Colloidally-induced fines release in porous media

Kartic C. Khilar¹, R.N. Vaidya² and H.S. Fogler²,³

¹Department of Chemical Engineering, Indian Institute of Technology, Bombay Powai, Bombay, 400 076 (India)
²Department of Chemical Engineering, The University of Michigan, Ann Arbor, Michigan 48109-2136 (U.S.A.)

(Accepted after revision June 9, 1989)

ABSTRACT


A critical value of the total ionic strength (CTIS) has been found to exist for mixed salt solutions flowing in porous media. If the ionic strength drops below this value, significant amounts of fines are released in-situ due to colloidal forces, causing drastic formation damage. For a NaCl/CaCl₂ system, the CTIS is strongly dependent on the relative amount of CaCl₂ present in the solution. The concept of a critical salt concentration (CSC) and the analysis based on DLVO theory has been extended to mixed salt systems to estimate the CTIS. The difference between critical flocculation concentration (CFC), and the present definition of CTIS has been pointed out. Predictions of this analysis are consistent with experimental observations.

Introduction

Colloidally-induced release and migration in porous media is important in numerous processes such as enhanced oil recovery, migration of organic waste from landfills, regeneration of filter beds, and erosion of earthen embankments (Khilar and Fogler, 1984, 1987; Khilar et al., 1985). The phenomenon of colloidally-induced fines migration is of significant importance in the petroleum industry as these released fines can migrate and plug regions in the formation causing damage and hence reduction in production. A number of studies using single salt systems (NaCl, KCl, etc.) have conclusively shown that colloidally-induced fines release is a threshold type of process that can occur when the salt concentration of the flowing solution decreases below a threshold (or a critical) value known as critical salt concentration (CSC) (Quirk and Schofield, 1955; Rowell et al., 1969; Hardcastle and Mitchell, 1974; Kolakowski and Matijevic, 1979; Khilar and Fogler, 1984). The latest of these studies has addressed the concept of critical salt concentration in detail and an experimental method has also been proposed to determine CSC for fines migration in Berea sandstone (Khilar and Fogler, 1984). The migrating fines in Berea sandstone were found predominantly to be kaolinite clay. In addition, an analysis has been formulated delineating the effects of flowrate, pH, temperature and, charge and size of cation on CSC in a single salt system. This analysis is based on DLVO theory of stability of lyphobic colloids and the CSC is analogous to the critical flocculation concentration (CFC) in colloid sol stability (Hiemenz, 1986).

Studies have been reported on colloidally-induced fines migration with a mixed salt system of NaCl/CaCl₂ (Quirk and Schofield, 1955; Jones, 1964; Kia et al., 1987b). These studies primarily emphasize the importance of
the presence of a minimum amount of Ca\(^{2+}\) ions in solution or on the surface of the fines (clay) to prevent their release and migration. Quirk and Schofield (1955) have observed that soil permeability decreases due to the clay swelling* and dispersion when the concentration of Ca\(^{2+}\) ions in the mixed salt solution decreases below a threshold value of \(2.5 \times 10^{-4}\) M. Their data showed that this threshold value is independent of the concentration of Na\(^+\) in the solution; which is rather unconvincing. Recent work of Kia et al. (1987b) focuses on the amount of Ca\(^{2+}\) ion on the surface rather than that in the bulk solution. This is a more reasonable approach, because the amount of Ca\(^{2+}\) ions on the surface of the fines determines the zeta potential of the fines which in turn controls the release process. Kia et al. have shown that if the solution composition is adjusted so that coverage on the surface by calcium ions is greater than a critical value of 75%, then the zeta potential is sufficiently reduced for the prevention of colloidally-induced fines release. The surface coverage of calcium ions depends strongly on the total ionic strength as well as on the calcium ionic fraction or percentage in the solution. Consequently, the threshold value of the concentration of Ca\(^{2+}\) to prevent fines release must depend on the mole percentage of calcium in the solution. Experimental work concerning a critical total ionic strength (CTIS) of a mixed salt system, the percentage of calcium in solution and its relationship with the phenomenon of colloidally-induced fines migration has not been reported, nor has an analysis been put forth that can be used to estimate the CTIS. This information is useful in many chemical, environmental and petroleum engineering operations involving flow of mixed salt solutions through a porous medium.

Continuing our earlier work on the CSC (Khilar and Fogler, 1984) we show here that there exists a critical total ionic strength (CTIS), below which colloidally-induced fines release may occur in Berea sandstone. We have

*Reduction in permeability due to clay swelling occurs because of reduction in flow cross-sectional area due to volume changes of the clay. In fines migration, the clay particles detach from the pore walls and migrate with the fluid until they are captured at pore constrictions, thereby reducing the flow cross-sectional area.
expanded our earlier analysis of the CSC to mixed salt systems consisting of symmetric and unsymmetric electrolytes. In a NaCl/CaCl₂ system, the CTIS strongly depends on the relative amount of CaCl₂ present in the solution (calcium molar percentage, %Ca). For example in a 5% calcium and 95% sodium solution, the CTIS is 0.025 M while it decreases significantly to 0.005 M for a 10% calcium and 90% sodium solution. As we will soon see the predictions using this analysis agree well with the experimental data.

**Measurement of the critical total ionic strength (CTIS)**

A schematic of the experimental system is shown in Fig. 1. It consists of a positive displacement pump for fluid injection, a Hassler cell in which the core is contained and, pressure and concentration measuring devices. For a constant injection rate, the pressure drop across the core was monitored continuously as a function of the ionic strength of the aqueous solution flowing through the core. All the Berea sandstone samples used for this study were from the same block, having an initial permeability of approximately 10 mD. The cores were not fired nor acidized prior to the experiments. The Berea samples had a clay content of approximately 8 wt%, and 75% of which is kaolinite clay.

The ionic strength of the solution is decreased in a stepwise manner, and this technique has been used successfully (Khilar, 1981; Khilar and Fogler, 1984) to determine the CSC of various single salt systems. The critical ionic strength is defined as the ionic strength at which there is a sharp decline in the relative permeability (K/Kₒ). A typical measurement is shown in Fig. 2 (Khilar, 1981). The value of the CSC for different cations, such as Li⁺, K⁺, NH₄⁺, Cs⁺, have been reported by Khilar (1981). In our present study, the concentrations of the ions (Ca²⁺ and Na⁺) were measured using specific ion electrodes. The particulate content of the effluent was analyzed using an Atomic Absorption Spectrometer (AAS)* and a Scanning Electron Microscope (SEM). The ionic strength at which the pressure drop across the core begins to increase and the clay particles appear in the effluent determines the critical concentration. A similar experimental procedure was used in this work.

In a typical experiment, a Berea sandstone core (2.54 cm both in diameter and length) was vacuum saturated with a NaCl/CaCl₂ salt solution of 0.10 M ionic strength (I) and at a particular mole percent of calcium. The saturated Berea sandstone was placed in a core holder and a NaCl/CaCl₂ salt solution was flown through the core at a superficial velocity of 19.2 cm h⁻¹ (15.1 ft day⁻¹). The temperature was maintained at 30°C by means of a constant temperature bath. The inlet pH was in the range 6–7 while the pH of the effluent was found to vary between 8 and 9. As de-

---

*The fines that are released were collected and acidized. This solution was then analyzed for Al³⁺ and Si⁴⁺ concentration using an AAS, and therefore estimate the amount of fines released.
Berea sandstone, temperature = 300 K
Ko = 10 mD, Calcium percentage = 5
2.54 cm diameter, 2.54 cm length

Table 1

<table>
<thead>
<tr>
<th>%Ca</th>
<th>%Na</th>
<th>CTIS (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>0.071</td>
</tr>
<tr>
<td>5</td>
<td>95</td>
<td>0.025</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>0.005</td>
</tr>
<tr>
<td>15</td>
<td>85</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

to obtain a range for the CTIS. Having obtained a coarse range, the ionic strength was then decreased in small steps within the range to determine the CTIS with an accuracy of ±0.0005 M.

Figures 3 and 4 show the values of CTIS measured at calcium percentages of 5 and 10, and all the results are summarized in Table 1. One observes from this table that CTIS decreases as the calcium percentage increases. That is, even at low ionic strength the fines are not released at higher calcium percentages. At 15% calcium/85% sodium, the CTIS could not be obtained as it appears to be much below the detection limit of the system.

The experimental results can be explained through a qualitative analysis, by comparing the zeta potentials (ζ) and the consequent variations in the double layer interactions. The zeta potentials of kaolinite and the Berea sandstone are strongly dependent on the extent of surface coverage of Ca²⁺ ions (Kia et al., 1987b), which in turn depends on the ion exchange equilibria between the particles and the mixed salt solution (Bolt, 1955; Wilemsky, 1982). The ionic condition of the fluid can be described by two parameters: the calcium percentage and the total ionic strength. The reduction in zeta potential with increasing calcium percentage causes the double layer repulsive potential to decrease and decreasing the probability of release. Therefore, the total ionic strength must be reduced to increase the diffuse double layer and increase the probability of release. Consequently, increasing the calcium percentage lowers the CTIS.
Extension of CSC analysis to estimate CTIS

The DLVO-type of analysis, used earlier by Khilar and Fogler (1984) to estimate the CSC, is extended to study the effects of calcium percentage on CTIS. The total energy \( (V_T) \) and the total force \( (F_T) \) are identically zero at CTIS:

\[
V_T = 0 \quad (1)
\]

\[
\frac{\partial V_T}{\partial h} = 0 = F_T \quad (2)
\]

where, \( h \) is the distance of separation between the pore wall and the particle. The total potential \( (V_T) \) can be obtained by simply adding the individual potentials:

\[
V_T = V_{\text{LVA}} + V_{\text{DLR}} + V_{\text{BR}} + V_{\text{HR}} \quad (3)
\]

where:

- \( V_{\text{LVA}} \): London–van der Waals attractive potential;
- \( V_{\text{DLR}} \): Double layer repulsive potential;
- \( V_{\text{BR}} \): Born repulsive potential; and
- \( V_{\text{HR}} \): Hydrodynamic repulsive potential.

It has been shown that, the contribution of the hydrodynamic potential becomes comparable to the colloidal forces only at very high flow-rates, that is superficial velocities greater than 1000 cm h\(^{-1}\) (Cerda, 1988). The experimental results of Khilar (1981), listed in Table 2, also show the weak dependence of velocity on the critical salt concentration. Since the experimental velocities in this study were much lower (19.2 cm h\(^{-1}\)), the effect of \( V_{\text{HR}} \) was neglected. When the distance of separation between the particle and the wall is of the order of 5 Å, the Born repulsive potential is comparable in magnitude to London–Van der Waals and Double layer potential. The inclusion of the Born repulsion term makes the primary minimum of the interaction potential finite. The existence of the finite primary minimum has been able to explain the observed adsorption/desorption of particles from surfaces and the flocculation behavior of colloidal suspensions (Hamaker, 1937; Ruckenstein and Prieve, 1976; Feke et al., 1984). Equation 3 reduces to:

\[
V_T = V_{\text{LVA}} + V_{\text{BR}} + V_{\text{DLR}} \quad (3a)
\]

Some investigators have modeled clay/clay interactions as either having a plate/plate or a cylinder/plate geometry (James and Williams, 1982). Typically, the clay particles are the order of one micron size and the pore to which they are attached have diameters approximately 30–40 microns. Therefore, the interaction between the particle (kaolinite clay) and the sandstone surface (Berea) were modeled to have a sphere/plate geometry as done by previous investigators (Khilar, 1981; Sharma et al., 1985). For such a system the London–Van der Waals potential is given by (Ruckenstein and Prieve, 1976):

\[
V_{\text{LVA}} = \frac{A}{6} \ln \left( \frac{h+2a}{h} \right) - 2a \left( \frac{h+a}{h} \right) \left( \frac{h+2a}{h} \right) \left( \frac{h+a}{h+2a} \right) \quad (4)
\]

where \( A \) is the Hamaker constant, \( a \) is the radius of the particle, and \( h \) is the distance of separation.

The double layer potential can be calculated, under certain approximations, using the following expression of Ruckenstein and Prieve (1976):

\[
V_{\text{DLR}} = 16\varepsilon \left( \frac{kT}{e} \right)^2 a \tanh \left( \frac{y_1}{4} \right) \tanh \left( \frac{y_2}{4} \right) e^{-kh} \quad (5)
\]
where:

\[ I = \frac{1}{2} \sum n_i^0 z_i^2 \]  
\[ \kappa^2 = \left( \frac{8\pi e^2 I}{ekT} \right) \]  
\[ \eta_j = \frac{e \Psi_j}{kT} \]

In these expression:

- \( n_i^0 \) bulk concentration of species, \( i \)
- \( \Psi_j \) surface potential of surface, \( j(j=1,2) \)
- \( z_i \) valency of species, \( i \)
- \( e \) electronic charge
- \( I \) total ionic strength
- \( k \) Boltzmann’s constant
- \( T \) absolute temperature
- \( \epsilon \) permittivity of the medium (all in cgs units)

The Born repulsion potential \( (V_{BR}) \), accounts for the short range structural or hydration forces due to the interaction of particles with adsorbed fluid layers (Feke et al., 1984). Assuming that these interactions can be linearly superimposed, Ruckenstein and Prieve (1976) obtained the following formula for a sphere–plate interaction geometry:

\[ V_{BR} = -\frac{A\sigma}{7560} \left[ \frac{8a+h}{(2a+h)^2} + \frac{6a-h}{(h)^2} \right] \]  

Here \( \sigma \) is the collision diameter, and is approximately 5–6 Å.

The ionic strength and the calcium percentage (%Ca) are related to the molarities of Na\(^+\) and Ca\(^{2+}\) \((M_{Na} \text{ and } M_{Ca})\) in the following manner:

\[ I = M_{Na} + 3M_{Ca} \]  
\[ \%Ca = 100 \left( \frac{2M_{Ca}}{M_{Na} + 2M_{Ca}} \right) \]

The total energy of interaction \( V_T \) was calculated by using Eqs. 3–6. The total energy of interaction may be evaluated as a function of the separation distance \( h \) for different values of ionic strength and at various calcium percentages.

The value of \( CTIS \) is determined as the value of the ionic strength \( I \) for which both the magnitude and the slope of the \( V_T/kT \) versus \( h \) plot become zero at some distance of separation (Eqs. 1 and 2). Figure 5 shows some typical interaction profiles that may be realized from Eqs. 3–6. One observes, that there is more than one situation when the conditions of Eqs. 1 and 2 are satisfied. The first situation arises when the maximum of the interaction potential curve satisfies the above conditions, and is shown as curve A. This salt concentration is generally referred to as the critical flocculation concentration \( (CFC) \) in colloidal studies related to aggregation of particles. As can be observed from Fig. 5, the primary minimum is still negative compared to the bulk potential (which is zero), and therefore the escape of particles from the primary minimum is minimal.
Reducing the ionic strength below the **CFC** results in the second situation, when the primary minimum satisfies the conditions of Eqs. 1 and 2. This is shown by curve B in Fig. 5. This ionic strength will be referred to as the critical total ionic strength (**CTIS**). Lowering the ionic strength below the **CTIS** makes the value of the potential at the primary minimum greater than the bulk potential. This condition now favors the detachment (or escape) of the particles from the primary minimum. The presence of a maximum in the interaction potential can slow the rate of release, since the particles have to diffuse over a potential barrier. For some ionic conditions, a secondary minimum may also be present and this could also have an effect on the rate of adsorption and desorption of particles (Ruckenstein, 1978). This effect results because the particles that are released form the primary minimum diffuse over the potential barrier and under certain circumstances may be captured in the secondary minimum, thus reducing release rates. From the above discussion, however, it is evident that, ionic strengths below **CTIS** will lead to the detachment of the clay fines from the sandstone surface. These released fines will diffuse into the bulk and flow with the fluid, consequently leading to formation damage.

Figures 6 and 7 show the total energy of interactions \( V_T \) as a function of distance of separation \( h \) for different values of total ionic strength \( I \) at 5 and 10% calcium percentage.

The values of zeta potentials were taken from the literature and at the calcium percentage of 5 and 10, the zeta potentials of kaolinite are approximately \(-16\) and \(-12\) mV, respectively, and those of Berea sandstone at \(-18\) and \(-14\) mV, respectively (Kia et al., 1987a, 1987b). The variation of zeta potential with total ionic strength (excluding the variations at very low values of \( I \)) was found to be very weak (Kia et al., 1987a) and was neglected in the calculations. A Hamaker’s constant, \( A \), of \( 0.6 \times 10^{-13} \) ergs, which lies in the reported range of \( 0.30-6.0 \times 10^{-13} \) ergs for clay–sandstone systems (Lyklema, 1968), was found to fit the observed experimental data satisfactorily.

The variations of interaction potential with the distance of separation and for different ionic strengths can be observed from any of these two figures. One observes from Fig. 6, the total interaction potential is negative or attractive (no release condition) at high values of ionic strength, while the potential is positive or repulsive (favoring release) at lower ionic strengths of the order of \( 0.001 \, M \).

The variation of total potential with distance of separation \( h \) follows the common trend of decrease in attractive energy as separation distance increases and the occurrence of maximum and minimum depending on the value of the zeta potential, ionic strength and Hamaker’s constant. Comparing Figs. 6 and 7, one observes that for the same value of ionic strength.
TABLE 3

Comparison of CFC and CTIS at various calcium percentages

<table>
<thead>
<tr>
<th>% Ca</th>
<th>CFC(M)</th>
<th>CTIS(M) (experimental)</th>
<th>CTIS(M) (predicted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.12</td>
<td>0.071</td>
<td>0.071</td>
</tr>
<tr>
<td>5</td>
<td>0.1</td>
<td>0.025</td>
<td>0.035</td>
</tr>
<tr>
<td>10</td>
<td>0.032</td>
<td>0.005</td>
<td>0.008</td>
</tr>
</tbody>
</table>

strength \( I \), the interaction potential \( V_T \) is more negative (increased attraction) at higher calcium percentages and decreases (becomes negative) with an increase in ionic strength.

One also observes from these figures that CTIS at 5 and 10% calcium can be taken equal to 0.035 and 0.008, respectively. These corresponding values calculated from DLVO theory compare well with the measured values of 0.025 and 0.005 M. For 15%Ca/85%Na the calculations showed that even at a low ionic strength of 0.001 M, the total energy of interactions is negative and hence the CTIS is below 0.001 M. The values in Table 3 give the ionic strength for the CFC and the CTIS, as has been defined previously, for various calcium percentages. As discussed earlier, an increase in concentration beyond the CFC enhances flocculation, while decreasing below the CTIS favors peptization (or detachment) of particles.

Although this very good agreement of theoretical predictions with data may be somewhat fortuitous, we wish to caution that the quantitative agreement depends on the estimated Hamaker’s constant, which can be determined accurately with great difficulty. Therefore like most other analyses based on the DLVO theory, this analysis can be considered as semi-quantitative predicting the relative change in CTIS at different colloidal conditions for a mixed salt system.

Conclusions

It can be concluded from the presented measurements and analysis that a critical total ionic strength (CTIS) for a mixed salt system of NaCl/CaCl2 flowing through Berea sandstone exists, below which fines are released due to colloidal forces. The value of CTIS is strongly dependent on the relative amount of CaCl2 present in the solution. For calcium molar percentage of 15 or higher, the molarity of the CTIS is virtually zero, while the maximum value (0.07 M) is at zero calcium percentage. Analysis based on the DLVO theory agree reasonably well with measurements. Although this study has been conducted for Berea-NaCl/CaCl2 system, the measurement technique and the analysis developed can be applied to other systems as well.

Acknowledgements

One of the authors, KCK, thanks the Department of Science and Technology, New Delhi, India for financial support (Sanction No. DST/STP/83/III) to carry out a part of this work. In addition KCK acknowledges with thanks the summer visiting faculty position offered by the department of Chemical Engineering at The University of Michigan. We also gratefully acknowledge the support from the National Science Foundation grant No. CBT-8516458.

References


