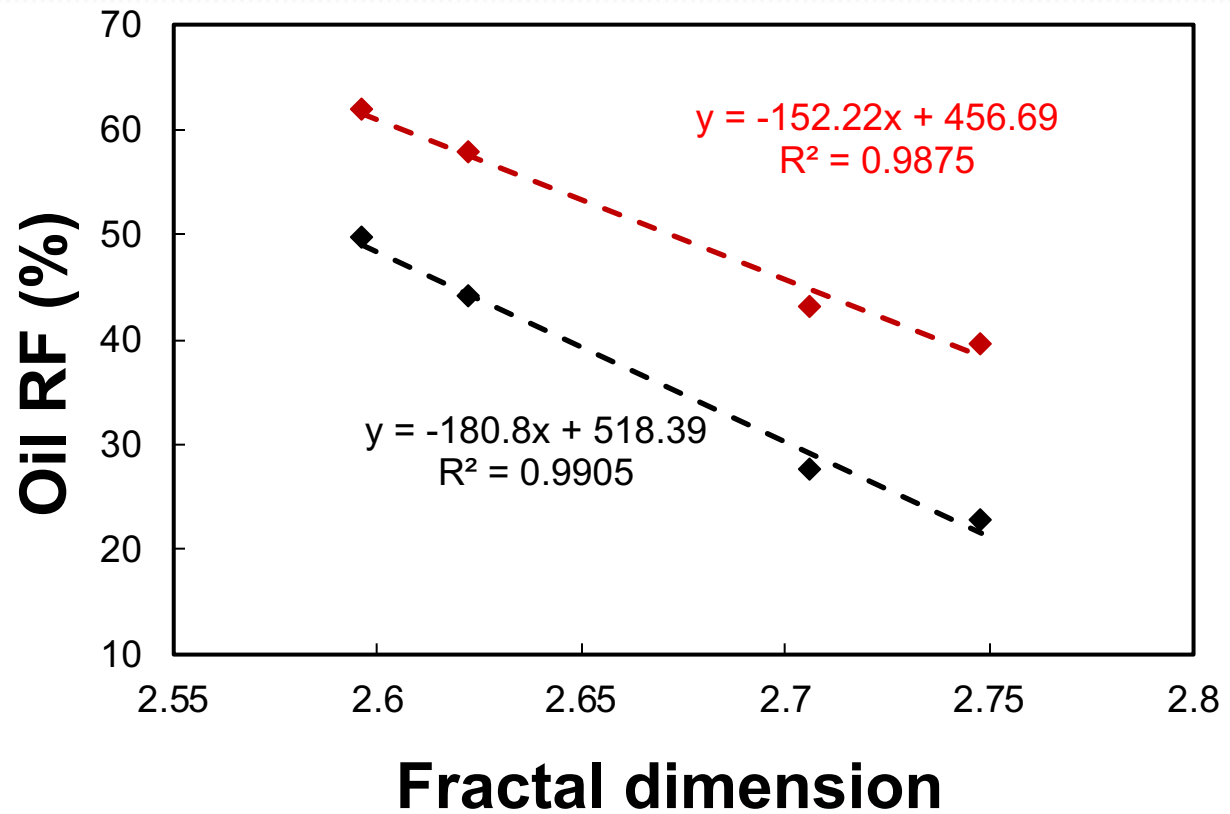
NMR T_2 spectra of fluid distribution in cores before immiscible flooding, residual oil and fluid re-saturation after **immiscible** flooding.

Core number	Fractal dimensions	$S_{oi}(\%)$	$S_{wc}(\%)$	Oil RF (%)	Residual Oil (%)	Asphaltene in produced oil (wt%)
H1	2.706	51.4	72.5	27.5	72.5	0.91
H2	2.622	62.9	55.9	44.1	55.9	1.01
H3	2.596	65.5	50.3	49.7	50.3	1.10
H4	2.748	42.3	77.2	22.8	77.2	0.83

Oil Recoveries in Pores of Different Sizes

The overall oil recovery of the core after miscible flooding is 12-17% higher than that after immiscible flooding. In addition, during the immiscible flooding, the contribution of large pores to the overall oil recovery is relatively higher, and this difference is reduced during miscible flooding, and the residual oil in the small pores is significantly lower than that after immiscible flooding.

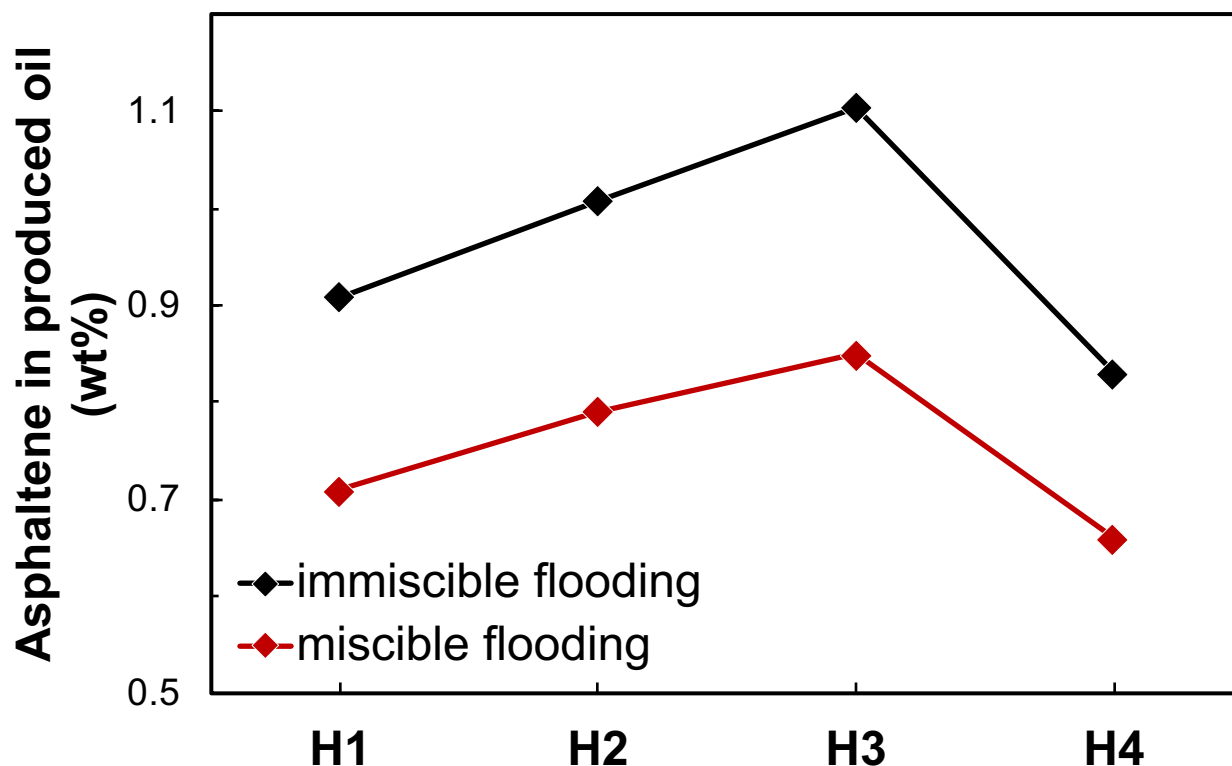




- ◆ immiscible flooding
- ◆ miscible flooding
- - 线性 (immiscible flooding)

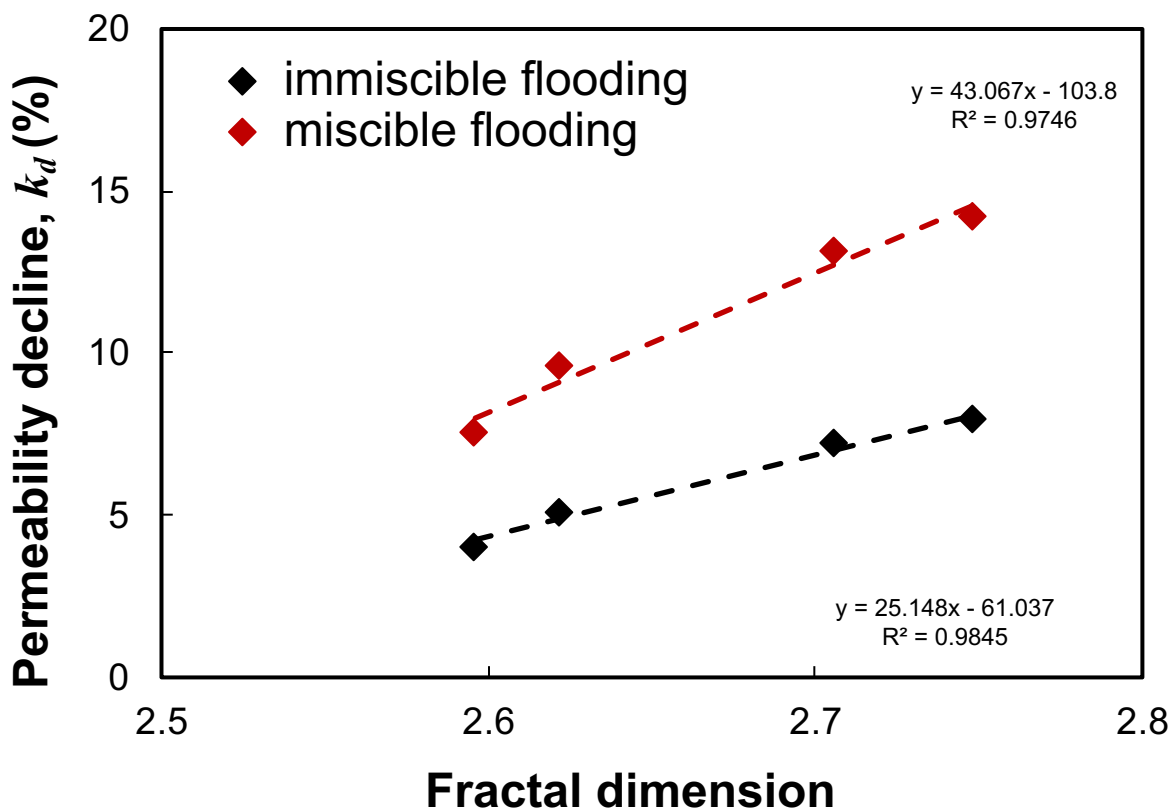
Under the same displacement conditions, the overall oil recovery and the fractal dimension of the core pore-throat structure show a good linear relationship. The core with a homogeneous pore-throat structure has a higher overall oil recovery rate. Under the miscible conditions, the pore-throat structure has a more obvious effect on the overall oil recovery. Under the miscible conditions, pores with different sizes in cores with the homogeneous pore-throat structure have good oil production performance.

Asphaltenes in Produced Oil

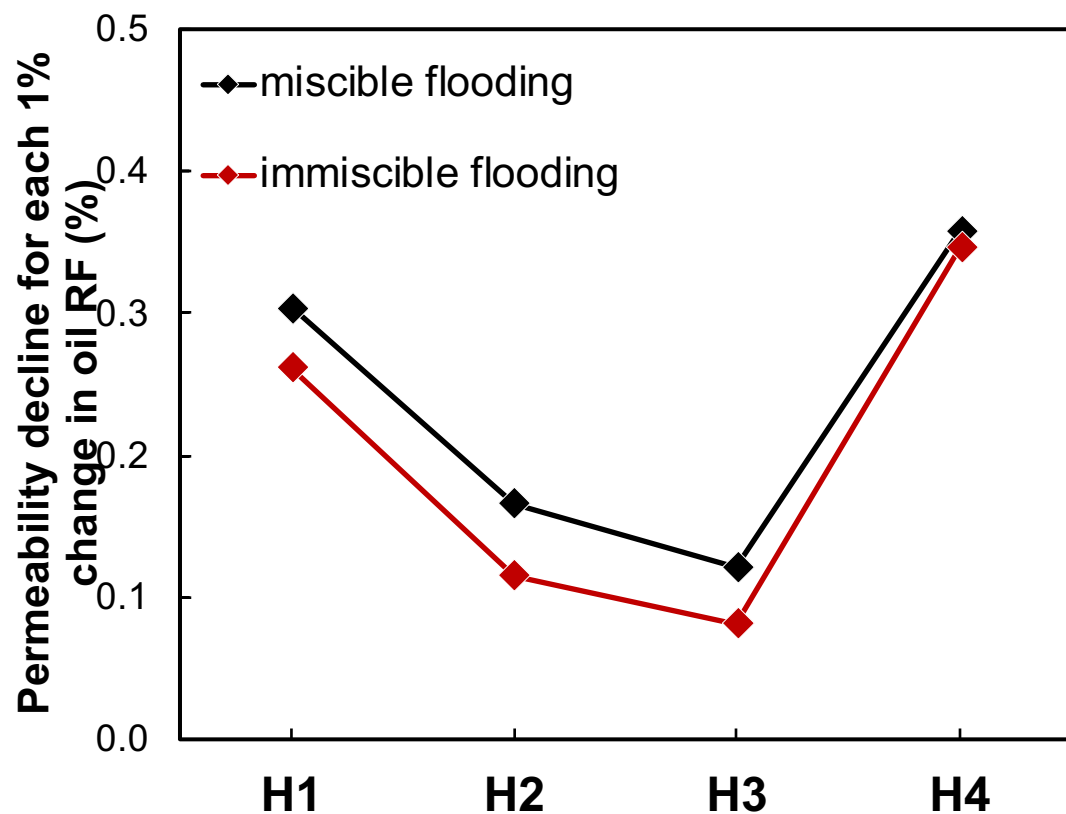


The initial value was 1.32 wt%.

For the same core, the content of asphaltenes in the produced oil after miscible displacement is lower than that after immiscible flooding. This is due to the fact that more CO_2 is dissolved in the pore crude oil during the miscible flooding and the stronger light hydrocarbon extraction of CO_2 to the crude oil. This causes more asphaltenes to precipitate from the crude oil and stay in the core pores. In addition, asphaltene precipitation during flooding is affected by pore size distribution and pore structure heterogeneity.



The permeability decline is consistent with the trend of fractal dimension of core pore-throat structure, and there is a good linear relationship between them. This indicates that differences in pore-throat structure of the four cores is the main factor influencing permeability decline, with less permeability damage being associated with larger and more homogeneous pore throat structures. The H1 and H4 pore throat structures have relatively strong heterogeneity. In the core with such pore-throat structure, the dominant seepage channel composed of several large pore throats contributes the most to the permeability. During the flooding, the path is blocked preferentially, the permeability of the reservoir rock is seriously damaged, and the permeability change of the core is more sensitive to the blockage by asphaltene precipitation.



The comprehensive effect of core pore-throat structure and miscible conditions on crude oil recovery and permeability damage is evaluated according to corresponding permeability decline by per 1% oil recovery.

At the miscible conditions, after the CO₂ breakthrough (BT), the crude oil will still be produced by the extraction of CO₂ on the light hydrocarbons, but this causes more serious asphaltene precipitation, resulting in a larger value.

At the same flooding conditions, H2 and H3 have smaller values, indicating that the pore-throat structure of H2 and H3 not only has advantages in crude oil recovery, but also has an advantage in resisting the decrease in permeability caused by asphaltene precipitation.

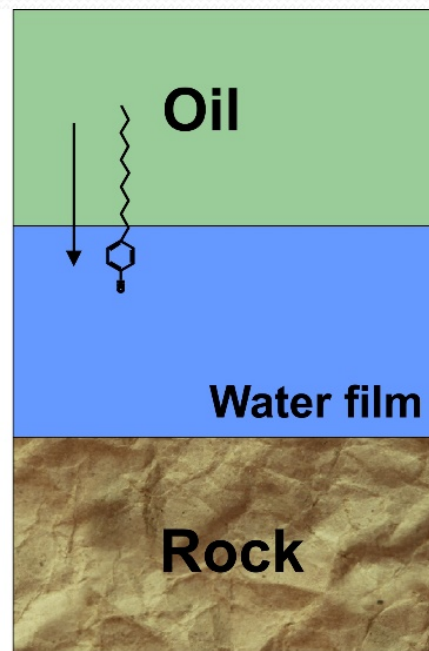
Cores	Amott-Harvey index (immiscible)			Amott-Harvey index (miscible)		
	before flooding	after flooding	decline (%)	before flooding	after flooding	decline (%)
H1	0.889	0.774	12.9	0.907	0.664	26.8
H2	0.693	0.587	15.3	0.679	0.273	59.8
H3	0.774	0.606	21.6	0.804	0.443	44.9
H4	0.812	0.727	10.5	0.805	0.534	33.7

The water-wetness of the rock is weakened after flooding, which is attributed to the adsorption of asphaltene precipitation on the pore surface of the rock. In all cores CO₂ core flooding weakened the overall water wettability of the core rather than making the core completely oil-wet, although for H2 the transformation towards oil wetness was considerable. Once the asphaltene precipitation had been removed from the cores by cleaning, the Amott-Harvey indexes returned to values very close to their initial values, showing that the water-wettability of the cores is restored.

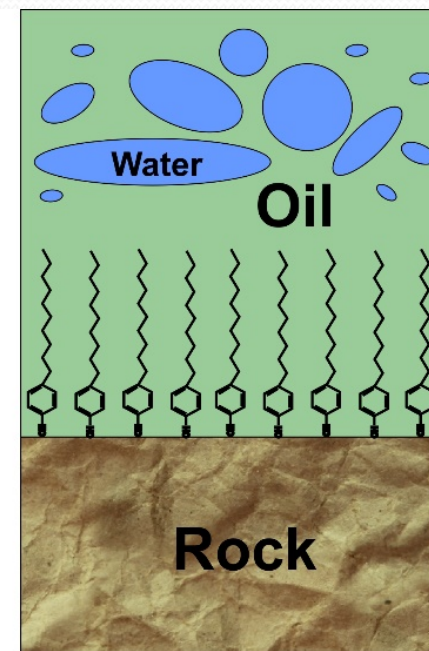
Changes in Wettability



Water-wet



Asphaltene deposits from oil

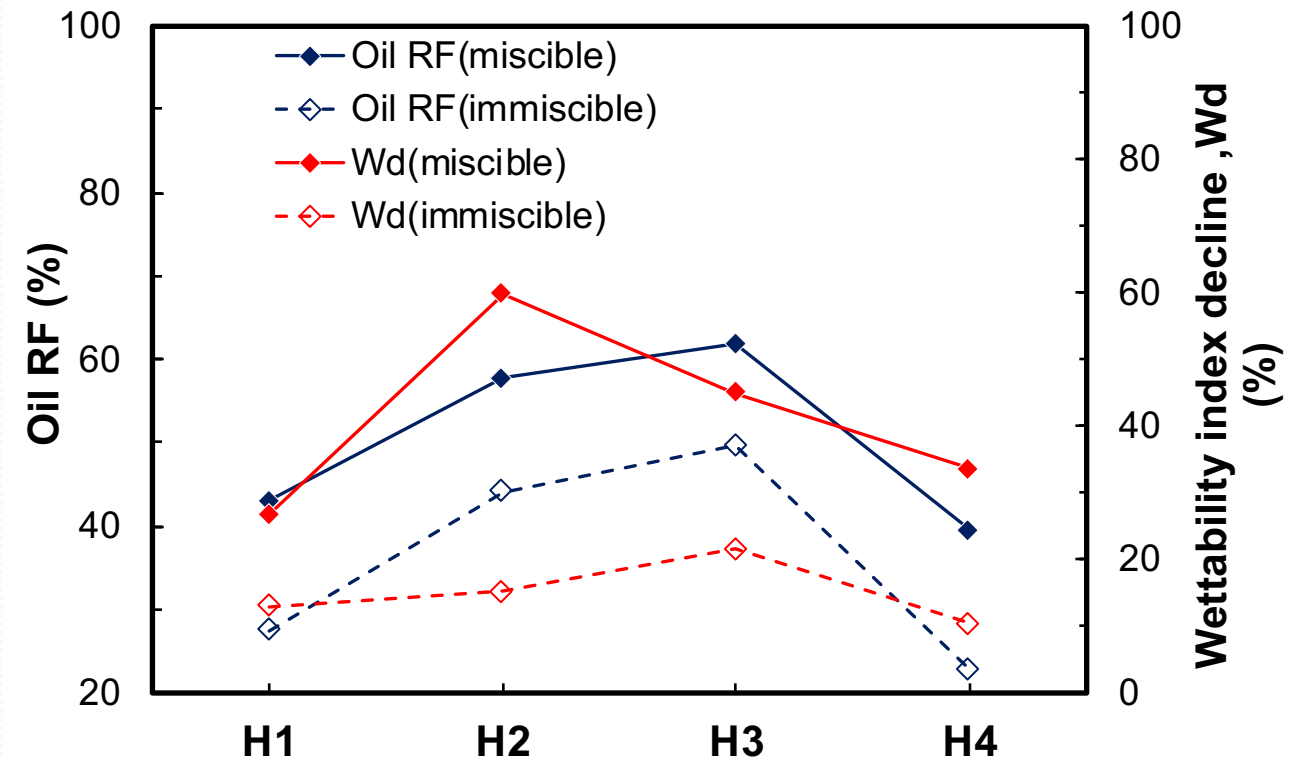


Oil-wet

The cores were initially water-wet, the pore surfaces were covered by a film of water, negatively charged and attached by hydrogen bonding. When CO_2 dissolves into the crude oil, the asphaltene molecules begin to aggregate. Due to the high polarity of asphaltene molecules, water films start to destabilize and eventually rupture. The polar ends of the asphaltene are positively charged and adsorbed on the pore surface, exposing the hydrocarbon end and making the surface more oil-wet.

The wettability of H2 and H3 changes more than that of H1 and H4, which is attributed to the difference in oil RFs caused by the difference in pore-throat structure. The magnitude of the wettability alteration of the four cores has the same trend as oil RFs. As the homogeneous pore-throat structure of H2 and H3 allows CO₂ to enter more and smaller pores and contact more crude oil more asphaltene precipitates adsorb to more pore surface, resulting in greater changes in overall wettability of cores.

The higher pressure causes more CO₂ to be dissolved in the crude oil, and the stronger extraction of light hydrocarbons results in more severe asphaltene precipitation during miscible flooding. The difference between the four core wettability index decreases is relatively small during the immiscible flooding, and the sensitivity of the change of wettability to the rock pore structure is relatively weak.

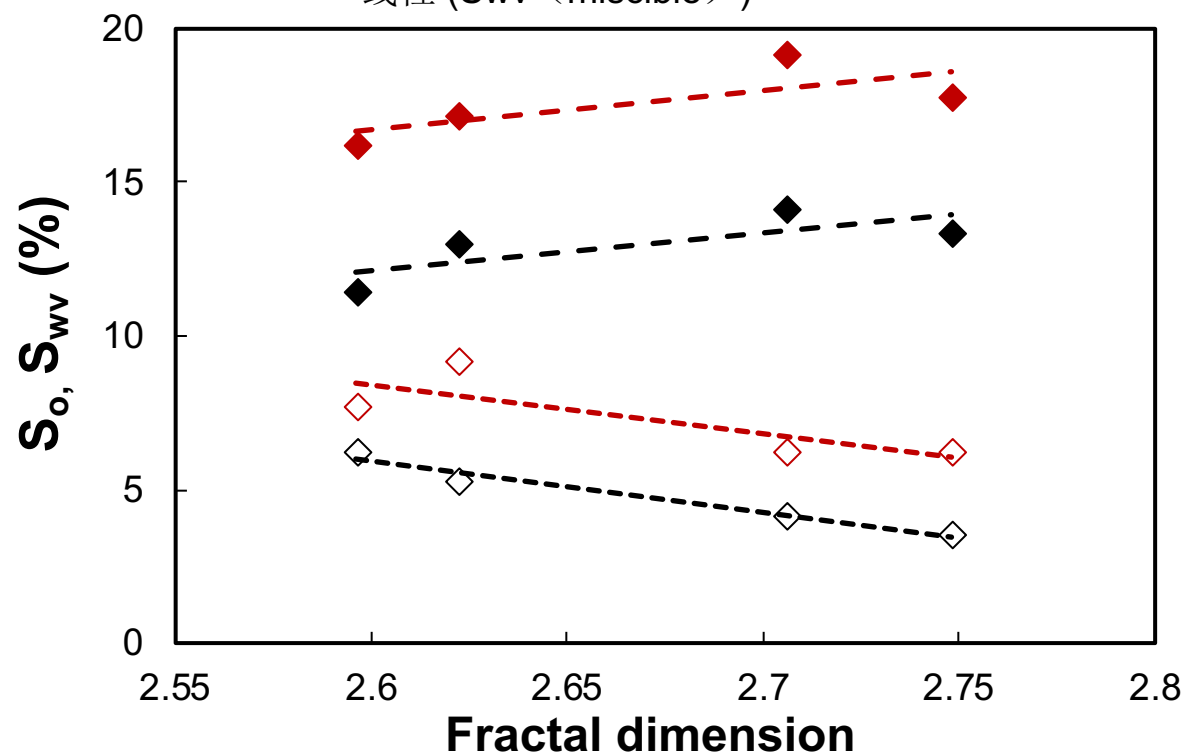


Flooding method	Cores	Fractal dimension	Oil RF (%)	S_{wv} (%)	S_{ov} (%)
Immiscible (14MPa)	H1	2.706	43.1	6.21	19.16
	H2	2.622	57.7	9.19	17.15
	H3	2.596	61.9	7.66	16.24
	H4	2.748	39.6	6.23	17.79
Miscible (18MPa)	H1	2.706	27.5	4.11	14.14
	H2	2.622	44.1	5.29	12.98
	H3	2.596	49.7	6.23	11.40
	H4	2.748	22.8	3.52	13.33

According to the distribution of initial oil and brine before flooding and re-saturated oil and brine after flooding. The variation in oil saturation (defined as S_{ov} , where $S_{ov} = S_{ob} - S_{oa}$, and S_{ob} is the initial oil saturation before flooding, and S_{oa} is the oil re-saturation after flooding) represents the degree of change in the oil saturation of the cores before and after flooding. As well as, the variation in brine saturation (S_{wv} , where $S_{wv} = S_{wb} - S_{wa}$, and S_{wb} is the brine saturation before flooding, and S_{wa} is the brine re-saturation after flooding) represents the degree of change in the brine saturation of the cores before and after flooding.

Oil and brine re-saturation after flooding is affected by two factors; (i) blockage of the pore throats, and (ii) changes to the wettability of cores. S_{wv} and S_{ov} represent the comprehensive changes in rock physical properties after flooding affected by these two factors generally reduced.

- ◆ Sov (immiscible)
- ◆ Sov (miscible)
- ◇ Swv (immiscible)
- ◇ Swv (miscible)
- - 线性 (Sov (immiscible))
- - 线性 (Sov (miscible))
- . - 线性 (Swv (immiscible))
- . - 线性 (Swv (miscible))



S_{ov} and S_{wv} of the four cores show opposite trends, H1 and H4 have large S_{ov} values, but the values of S_{wv} are smaller than those of H2 and H3. The pore space occupied and throats blocked by asphaltene deposition are constant during brine and oil re-saturation after flooding, so that the S_{ov} and S_{wv} of four cores should share similar trends in the case of eliminating the factor of wettability changes, theoretically. This is attributed to the fact that changes in wettability increase S_{wv} but decrease S_{ov} .

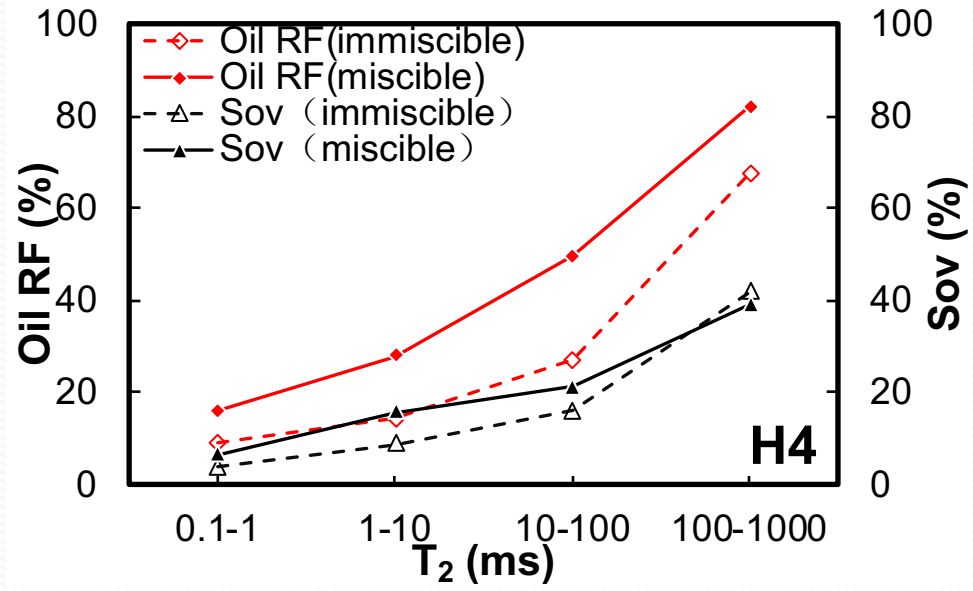
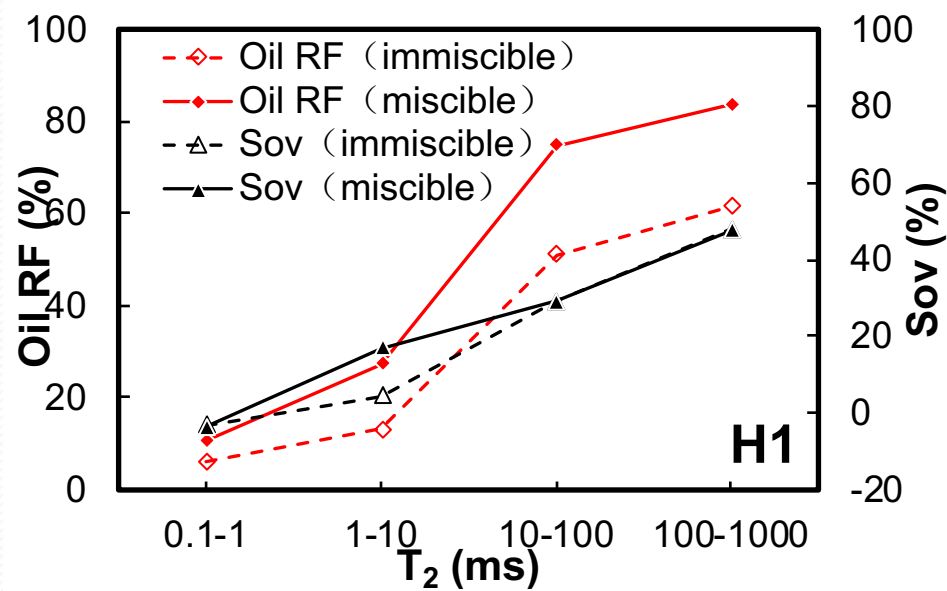
High oil RF is likely to result in more blockage of asphaltene particles at throats and large wettability variation under the same displacement pattern. However, the oil RFs of H2 and H3 are higher than that of H1 and H4, but H2 and H3 have smaller S_{ov} values. The result may be attributed to the difference in pore-throat structure between H2, H3 and H1, H4.

On the one hand, although more oil production means more asphaltene precipitation in H2 and H3 during the flooding process, these asphaltene precipitates did not form severe blockage as in H1 and H4, causing serious damage to the pore-throats structure of rocks, which implies that the type of pore-throat microstructure of H2 and H3, especially H3, is more resistant to damage to rock properties by the migration of asphaltene precipitation.

Moreover, more asphaltene precipitation also implies that H2 and H3 undergo large changes in wettability, which aids oil re-saturation. Consequently, S_{ov} decreases with increasing oil RF and increases with increasing fractal dimension.

Changes in Key Petrophysical Properties IV

Oil recovery and S_{ov} in different sizes of pores



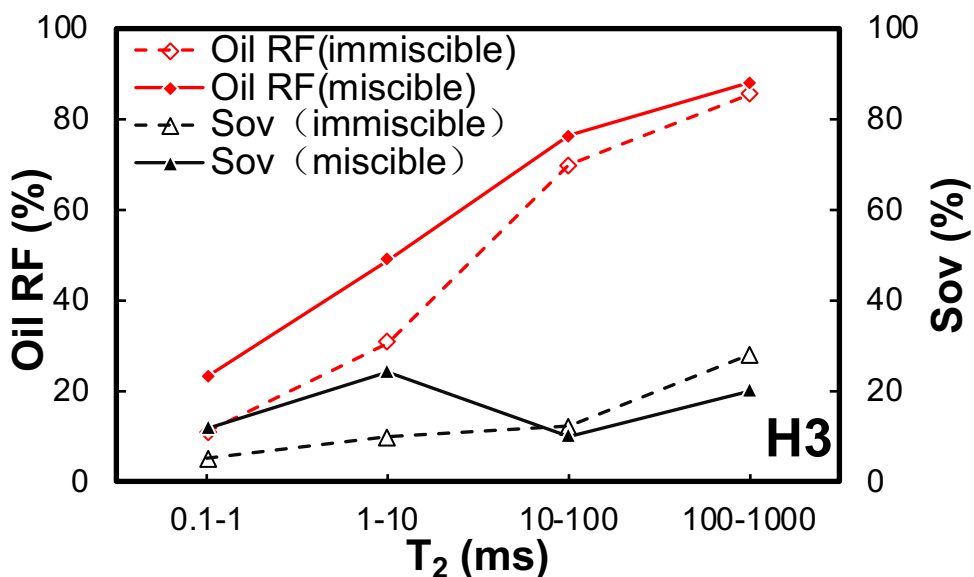
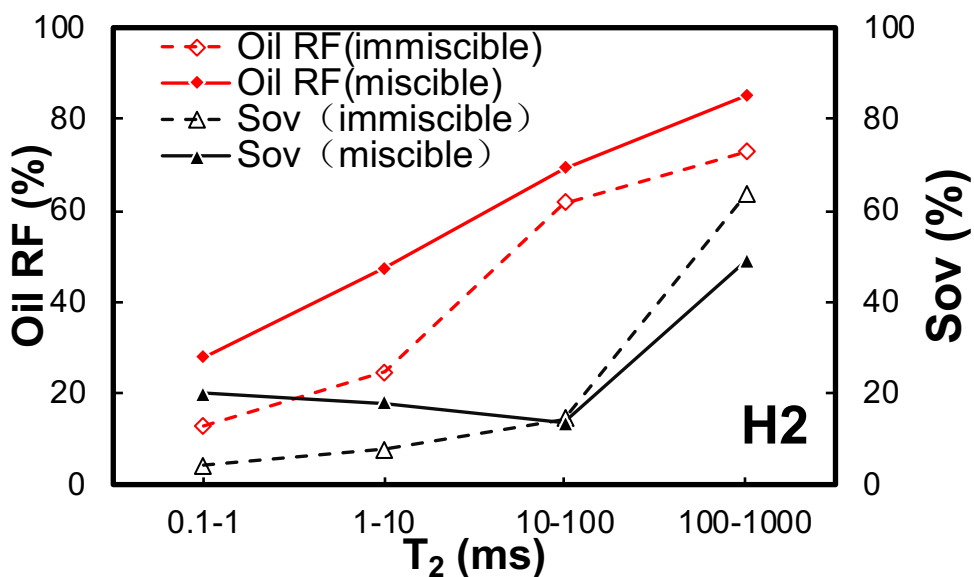
The values of S_{ov} of pores with different sizes in H1 and H4 increase with the oil RFs. The smaller S_{ov} in the small pores of H1 and H4 is caused by little oil production. Small pores and associated pore throats are difficult to sweep of oil during flooding, resulting in less asphaltene precipitation and small S_{ov} values.

The large RF in the large pores indicates that these large pores are the main producers of oil, and by implication they are also the main pathways of fluid flow. Such pathways are also the main locations where asphaltene precipitation, migration and adsorption occur.

The structure of these pores and associated pore throats is more likely to be modified by asphaltene precipitation, resulting in large S_{ov} values.

Changes in Key Petrophysical Properties V

Oil recovery and S_{ov} in different sizes of pores



However, the values of S_{ov} do not increase strictly with the increase of oil RFs in H2 and H3, especially in H3. Although the pore throats are partially blocked and the permeability is reduced, it seems that the oil re-saturation of the larger pores is not greatly affected, and the difference in S_{ov} in pores of different sizes is relatively small. Blockage at pore throats and wettability changes evenly across pores of all sizes, indicating that a homogeneous pore-throat structure is advantageous for the large pores and associated pore throats to resist the changes in the pore-throat structure caused by asphaltene precipitation and migration.

Under miscible conditions, the S_{ov} of small pores is greater than that of immiscible flooding, while the S_{ov} of large pores is close to or less than that of immiscible flooding with higher oil RFs. During miscible flooding, the change of core comprehensive physical properties is more evenly distributed, and the homogeneous pore-throat structure enhances this advantage.

The overall oil RFs of the core After the miscible flooding are 12-17% higher than that of after immiscible flooding.

Under the same flooding conditions, the residual oil of cores have a good apparently linear relationship with the fractal dimension of the core pore-throat structure.

The oil RFs of cores with homogeneous pore-throat structure are 18-27% higher than that of cores with strong heterogeneity. Under the immiscible conditions, the oil RFs are more sensitive to the pore-throat structure.

Due to the blockage of the pores and throats caused by the asphaltene precipitation, the permeability decreased by 7-15% and 4-8% after miscible and immiscible flooding, respectively.

The decrease in permeability have a good apparently linear relationship with the fractal dimension of the pore-throat structure, and the permeability decrease of the core with a homogeneous pore-throat structure is 2-7% smaller.

The Amott-Harvey indexes of cores decrease by 25-60%, with the cores with larger and more homogeneous pore-throat microstructure becoming less water-wet due to greater degrees of asphaltene precipitation adsorbed onto a greater pore surface area, which is ultimately caused by the larger sweep volume of injected CO₂.

Cores with larger and more homogeneous and pore-throat microstructures have a more homogeneous distribution of petrophysical variation in pores of different size, with greater petrophysical variation being controlled mainly by large pores in heterogeneous cores.

Overall, the distribution of core physical properties changes is more uniform, but it is more sensitive to the pore-throat structure under miscible conditions. The cores with homogeneous pore-throat structure have more significant CO₂ flooding effect with less damage of asphaltene precipitation to the core physical properties.

THANK
YOU!