

Article

# Influence of Individual Ions on Silica Nanoparticles Interaction with Berea Sandstone Minerals

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**Abstract:** Nanofluids are prepared by dispersing silica nanoparticles in aqueous media (brines). The purpose of this work is to address brine/rock interactions in presence of nanoparticles. Our previous studies have shown that silica nanofluids are effective in reducing formation damage in sandstone reservoirs. This study addresses effect of individual ions on dispersed silica nanoparticles' interaction with Berea Sandstone minerals. The selected ions are  $Mg^{2+}$ ,  $SO_4^{2-}$  and  $Na^+$ , in  $MgCl_2$ ,  $Na_2SO_4$  and  $NaCl$ , which are the major constituents of seawater. Three flooding stages for Berea Sandstone cores were followed. The first flooding stage was without nanoparticles, the second one was a slug of the nanoparticles with tracer and the third stage was a post-flushing of the core with the respective ion. The effluent tracer concentration, nanoparticle content, ion concentrations and pH reflect the effect of individual ions on nanoparticle/mineral interaction which were used for suggesting possible interaction mechanisms. Presence of  $Mg^{2+}$  and  $SO_4^{2-}$  ions improved the adsorption of nanoparticles on minerals, however the effect of  $Na^+$  was lesser. In general, in all the cases nanoparticles reduced the mineral dissolution and associated fine migration/possible formation damage.

**Keywords:** silica; nanoparticles; adsorption; fluid/rock interaction;  $Mg^{2+}$ ;  $Na^+$ ;  $SO_4^{2-}$

## 1. Introduction

The fall in oil prices over the last few years has led to increased focus on developing efficient enhanced oil recovery (EOR) techniques that can make oil production from maturing oil fields economically attractive [1–3]. Silica nanoparticles (NPs) dispersed in various fluids have emerged as an attractive option since they have the potential to be effective at very low volume concentrations [4] thereby reducing the cost of applying this technology. Potential applications of silica nanofluids (NFs) include: (a) surface modification to alter wettability [5–7]; (b) Interfacial Tension (IFT) reduction [8,9]; (c) increasing structural disjoining pressure for increasing oil recovery [10–12]; (d) mitigating formation damage [13–16]; and (e) improving the performance of low salinity water floods [17–19].

Water flooding is a well-established secondary oil recovery method for reservoir pressure maintenance post-primary production phase. Most offshore oil reservoirs are flooded with seawater due to easy availability and low cost. It is well established in the literature that ionic composition of injection brine affects the crude oil brine system [20–22]. Lowering injection brine salinity is a popular EOR method [23,24], but it may have some detrimental effects in the reservoir. Khilar and Fogler [25] proposed a limit on brine salinity for injection in sandstones known as critical salt concentration (CSC). They proposed that if the injected salinity below was below CSC, there may be a release of clay particles and this may cause formation damage. Formation damage by lowering injection brine salinity has also been reported by other research groups [26–28].

Silica nanofluids are prepared by dispersing silica NPs in appropriated brines. Therefore, it stands to reason that the ionic composition of brine used to prepare the nanofluid would itself affect fluid/rock

interaction in the reservoir. Previous work in our lab identified that adding silica NPs to low salinity water can reduce fine migration and mineral dissolution in Berea Sandstone [18]. Low salinity water is in itself a promising EOR method. However implementing this method can incur high investment involved in setting up desalination plants and transport infrastructure especially in off shore environments [29]. Therefore, adding silica NPs to cheaply available seawater presents a more cost-effective solution. Many researchers have reported that silica NPs can be effective in increasing oil recovery from sandstones reservoirs dispersed in seawater [12,30–33]. Wettability alteration is the major mechanism attributed to the effectiveness of silica nanofluid [5–7]. Wettability alteration depends on the surface modification of Berea Sandstone due to the adsorption of silica NPs on mineral surface. Therefore, the adsorption behavior critically controls the effectiveness of silica nanofluid as an EOR. Monfared, et al. [34] showed that for single salt NaCl brine NP adsorption on calcite mineral increases with salinity. Previous work in our lab [35] investigated the kinetic adsorption of silica NPs on Berea Sandstone as the salinity of multicomponent brines was increased from DIW (no added salts) to low salinity (1:10 diluted seawater) and finally high salinity (seawater). We reported that both rate and equilibrium adsorption increased with salinity. Seawater is a multicomponent brine and therefore the different ions present in seawater have a combined and complicated effect on the performance of the nanofluid flood. Hence, it is important to address the role played by the major ion present in seawater, as this would enable operator to design a more effective brine for dispersing silica NPs and preparing more effective nanofluid for EOR application. However, to the best of our knowledge, the effect of silica NPs dispersed in seawater on fluid/rock interaction and its adsorption in Berea Sandstone has not been addressed in the literature.

The objectives of this work are to address individual ions such as magnesium, sulphate and sodium on NP adsorption and NP/mineral interaction associated with the injection of silica nanofluids in Berea Sandstone cores. These ions were selected since they are the major constituents of seawater and are therefore expected to have direct effect on the performance of silica nanofluid injection. Single ion brines of these ions were considered as stabilizing fluids for NPs. This work contributes to isolate and understand the influence of the individual ions on the NPs/mineral interaction and their mechanism(s).

In the following sections, the materials used for this study and the experimental methodology for core flooding are outlined followed by the results. The results include the detailed quantitative analysis of the effluent characterization. The produced effluent characterization included determining NPs concentration, ion concentration and pH. Additionally, the particle size of the NPs dispersed in various brines and the zeta potential of the NPs and crushed Berea powder dispersed in different brines was measured. The data from these measurements were used to determine the electric double layer interaction between the silica NPs and the Berea. Finally, the summary and conclusions of this study are presented in the final section.

## 2. Materials and Methods

The Silica NPs (DP 9711) used in this work was provided by Nyacol Nano Technologies (Ashland, MA, USA) at 30 wt% concentration, dispersed in deionized water (DIW). The stock fluid was supplied at pH 3. The manufacturer claimed NP size was about 20 nm. The nanofluids used in this study were prepared from the stock fluid by diluting it with appropriate brines. Synthetic seawater (SSW) brine was prepared by dissolving NaCl (AnalaR NORMAPUR, VWR Chemicals, Oslo, Norway), Na<sub>2</sub>SO<sub>4</sub> (Honeywell Fluka, Oslo, Norway), NaHCO<sub>3</sub> (Honeywell Riedel-de-Haën, Oslo, Norway), KCl (Sigma-Aldrich, Oslo, Norway), MgCl<sub>2</sub>·6H<sub>2</sub>O (AnalaR NORMAPUR, VWR Chemicals, Oslo, Norway) and CaCl<sub>2</sub>·2H<sub>2</sub>O (AnalaR NORMAPUR, VWR Chemicals, Oslo, Norway) at appropriate concentration in DIW and filtering the brine before use with 0.22 µm filter paper. The single salt brines were prepared by dissolving NaCl, MgCl<sub>2</sub>·6H<sub>2</sub>O and Na<sub>2</sub>SO<sub>4</sub> in DIW for Na Brine, Mg Brine and SO<sub>4</sub> brine respectively. The single salt brines were also filtered with 0.22 µm filter paper. The ionic composition and ionic strength of the brines used in this study are listed in Table 1. Berea Sandstone outcrop cores obtained from Koucurek Industries Inc., Caldwell, TX, USA were used as the porous

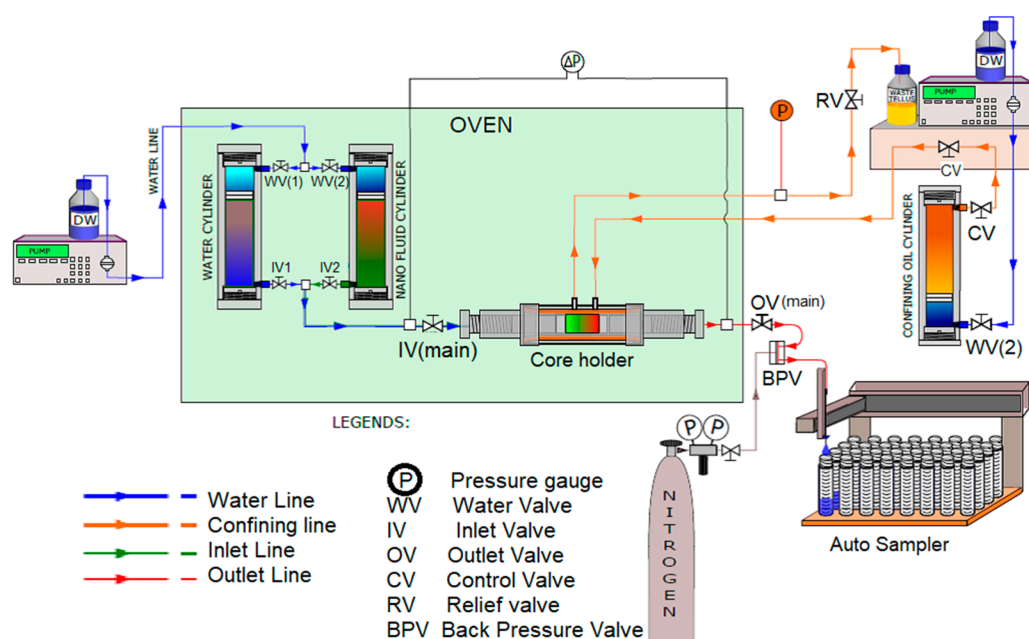
media for performing injection experiments. Zetasizer Nano ZSP from Malvern Instruments (Malvern, Worcestershire, UK) was used to measure the average particle size and zeta potential of the NPs and the zeta potential of the Berea mineral dispersed in different brines and Berea mineral which was modified by silica NPs. The detailed method for modifying the Berea mineral with silica NPs and measuring zeta potential can be found elsewhere [18].

**Table 1.** Ion concentration the brines.

Ion	SSW (mol/L)	Na Brine (mol/L)	Mg Brine (mol/L)	SO <sub>4</sub> Brine (mol/L)
HCO <sub>3</sub> <sup>3-</sup>	0.002	0	0	0
Cl <sup>-</sup>	0.525	0.400068	0.089033	0
SO <sub>4</sub> <sup>2-</sup>	0.0240	0	0	0.096
Mg <sup>2+</sup>	0.045	0	0.178066	0
Ca <sup>2+</sup>	0.013	0	0	0
Na <sup>+</sup>	0.450	0.400068	0	0.048
K <sup>+</sup>	0.010	0	0	0
Ionic strength	0.68	0.4	0.13	0.072

### 2.1. Nanoparticle Slug Injection

The objectives of the tests were to study the adsorption profile of the injected NPs and the interaction between NPs and the minerals present in Berea Sandstone. The schematic of the core flooding setup used this study is shown in Figure 1. Prior to loading the cores in the flooding setup, the cores were dried in a vacuum oven at 100 °C until the weight stabilized. Thereafter, the core was vacuum saturated with SSW. The difference between the dry weight and the saturated weight was used to determine the pore volume (PV) of the core. The SSW saturated core was then loaded into the core holder and a confining pressure of 25 bar was applied. After injecting several PVs of brine (pre-flush), 1.5 pore volume (PV) of slug with LiCl (AnalaR NORMAPUR, VWR Chemicals, Oslo, Norway) tracer was injected. Thereafter, the injection was switched to the original fluid to conduct a post-flush. Both brine and nanofluid slug injection was performed at a constant flow rate of 10 PV/day and at room temperature. Details of the experiment are listed in Table 2.



**Figure 1.** Schematic of the core flooding setup.

**Table 2.** Flooding experiments.

Name	Initial Saturating Fluid	Pre-flush Fluid	NP Slug	Post-Flush Fluid
BRT 1	SSW	Mg Brine	1 (g/L) NP in Mg Brine with 0.1 M LiCl tracer	Mg Brine
OBRT 2	SSW	SO <sub>4</sub> Brine	1 (g/L) NP in SO <sub>4</sub> Brine with 0.1 M LiCl tracer	SO <sub>4</sub> Brine
BRT 3	SSW	Na Brine	1 (g/L) NP in Na Brine with 0.1 M LiCl tracer	Na Brine
BRT 4	SSW	SSW	1 (g/L) NP in SSW with 0.1 M LiCl tracer	SSW

SSW: Synthetic seawater

The effluents were analyzed for NP concentration, ion concentration and pH. NPs concentration measurement was performed using a dual beam UV-Vis 1700 spectrophotometer from Shimadzu Corporation (Nakagyo-ku, Kyoto, Japan). The concentration of the ions produced in the effluents from the flooding experiments was determined by using a Dionex ICS-5000 ion chromatograph from Thermo Fisher Scientific (Waltham, MA, USA).

## 2.2. Electric Double Layer Interaction

The theory of surface forces was used in this work to estimate the electric double layer interaction between the NPs and the Berea minerals. There is a significant size difference between the NPs and the mineral surfaces. Therefore, the curvature of the mineral surface can be neglected so that the double layer interaction between the NPs (sphere) and mineral (plate) can be modelled based on the sphere–plate collector geometry [36]. The electric double layer interaction ( $V_{EDL}$ ) can be calculated as [34,37]:

$$V_{EDL}(h) = \pi \epsilon_0 \epsilon_1 \kappa (\zeta_p^2 + \zeta_s^2) \int_0^{a_p} \left( \begin{array}{l} -\coth \left[ \kappa \left( h + a_p - a_p \sqrt{1 - (r/a_p)^2} \right) \right] \\ + \coth \left[ \kappa \left( h + a_p + a_p \sqrt{1 - (r/a_p)^2} \right) \right] \\ + \frac{\zeta_p \zeta_s}{\zeta_p^2 + \zeta_s^2} \operatorname{csch} \left[ \kappa \left( h + a_p - a_p \sqrt{1 - (r/a_p)^2} \right) \right] \\ - \frac{\zeta_p \zeta_s}{\zeta_p^2 + \zeta_s^2} \operatorname{csch} \left[ \kappa \left( h + a_p + a_p \sqrt{1 - (r/a_p)^2} \right) \right] \end{array} \right) r \cdot dr \quad (1)$$

where  $\epsilon_0$  and  $\epsilon_1$  represent the vacuum permittivity and relative permittivity of water;  $h$  is the separation distance between the surfaces;  $\zeta_p$  and  $\zeta_s$  are the surface potentials of the NP and mineral, respectively, which can be approximated as their respective zeta potential;  $a_p$  is the NP radius; and  $\kappa$  is the inverse Debye length. For brines, the inverse Debye length depends on the salinity of the intervening medium:

$$\kappa^{-1} = \sqrt{\frac{\epsilon_0 \epsilon_1 k_B T}{2e^2 N_a I}} \quad (2)$$

where  $e$  is the elementary charge of an electron (C),  $k_B$  is the Boltzmann constant,  $N_a$  is the Avogadro constant,  $T$  is temperature and  $I$  is the ionic strength of the medium.

$$I = \frac{1}{2} \sum c_i Z_i^2, \quad (3)$$

where,  $c_i$  is the ion concentration of the  $i^{\text{th}}$  species and  $Z_i$  is the valence number of the  $i^{\text{th}}$  species as listed in Table 1. Finally, the non-dimensional double layer interaction energy ( $V_{EDL,ND}$ ) can be calculated as follows:

$$V_{EDL,ND}(h) = \frac{V_{EDL}(h)}{k_B * T}. \quad (4)$$

### 3. Results and Discussions

Core flood investigations were conducted in this work to address the performance of silica NPs dispersed in single salt brines ( $\text{MgCl}_2$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$ ) and SSW (used in some sections here as a reference). The effluent samples were analyzed for NPs concentration by UV-Vis. Ion concentrations and tracer ( $\text{LiCl}$ ) presence in the effluent were determined by ion chromatogram and the pH level was measured. This section is divided into three subsections, NPs and tracer concentration profiles, double layer interaction and NPs/mineral interaction with possible mechanism(s).

#### 3.1. Nanoparticle and Tracer Profiles

The NPs and tracer profiles for the flood conducted in this work are shown in Figure 2. In our previous work [18] with dispersed NPs in low salinity water injected into Berea Sandstone, we observed significant NP production after tracer had ceased to produce. Figure 2 shows that percentage of retained/adsorbed NPs varied with the dispersing fluid. The amount of retained NPs in the core is estimated by integrating the area under the NPs production curves and comparing with the known injected amount of NPs into the core. The estimated amounts of NPs retained are shown in Table 3.

SSW and Mg brine flooding showed maximum NP retention/adsorption of about 81%. Flooding with  $\text{SO}_4$  brine showed an intermediate NP retention/adsorption of about 68% and the lowest NP retention/adsorption of about 34% was estimated for the case of Na brine flooding. Figure 3 shows the influences of the ionic strength (salinity) of the NPs dispersing brines on Debye length. Previous studies have shown that NP adsorption increases with salinity [34,37]. However, from Table 3, the level of NPs adsorption was similar (~80%) in the case of SSW and Mg as dispersing brines, in spite of the significant difference in their ionic strength. In addition, high salinity in the case of  $\text{Na}^+$  brine (salinity = 0.4) corresponds to the lowest adsorption (~34%) while  $\text{SO}_4$  brine with the lowest salinity (0.072) showed an intermediate NP adsorption (68%). Therefore, these results may indicate that the salinity of the NPs' dispersing medium may not be the main factor that influences NP adsorption on mineral surfaces. The composition of the dispersing brines affects zeta potential of the interacting NP, fluid and mineral surfaces, as demonstrated in Figure 4.

Figure 4 shows the zeta potential for NPs/brines, Berea/brines and modified Berea with NPs/brines. Zeta potentials for all brines used in this study were negative. The average zeta potential of NP-modified Berea for the single ion brines was about  $23 \pm 2$  mV while SSW with multiple-ion composition exhibited the lowest zeta potential, and also had the highest amount of retained/adsorbed particles. From this point on in the manuscript, the term adsorption will be used. The term retained may give impression of core damage. The term adsorption is justified based on our previous work [16–18] where a decrease in pressure drop across the core was detected when flooding with silica NPs, rather than an increase in pressure drop which would be indicative of core damage.

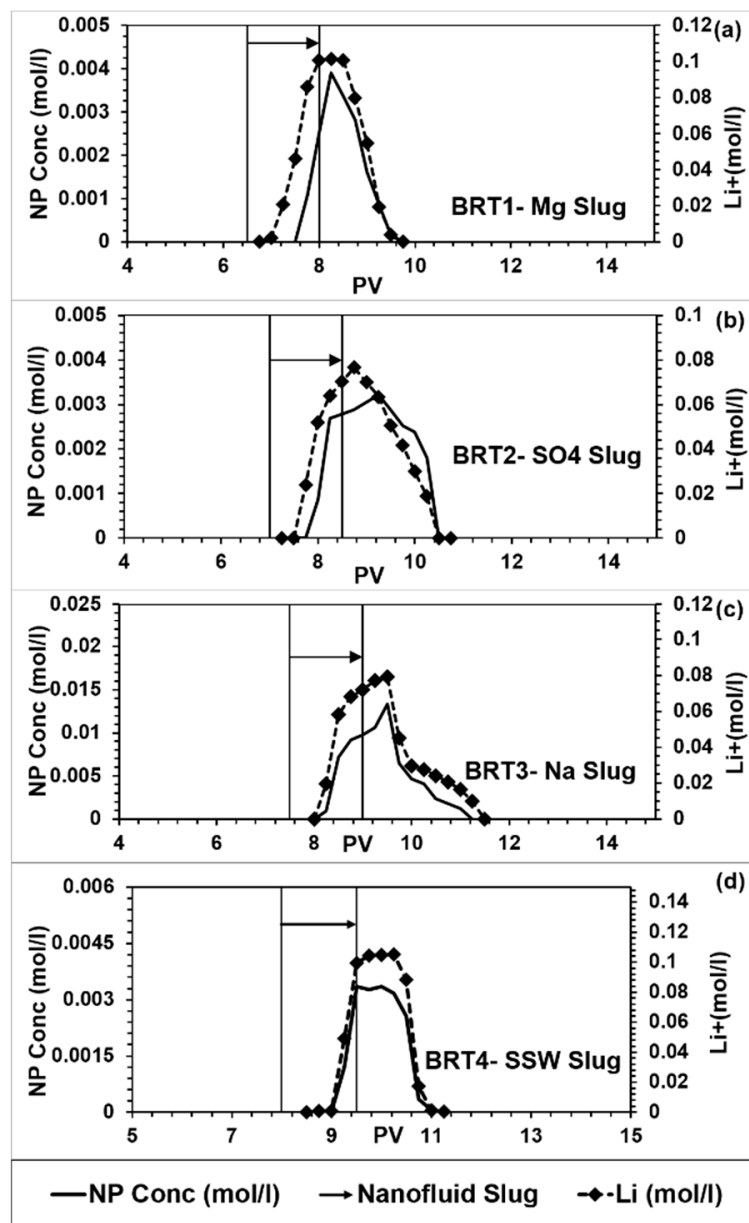


Figure 2. Nanoparticle (NP) and tracer concentrations from flooding of (a) BRT1; (b) BRT2; (c) BRT3; (d) BRT4.

Table 3. Percent of nanoparticles retained/adsorbed in the core.

Experiment	% Nanoparticles Retained in the Core
BRT1 SSW Slug	81.7
BRT2 MG Slug	81.3
BRT3 SO <sub>4</sub> Slug	68.2
BRT4 Na Slug	33.9

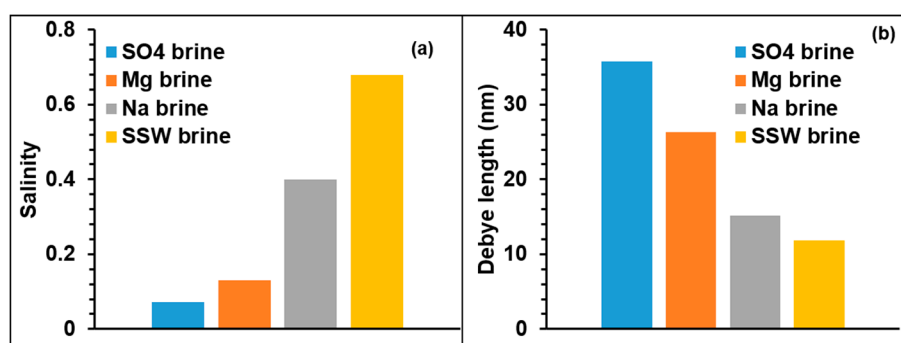


Figure 3. (a) Salinity for different brines; (b) Debye lengths for different brines.

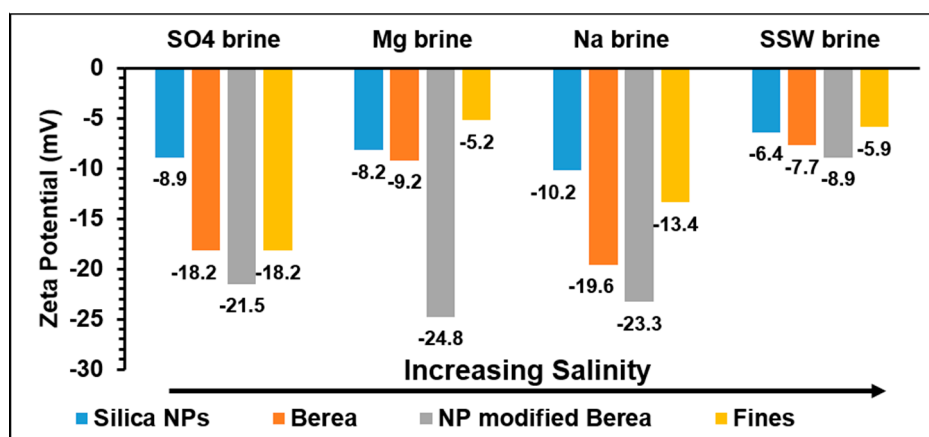


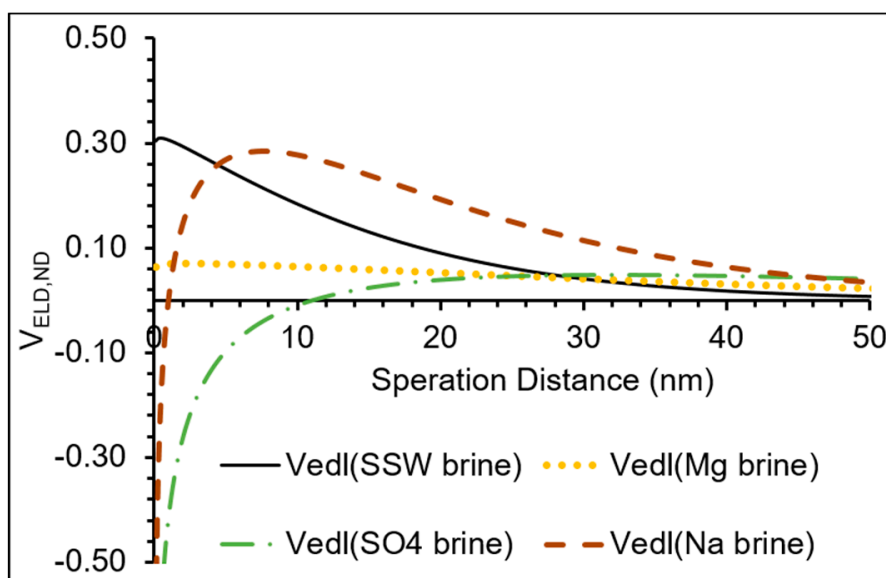
Figure 4. Zeta potential for the different fluids.

### 3.2. Double Layer Interaction

Based on the Debye lengths (Figure 3b), NPs’ sizes dispersed in different brines (Table 4) and the zeta potential (Figure 4), NPs–mineral surfaces double layer interactions were estimated by Equation (1). The results are shown in Figure 5.

Table 4. Particle size of the dispersed silica NPs.

Dispersing Fluid	Average Hydrodynamic Radius of the NPs (nm)
SSW	28.2
Na Brine	19.6
Mg Brine	19.4
SO <sub>4</sub> Brine	19.5



**Figure 5.** Double layer interactions for NPs/mineral surfaces in different brines.

Figure 5 shows that the interaction is mostly repulsive in the case of Na brine, while it is less repulsive in the case of the other brines. It is interesting to note that in the case of Mg brine, the double layer interaction remains almost constant at all the separation distances. This is difficult to explain, however it may have been caused by a homogenous fluid around the mineral (approximately 10 nm from mineral surface) which caused the diffused product of the exchange reaction between  $Mg^{2+}$  and the calcium in the carbonate (cementing material in Berea) hence reducing the potential difference around the minerals. This may also explain the highest adsorption in the case of the Mg brine where NPs in Mg brine diffuse into the minerals, where the exchange between  $Mg^{2+}/Ca^{2+}$  takes place, hence increasing the contact surface area between NPs and the silicate mineral surfaces.

Delays of NPs' breakthrough occurred at different time from the tracer's breakthrough indicating possible interactions with the minerals (Figure 2). In the case of Mg brine, there was a delay of approximately 0.5 PV (Figure 2a) for NPs' breakthrough to occur. A similar delay of NPs' breakthrough of 0.5 PV also occurred in the case of  $SO_4$  brine (Figure 2b). The next subsection addresses possible mechanisms of interaction for individual brines.

### 3.3. NPs/Mineral Interaction and Possible Mechanism(s)

This section addresses the interaction ion products and pH as a function of the stabilizing single ion brines to understand the mechanism(s) and the contribution of the different ions of the single ion brines in the interaction between NPs/mineral. It was decided, therefore, to exclude the multiple ion brines such as SSW, in this study. However, the multiple ion brines will be addressed in a different study. The effluent pH and ion concentration profiles for the floods are shown in Figures 6–9. All flooding with nanoparticles showed large reductions of  $K^+$  ion concentrations. This perhaps indicates less mineral dissolution, hence possible reduction of fine migration or formation damage (discussed in detail later).



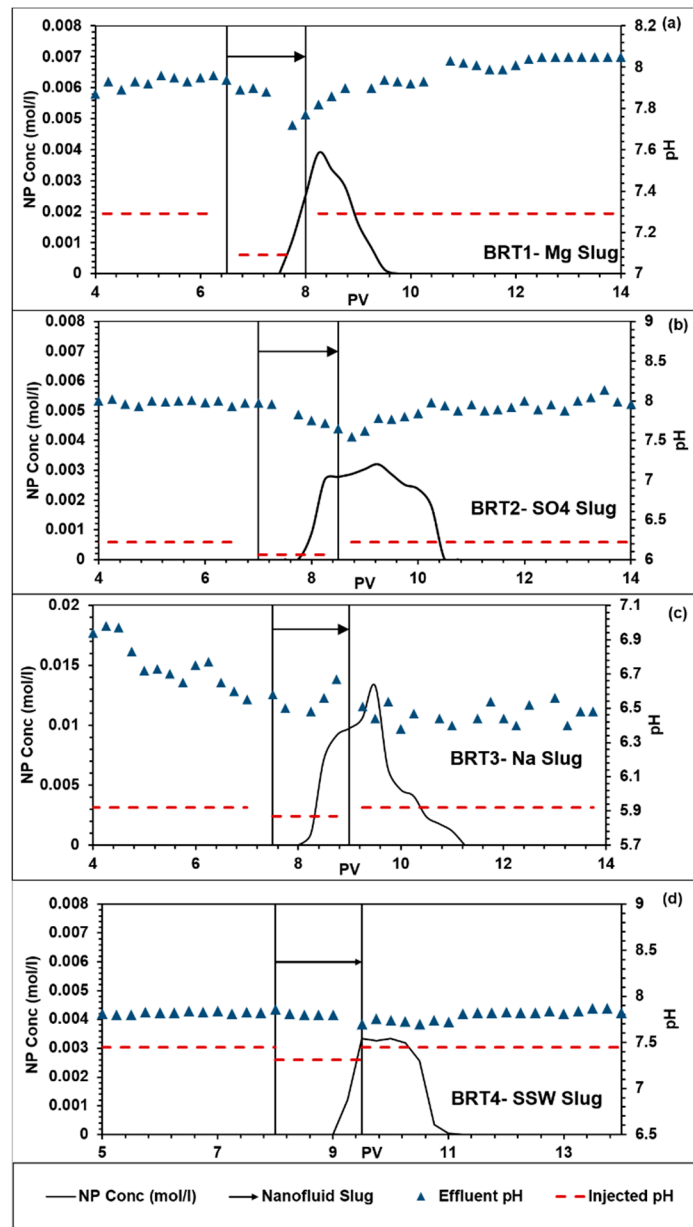


Figure 6. Effluent pH profiles for (a) BRT1; (b) BRT2; (c) BRT3; (d) BRT4.

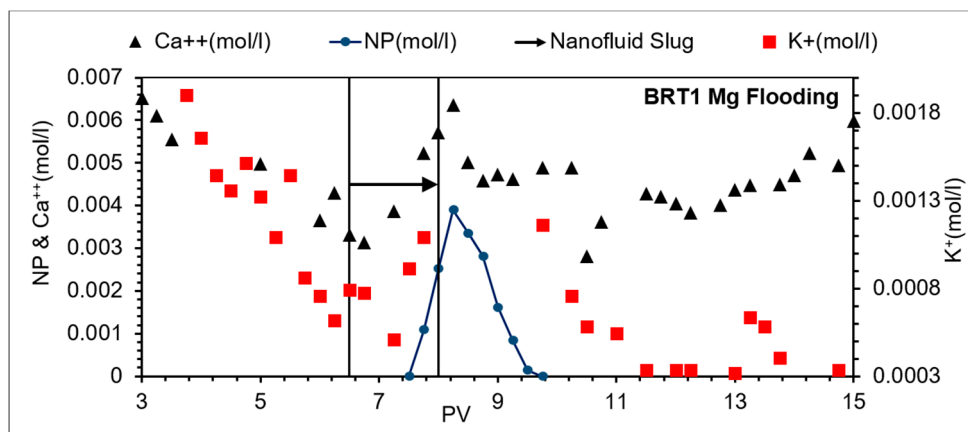


Figure 7. Effluent concentrations of NPs and ions for BRT1; Mg brine flooding.

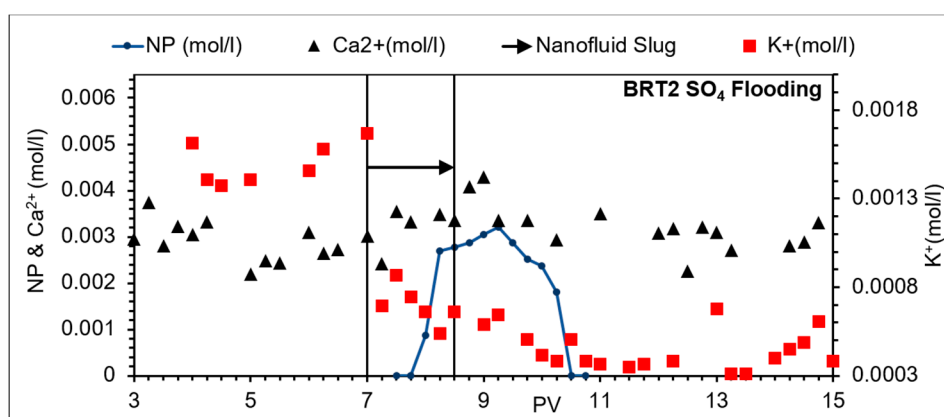


Figure 8. Effluent ion composition, BRT2; SO<sub>4</sub> brine flooding.

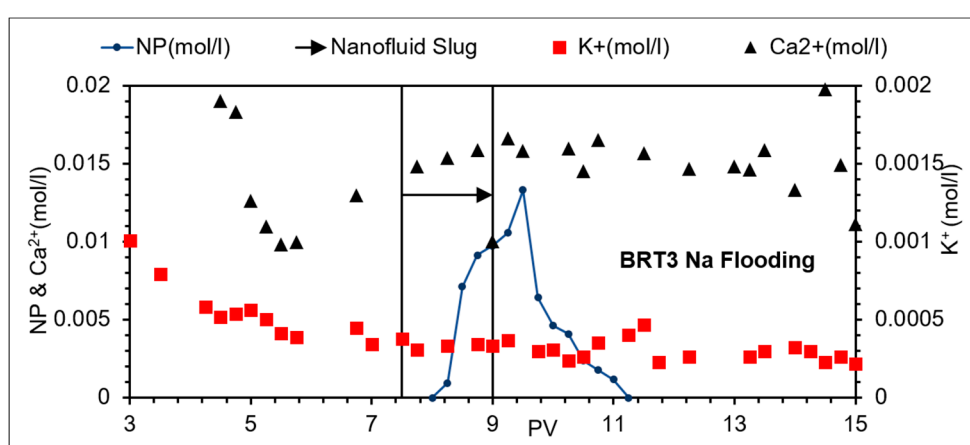
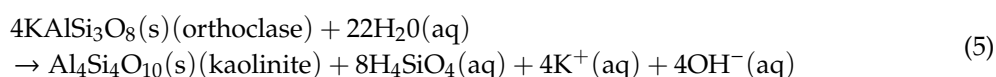


Figure 9. Effluent ion composition, BRT3 Na brine flooding.

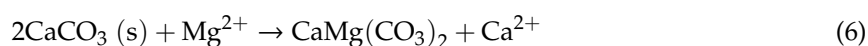
Figure 7 (Mg flooding) shows a higher concentration of K<sup>+</sup> in the effluent at the pre-flush stage of the flooding. There are two possible sources of K<sup>+</sup> ions: (1) production of residual K<sup>+</sup> from the initial core saturation fluid (SSW); and (2) production of K<sup>+</sup> from K-feldspar dissolution. Previous studies [38] suggested the following equation for the K-feldspar dissolution. This equation also explains the rise of the pH from all brines (Figure 6) excluding (Figure 6c) which is for Na brine (addressed in a later subsection).



### 3.3.1. MgCl<sub>2</sub> Brine

Using Mg brine as NPs' stabilizing fluid showed a delay of NPs breakthrough of about 0.5 PV relative to the tracer breakthrough (as mentioned above); lowest zeta potential with Berea's minerals; a constant double layer effect over a separation distance of about 40 nm; and pH before/after the NP slug being almost the same at approximately 8.0 (Figure 6a).

The effluent Ca<sup>2+</sup> (Figure 7) shows slightly higher average concentration (~0.005 mol/L) at the post-flush compared to about 0.004 mol/L prior to the slug, which may suggest an exchange reaction. The exchange reaction may lead to formation of dolomite or magnesian, depending on the Mg<sup>2+</sup>/Ca<sup>2+</sup> ratio. Since, Mg<sup>2+</sup> is constantly injected, it is difficult to relate the concentration ratio, therefore the exchange equation considered here is for the formation of dolomite, according to the following [39]:



The exchange reaction due to injection of Mg brine as a mechanism seems to explain the following observations: the highest adsorption and constant double layer for about 40 nm separation distance from the mineral surface (explanation is suggested in the previous subsection), and the higher concentration of calcium ions in the post-flush, which can be explained by Equation (6).

### 3.3.2. Na<sub>2</sub>SO<sub>4</sub> Brine

Observations of flooding with Na<sub>2</sub>SO<sub>4</sub> brine, as NPs stabilizing are as follows. A delayed NP breakthrough about 0.5 PV relative to the tracer breakthrough (indicating interaction between the NPs and mineral surfaces) was observed, and there was less repulsive double layer interaction than in the cases of other brines (Figure 5). The effluent had almost stable average pH at about 8 except within the slug window, where the pH value was reduced by about 0.5 (Figure 6b). There was an almost stable calcium concentration at about 0.003 mol/L (Figure 8). Zeta potentials for cation/minerals were more negative than that in the case of SO<sub>4</sub><sup>2-</sup> (Figure 4), opposite to what was expected.

Anions must be capable of accepting or donating protons to be adsorbed on minerals [40]. Sulphate adsorbs on kaolinite and releases OH<sup>-</sup> [41]. Researchers suggested that the change of the surface charge (negative charge) is neutralized by participation of neighboring Al ions resulting in ring formation [42].

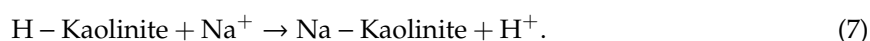
The suggested mechanism here is that SO<sub>4</sub><sup>2-</sup> ions adsorb on kaolinite and release OH<sup>-</sup>. These in turn increase the pH = 8 as observed in this work and keep it almost constant, since SO<sub>4</sub><sup>2-</sup> ions are injected. It partially reacts with Ca<sup>2+</sup> ions. Ca<sup>2+</sup> ions concentration remained almost same (0.003 mol/L) before and after the slug treatment.

As mentioned earlier that the zeta potentials of the cation/minerals are consistently and slightly more negative than that in the case of SO<sub>4</sub><sup>2-</sup>, which is opposite to what is expected. This actually agrees with the suggested mechanism where in the first step after adsorption of SO<sub>4</sub><sup>2-</sup>, a negative-charged compound is formed, which then is neutralized by the neighboring Al, resulting in ring formation [41].

### 3.3.3. NaCl Brine

While flooding with NaCl brine, NPs' breakthrough occurred at the same time and had almost the same shape as the tracer indicating minimum NP/mineral interaction (Figure 2c). The highest double layer repulsion was observed, relative to that for all the other brines (Figure 5). A declining of the average pH profile was also observed. The pH was approximately 7 in the pre-flush stage and was reduced to about 6.5 in the post-flush stage, however a slight increase in pH was observed in the slug window (Figure 6c). In contrast, other brines investigated here showed an increasing pH profile (apart from during the slug injection window (Figure 6)) to different degrees. Ca<sup>2+</sup> concentration, in general, showed a slight increasing trend from an average of about 0.001 mol/L to an average of approximately 0.002 mol/L (Figure 9), which may relate to the slight reduction of the pH.

The measured zeta potential of Na brine/minerals was more negative than that for other brines. Reid [43] and Hanna and Somasundaran [44] explained the source of the acidity. Clay minerals have exchangeable cations, so addition of NaCl follows this equation:



The released hydrogen ions are related to the ion exchange capacity of the clay minerals and this process is a fast one. This process changes the surface charge distribution, hence affecting the adsorption of material such as for example NPs. In the case of Na brine, the lowest adsorption of NPs (~34%) was observed. The two other observations that may support the exchange mechanism are the domination of the repulsive double layer (Figure 5) and highest negative zeta potential for NPs/Berea in presence of NaCl. In Figure 6, all floods except Na flooding show similar behavior: the pH stabilizes in the pre-flush region followed by a decline after nanofluid injection. Thereafter, the pH rises and then stabilizes in the post-flush region.

The results from this work help to identify the effect of major ions present in seawater on performance of NPs adsorption and mechanisms for NP/mineral interaction by selecting major constituents of seawater. Thus, this study improves the understanding of the influence of the individual ions on the NPs/mineral interaction and their mechanism(s). For each of the single salt brine, the salinity varied as shown in Figure 3. This study was performed at ambient conditions and may be considered as a first step of the influence of seawaters' major ions on NP interactions with the minerals in absence of oil. So, future work may consider this approach in presence of oil. This would enable studying oil recovery along with NP adsorption and NP/mineral interactions.

#### 4. Summary and Conclusions

This study investigated the effect of single salt brines,  $MgCl_2$ ,  $Na_2SO_4$  and  $NaCl$ , as stabilizing fluids which are the major ion constituents of SSW on silica NP performance. The results from this study show that:

1. All the used single salt brines showed reduced mineral dissolution, however to different degrees. This is related to the degree of adsorption on the minerals, where the highest were about 82% in the cases of  $Mg$  and  $SO_4$  single brines, compared to about 34% in the case of  $Na$  single brine. It is demonstrated that specific ions rather than brine ionic strength/salinity are the major influencing factor on adsorption of silica NPs on Berea mineral surface.
2. The possible mechanism for the influence of  $Mg^{2+}$  on the adsorption is due to renewing and increasing of the contacted surface area at the mineral surfaces by a possible exchange reaction between  $Ca^{2+}$  and  $Mg^{2+}$ . The mechanism in the case of  $SO_4^{2-}$  ions, is due to their adsorption on kaolinite and release of  $OH^-$ , which is followed by neutralization of the resulted negative charge by participation of neighboring  $Al$  ions resulting in ring formation, as suggested in the literature. This may also be supported by the increasing trends of the pH and the zeta potentials of the cations/minerals which are more negative than that in the case of  $SO_4$  brine. Another possible supporting point is that in the case of  $SO_4$  brine, the double layer interaction is less repulsive than those of the other brines.
3. Clay minerals have exchangeable cations so for the addition of sodium brine, an exchange between  $Na^+$  with  $H^+$  releases hydrogen ions. This process changes the surface charge distribution; hence affecting the adsorption of materials such as NPs. This is supported by that in the case of  $Na$  brine, the lowest adsorption of NPs (~34%) occurred. The two other observations that may support the exchange mechanism are the domination of the repulsive double layer (Figure 5) and that  $Na$  brine has the highest negative zeta potential, for NPs/Berea in presence of  $NaCl$  as stabilizing fluid.

The results from this study can aid in design of nanofluid flooding in sandstone reservoirs. The presence of  $Mg^{2+}$  and  $SO_4^{2-}$  ions in the brine used for preparing nanofluids may improve the adsorption of silica NPs injected into sandstone reservoirs for controlling formation damage.

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