

# **Experimental Investigation of Stability of Silica Nanoparticles at Reservoir Conditions for Enhanced Oil Recovery Applications**

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## **ABSTRACT**

To be effective enhanced oil recovery (EOR) agents, nanoparticles must be stable and transported through the reservoir. However, the stability of a nanoparticle suspension at reservoir salinity and temperature is still a challenge and how it is affected by reservoir rock and crude oil is not well understood. The objective of this study is to investigate ways to stabilize nanoparticle suspensions at reservoir conditions for EOR applications.

The stability of nanoparticle suspensions was screened in test tubes at 70°C and 3.8 wt. % salinity in the presence of rock and crude oil. Rock and oil samples used included Berea sandstones, shale, chalk, and limestone and crudes with different properties. Fumed silica nanoparticles in suspension with hydrochloric acid (HCl), polymer modified fumed nanoparticles and amide functionalized silica colloidal nanoparticles were studied. The size and pH of nanoparticle suspension in contact with rock samples were measured to determine the mechanisms for stabilization or destabilization of nanoparticles. A turbidity scanner was used to quantify stability of nanoparticle suspension.

Results showed that both HCl and polymer surface modification can improve nanoparticles stability under synthetic seawater salinity and 70°C. Suspensions of polymer modified nanoparticles were stable for months. It was found that pH is a key parameter influencing nanoparticle stability. Rock samples with carbonate destabilized unmodified nanoparticles. Crude oils have limited effect on nanoparticles stability and no obvious trend was observed. Some components of crude oil migrated into the aqueous phase consisting of amide functionalized silica colloidal nanoparticles suspension.

This is the first time the effect of rock and crude oil on the stability of silica nanoparticle suspension has been reported. The feasibility of using a low pH environment to stabilize a nanoparticle suspension in a porous medium will be further investigated. This study constitutes part of a continuing effort to determine the feasibility of using nanoparticle suspensions as EOR agents.

## **INTRODUCTION**

In recent years, nanotechnology research on EOR has shown promise in the laboratory. Some EOR experiments with silica nanoparticles have been performed and showed positive results in increasing oil recovery. The proposed EOR mechanisms for silica nanoparticles include interfacial tension reduction, wettability alteration, plugging of pore channels and emulsification. The precondition of these mechanisms working well in the reservoir is that nanoparticles should be stable and maintain their surface properties at reservoir condition. However, the high temperature and high salinity condition in the reservoir is unfavorable for nanoparticles stability. According to DLVO theory (named after Derjaguin, Landau, Verwey and Overbeek) [1, 2], presence of cations in a nanoparticle suspension will lead to a thinner double layer. Divalent cations such as  $Mg^{2+}$ ,  $Ca^{2+}$ , and  $Ba^{2+}$  are effective in suppressing the double layers and result in nanoparticle aggregation [3]. A high temperature also increases the aggregation rate of nanoparticles. At the same salinity, nanoparticles at 70 °C are much larger than those at 25 °C [3].

Some approaches have been conducted to improve stability of nanoparticle suspension under a high-temperature and high-salinity condition. Kim *et al.* (2017) used HCl to stabilize nanoparticles in about 3.6 wt. % sea water and 9.3% additional oil was produced during 0.03 wt. % nanofluid flooding [4]. Surface modification of nanoparticles is another method to stabilize nanoparticles. Silica nanoparticles with surface modification by adding zwitterionic monomers had long-term stability at salt concentrations up to 120g/l at 90°C [5]. However, since reservoir rock and crude oil were absent in these nanoparticle stability experiments, it is not clear whether these have an effect on nanoparticles stability. In this study several reservoir rock and crude oil samples from different fields were used to investigate their effects on nanoparticles stability under a high-temperature and high-salinity condition.

## **EXPERIMENTAL MATERIALS AND METHODS**

### **Experimental Materials**

1. Nanoparticle: Fumed hydrophilic silica nanoparticles (FNP) produced by Evonik Industries and an amide functionalized silica nanoparticles (ANP) dispersion purchased from Sigma-Aldrich were used in this study. Primary particle size of FNP is about 7 nm, but in suspension nanoparticle size may increase to more than 100 nm. The specific surface area of FNP is around 300m<sup>2</sup>/g. The particle size of ANP is less than 30 nm. Surface modified FNP with zwitterionic monomers (FNP-MD) was prepared and used in this study. HCl was utilized as a stabilizer for nanoparticles in our experiments. These three nanoparticles have been characterized by using Cryogenic transmission electron microscopy (Cryo-TEM) and Scanning Electron Microscope (SEM). Images are shown in Figures 1 and 2.

2. Nanoparticles suspension: In this study five concentrations were used (0.1, 0.2, 0.3, 0.4 and 0.5 wt. %) and nanoparticles were dispersed in 3.8 wt. % synthetic seawater (SSW). The recipe of SSW is given in Table 1. For FNP and FNP-MD, nanoparticles were weighed and then dispersed in SSW by using a sonicator. For some FNP suspension samples (FNP-HCl), HCl was used as a stabilizer with pH=2.0.

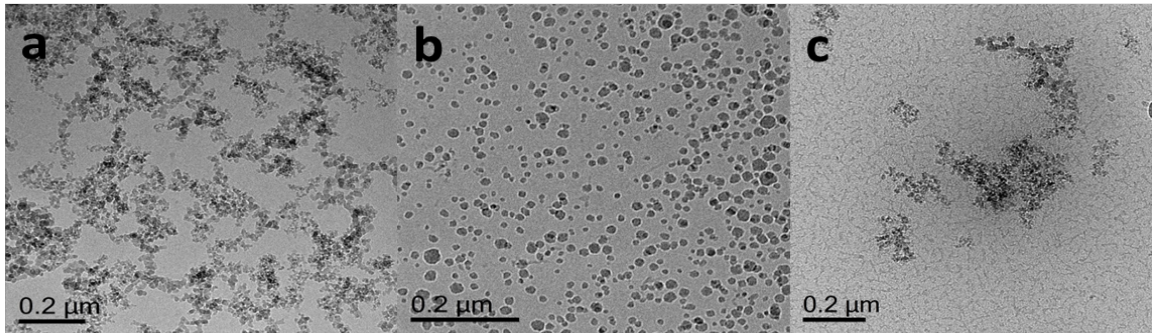


Figure 1 Cryo-TEM image of nanoparticles: (a) FNP; (b) ANP; (c) FNP-MD.

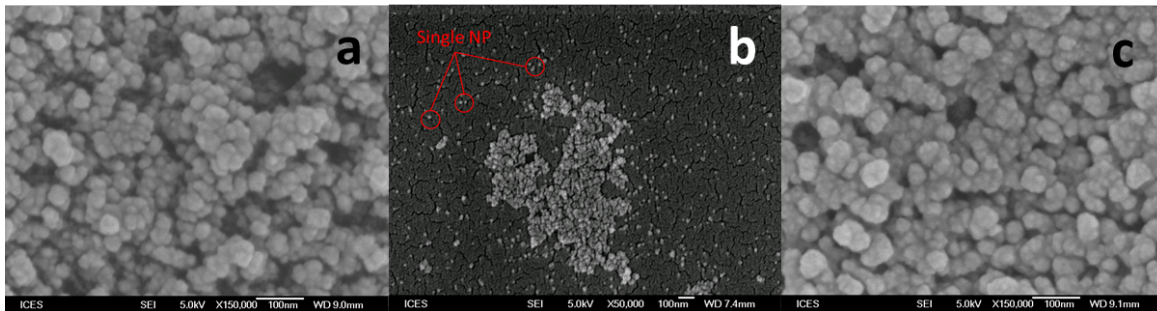


Figure 2 SEM image of nanoparticles: (a) FNP; (b) ANP; (c) FNP-MD.

The ANP suspension was prepared by a dilution of concentrated suspension to lower the suspension concentration. Nanoparticles size in suspension was measured with dynamic light scattering (DLS) and values are 142.5 nm, 168.3 nm and 21.4 nm, respectively.

Table 1 Synthetic seawater recipe

Salts	Concentration (g/l)	Salts	Concentration (g/l)
CaCl <sub>2</sub> · 2H <sub>2</sub> O	1.76	Na <sub>2</sub> SO <sub>4</sub>	4.81
MgCl <sub>2</sub> · 6H <sub>2</sub> O	11.23	NaCl	27.03

3. Reservoir rocks: Two Berea sandstones (BSS) were used in this experiment; BSS 1 has a lower permeability and BSS 2 has a higher permeability. Chalk, limestone and shale were also used in this study. The X-ray diffraction results for rocks are shown in Table 2.

Table 2 Mineral components of rock samples

%	BSS1	BSS2	Chalk	Limestone	Shale
SiO <sub>2</sub> Quartz	90.87	90.31	--	0.69	2.84
Na AlSi <sub>3</sub> O <sub>8</sub> Albite	0.89	1.89	--	--	--
KAlSiO <sub>8</sub> Sanidine	0.46	0.74	--	--	--
KAl <sub>2</sub> (Si <sub>3</sub> Al)O <sub>10</sub> (OH,F) <sub>2</sub> Muscovite	3.75	3.6	--	--	2.07
Al <sub>2</sub> SiO <sub>5</sub> (OH) <sub>4</sub> Kaolinite	1.92	2.29	--	--	1.48
(Mg,Fe) <sub>5</sub> Al(Si <sub>3</sub> Al)O <sub>10</sub> (OH) <sub>8</sub> Clinocllore	0.97	0.89	--	--	--
CaMg(CO <sub>3</sub> ) <sub>2</sub> Dolomite	1.13	0.28	--	--	1.89
CaCO <sub>3</sub> Calcite	--	--	100	99.31	89.28
Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH) <sub>2</sub> Apatite	--	--	--	--	2.44

4. Oil: Decane and eight types of crude oil were used in this experiment. Crude oil properties are given in Table 3.

Table 3 Crude oil properties

	Penara (PEN)	Tembikai (TMB)	Bunga Raya (BR)	Miri Light (ML)	Tapis Blend (TB)	Van Gogh (VG)	Wandoo (WD)
Saturates	60.66	75.72	84.61	38.48	74.79	26.37	32.94
Aromatics	10.52	17.43	12.76	56.13	19.79	51.90	52.26
Resins	9.68	3.85	2.32	5.33	5.06	20.76	14.80
Asphaltenes	19.15	3.00	0.31	0.07	0.36	1.09	0.00
API @15°C	31.80	38.01	39.36	27.30	40.10	16.11	19.48
Viscosity @70°C	7.66	2.47	1.90	2.43	1.51	35.61	13.06
Sulphur content (ppm)	657	491	655	1300	574	3325	1900
Total Acid Number (mg/mg KOH)	0.064	0.475	0.103	0.260	0.239	1.720	1.702

## Experimental Methods

1. Nanoparticles suspension stability: Nanoparticle suspension stability tests were performed by using visual observation and turbidity scanning. For each type of nanoparticle (FNP, FNP-HCl, FNP-MD and ANP), samples with five different concentrations (0.1, 0.2, 0.3, 0.4 and 0.5 wt. %) were put into test tubes and placed in a heat cabinet under 70°C. Photographs were taken to show their stability over time. A Turbiscan instrument was used to quantify nanoparticle suspension stability. Samples of nanoparticle suspension were scanned at 60°C with a 880 nm near-infrared LED source and the transmission and backscattered signals were received by detectors. Since nanoparticle size can affect these signals, delta transmission and backscattering were used to show nanoparticle stability. Turbiscan Stability Index (TSI) calculated with Turbiscan software was used to compare stability of different nanoparticle suspensions. The smaller TSI value indicates better nanoparticles stability.

2. Effect of reservoir rocks and crude oils on nanoparticles stability: FNP, FNP-MD and ANP suspensions at 0.1 wt. % concentration were used in this study. A 7 ml nanoparticle suspension was placed in a test tube and 0.2 gram of rock sample was put inside test tube. Pure quartz was used as reference rock sample. Another set of samples were prepared with 5 ml nanoparticle suspension and 2 ml oil. Decane was used as reference oil. All of these test tubes were put in a heat cabinet at 70°C.

3. Particles size and pH measurement of nanoparticles: The particles size and pH of nanoparticle samples with rock samples were measured by using DLS and pH meter, respectively.

4. Preparation of polymer modified nanoparticles: [2-(Methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide (MEDSAH, 95%, Aldrich), 2-(2-Carboxyethylsulfanylthiocarbonylsulfanyl)propionic acid (CTA, 95%, Aldrich), 3-(Trimethoxysilyl)propyl methacrylate (MPS, 98%, Aldrich), 2,2'-Azobis(2-methylpropionamide)dihydrochloride (V50, Wako Chemicals), fumed silica (FNP), toluene (HPLC, VWR Chemicals) were used as received.

In a sealed Schlenk flask, fumed silica was dried under vacuum at 120°C for at least 24 hrs before being used. To a dispersion of dried silica (2 g) in toluene (100 ml) being stirred (1000 rpm) and under argon protection, MPS (3 g) was added using an argon-purged syringe. The mixture was then heated to 100°C for 12 hrs. After cooling to room temperature, the dispersion was centrifuged and washed with fresh toluene (3 times), followed by ethanol rinsing (3 times). The methacrylate-functionalized silica (SiO<sub>2</sub>-MPS) was dried under vacuum at 60°C for 12 hrs. As-prepared SiO<sub>2</sub>-MPS (0.5 g) was dispersed in deionized water (25 ml) under sonication for 2 hr. MEDSAH (2 g), CTA (36.6 mg), V50 (7.8 mg) [MEDSAH/CTA/V50=50/1/0.2] were placed into a dry Schlenk flask. The flask was sealed with a rubber septum and subjected to 4 vacuum/argon cycles. SiO<sub>2</sub>-MPS dispersion was deoxygenated by bubbling argon for about 1 hr and added to the Schlenk flask using an argon-purged syringe. The mixture was heated at 60°C under a stirring rate of 700 rpm. After 24 hrs, the dispersion was cooled to room temperature, and washed with deionized water for 8 times. The polymer-coated silica (SiO<sub>2</sub>-MEDSAH) was dried under vacuum at 80°C for 24 hrs.

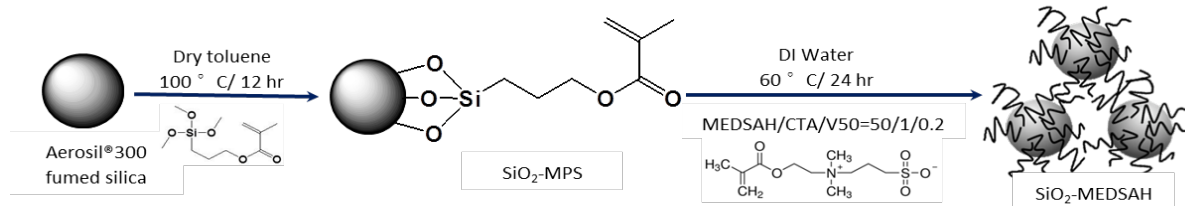


Figure 3 Schematic of preparation polymer modified nanoparticles.

## RESULTS AND DISCUSSION

### Nanoparticles suspension stability test

Four types of nanoparticle suspensions (FNP, FNP-MD, ANP and FNP-HCl) were used in this stability test. Stability observation of test tubes and stability quantification by using turbidity scanning were undertaken. The time when nanoparticle aggregation occurred for each sample was recorded and given in Table 4. It can be seen that FNP suspensions had the worst stability, all samples aggregated within two days. FNP-MD suspensions had the best stability, five samples were still stable after thirty days. Compared with FNP cases, adding HCl into FNP can delay nanoparticle aggregation and the lower the HCl concentration the longer is the stabilization time. However, ANP suspensions showed the opposite trend. The reason is that acid was used to stabilize concentrated ANP suspension, so 0.5 wt. % diluted sample had a lower pH than the 0.1 wt. % sample and a lower pH stabilizes ANP.

Table 4 Nanoparticles stability screening test

NPs Conc. (wt. %)	FNP	FNP-MD	FNP-HCl	ANP
0.1	day 2	--	--	day 2
0.2	day 1	--	day 25	day 8
0.3	less than 1 day	--	day 15	day 25
0.4	less than 1 day	--	day 12	--
0.5	less than 1 day	--	day 10	--

--: no nanoparticles aggregation was observed within 30 days

The turbidity scanning tests were performed for four types of nanoparticle suspension at 0.1 wt. % concentration and the TSI versus time is shown in Figure 4. It can be seen that both FNP-HCl and FNP-MD had very low TSI, which means that these two samples had good stability. However, TSI value for FNP and ANP samples increased very fast to a plateau and was constant after day 2, which means that the nanoparticles have aggregated and lost their stability. This result is consistent with test tube observations.

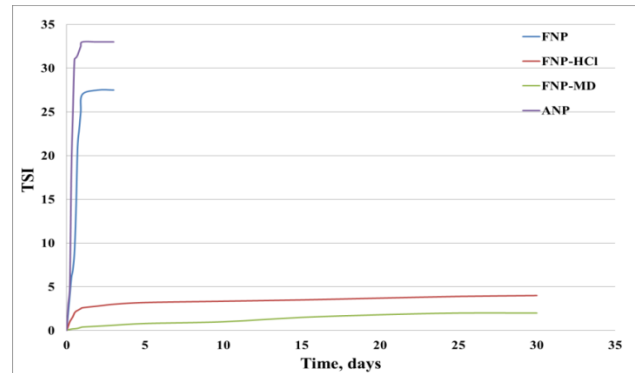


Figure 4 TSI results for nanoparticles suspensions.

### Effect of reservoir rocks on nanoparticles stability

Five reservoir rocks (Berea sandstone 1 and 2, chalk, limestone and shale), as well as pure quartz used as reference sample, were used in this experiment. And FNP, FNP-MD and ANP suspension with 0.1 wt. % concentration were used. Photographs of all samples in test tubes were taken for nanoparticles stability observation. Particle size and pH of nanoparticles suspension were measured to investigate the mechanisms for stabilization or destabilization of nanoparticles due to the presence of rock samples. The photographs for FNP, FNP-MD and ANP suspensions with rock samples are shown in Figure 5-7. Results of pH and particle size measurements are shown in Figures 8-10. As shown in Figures 5 and 7, reservoir rocks had a significant effect on nanoparticle stability, especially for limestone, chalk and shale. As listed in Table 2, all of these three rocks have very high calcite percentage, so they reacted with  $H^+$  in nanoparticle suspensions. In Figures 8 and 10, the pH value of limestone, chalk and shale samples increased to 7 quickly, and this neutral pH is not favorable for nanoparticles stability. Thus fast nanoparticles aggregation was observed. Berea sandstones also had an effect on FNP and ANP suspension stability. Faster nanoparticles aggregation was observed in BSS1 sample, the reason might be due to higher dolomite content in BSS1, which leads to a quicker pH increase of suspension. No significant effect of quartz on nanoparticle stability was observed, so dolomite must be the main source of nanoparticle destabilization by Berea sandstone, due to its reaction with nanofluid. For FNP-MD suspension (Figure 6), almost no rock sample affected its stability except limestone. As shown in Figure 9, pH increased in all reservoir rock samples while FNP-MD was still stable after 30 days in the heating cabinet even though the particle size increased in chalk and shale samples. For some unknown reason, limestone destabilized the FNP-MD suspension. Since limestone has the similar mineral component with chalk, more tests need to be done to determine the mechanism.



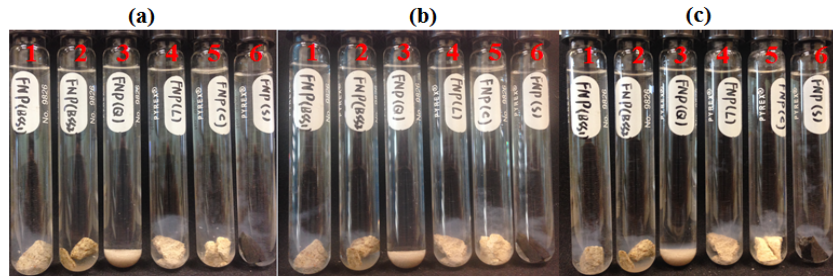


Figure 5 FNP suspensions with reservoir rocks: (a), Day 1; (b), Day 2; (c), Day 4. (1: BBS1; 2: BSS2; 3: quartz; 4: limestone; 5: chalk; 6: shale).

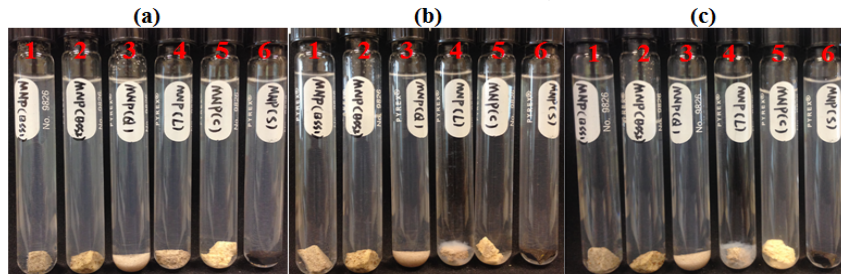


Figure 6 FNP-MD suspensions with reservoir rocks: (a), Day 1; (b), Day 7; (c), Day 30. (1: BBS1; 2: BSS2; 3: quartz; 4: limestone; 5: chalk; 6: shale).

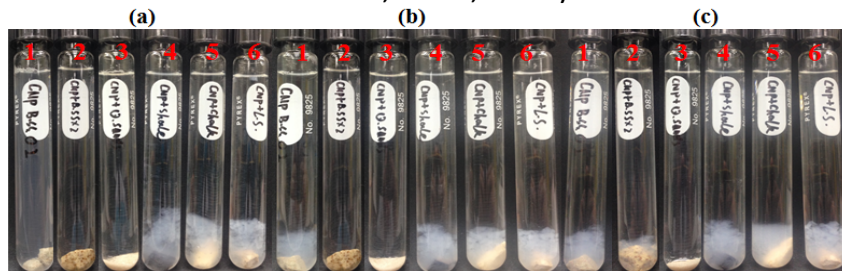


Figure 7 ANP suspensions with reservoir rocks: (a), Day 0; (b), Day 1; (c), Day 2. (1: BBS1; 2: BSS2; 3: quartz; 4: shale; 5: chalk; 6: limestone).

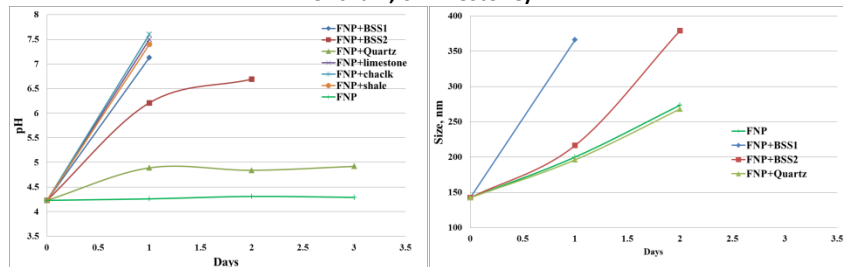


Figure 8 pH and particle size measurements for FNP suspension with different rocks.

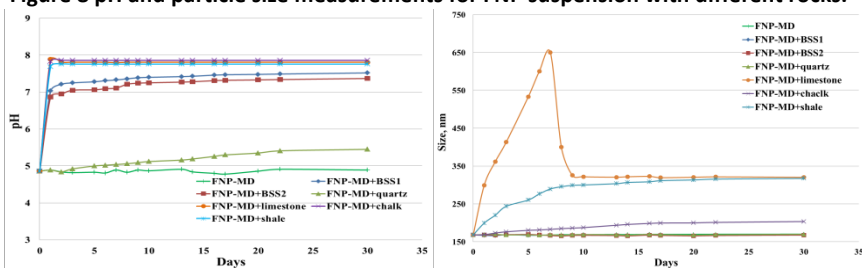


Figure 9 pH and particle size measurements for FNP-MD suspension with different rocks.

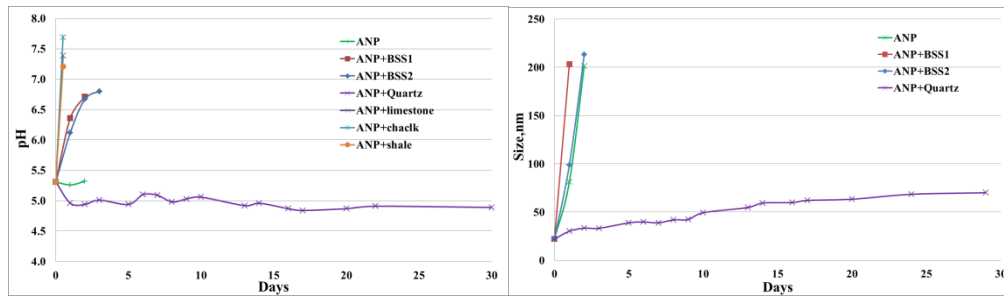


Figure 10 pH and particle size measurements for ANP suspension with different rocks.

### Effect of crude oils on nanoparticles stability

Seven crude oils with different properties were employed in this study, and decane was used as reference oil. FNP, FNP-MD and ANP suspension with 0.1 wt. % concentration were used. Photographs of all samples in test tubes were taken for nanoparticles stability observation. For FNP suspension (Figure 11), crude oils had no obvious effect on stability. Only nanoparticle aggregation delay was observed in the ML sample. FNP-MD had good stability in the presence of crude oils and was still stable after 30 days in the heating cabinet (Figure 12). For ANP suspension, nanoparticle aggregation occurred in PEN and decane samples at day 1, and all samples aggregated at day 3 (Figure 13). For samples with BR, TB and ML, nanoparticles aggregation (at bottom of test tube) appeared yellowish, which might be due to migration of some components of crude oil into the aqueous suspension.



Figure 11 FNP suspensions stability screening with different type of oils: (a), Day 1; (b), Day 2; (1: PEN; 2: TMB; 3: BR; 4: ML; 5: TB; 6: WD; 7: VG; 8: Decane).



Figure 12 FNP-MD suspensions stability screening with different type of oils: (a), Day 1; (b), Day 30; (1: PEN; 2: TMB; 3: BR; 4: ML; 5: TB; 6: VG; 7: WD; 8: Decane).



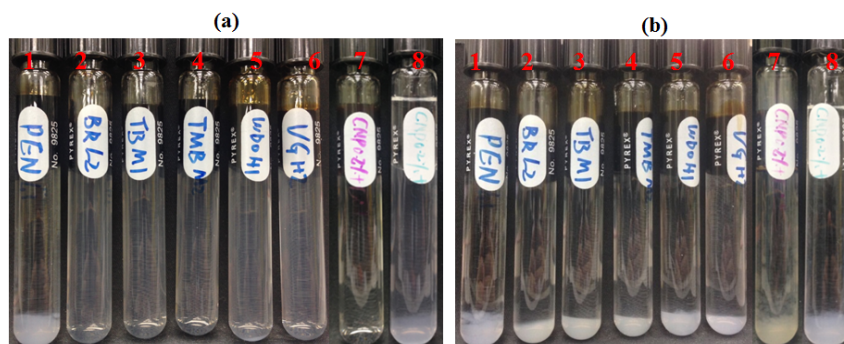


Figure 13 ANP suspensions stability screening with different type of oils: (a), Day 1; (b), Day 3; (1: PEN; 2: BR; 3: TB; 4: TMB; 5: WD; 6: VG; 7: ML; 8: Decane).

## CONCLUSIONS

Stability screening test was performed for surface modified nanoparticles and nanoparticles with a stabilizer. The effect of reservoir rock samples and crude oils on nanoparticle stability was also examined. It was found that both surface modification and the presence of a stabilizer can increase nanoparticle stability under high-temperature and high-salinity. Reservoir rocks containing carbonate can react with nanoparticle suspension to increase the pH and destabilized the nanoparticles. However, reservoir rocks had no significant effect on FNP-MD stability. Crude oils had limited effect on nanoparticle stability and no obvious trend was observed. Some components of crude oil migrated into the ANP suspension.

## REFERENCES

1. Deryaguin, B. V., and Landac, L. 1993. Theory of the stability of strongly charged lyophobic sols and the adhesion of strongly charged particles in solutions of electrolytes. *Progress in Surface Science* **43** (1-4): 30-59.
2. Verwey, E. J. W., and Overbeek, J. Th. G. 1948. *Theory of the stability of lyophobic colloids*. Amsterdam: Elsevier publishing Co. (Reprint).
3. Metin, C. O., Lake, L. W., Nguyen, Q. P. Stability of aqueous silica nanoparticle dispersions. *J Nanopart Res* (2011) 13:839–850.
4. Ranka, M., Brown P., Hatton, T. A. Responsive Stabilization of Nanoparticles for Extreme Salinity and High-Temperature Reservoir Applications. *ACS Appl. Mater. Interfaces* (2015), 7, 19651–19658.
5. Kim, H., Sivira, D.J., James, L.A., Zhang, Y. Experimental Investigation of EOR by Injecting SiO<sub>2</sub> Nanoparticles as Water Additive with Application to the Hebron Field. 19th European Symposium on Improved Oil Recovery 24-27 April 2017, Norway.