

Functional Nanoparticle-Augmented Surfactant Fluid for Enhanced Oil Recovery in Williston Basin

Quarterly Status Report

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Summary of Current Progress

During the past quarter, our primary goals were to test the oil recovery of novel nanofluid by physical simulation and to analyze flow mechanisms of Middle Bakken formation by numerical simulation. Specifically, we tested the performances of surfactant-coated silica nanofluid at high salinity brine, carried out spontaneous imbibition experiment of Berea and numerical simulation of tight Bakken formation. We also studied the NMR characteristics of tight Bakken core samples.

We mainly focused on the following tasks:

- 1) Performance of surfactant coated silica nanofluid at high salinity brine
 - a.) Interfacial tension change
 - b.) Contact angle change
- 2) Spontaneous imbibition test of Berea
- 3) Evaluation and optimization of the nanoparticle-surfactant hybrid for EOR
- 4) Numerical simulation of spontaneous imbibition in tight Bakken core samples
- 5) NMR study of tight Bakken formation

Below are the detailed results of the tasks.

1. Performance of surfactant coated silica nanofluid at high salinity brine

1.1 Introduction

A surfactant-coated SiO₂ nanofluid (SBSNF) was formulated. SBSNF was prepared by adding different concentration SiO₂ NPs modified with amino into 0.2wt% 964-surfactant solution in 15wt% NaCl brine. All of them were magnetic stirred for 2 hours and then ultrasonicated for 2 hours.

1.2 Summary and discussion

(1) Interfacial tension

Oil-water interfacial tension (IFT) is an important parameter to oil recovery because the lowering of IFT can positively affect oil mobilization. Table 1 shows the oil–water interfacial tension of SBSNF. The oil–water interfacial tension between 0.2wt% 964-surfactant dissolved in 15wt% NaCl brine and Bakken crude oil was 0.78mN/m in the absence of SiO₂ NPs. With the addition of SiO₂ NPs, a decrease trend was observed and the minimum value was 0.02 mN/m at 0.05 wt% NPs. The decreased oil-water interfacial tension indicates that SBSNF would have better potential to displace oil from rocks.

Table 1. Oil-water Interfacial Tension of Different Concentration of SiO₂ NPs in 15wt% NaCl at 65°C

Concentration of modified SiO ₂ NPs (wt%)	0	0.005	0.01	0.015	0.02	0.025	0.03	0.035	0.04	0.045	0.05
Oil-water interfacial tension of SBSNF (mN/m)	0.78	0.61	0.42	0.24	0.13	0.09	0.07	0.05	0.04	0.03	0.02

(2) Contact angle

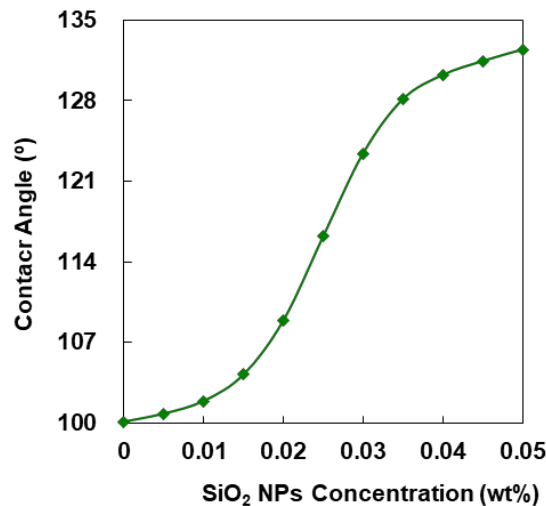


Figure 1. Contact angles of Bakken crude oil drop with oil-wet surface in different concentrations of SiO₂ NPs

SiO₂ NPs also can augment surfactants' ability to alter the formation wettability. Figure 1 shows that the contact angle of 964-surfactant in 15wt% NaCl brine was 100.1° (no SiO₂ NPs in SBSNF). It indicated that 964-surfactant can alter the oil-wet formation to intermediate wet. When the SiO₂ NPs was added into the solution, the contact angle showed an increase with a “S-curve” trend. The largest contact angle was achieved to 130.2° when the concentration of SiO₂ NPs is 0.04%, indicating water-wet. Therefore, in the following experiments, 0.04wt% SiO₂ NPs was used as the optimal concentration. Compared with the contact angle of 964-surfactant, the wettability was altered from intermediate wet to water-wet by adding of SiO₂ NPs.

2. Spontaneous imbibition test of Berea

2.1 Introduction

The spontaneous imbibition experiments for Berea core samples were conducted in 0.2wt% 964-surfactant and SBSNF (0.04wt% SiO₂ NPs dispersed in 0.2wt% 964-surfactant in 15 wt% NaCl) at 65°C.

2.2 Summary and discussion

Figure 2 shows that the oil recovery of two spontaneous imbibition tests. For 0.2wt% 964-surfactant, imbibition mainly occurred in the first 3 days. From the 5th to 10th days, the recovery increased slightly. After 10 days, the recover changed a little or unchanged. For SBSNS, the imbibition mainly occurred in the first 12 days. From 12th to 15th days, the recovery increased slightly. After 20 days, the oil recovery unchanged. The final oil recoveries of 0.2wt% 964-surfactant and SBSNS were 22.89%OOIP and 46.61%OOIP, respectively. Comparing with 0.2wt% 964-surfactant, SBSNS can enhance 20.72%OOIP, which almost doubled the oil recovery efficiency by using the 964-surfactant alone. This indicates the SBSNS is a promising and efficient chemical agent for EOR.

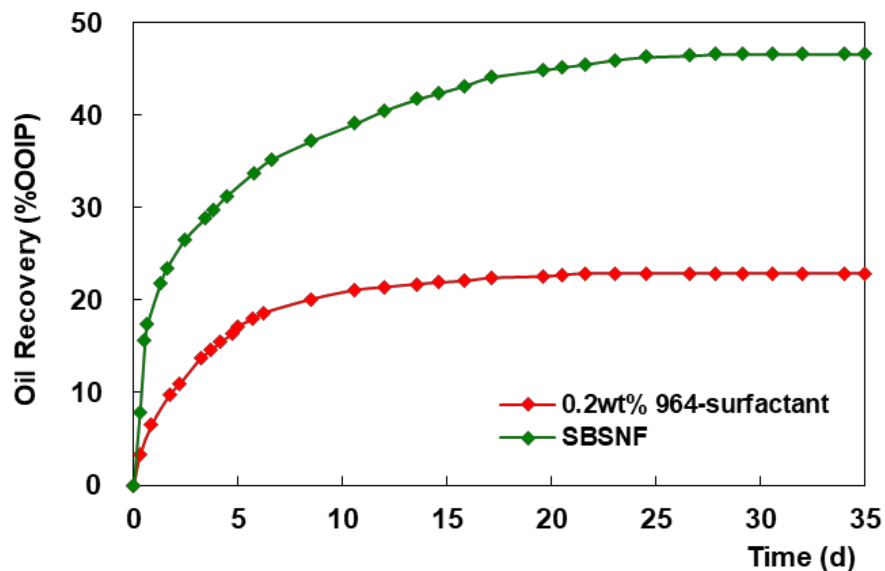


Figure 2. Oil recoveries of spontaneous imbibition experiments

3. Evaluation and optimization of the nanoparticle-surfactant hybrid for EOR

3.1 Introduction

Considering the fact that surfactants have relatively high adsorption on Bakken minerals, thus, the residual effective surfactant concentrations are pretty low, which results in reduction of the surfactants' amount. Nanoparticles are well known to be an effective additive. Therefore, the compatibility between various commercial nanoparticles and various types of surfactants in DI water were evaluated through zeta potential test.

3.2 Summary and discussions

The adsorption data were further analyzed by Minitab 2016 to compare the impacts of different factors (temperature, concentration, mineral type and surfactant structure). The interactions between various parameters were also investigated. According to the results, concentration, mineral type and concentration-mineral interaction are the three most dominant factors.

Table 2 shows zeta potential of different nanoparticles in different surfactants solution. The concentrations of surfactant and nanoparticle were maintained to be 1000 mg/L and 500 mg/L, respectively.

Table 2. Zeta potential of nanoparticles

Nanoparticles	Surfactants				
	DI	HCS	27000A	964	Betaine
ST-O	-37.30±4.50	-10.17±2.05	-10.04±1.54	-30.33±6.06	18.33±0.55
ST-30LH	-37.83±4.91	-32.60±1.71	-45.10±2.80	-36.47±0.64	12.53±0.85
Nexil 6	-15.95±1.91	-12.64±3.01	-12.64±3.01	-66.37±3.78	-25.5±0.96
Nexil 12	-21.67±5.43	-21.0±0.72	-17.10±0.82	-23.57±0.50	12.83±0.21
TiO ₂	35.03±3.02	40.50±2.76	-40.23±0.47	-4.62±2.82	22.77±0.61
ZrO ₂	17.10±9.11	28.13±2.50	-27.13±0.55	35.53±0.86	35.60±1.71

Negatively charged nanoparticles tend to be more stable with anionic surfactants while positively charged ones are more suitable to work together with nonionic ones as shown in Table 2. However, in the high salinity solution, pure nanoparticle alone with surfactants were not stable enough due to the charge shielding effect of cationic ions especially those divalent ones, indicating the necessity for particle surface modification.

4. Numerical simulation of spontaneous imbibition with tight Bakken formation

4.1 Introduction

In order to study flow mechanisms of middle Bakken formation, radial spontaneous imbibition was numerically studied.

4.2 Summary

The governing equation of radial spontaneous counter-current imbibition is as following:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(rK \frac{\lambda_w \lambda_g}{\lambda_t} \frac{dp_c}{dS_w} \frac{\partial S_w}{\partial r} \right) = \phi \frac{\partial S_w}{\partial t} \quad (1)$$

Where $\lambda_w = K \frac{k_{rw}}{\mu_w}$, $\lambda_g = K \frac{k_{rg}}{\mu_g}$, $\lambda_t = \lambda_w + \lambda_g$.

K —rock permeability;

k_{rw} — water relative permeability, $k_{rw} = k_{rw,max} \left(\frac{S_w - S_{wir}}{1 - S_{wir} - S_{or}} \right)^{\beta_w}$;

k_{rg} — gas relative permeability, $k_{rg} = k_{rg,max} \left(\frac{S_w - S_{wir}}{1 - S_{wir} - S_{gr}} \right)^{\beta_g}$;

p_c — the capillary pressure, $p_c = p_{c,entry} \left(\frac{S_w - S_{wir}}{1 - S_{wir} - S_{gr}} \right)^{\beta_{pc}}$.

Through adjusting the parameters of $k_{rw,max}$, β_w , $k_{rg,max}$, β_g , $p_{c,entry}$, β_{pc} , the numerical simulation results match the experimental results, as shown in Figure 3. Therefore, the established model meets the actual imbibition experimental conditions and can predict the relevant results, as shown in Figure 4-Figure 6. Figures 4 5 show the capillary pressure and relative permeability trends with water saturation, respectively. Using this model, the water saturation trend of Bakken formation core sample with the radius of 1.91mm was predicted under different imbibition time, as shown in Figure 6.

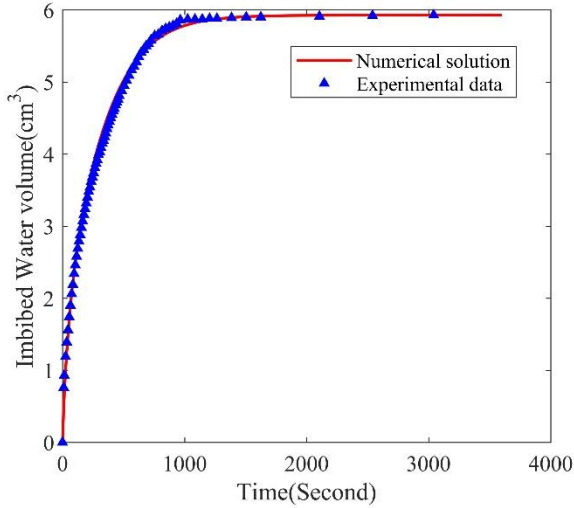


Figure 3. Experimental data and Numerical solution of imbibed water volume

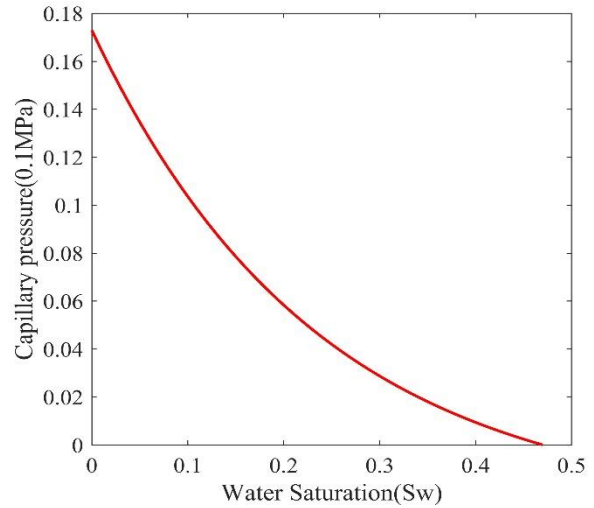


Figure 4. Capillary pressure curve plotted vs S_w .

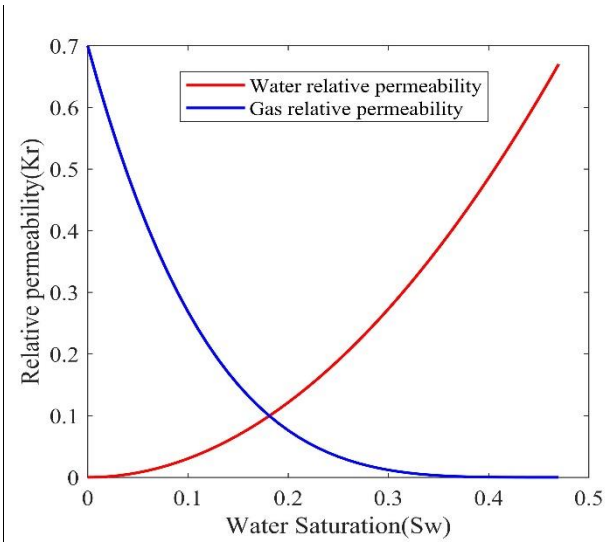


Figure 5. Relative permeability curve

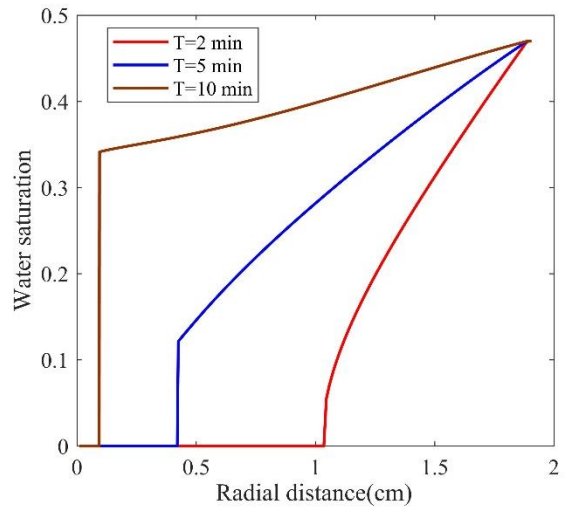


Figure 6. Water saturation with the radius

5. NMR study of tight Bakken formation

5.1 Introduction

NMR method can be used to study pore size distribution [1-2]. In order to study fluid distribution in pore structure, NMR study of the Bakken formation rock was carried out. Properties of four samples from the same well are shown in Table 3. The core samples were fully saturated with brine, followed by the T2 distribution test.

Table 3. Properties of Bakken formation sample

Sample	Well	Depth	Diameter(in)	Length(in)	Mass(g)
# 1	24022	10314	1.487	1.486	59.69
# 2	24022	10314	1.491	1.238	81.67
# 4	24022	10322	1.490	0.706	51.94
# 5	24022	10322	1.483	1.690	125.03

5.2 Summary

Figures 11-14 show the NMR results of the four Bakken core samples. The larger the value of NMR T2, the bigger the pore and vice versa. For cores # 1 and # 2, T2 is less than 40 ms. For cores # 4 and # 5, T2 is less than 10 ms. The cumulative porosity for cores # 1 and # 2 are higher than cores # 4 and # 5. These results indicate porosity and pore size of cores # 4 and # 5 are smaller than cores # 1 and # 2.

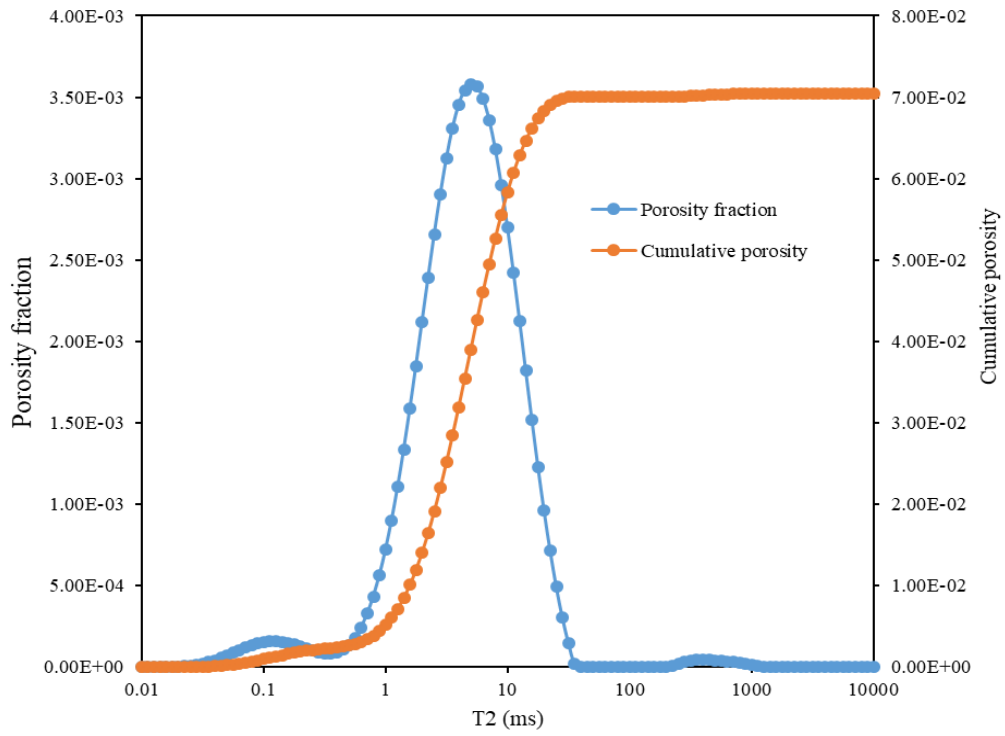


Figure 11. NMR analysis of Core# 1

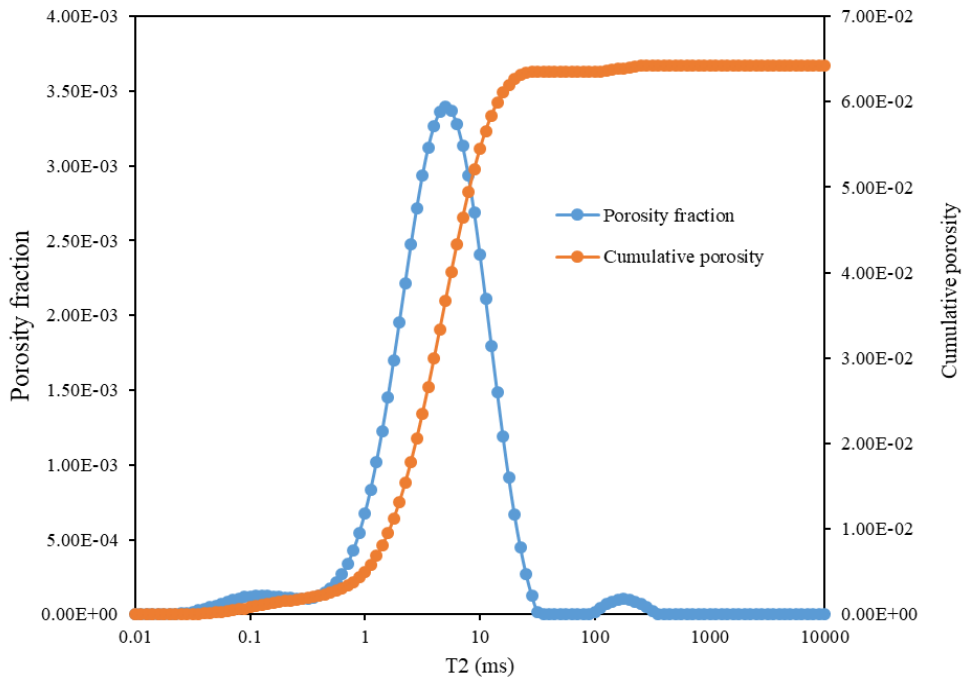


Figure 12. NMR analysis of Core# 2

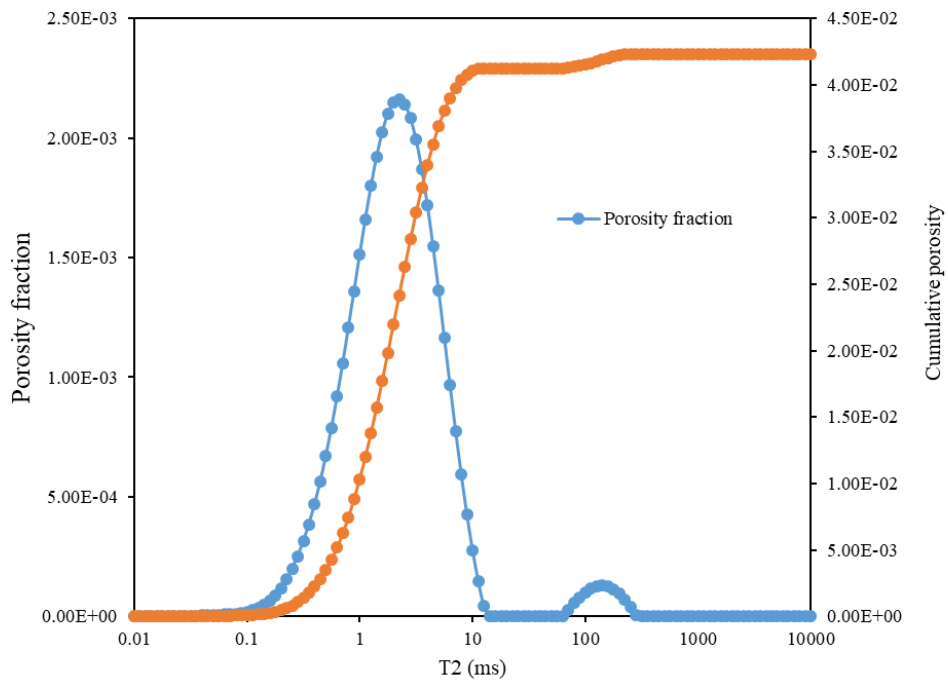


Figure 13. NMR analysis of Core# 4

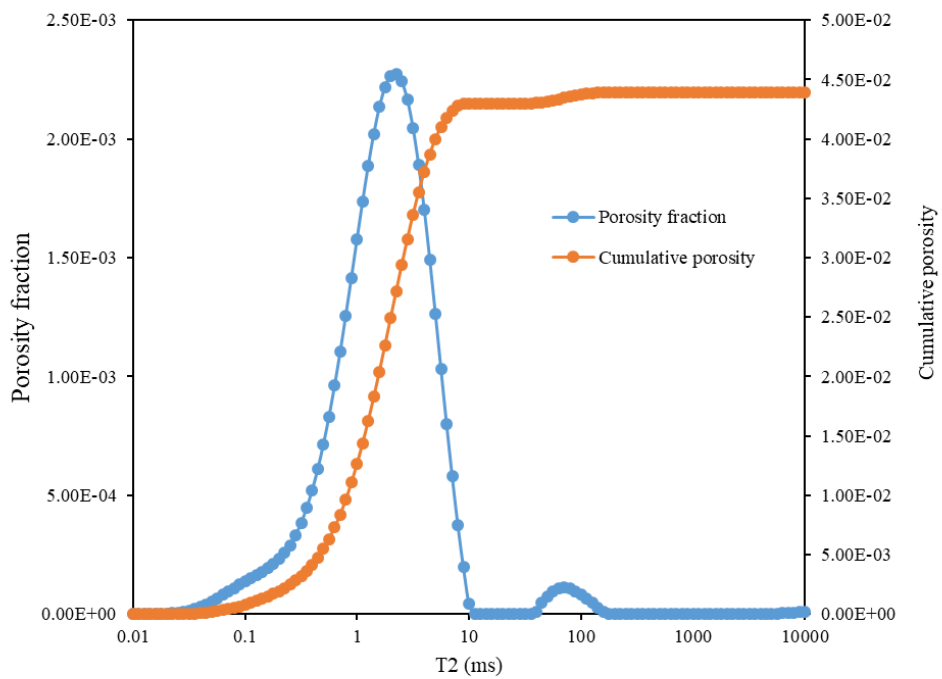


Figure 14. NMR analysis of Core# 5

Future Work

1. Synthesis of polymer nanoparticles.
2. Performance of zwitterionic surfactant coated nanofluid.
3. Synthesis of small silica nanoparticles (<20 nm) with relative high yield.
4. Water imbibition experiment using different depth Middle Bakken core samples.
5. NMR test of Middle Bakken samples.
6. Mathematical model improvement of the imbibition experiment.

References

- [1] Schmid, K. S., Alyafei, N., Geiger, S., Blunt, M. J. (2016). Analytical solutions for spontaneous imbibition: fractional-flow theory and experimental analysis. *Spe Journal*, 2016,21(6),2308-2316.
- [2] Lyu, C., Ning, Z., Wang, Q., Chen, M. (2018). Application of nmr t2 to pore size distribution and movable fluid distribution in tight sandstones. *Energy & Fuels*. 2018,32(2), 1395–1405.