Formation Damage due to Colloidally Induced Fines Migration

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ABSTRACT

The in-situ release of fine particles in a porous medium resulting from changes in the colloidal character of fines induced by changes in the electrolytic condition of the permeating fluid and its effects on processes related to enhanced oil recovery (EOR) are examined. Experimental results show that high pH and low salinity cause fines to be released which, in turn, causes a drastic decline in the permeability of the medium. These results and other key experiments establish the interplay between salinity changes, cation exchange, and pH during a water shock, and elucidate the vital role of the ion-exchange process in formation damage. A physico-chemical model based on the fundamental principles of ion exchange and colloidal chemistry shows qualitative agreement with experimental observations. The results of this study will find use in various areas such as: bacteria migration in soils, failure of earthen embankments, and contaminant transport during ground water flow.

INTRODUCTION

A reduction in the permeability or hydraulic conductivity of a formation is of great concern in many oil field processes, and its control is necessary for the successful economic operation of oil and gas wells. This reduction in permeability is frequently referred to as formation damage in the petroleum industry. An overview of the various causes of formation damage and its effect on well productivity has been discussed by Krueger [1]. Although there are numerous causes for formation damage [1–4], changes in the ionic conditions of the permeating fluid are responsible for the majority of the cases. It has been observed that the flow of fresh (deionized water) or low salinity water through an initially brine-saturated Berea sandstone rock causes a drastic reduction in permeability of the sandstone. A typical result is shown in Fig. 1. The abrupt change in salinity which leads to this drastic decline in permeability is called a “water shock” and the phenomenon is called “water sensitivity”. Similar findings on a different sandstone are also reported in the literature [5]. Phe-
nomena such as migration of toxic waste from dump sites, failure of earthen embankments [26], etc., are also attributed to the process of fines migration [6]. Consequently the phenomenon of “water sensitivity” is of significant scientific and industrial importance.

A scanning electron microscope analysis of Berea sandstone samples after a water shock has shown that the permeability reduction occurs due to blockage of fluid paths by micron sized kaolinite clay [7]. In an undisturbed state, these clay particles (fines) line the pore walls of the sandstone surface. However, when they are brought in contact with low salinity water they detach from the surface. These released fines are then carried with the fluid flow and subsequently captured at pore throats or pore constrictions, causing formation damage. The phenomenon of water sensitivity (i.e., reduction in permeability during a water shock) has been explained by using the DLVO theory of lyophobic colloids [6–10]. The salt concentration below which such a drastic decline in permeability occurs is known as the critical salt concentration (c.s.c.) and is analogous to the critical flocculation concentration (c.f.c.) of the DLVO theory for colloids [7,8,26]. The phenomenon of adsorption and desorption of particles, subjected to colloidal and electrical forces, has been extensively studied both experimentally and theoretically [11–19]. While a review of the topic is beyond the scope of this paper, the important points to note here are that: (i) at certain ionic conditions of the permeating fluid the release of fines occurs; and (ii) the released fines can be captured downstream and cause catastrophic loss in the permeability of the porous medium.

Previous work in our laboratory and by other workers has focussed upon the effects of the salinity and pH of the permeating fluid on formation damage. Specifically, during fresh water flow displacing brine in an initially brine-saturated core, it was observed that: (1) a drastic decline in permeability was accompanied by a dramatic increase in the pH of the effluent fluid during a fresh water shock (Fig. 2); and (2) the permeability decline during a water shock can be minimized by lowering the pII of the injected fluid [8].
The sudden decrease in salinity from brine to fresh water not only caused formation damage, but also modified the pH of the permeating fluid, probably through an ion-exchange process involving surface cations ($\text{Na}^{+}$) and the protons in water [8]. It, therefore, became apparent that in a system containing exchangeable cations, the salinity and the pH of the medium can be expected to have correlative effects; effects that have not been previously considered. In other words, a salinity decrease causes increased double-layer repulsion between the wall and the particle. This repulsive force can be further compounded by the change in surface potentials of both the particle and the wall due to the increase in pH of the permeating fluid. Thus, it is critical to study the combined effects of salinity and pH and address them in tandem, and not separately as done previously [7–10].

In this study, we present a systematic investigation that encompasses the combined effects of pH and changes in salinity of the injection fluid. This work clearly elucidates the importance of ion exchange resulting in a change of pH of the permeating fluid and its effect on formation damage. A physico-chemical model has been developed that can explain all the current and past experimental observations with regard to the water sensitivity in a unified manner. It is anticipated that further predictive relationships can be easily determined by an extension of the model. Results of this study will have a significant impact in designing injection strategies for alkaline floods, drilling muds, and modelling contaminant transport during ground water flow.

BACKGROUND

The two important parameters that have been widely studied and which characterize the ionic conditions of the permeating fluid are: (i) pH; and (ii)
salinity (electrolyte concentration). If the permeating fluid has a mixture of ions, then their molar ratios and their valency also become important [9,20,21]. However, in this study we limit ourselves to a single (1:1) monovalent salt (NaCl). For a detailed review of earlier results, we refer the reader to the paper by Khilar and Fogler [6]. In this work we will discuss these earlier results briefly to aid in understanding the current results and to contrast these results with earlier published work.

(i) Effect of pH

First, it was found that when the pH of the injected fluid is below 2.6, no significant damage occurs in Berea sandstone during a water shock [8,22-24]. Second, it was observed that the pH of the effluent increased during a water shock [8]. This increase, which was much beyond the initial value*, occurred at the same time as the drastic reduction in permeability. No previous attempts have been made either to model this effluent pH transient or to analyze the effect of other parameters on this process (pH change). As we will show later, this result is of great importance and influences the magnitude of formation damage.

(ii) Effect of rate of salinity decrease

When the salinity of the injected fluid is reduced gradually, the resulting permeability reduction is marginal in comparison to that obtained due to a water shock [7,23,25]. This gradual change in salinity can be achieved by having a CSTR (continuous stirred tank reactor) upstream to the core. Such a configuration causes the salinity to decay exponentially with time, the rate being dependent on the time constant $\tau^{**}$ for the CSTR. A more detailed description of the experimental setup is available in Ref. [7]. It has been shown that there exists a “critical rate of salinity decrease” (CRSD), above which the damage due to a water shock is minimized or totally eliminated [7].

One explanation for the CRSD is that when the salinity is decreased gradually, the fines are released at a slower rate and, therefore, the concentration of fines in the flowing suspension is low. This lower concentration of the released fines in the suspension inhibits the “log-jam” of particles at the pore throats, allowing the particles to be transported through the core without being

*An increase of 2-3 pH units, corresponding to a 100-1000 fold decrease in H⁺ concentration, is observed.

**The time constant, $\tau$, is called the mean residence time and is equal to $V/Q$, where $V$ is the volume of the CSTR and $Q$ is the volumetric flow rate through the CSTR.
captured (also referred to as piping, [26]) thereby reducing the extent of damage.

Mungan [23] reported similar interesting results on permeability reduction during gradual salinity decrease. Mungan did not observe any decline in permeability at a salt concentration of 1 ppm when the salinity was achieved by reducing it gradually from 30 000 ppm. The experiment on the same core was further continued, by first re-sensitizing the core by flowing 30 000 ppm brine. Next, the fluid flowing through this core was suddenly switched to 1 ppm brine (essentially a water shock) whereby a drastic reduction in the permeability similar to the one shown in Fig. 1 occurred.

If only the final ionic conditions had been important then we should not have seen any damage when the core was reflushed with 1 ppm brine. This result of Mungan deviates from the wash-out hypothesis proposed by Khilar et al. [27]. Neither Mungan nor Khilar considered the effect of ion exchange between adsorbed Na+ ions and the protons (H+) in solution. However, the model proposed in this paper can predict and satisfactorily explain the above conflicting observations.

MATERIALS AND METHODS

In the following section we describe experiments which give new insight to the phenomenon of water sensitivity. Besides gaining an in-depth understanding of the phenomenon of water sensitivity due to colloidally induced fines migration, these experiments also establish the validity of the proposed Na+/H+ exchange model.

Experimental setup and procedure

The schematic of the experimental setup in Fig. 3 shows the arrangement of constant displacement pumps (FDS-210 from Core Labs and Programmable 116 from Beckmann), a 2 ft long Hassler core holder, a flow-through pH electrode, a flow-through conductivity cell, digital pressure measuring devices, and a data acquisition system (linked to an IBM-PC). The following experimental procedure was usually adopted for the experiments. A Berea sandstone sample (1" diameter and 2" long) was vacuum saturated in 0.51 M NaCl (or other salt) solution and placed in the core holder. The permeating fluid (0.51 M brine) is injected through the core at a constant flow rate. The fluid passes through a 0.22 μm filter to remove suspended solids before injection into the core. Next an acidified brine solution (pH ~ 2-3, and 1 M NaCl) is injected to remove most of the carbonates (e.g., calcite). After this pretreatment, the core is subjected to a flow of more than 150 pore volumes of 0.51 M NaCl at near neutral pH to restore the core to a sodium saturated state. This brine-saturated core will be referred to as the brine-conditioned core.
Two sets of experiments were performed. In one set, the pH of the solution was increased in steps and in the other set of experiments the salinity (sodium chloride concentration) is reduced gradually. The ionic condition (pH and salinity) of the fluid injected into the core could be changed gradually by continuously adding small amounts of a different fluid into the stirred tank (CSTR), which is placed upstream of the core.

The permeability of the core was measured by monitoring the pressure drop across the core at a constant injection flow rate. The permeability ratio $K/K_0$, at any time can be computed easily from Darcy's law. At a constant flow rate, an increase in pressure drop would imply a decrease in permeability (or hydraulic conductivity).

RESULTS

**Effect of injection pH**

*(i) Step changes in injection pH*

The pH of distilled water used for these sets of experiments was adjusted by using HCl for pH values below 7, and NaOH for pH values above 7. When the brine-conditioned core is exposed to fresh water at pH 2.0 (zero NaCl concentration), no decline in permeability is observed, which is in agreement with the results of Kia et al. [8]. However, when we continued to increase the pH of the injected fluid in step increments with no salt present, a surprising result
was observed as is shown in Fig. 4. Although there was no appreciable change in pressure drop until a pH of 9.0, at a pH greater than 11.0, a rapid and drastic increase in the pressure drop similar to that for a water shock was observed. This implies that severe damage is caused on contact with the high pH fluid when no salt is present. Data from other similar experiments show comparable results.

To study the effect of other cations, other alkaline solutions such as KOH, NH$_4$OH and Ca(OH)$_2$ were also used to change the pH of the injected fluid. Results of these experiments are summarized in Table 1. Both K$^+$ and NH$_4^+$ showed results similar to those obtained for Na$^+$. However, when Ca$^{2+}$ was used, no damage occurred even at pH values greater than 12 (Fig. 5). To be sure that the core was still susceptible to damage, the core was resensitized by flowing 1.0 M NaCl solution and subjected to a fresh water shock. As can be observed from Fig. 5, there was indeed a drastic reduction in permeability during fresh water flow. The zeta potential measurements, which are described later, will enable us to interpret and understand the above results, especially the result that no damage was observed when Ca$^{2+}$ was used.

\(\text{(ii) Continuous changes in injection pH}\)

In another experiment, the brine-conditioned core was subjected to fresh water flow at pH ~ 2.0, and the pH was increased gradually and continuously.
from this value. This was achieved by adding continuously a pH 12 solution to
the feed solution which is initially at pH 2. Figure 6 shows the permeability
response, and again, drastic and rapid changes in pressure drop indicating
damage commences around an inlet pH of 11. This result is consistent with
the results in Fig. 5.

We also observe in this figure that the breakthrough of the pH front lags the
inlet pH by approximately 20–22 pore volumes. Such delays in the break-
through of alkaline fronts have been observed during alkaline flooding [33].
An order of magnitude estimate for the cation exchange capacity for the sand-
stone may be evaluated from such a curve. Such an estimation gives a value of
1.2 meq/100 g of sandstone*, which though slightly high, is in the range of
values reported for Berea sandstone [34].

*The median of the effluent curve is approximately 18 pore volumes and the exchange capacity
based on the median is 1.0 meq/100 g.
Our results (Figs 4 and 6 and Table 1) indicate that the permeability is unaffected by flow of fresh water at near neutral pH, and that the conditions of high pH and low salinity are required to cause drastic and significant damage in Berea sandstone. At first glance, our results seem to differ from those which show drastic permeability changes during a water shock, even though the injection pH is near neutral [7,8]. However, a detailed inspection of the results of a water shock (Fig. 2) can easily resolve the paradox.

In our experiments (Table 1) the high pH is externally imposed by changing the pH of the injection fluid, while during a water shock the high pH is generated in situ (see Fig. 2, the effluent pH increases to 10.4). Therefore, during a water shock we have the presence of both low salinity and a high pH, and these conditions lead to a drastic decline in permeability. Thus, the ionic conditions in the core during a water shock are no different than those in our experiments (Table 1), satisfactorily explaining the paradox between them.

Results of CRSD experiments

Salinity decrease experiments similar to those of Khilar et al. [7,27] were carried out with a slight modification in the procedure. The experiments were performed in two stages. In the first stage, the salinity was reduced gradually by using a CSTR until the salt concentration had decreased significantly below the c.s.c. (i.e., < 500 ppm, or $9 \times 10^{-3} M$) [7,8]. Then (second stage) the salinity is changed abruptly by switching the flow to fresh water. The results of typical experiments are shown in Fig. 7.

In this experiment, the injection fluid was switched to fresh water (DDI water) when the salt concentration of the permeating solution was approximately $10^{-4} M$ (which is two orders of magnitude lower than the reported

![Fig. 7. Permeability changes during CRSD followed by a water shock (NaCl concentration before switch $\sim 7.6 \times 10^{-5} M$).](image-url)
Note, that during the gradual decrease in salinity the pH of the effluent does not show a significant increase (i.e., pH remains below 9.0) which is in contrast to the results of a fresh water shock (pH increased beyond 10.3). Since there is no significant increase in pH in this case, no drastic reduction in permeability occurs during this time period. Further, during the second stage, i.e., switching the injection fluid to fresh water, only a marginal decline in permeability occurs, which is in phase with the small increase in effluent pH.

Similar experimental results for the second stage, in which the switch to fresh water is carried out at initial salt concentrations of $10^{-3}$ and $3 \times 10^{-5}$ M, are summarized in Table 2. When the salinity of the initially flowing brine is $10^{-3}$ M, the change in permeability is drastic during the water shock, while when the salinity of the initially permeating brine was $3 \times 10^{-5}$ M there is no change in permeability during the water shock. These results indicate: (i) the reduction in permeability can be minimized by gradually decreasing the injection salinity; and (ii) that the magnitude of the reduction in permeability is dependent on the salinity of the brine permeating before the switch to fresh water. This dependency holds even though the salinity of the permeating brine was much below the c.s.c.

**DISCUSSION AND ANALYSIS OF RESULTS**

To analyze our results we will first focus our attention on the cation exchange process between the adsorbed sodium ions and the ions in solution and the resulting effect on colloidally induced fines migration. During the fresh water shock of an initially brine (NaCl) saturated core, there is an exchange between the adsorbed Na$^+$ and the H$^+$ ions in solution. This exchange and the constraint imposed by the equilibrium relationship for the dissociation of water, results in an increase of the OH$^-$ ion concentration in the bulk solution phase, as has been experimentally observed from the analysis of the effluent pH (Fig. 2).

**TABLE 2**

Summary of results for water shock experiments at various initial brine salinities

<table>
<thead>
<tr>
<th>Concentration of salt before switch to DDI</th>
<th>Permeability change $(AK/K_0)^b$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$(\text{after switch} - \text{before switch})/\text{before switch}$</td>
<td></td>
</tr>
<tr>
<td>$1.0 \times 10^{-3}$</td>
<td>$-0.95$</td>
<td>drastic reduction</td>
</tr>
<tr>
<td>$7.6 \times 10^{-5}$</td>
<td>$-0.16$</td>
<td>marginal reduction</td>
</tr>
<tr>
<td>$3.0 \times 10^{-5}$</td>
<td>$0$</td>
<td>no reduction</td>
</tr>
</tbody>
</table>

$^a$DDI refers to fresh water.

$^b$ $K_0$ refers to initial permeability before switching to fresh water.
To learn the consequences and ramifications of this pH transient, we now focus our attention on the surface potential as a function of the pH of the suspension. For mineral oxides it is known that $H^+$ and $OH^-$ are the potential determining ions and, therefore, pH will have a significant influence on the surface potentials. The zeta potential of kaolinite*, which may be considered to correspond to the surface potential, is shown as a function of pH in Fig. 8. One observes that as the pH increases the zeta potential becomes increasingly negative, in qualitative agreement with other published results [28–30]. This is true in the presence of $Na^-$, $K^+$, and $NH_4^+$ cations. However, for $Ca^{2+}$ ions the zeta potentials remain fairly low even at high pH, most likely due to the fact that calcium is a divalent ion and can exhibit specific binding to clay surfaces.

Based on the above mechanism for ion exchange and using the principles of colloid chemistry, we can now easily explain all our observations. We shall start with the results shown in Fig. 4. When the brine-saturated core is flushed with pH 2 solution, the usual ion exchange between adsorbed $Na^+$ and $H^+$ takes place. However, the excess of $H^+$ prevents the solution from becoming highly alkaline during the exchange. Since the pH remains low during and after the exchange, the surface potential remains low. Thus, fines release does not occur, avoiding damage.

When the pH of the injection fluid is now increased above 2, there is no adsorbed sodium to exchange, consequently the alkalinity of the permeating solution will not increase beyond the injection value. Although the surface potentials increase with pH they are still low, and hence, no significant damage is observed. Finally, when the injection pH reaches a high value, the surface

![Fig. 8. Zeta potential measurements on kaolinite as a function of pH.](image)

*It is recognized that the measured zeta potential of kaolinite reflects the combined value for the surface and edge potentials. Since the purpose of the measurement here is to illustrate the changes in average total interaction between two surfaces under different colloidal conditions, the zeta potential measurements may be considered to be adequate and satisfactory.
potentials of the Berea sandstone and the fines become highly negative. This change in the surface potentials produces a significant repulsive force causing colloidally induced detachment of fines, ultimately leading to catastrophic reduction in permeability. An interesting discussion on the role of surface chemistry on particle release and deposition can also be found in the paper by Prieve and Ruckenstein [31].

Figure 9 shows the total interaction potential for two equipotential surfaces ($\psi_1 = \psi_2$). Here the total potential is the sum of van der Waals attractive potential, the Born repulsive potential, and the double-layer repulsive potential [13,14]. The hydrodynamic potential can be neglected since it is only important at high velocities or for very large particles [7,32]. A Hamaker constant of $2.4 \cdot 10^{-13}$ ergs, which is comparable to the value of $2.6 \cdot 10^{-13}$ of Khilar [7] was used for these computations. One observes from Fig. 9 that the interaction potential becomes increasingly repulsive with an increase in pH owing to the change in surface (zeta) potential. The DLVO analysis also predicts that at pH 11 both the total interaction potential and the force at the primary minimum are zero, conditions which favor the release of particles*. Thus, at this high pH, drastic reduction in permeability occurs. For Ca(OH)$_2$, the zeta po-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{interaction_potential.png}
\caption{Plot of interaction potential versus distance of separation at various pH.}
\end{figure}

*The result reveals that instantaneous and significant release of fines occurs when a critical or a threshold surface potential is achieved, approximately $-39$ mV in our case. In the case of Na$^+$ and K$^+$ this occurs around pH 11, while for NH$_4^+$ it occurs around pH 10 (Fig. 8). Thus the above predictions are in agreement with the results in Table 1.
tentials were low (0 to -20 mV), even at high pH. As a result, the particles remain in a state of attraction with the wall. Therefore, no release of fines occurs and damage is eliminated.

In the case of the CRSD experiments where the salinity is reduced gradually, the exchange between adsorbed $\text{Na}^+$ and $\text{H}^+$ occurs over a large number of pore volumes of fluid ($\sim 500-1000$). The salinity changes experienced by the core are small and, therefore, the change in pH of the permeating fluid is small and gradual. Since the pH never increases significantly to reach high values (cf. Fig. 7), the release of fines is minimal as is the reduction in permeability.

The above discussion can be extended to explain the results of Mungan [23]. During the initial gradual salinity decrease from 30 000 ppm to 1 ppm no damage was observed, since the pH change is not significant. However, when the core was resensitized with 30 000 ppm NaCl ($0.51 \text{ M}$) solution and subjected to a water shock (1 ppm NaCl), a significant pH increase is generated to cause the surface potentials to become highly negative and release the particles of the wall. Therefore, during this step a significant reduction in permeability is expected, as was observed by Mungan. Thus, we have explained the results of Mungan and the reason for the deviation from the results of Khilar et al. [27].

From all the above results we conclude that the drastic reduction in permeability during a water shock occurs, not only due to the decrease in salinity alone, but is further compounded by the presence of high pH during the water shock. It also implies that the damage can be minimized if the salinity can be lowered without allowing the pH to increase.

Further evidence and verification that low salinity and high pH are responsible for the drastic reduction in permeability was demonstrated with the following experiment. The cation concentration (hence salinity) is decreased by a water shock without allowing the effluent pH to change (i.e., increase). This experiment enables us to measure permeability changes associated with sal-

Fig. 10. Water shock in the presence of a buffer (boric acid).
inity changes alone. A constant pH was achieved by adding a buffer to water during the water shock. The idea here is that the H\(^+\) required for the exchange is provided by the dissociation of the buffer. The core is first exposed to a 0.2 M NaCl solution and later shocked with water containing boric acid (solution pH ~ 6.0)*. The effluent pH and the pressure drop did not show any significant change during this stage. This clearly indicates that the salinity change by itself does not produce a drastic reduction in permeability. The experiment was further continued, and the injection fluid was switched to distilled water at pH ~ 12.0 (adjusted using NaOH). As can be seen from Fig. 10, a drastic increase in pressure drop (hence a reduction in permeability) was observed at this time.

This result is consistent with the hypothesis and the mechanism for initiation of formation damage proposed in this paper, viz. a salinity reduction induces a pH increase which amplifies the release of fines and leads to a drastic reduction in permeability. In a subsequent publication we will present a quantitative mathematical model, incorporating ion exchange, mass transfer kinetics, dispersion and convective transport, to predict the observations of salinity changes and its influence on the pH of the permeating fluid.

SUMMARY AND CONCLUSIONS

The drastic decline in permeability \((K/K_0 \sim 0.01)\) can be caused by a combination of salinity and pH changes. An abrupt decrease in salt concentration, even if the salt concentration before the change is below the c.s.c., can cause significant damage. However, the extent of damage will be dependent upon the magnitude of salinity change, the salinity of the permeating fluid, and the electro-kinetic properties under these conditions.

1. Low salinity and high pH can cause a significant amount of fines to be released leading to drastic formation damage.

2. A model describing the ion-exchange process shows agreement with the experimental data. It also implies that the mechanism and the degree of damage due to a fresh water shock may be vastly different than the damage due to a gradual decrease in salinity.

3. Although previous work focused on salinity and pH independently, it was conclusively shown here that a salinity change through the process of ion exchange influences the pH. Hence, these parameters should be addressed simultaneously when developing a model for formation damage or when designing injection strategies to minimize damage.

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* Using \(5.26 \cdot 10^{-10}\) [35] as the dissociation constant for boric acid, gives a concentration of \(1.73 \cdot 10^{-3} \) M.
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