Particle clogging in porous media

Filtration of a smectite solution

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SKB

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Summary

The goal of this project is to find out if it is possible for bentonite clay to self heal during leaching with deionized water. The investigation has focused on the formation of a filter cake made of accessory material from MX 80 and the separation of solid material when a smectite solution (1%) is pushed through the cake using a pressure difference of 5 bar. It was also in the scope of this project to design and build the necessary equipment for these experiments.

In the literature review it was not found any example that the phenomenon of clogging has been used as a self-healing method previously. It was rather separated also between the clogging of a filter cake (deep bed filtration or cake filtration) and the filtration of colloidal particles. Probably because the latter are in such low concentrations in natural systems and the focus have mainly been in the transport properties of colloids within a filter cake or deep bed filter.

An experimental equipment was designed and built. It consists of seven filtration cells that could operate in parallel. All of them are connected to the same source of pressure to ensure equal conditions. A system was also prepared to prevent air from dissolving in the solution because it could create an unwanted expansion in the filter cake due to lower solubility at lower pressure.

The experiment showed good separation of smectite particles from the solution when it passed through the filter cake. In all tested cases, the separation was almost complete after long enough time, indicating that the cake has small enough pores to act as a geometrical hinder for the small particles. Comparison between the materials prepared at Chalmers University of Technology and at Clay Technology showed a very good agreement indicating similar properties of the produced smectite.

Sammanfattning

Målet med detta projekt är att utröna om bentonitlera har möjlighet att självläka vid lakning med avjoniserat vatten. Undersökningen har fokuserat på bildandet av en filterkaka från assessoriska partiklar i MX-80 och separationen av fast material för en lösning innehållande 1% smektit som passerar filterkakan vid en tryckskillnad på 5 bar. Inom projektet skulle också nödvändig utrustning för ändamålet utformas och byggas.

I litteraturgenomgången hittades inget exempel på fenomenet att igensättning använts som metod för självläkning i dessa system. Det fanns framför allt två ytterlighetsfall som studerats; igentäppning av en filterkaka (djupbäddsfiltrering eller ytfiltrering) och filtrering av kolloidala partiklar. Detta beror troligtvis på att den senare har låga koncentrationer i de naturliga systemen och fokus där är transportegenskaper inuti en filterkaka eller djupfilter (t.ex. sandbädd).

En försöksutrustning var konstruerat och byggd inom projektet. Den består av sju filtrerceller som kan fungera parallellt med varandra. Alla är i förbindelse med samma tryckkärl för att säkerhetsställa likartade villkor. Ett säkerhetssystem var också konstruerat för att förhindra att gas fanns närvarande i smektitlösningen i högre koncentration än vad som råder vid jämvikt vid atmosfärstryck. Anledningen till detta var att förhindra en plötslig gasbildning i filterkakan när trycket minskas.

Experimenten visade en bra separation av smektit partiklar från lösningen när den passerade filterkakan. För alla testade fall blev separationen nästintill fullständig efter tillräckligt lång tid. Detta indikerar att filterkakan hade tillräckligt små porer för att fungera som ett geometriskt hinder för de små partiklarna. Jämförelser mellan smektit framställt på Chalmers tekniska högskola och på Clay Technology visade en bra överensstämmelse och därigenom indikerade på likartade egenskaper för den producerade smektiten.

Contents

1 Introduction

In the Swedish design of a final repository for spent nuclear fuel the spent fuel is encased in copper canisters that are stored about 500 m underground in granitic rock.

The Swedish model is called KBS-3 and consists of three different protection layers, solid rock, bentonite clay and a copper canister. The bentonite clay has an attractive characteristic, namely that it will swell in contact with water and thereby fill out all voids and formed cracks in the rock and thereby make a more stable environment for the copper canister. However, if a fracture is present within the rock and water with a low salinity is constantly passing by during a long time, the smectite particles in the bentonite clay may start to diffuse out into the flowing water and be carried away. This, of course, is no ideal situation because the bentonite clay consists roughly of 75% of these small particles (a smectite particle is only a few nm thick and about 200 nm long) and the protection clay layer might then vanish, leaving the copper canister open for corrosion attacks.

It is, however, a possibility that the remaining particles in the clay, the accessory particle, which are larger in size (mean size of about 20 μm) will be left behind and can form a filter cake and thereby prevent further losses of smectite. When particles form a filter cake, they can be ordered in special ways depending on their geometrical shape. This will give a certain pore size distribution. If the solid material has small enough size, the pore sizes will decrease and it will virtually be impossible for more smectite particles to penetrate filter cake. The plugging of the pores by smaller particles is called clogging. This will significantly reduce the permeability of the cake and eventually hinder all minor particles to pass through the bed. A way to enhance this behaviour is to seed the original clay with inert material at a certain pore size distribution to faster achieve the wanted clogging.

1.1 Aims and scope

The purpose is first to get an overview of the clogging phenomena during filtration. After that, the experimental equipment should be designed and built where a suspension of smectite in water should be filtrated through a filter cake made of accessory material. The tested cases, which aim at a total separation of the solid material, are made for bentonite clay using both large particles (accessory minerals) and montmorillonite (smectite). Tests will also be made to see if addition of other material further improves the separation.

1.1.1 Motivation

The motivation of this project is to establish if the accessory particles can form an impermeable filter cake with respect to the much smaller smectite particles. It will therefore investigate the phenomena from one extreme point of view, namely a pre formation of the filter cake by the larger particles and then force a fluid of smectite and water through this by a pressure difference equal to the estimated swelling pressure inside the bentonite clay. Thus, the results are more on the theoretical level and will be a base for further investigations closer to the real scenario. If this investigation show no possible separation further studies are not necessary.

2 Particle clogging in porous media

Today, there is no general model that can predict the behaviour of clogging for all kinds of system, ranging from small colloid particles to larger biological microbial matter, /Mays and Hunt 2005/. Such a model must be based on first principles but is still too blunt to describe the structural complexity of the deposits and quantify the relation between the flow and the deposits. So far, the models have been based on the Kozeny-Carman equation.

$$-\frac{\mathrm{d}p}{\mathrm{d}z} = K' S_\mathrm{p}^2 \mu \frac{(1-\varepsilon)^2}{\varepsilon^3} u \qquad\qquad 2\text{-}1$$

In the above equation, K' is the Kozeny constant, p is the static pressure, z is a spatial co-ordinate, S_p is the specific surface area of the solid material, μ is the fluid viscosity, ε the bed porosity and u the superficial velocity. It is then possible to describe the permeability of the bed, K, as:

$$K = \frac{\varepsilon^3}{K' S_\mathrm{p}^2 (1-\varepsilon)^2} \qquad\qquad 2\text{-}2$$

The specific filtration resistance, α_avg, becomes:

$$\alpha_\mathrm{avg} = \frac{K' S_\mathrm{p}^2 (1-\varepsilon)}{\rho_\mathrm{s} \varepsilon^3} \qquad\qquad 2\text{-}3$$

In this method, an empirical constant is present, namely the Kozeny constant. It is also derived on the basis of homogenous spheres that are packed in the same way all through the bed, and hence the specific surface area and the bed porosity are constant in the bed.

Two different kinds of models are most common: the deep-bed filtration model and the cake filtration model.

2.1 Deep-bed filtration

The permeability of a filter bed is inversely dependent on the square of the surface area in the filter, see Equation 2-2.

$$K \propto S_\mathrm{p}^{-2} \qquad\qquad 2\text{-}4$$

This gives a relation between the actual permeability and the clean bed permeability as:

$$\frac{K_0}{K} = \left(\frac{S_\mathrm{p}}{S_{\mathrm{p},0}}\right)^2 \qquad\qquad 2\text{-}5$$

A theoretical system composed of spherical collectors with a radius, a_c, have a specific surface area as:

$$S_{\mathrm{p},0} = \frac{3(1-\varepsilon)}{a_\mathrm{c}} \qquad\qquad 2\text{-}6$$

When particles are accumulated to the collector surfaces the total specific surface area increases. This increase is proportional to the number of deposited particles /Mays and Hunt 2005/.

$$S_{\mathrm{p,c}} = 4\pi a_\mathrm{c}^2 + \beta' N S_{\mathrm{p,p}} \qquad\qquad 2\text{-}7$$

Index c refers to the collector and index p to the particle, β' is an empirical coefficient to describe the increase of specific surface area due to a single retained particle and N is number of particles on each collector.

The total specific area for the whole filter will then be described as (assuming homogenous conditions in the whole bed):

$$S_\mathrm{p} = 3(1-\varepsilon)\left(\frac{1}{a_\mathrm{c}} + \frac{\beta' N S_{\mathrm{p,p}}}{4\pi a_\mathrm{c}^3}\right) \qquad\qquad 2\text{-}8$$

If the flow velocity is kept constant, the head loss is, according to Equation 2-1, directly proportional to the square of the specific surface area and with a homogeneous bed the total head loss, Δp, can be rewritten as:

$$\frac{\Delta p}{\Delta p_0} - 1 = 2\gamma\sigma + (\gamma\sigma)^2 \qquad \text{2-9}$$

where

$$\gamma \equiv \frac{\beta' a_c}{3(1-\varepsilon)} \frac{S_p}{V_p} \qquad \text{2-10}$$

$$\sigma = \frac{3N(1-\varepsilon)V_p}{4\pi a_c^3} \qquad \text{2-11}$$

Here, V_p is the volume of a single particle and σ is the specific deposits.

2.2   Cake filtration model

The cake filtration model is usually used to describe membrane separation systems with particle accumulation occurring above the filter medium. The membrane filter permeability is thus constant all through the filtration period but the total head loss increases due to the formation of a deposits bed that increases in thickness as more and more particles accumulate.

The head loss of the filter cake can be written as:

$$\Delta p_c = \frac{u\mu L \sigma}{\rho g k_{c,0}(1-\varepsilon_c)} \sqrt{1 + \frac{\Delta p_c}{\Theta}} \qquad \text{2-12}$$

$k_{c,0}$ is the cake permeability when the head loss is zero, L is the cake height and Θ is an empirical constant to describe the cake deformation. The investigated system in this study has most of the filter bed resistance within the filter cake and the deep bed filtration model will therefore be used for further descriptions.

2.3   Deposits distribution

In the previous subchapters, it was assumed that the deposits were evenly distributed in the bed and that an average filtration resistance could be used. However, that is not the case and there will always be a distribution within the filter. The idea to solve this is to assume local validity, i.e. the filtration model is valid for a sufficiently thin portion of the filter bed. The head losses, at constant flow rate, can thus describe the deposits distribution /e.g. Bedrikovetsky et al. 2001/.

For a local description, Equation 2-9 becomes:

$$\frac{dp}{dz} = \frac{dp_0}{dz}[1 + \gamma_2\sigma(z)]^2 \qquad \text{2-13}$$

where γ_2 is the corresponding morphology coefficient valid in this local model (compare the definition in Equation 2-10 for a global model).

Earlier findings /see references in Myas and Hunt 2005/ show an exponential decay of specific deposition with filter bed depth.

$$\sigma(z,t) = \sigma_0(t)e^{-\frac{z}{\delta}} \qquad \text{2-14}$$

In Equation 2-14, δ is the characteristic depth of particle penetration. The total head loss of a bed with total height L can thus be written as:

$$\frac{\Delta p}{\Delta p_0} = 1 + 2\gamma_2\sigma + \frac{\gamma_2^2\sigma^2 L}{2\delta} \frac{(1 - e^{-2L/\delta})}{(1 - e^{-L/\delta})^2} \qquad \text{2-15}$$

3 Classical colloid filtration theory

In this approach the filter bed consists of collectors with known geometry and flow around these particles is in the low Reynolds number region. The general convective diffusion equation used to describe such a system is found below.

$$\frac{\partial C}{\partial t} + \nabla \cdot \boldsymbol{J} = Q \qquad\qquad 3\text{-}1$$

C is the particle number concentration, t is time, $\boldsymbol{J}$ is the particle flux vector and Q is the source. The particle flux vector can be described as:

$$\boldsymbol{J} = -\boldsymbol{D} \cdot \nabla C + \boldsymbol{u}C + \frac{\boldsymbol{D} \cdot \boldsymbol{F}}{k_B T} C \qquad\qquad 3\text{-}2$$

$\boldsymbol{D}$ is the diffusion tensor, $\boldsymbol{u}$ is the particle velocity induced by the fluid flow, k_B is the Boltzmann constant, T is temperature and $\boldsymbol{F}$ is the external force vector.

If no source exists, the convective diffusion equation becomes:

$$\frac{\partial C}{\partial t} + \nabla \cdot (\boldsymbol{u}C) = \nabla \cdot (\boldsymbol{D} \cdot \nabla C) - \nabla \cdot \left(\frac{\boldsymbol{D} \cdot \boldsymbol{F}}{k_B T} C \right) \qquad\qquad 3\text{-}3$$

However as stated in /Elimenlech 1994/, steady state is usually established after a short period of time and the equation can be further simplified to:

$$\nabla \cdot (\boldsymbol{u}C) = \nabla \cdot (\boldsymbol{D} \cdot \nabla C) - \nabla \cdot \left(\frac{\boldsymbol{D} \cdot \boldsymbol{F}}{k_B T} C \right) \qquad\qquad 3\text{-}4$$

This is also the model that has been most widely used for particle deposition.

The external forces involved in colloid filtration are colloidal forces and gravitational forces.

$$\boldsymbol{F} = \boldsymbol{F}_{col} + \boldsymbol{F}_G \qquad\qquad 3\text{-}5$$

Small particles, assumed spherical and neutral, are removed from the suspension by interception, sedimentation and diffusion to the collector surface where they can stick. A single particle in an uncharged system will only have gravitational forces as external force and the resulting convective diffusion equation will look like /Yao et al. 1971/:

$$\frac{\partial C}{\partial t} + \boldsymbol{v} \cdot \nabla C = D_{bm} \nabla^2 C + \left(1 - \frac{\rho}{\rho_p} \right) \frac{mg}{3\pi \mu d_p} \frac{\partial C}{\partial z} \qquad\qquad 3\text{-}6$$

D_{bm} is the diffusion coefficient of the suspended particle, ρ is the density of water and particle (using index p), μ is water viscosity, m and d_p are mass and diameter of the particle, g is the gravitational force acting in the z direction. This is only valid if the velocity vector and the diffusion coefficient are space invariant.

The particle diffusivity has been taken as:

$$D_{bm} = \frac{k_B T}{3\pi \mu d_p} \qquad\qquad 3\text{-}7$$

However, not even the simplified equation above (Equation 3-6) can be solved analytically and further simplifications must be made unless a numerical solution can be accepted.

3.1 Single-collector efficiency

The removal efficiency of the collector (particle) is usually denoted as η and describes the amount of colloid deposit. It is defined as the ratio between the particle deposition rate on the collector and the projected area of the collector. The efficiency for a single isolated and spherical collector particle is thus:

$$\eta = \frac{I}{UC_0 \pi a_c^2}$$ 3-8

where U is the fluid approach velocity, C_0 is the bulk concentration, I the actual deposition rate on a collector with radius, a_c. If this will be used in a packed bed, the concentration profile in the bed can be described by /Yao et al. 1971/:

$$\ln \frac{C}{C_0} = -\frac{3}{4}(1-\varepsilon)\eta \frac{L}{a_c}$$ 3-9

Where ε is the bed porosity and L is the bed depth. The equation does not take into consideration any chemical surface interaction and attempts to use the equation will fail; especially for system with predominate double layer interactions /Ryan and Elimelech 1996/. If these are included another factor, the empirical collision efficiency factor, α, must be added:

$$\ln \frac{C}{C_0} = -\frac{3}{4}(1-\varepsilon)\alpha\eta \frac{L}{a_c}$$ 3-10

The empirical collision factor can be determined experimentally and is usually between 10^{-3} and 1 /Elimelech and O'Melia 1990/.

3.2 Packed-bed efficiency

However, the flow field around a single collector in a packed bed is affected by the nearby collectors. Of the various models derived, the most common /Ryan and Elimelech 1996/ is the Happels's sphere in a shell model. The model is based on the assumption that the porous media is built up by identical particles all with a small layer of liquid around them, see Figure 3-1. The shell thickness, b, can be determined as:

$$b = a_c(1-\varepsilon)^{-1/3}$$ 3-11

This model has been successfully used in several filtration studies.

The colloidal force vector, $\boldsymbol{F}_{col}$, can be described from the total interaction potential, Φ_T.

$$\boldsymbol{F}_{col} = -\nabla \Phi_T$$ 3-12

3.3 DLVO theory

The DLVO theory, named after Derjaguin, Landau, Verwey and Overbeek, focuses on the total interaction between two surfaces and calculates if the system is unstable (i.e. surfaces are attracted to each other) or stable (i.e. surfaces are repelled from each other). In an intermolecular system, attractive van der Waals forces are always present and must therefore be considered (other intermolecular forces like the Coulombic and the hydrogen bonding are usually stronger if present). In reality, it is therefore only in very few cases where the van der Waals forces alone determine the interaction. For example when colloidal particles are present, the fluid phase introduces a complexity. The reason is that the surfaces become charged either by dissociation of functional groups that becomes ionized, due to permant charge deficiency in the crystal structure as in smectite sheets or when ions adsorb on an uncharged surface.
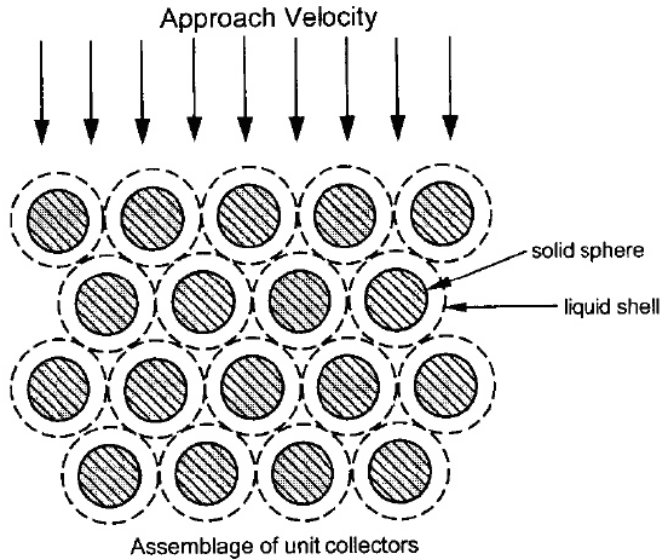
Figure 3-1. Schematic description of the sphere in a shell approach to describe the fluid flow in a packed bed /picture from Ryan and Elimelech 1996/.

3.4 Boundary conditions

Within the colloid particle deposition rate numerical calculations, two boundary conditions are most frequent /Ryan and Elimelech 1996/. These are the perfect sink and the non-penetration model.

3.4.1 Perfect sink model

The perfect sink model is the most common to be used and assumes that the particles are trapped by an infinite energy sink and thereby disappear from the system. The boundary conditions will be $C=0$ at $h=\delta$ (sometimes $h=0$ is used), where δ is the primary energy minimum between a collector surface and a particle. This means that particles that come sufficiently close to a surface are irreversible captured. This assumption has given rise to approximate suspension where the two most famous are the Smoluchowski-Levich and the Interaction force boundary layer (IFBL).

IFBL

This method, the Interaction force boundary layer method, is used to approximate the deposition rate of Brownian particles in the presence of a repulsive energy barrier. It is built on the fact that colloidal forces operate over short distances from the collector surface (only several tens of nanometres) where the convective transport is negligible. This inner layer is taken as the size of the double layer thickness and the outer layer, where the convective transport is important, are in the order of the diffusion boundary layer. It is then possible to obtain an analytical solution for some simple geometries. In case of spherical collectors the single collector removal efficiency will be /Ryan and Elimelech 1996/:

$$\eta = 4.0 A_S^{1/3} \left(\frac{D_\infty}{2a_c U} \right)^{2/3} \left(\frac{\beta}{1+\beta} \right) S(\beta) \qquad \text{3-13}$$

Where β can be found in /Spielman and Friedlander 1974/ as:

$$\beta = \frac{1}{3}(2)^{1/3} \Gamma\left(\frac{1}{3}\right) A_S^{-1/3} \left(\frac{D_\infty}{Ua_c} \right)^{1/3} \left(\frac{k_F a_c}{D_\infty} \right) \qquad \text{3-14}$$

k_F is a pseudo first order rate constant, A_S is a porosity dependent parameter in the Happel's model, D_∞ is the colloid bulk diffusion coefficient and $S(\beta)$ is a function defined as:

$$S(\beta) = \frac{3}{\Gamma\left(\frac{1}{3}\right)} \left(\frac{\pi}{4} \right)^{2/3} + \int_0^{\frac{\pi}{2}} \Psi(t) dt \qquad \text{3-15}$$

$\Psi(t)$ is obtained by solving the equation below using specific values of β.

$$\Psi(t) + \frac{\beta^{\frac{1}{3}}\beta}{\Gamma(\frac{1}{3})\Gamma(\frac{2}{3})} \int_0^t \frac{\Psi(\mu)d\mu}{\sin\theta(t-\mu)^{\frac{2}{3}}} = -\frac{2^{\frac{1}{3}}}{\Gamma(\frac{1}{3})}t^{-\frac{1}{3}} + \frac{6}{\sin\theta\,\Gamma(\frac{1}{3})} \qquad \text{3-16}$$

Smoluchowski-Levich

If there are no colloidal and hydrodynamic interactions, β→∞ and S(β)→1 leading to the common solution:

$$\eta = 4.0 A_S^{\frac{1}{3}} \left(\frac{D_\infty}{2a_c U} \right)^{\frac{2}{3}}$$

3.4.2 Non-penetration model

A problem with the perfect sink model is that it does not take into account the accumulation of immobilized particles at the collector interface. The non-penetration model was therefore introduced, /Adamczyk et al. 1983/. In the non-penetration model, the particles are assumed not to penetrate through the solid surface of the collector. The boundary condition will be that the particle flux at the surface vanishes:

$$\boldsymbol{J}_\perp = 0 \quad \text{at} \quad h = 0 \qquad \text{3-17}$$

This model also incorporate the source term, Q, in the convective diffusion equation to account for the complex interaction at the collector surface that give rise to immobilization and to account for the release rate.

3.5 Comparison of models and experiments

/Adamczyk and Weronski 1999/ conclude that the DLVO description together with the convective diffusion equation predicts the right magnitude of colloidal removal efficiency when no energy barrier exists. However, when these exist, the discrepancy is large. It might be due to the heterogeneous surface of the collector or that the surface properties of the particles are not evenly distributed. Furthermore, the potential blocking effect is not taken into account.

4 Experimental

4.1 Description of experimental equipment

The experimental equipment is shown in Figure 4-1. The columns to the left are filtration columns with smectite suspension and equipped with a filtration cell. The column to the right is used to transfer pressure from gas phase to water phase (it is important that there is less gas in the water compared to what is soluble at higher pressure otherwise there may be an expansion in the filter cake lead to bubble formation, which would lead to ruptures and cracks). This column is followed by a four meter long horizontal tube (0.8 dm^3) to prevent any thermally induced mixing. The second column from the right is used for filter cake preparation and contains deionized water where the air has been removed. All columns are connected to the same source of pressure but can be operated individually.

The filtering experiments start with forming a filter cake of detritus material. This filter cake is used to filtrate the suspension of the small smectite particles. The rate of water flowrate through the cake is monitored and the smectite content in the filtrate is measured.

The filtration unit can be seen in Figure 4-2 and Figure 4-3. It has an inner diameter of 16 mm, which then will be the size of the filter cake. An inner tube is used for two reasons; one is to simplify the removal of filter cake after the experiment (it will come together with the tube when it is removed from the filter cell) and to support the filtration media (a membrane filter that lies on a support plate).

Figure 4-1. *Experimental set-up.*

Figure 4-2. *The filtration cell.*   ***Figure 4-3.*** *Parts included in the filtration cell.*

4.2   Preparation of material

1) The first step to prepare the material was to mix 1 part of bentonite clay (MX-80) in 100 parts of 1M NaCl solution to ion-exchange the clay to sodium base. The slurry was then stirred thoroughly both with stirrer and in an ultrasonic bath. After this, the bottle was put into a centrifuge for 15 minutes. This rendered three phases, one clear water phase and two solid phases of which one is light and one is dark, see Figure 4-4. Then as much of the water as possible was removed.

2) As a second step, the solid residue was diluted with deionized water to the same volume as in the first step and mixed thoroughly. This was followed by a centrifugation and a separation of the solid and liquid.

3) The third step was a new dilution followed by mixing and centrifugation as in the second step. After the separation of the liquid phase, a manual separation of the two different solid phases was made and the material was saved in separate bottles. The light phase is the smectite portion (montmorillonite in this case) and the dark phase is the accessory particles.

4) Step four includes a dilution of each of the solid fractions with deionized water followed by a new centrifugation. The water was then removed. This step was repeated until only one solid phase was found.

5) As a final stage, the solid phases were dried in an oven at 85°C. After the samples were dried, they were gently pestled for a more easy usage (if there are too large chunks it is difficult to mix them with water afterward and form either a homogeneous suspension or a slurry for the filter cake formation).

Figure 4-4. *Remaining solid phases after removal of water from a MX-80 suspension.*

4.3 Preparation of experiment

4.3.1 Usage of material

The montmorillonite was diluted 1:100 and mixed to a homogeneous solution. A slurry with a rather high concentration of the accessory particles was prepared (enough to have a homogeneous suspension with as little water as possible).

4.3.2 Preparation of filter cake

The filtration cell was filled with a slurry made from the accessory particles and deionized water. It was then mounted below the water column and the pressure was increased to 5 bar. If not enough material could be placed in the filtration cell directly as part of the material goes through the membrane filter (the accessory particles have a wide particle size distribution) depressurize the column, the filtration cell was removed and refilled with the remaining suspension.

4.4 Experimental procedure

The column was filled with the formed montmorillonite suspension. Two pistons were placed in the column and the space between them was filled with the same suspension (this was to prevent mixing with the incoming water). The filtration cell with the formed filter cake was moved from the preparation column (the water column) to the filtration column (the column filled with montmorillonite suspension) and the system was pressurized. Due to a reformation of the filter cake some material will pass through in the beginning. The filtrate was collected in a beaker supplied with a lid to prevent evaporation. The beaker was weighed approximately once a day. When enough filtrate had passed through, a dry content test was performed (the filtrate was evaporated in an oven).

4.5 Performed experiments

The experimental set consisted of two major tasks. First was the investigation to study the clogging of the filter cake made of detritus material . In that part, different filter cake thicknesses were investigated and also filtration at different pH levels. The second task included addition of new material to improve the separation properties of the filter cake.

4.5.1 Accessory material

The intention with these experiments was to investigate the long time behaviour of filter cakes made by accessory material only. Initially, eight experiments were planned and conducted according to Table 4-1.

In addition to these experiments, one more experiment in this section was conducted. It was a test to see if the gravity had any effect on the filtration and separation properties. Therefore, one experiment was performed where the filter cell and suspension tank was turned up-side down.

Table 4-1. Experimental plan.

Experiment	Amount of material in filter cake	Corresponding cake height	Material in suspension	pH
1	1.5 g	5 mm	Chalmers	8.6
2	3 g	10 mm	Chalmers	8.6
3	1.5 g	5 mm	Clay technology	8.6
4	1.5 g	5 mm	only water	7
5	1.5 g	5 mm	Chalmers	~8.3
6	1.5 g	5 mm	Chalmers	~5
7	1 g	3 mm	Chalmers	8.6
8	0.5 g	1.5 mm	Chalmers	8.6

4.5.2 Added material

Five different materials were selected; Kaolin clay, $CaSiO_2$, TiO_2, Al_2O_3 and SiO_2 (diatomaceaous earth non-washed). To see if the material had any effect at all on the filtration and separation properties, a series of preliminary experiments were performed. These can be found in Table 4-2.

These experiments gave further insight and a complete experimental plan was then made, Table 4-3. All experiments were duplicated.

Table 4-2. Preliminary experiments with added material.

Experiment	Accessory Material (g)	Kaolin (g)	CaSiO₂ (g)	TiO₂ (g)	Al₂O₃ (g)	SiO₂ (g)
1	0.5	–	–	–	–	–
2	–	0.5	–	–	–	–
3	1.5	–	–	–	–	–
4	–	1	–	–	–	–
5	1.5	–	–	–	–	–
6	0.5	–	–	–	–	–
7	0.3	–	0.3	–	–	–
8	0.3	0.3		–	–	–
9	–	–	0.5	–	–	–
10	1	–	–	0.3	–	–
11	1	–	–	0.4	–	–
12	1	–	–	0.5	–	–
13	–	–	–	0.5	–	–
14	1	–	–	–	0.5	–
15	1	–	–	–	–	0.5
16	1	–	–	–	–	0.5
17	1	–	–	–	0.5	–
18	–	–	–	–	0.5	–
19	–	–	–	–	–	0.5
20	–	0.75	–	–	–	–

Table 4-3. Complete experimental plan with added material.

Experiment	Accessory Material (g)	TiO₂ (g)	CaSiO₂ (g)	SiO₂ (g)	Al₂O₃ (g)	Kaolin (g)
1	0.3	–	–	–	–	–
2	0.3	0.2	–	–	–	–
3	0.3	–	0.2	–	–	–
4	0.3	–	–	0.2	–	–
5	0.3	–	–	–	0.2	–
6	0.3	–	–	–	–	0.2
7	0.4	–	–	–	–	–
8	0.4	0.1	–	–	–	–
9	0.4	–	0.1	–	–	–
10	0.4	–	–	0.1	–	–
11	0.4	–	–	–	0.1	–
12	0.4	–	–	–	–	0.1
13	0.2	–	–	–	–	–
14	0.2	0.3	–	–	–	–
15	0.2	–	0.3	–	–	–
16	0.2	–	–	0.3	–	–
17	0.2	–	–	–	0.3	–
18	0.2	–	–	–	–	0.3

5 Experimental Results and Discussion

5.1 Sample preparation

It is important to verify that all introduced chloride ions are removed from the samples before they are used. This was made by analysis of the Na ion concentration in the solution in an AAS. This will give a too high value of the concentration of Cl ions since ion exchange occurs in the bentonite clay between Na and Ca in the procedure. It could, however, be concluded that the value of Na ions decreased more than three orders of magnitudes, Figure 5-1, leading to the conclusion that the amount of Cl ions is negligible.

The used procedure will only recover about 55% of the original material, Figure 5-2. There are several reasons of this, but one is that material is lost during the manual separation between the phases to prevent material mixing. Some material might also be lost in the removed water phase. Of the recovered material, more than 75% is the smectite phase.
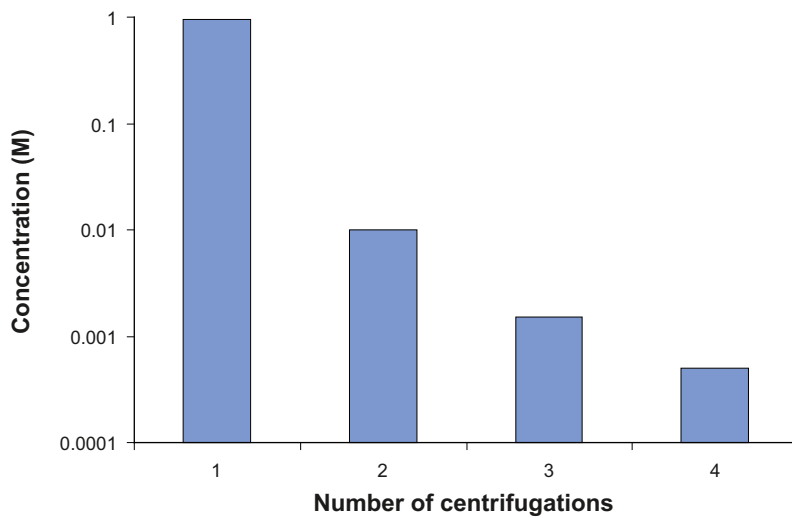

Figure 5-1. *Amount of Na in solution during sample preparation at different stages.*
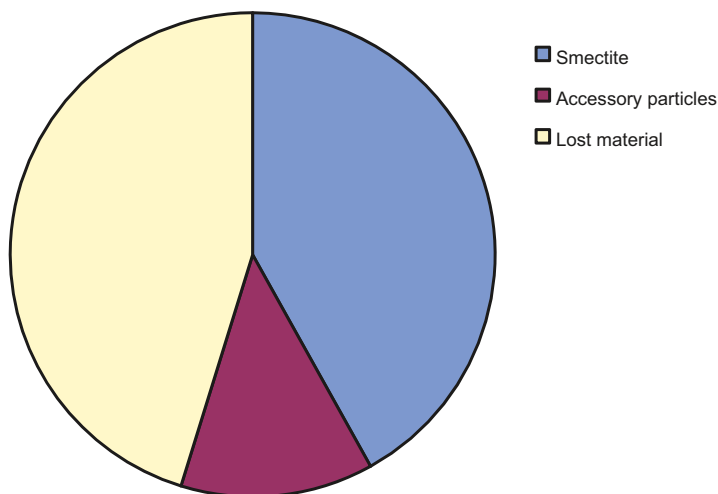

Figure 5-2. *Recovered and lost material during sample preparation.*

5.2   Material properties

5.2.1   Particle size distribution

The particle size distribution of the accessory particles in the bentonite clay (MX-80) was measured on a Malvern 2600. Three measurements were performed (a, b and c) and can be seen in Figure 5-3. It is clear that the different samples had the same size distribution and that it mainly consisted of particles with sizes less than 20 µm (the two peaks are found at 5 and 10 µm). This means that the sizes are much larger than the smectite particles (where the sizes are up to 200 nm). It must be emphasized that the measured particle size is a conversion from the actual geometry to a spherical geometry and the particles may have another shape that significantly differs from a sphere.

The particles size distribution of the added materials can be found in Figure 5-4 and Figure 5-5. Each material was analyzed from two samples (a and b). It is clear that they have very large variation in their distribution with some having larger mean size (especially SiO_2 but also TiO_2 has a larger mean size than the accessory particles) and other having a lower. The width of the distribution also varies (SiO_2 has a wide variation while Al_2O_3 is very narrow).

5.2.2   Surface area

The different material showed a large variation in BET surface area, ranging from 0.5 up to 12.5 m²/g. It was measured on a Micromeretics TriStar 3000.

	SiO_2	$CaSiO_2$	Al_2O_3	Kaolin	TiO_2	AP
BET m²/g	1.13	65.16	0.45	12.47	2.45	11.32

5.2.3   Particle solid density

The tested materials varied in solid density from 2.3 up to 4.3 g/cm³. The measurements were performed on a Micromeretics AccuPyc 1330.

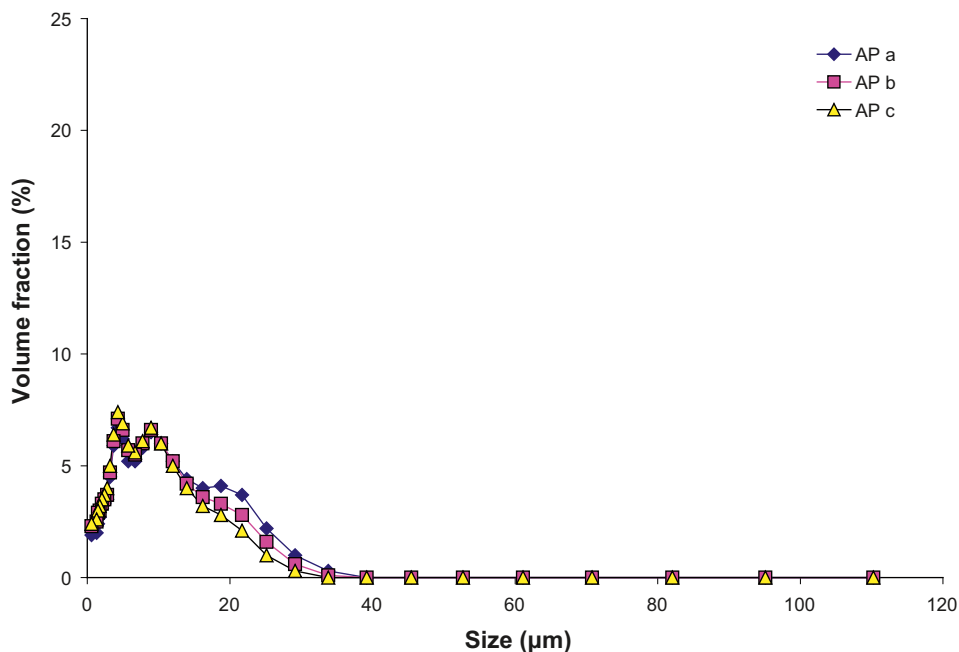|	SiO_2	$CaSiO_2$	Al_2O_3	Kaolin	TiO_2	AP
Density g/cm³	2.316	2.613	3.992	2.746	4.308	2.696

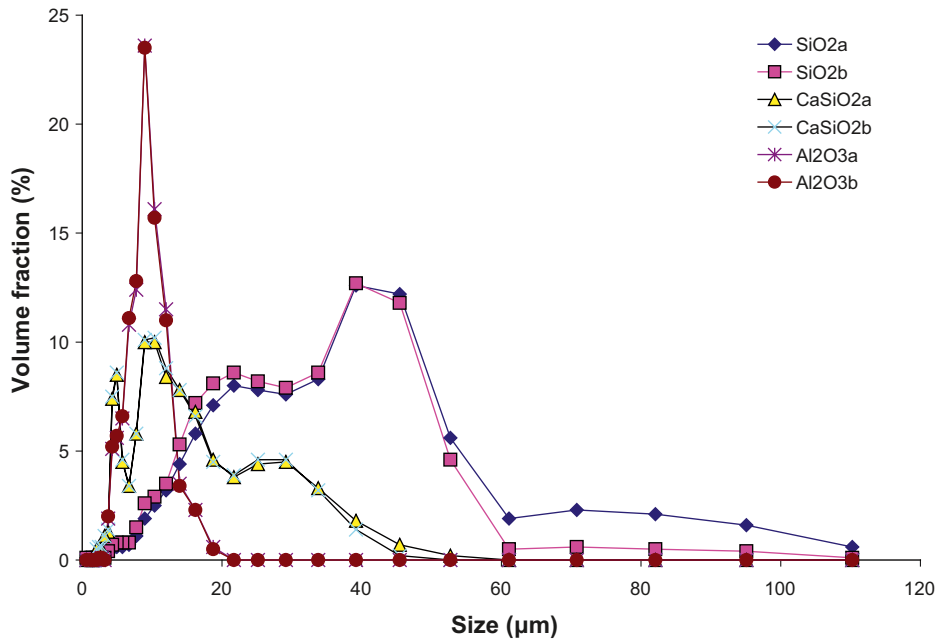***Figure 5-3.** Particle size distribution for accessory particles (AP).*

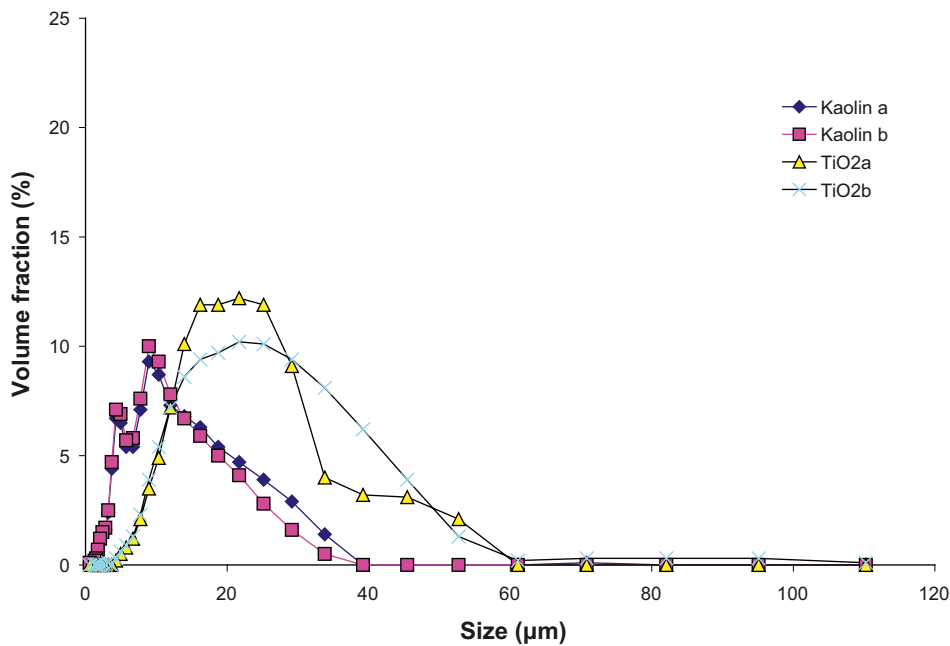***Figure 5-4.*** *Particle size distribution for added materials.*

Figure 5-5. *Particle size distribution for added materials.*

It then becomes clear that the particle with large particle size distribution and low BET surface area showed a low density as well (SiO$_2$). Especially a correlation between particle size distribution and BET surface area would be expected for particles with homogeneous geometry and density. If however the particle size distribution and BET surface area both are small the resulting density becomes high (Al$_2$O$_3$) which is in accordance with what could be expected (small particles sizes would likely be yielding large surface areas but if the density is high the surface area per mass of material decreases). Of the tested materials, kaolin is the one which mostly resembles the accessory material particles (originated from the bentonite clay). The largest difference between these two materials is that the accessory particles have more material below detection limit of the instrument (1.2 μm). One reason for this is that it is sensitive to erosion and the material must be stirred during tests and also during sample preparations.

5.3 Filtration experiments (accessory particles)

In total, eight filtration experiments were performed. One used only water to estimate the filtration resistance in the filter cake of accessory minerals. Using the traditional filtration equation, Equation 5-1, (where the filtration media resistance is neglected), the average specific filtration resistance became $1.7 \cdot 10^{13}$ m/kg which is a medium resistance indicating the presence of small pores in the system.

$$\frac{dV}{dt} = \frac{A \cdot \Delta P}{\mu \cdot \alpha_{avg} w_c} \qquad\qquad 5\text{-}1$$

V is the filtrate volume, t is the filtration time, A is filter area, P is pressure, μ is the viscosity, α_{avg} is the average filtration resistance and w_c is the weight of the filter cake.

Figure 5-6 shows the amount of filtrate from filtration experiments using a different amount of solid material in the filter cake. A cake height of 5 mm corresponds to 1.5 g of solid material. In the graph, an experiment using prepared montmorillonite from Clay Technology AB is also included (5 mm C tech) to see if there are any differences between the sample preparation methods. It is clear that the more material in the cake the less filtrate will penetrate. One deviation from this comes from the filter cake with the lowest amount of material used (1.5 mm height) where the filtrate penetration is lower compared to filter cakes containing more material. No explanation are found to this behaviour but it is likely to depend on the formation of the filter cake which is crucial in these tests (boundary effects are non-negligible). It is also found that there seems to be the same filtration behaviour between the two experiments using montmorillonite prepared by two different methods. The material from Clay Technology AB is also membrane filtrated to retain the smallest particles.

Tests were also performed to investigate the impact of a variation in pH of the incoming suspension, Figure 5-7. pH 7 and pH 5 represent the initial decrease in pH (using HCl) of the montmorillonite suspension. However, the system has a buffering capacity and pH increases with time leading to final values of 8.3 and more than 6 (it was then re-acidified to 5 again) respectively in the two cases. There seems to only be a very small initial effect on the filtration behaviour when pH is decreased but the effect seems not to be permanent (the filtration curves are coming closer to each other with increasing time) and a further decrease has no additional effect. It should be noted that the experimental values in Figure 5-6 has been modified by subtracting the values of the first experimental point due to irregularities in the cake when it was moved from the preparation column to the filtration column. This was not done in Figure 5-7 because measurements started day 3.
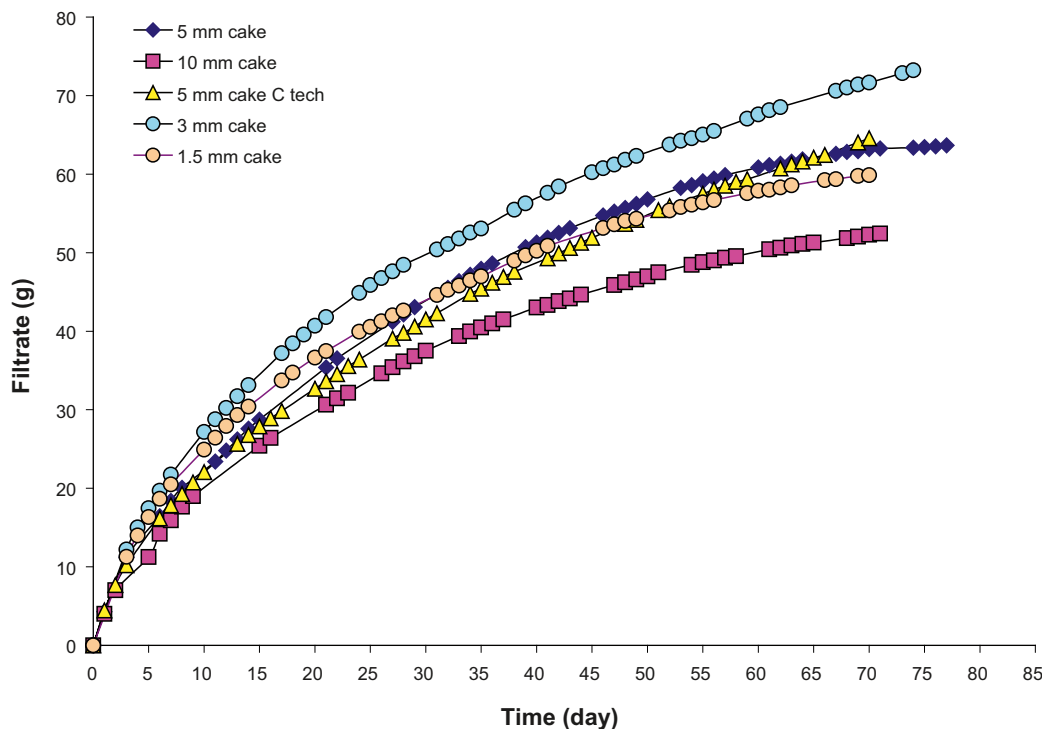

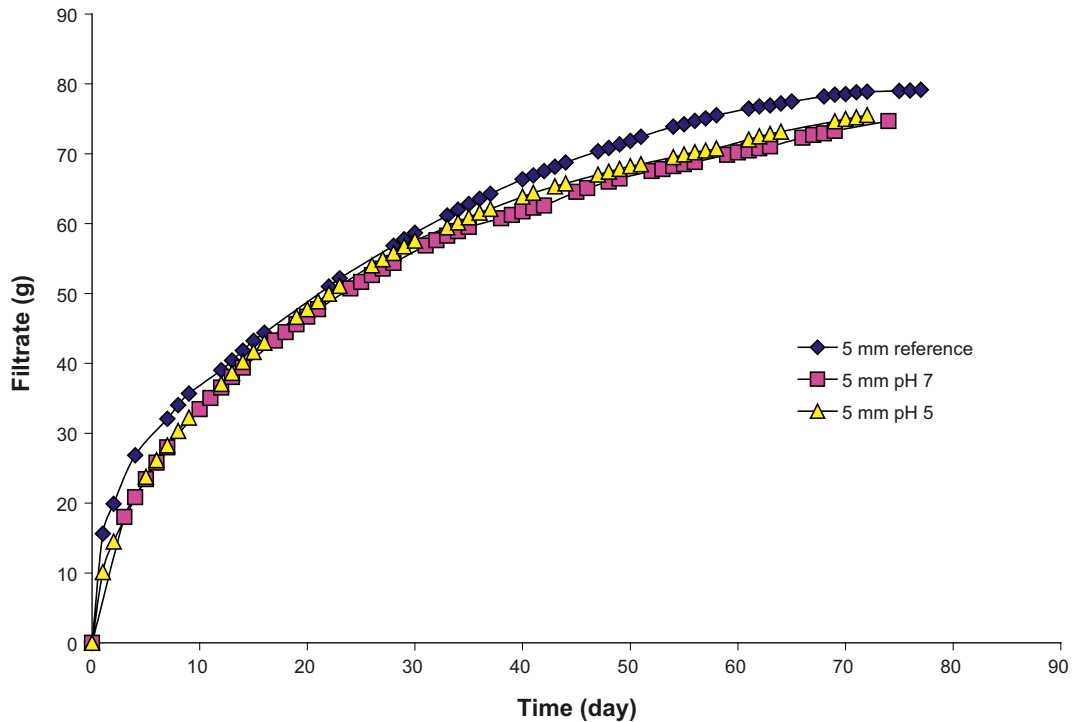***Figure 5-6.*** *Amount of filtrate by time at different cake heights.*

Figure 5-7. *Amount of filtrate by time at different pH.*

To determine the filtration resistance, the filtration equation is integrated and the specific mass of the filter cake (w_c) is expressed as a function of slurry concentration (concentration of montmorillonite) and amount of filtrate.

$$\frac{dV}{dt} = \frac{A^2 \Delta P}{\mu(\alpha_{av} c V + R_m A)} \qquad\qquad 5\text{-}2$$

$$\frac{t_2 - t_1}{V_2 - V_1} = \frac{\mu}{A^2 \Delta P}\left[\frac{\alpha_{av} c}{2}(V_2 - V_1) + c\alpha_{av}V_1 + R_m A\right] \qquad\qquad 5\text{-}3$$

The specific filtration resistance is then given by the slope between time over filtrate volume against the filtrate volume (if the density is constant the mass can be used instead).

Figure 5-8 should consist of straight lines if ideal conditions were achieved and the specific filtration resistance could then be determined from the slope. This is not the case here indicating a compression of the filter cake or a clogging of the filter medium (the bed of accessory minerals). If the lines are divided in two parts, the filtration resistance can then be estimated for each section. It can clearly be seen, Figure 5-9, that there is a difference between the two parts (initial and end part of the filtration curves) but also that the filtration resistance values are higher than the filtration resistance of the bed material (the accessory mineral had a filtration resistance of $1.7 \cdot 10^{13}$ m/kg).

The main aim of this task was however, not to test filtration resistance and amount of filtrate passing through the filter but to investigate the amount of solid material that passes with the filtrate. The filtrate was therefore collected and analyzed on dry substance by evaporation. Due to the low amount of solid material in the initial suspension (1:100) it was necessary to have at least 25 ml of filtrate to have low measurement errors. The result, Table 4-3, showed a clear decrease of the initial solid concentration (1%) in all cases. In two cases, the solid concentration was higher the first day (could also be seen as a higher flow rate) indicating that the structure of the filter cake was not homogeneous and material could therefore pass.
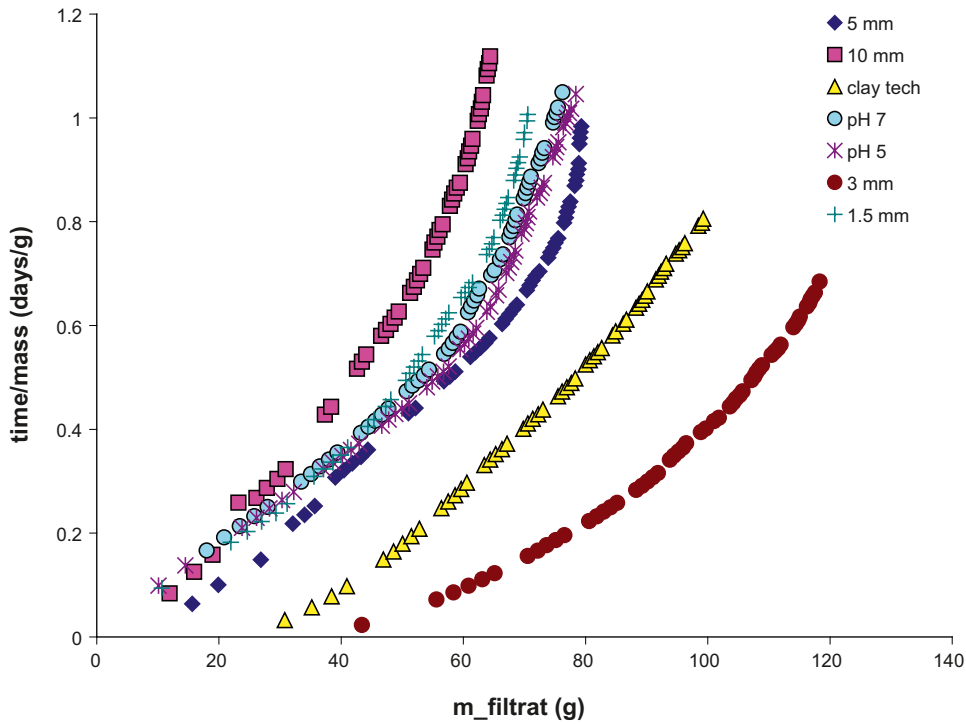
Figure 5-8. *The ratio of time and mass of filtrate against the amount of filtrate to determine the specific resistance during filtration of a montmorillonite suspension.*
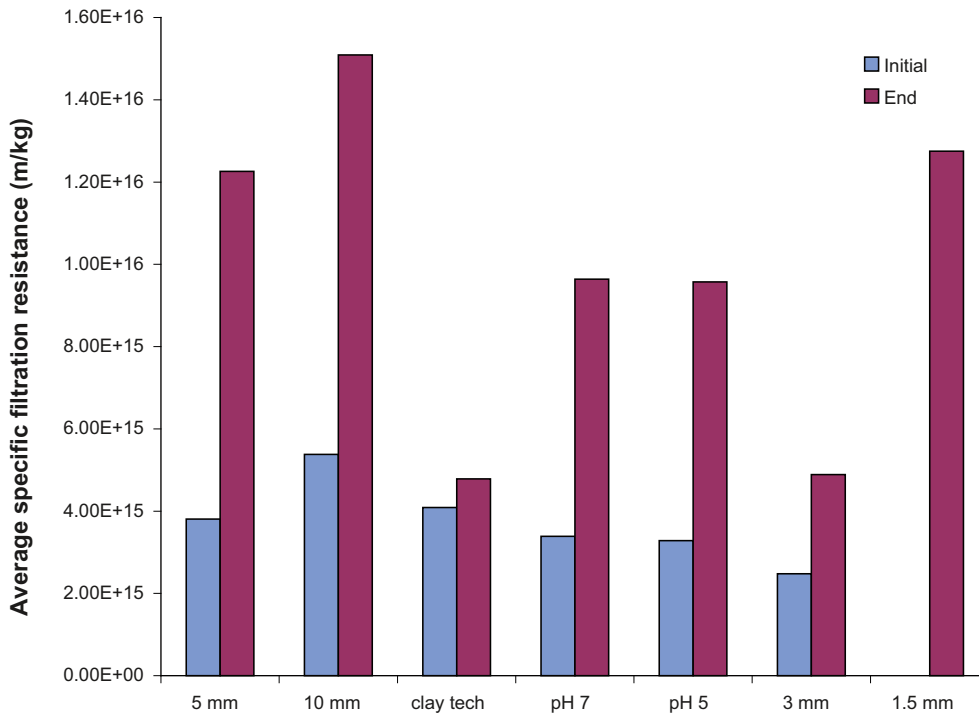

**Figure 5-9.** *Determined average specific filtration resistances of the performed filtration experiments.*

Due to the fact that some montmorillonite actually passes through the bed of accessory minerals it is important to determine how far into the bed they penetrate. Therefore, some filter cakes were further analyzed. They were divided in several parts which included both the original filter bed material (accessory minerals) and the formed filter cake of montmorillonite. The material was analyzed in two ways, one where the solid content was measured through evaporation and one where the amount of particles was

measured in a suspension consisting of cake material and distilled water. The particles were measured with a turbidity meter at Clay Technology AB. The reason to have both methods was to separate the montmorillonite and the accessory minerals from each other (the montmorillonite was expected to stay in the diluted suspension after 24 hours while the accessory minerals were expected to sediment). It was then found that the dry content in the filter cake increased with increasing depth. A sharp transition was found between the formed montmorillonite cake and the original accessory minerals, Figure 5-10. The original cake contained a low amount of montmorillonite even though there was an initial penetration. The smectite concentration in the filter cake was between 5 and 8 wt%.

It was then further tested whether or not the position of the filter cell had any impact on the filtration behaviour. Therefore, one experiment was performed where the filtration occurs upwards. As can be seen in Figure 5-11, there is a large difference between the two experiments and it seems to be a much faster filtration when the filtration is upwards, indicating a large effect of e.g. sedimentation. However, according to the results from Table 5-1, a good separation was achieved. Initially the separation was a little lower compared to the reference downwards filtration but the level goes down to a very low level (last measurement was 0.021% of solid material from a 1% suspension). It shall be stressed that this are measurements from a single experiment and it is difficult to form a homogeneous filter cake so it is difficult to determine the effect in more detail.

5.4 Filtration experiments (added material)

The initial experiments, according to Table 4-2, did show a potential of separating the smectite particles at low amounts of accessory material. However, the results were non conclusive and it also included a high amount of accessory particles. Therefore, a larger experimental plan was executed where the amount of accessory particles varied from 0.4 down to 0.2 g and other material was added to achieve a total weight of 0.5 g representing a filter cake height of about 1.5 mm. The result can be found in Table 5-2 (AP stands for accessory particles). An X indicates that the separation succeeded (two cases occurred either the smectite suspension penetrated fast yielding no separation or it was slow and then the separation was higher than 99% with respect to the smectite particles). A double X means that the result was similar in both duplicates.
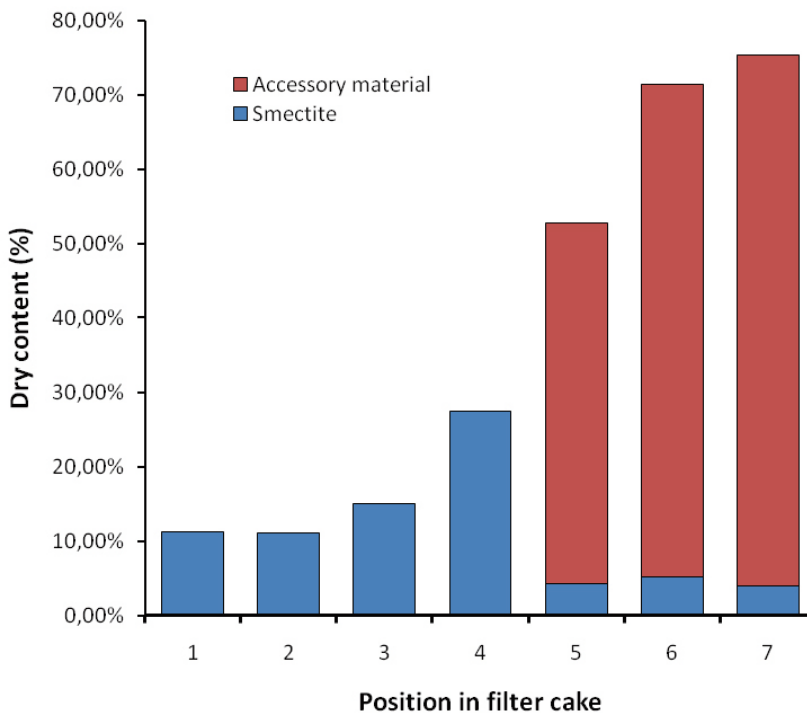
Figure 5-10. Dry content in different places in a filter cake (a higher number represent further down in the cake). Number 4 represent the boundary layer between the original filter cake and the formed cake of montmorillonite.
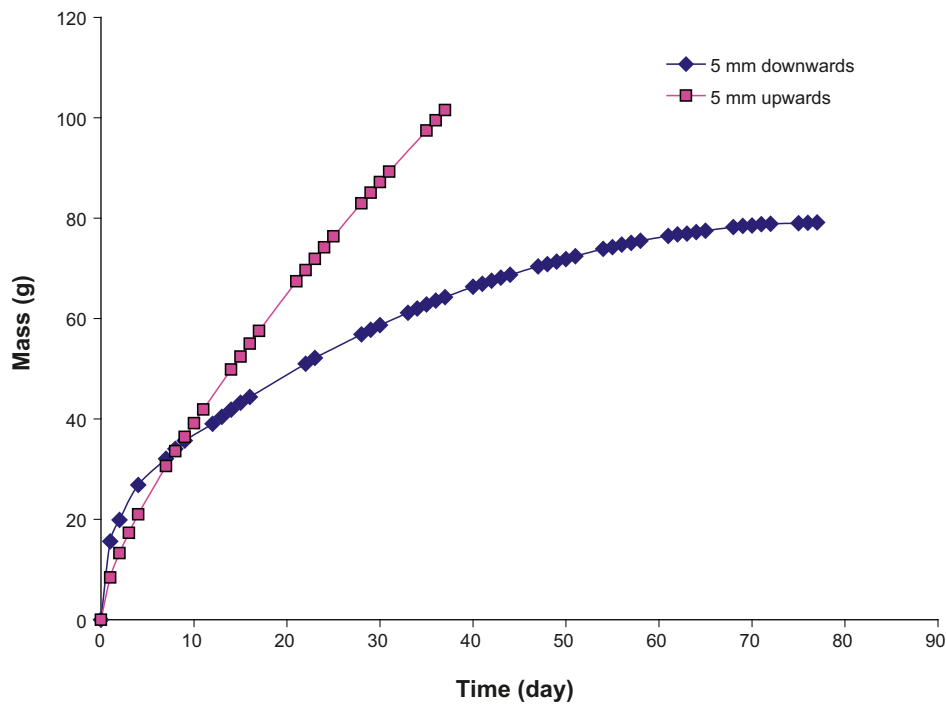
Figure 5-11. *Filtration of montmorillonite in a bed of accessory minerals in two directions.*

Table 5-1. Solid material in filtrate.

Filter cake	Sampling days	Amount of filtrate (g)	Solid concentration in filtrate (%)
1.5 g	1–4	28.86	0.06
1.5 g	4–49	44.47	0.02
3 g	1–9	29.59	0.008
1.5 g clay tech	1	30.75	0.7
1.5 g clay tech	2–21	32.68	0.017
1.5 g pH 7	1–12	36.52	0.05
1.5 g pH 5	1–13	38.62	0.058
1 g	1	43.39	0.84
1 g	2–14	31.73	0.02
0.5 g	1–6	26.98	0.082
0.5 g	7–	30.65	0.02
3 g upwards	1–10	36.67	0.05
3 g upwards	11–		0.0021

Table 5-2. Filtration of smectite suspension through filter cakes of different composition.

	AP 0	AP 0.2	AP 0.3	AP 0.4
no addition			X X	X
TiO$_2$			X X	
CaSiO$_2$				X
SiO$_2$			X	
Al$_2$O$_3$		X		
Kaolin		X	X	X

From this it is still difficult to draw any conclusions regarding if addition of material really improve the separation. However, as can be seen in Table 5-2, complete separation does occur when other material added which indicate that there is an effect. This is important if more material are added into the bentonite clay from the beginning (even though the material itself may not form a good filter it can be used in combination with the accessory material and become effective).

# 6	Conclusions

The experimental equipment was designed and built. It can handle seven samples in parallel using up to 1.5 dm³ of suspension for each experiment. It is easy to handle and has a high capacity. The difficulties are formation of filter cake and changing the suspension between water (used in the formation stage) and the smectite suspension. The single pressure reservoir also could impose sudden pressure changes in the on-going experiments when a new experiment is started.

The amount of material in the filter cake has, as expected, an impact of the filtration rate. More material decreased the filtration rate.

The separation of smectite particles was almost complete in all tested cases (cakes of accessory material particles with a weight of 0.4 g corresponding to less than 1.5 mm). Only a fraction of the solid concentration in the suspension was found in the filtrate.

pH had almost no influence on the clogging phenomena. The amount of solid particles in the filtrate and the filtration rates were comparable for all different pH levels.

Gravitation may influence the filtration rate. However, the separation quality is equally good regardless if the filtration is performed upwards or downwards.

It is possible to achieve a good separation of smectite particles from a water suspension with a mixture of different materials. The one most promising seems to be kaolin. This is also the material of the investigated materials that resembles the properties of the accessory material particles the most.

7   Nomenclature

Roman letters

a	radius (m)
A	area (m^2)
A_s	porosity dependent parameter
b	shell thickness
c	slurry concentration (kg/m^3)
C	number concentration (m^{-3})
d	diameter (m)
D	diffusion (m^2/s)
F	external force (N)
g	gravity acceleration (m/s^2)
I	deposition rate (s^{-1})
J	particle flux vector ($m^{-2}s^{-1}$)
K'	Kozeny constant
k_B	Boltzman constant
$k_{c,0}$	cake permeability at no head loss (m^2)
k_F	first order rate constant
L	total height of filter cake equal to bed depth (m)
m	mass (kg)
N	number on particles on the collector (–)
p	static pressure (Pa)
Q	source ($m^{-3}s^{-1}$)
R_m	filtration media resistance (m^{-1})
Sp	specific surface area (m^2/g)
t	time (s)
T	temperature (K)
u	superficial velocity (m/s)
U	velocity (m/s)
V	volume (m^3)
w_c	specific weight (kg/m^2)
z	spatial coordinate (m)

Greek letters

α_{avg}	average specific filtration resistance (m/kg)
β	empirical coefficient
ε	porosity (–)
Φ	interaction potential (J)
η	efficiency
μ	viscosity (Pa s)
Θ	empirical constant to describe deformation in the cake (bar)
σ	specific deposits (–)

Subscript

0	initial condition
∞	bulk
bm	suspended particle
c	collector, cake
col	colloidal
g	gravitational
p	particle
T	total

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