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KAOLINITE MOBILISATION IN SANDSTONE: PORE PLUGGING VS SUSPENDED PARTICLES

Esther Rosenbrand¹, Ida Lykke Fabricius¹, Frans Kets²

¹Technical University of Denmark,
Dept. of Civil Engineering, Brovej 118
Kongens Lyngby, 2800, Denmark
esro@byg.dtu.dk

²University of Leeds
School of Earth and Environment
Leeds LS2 9JT, United Kingdom

ABSTRACT

The effect of temperature and salinity on sandstone permeability is critical to the feasibility of heat storage in geothermal aquifers. Permeability reduction has been observed in Berea sandstone when the salinity of the pore water is reduced as well as when the sample is heated. Several authors suggest that this effect is due to kaolinite clay mobilisation from the quartz grain surface; the mobilised particles subsequently plug the pore throats and reduce the permeability irreversibly. The expected hysteresis is observed when the salinity is reduced and increased; however, in contradiction with the throat plugging theory, the effect of heating is found to be reversible with cooling. In laboratory experiments we heated Berea sandstone from 20°C to 80°C and observed a reversible permeability reduction. The permeability of the heated samples increased at higher flow rates. We propose that in this case the mobilised kaolinite particles either remain suspended and thereby increase the fluid viscosity, or form porous aggregates that can be destabilized by hydrodynamic forces.

To address how the pore scale distribution of kaolinite relates to the permeability of the entire sample, we relate permeability to the effective specific surface, S_p . The effective specific surface represents the average surface area that resists the flow through the sample of a volume of fluid. We propose that flow paths with a small S_p contribute more than proportionately to the total volume flux. Kaolinite mobilisation in pores with a small S_p diverts fluid flow through pores with a higher S_p , and thereby reduces permeability of the entire sample.

In this paper, we use the DLVO theory to compare how temperature and salinity affect the surface interaction forces between quartz and kaolinite, as well as the interaction forces among kaolinite particles to evaluate whether heating can be expected

to a) mobilise particles and b) result in kaolinite forming a suspension rather than plugging the pore throats.

INTRODUCTION

The permeability of a sandstone aquifer is critical to the successful extraction of water for geothermal energy production. Mineral-fluid interaction alters permeability when this causes dissolution or precipitation (Milsch et al. 2009), clay swelling, or clay mobilisation (Mungan, 1965; Gray and Rex, 1966; Khilar and Fogler, 1983, 1984; Kia et al. 1987; Schembre and Kovscek, 2005). We address the mechanism by which kaolinite mobilisation affects the permeability of the Berea sandstone. Kaolinite is the dominant clay mineral in the Berea sandstone, and accounts for approximately 6% (Baudracco and Aoubouazza, 1995) to 9% of the solid mass (Shaw et al., 1991).

Kaolinite particles are mobilised by an increase in the electrical double layer (EDL) repulsive force between quartz and kaolinite (Kia et al., 1987; Schembre and Kovscek, 2005). The EDL force acts between electrically charged surfaces. Kaolinite and quartz surfaces have broken bonds that interact with water molecules. The resulting surface groups have a charge that depends on their protonation. The equilibrium constants for the protonation reactions depend on both the pH and on the temperature (Brady et al., 1996). The surface charge attracts oppositely charged ions. These ions form the EDL on the surface that counters the surface charge. Inside the EDL the potential falls with distance from the surface. The distance over which the surface potential is reduced by a factor $1/e$ is given by the Debye length, which characterizes the thickness of the EDL (Lyklema et al., 1995). The concentration of counterions at a given point inside the EDL depends on the surface potential and the ionic strength of the solution. As two surfaces with the same charge

approach, the overlap of their double layers causes a repulsive force between the EDLs (Israelachvili, 2011). Reducing the ionic strength increases the EDL thickness and the magnitude of the EDL repulsion. Heating reduces the EDL thickness. However, data on the surface charge of kaolinite (Brady et al., 1996), as well as data on the surface potential of both kaolinite and quartz show a significant increase in the magnitude of these with heating (Rodríguez and Araujo, 2006). This increase can offset the reduction of the EDL thickness, and can result in a net increase of the EDL repulsion (Khilar and Fogler, 1984; Schembre and Kovscek, 2005).

According to the DLVO (Derjaguin and Landau, 1941, 1993; Verwey and Overbeek, 1948) theory, the EDL repulsion is counteracted by van der Waals attraction. Changes in the ionic strength or temperature, in the 20°C to 80°C range, are assumed to have a negligible effect on the magnitude of the van der Waals attraction between mineral surfaces interacting across water or brine (Khilar and Fogler, 1984; Schembre and Kovscek, 2005; Israelachvili, 2011). When the EDL repulsion exceeds the van der Waals attraction, kaolinite particles are mobilised. Due to the different rates by which the magnitude of the EDL and the van der Waals force fall with separation between the surfaces, the net interaction energy typically shows an attractive primary energy minimum at short separations where van der Waals forces dominate (negative interaction energy represents attraction). At greater separation the EDL force causes a peak in the interaction energy (Israelachvili, 2011). The net interaction energy is considered to be repulsive when the peak is positive, even if there is attraction at smaller and larger separations (Khilar and Fogler, 1983, 1984; Kia et al. 1987; Schembre and Kovscek, 2005).

Currently it is assumed that the mobilised particles form plugs in the pore throats, resulting in a sharp drop in permeability (Mungan, 1965; Gray and Rex, 1966; Khilar and Fogler, 1984; Schembre and Kovscek, 2005). Rosenbrand et al (submitted) found that reducing the ionic strength at 20°C causes a permeability reduction that is not reversed by increasing the ionic strength. This hysteresis is expected for plugged pores, and is also observed in the Berea sandstone by e.g., Mungan (1965) and by Khilar and Fogler (1984). The permeability only increases significantly when the flow direction was reversed both in our experiment and in tests by Khilar and Fogler (1983). Rosenbrand et al. (under review) found that heating the sandstone from 20°C to 80°C causes a smaller permeability reduction than reducing the ionic strength does, and that the effect of temperature is reversible with cooling. A reversible effect of temperature is also found by Aruna (1976), Baudracco and Aoubouazza (1995) and Cassé and Ramey (1979). This reversibility is not predicted by the particle plugging hypothesis. Furthermore, reversing the flow direction did not significantly

affect permeability, but increasing the flow velocity improved permeability significantly.

At elevated temperature, the permeability remained approximately constant as the ionic strength was reduced from 2.0M to 0.002 M NaCl and increased again (Rosenbrand et al., submitted). If heating only mobilised a fraction of the kaolinite, the reduction of the ionic strength would be expected to affect permeability in the heated samples by mobilising the remaining kaolinite. This suggests that the kaolinite is present as unstable aggregates or in suspension rather than as stable plugs in the pore throats.

A more negative surface charge on the kaolinite at 80°C, and thereby a higher EDL repulsion, could account for these observations. A higher EDL repulsive force among kaolinite particles may prevent mobilised kaolinite from forming stable aggregates. Individual particles may be small enough to pass through the pore constrictions, however, when the concentration of suspended particles is high, the particles can obstruct each others' passage through the pore and form particle bridges (McDowell-Boyer et al., 1986). Particle bridges can be destabilized by increasing the hydrodynamic drag forces (Sen and Khilar, 2006).

Rather than being transported to the pore constrictions, the suspended kaolinite may alter the rheology of the pore fluid. Kaolinite suspensions behave as non-Newtonian fluids that only shear when a yield stress is exceeded (Johnson et al., 1998). Both unstable particle bridges as well as a non-Newtonian suspension can account for the increase in permeability with flow velocity observed in our experiments.

The interaction forces between kaolinite particles are affected by the crystal shape of the kaolinite. Kaolinite particles are typically hexagonal platelets, made up of layers with one silica sheet bonded to an alumina sheet. A particle consists of a number of such layers that are connected by hydrogen bonds between adjacent alumina and silica sheets. The particle thereby has one silica face and one alumina face, and the edges have broken bonds where the mineral structure is interrupted. This results in different surface charges on the two faces and on the edges of the particle (Brady et al., 1996) and hence in different EDL interaction forces. Kaolinite forms compact stacked aggregates when there is attraction among the faces, and larger 'card house' structures when there is attraction between the edges and the faces (Schofield and Samson 1954, Wang and Siu, 2006; Gupta et al., 2011). In the untested Berea sandstone, compact stacks of kaolinite particles are observed by Shaw et al. (1991). If these reorient to card houses, this reduces porosity and increases the effective surface area in contact with the fluid.

In this paper we show how the distribution of kaolinite on the pore scale affects the effective specific surface that resists fluid flow. We use the Kozeny (1927) equation to relate the effective

specific surface per unit pore volume, S_p , to the sample permeability. We then use the DLVO theory to compare the effects of ionic strength and of temperature on the interaction energy between charged surfaces in order to evaluate the likelihood of the different scenarios for the kaolinite distribution.

METHOD

Effective specific surface

Kozeny's (1927) equation (Eq. 1) relates the effective specific surface per unit of rock volume, S , to the porosity, ϕ , and permeability, k , for a homogeneous porous medium. Following Mortensen et al. (1998) the parameter c is taken to depend on the porosity. The porosity can be assumed constant during experiments where the sample is allowed to expand whilst it is heated. The permeability change is due to change in the effective specific surface area.

$$k = \frac{c\phi^3}{S^2} \quad (\text{Eq. 1})$$

The ratio $S_p = S/\phi$, is the effective specific surface area per unit of pore volume. S_p is inversely proportional to the average pore diameter. The permeability is determined using Darcy's law (Eq.2) from the volumetric flow rate, Q , through the sample. Here, A is the cross sectional area, ΔP is the pressure difference over the sample length, L , and μ is the fluid viscosity.

$$k = \mu \frac{Q}{A} \frac{L}{\Delta P} \quad (\text{Eq. 2})$$

The fluid on the solid surface is stationary according to Poiseuille's law. Therefore we expect a higher flow rate in pores with a lower S_p . Thereby, the pores with a smaller specific surface can be expected to contribute more to the total flow rate, *and* the average permeability is expected to be dominated by the flow through pores with a smaller specific surface.

Kaolinite mobilisation can directly increase the effective surface area in a pore, when compact aggregates are dispersed. It can also plug a pore with a low S_p , and divert flow through pores with a larger S_p . In both cases the effective specific surface of the sample is increased, and the permeability in Eq. 1 is reduced.

Kaolinite distribution

Kaolinite in the Berea sandstone is often observed in locally high concentrations (Schembre and Kovscek, 2005). The kaolinite particles are present in compact stacks (Shaw et al., 1991) and present a relatively

small effective surface area. This is the initial condition in the permeability experiments at 20°C and high ionic strength. The net interaction force among kaolinite particles, as well as between quartz and kaolinite can be expected to be attractive in these conditions.

Both reducing the ionic strength at 20°C, and heating to 80°C reduce the permeability, indicating kaolinite is mobilised. This is generally attributed to repulsion between the quartz and kaolinite surfaces. (Khilar and Fogler, 1983, 1984; Schembre and Kovscek, 2005; Rosenbrand et al., under review).

At 20°C, mobilised kaolinite is perceived to form aggregates that plug the pore throats (e.g., Khilar and Fogler, 1984). The mobilised kaolinite particles may flocculate and form aggregates that are too large to pass through the pore throats as shown in Scenario 1 (Figure 1a). Flocculation can occur even if there is repulsive interaction energy at a given separation between surfaces subject to the conditions that the repulsive energy is small relative to the thermal energy and that there is attraction for smaller separations (Hogg et al. 1966). In our case, due to flow, collisions between particles may have sufficient energy to overcome the repulsive energy barrier and attach in the energy minimum at close separation. Alternatively, if the suspended particles repel each other strongly enough to prevent aggregation, they may form particle bridges in the pore constrictions as shown in Scenario 2 (Figure 1b). The key difference between these two scenarios is the stability of the particle aggregates. The relatively high repulsion among particles in Scenario 2 implies that the particle bridges can be destabilised and removed from the pore constriction by an increase in hydrodynamic forces (Sen and Khilar, 2006), whereas stable aggregates that are strained in the pore constriction are not expected to be remobilised (Bedrikovetsky et al., 2012). In Scenarios 1 and 2, the S_p increases primarily due to a diversion of fluid flow through pores with a higher S_p .

Scenario 3 (Figure 1c) shows kaolinite forming the voluminous card-house aggregates described by Schofield and Samson (1954) and Wang and Siu (2006). These form when there is attraction between kaolinite edges and faces, but repulsion among the kaolinite faces. The hydrodynamic forces are insufficient to overcome the gravitational forces on these larger aggregates, and/or the attractive forces tying the aggregate to the quartz, and they are not transported to the pore throats. In Scenario 3, the S_p is increased because the surface area of the kaolinite in contact with the fluid is increased and the effective porosity is reduced by the more voluminous kaolinite aggregate.

Scenario 4 (Figure 1d) shows a kaolinite suspension where the kaolinite particles repel each other, as in Scenario 2. In Scenario 4, however, the strong repulsive interaction energy prevents the formation of particle bridges in the pore throats. The surface area

of the kaolinite in contact with the fluid is increased, increasing S_p . Even when the EDL repulsion among kaolinite particles is high, interactions among the suspended particles result in a yield stress of the suspension (Johnson et al., 1998). Zbik and Frost (2009) observed that kaolinite particles form a structured network even in stable suspensions. Interactions between the electrical double layers of the particles can be expected to affect the orientation of the suspended particles.

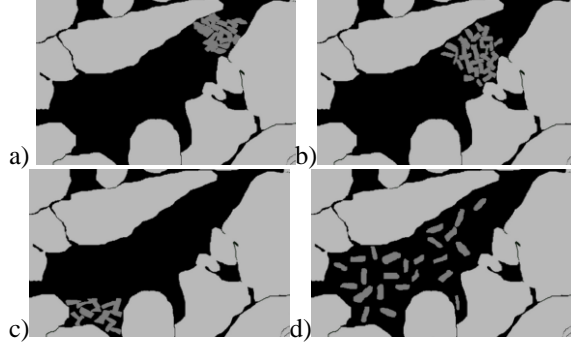


Figure 1: a) stable kaolinite aggregates that are too large to pass the pore constriction. b) kaolinite particles forming a particle bridge c) voluminous kaolinite aggregates in the pore body. d) kaolinite suspension in the pore body. Modified from Rosenbrand et al. (submitted)

Interaction energy

The DLVO theory is used to compare the effect of temperature and ionic strength on the net interaction energy between two surfaces. As a first approximation we consider the interaction forces between parallel plates. Kaolinite particles are platelets rather than spherical particles, and the radius of quartz grains relative to the kaolinite size is large, so that the surface can be approximated as a plane.

Van der Waals interaction

As a first approximation, we assume the van der Waals interaction is not affected by heating or by ionic strength. Atomic force microscopy (AFM) measurements on mica plates indicate that the van der Waals forces are not significantly affected by ionic strength (Israelachvili and Adams, 1978). The van der Waals interaction energy, E_{vdW} , between plates per square meter is given by Eq. 3 (Israelachvili, 2011):

$$E_{vdW} = -\frac{A_H}{12\pi h^2} \quad (Eq. 3)$$

The separation between the mineral surfaces is given by h . A_H is the Hamaker constant that is determined

by the intrinsic properties the two surfaces and the intervening medium. We use $A_H = 2.2 \times 10^{-20}$ J; this is comparable to values that are used for interactions between kaolinite and quartz in aqueous NaCl solution by Kia et al. (1987) and by Schembre and Kovscek (2005).

EDL interaction

We consider the electrical double layer as composed of two layers based on the Stern model (Stern (1924) in Lyklema (1995)). The Stern layer, the distance between the surface and the Stern plane, accounts for small-scale surface roughness, directly adsorbed water molecules and the size of the hydrated counterions. Beyond the Stern plane, the ions in the diffuse part of the double layer are treated as point charges after the Gouy-Chapman theory (Gouy (1909), Chapman (1913) in Lyklema, 1995). In the diffuse part of the EDL, the potential drop with distance is characterized by the Debye length, κ^{-1} (Eq. 4).

$$\kappa^{-1} = \sqrt{\frac{\epsilon_0 \epsilon k_B T}{2N_A e^2 I}} \quad (Eq. 4)$$

Here ϵ is the relative permittivity of the solution, ϵ_0 is the vacuum permittivity, k_B is Boltzmann's constant, T , is the absolute temperature, N_A , is Avogadro's number, e , is the electron charge and I is the ionic

strength of the solution $I = \frac{1}{2} \sum C_i z_i^2$ where C is

the concentration and z the valence of the ions. Temperature and ionic strength directly affect κ^{-1} , and they also influence ϵ . We calculate the permittivity as a function of T and I after Michelsen and Mollerup (2007).

The interaction energy due to the overlapping double layers can be calculated exactly by solving the Poisson-Boltzmann equation. This requires numerical methods, but analytical solutions based on simplifications can give results closely approximating the exact solution (Gregory, 1975). The boundary conditions that are required for both the numerical and the analytical solutions have a significant effect on the interaction at small separations. The assumption that the charge in the double layers is constant as the surfaces approach results in an estimate of the upper bound for the EDL repulsion. The lower bound is obtained by the assumption that the potential at the Stern plane is constant. This assumption, however, leads to the prediction that the EDL force between surfaces with different magnitude charge of the same sign, flips from repulsion to attraction at short separations. Gregory (1975) suggests the use of an intermediate condition, represented by the linear superposition approximation

(LSA) Eq. 5. This solution does not lead to a change of sign of the EDL interaction force with separation distance. Rather than assuming constant potential or charge on the surfaces, the potential midway between the Stern planes is assumed to be given by the summation of the potentials of the individual double layers at this position. The assumption that the double layers do not affect each other is probably not valid for separations less than κ^{-1} (Elimelech et al., 1995).

$$E_{EDL} = \frac{64000N_A C}{\kappa} \gamma_1 \gamma_2 \exp(-\kappa D) \quad (Eq. 5)$$

Here, C is the concentration of the monovalent electrolyte in moles per litre, D is the separation between the Stern planes, and γ_i is the reduced surface potential which for monovalent electrolyte solutions is given by:

$$\gamma_i = \tanh\left(\frac{e\psi_{0,i}}{4k_B T}\right) \quad (Eq. 6)$$

The potential at the Stern plane should be used for the surface potential, ψ_0 , according to Frens and Overbeek (1972). The zeta potential ζ , is generally used to estimate the ψ_0 , (Elimelech et al., 1995). This can be measured using particle electrophoresis experiments. The ζ values reported in the literature for kaolinite at pH 8 vary significantly. This is partially because the ψ_0 depends on the ionic strength as well as on ψ_0 (Frens and Overbeek, 1972). To compare data from experiments at different electrolyte concentrations we used the relation between the ψ_0 and the charge on the Stern plane, σ_0 after Grahame (1947).

$$\sigma_0 = \sqrt{8000N_A \epsilon_0 \epsilon k_B T C^+} \sinh\left(\frac{e\psi_0}{2k_B T}\right) \quad (Eq. 7)$$

By comparing the σ_0 rather than the ζ we reduced the variation that is due to the different ionic strengths used to measure the ζ . Still, at pH 8, the values of the σ_0 for kaolinite from different investigations (Johnson et al., 1998; Rodríguez and Araujo 2006; Zbik and Frost, 2009) vary in the range between 11 mC/m² and 22 mC/m². This can be expected to be caused by differences in the particle shape and size. The value of the ζ is an average for the entire particle, but the different sides of kaolinite particles have different charge densities. Gupta and Miller (2010) measure the σ_0 on both the alumina and the silica faces using AFM. Gupta et al. (2011) conclude that the σ_0 on the edges must be significantly higher than the σ_0 on the faces to account for the value of the ζ at pH 8. Particles with a larger ratio of edge to face surface area can therefore be expected to have a higher

average σ_0 , and therefore a higher ζ . Brady et al. (2006) observe that the faces of their kaolinite particles are not planar but show steps. This effectively adds broken bonds or edge surface to the particle faces and can be expected to increase both the face σ_0 and the average σ_0 for the particle. Brady et al. (2006) use potentiometric titration in combination with chemical modelling to estimate distribution of surface charge. Their data suggests that the σ_0 on the edges is in the order of 3 times as high as the average σ_0 .

Heating is observed to increase the ζ by a factor 2 for both kaolinite and for quartz when these are heated from 20°C to 45°C (Rodríguez and Araujo, 2006). Brady et al. (2006) observe an approximate doubling of the σ_0 of kaolinite for a temperature increase from 25°C to 70°C.

We calculated the value of the ψ_0 from the $\sigma_{0,20}$ at 20°C using Eq. 7. We assumed that the Stern plane is 0.5 nm removed from the surface. This corresponds approximately to one layer of adsorbed water plus the radius of the hydrated counter-ions. Thereby the distance, D , for the EDL force as defined in Eq. 5 is 1 nm less than the separation between mineral surfaces, h . The net interaction energy was calculated for kaolinite with $\sigma_{0,20}$ ranging from $\sigma_{0,20} = 7$ mC/m² to $\sigma_{0,20} = 22$ mC/m². The lower values can be expected only on the faces, whereas the higher values correspond to measured ζ values. To account for the significantly higher edge charge density values between $\sigma_{0,20} = 27$ mC/m² and $\sigma_{0,20} = 37$ mC/m² were used. However, the interaction energy of the edges was scaled by 0.2 μm^2 whereas that for the faces is scaled by 4 μm^2 to account for the difference in surface area. For quartz we used $\sigma_{0,20} = 22$ mC/m² to $\sigma_{0,20} = 32$ mC/m² based on data from Rodríguez and Araujo (2006) and from House and Orr (1992).

We calculated the interaction energy at 80°C for both the same $\sigma_{0,20}$ as at 20°C as well as for a two- and for a four-fold increase in $\sigma_{0,20}$ that may result from heating.

RESULTS

Reducing the ionic strength causes a significant increase of the κ^{-1} , whereas heating has a negligible effect (Figure 2a; Eq. 4). For a constant σ_0 , the magnitude of the ψ_0 increases significantly when ionic strength is reduced according to Eq. 7. Heating to 80°C also increases the magnitude of the ψ_0 but to a lesser extent (Figure 2b).

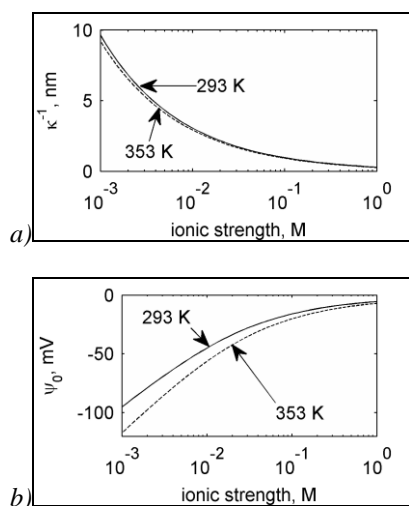


Figure 2: (a) the reduction of the ionic strength increases the Debye length, κ^{-1} .
 (b) reducing the ionic strength also increases the magnitude of the surface potential, ψ_0 at a constant surface charge. The effect of heating on κ^{-1} and ψ_0 is less significant than the effect of ionic strength.

Figure 3 shows the effect of ionic strength on the net interaction energy between quartz and kaolinite at 20°C. At high ionic strength, both κ^{-1} and ψ_0 are low and the van der Waals forces dominate. The peak of the interaction energy profile switches from attraction (negative interaction energy) to repulsion (positive interaction energy) between ionic strengths 0.2 and 0.02 M. Due to the thickness of the Stern layer, the minimum separation between surfaces is 1 nm. For separations between Stern planes, D , that are less than approximately κ^{-1} , (indicated by the vertical dotted line in the figures) the calculated EDL interaction energy depends strongly on the assumption of constant potential or constant charge (Gregory, 1975). We limit the analysis to the interaction energies at greater separations. Therefore we do not compare the maximum height of the interaction barriers, but rather the interaction values at a larger separation.

The value of the $\sigma_{0,20}$ of kaolinite varies in literature, however, this variation does not change the sign of the interaction energy at 3 nm separation between the

kaolinite and quartz surfaces, ($D=h-1$ nm) at 0.2 M (Figure 4a) and 0.02 M (Figure 4b). These figures show an attractive interaction at 0.2 M and repulsion at 0.02 M ionic strength for the range of $\sigma_{0,20}$ that we consider representative of faces or of the average charge. Only for the relatively high negative $\sigma_{0,20}$ that can be expected on the edges, there is repulsion at both ionic strengths. The interaction energy is calculated as energy per square meter, and the total energy is therefore scaled by the interacting areas. Due to the smaller surface area of the edges, $0.2 \mu\text{m}^2$, compared to the faces, $4 \mu\text{m}^2$, the energy for the interactions between the edges of kaolinite and quartz is lower than for the interaction between the faces of kaolinite and quartz. This does not imply that attachment between quartz and the edges is more probable than between quartz and the faces. The difference is comparable to the difference between pressure and force.

Mobilisation due to heating was observed even at high ionic strengths (Rosenbrand et al, under review). Figure 5a shows that the interaction energy between quartz and kaolinite remains negative when the temperature is increased from 20°C to 80°C at 0.34 M ionic strength. Heating only causes repulsion when the σ_0 increases due to heating. Figure 5b shows that the increase in the surface charge density σ_0 , required for repulsive interaction energy at 2.0 M ionic strength is four times $\sigma_{0,20}$ rather than the twofold increase that caused repulsion at 0.34 M ionic strength. At larger separations (4-7 nm) this curve shows a negative minimum, a minimum at this distance may indicate a stable configuration at this distance (Hahn and O'Melia, 2004).

If heating increases the σ_0 , this also increases the repulsive interaction among kaolinite particles. Figure 6a shows the calculated interaction energy between a kaolinite face with a $\sigma_{0,20}$ 11 mC/m²; which corresponds to the lower range of the ζ in literature, and all sides of the kaolinite particle at 20°C and 0.02 M ionic strength, which is repulsive at all separation distances. Assuming that heating to 80°C increases the surface potential by a factor four, the interaction energy at close separations increases sharply even when partly compensated by the effect of a relatively high, 0.2 M, ionic strength (Figure 6b).

At 20°C the kaolinite particles are expected to form relatively stable aggregates even at a low ionic strength. The interaction energy at 20°C and 0.02 M is less repulsive than the interaction energy at 80°C and 0.2 M, which can be expected to result in a higher aggregate stability at 20°C. The difference between the interaction energy at 20°C and 0.02 M ionic strength and the energy at 80°C and 0.2 M depends on the separation distance, (Figure 6c). At small separations, the interaction energy is higher in the heated sample due to the higher σ_0 . At greater separations the effect of the higher ionic strength at 80°C outweighs the effect of the higher σ_0 and there is a higher repulsion at 20°C.

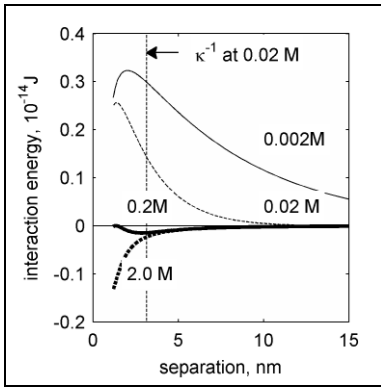
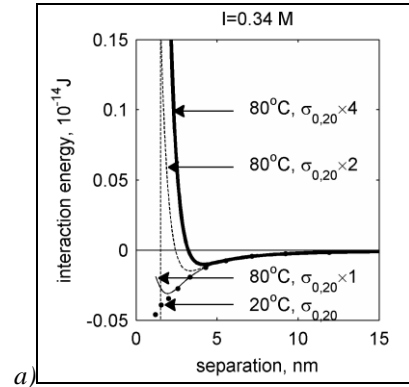
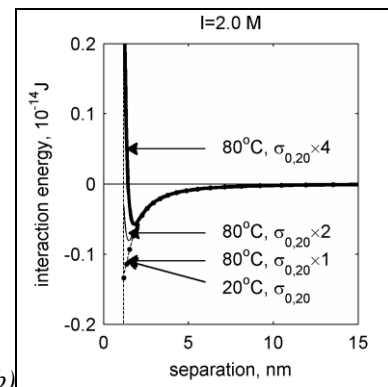


Figure 3 interaction energy as a function of separation between surfaces of kaolinite and quartz with $\sigma_{0,20}$ between 11 mC/m^2 and 27 mC/m^2 . The Debye length increases as the ionic strength falls.

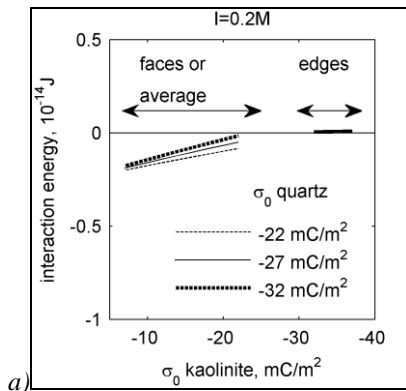


a)

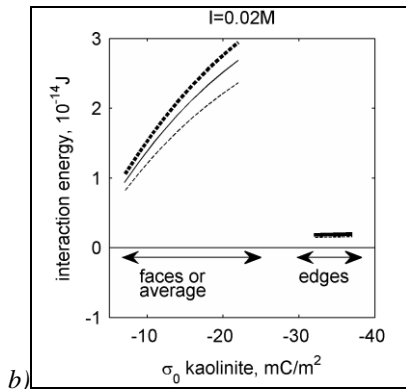


b)

Figure 5: Heating can increase the surface charge density and thereby result in a repulsive interaction energy between kaolinite and quartz at small separations. At 0.34 M ionic strength, a), the interaction energy becomes repulsive if heating increases σ_0 by a factor two compared to $\sigma_{0,20}$. At 2.0 M ionic strength there is only repulsion for a fourfold increase in $\sigma_{0,20}$.



a)



b)

Figure 4 the interaction energy between kaolinite faces and quartz at 2 nm between Stern planes (3 nm between surfaces) is attractive at 0.2 M (a) and repulsive at 0.02 M (b) for the range of $\sigma_{0,20}$ based on face or average particle charge. For the edges with a higher surface charge density there is repulsion both at 0.2 M and 0.02 M .

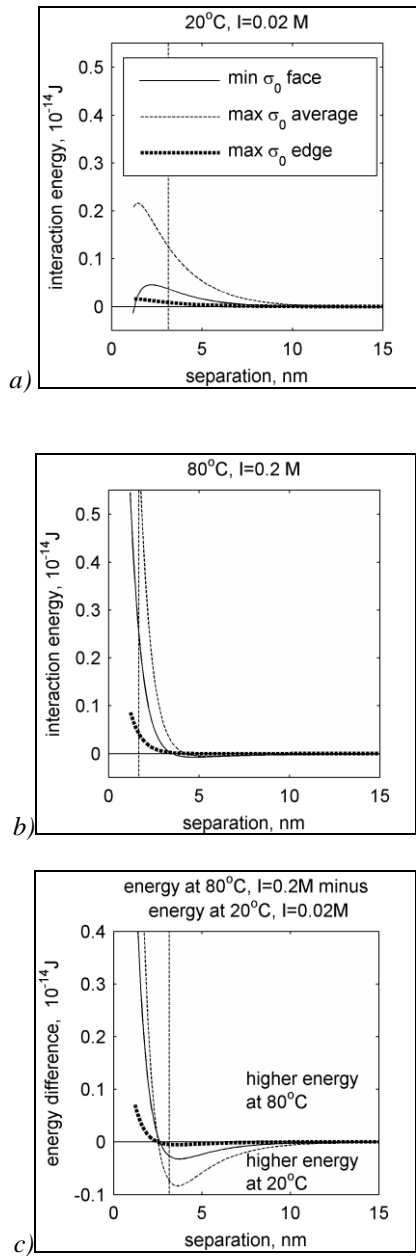


Figure 6: Comparison of the interaction energy among kaolinite particles at 20°C and 0.02 M ionic strength (a) to the interaction energy at 80°C (b) and 0.2 M ionic strength. The repulsive interaction energy is highest in the heated sample for small separations (c) (when the surface charge density increases by a factor 4 compared to the surface charge density at 20°C).

DISCUSSION

Heating from 20°C to 80°C has less effect on the Debye length, κ^{-1} , than ionic strength does, according to Eq. 4 (Figure 1a). However, Israelachvili and Adams (1978) suggest that Eq. 4 may under-predict

the thickness of the double layer at higher ionic strengths. Their measurements of the forces between mica surfaces indicate that the potential in the double layer falls less steeply than predicted by Eq. 4. A greater double layer thickness would result in greater repulsive interaction energy between surfaces with the same sign charge than we calculated. This effect would be greatest for our calculation of the interaction energy at 2.0 M.

The permeability reduction due to reduction of ionic strength, at 20°C, that was observed in experiments has been interpreted as kaolinite mobilisation. The calculated net interaction energy switched from attractive to repulsive between these ionic strengths (Figure 3a). Furthermore, Figure 4a and Figure 4b show that the switch from an attractive to a repulsive interaction energy can be expected to occur between these ionic strengths for a wide range of surface charge densities representative for the quartz-kaolinite system. Repulsion dominated the quartz to kaolinite edge interaction even at 0.2 M ionic strength. This suggests that the average charge on the kaolinite particle or possibly only the charge on the faces is relevant to predict mobilisation. Currently the zeta potential, ζ , which represents the average surface charge, is often used to predict kaolinite mobilisation in Berea sandstone (e.g., Kia et al. 1987; Schembre and Kovsky, 2005).

Heating from 20°C to 80°C was observed to reduce permeability in experiments with distilled water, as well as in tests with solutions of 0.34 M and 2.0 M NaCl. With a constant σ_0 , Eq. 7 predicts that the surface potential, ψ_0 is higher at 20°C than at 80°C (Figure 1b). Figure 4 shows that this increase was not sufficient to cause repulsion at either 0.34 M or 2 M ionic strength. A doubling of the $\sigma_{0,20}$ was sufficient to cause a repulsive interaction at 0.34 M, but the mobilisation we observed at 2.0 M ionic strength would require a fourfold increase in the $\sigma_{0,20}$ to obtain a repulsive interaction energy for the minimum separation between surfaces. We limit ourselves to the distance range beyond twice the 0.5 nm Stern layer. No quantification is made of attractive forces at smaller distances, but we note that at closer approach the van der Waals interaction suggests strong attraction (Eq. 3). Figures 5a and 5b do show another minimum for separations around 4-7 and 2-4 nm separation respectively. It has been suggested that particles can be loosely attached in this secondary minimum, from where they are more easily mobilised by hydrodynamic forces (Hahn and O'Melia, 2004). It appears unlikely that particles were attached in the secondary minimum at 80°C because the ionic strength had no effect on permeability whereas the secondary minimum is eliminated at low ionic strength. The secondary minimum is only present for a narrow range of separations; surface roughness can be expected to cause variation in the separation. The higher repulsive interaction at smaller distances may be expected to have a dominant effect.

The effect of heating on the surface potential can be significant. Electrophoresis data from Rodríguez and Araujo (2006) indicate that the ζ increases by a factor 2 when the sample is heated from 20°C to 45°C. This might possibly be extrapolated to match the increase required at 2.0 M. However, potentiometric titrations indicate only an approximate doubling of the surface charge when a sample is heated from 25°C to 70°C (Brady et al., 1996). The effect of a change in σ_0 on the interaction energy depends on the EDL thickness, which may be under-predicted by Eq. 4 at 2.0 M ionic strength. In that case a smaller change in σ_0 could cause mobilization. Furthermore, we have assumed that the effect of heating on the van der Waals interaction was negligible. We have also assumed that the Stern layer thickness was not affected by heating, and that the dielectric properties of fluid in the Stern layer were the same as the dielectric properties of the bulk fluid. All of these assumptions can be challenged; however, we lacked the evidence to support alternative assumptions. With these assumptions, Figure 5 indicates that the effect of heating on the EDL interaction is less than the effect of ionic strength on the EDL interaction if the σ_0 is constant. However, heating does increase the σ_0 ; whether the increase is sufficient to cause particle mobilisation is subject to discussion.

Scenario 1 can explain the stability of the aggregates at 20°C; here there is attraction among kaolinite particles even at low ionic strength. Figure 6a shows a small repulsive interaction energy between a kaolinite surface with a σ_0 representative of the faces and kaolinite surfaces with values representative of the average σ_0 and of the σ_0 on the edges at 20°C and 0.02 M ionic strength. The interaction between the surface and another surface with a kaolinite face σ_0 was attractive at short separations. However, the divergence between the different formulations for the EDL force is particularly significant at separations less than κ^{-1} (Gregory, 1975). We consider the interaction energy in this region to be more uncertain than those at larger separations. At greater separations there is repulsive interaction energy. However, suspended particles may aggregate despite a repulsive interaction energy barrier if their thermal energy is sufficient to overcome this (Hogg et al. 1966). Therefore, we do not rule out Scenario 1 based on these calculations. Even if particles do not aggregate due to the repulsive interaction, particles transported to the pore constrictions may still form particle bridges as in Scenario 2.

Scenario 3 appears unlikely. The repulsive interaction energy for the edges is lower than for the faces due to their smaller area. However, as also noted by Gupta et al. (2011), at pH 8 the edges have a high negative charge density, which makes it unlikely that they attach to the negatively charged faces. The observation that the permeability of the heated samples does not depend on the ionic strength also indicates that Scenario 3 is less likely. The stability

of the aggregates can be presumed to depend on the interaction energy among kaolinite particles and thereby on the double layer length. Scenario 4 is more plausible with repulsion among kaolinite particles.

As the DLVO calculations did not rule out Scenarios 1, 2 or 4, we considered these in combination with the permeability test data. Particles had been mobilised at 20°C by the reduction of the ionic strength and at 80°C they had been mobilised by heating.

At 20 °C increasing the ionic strength to 0.2 M or 2.0 did not improve the permeability. Figure 3 shows there is attraction between kaolinite and quartz at 0.2 and 2.0 M ionic strength. In the case of Scenario 4, the particles would be expected to re-attach to the grain surface. This can be expected to reduce specific surface and improve permeability, however, we did not observe a permeability recovery. The combination of DLVO theory and experimental observations rather suggests Scenarios 1 or 2 dominate at 20°C. These predict an irreversible permeability reduction. These scenarios are comparable to the current models for particle plugging (e.g. Khilar and Fogler 1984). At 80 °C the permeability reduction is reversible, and furthermore permeability increases at higher flow rates. This allows us to rule out Scenario 1, of stable aggregates. Scenario 3 has been ruled out based on the repulsive interaction energy between the edges and faces, leaving Scenarios 2 and 4. The observed reversibility with cooling suggests the particles are in suspension rather than as particle bridges. A reduction in the repulsive EDL force due to cooling would make the bridges more stable, rather than improve the permeability. This suggestion is supported by the observation that changing the flow direction had no significant effect on permeability at 80°C. However, the improvement in permeability with cooling may be due to removal of particle bridges by the increase in fluid viscosity and hydrodynamic forces. The lack of effect of flow direction may be due to the fact that when this was done at 80°C the particles formed bridges at the other side of the pore, since they were still repelled by the quartz surface. At 20°C the flow direction was reversed at high ionic strength so that particles could re-attach to the quartz grains. Scenario 2 might therefore prevail at both 20°C and 80°C, whereby the difference in the effect of flow velocity on permeability was due to the difference in the magnitude of the EDL repulsion.

Four different scenarios were proposed to explain permeability data in terms of kaolinite distribution. The permeability data suggest that a repulsive interaction energy prevails between kaolinite particles at high ionic strength at 80°C. This is supported by data showing that the surface charge density of the minerals increases with heating and by DLVO calculations based on this. The DLVO theory

is successful in predicting the kaolinite mobilization caused by the reduction in ionic strength at room temperature (Khilar and Fogler, 1984, Kia et al. 1987). We applied the DLVO theory to predict kaolinite mobilization for a range of different surface charge densities at 20°C and found that the ionic strength interval where mobilisation occurs was robust to the variation that can be expected for the kaolinite surface charge density. We then used the same EDL model and parameters to investigate kaolinite mobilization due to heating, and to investigate kaolinite aggregation at 20°C and at 80°C. The high uncertainty in the effect of heating on the relevant parameters, ζ and A , limits even a qualitative comparison of the effects of ionic strength and temperature.

CONCLUSION

The ionic strength at which permeability reduction occurs in laboratory experiments is within the same order of magnitude as the ionic strength that causes a repulsive interaction energy between kaolinite and quartz at 20°C. This ionic strength is robust for the range of surface potentials reported for different kaolinites in literature.

Heating can be expected to increase the surface charge density. In the framework of the DLVO theory this can lead to particle mobilisation and prevent particles aggregation. This would imply that at elevated temperature, pore throat plugging by stable particle aggregates is an unlikely mechanism of permeability reduction. The effect of temperature on other relevant parameters is not established well enough to make reliable estimates of inter-particle forces at elevated temperature.

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