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REVIEW

Effect of nanoparticles on clay swelling and migration

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KEYWORDS

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Swelling index;
Core flood;
Micro model

Abstract Clay migration/swelling has been widely documented as the main reason leading to oil recovery impairment. Interactions of clay particles with the medium surface in the presence of permeating fluid have been recognized as a critical parameter controlling the fate of clay particles. These interactions are strongly functions of the ionic strength of the permeating fluid. It is widely reported that reducing the salinity of the reservoir environment facilitates the challenges induced by clay particles. On the other hand, low salinity reservoir environment has been recognized as a very favorable condition for oil recovery. Accordingly, one should consider the positive effect of reducing salinity on oil recovery and its deteriorative effect on clay particles at the same time to improve oil recovery in a controlled formation damage mode. This experimental work aims to investigate the potential remedial effect of different metal oxide nanoparticles to treat clay swelling. Several core flood experiments and micro-model tests have been conducted to achieve the mentioned goal. Furthermore, swelling tests were quantified in terms of swelling indices to explain the effect of nanoparticles on clay swelling. We concluded that although nanoparticles can be used as a permanent stabilizer to prevent clay migration, they are not able to prevent clay swelling and may also increase the pressure drop due to fitting between clay crystals and blocking pores.
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1. Introduction

Formation damage mechanisms affect reservoir permeability especially in the near wellbore area and may happen during different operations such as drilling and production. It has been reported that approximately 97% of all petroleum reservoirs contain clay minerals and they are categorized into swelling and non-swelling groups [1]. Non-swelling clays such as kaolinite may migrate during water flooding because of repulsive forces between clays and pore walls and block pores in the reservoir, as schematically shown in Fig. 1a. Swelling clays such as montmorillonite may swell in contact with the invaded water up to 20 times the original volume, as shown in Fig. 1b, and may also migrate. Both these effects reduce porosity and permeability in the formation.

The reason for this special behavior of the clays is due to their unique structures. The crystal structure of swelling clays consists of Al–OH or Fe–OH or Mg–OH octahedral, sandwiched by two Si–O tetrahedral layers, as shown in Fig. 2. These layers are always deficient in positive charges because of cation substitution. Interlayer cations are required to balance the negative layer charges. When the exchangeable cations are hydrated during water injection and water molecules enter the space between the structure layers, the distance between the two layers increases leading to clay swelling. The swelling process comprises two main stages: the first stage is crystalline swelling, which is a reversible process; the second is osmotic swelling whereby the particles disperse and migrate with flow, and is an irreversible process, as shown in Fig. 3.

Three main mechanisms are used to reduce clay swelling which are ion exchange, coating of the clay particles by stabilizers, and modification of surface affinity toward water [2]. These methods can also be categorized into temporary and permanent remedies. Temporary clay stabilizer additives are materials that prevent swelling and migration of clays but are easily removed by the formation-produced fluids following the treatment. The most common temporary clay stabilizers are simple inorganic salts such as NaCl, KCl, ammonium chloride (NH_4Cl), and calcium chloride ($CaCl_2$). The most recent advances in clay stabilization have been focused on the area of permanent clay stabilizer additives. The most common permanent clay stabilizers are quaternary amine polymers. A monomolecular film of these polymers tightly binds with the clay surface by means of cation exchange and is not removed by the produced fluid [3]. Zhou (1995) divided clay stabilizers into different classes and described their advantages and disadvantages [4].

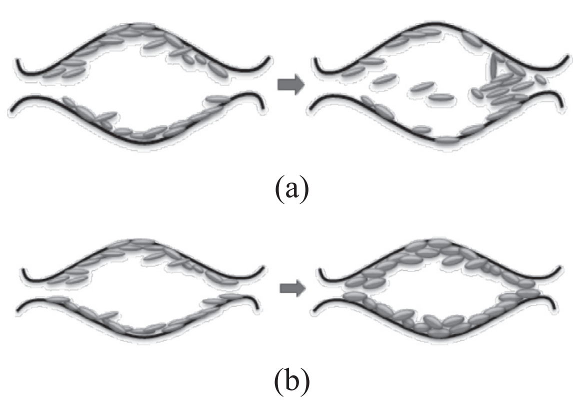


Figure 1 Schematic of formation damage by clay mechanisms: (a) migration; (b) swelling.

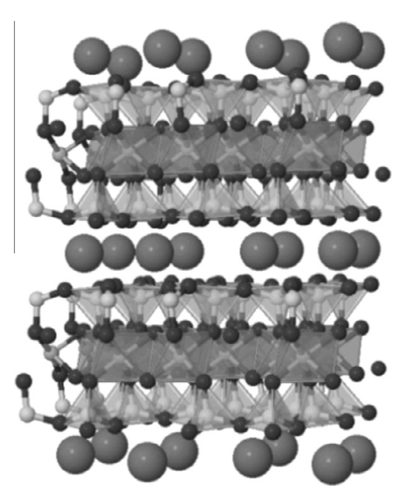


Figure 2 Schematic of clay structure.

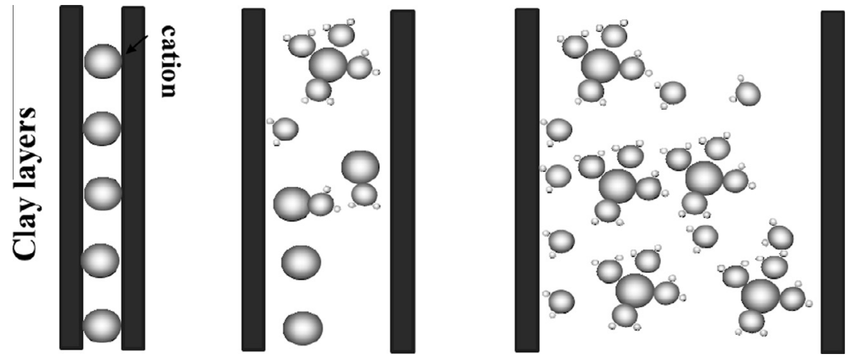


Figure 3 Swelling process.

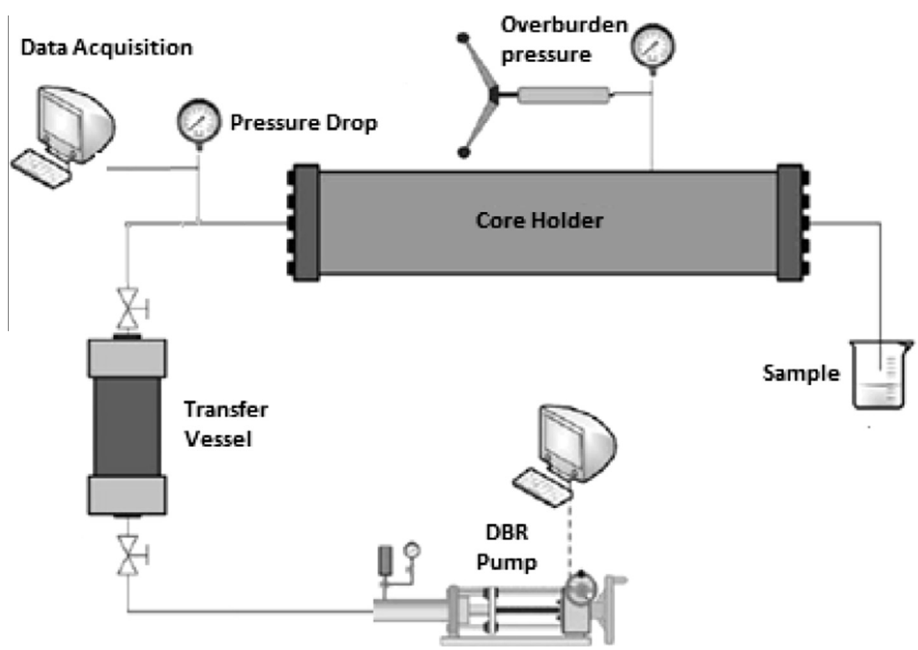


Figure 4 Schematic of core flooding set-up.

Nanoparticles have been recognized as very efficient agents to remedy the colloidal particles migration through the medium. Habibi et al. (2013) investigated the effects of various nanoparticles such as MgO, SiO_2 and Al_2O_3 on reduction of fines migration. They concluded that the MgO nanoparticle is an effective agent for controlling fines migration [5]. Ahmadi et al. (2011) studied the zeta potential effects on fine migration reduction [6]. Assef et al. (2013) extended the study to include the performance of nanoparticles in formation damage control under various PH and salinity conditions [7]. Recently, similar attempts have been made to control clay swelling with nanoparticles, with contradictory results. Sensoy et al. (2009) tried to use nanoparticles to control clay swelling during water invasion in drilling shale formations. They concluded that injection of nanoparticles could not directly solve the swelling problem and just increased the pressure drop due to pore plugging in the shale formation [8]. On the other hand, Huang (2011) studied the ability of nanoparticles to reduce clay swelling in proppant application during water flooding of cores and observed that nanoparticles reduce the pressure drop in cores [9]. Therefore, the basic question remains: "Can nanoparticles permanently reduce clay swelling and

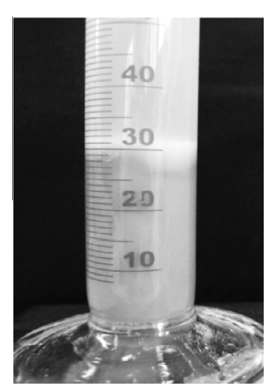


Figure 5 Swelling index.

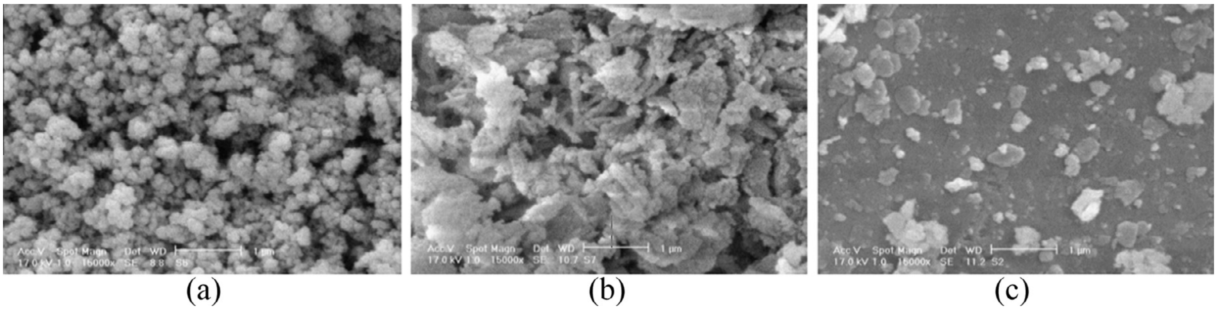


Figure 6 SEM from Nanoparticles: (a) SiO_2 (b) MgO (c) Al_2O_3.

migration?". In this work, we have applied different experimental approaches to answer this question.

In the first step, we did several water flooding tests in the core scale to study the pressure drops due to clay swelling and migration. Then we studied the effects of nanoparticles on damage caused by swelling and migration, and conducted core flooding tests. The effects of nanoparticles were also compared with those of other common stablizers. Micro-model experiments were performed to study different processes for recovering residual oil inside the porous medium during EOR or stimulation operations to study fluid flow in porous medium. We also did several tests in micro-model scale for better visualization of the process of fluid flow.

2. Materials and experiments

2.1. Core flood primary tests

This preliminary phase studied the effect of clay swelling and migration on pressure drop during injection. Results were the reference for our proposed method of remediation. In this experiment we made a synthetic porous medium from glass beads with US mesh size between 150 and 200 (74–90 μm). We also used experimental bentonite as clay (Density: 620 g/l, Swelling Volume: 10–15 cc). The porous medium was prepared with 90% glass beads and 10% by weight bentonite powder. The porous medium was well homogenized in a core holder measuring 3.81 cm in diameter and 11 cm in length. Then we applied 800 psi overburden pressure to the core. The flooding system is shown schematically in Fig. 4.

Table 1 Permeability results for different injections.

	Permeability (mD)
Fresh water	66
KCl	405
Nano fluid	57

2.2. Swelling index test

A series of swelling index tests were performed to study the performance of our approach to control the swelling of bentonite in comparison with other common methods. The swelling index test is a simple standard test (ASTM D5890-11), which is used to measure the swelling tendency of clays. To perform these tests, a 2 g sample of dry and finely ground bentonite clay was added to water in a 100 ml cylinder, as shown in Fig. 5. The sample was then covered and protected from disturbances for a period of 16–24 h. After the complete hydration and swelling of the clays, the increase in the mixture's volume was measured as an indicator of the swelling.

For studying the effect of nanoparticle treatment on the swelling mechanism of bentonite, three types of nanoparticles, MgO, SiO_2 and Al_2O_3 prepared from Nanoshell company, were selected because of their accessibility and previous studies regarding their effects on fines migration prevention [5]. SEM pictures of the used nanoparticles are shown in Fig. 6.

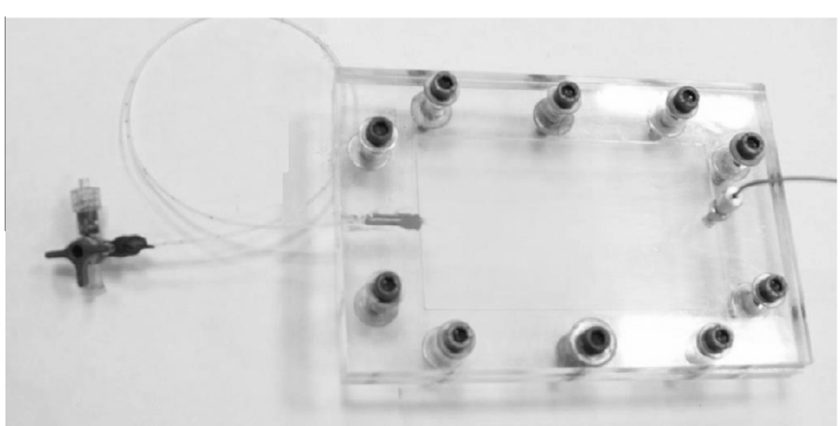


Figure 7 Micromodel set-up.

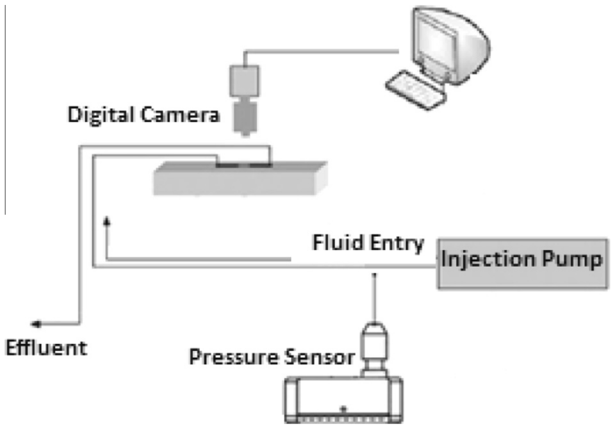


Figure 8 Schematic of the apparatus used in the experiments.

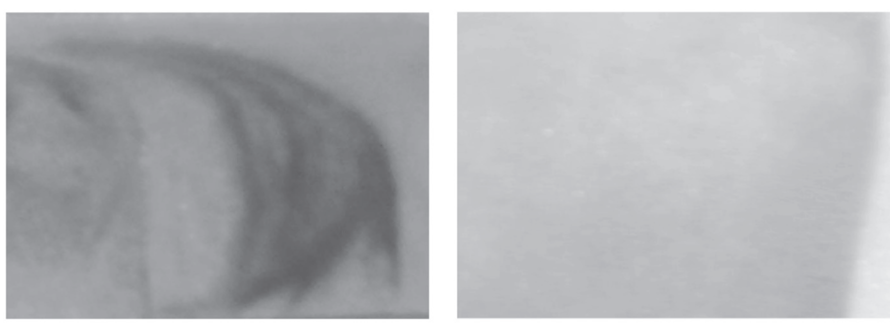
2.3. Final core flooding test

A core flooding test was designed to study both phenomena, swelling and migration simultaneously. The same synthetic porous medium with 10% clay and 90% glass beads with 150–200 US mesh and 30% porosity was prepared for the experiments. The glass bead and bentonite were mixed and well packed in the core holder system. First the porous media was vacuumed and then saturated by fluid injection. The materials including brine and nanofluid were flooded to the synthetic core. During each experiment the pressure drop along the core was measured.

2.4. Micromodel tests

In order to visually investigate the effect of nanoparticles, a low-pressure micromodel was prepared and used as shown in Fig. 7. All injection experiments were carried out at ambient temperature under a constant flow rate. The micromodel used in the experiments was constructed from two Plexiglass slides of roughly the same size. On both slides 10 holes were made to accommodate screws. Each slide's thickness was 10 mm and a Plexiglass plate with a thickness of 1 mm was used to fill the micromodel with glass beads.

Table 1 shows the permeability and porosity of the micromodel. In this table the properties of the micromodel are presented before various fluid floodings including water and stabilizers.



(a) (b)

Figure 9 (a) Improper clay distribution; (b) homogenized clay distribution.

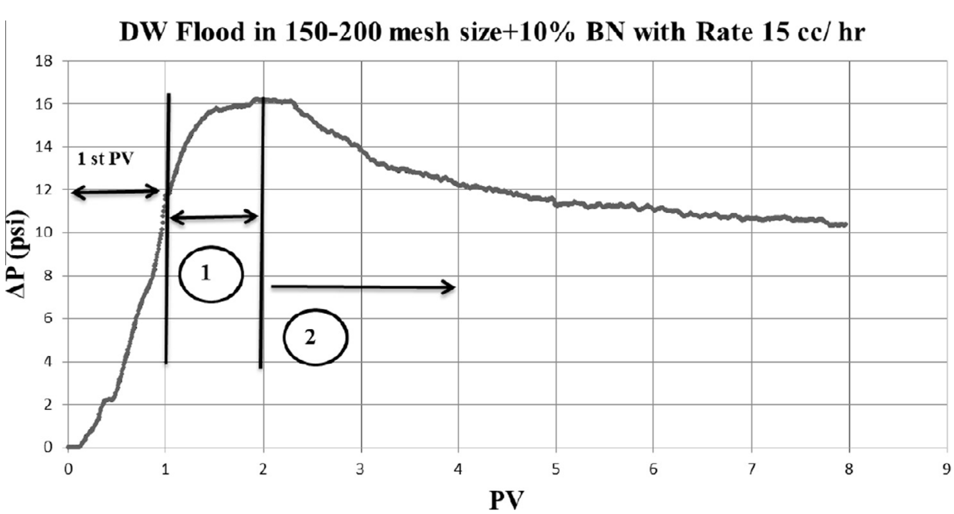


Figure 10 Pressure drop in porous medium during distilled water injection.

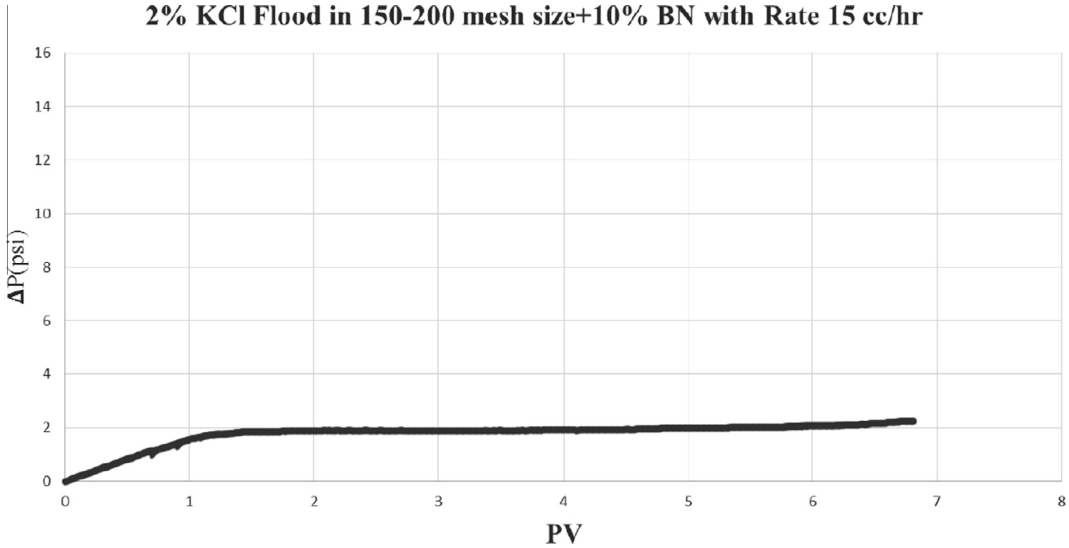


Figure 11 Pressure drop in porous medium during brine (2% KCl) injection.

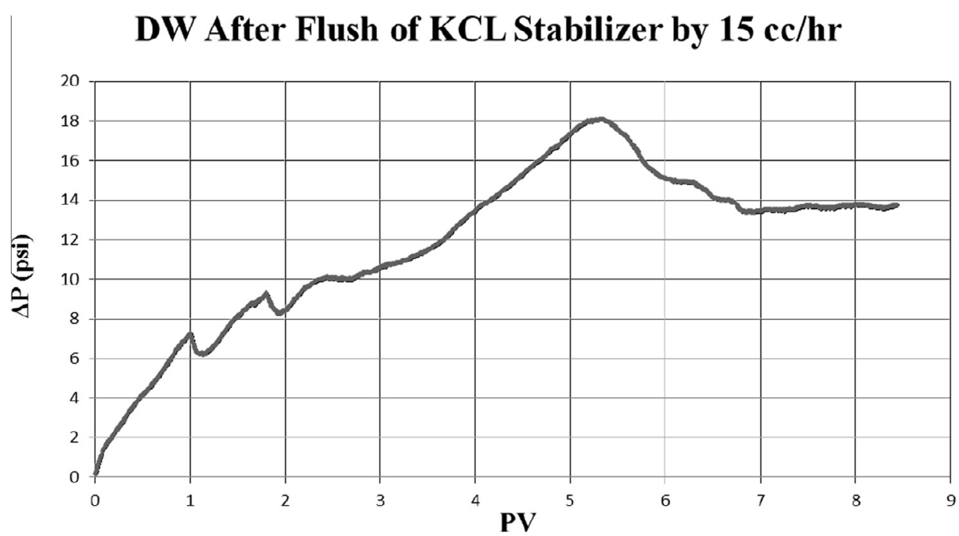


Figure 12 Pressure drop in porous medium during re-injection of distilled water.

Table 2 Swelling index test results.

Fluids	SI (ml/2 g bn)
Distilled water	32
2% KCl solution	8
0.1% SiO_2 suspension	32
0.1% MgO suspension	32
0.1% Al_2O_3 suspension	32

A schematic diagram of the experimental set-up is shown in Fig. 8. The micromodel set-up was composed of three parts comprising fluid injection section, micromodel and imaging system.

A Nexus 6000 syringe pump was used which can provide injection rates between 0.01 μl/min and 200 μl/min. Pictures from the top of the micromodel were taken while it was illuminated with UV light. Glass beads with a diameter of 0.4–0.59 mm were dry-mixed with 10 wt% bentonite clays and then packed into the micromodel. The clay should be quite homogeneous among the glass beads. Fig. 9a shows incorrect position of the clay in the micromodel and Fig. 9b shows a homogenized distribution. The micromodel was vacuumed prior to fluid injection.

Table 3 SI results for different types and concentrations of nanoparticles.

Fluids	SI	Fluids	SI	Fluids	SI
0.1% ZnO	33	0.1% TiO_2	35	0.01% Alumina (size 30 nm)	33
0.1% ZrO_2	32	0.01%TiO_2 + 5% LA	29	0.05% alumina	32
0.1% CeO_2	34	0.1% alumina + 0.4% SDBS	33	0.2% alumina	34
0.1% ZH	31	0.1% alumina + 0.5% CTAB	32	0.05% alumina (size 8 nm)	32

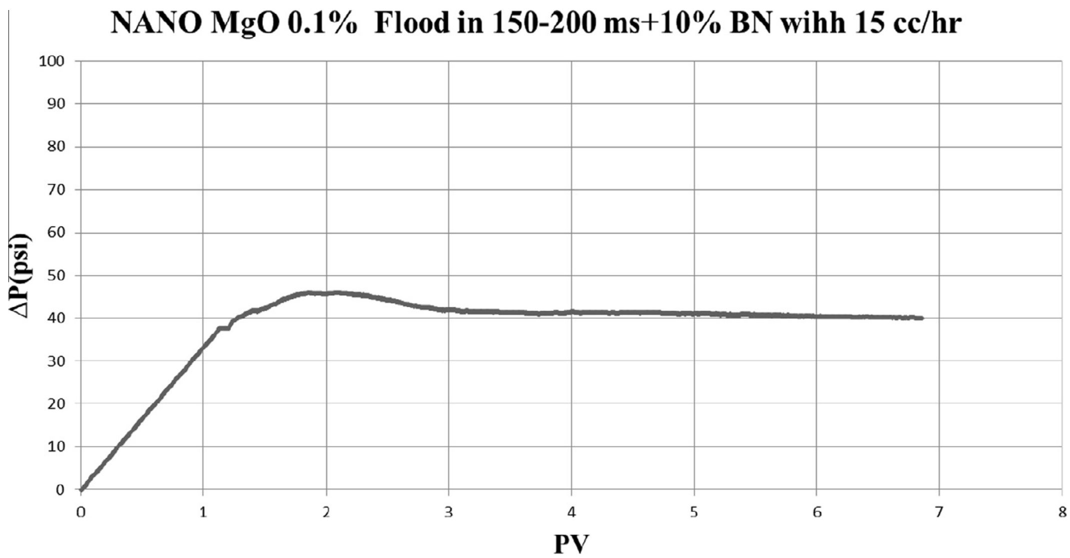


Figure 13 Pressure drop along the core during injection of water and 0.1% MgO nanoparticles.

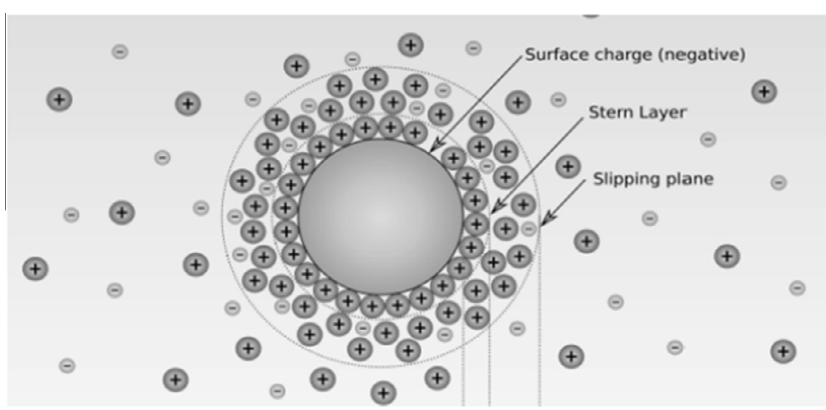


Figure 14 Radius of nanoparticle charge effect.

3. Results and discussions

3.1. Core flood primary tests

In the first test the prepared porous medium was flooded by distilled water at the rate of 15 cc/h. Fig. 10 shows the pressure drop across the core. Flooding was initiated by saturation of the core by vacuum. Due to swelling of clays in the presence of distilled water, the saturating procedure failed. Hence, first the porous media was vacuumed and then saturated by water injection.

Clay behavior can be divided into two sections. In the first stage, after one pore volume of injection, crystalline swelling occurs and the distance between bentonite plates increases which leads to a pressure drop. In the second part, osmosic swelling starts, the clay structure collapses and plates migrate through the porous medium. As the clays break through, the porosity starts to increase and the pressure drop decreases, as shown in Fig. 10.

In the second test, we measured the pressure drop in the core during flooding with 2% KCl brine solution as a temporary stabilizer at the rate of 15 cc/h. As shown in Fig. 11, the pressure drop reduced from 16 psi to 2 psi which means that the clay swelling is controlled by KCl. Similarly, we can observe two different behaviors of the clays similar to the first experiment that initially, a pressure drop hump occurs because of the clay swelling and then it stabilizes because of the migration of the clays out of the porous medium.

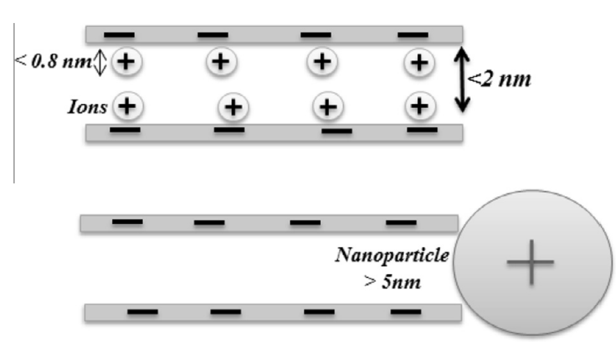


Figure 15 Schematic of clay crystals in contact with ions and nanoparticles.

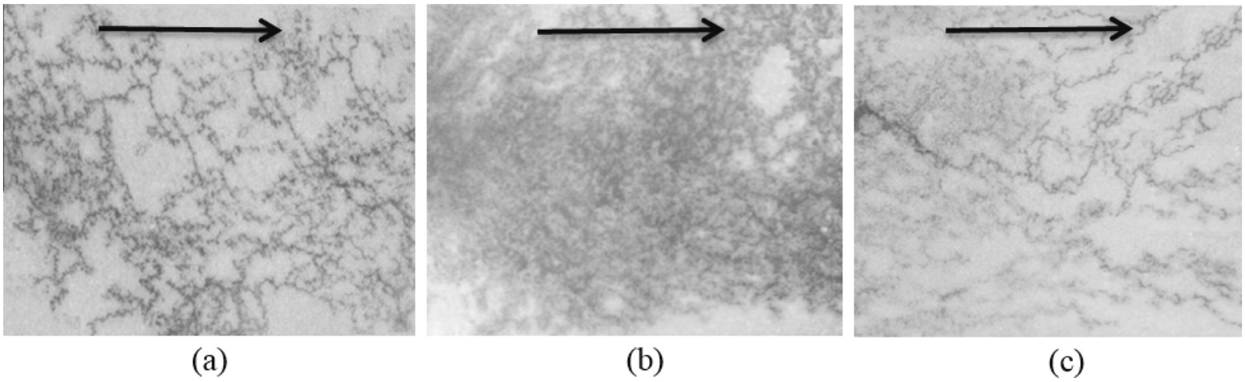


Figure 16 Paraffin injection in different conditions: (a) after distilled water injection, (b) after KCl injection, (c) after MgO nanofluid injection.

Fig. 12 shows the pressure drop measurements for the re-injection of distilled water after KCl flooding in the second experiment. This figure shows that the remedial action of KCl is temporary and clays are swelling again.

3.2. Swelling index test

In the first experiment, we measured the swelling index (SI) of bentonite (bn) in distilled water and in 2% KCl solution. These experiments were treated as a reference for comparison with the nanoparticle-treated cases. Table 2 shows SI results of these cases. As can be seen, adding KCl can control the swelling of bentonite.

As shown in Table 2, no remedial effect of this new approach was observed for the swollen clays.

We checked different nanoparticles at different concentrations and diameter sizes. Also, we tried to change the surfactant types used for nanofluid preparation. As shown in Table 3, none of them reduced swelling index (SI) in a noticeable manner.

Our preliminary experiments showed that nanoparticles are not able to prevent clay swelling at any concentration. As mentioned earlier, other research has shown that nanoparticles are effective in controlling fines migration during water movement but for the swelling we have not seen any noticeable effect.

3.3. Final core flooding test

From the basic tests we concluded that nanoparticles are unable to reduce swelling but they can stabilize the clay plates from migration and act as a permanent stabilizer.

Fig. 13 shows the pressure drop along the core during water and 0.1% MgO nanoparticle dispersed in water injection.

It can be seen that a pressure drop equal to 40 psi occurred along the core, which is much higher than the reference case in Fig. 10 which was about 16 psi. This excessive pressure drop reveals that although the nanoparticles reduce the clays' migration they are not effective at controlling formation damage caused by high clay swelling and pore-blocking. In formations containing swelling clays, injection of nanoparticles will increase the pressure drop due to the additional pluggings in pore throat spaces. Hence, this approach is not recommended as a remedial method to prevent formation damage caused by clay swelling.

Table 4 Porous medium properties.

Porous medium	US mesh size (30–40)
Permeability without clay (*D*)	8.37
Porosity without clay (%)	37
Permeability with clay (*D*)	2.8
Porosity with clay (%)	14

During the contact between low salinity water and clays, as the concentration of ions between clay sheets is higher than ion in the bulk, water molecules diffuse into the clay structure because of the osmotic pressure difference which causes clay swelling. Increasing the salinity can solve this problem, as it also increases the ion concentration in the whole bulk region. With nanoparticles, however, change in the charges did not happen in all sections of the bulk water: osmotic behavior occurred and clays started to swell. Fig. 14 shows this phenomenon schematically. The effects of the nanoparticles are noticeably very close to them. Hence, they cannot affect the fluid bulk.

Generally as shown in Fig. 15, after the swelling of the clays, the distance between the plates is less than 2 nm. Positive ions can enter between the sheets due to ions size and reduce the distance between them thanks to their charges but our experiments showed that this process does not happen during nanoparticle injection [10]. Nanoparticles are normally larger than 5 nm in size. Hence, nanoparticles cannot enter between the sheets to neutralize the negative charges between them.

3.4. Micromodel tests

The porous medium was injected with different fluids such as fresh water, 2% potassium chloride solution and 0.01% MgO nanofluid. After saturation with different fluids, paraffin was flushed through the micromodel to display its advance into the medium. Fig. 16 shows the open sections of the porous medium to the movement of paraffin. Hence, this figure shows clearly the sections which are blocked by clay swelling and migration.

The movement of the liquid paraffin into the micromodel pore spaces is clearly influenced by the presence of the clay. Porous media properties are shown in Table 4. Permeability in the presence of clay was measured by KCl injection. KCl is used to prevent clays swelling and migration. During the nanofluid injection due to the clays migration and pores plugging, the pressure drop along the core was not stable. Hence, it is not possible to measure the permeability in these cases. Fig. 16a shows the situation after the distilled water injection. It can be seen that the movement of the paraffin is limited and different sections of the porous media are damaged because of swollen clay. After injection of KCl according to Fig. 16b, it can be seen that the fluid flow in porous medium is more homogeneous and this treatment controls the swelling process. Fig. 16c shows the performance of the paraffin injection after treatment by nanofluids. Flow paths are limited and permeability reduces in all sections of the medium. This experiment proves that nanoparticles are not effective for controlling damage caused by clay swelling. Permeability in all three cases was measured and is shown in Table 4. Nanofluid injection decreases the permeability of the porous medium because of plugged pores.

4. Conclusions

This work aims to investigate nanoparticle treatment of clay swelling and/or migration. The following can be inferred based on the conducted measurements including swelling index test, segregation test, core flood test, and micromodel experiments:

1. The swelling index test proved that nanoparticles cannot prevent swelling. Nanoparticle suspensions do not act as a single phase fluid to diffuse between the clay crystals as salt solutions do. The size of the smallest nanoparticles is larger than the size of the largest ions and therefore they are not able to diffuse into the clay crystals.
2. Segregation tests showed that nanoparticles are effective as permanent stabilizers to prevent clay migration compared with salt solutions, which are temporary stabilizers.
3. Core flooding tests showed that the presence of nanoparticles cannot decrease the tendency to clay swelling. Hence, nanoparticles do not have positive effects in terms of remedying formation damage caused by clay swelling. Our observations support the findings of Sensoy et al. [8].
4. Nanofluid injection decreased the permeability of the porous medium due to plugging of the pores.

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References

[1] K.K. Mohan, R.N. Vaidya, M. Reed, H.S. Fogler, Colloids Surf. A Physicochem. Eng. Aspects 73 (1993) 237–254.
[2] A. Zaltoun, N. Berton, SPE Prod. Eng. 7 (2) (1992) 160–166.
[3] S. Berry, J. Boles, H. Brannon, B. Beall, Performance evaluation of ionic liquids as a clay stabilizer and shale inhibitor, in: SPE International Symposium and Exhibition on Formation Damage Control, 2008.
[4] Z. Zhou, W. Gunter, R. Jonasson, Controlling formation damage using clay stabilizers: a review, in: Annual Technical Meeting, 1995.
[5] A. Habibi, M. Ahmadi, P. Pourafshary, S. Ayatollahi, Y. Al-Wahaibi, SPE J. 18 (2) (2013) 309–318.
[6] M. Ahmadi, A. Habibi, P. Pourafshary, S. Ayatollahi, Zeta potential investigation and mathematical modeling of nanoparticles deposited on the rock surface to reduce fine migration, in: SPE Middle East Oil and Gas Show and Conference, 2011.
[7] S. Ayatollahi, Y. Assef, P. Pourafshary, Reduction of fine migration in different pH and salinity conditions using nanofluid, in: 10th SPE International Conference and Exhibition on European Formation Damage. 2013.
[8] T. Sensoy, M. Chenevert, M. Sharma, Minimizing water invasion in shales using nanoparticles, in: SPE Annual Technical Conference and Exhibition, 2009.
[9] T. Huang, Clay Stabilization with Nanoparticles, Patent Application publication, Pub No. US 2012/0178651 A1, 2011.
[10] Y. Lu, Study of property of cationic surfactant for preventing clay from swelling, in: International Meeting on Petroleum Engineering, 1988.