

PHYSICO-CHEMICAL ASPECTS OF CLAY MIGRATION AND INJECTIVITY DECREASE OF GEOTHERMAL CLASTIC RESERVOIRS

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Abstract

Geothermal energy will play an increasingly important role in carbon dioxide emission-free energy production in the new millennium. High fluid production rates are essential for circulating geothermal systems to be economically viable. However the financial viability of the geothermal systems often suffers from a permeability decrease of clastic reservoirs, particularly in the vicinity of an injection well. Moreover, a number of projects that dealt with development of low enthalpy aquifers in Europe were abandoned because of the drastic drop of the aquifers' permeability during their exploitation. The decline of well injectivity is commonly caused by transport of clay particles, which are always present in sedimentary rocks. In spite of extensive research, internal clay and colloidal particle transport is still one of the issues that is poorly understood. Therefore development of reliable methods preventing clay plugging can significantly improve geothermal economics.

In the paper we highlight the effect of the main physico-chemical factors, such as salinity, type of exchangeable cations, pH and temperature, on the stability of clay particles in sandstone and their influence on the rock permeability. Through percolation experiments with Bentheim sandstone, combined with scanning electron microscope image analysis, we have found a strong correlation between the effect of the physico-chemical factors on the permeability and the parameters of the rock microstructure. The applied integrated approach that incorporates physical modeling, DLVO theory, and rock microstructure analysis, is a reliable tool for interpretation of the laboratory as well as field experiments. The formulated physico-chemical rules of clay particle stability and transport will help reservoir engineers to develop the best strategy for clastic reservoir exploitation and minimize the formation damage caused by clay migration.

Introduction

Environmentally safe production water re-injection is an important issue in geothermal energy exploitation. The injectivity of an injection well often decreases as a result of formation damage caused by in-situ clay particles released from the rock matrix. Clay transport is a common cause of soil dam damage. There is also evidence that the clays can be responsible for transportation of toxins in aquifers and contamination of drinking water in wells. Therefore clay particle transport in porous rock media is of scientific, industrial and environmental significance.

The rate of permeability decline caused by internal clays depends on the intrinsic fluid velocity and physico-chemical factors controlling the electrical double layer around the clay particles. The quantitative theory of colloidal particle interactions was developed by Derjagin B.V. (1937), Landau L.D. (1941), Verwey J.J.W. and Overbeek J.Th.G. (1948) (DLVO theory). Later on, based on the DLVO theory principles, the theory of clay particle interaction and clay rock properties was developed (H. van Olphen, 1963; J.K. Mitchell, 1976; V. I Osipov, 1979). It is well known now that the stability of clay particles in water suspensions and sandstone reservoirs is determined by the balance between the attraction Van der Waals-London forces on one side and the repulsion electrostatic forces as well as structural forces of bound water on another side.

In this paper we highlight the mechanisms of formation of clay surface charge and the clay particle electrical double layer (EDL). Then we consider the influence of physico-chemical factors on coagulation-dispersion processes and the rate of pore throat bridging by internal clays. In particular we describe the effect of the ionic strength, chemical composition, pH and temperature of the permeating fluid, as well as clay mineralogy and composition of the exchangeable cations. Further we describe the effect on clay stability of structural forces of adsorbed water layers, which are often ignored in reservoir engineering literature. Finally we present our experimental data concerning the effect of salinity of the injected fluid on release and migration of different micro-morphological types of clays in Bentheim sandstone.

THEORY OF CLAY-INDUCED FORMATION DAMAGE

The porous medium of sandstone can be represented as a network consisting of pores connected with each other by narrower pore channels (or throats). The widely accepted model of in-situ clay-induced formation damage supposes that the permeability reduction occurs due to release of clay particles from pore walls and their subsequent re-deposition downstream in pore throats, which presumably have smaller diameters than the pores (Priisholm et al. 1987).

The stability (or, on the contrary, detachment) of the in-situ clay particles in a reservoir is determined by the balance between the forces affecting the clay particles. The interaction between a clay particle and a pore surface can be described by the following equation:

$$F_{\text{total}}(h) = F_{\text{LVA}}(h) + F_{\text{DLR}}(h) + F_{\text{BR}}(h) + F_{\text{HR}}(h) + F_{\text{IHL}}(h),$$

where

$F_{\text{total}}(h)$ - the resulting force of a clay particle-pore wall interaction (positive if repulsion dominates, and negative if attraction dominates); $F_{\text{LVA}}(h)$ - London - van der Waals attraction; $F_{\text{DLR}}(h)$ - repulsive force due to overlap of double

electrical layers of like charged surfaces (i.e. clay and mineral matrix); $F_{BR}(h)$ - Born Repulsion (significant at a distance of less than 5 Å); $F_{HR}(h)$ - hydrodynamic force (depends on the interstitial velocity of the permeating liquid); $F_{IHL}(h)$ - structural force of the interfacial hydrate layers; h - distance between a single particle and a pore wall. The London-van der Waals attraction force has a negative sign, all other repulsion forces a positive one.

A similar equation in terms of potentials was introduced by Khilar K.S. and Fogler H.S. (1987). However, they ignored the effect of the interfacial hydrate layers (Derjagin B.V. & Titievskaja A.S. 1953) that also play an important role in interaction between clay particles and pore matrix.

Most of the entities of the equation are mathematically described by the DLVO theory (Derjagin 1937, Derjaguin and Landau, 1941; Verwey & Overbeek, 1948). Unfortunately it is rather difficult to measure many of the parameters (e.g. Hamaker constant) which determine these entities. Hence it can be used mostly for semiquantitative evaluation of clay particle stability in porous media. Nevertheless it allows us to analyze the influence of the physico-chemical factors and flow rate on the sandstone permeability.

The equation shows that the rate of clay particle release (and permeability decline) depends both on the interstitial fluid velocity and the physico-chemical factors controlling the double electrical layer structure around clay particles (and therefore F_{DLR}). For example, the internal clay particles start being released if a so-called critical flow rate (CFR) is exceeded (Vernoux J.F. & Ochi J. 1994). The value of the critical flow rate (or critical fluid velocity, CFV) depends on the physico-chemical conditions in the reservoir, the clay and rock matrix mineralogy as well as pore size distribution. Pore size distribution is important because it controls the distribution of the interstitial fluid velocity within the porous medium and determines hydrodynamic forces affecting the clay particles.

Clays can also cause pore plugging if the salt concentration in the permeating fluid falls below a critical salt concentration (CSC), even if the flow rate is relatively small. The value of the CSC depends significantly on the type of salts dissolved in the permeating fluid (Khilar & Fogler, 1987).

The effect of the physico-chemical properties of the injected fluid on the particle transport was intensively investigated in petroleum engineering. Strong correlation was found between the permeability and the salinity. However, in geothermal and disposal wells injection rates are much higher than in injectors at oilfields. It means that particle release can occur purely due to high hydrodynamic forces (FHR), even if the physico-chemical conditions do not change (Priisholm et al. 1987).

It is a well documented fact (e.g. by Mungan, 1965) that at low flow rates an abrupt salinity drop causes drastic permeability reduction due to increase of the electrostatic repulsion (F_{DLR}) between clay and sand surfaces. It still is not clear, however, what happens if the salinity of the injected fluid is reduced gradually and whether it has any significant effect on the permeability if the flow rate is primarily higher than the initial critical value for the reservoir.

Mechanisms of clay surface charge

Clay face surfaces

Theoretically, the electrical double layer (EDL) can be represented as a "condenser" where the negatively charged inner layer of the condenser is built up by a clay crystal surface and a positively charged outside layer is formed by exchangeable cations (Fig. 1). The charge of a clay face surface mainly depends on the isomorphous changes occurring in the clay crystal. For example, the Si^{4+} cation can be substituted by Al^{3+} , Mg^{2+} , etc. As a result the crystal structure gets a negative charge that is compensated by exchangeable cations in dry conditions. In the presence of water (e.g. in aqueous suspension) the exchangeable cations dissociate and the clay crystal surface gets negatively charged.

Clay edges

When a clay crystal edge interacts with water, $(-SiO)$ groups are hydrated and form $(-SiOH)$ groups on the crystal edge surface: $2(-SiO) + H_2O \rightarrow 2(-SiOH)$. In base conditions the formed poly-silicon acid partially dissociates: $(-SiOH) \rightarrow SiO^- + H^+$. The produced H^+ ions (or H_3O^+) transit to the aqueous phase, but under the electrostatic attraction of $(-SiO^-)$ -groups they remain nearby the crystal surface.

The concentration of OH^- and H^+ -ions in the solution affects the degree of dissociation of the $(-SiOH)$ group and thus determines the potential of the silicon surface (i.e. clay edge charge). An increase of pH (i.e. concentration of the OH^- ions) increases the silicon surface negative potential and thus stabilizes clays in aqueous suspensions. The dispersion effect of diluted alkaline solutions can complicate purification of the injection water from clays. In clayey sandstone it can lead to the detachment of internal clay particles from the sand grains and cause clay-induced formation damage.

If Si^{4+} is isomorphically changed with Al^{3+} , the type of the $(-AlOH)$ group dissociation depends on the pH. In base conditions the $(-AlOH)$ group dissociates by the acid type ($Al(OH)_3 \leftrightarrow Al(OH)_2O^- + H^+$), and in acid condition by the base type ($Al(OH)_3 \leftrightarrow Al(OH)_2^+ + OH^-$). In the second case the edges of the clay particles get positively charged.

In many minerals (e.g. in montmorillonites) the isomorphous exchange of Si^{4+} for Al^{3+} occurs only in octahedral layers. If there are no isomorphous exchanges for Al^{3+} in tetrahedral positions, the edges of tetrahedral layers remain neutral in acid environment and get negatively charged in base conditions. Nevertheless it is important to notice that in mica and hydromica isomorphous exchange of Si^{4+} for Al^{3+} can be present in tetrahedral layers as well, and thus the edges of these layers behave similar to octahedral ones.

Besides those described above, there are also some other mechanisms of charge formation in clay minerals that are considered in detail in clay mineralogy literature (Sergeev, 1983).

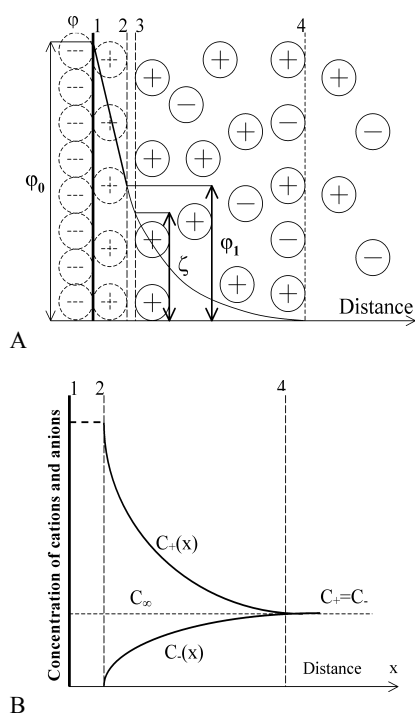
Clay particle electrical double layer structure

In an aqueous environment, hydration reduces the strength of bonds between a clay surface and exchangeable cations (cations-compensators or counterions). While some of the cations remain attached to the clay surface and form the adsorbed cation (or so-called Stern) layer, others transit at

some distance from the clay surface and form the diffuse ionic layer (Fig. 1, A). The distribution of the dissociated cations near a clay particle surface is determined by the balance between electrostatic attraction of the clay surface and thermal motion of the ions tending to spread the ions away from the surface and equalize their concentration in the solution. Consequently the concentration of the dissociated cations decreases with the distance from the particle, attaining the concentration of the similar cations in the solution (Fig. 1, B). The concentration of the anions on the contrary decreases in the direction towards the surface.

The clay surface charge is balanced by an equivalent number of oppositely charged cations in adsorption and diffusion layers. The part of the clay surface (or thermodynamic) potential which is compensated by the adsorbed cation layer, is called consequently the adsorption potential. The remaining part of the potential, at the boundary between adsorbed and diffusion layers, is called Stern potential.

The interaction between charged particles is governed predominantly by the overlap of their diffusion layers, so the Stern potential is often considered as the most relevant to the interaction (Gregory, 1989). Nevertheless, there are no direct methods for determining thermodynamic or Stern potentials. Instead of the Stern potential, the electrokinetic or ζ -potential is often used for calculations. The electrokinetic potential is that at the plane of shear between a particle and a fluid when there is relative motion between them (e.g. due to electrophoretic clay transport or electro-osmotic fluid flow). Consequently, the ζ -potential of clays can be found by means of electrophoresis or electro-osmosis techniques. In spite on the fact that the shear plane does not coincide precisely with the adsorption layer boundary (the Stern plane), ζ -potential can be used in many cases as an adequate substitute for the Stern potential.



Effect of physico-chemical factors on ξ -potential, EDL properties, and stability of clay particles.

The electrokinetic potential is one of the main parameters that determine clay particle stability in suspensions and the strength of clay-mineral skeleton contacts in sandstone reservoirs. An increase of the ξ -potential adds to the electrostatic repulsion between clay particles and thus stabilises clay suspensions and complicates injection water filtration. In a sandstone an increase of the ξ -potential of clay particles and the rock matrix grains can lead to release of the clays from the pore walls and cause pore throat plugging.

The value of ξ -potential and thickness of the diffuse layer are controlled mainly by the following factors: clay surface potential (i.e. mineralogy); type of the exchangeable cations; concentration and chemical composition of the pore solution; dielectric constant of the solution, pH and temperature. In the following paragraphs we consider the influence of these factors on the ξ -potential, EDL structure and stability of clay particles.

Clay mineralogy and composition of the exchangeable cations

The value of the surface potential of clay minerals generally increases with the number of hetero-valence isomorphic changes in their crystal structure. Nevertheless one should be aware that the excessive charge of the octahedral layers can be significantly screened by tetrahedral ones, e.g. in the minerals with 2 (tetrahedral layers) : 1 (octahedral layer) structure. However the montmorillonite minerals, because of a large specific surface, have better developed diffuse layers and exhibit rather larger swelling (and consequently swelling induced formation damage) relative to kaolinite and hydromica.

The value of the ξ -potential at the face surfaces (ξ_{001}) varies significantly for different cation forms of the same mineral. Increase of valence of exchangeable cations strengthens bonds between the cations and the clay surface and consequently reduces the ξ -potential and the diffuse layer thickness.

Polarizability of a cation increases and its hydration ability decreases with increasing of the cation radius. Larger polarizability and less hydration ability of a cation contributes to strengthening of its adsorption bonds with a clay surface. Therefore, if the exchangeable cations have the same valence, the increase of their radius should lead to decrease of ξ -potential and the diffusion layer thickness (except H^+).

Figure 1. A principle scheme (Stern model) of the electrical double layer on the boundary clay face surface - aqueous solution.

A - cation and electrical potential distribution near a charged surface.

B - cation (C_+) and anion (C_-) concentration as a function of a distance from the surface.

ϕ_0 = surface potential; ϕ_1 = Stern potential; ξ = electrokinetic potential; 1 - clay surface; 2 - Stern plane; 3 - plane of shear, between a particle and fluid; 4 - boundary between a diffuse layer and free solution.

These theoretical propositions were confirmed by numerous experimental investigations. Ovcharenko, Poliakov and Alekseev (1971) show that at equal concentrations of the pore solution the ξ -potential of different ionic forms of vermiculite decreases as follows: $\text{Li} > \text{Na} > \text{NH}_4 > \text{Ca} > \text{Cu} > \text{Mn} > \text{Co}$, and for palygorskite: $\text{NH}_4 > \text{Ca} > \text{Mn} > \text{Co} > \text{Cu}$.

Quirk and Schofield (1955), Khilar and Fogler (1987) found experimentally that there is a critical ionic strength below which clays start being released and transported in sandstone; that for KCl solutions is rather lower than for NaCl solutions.

According to Efremov I. F and Zon I.R. (1983), for mono-ionic forms (Li, Na, Cs, H) of kaolinite the ξ -potential reduces in the following order:

$\text{Li} (\xi = -71 \text{ mV}) > \text{Na} (\xi = -48 \text{ mV}) \approx \text{Cs} (-49 \text{ mV}) > \text{H} (-24 \text{ mV})$.

Many scientists claim that the surface charge of kaolinite is mainly concentrated on the edges of clay particles where the valence bonds are not filled. Because there are a few isomorphous changes in the kaolinite structure, the face surfaces have relatively small charge and the exchangeable cations are mainly adsorbed on the crystal edges. This specific charge distribution distinguishes kaolinite from most other clay minerals which have higher values of ξ -potential on face surfaces (Osipov et al., 1985; Grim, 1963.)

Zlotchevskaia and Korolev (1988) have found that ξ -potential also depends on the water saturation of the rocks. According to their electro-osmotic tests (which can measure only the averaged value of ξ -potential of clay face surfaces and edges) ξ -potential changes from 10 to 50 mV for kaolinite, and from 15 up to 100 mV for montmorillonite, depending on the moisture of the investigated samples.

Effect of pH

As mentioned above, the edges of clay minerals are negatively charged in alkaline solutions and positively charged in acid solutions. The value of the iso-electric point can vary significantly depending on the mineralogy and crystal structure of clays. According to Osipov (1979), for montmorillonite the iso-electric point is equal to 6.5, for hydromica it is 6 and for kaolinite about 8. D. Williams and K. Williams (1977) found from electrophoretic measurements that the iso-electric point of kaolinite amounts to 7.4.

It is important that high concentrations of some polyvalent cations in pore solution can also cause a change of sign of ξ -potential of natural minerals. For instance, it has been shown experimentally that surfaces of quartz grains become positively charged in highly concentrated solutions of AlCl_3 (Tchistiakov et al., 1983).

Change of the charge sign at the clay edges to a positive one causes coagulation of clay suspensions and consequently simplifies the process of the injected water filtration. In acid environment clay suspensions form a sediment with highly porous but strong microstructure where face-edge type of contacts dominates. The strength of the contacts between the oppositely charged surfaces is much higher than the strength of the contacts formed due only to Van der Waals-London attraction in base conditions (Osipov, 1979, Sokolov, 1989, Tchistiakov, 1994). In sandstone reservoirs with acid fluid in the porous medium, the internal clays should be more stable relative to alkaline conditions if the pore walls (e.g. quartz)

remain negatively charged. Nevertheless it is important to emphasize that injection of fresh water, particularly at high flow rate, can cause clay release even if the pH of the injected fluid is lower than the isoelectrical point. Moreover, extreme pH conditions (both alkaline and acid) can cause clay disintegration or their transformation to other mineralogical forms and consequent formation damage (Hayatdavoudi and Ghalambor, 1996).

Effect of the salt concentration in the pore solution.

Here we consider the effect of salts, which do not change the surface potential of clay particles themselves (indifferent electrolytes) but affect the thickness of the EDL. Generally, if the other physico-chemical conditions (moisture, temperature, particle size, pH, surface potential) are constant, the increase of salt concentration causes reduction of the double ionic layer and a decrease of the ξ -potential (Gregory, 1989). This is explained by the fact that, if the salt concentration in the pore solution increases, some of the cations move from the diffuse layer to the adsorption layer and consequently the ξ -potential decreases (for simplification we presume that the exchangeable cations and the cations in the pore solution are the same).

Nevertheless it is important to emphasize that some experiments show that replacement of distilled water by dilute solutions of NaCl in Na-forms of clays can cause increase of ξ -potential and enlargement of the diffusion ionic layer (Zlotchevskaia and Korolev, 1988). For different minerals the NaCl dispersing effect on clay soils and suspensions was observed at concentrations between 0.001 M and 0.01 M. (Zlotchevskaia and Korolev, 1988; Tchistiakov 1994). For the Na-form of the minerals a possible mechanism of this phenomenon may be the following. While only distilled water is present in a pore medium, some of the H^+ diffuses to the exchange complex of clay minerals. The permeating of NaCl solution causes exchange of some H^+ for Na^+ , which leads to increase of the clay zeta potential (see above). Further increase of NaCl causes successive reduction of ξ -potential. A similar mechanism of the NaCl dispersion effect can be suggested for polyvalent forms of clay minerals.

Effect of cation exchange reactions on the clay stability

In practice we usually deal with aqueous solutions which contain several salts. The cations of the most common salts can be distributed in the following order according to their adsorption capacity (or energy of their adsorption at clays): $\text{Fe}^{3+} > \text{Al}^{3+} > \text{H}^+ > \text{Ba}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ (Sergeev, 1983). Thus the mono-valence cations (other than H^+) can more easily desorb from a clay surface and go to the diffuse layer around the clay particle. This means that, if the concentration of the cations in the solution is equal, the equilibrium in the exchange reactions is always shifted to polyvalent cations.

The critical coagulation concentration of salts, above which clay suspensions coagulate, depends strongly on the valency of the cations present in the solution. The value of the coagulation limit decreases with increase of the cation valency and consequently with the partial concentration of the polyvalent salts in the solution. That is why polyvalent salts are widely used to purify water from clays (Babenkov, 1977).

It is reasonable to suggest that salts containing polyvalent cations have a stabilizing effect on clay particles in sandstones due to strengthening of the clay-matrix bonds, and therefore can be considered as chemicals that counteract formation damage caused by in-situ clays. Khilar and Fogler (1987) experimentally proved this theoretical proposition. They have shown that the increase of the partial concentration of CaCl_2 in the mixture with NaCl reduces the value of the critical ionic strength of the solution permeating through the illite soil bed.

Effect of temperature

Based on the results of electro-osmosis measurements in Na-forms of kaolinite and montmorillonite, Zlotchevskaia and Korolev (1988) show that the ξ -potential grows almost linearly when the temperature increases from 5°C to 70°C. The increase of the ξ -potential for kaolinite amounts to 40% and for montmorillonite reaches 55%. Fazilova (1976) and Sidorova and Fridrikhsberg (1980) also detected growth of the ξ -potential for quartz fibres with increase of temperature.

Based on these data it is possible to suggest that an increase of temperature should increase the stability of clay particles in suspension. In sandstone, therefore, temperature increase should stimulate clay particle dispersion from the mineral grains.

Nevertheless, Korolev (1988) together with Tchistiakov (1991) have found experimentally that the effect of temperature on stability of clay suspensions is much less evident than the effect of other physico-chemical factors. It depends on the mineralogy of clay particles and the ionic strength of the solution as well as on the interval of the temperature. For example, they have shown that the increase of ionic strength of aqueous clay suspensions significantly reduces the effect of temperature on the coagulation processes.

On one hand a rise of temperature increases the value the ξ -potential and contributes to dispersion of clay particles. On the other hand the temperature increase reduces the splitting effect of bound water layers around the clay particle (see below). Thus the total effect of the temperature on clay particle stability will depend on the dominance of one of these factors in particle-particle (or particle-matrix) interactions.

Cho et al. (1999) has shown that with an increase of temperature from 20°C up to 80°C the mobility of a Ca-bentonite bed increases as much as three times. From these data it is possible to suggest that the mobility of the Ca-bentonite is controlled mainly by variation of dynamic viscosity with temperature but not clay swelling-shrinkage processes. This conclusion is in agreement with the experimental results obtained by Zlotchevskaia and Korolev (1988). They have shown that the temperature significantly affects only the swelling of Na-montmorillonite and does not have almost no influence on swelling of Ca-montmorillonite or Ca-kaolinite.

Beside physico-chemical researches, the effect of temperature on clay particle stability and formation damage has been investigated intensively in reservoir engineering. Anuj Gupta and Faruk Civan (1994) give an extensive theoretical overview on temperature sensitivity of sandstones. Unfortunately there is still no robust agreement between experimental results and theory concerning the effect of temperature on clay transport.

Effect of structural forces on clay particle stability

In an aqueous environment, clay minerals adsorb water molecules, and water films form on the particle surfaces (Fig. 2). Many authors distinguish two main structural water layers: adsorption (or "firmly bonded") water layer, and "osmosis" (or loosely bonded) water layer. B.V. Derjagin (1984) calls the first layer α -film and the second one β -film. These two types of water films are characterized by different physico-mechanical properties and strengths of contact with a clay surface.

Within the α -film we can distinguish theoretically two layers. The water layer closest to a clay surface is formed by molecules which hydrate the clay crystal surface and adsorbed cations. The water molecules are firmly attached to the clay particles, mainly by hydrogen and ion-dipole bonds. The outer layers of the α -film are formed by water molecules which are highly oriented toward the clay surface due to dipole-dipole interactions with the water molecules attached immediately to the clay.

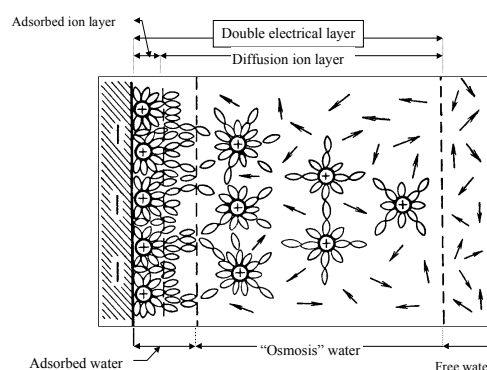


Figure. 2. Structure of water films near a clay face surface (after Zlotchevskaia and Korolev, 1977)

The thickness of the α -film depends on the crystallographic parameters of the clay particle and the physico-chemical properties of the pore solution. Derjagin (1984) shows experimentally that for a pure silicon surface the thickness can vary from 1.5 - 8 up to 30 nanometres. Because of the forced orientation of the water molecules within the α -film, the adsorbed water has higher values of viscosity and shear yield limit relative to "free" water. Bondarenko (1973) determined experimentally an α -film shear yield limit of 9.5-13 Pa. The shear yield limit of free water is rather less, equal to 10^{-3} Pa. The dielectric constant of adsorbed water films in montmorillonite, which have a thickness of 5-8 nanometres, amounts to only 24 (while for water it is 81). Many other parameters of the adsorbed water, e.g. freezing temperature and thermal conductivity, also differ significantly from properties of free water.

The β -film is a transition layer between the highly structured water of the adsorption layer and free water. Within the β -film some of the water molecules are associated with the diffused exchangeable cations, which causes distortions in the water structure. The exterior boundary of the osmosis water theoretically coincides with the outward boundary of the

diffuse ionic layer. The physical properties of the osmosis layer and free water are comparable.

If the base surface of a clay particle can be considered as a plate, the clay particle edge can be approximated as a convex cylindrical surface. In this case the thickness of water films will be determined by (inter alia) capillary forces acting at the cylindrical interfacial surfaces. Because of the capillary effect, water films are less stable on a convex surface than on a plate (Derjagin and Churaiev, 1984). This is the reason why the water films on clay edges are rather thinner than on face surfaces. Sokolov (1989), for instance, shows that the water film at the clay edges can be ten times thinner than at the face surfaces.

The structural forces associated with the water films have a splitting (repulsion) effect on the clay particles and thus the balance between coagulation-dispersion processes depends on the thickness of the films (Derjagin and Titievskaia, 1953). Because the film thickness at the clay edges is much smaller, clay particles in suspensions are less stable against coagulation at their edges (Tchistiakov, 1994). In sandstone, clay micro-aggregates often interact with the rock matrix predominantly along their edges.

The boundaries between different types of the film water layers have a kinetic nature. The water molecules can diffuse from the adsorption water layer to the "osmosis" water layer, from the "osmosis" layers to free water, and reverse. A temperature increase intensifies diffusion of the water molecules away from the clay surface and thus causes degradation of the water films and reduction of their total splitting effect.

In spite of intensive investigation of the effect of water films on clay and colloidal stability, the quantitative theory of elastic and rheological properties of the adsorbed water layers is still not very well developed. Nevertheless, their effect on clay stability can not be ignored in formation damage evaluation.

EXPERIMENTAL

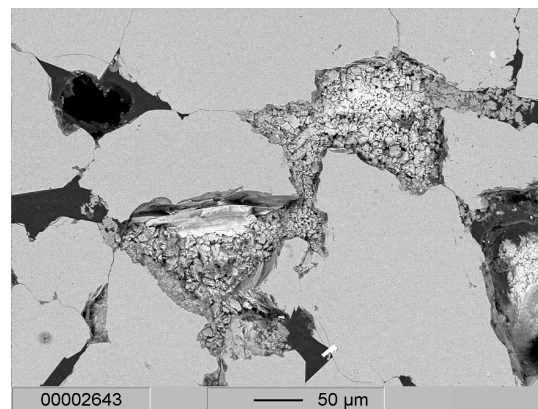
Rock characteristic

In our experiments we use Bentheim sandstone, collected in the western part of Germany. The sandstone consists of α -quartz (97.2%), 1.4% kaolinite and 1.3% microcline. The sandstone is well sorted with grain shapes varying from subrounded to rounded. The contacts between grains are formed as a result of quartz overgrowth or pressure dissolution (both types of contacts are clearly observed in the SEM images). Clay cement is also present but has a minor importance. The clay fraction is represented mainly by kaolinite, which can easily be identified by the hexagonal shape of the individual particles and "booklet" like aggregates.

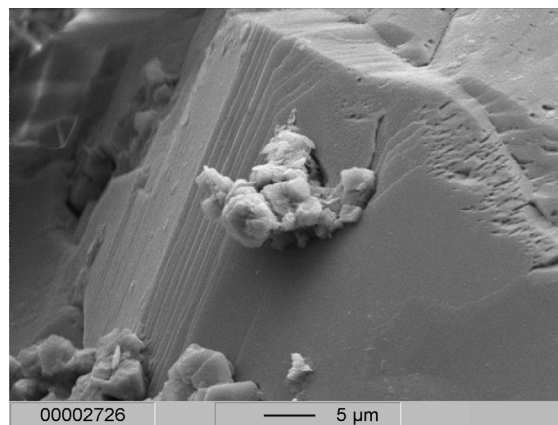
Kaolinite is formed as a result of weathering of feldspar grains. If a clay aggregate replacing a feldspar grain is not afterwards eroded, it remains where it was formed and consequently the whole clay aggregate inherits the shape of the original feldspar grain (Fig. 3a). The aggregates are surrounded by quartz grains and form rather isolated clay "pockets" in the sand

structure. The clay pockets have a compact microstructure formed by kaolinite booklets.

Part of the kaolinite microaggregates and particles were eroded and subsequently re-deposited at sand grains (Fig. 3b). This class of clays we call "discretely dispersed" (after Neasham, 1977). The exchange complex of the clays is represented mainly by Na^+ and Mg^{2+} .



a. Clay pocket (backscattering electron microscope image)



b. Discretely dispersed clays

Figure 3. Microstructure of the original Bentheim sandstone before flooding.

Experimental set-up and procedure

Percolation experiments were performed on Bentheim sandstone cores with a diameter of 1" and length of 3". We flooded the cores with aqueous NaCl solutions of different concentrations at flow rate of 10 l/h. This laboratory flow rate value corresponds to the injection rate of 150 m³/h at a well with a diameter of 0.1 m and an injection interval of 30 m (Vernoux and Ochi, 1994). We successively reduced the NaCl concentration in the injected fluid from 1 M to zero (1 M, 0.5 M, 0.1 M, 0.05 M, 0.01 M, and distilled water). Then, after injection of distilled water, we again injected again 1 M NaCl solution.

At every stage of the experiments we injected about 2000-3000 pore volumes of the fluid, until permeability had stabilized. We ran the experiments at 25°C. The pH and temperature were monitored and viscosity correction was applied during the calculation of Darcy permeability.

Results and discussion

Effect of decreasing salt concentration

The percolation experiments show that successive reduction of the NaCl concentration in the permeating fluid causes consecutive reduction of the permeability (Fig. 4). The most obvious permeability drop (20%) occurs after switching from 0.01 M NaCl solution to distilled water. When we inject again the 1 M NaCl solution following the distilled water we detect some recovery of the permeability (Fig. 4).

The SEM images of the percolated samples show that many of the pore throats are plugged by re-deposited clays that were discretely dispersed in the original sandstone (Fig. 5b). Nevertheless numerous clay pockets as well as some of the discretely dispersed clay particles are still present in the rock (Fig. 5b).

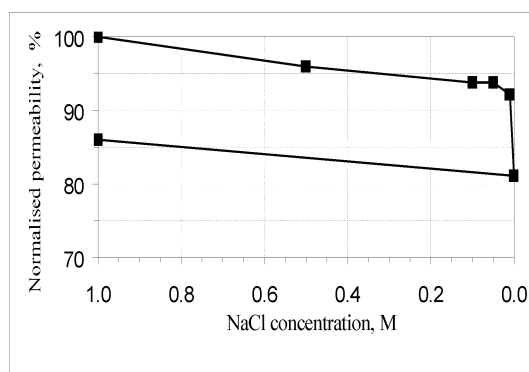


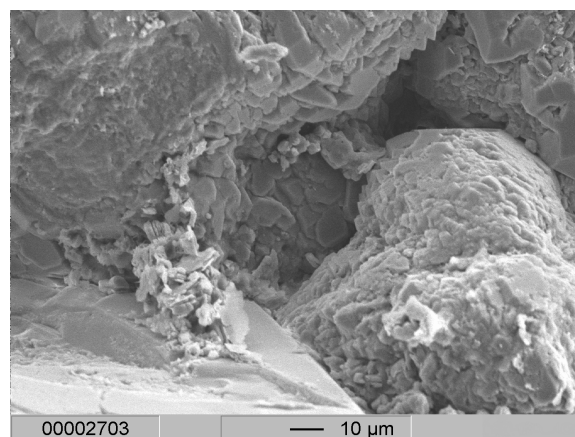
Figure 4. Effect of NaCl concentration on the sandstone permeability. Normalized permeability (k_n) is the ratio of the end permeability (k), corresponding to each NaCl concentration, to the permeability value calculated for 1 M NaCl solution. $k_0=1.85$ D, $k_n = (k/k_0) \times 100\%$

X-ray microanalysis of the clay plugs and the filtrate show that the migratory fines are mainly kaolinite. Besides the kaolinite a few fine grains of quartz and feldspar are also traced in the filtrate.

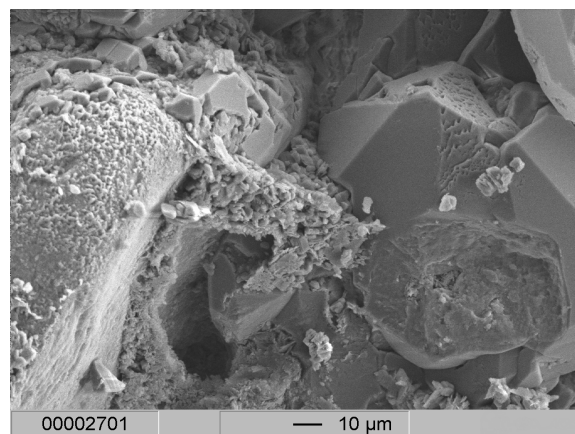
The release of the clay particles from the rock mineral skeleton can be explained by the cation exchange reactions occurring during saturation of the rock with highly concentrated NaCl solutions and further percolation with distilled water. The exchange of Mg^{2+} for Na^+ in kaolinite (in highly concentrated solutions), followed by successive reduction of the ionic strength of the permeating fluid, causes increase of the clay ξ -potential (Zlotchevskaia and Korolev, 1988). This consequently increases electrostatic repulsion between kaolinite particles, microaggregates and quartz grains (FDLR). Increase of the interfacial water layer thickness as a result of cation exchange for Na^+ in kaolinite also contributes

to Na-kaolinite dispersion due to splitting effect of the bonded water layers (FIHL).

While the discretely dispersed clay particles can be easily detached from sand grains by hydrodynamic forces, the clay pockets, being isolated by surrounding grains, remain in many cases preserved.



a. Clays bridging a pore throat

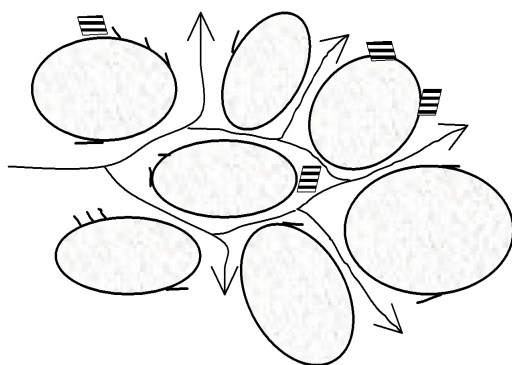


b. Clay pocket remained undisturbed during flooding

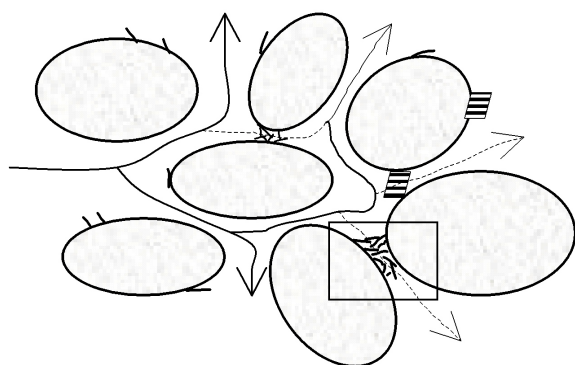
Figure 5. Microstructure of the sandstone after flooding

Effect of increasing salt concentration

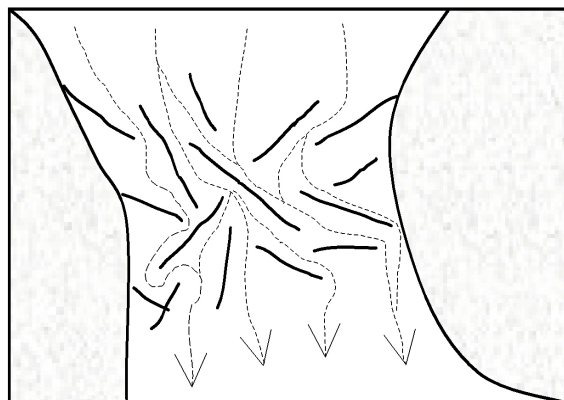
The experiment shows that the injection of 1 M NaCl solution after distilled water causes some recovery (5%) of the permeability (Fig. 6). We can give the following explanation to this phenomenon. The total permeability of the original sandstone is determined mainly by the inter-granular pore flow, because the total clay content is less than 2% (Fig. 6a). The swelling of kaolinite is very small (Sergeev et al., 1983). Therefore the swelling effect of the discretely dispersed clays on the porosity and permeability of the original sandstone is negligible.



a. Flow pattern in the original sandstone



b. Flow pattern in the "damaged" sandstone



c. Flow pattern within a throat plugged by clay particle and micro-aggregates.

Figure 6. Flow micromorphology in the Bentheim sandstone. *It is important to emphasize that the picture does not reflect the real ratio between sizes of clay and sand particles.*

After the discretely dispersed clay particles have been released from pore walls, and consequently part of the pore throats has been plugged, the micromorphology of the flow changes significantly. In this case within the pores the permeability is still determined by the inter-granular flow, but within the plugged pore throats it is controlled by inter-clay microaggregate flow (Fig. 6 b and c).

The permeability within the pore throats depends on the thickness of the interfacial hydrate layers around the clay particles and microaggregates (i.e. swelling of the clay particles). Thus the factors which influence the swelling of the clay affect the permeability of the sandstone as well. It is well known that the saturation of clay soils with highly concentrated brines causes reduction of the double electrical layer (Olphen, 1963) and interfacial hydrate layers (Derjagin and Churaiev, 1985). This consequently reduces swelling of the clay soils (Osipov et al., 1989).

While the Na-kaolinite plugs are saturated with distilled water the clay particles have well-developed interfacial hydrate layers. Thus the inter-particle pore space is blocked (partly or completely) by the adsorbed water, which has much higher viscosity than free water. The injection of 1 M solution of NaCl (after distilled water) causes reduction of the thickness of the interfacial hydrate layers and closer attachment of the clay particles within the microaggregates. This consequently increases the effective inter-microaggregate pore diameters and permeability of the pore throats. We believe that this is the main reason for the partial recovery of permeability of the sandstone after repeated injection of the highly concentrated sodium chloride solution.

Summary

Physico-chemical conditions determine clay particle stability in sandstone reservoirs. Thus, even if the fluid velocity in the reservoir is relatively low, changing these conditions can cause clay particle detachment and subsequent formation damage. The permeability of the rock is therefore a function of the hydrodynamic parameters as well as the physico-chemical properties of the permeating fluid and the rock material. In our opinion, only tests with samples of natural rocks reproducing the maximum number of factors affecting permeability can give reasonably reliable information about the formation reaction to fluid injection. Unfortunately, laboratory experiments and existing reservoir models are not really able to reproduce or take into account the whole variety of the physico-chemical micro- and macro-conditions occurring in reality. This significantly complicates up-scaling of the laboratory results to the reservoir level. Hence a specific approach is required for every formation.

The permeability damage potential can be evaluated only via broad-minded and interdisciplinary thinking, rather than through automatic application of mathematical equations and laboratory test results. We are convinced that better understanding of the fundamental physico-chemical principles of clay particle stability and transport in porous media will help the reservoir specialists to develop better techniques and apply more effective existing ones for preventing in-situ clay induced formation damage of geothermal reservoirs.

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