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# Enhancement of the electrodewatering properties of synthetic and municipal sludges by the addition of metal cations

by

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# Abstract

Electrodewatering consists on the application of both pressure (mechanical effect) and electrical current (electrokinetic phenomena) to colloidal systems, such as municipal sludge, in order to achieve higher solid content (also designated by dryness). The influence of metal cations and its salts on the electrodewatering characteristics was systematically studied for municipal sludge and for two potential synthetic sludges, one composed of kaolin and the other of kaolin plus xanthan gum. The effect of the size, charge and concentration of the metal cations were studied in the three types of sludge. The effect of pH was also briefly addressed. The results were explained by the selective adsorption of metal cations to the surface of the dispersed particles. The adsorption was studied by ICP-AES (Inductively Coupled Plasma with Atomic Emission Spectrometer) metal analysis. This project was performed in collaboration with Ovivo.

The first type of synthetic sludge was prepared by mixing kaolin powder with an electrolyte, where the nature of the salt and its concentration (from 0.0 to 0.2 M) were varied. In the presence of deionized water, the dryness of the sludge increases by 20%, from 62 to 74%. In general, the addition of salts of monovalent cations, such as MCl, where M=$Li^+$, $Na^+$, $K^+$ and $Rb^+$, causes an increase of the amount of water extracted from the sludge as long as the salt concentration is below 0.1 M. In the case of CsCl, the amount of water extracted decreases constantly with an increase in concentration. At the same concentration, the volume of water extracted is highest for cations with the largest hydrated radius: $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. This series represents the opposite trend observed for the relative adsorption affinity of cations for the surface of the kaolin: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. Therefore, electrodewatering is favored in the presence of poorly adsorbed metal cations as a direct result of improvement of the electromigration. Moreover, for concentration in the range 0.0 to 0.2M, a charge increase on the cation of the chloride salts (NaCl, $CaCl_2$ et $CeCl_3$) results in a decrease in the volume of extracted water: $Na^+ > Ca^{2+} > Ce^{3+}$, The adsorption of these cations to the kaolin surface is more significant for the cations with the highest charge: $Na^+ < Ca^{2+} < Ce^{3+}$. Once again, the electrodewatering is favored in presence of cations that do not adsorb to the kaolin surface.

The electrodewatering of kaolin is also dependent on the pH that should be between 2 and 7. As a consequence, the addition of different sodium salts (NaCl, $NaNO_3$, $NaClO_3$, $Na_2SO_4$, $NaHCO_3$, NaOH, $Na_2CO_3$) causes a decrease of the extracted water if the pH of the electrolyte is higher than 8, which is the case of $NaHCO_3$, NaOH and $Na_2CO_3$.. In general, the extracted water decreases in the series: $Cl^-$, $NO_3^-$, $ClO_3^- > SO_4^{2-} >> HCO_3^- >> OH^-$, $CO_3^{2-}$.

The energy spent in the electrodewatering process of kaolin mixed with deionized water is 0.9±0.1 kWh per kilogram of extracted water. However, 96% of the water is extracted in the first 10 minutes of electrodewatering with an energy consumption of 0.20±0.02 kWh/kg of extracted water, which corresponds roughly to 20% of the energy spent in the 60-minute experiments. Furthermore, the addition of the electrolyte solutions to kaolin causes an increase in the energy consumption. As an example, the addition of LiCl 0.2 M to kaolin leads to an increase of extracted water from 6.9 g without any salt to 8.0 g. At the same time the energy consumed is 1.1 and 2.1 kWh per kilogram of extracted water for the ten- and sixty-minute experiment, respectively. Therefore, the composition of sludge and the operation time are both crucial for the energy performance.

The electrodewatering properties of kaolin are changed upon addition of a small amounts of xanthan gum (4.4 wt%). For example, a sludge composed of kaolin plus xanthan gum does not dewater by the application of pressure alone, which is the opposite of what happens with the kaolin sludge. The xanthan gum is helping to disperse the kaolin particles in solution, making the dewatering more difficult. Moreover, the total water extracted from kaolin plus xanthan gum sludge is 2.7 g, which is 2.6 times less water when compared to the water extracted from the kaolin sludge (7.2 g).

All the salts of monovalent cations (MCl, with M=$Li^+$, $Na^+$, $K^+$, $Rb^+$, and $Cs^+$) have a similar effect on electrodewatering of kaolin plus xanthan gum sludge ($Li^+=Na^+=K^+=Rb^+=Cs^+$) when compared at the same concentration. On the other hand, an increase of the charge of the metal cation results in an increase of extracted water: $Na^+ < Ca^{2+} < Ce^{3+}$. In this case, the amount of extracted water increases with an increase of the concentration of added salt (from 0 to 0.2 M). The final dryness is 74.2% when $CeCl_3$ 0.2 M is added, compared to 66.2% with deionized water. The presence of cations that adsorb strongly to the surface of the kaolin, such as $Ce^{3+}$, facilitates the aggregation of the kaolin and xanthan gum particles, which results in an increase of electrodewatering.

The replacement of chloride ion in NaCl was also studied. The amount of extracted water decreases in the series: $Cl^- > NO_3^- > ClO_3^-$ , $SO_4^{2-} \gg HCO_3^- > CO_3^{2-} > OH^-$. The electrodewatering of kaolin plus xanthan gum is favored by more acidic pH's. The water lost by evaporation, as a result of the increase in temperature during the drying process, may represent more than 20% of the total extracted water. The energy consumed per kilogram of water extracted is 2.9±0.1 kWh in the presence of deionized water.

The electrodewatering properties of municipal sludge from La Prairie, Quebec, were studied. This sludge has an initial dryness of 14.3%. Upon electrodewatering, the dryness of the sludge practically doubles (final dryness of 26±3%) and the initial volume is reduced by half. Twenty percent of the total extracted water is lost by evaporation. The energy consumed in the process is 0.29 kWh per kilogram of extracted water, which represents about four times less energy when compared to a thermal drying method.

All monovalent cations have a similar effect on the electrodewatering of municipal sludge: $Li^+=Na^+=K^+=Rb^+=Cs^+$. Furthermore, the +2 and +3 cations are more efficient in the dewatering of municipal sludge than +1 cations: $Ce^{3+}$, $Ca^{2+} > Na^+$. A bell shape curve is obtained for the dependency of extracted water with the amount of added metal cation. The highest dewatering is achieved at 4.4-7.5, 2.2-4.4, and 1.5-4.4 mmol of added, NaCl, $CaCl_2$ and $CeCl_3$, respectively. For example, the final dryness of the sludge reaches 42% upon addition of 4.4 mmol of NaCl. This represents a three times increase in dryness relative to the initial value. In these conditions, the volume of the sludge is reduced by 70%. For the optimal concentrations, the energy consumed per kilogram of extracted water is 0.32, 0.36-0.43 and 0.33-0.39 kWh for $Na^+$, $Ca^{2+}$ and $Ce^{3+}$, respectively, values that are close to the one observed with deionized water. The energy consumption is still less than the case of thermal drying. Thus, electrodewatering of municipal sludge is an attractive method to treat municipal sludge residues and in fact the process may be successfully optimized by the addition of metal cations prior to treatment.

Kaolin plus xanthan gum sludge and municipal sludge behave similarly in electrodewatering. The synthetic sludge is a useful tool that can be used in the understanding of the fundamental phenomena taking place in electrodewatering.

Student

Director of Research

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# Table of Contents

# List of Figures

# List of Tables

# Chapter 1 – Fundamentals of Electroosmotic Pressure Enhanced Dewatering in Wastewater Treatment

## 1.1 Introduction

Wastewater sludge is formed in the process of sewage treatment. This byproduct of water treatment is commonly used as fertilizer in agricultural lands, or as an alternative it can be disposed of by incineration or by depositing in landfill. However, deposition sites are usually far from wastewater treatment facilities. This results in the need to transport the sludge and because of its high water content (67- 87 wt%), the energy needed in the transportation process per kg of solid material is high (as well as the energy needed in incineration) [1]. For this reason, and also as a mean to reduce the volume of the sludge, it is of interest to remove as much water as possible from the sludge before moving it from one place to the other [2].

Different methods are available to dry sludges. These methods involve the combined use of mechanical (such as centrifugation and pressure belt filtration) and thermal methods. However, there is a limit to the amount of water that it is possible to remove from a sludge using mechanical methods. Moreover, these methods are usually energy demanding. As an example, to remove 1 kg of water from sludge by evaporation, 1.2 kWh of energy is required [3].

An attractive approach for the dewatering of municipal sludge is called electrokinetic dewatering (or electroosmotic dewatering or more simply electrodewatering). In this process, a potential difference is applied to the sludge cake that is compressed between two metal plates. A series of electrokinetic phenomena take place that account for the increase in the solid content of the sludge. Two main advantages arise from electrodewatering: higher dry solid content is achieved with less energy spent in the process. Recently published results showed that it is possible to achieve sludge with solid content as high as 55 wt% (for 1.5 hour experiments at 400 kPa and 50 V) spending as little as 0.34 kWh/kg of extracted water [4]. For comparison, the maximum dry solid content achieved by the three most common mechanical methods (centrifugation, belt press filtration and press filtration) is 35 wt% [4].

(Note: municipal sludge, sewage sludge or wastewater sludge are used interchangeably.)

## 1.2 Electrokinetic phenomena in electrodewatering

Electrodewatering is a process that combines the application of a potential difference with that of pressure to increase the solid content of sludge. The application of an electric field to a colloidal system, such as a municipal sludge, gives rise to physico-chemical phenomena that result in the conduction of an electric current, with an intensity dependent on the nature of the colloidal system and on the intensity of the electrical field. An electrodewatering cell is basically composed of two metal plates that act as anode and cathode upon the application of an electrical potential difference. The cathode is perforated to allow drainage of water, and thus, the solid content of the sludge is increased. Pressure is used to guarantee a good electrical contact between all parts of the system. The above mentioned physico-chemical modifications are called electrokinetic phenomena and these include **electroosmosis** (movement of water towards the cathode), **electromigration** or **electrophoresis** (movement of charged particles towards the electrode of opposite sign; electromigration can be seen as a particular case of electrophoresis when the particle size is close to zero), **streaming potential** (formation of an electrical potential difference by the forced movement of an electrolyte, by the application, for example of a pressure difference to the colloidal system), and **sedimentation potential** (potential difference generated as the result of the migration of charged particles, for instance during gravitational settling). **Electrochemical reactions** also take place, namely water hydrolysis due to the potential reached by each electrode. The streaming potential and sedimentation potential are less important in the understanding of electrodewatering and will not be further discussed [5]. Figure 1.1 describes schematically the more relevant phenomena taking place during electrodewatering.

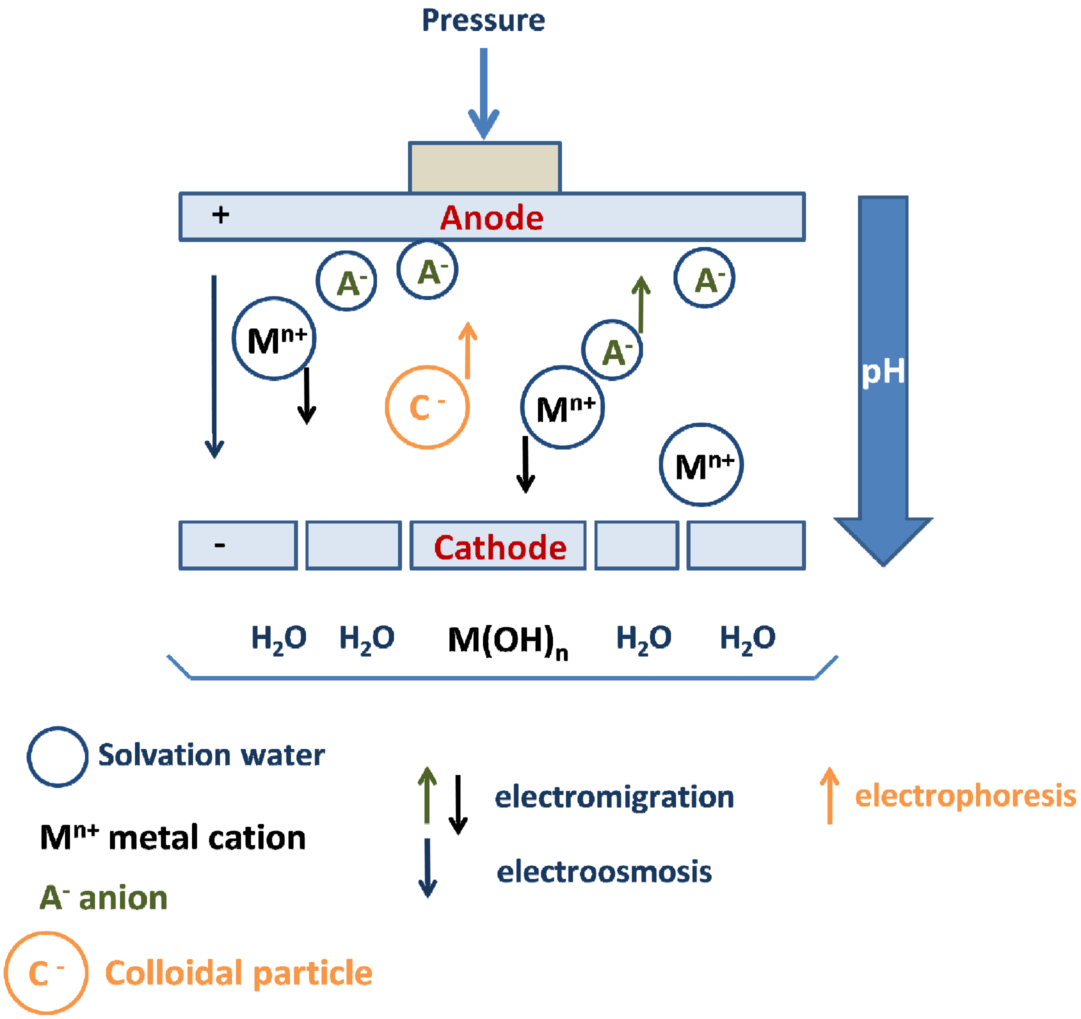

**Figure 1.1** Schematic representation of the electrochemical phenomena taking place in an electrodewatering cell. The perforated cathode allows the removal of water from the colloidal system, thus resulting in an increase of the solid content.

Water in municipal sludge can be categorized in four different types: (i) free water, (ii) interstitial water (bound to sludge particles within the flocs by capillary forces), (iii) surface water (adsorbed on sludge particles), and (iv) intercellular water (chemically bound to sludge particles) [1, 5]. The surface and intercellular water can only be removed by high energy thermal methods and mechanical methods only remove free water. Electrodewatering is able to remove interstitial water as well, which makes this technique very promising to achieve higher solid content. Indeed, due to its characteristics, electrodewatering is an attractive process in the dewatering of materials that present a low hydraulic permeability [6], such as municipal sludges.

Water flows from the anode to the cathode by electroosmosis, which is also the result of electromigration. Moreover, the passage of an electric current through the sludge will cause an increase in temperature. This may lead to the evaporation of water, resulting in a further increase of the dryness. Furthermore, an increase in temperature also reduces the viscosity of water, which will further facilitate the dewatering process [7].

### 1.2.1 Electrochemical reactions

An electrodewatering cell operates at voltages that allow water electrolysis, represented by Equations 1 and 2 [5].

Anode: $2\ H_2O\ (l) \rightarrow 4\ H^+(aq) + O_2\ (g) + 4\ e^-$ (for acidic pH, $E_{0/SHE} = +1.23$ V;) (Equation 1.1)

Cathode: $2\ H_2O\ (l) + 2\ e^- \rightarrow H_2\ (g) + 2\ OH^-\ (aq)$ (for basic pH, $E_{0/SHE} = 0.0$ V;) (Equation 1.2)

Overall reaction: $2\ H_2O \rightarrow 2\ H_2\ (g) + O_2\ (g)$ (Equation 1.3)

As a result of water decomposition, protons and hydroxide ions are formed at the anode and cathode, respectively. These $H^+$ and $OH^-$ lead to a modification of the pH of the sludge cake near the electrodes that become more acidic at the anode and more basic at the cathode. Oxygen and hydrogen gases are also formed at the anode and cathode, respectively. The evolution of gases does not pose a safety hazard, as long as good ventilation of the facilities is ensured. However, the accumulation of gas at the anode can create an insulating layer between the sludge and the anode, which increases the resistivity of the system and limits the dewatering process (and increases the consumption of energy). The application of pressure in an electrodewatering cell is thus justified to avoid the accumulation of gas around the anode. This problem is not relevant for the cathode side because the cathode is perforated to allow water to be drained from the sludge.

Other electrochemical reactions are possible depending on the electroactive species present in solution. In the presence of chloride, $Cl_2$ evolution could occur (Equation 1.4), which may cause corrosion problems.

$2\ Cl^- \rightarrow Cl_2\ (g) + 2\ e^-$ ($E_0 = 1.36$ V vs SHE) (Equation 1.4)

Oxidation of the anode may occur (Equation 1.5) depending on the material chosen. To avoid oxidation, Dimensionally Stable Anodes (DSA®) were used (Chapter 2). On the other hand, metallic deposition may occur at the cathode (Equation 1.6).

$M \rightarrow M^{n+} + ne^-$ (Equation 1.5)

$M^{n+} + ne^- \rightarrow M$ (Equation 1.6)

### 1.2.2 Electromigration

The ions present in solution will migrate to the electrode of opposite charge in a process called electromigration. As a result, cations will move towards the cathode, and anions towards the anode. Hydroxyl and protons formed during the decomposition of water (section 1.2.1) will also migrate, which will result in the formation of a pH gradient throughout the sludge, being lowest at the anode and highest at the cathode. Both anions and cations have hydration spheres and as a result water molecules are also being displaced (the movement of water is called electroosmosis which is further explained below – section 1.2.3). Cations reaching the cathode may precipitate in the form of hydroxides because of their low solubility at high pH.

The electromigration depends on the applied electric field, the nature of the moving ion and its concentration (Equation 1.7 derived from Nernst-Planck equation) [5].

$\vec{N_i} = -z_i u_i^* F c_i \nabla\phi$ (Equation 1.7)

where, $\vec{N_i}$ is the flux of species i, $u_i^*$ its effective ionic mobility $c_i$ its ionic concentration, $z_i$ its charge number, $\nabla\phi$ is the applied electrical field, and $F$ is the Faraday's constant.

The electrical conductivity of the colloidal system will dictate the intensity of the current generated by the moving ions (Ohm's law)

$\vec{\imath} = -k\nabla\phi$ (Equation 1.8) where, $\vec{\iota}$ is the current density and $k$ is the electrical conductivity of the continuous phase of the colloidal system and is dependent on the composition of the electrolyte (Equation 1.9):

$k = F^2 \sum_i z_i^2 u_i^* c_i$ (Equation 1.9).

It is expected that electrodewatering is facilitated in the presence of ions with the highest hydrated radius, because water molecules are being dragged along with the migrating ions under the action of the electric field. For example, the hydrated radius of alkali metal cations decreases with increasing atomic number: $Li^+ > Na^+ > K^+ > Rb^+$, $Cs^+$ [8]. Accordingly, electrodewatering should be enhanced in the presence of $Li^+$ compared to $Cs^+$. This effect will be tested in the electrodewatering of kaolin, kaolin plus xanthan gum and municipal sludges (Chapters 3, 4 and 5, respectively).

### 1.2.3 Electroosmosis

Electroosmosis is the movement of water towards the cathode as a result of movement of ions and their hydration water. Whenever the water reaches the cathode, and because the cathode is perforated, the water will be removed from the system, and the solid content of the sludge will improve.

Helmholtz (1879) and Smoluchowski (1914) developed a theory to help understand the electroosmotic effect in capillaries filled with liquid [9]. The electroosmotic flow rate, $Q_e$, will be the outcome of two opposing forces: the electrical force that causes water movement and friction that prevents it. The electroosmotic flow rate is given by equation 1.10.

$Q_e = k_e i_e A$ (Equation 1.10).

where, $k_e$ is the coefficient of electroosmotic conductivity, $i_e$ is the electrical potential gradient, and $A$ is the cross-sectional area. Equation 1.10 has the same form as Darcy's Law for hydraulic flow rate $Q_h$ :

$Q_h = k_h i_h A$ (Equation 1.11).

where, $k_h$ is the coefficient of hydraulic conductivity, $i_h$ is the hydraulic gradient (for example the one imposed to the sludge by the application of pressure), and $A$ is the cross-sectional area.

The coefficient of electroosmotic conductivity is given by:

$k_e = \frac{\zeta D}{\eta} n$ (Equation 1.12).

where, $\zeta$ is the zeta-potential (further discussed in section 1.3.), $D$ is the dielectric constant of the pore fluid and $\eta$ is its viscosity, and $n$ is the porosity of the solid material composing the sludge.

Electroosmosis is enhanced in the presence of strong electric fields and from equation 1.10, a linear relation should be observed between the intensity of the applied electric field and the electroosmotic flow rate or the volume of water extracted per unit time. The electroosmotic conductivity, $k_e$, is dependent on the porosity of the medium but it is not dependent on the pore size, the opposite trend of what happens with the hydraulic conductivity coefficient. This is why higher solid content (more extensive dewatering) can be achieved by the application of an electric field as opposed to the application of pressure alone. Electroosmosis is also enhanced by an increase of the zeta-potential. In general, the extent at which electrodewatering occurs can be modified by changing one of the two parameters that influence electrosmosis: the zeta-potential and the applied electric field.

### 1.2.4 Electrophoresis

The movement of charged particles by the application of an electric field is called electrophoresis. As municipal sludge particles are usually negatively charged at their surfaces, the particles are attracted to the anode. The electrophoretic velocity,$v_{ef}$, is thus equal to the electroosmotic velocity, $v_{eo}$, but of opposite sign [5]. From the Helmholtz-Smoluchowski theory:

$v_{ef} = -v_{eo} = \frac{\zeta D}{4\pi\eta} i_e$ (Equation 1.13)

In the configuration of an electrodewatering cell, where water is only recovered at the cathode, electrophoresis has a limited role on the cake's final dryness. However, it may prevent clogging of the filter, because electrophoresis is preventing particles to settle near the cathode, as they are being directed towards the anode [10].

## 1.3 Electrical Double Layer (EDL) and zeta-potential

Colloidal particles are charged at their surfaces and municipal sludge particles are usually negative. As a result, cations will surround the sludge particles. The two-zone region composed of the negative charge on the surface of the sludge particles surrounded by the positive charge of the adsorbed cations is called the electrical double layer (EDL; a schematic representation of the EDL can be found in [5]). There are three different models used in the understanding of the charge distribution around colloidal particles: Helmholtz, Gouy-Chapman (1910-1913), and Stern models [9]. The following is a short description of the Stern model which accounts for aspects of the other two models.

Immediately next to the negatively charged surface there is a layer of specifically adsorbed non-hydrated cations. This layer is called the Stern layer and is surrounded by a diffuse shell of hydrated cations and anions. The neutrality of the solution is not observed in the electrical double layer: the cations concentration is larger closer to the colloidal particles and decreases to the bulk solution value as the distance from the particle is increased. The anion concentration profile is the mirror image of the one for cations: it increases with the distance from the particle until it reaches the bulk value. As a result of the locally unbalanced charges, there is a potential difference between the particles' surface and the solution's bulk.

Upon the application of an electric field, a colloidal particle will move towards one of the electrodes, in a process called electrophoresis (section 1.2.4). Part of the solvation shell of the colloidal particle will move with the colloidal particle while the other part of it will not. The plane at which this separation occurs is a shear plane and the potential difference between that plane and the bulk of the solution is called the zeta-potential ($\zeta$). The shear plane is located in the diffuse layer region but its exact position is unknown [11]. The zeta-potential can be determined experimentally by measuring the electrophoretic mobility, and using the Helmholtz-Smoluchowski theory by means of Equation 1.13. Furthermore the thickness, $r_D$, of the EDL varies with the ionic strength, $I$, of the solution [12]:

$$r_D = \left(\frac{\varepsilon RT}{2\rho F^2 I}\right)^{1/2} \text{(Equation 1.14).}$$

where, $\rho$ is the solution mass density. An increase of the ionic strength will give rise to a decrease in the thickness of the double layer, which may bear consequences to the stability of the colloidal suspension, depending on the forces at play.

The DLVO theory (Derjaguin and Landau (1941) and Verwey and Overbeek (1948)) rationalizes the stability of a colloidal suspension as a balance between repulsive and attractive forces of interaction among colloidal particles. Thus the total interaction energy, $V_{total}$, is given by:

$$V_{total} = V_{ER} + V_{VA} \text{ (Equation 1.15).}$$

where, $V_{ER}$ is the repulsion provided by neighboring electrical double layers, and $V_{VA}$ is the attraction arising from intermolecular van der Waals interactions. When the EDL is contracted by an increase of the ionic strength, flocculation or even coagulation (the difference between flocculation and coagulation is that in the first case the colloidal suspension may be redispersed by mechanical means, whereas the second case is irreversible) may occur if the attractive interactions are strong enough. For example, high valence metal cations, such as $Al^{3+}$ are known to induce coagulation and to decrease the zeta-potential. In turn, this decrease of the zeta potential will cause a decrease of the electroosmotic flow that will affect negatively the electrodewatering. However, an increase in coagulation can also facilitate hydraulic dewatering because less water molecules are retained within the flocs of the sludge and the removal of water by pressure is thus facilitated.

## 1.4 Published Results

Kaolin has been used in the studies of electrodewatering [13-21]. It was shown that an increase in voltage results in an increase of the solids content, for example, from 47 wt% at 1 V to 67 wt% at 50 V [13]. The energy consumed is highly dependent on the experimental conditions and a voltage step increase from 1 to 50 V may result in a reduction (by a factor of five) of the energy consumed to remove a fixed amount of water compared to the application of a fixed voltage (50 V) [13]. Furthermore, the addition of acid or electrolyte, such as NaCl, up to 0.01 M, is beneficial for electrodewatering that shows better performances at same voltages when compared to pure water [14].

The electrokinetic properties of kaolin have been also thoroughly studied. The impact of pH, electrolyte type, valence and concentration of added cation on the value of the zeta-potential was evaluated [11, 22-31]. More specifically, it was shown that in presence of NaCl, the zeta-potential increases with an increase of concentration up to 0.1 M, after which the zeta-potential decreases [31]. In the presence of divalent cations there is a charge reversal of the zeta-potential at about 0.2 M [31]. However, the impact of the changes of the zeta-potential on the electrodewatering characteristics of kaolin were not fully addressed yet and it will be one of the topics of the current project.

Electrodewatering is an effective method to dry municipal sludges. The electrodewatering performance has been evaluated in terms of rate, final dryness and energy consumption. All of these vary with respect to the experimental conditions, such as the duration, the time of application and the strength of the electric field, and the pressure applied. In general, the various studies have shown that an increase in voltage (or current) and an increase in pressure result in the increase of the dryness of the sludge cake [1-5, 32-35]. For example, recently published data show that by increasing the voltage five times the final dryness increases more than three times [4]. At the same voltage, with a six times increase in pressure the final dryness of the sludge cake increased from 55 to 64% [4]. The reported energy consumption to extract a given amount of water is a function of the applied pressure and voltage and is between 0.034 and 0.488 kWh/kg of extracted water [4]. The energy consumed is always lower in comparison to a thermal process (1.2 kWh/kg of extracted water) [3].

It was shown that the addition of sodium sulfate improves the electrodewatering process. For example, the final dryness increases from 45 to 53% when the conductivity of the sludge increases from 0.3 to 9.5 mS $cm^{-1}$ as a result of an increase in salt concentration [36]. The increase in dryness is accompanied by an increase in the energy consumption from 0.27 to 0.45 kWh/kg of extracted water but the higher value is still lower than the one observed in thermal drying. The effect of the addition of other salts was further investigated in the present work.

Synthetic sludges that mimic the properties of municipal sludge are described in the literature and can be prepared by mixing polystyrene latex particles, alginate, calcium ions and cellulose fibers [37]. In the current project, this approach was simplified and a model for municipal sludge was created by mixing kaolin and xanthan gum. Xanthan gum is as natural polysaccharide that finds many applications in the industry especially as a rheology modifier [38-40]. Polysaccharides are known to adsorb on the surface of minerals [40]. In particular, the adsorption of starch (and derivatives) onto kaolin has been studied [42-44]. The interaction starch-kaolin can be electrostatic and/or by hydrogen bonding [42]. Ionic strength and pH both influence the adsorption of starch onto kaolin [43, 44]. Starch adsorption increases with decreasing pH and increasing ionic strength [43]. In the presence of hydrolysable metal cations, such as calcium and magnesium, the adsorption is also favored [44]. To our knowledge no electrodewatering experiments have been reported in the literature that use kaolin combined with a polysaccharide and more specifically with xanthan gum. In this project, the open literature of the adsorption of polysaccharides on kaolin was used as a starting point and its influence on the electrodewatering properties was investigated under different conditions of pH and ionic strength.

## 1.5 Objectives

The ultimate goal of this project is to improve the electrodewatering properties of municipal sludge in order to make this process even more efficient and competitive. To achieve this, an experimental setup was designed and built purposefully for the electrodewatering tests. Then, it was mandatory to identify a synthetic sludge whose electrodewatering behavior would mimic that of municipal sludge. Subsequently, the effect of the addition of mono-, di- and trivalent metal cations to the synthetic sludge is going to be evaluated in an effort to identify the best operating conditions. Tests will then be performed on municipal sludge in the installation of our industrial partner (Ovivo) to identify which of the synthetic sludges is a better model of municipal sludge and to identify which metal cations (and at what concentrations) positively affect the electrodewatering characteristics of that medium. Finally, the behavior of the different metal cations at a microscopic level will be explained by relying in ICP-AES (Inductively Coupled Plasma – Atomic Emission Spectroscopy) method to measure the adsorption of the various metal cations.

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# Chapter 2 – Experimental part

## 2.1 Electrodewatering experiments

### 2.1.1 Laboratory cell setup (cell 1 and cell 2)

An electrodewatering cell is a device that combines mechanical pressure with an electrical potential difference to achieve higher solid contents. The basic components on an electrodewatering cell include two metal plates, between which the sludge is compressed by action of the applied pressure. Two cells were designed and built during this project (cell 1 and cell 2; Figure 2.1 A, B, C and D). In both cells, the anode used was a commercially available DSA®-type anode (Dimensionally Stable Anode) consisting of a 28.2 mm Ti disk coated with a mixture of $Ta_2O_5$ (approximately 20 at%) and $IrO_2$ (80 at%). The anode is assembled in the anode block which is made of Teflon®. One side of the anode is in contact with a Pt wire that allows the connection to a power source (Agilent AC Power Source/Analyzer 6811B), through which the potential difference is applied. The other side of the anode is in contact with the sludge. Pressure is applied on the anode block using compressed air (cell 1) or masses made of stainless steel blocks (cell 2). In cell 1, the anode block is inserted in a glass tube, whereas in cell 2 a Teflon®- carbon fiber tube was preferred that minimizes the friction between the sliding anode block and the tube (in cell 1, the inner wall of the glass tube was covered with a Teflon® lubricant to reduce the friction). The cathode is composed of a perforated stainless steel disk that allows drainage of water. A filter paper is inserted on top of the cathode to prevent the sludge to go through the cathode. Although equivalent in principles, cell 2 is easier to operate.

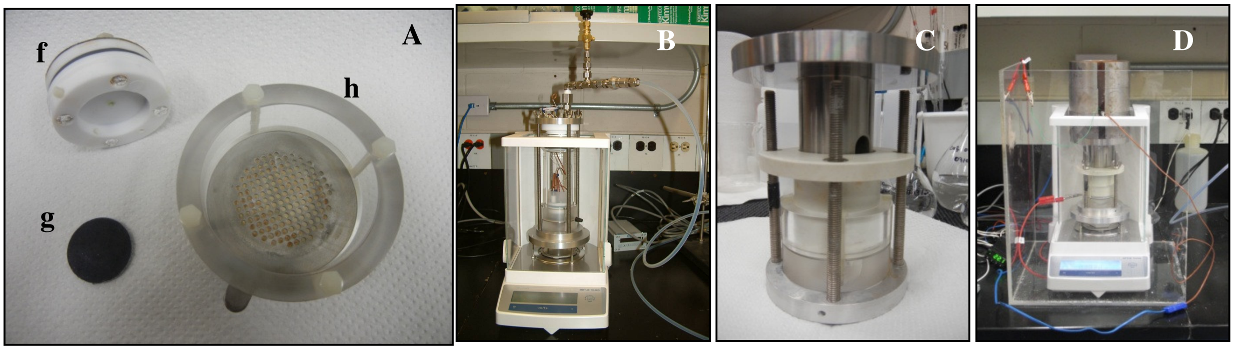

**Figure 2.1** **A**: electrodewatering cell parts common to both cell 1 and 2 – anode block (**f**), 28.2 mm anode disk (**g**), cathode support (top view, **h**); **B**: assembled cell 1; **C** and **D**: assembled cell 2; **C** clearly shows the weights required to apply pressure; **D** shows the air pressure system through which the pressure is applied.

The temperature of the sludge cake, the current passing through the sludge and the mass of the recovered water were measured throughout the duration of all experiments. The data were automatically collected with the help of a computer at a frequency of 1 Hz. The temperature was measured with a type T-thermocouple from Omega Environmental, Inc., while the mass of the filtered water passing through the cathode was measured with a Mettler Toledo balance (AB204-S/FACT). All tests were performed at room temperature and at a pressure of 70 kPa (cell 1) or 77-78 kPa (cell 2). Cell 1 and cell 2 were mostly used to study the dewatering properties of the synthetic sludges.

### 2.1.2 Ovivo-laboratory cell setup

Ovivo-laboratory cell (CINETIK® CK-LAB technology; Figure 2.2) operates according to the same principles as cell 1 or cell 2. DSA®-type anode (Ti support, coated with $IrO_2$ mixed with about 20% $Ta_2O_5$) and stainless steel cathode were also used. The anode is quadrangular in shape with a surface area of 122 $cm^2$. Pressure is applied by a compressed air system. Ovivo cell was used exclusively for the electrodewatering of municipal sludge. The current passing through the sludge and the mass of the recovered water collected at the cathode were measured during each experiment. An estimation of the volume reduction that occurs as a result of water loss was made by monitoring the sludge cake thickness.

**Figure 2.2** Representation of CINETIK® electrodewatering cell system used in experiments with municipal sludge at Ovivo's laboratory. The power source is shown on the left; on the right is the electrodewatering cell; the scale is used to measure the water extracted at the cathode. (From [1])

### 2.1.3 Operating conditions

The general experimental operating conditions are summarized in Table 2.1.

**Table 2.1** Operating conditions of the electrodewatering cells.

| | **Cell 1** | **Cell 2** | **Ovivo cell** |
|---|---|---|---|
| Temperature | Room temperature | Room temperature | Room temperature |
| Pressure (kPa) | 70 | 77-78 | 116±4 |
| Voltage (V) | 50 | 50 | 50 |
| Maximum current (A) | 4.1 | 4.1 | 6.1 |
| Anode surface area (cm$^2$) | 6.25 | 6.25 | 122 |
| Filter | Whatman® filter paper #5 | Whatman® filter paper #5 | Filter cloth Exxtreme 5 from Weavexx ** |
| Sludge type used | Synthetic sludge* | Synthetic sludge | Municipal sludge |
| Sludge initial mass (g) | 43.15 | 43.15 | 150 |
| Sludge initial dryness (%)*** | 62 | 62 | 14-15 |

*One test was also performed with municipal sludge to directly compare results with the synthetic models.

**The filter is made of polyphenylene sulfide; it is drenched in tap water before use as a way to increase its electrical conductivity.

***The sludge dryness is the percentage of solids present in the sludge (explained below).

### 2.1.4 Synthetic sludge preparation

The synthetic sludge was prepared by mixing kaolin (or kaolin plus xanthan gum) with a given amount of electrolyte with a known concentration. In a typical preparation, 35.15 g of kaolin (or 32.65 g of kaolin plus 2.50 g of xanthan gum) were mixed with 21.50 g of electrolyte and stirred till a homogeneous cake was obtained. The sludge was prepared immediately before the electrodewatering test. Two different batches of kaolin were used: batch A – EMD Chemicals lot # 48220930; and batch B – Fluka lot # 424080/1. Xanthan gum (food grade) was purchased from Bob's Red Mill Natural Foods, Inc. Milwaukie, OR, USA; all other chemicals (ACS grade) were purchased from Aldrich. The electrolyte solutions were prepared in the concentration range 0-0.2 M.

### 2.1.5 Calculations performed

#### *2.1.5.1 Electrodewatering experiments with synthetic sludge*

The water reaching the cathode during an electrodewatering test is collected and continuously weighted. At the end of the experiment the cumulative mass of water thus recovered is called filtered water. The total extracted water can be determined by weighing the electrodewatering cell before and after each experiment, as illustrated by Equation 2.1.

$$Total\ extracted\ water\ = M1 - M2 \quad \text{(Equation 2.1)}$$

In equation 2.1, $M1$ and $M2$ are the mass of the electrodewatering cell, before and after the electrodewatering test, respectively. The total extracted water is always higher than the filtered water and the difference was assumed to be an estimation of the water that was lost by evaporation (evaporated water), as it is shown by Equation 2.2.

$$Mass\ of\ evaporated\ water = Total\ extracted\ water\ -\ Mass\ of\ filtered\ water$$
(Equation 2.2)

The percentage of water lost by evaporation is given by Equation 2.3.

$$Water\ lost\ by\ evaporation = \frac{Mass\ of\ evaporated\ water}{Total\ mass\ of\ extracted\ water} \times 100 \text{ (Equation 2.3)}$$

In several experiments, especially with kaolin sludge, the evaporated water represents less than 5% of the total extracted water. In those cases, the filtered water was considered to be equal to the total extracted water.

In some experiments (with kaolin plus xanthan gum), it was necessary to account for the presence of solid particles in the filtrate. Thus, the mass of filtered water was corrected for the soluble solid present in the filtrate (Equation 2.4).

$$Corrected\ mass\ of\ filtered\ water = Mass\ of\ filtered\ water - M3 \text{ (Equation 2.4)}$$

In Equation 2.4, *M3* is the mass of solid residue present in the filtrate, determined by weighing the residue left after evaporating the filtrate to dryness.

The sludge dryness is defined as the mass percentage (expressed as weight percent, wt%) of solids present in the sludge. The calculation of initial dryness is straightforward from the knowledge of the composition of the synthetic sludge, that is, from knowing the mass of solids and the mass of electrolyte used in the preparation. Therefore, the initial dryness is calculated according to Equation 2.5.

$$Initial\ dryness = \frac{Mass\ solids}{Mass\ solids + Mass\ electrolyte} \times 100 \text{ (Equation 2.5)}$$

The knowledge of the total mass of extracted water allows the calculation of the sludge final dryness, as given by Equation 2.6.

$$Final\ dryness = \frac{Mass\ solids}{Mass\ solids + Mass\ electrolyte - Total\ mass\ of\ extracted\ water} \times 100$$

(Equation 2.6)

The total energy spent per mass of extracted water is given by Equation 2.7.

$$Total\ energy\ per\ mass\ of\ extracted\ water = \frac{\int V_n \times i_n \times t}{Total\ mass\ of\ extracted\ water}$$

(Equation 2.7)

where, $V_n$ and $i_n$ are the voltage (V) and the current intensity (A) at time point $n$, and $t$ (h) is the time between each data point (one readout is made each second), respectively. Thus defined, the total energy per mass of extracted water has the units of Wh/g, which is equivalent to kWh/kg.

#### *2.1.5.2 Electrodewatering experiments with municipal sludge*

The dryness of the municipal sludge is determined by a gravimetric method [2]. One sample of municipal sludge is dried at 105°C for 24 hours in a beaker of known mass. Afterwards, the sample is left to cool down to room temperature for 4 hours inside a desiccator before measurement of the final mass. The solid content of the sludge is determined by Equation 2.8.

$$Dryness = \frac{B-A}{C-A} \times 100 \text{ (Equation 2.8)}$$

where, $A$ is the mass of the beaker, $B$ is the mass of the beaker plus the sludge after thermal treatment, and $C$ is the initial mass of the beaker plus sludge. Triplicates were performed. The dryness of the municipal sludge is measured before and after the electrodewatering experiment, using the method described above.

The mass of water loss through evaporation (evaporated water) is estimated by using a mass balance equation for water (Equation 2.9).

$$Evaporated\ water = w1 + w2 + w3 - w4 - w5 - w6 \text{ (Equation 2.9)}$$

where, *w1* is the initial water present in the sludge, calculated from the knowledge of the measured initial dryness and the initial sludge mass; *w2* is the initial water present in the filter (because the filter is initially drenched in water); *w3* is the initial mass of water present in any additive used in the experiments (for instance the mass of added electrolyte solution); *w4* is the cumulative mass of the filtrate collected at the cathode; *w5* is the final water present in the sludge, calculated from the values of final dryness and mass of final sludge; and *w6* is the mass of water retained at the filter after the electrodewatering test.

The mass of the filtered water was also corrected using Equation 2.4. The energy consumed in an electrodewatering experiment is calculated using Equation 2.7 as well. In this case, data points are collected every two seconds.

## 2.2 Physical-Chemical characterization

### 2.2.1 pH

Following the definition of Brønsted-Lowry, an acid, HA, is any substance that can donate a proton, and a base, $A^-$, is any substance that can accept one. Dissociation or ionization of the acid occurs in aqueous media (Equation 2.10) and the extent of that dissociation depends on the acid [3].

$$HA \rightarrow H^+ + A^- \text{ (Equation 2.10)}$$

The pH as defined by Sørenson [3] is a measure of the concentration of $H^+$ (or $H_3O^+$, the hydrated form of the proton) in solution and is given by Equation 2.11.

$$pH = -\log [H^+] \text{ (Equation 2.11)}$$

At pH 7 the solution is considered neutral; if the pH is lower than 7 the solution is classified as acidic, and if higher, the solution is considered basic. pH measurements were performed using an instrument from Metler-Toledo (model FE20) that was calibrated with buffers at pH 4.00 and pH 7.00 (both bought from Fischer Scientific).

### 2.2.2 X-Ray Diffraction

The structure of kaolin was confirmed by X-Ray Diffraction (XRD). A diffractometer from Bruker D8 Advance was used with a copper $K_\alpha$ source ($\lambda$=0.15406 nm) operating at 40 kV and 40 mA. Data was collected between 15° and 90° ($2\theta$) in a step mode (0.02°/step and 2 s/step).

### 2.2.3 Zeta-potential

Zeta-potential measurements were performed with ZetaPlus, from Brookhaven Instruments Corporation, that uses Electrophoretic Light Scattering [4]. Briefly, a laser beam is made to pass through a colloidal suspension that is under the influence of an electric field. Due to the movement of particles, scattered light will suffer a Doppler shift. The scattered light is mixed with a reference beam, producing a beat pattern with frequency $f_e$. This parameter is measured experimentally and is related to the electrophoretic velocity of the moving particles, as shown by Equation 2.12:

$$v_{ef} = \frac{2\pi f_e}{Ekcos\alpha} \text{ (Equation 2.12)}$$

where, $E$ is the intensity of the applied electric field; $k$ is the modulus of the scattering vector $\vec{k}$ (the difference between the wave vectors of scattered and incident light); and $\alpha$ is the angle between $\vec{k}$ and the direction of electrophoresis [5]. The zeta-potential is automatically calculated by the instrument's software applying the equation derived from Helmholtz-Smoluchowski theory, already presented in Chapter 1 (Equation 1.13). Samples of kaolin (0.05 g/L) in NaCl, $CaCl_2$ or $CeCl_3$ 0.002M were analyzed immediately after preparation. Three independent measurements of each solution were performed.

### 2.2.4 Inductively Coupled Plasma with Atomic Emission Spectrometer (ICP-AES)

A plasma is a mixture of a gas, its neutral species, positive ions and electrons, formed as a consequence of the ionization of that gas by the application of an electrical discharge [6]. Inductively coupled plasma (ICP) is one of the most used plasma sources in atomic spectroscopy, where an alternating current is applied (27 to 40 MHz), after the initial spark. Plasma temperatures reach 7000-10000K, which allows atomization of the sample and atomic excitation. The lifetime of the excited states is usually $10^{-8}$ s, and the return to the ground state is accompanied by the emission of radiation of a precise wavelength, which is specific to each element [6]. This allows the identification and quantification of the different elements present in a sample.

Analytical methods were developed for the analysis of lithium, sodium, calcium and cerium, using Varian 725 ES from Agilent with radial plasma quartz torch. The operating parameters were automatically optimized by the instruments supplied software and they are summarized in Table 2.2. All samples were dissolved in $HNO_3$ 2% v/v and filtered using a 45 µm pore size filter with nylon membrane prior to injection in the ICP.

**Table 2.2** Experimental parameters for the ICP analysis of Li, Na, Ca and Ce.

| Parameters | Li | Na | Ca | Ce |
|---|---|---|---|---|
| Power (kW) | 1.20 | 1.05 | 1.15 | 1.45 |
| Nebulizer flow (L/min) | 0.85 | 0.75 | 0.80 | 0.65 |
| Viewing height (mm) | 9 | 10 | 5 | 5 |
| Wavelength (nm) | 670.783 (<10 ppm) and<br>610.365 (>10 ppm) | 589.592 | 422.673 | 418.659 |

For each element, calibration curves were recorded from 3 standards (1, 10 and 100 ppm). Standards were prepared by dilution from concentrated commercially available stock solutions (1000 and 10 000 ppm bought from High-Purity Standards), using nitric acid 2% (v/v) as the solvent. All calibration curves are within ±5% error (for all concentrations).

The existence of possible interferences in the quantification of the different elements was assessed. First, 10 ppm (10 mg of metal per liter of solution; designated "prepared concentration" in Equation 2.13) solutions of lithium, calcium or cerium were spiked with sodium in the concentration range 30-1000 ppm. The Li, Ca and Ce content of these spiked solutions was then experimentally measured (designated "measured concentration" in Equation 2.13), and the variation or error was calculated using equation 2.13. The results are shown in figure 2.3.

$$\%Error = \frac{measured\ concentration - prepared\ concentration}{prepared\ concentration} \times 100 \text{ (Equation 2.13)}$$

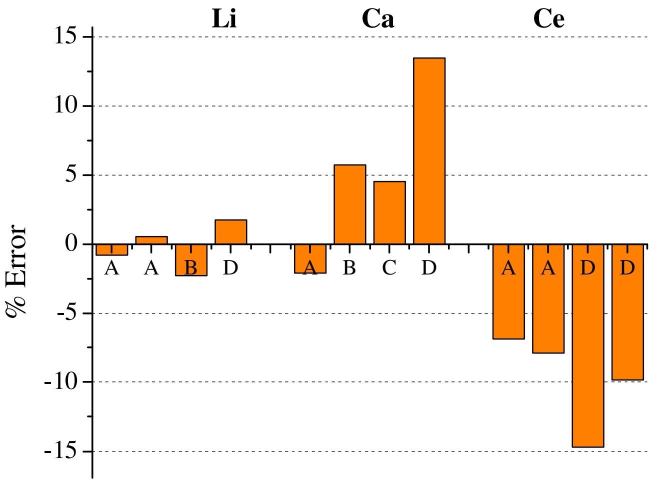

**Figure 2.3** Percent error in the determination of the Li, Ca and Ce content in presence of sodium at three different concentrations; A=30 ppm, B=100 ppm, C=300 ppm, D=1000 ppm. The initial 10 ppm Li, Ca and Ce solutions were spiked with sodium at 30, 100, 300 or 1000 ppm.

As shown in Fig. 2.3, the Ca concentration is overestimated in the presence of high concentrations of sodium, while the Ce content is underestimated. The determination of the Li content is not affected by the presence of Na, because the error is lower than 5%. These effects are current in ICP analysis.

The error made on the determination of the sodium concentration when the solutions are spiked with 1000 ppm of Li, Ca and Ce was also assessed. To do this, a 10 ppm solution of sodium was spiked with the different elements and then sodium content was measured. The percent error (Equation 2.13) in the determination of the Na content is shown in Figure 2.4.

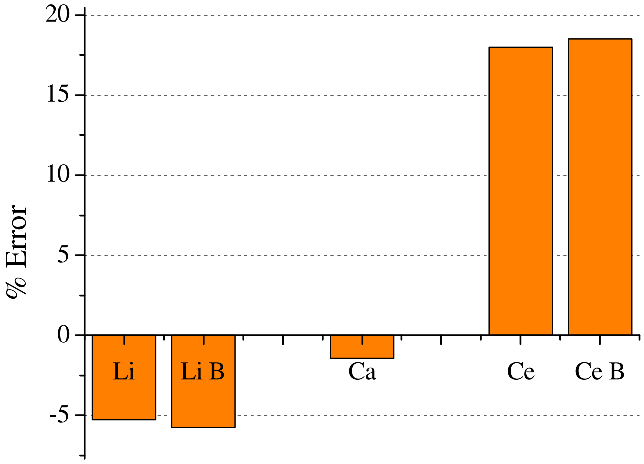

**Figure 2.4** Percent error in the determination of the Na content in the presence of Li, Ca and Ce (1000 ppm). In each case, 10 ppm solutions of Na were initially prepared.

As seen in Fig. 2.4, the sodium content is overestimated in the presence of cerium. Li and calcium do not interfere with the determination of the Na content although the error is close to the acceptable limit in the case of Li.

## 2.3 References

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# Chapter 3 – Electrodewatering of kaolin sludge

## 3.1 Introduction

Kaolin is a clay mineral naturally present in many types of soils. It has several applications in the industry where it is used as paper filler, additives in paint and ink [1], and even in the pharmaceutical industry [2]. Most importantly, it is a major component of ceramics. Kaolin is an aluminosilicate with general chemical formula $Al_2(OH)_4Si_2O_5$ [3]. It is composed of one layer of silicon and one layer of aluminum cations covalently bonded by shared oxygens (Figure 3.1). One of the layers contains Si tetrahedrally coordinated to oxygen atoms – called silica sheet, whereas the other layer contains octahedrally coordinated Al cations that are bound to two oxygen atoms and four hydroxyl groups – called alumina or gibbsite sheet. Two of these hydroxyl groups are shared with neighboring aluminum atoms, and one of the oxygen atoms is shared between one silicon and one aluminum atoms. The two layers form a platelet, and different platelets can be stacked together through van der Waals' forces and hydrogen bonding [4]. At the edge of the platelets, bonds are broken and there will be oxygen atoms with incomplete valence that can react with protons, forming hydroxyls. Around 10% of kaolin particle surface area is due to these edges [1].

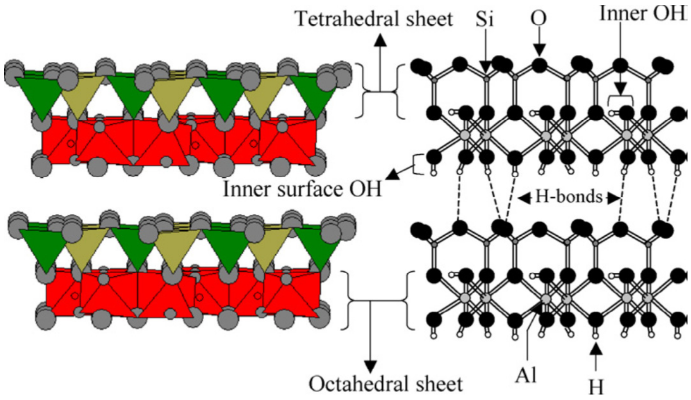

**Figure 3.1** Kaolin structure showing the stacking of two adjacent platelets by hydrogen bonding. Each platelet is composed of one tetrahedrally (Si) and one octahedrally coordinated (Al) layers of atoms covalently bonded by shared oxygens. (From [5])

The surface of kaolin particles is charged. This charge is due to the presence of hydroxyl groups at the edges or at the gibbsite-layer that can be protonated/deprotonated. The hydroxyls from the gibbsite layer are usually less reactive than the hydroxyls at the edges of the kaolin platelets [6]. The charge on kaolin surface also arises from the isomorphic replacement of $Si^{4+}$ with $Al^{3+}$. The protonation/deprotonation of the hydroxyl groups is pH dependent (further explained below), whereas the charge arising from isomorphic replacement is not (permanent charge).

A negative charge arises from the isomorphic replacement of $Si^{4+}$ by $Al^{3+}$. It is then counterbalanced by the presence of $Na^+$, $K^+$ or even $Ca^{2+}$, commonly designated as exchangeable cations. The cation exchange capacity (CEC) is 1-10 mequiv/100 g of kaolin and gives an approximate measure of the amount of silicon atoms that have undergone isomorphic substitution [4].

The hydroxyl groups at the edges of the kaolin platelets behave differently whether they are bonded to aluminum or silicon atoms. Aluminol groups (AlOH) are amphoteric and silanol groups (SiOH) are usually acidic [6]. Aluminol groups present a positive charge due to protonation in aqueous media with pH lower than 8.7 (Equation 3.1) and a negative charge at higher pH (Equation 3.2). Silanol groups have a positive charge at pH lower than pH 2 (Equation 3.3) and a negative charge at higher pH (Equation 3.4 ).

$-AlOH + H^+ \rightarrow -AlOH_2^+$  $pH < 8.7$ (Equation 3.1)

$-AlOH \rightarrow -AlO^- + H^+$  $pH > 9$ (Equation 3.2)

$-SiOH + H^+ \rightarrow -SiOH_2^+$  $pH < 2$ (Equation 3.3)

$-SiOH \rightarrow -SiO^- + H^+$  $pH > 2$ (Equation 3.4)

As a consequence of the protonation/deprotonation reactions, at certain pH values there could be positively charged groups at the edges of the kaolin platelets and a (permanent) negative charge on the faces of the platelets due to isomorphic replacements. For this reason, kaolin particles are said to have dual charge on the surface. Nonetheless, kaolin sols usually have a negative zeta-potential. Published measurements of the absolute value of the zeta-potential show that it is decreasing with decreasing pH, reaching zero at pH 2-4 (isoelectric point) [1]. The presence of dual charge on kaolin platelets may also result in the production of aggregates or flocs where the positive edge of a platelet interacts electrostatically with the negative face of another platelet [7]. Due to the presence of both positive and negative charges at the surface of the kaolin, calculations of zeta-potential by application of the Helmholtz-Smoluchowski theory (section 1.3.) have been questioned by some authors.

The surface charge, and hence the zeta-potential, is also influenced by the presence of metal cations, and their valence state and concentration in the solution are of the utmost importance in determining the properties of the kaolin. Hydroxyl groups at the edges may react with metal cations in solution [7]:

$\text{-S-OH} + M^{n+} \rightarrow \text{-S-OM}^{(n-1)} + H^+$ (Equation 3.5)

$\text{-S-OH} + M^{n+} + L^- \rightarrow \text{-S-L-M}^{n+} + OH^-$ (Equation 3.6)

If the interaction of the metal cation with the kaolin surface results in the displacement of the protons (Equation 3.5) then the pH of the solution decreases. On the other hand, if ligand exchange occurs (Equation 3.6), the pH of the solution is expected to increase as a result of the displacement of $OH^-$ groups from the kaolin surface to the solution. Metal cations can also interact with the kaolin surface by exchange with the cations that counterbalance the permanent negative charge mentioned previously. The effect of metal cation adsorption on electrodewatering will be further discussed in Chapter 6.

The zeta-potential of kaolin particles has been measured in the presence of different metal cations in a range of concentrations and pH. In general, for the same metal valency, the absolute value of the zeta potential decreases with increasing polarizability [4]. A polarizability increase of the metal cation is also accompanied by an increase in clay-cation interaction [7]. A signal reversal of the zeta-potential can occur with high valence metal cations because of the interaction illustrated by Equations 3.5 and 3.6, which lead to a change of the global surface charge. Increase of the metal cations concentration leads to a decrease of zeta-potential but it is not always the case [8]. The influence of polarizability, metal valence, and concentration on zeta-potential (and electrodewatering) will be fully discussed in the following sections.

## 3.2 Results

### 3.2.1 Physical-chemical characterization of kaolin

Two batches of kaolin – batch A and batch B – were used in the electrodewatering experiments. The structure of the as-received material was characterized by XRD and the X-Ray diffractograms do not show any difference between the two batches (Figure 3.1). Further characterization was performed in solution. Both samples were suspended in water at 50 g/L and stirred overnight. Measurements of the pH and of the sodium present in solution were performed. The kaolin suspensions were inspected visually for stability. The results are shown in Table 3.1.

**Table 3.1** pH values and sodium content for 50 g/L suspensions of kaolin stirred overnight. Values are average ± standard deviation for two independent measurements of the same solution. Stability of suspension was visually evaluated.

| Kaolin | pH | Na content (mg) | Macroscopic properties |
|---|---|---|---|
| Batch A | 9.71±0.06 | 14.72±0.07 | Stable suspension |
| Batch B | 6.6±0.1 | 1.130±0.005 | Kaolin separates from solution |

The pH of a 50 g/L suspension of kaolin is more basic for batch A than it is for batch B and the suspension of batch A is about 13 times more concentrated in sodium than batch B. Furthermore, kaolin batch B suspension settles rapidly (less than 10 minutes), whereas kaolin batch A suspension is stable for about 1 day.

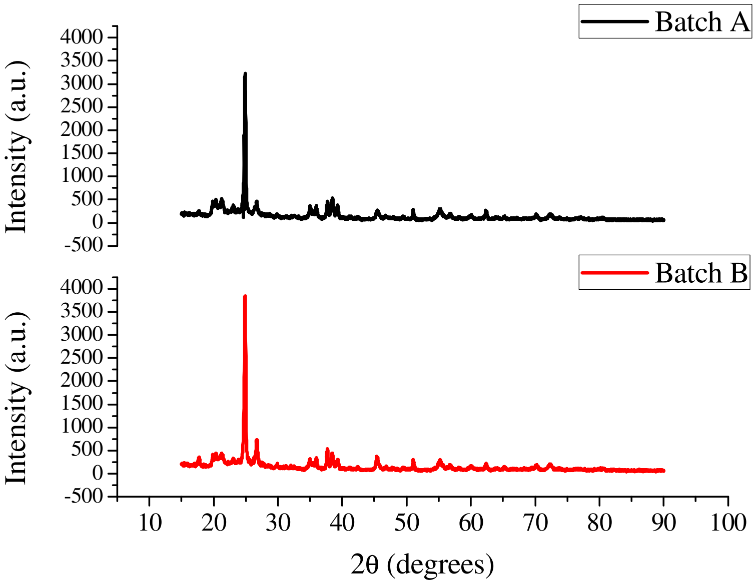

**Figure 3.2** X-Ray diffractograms for batch A and batch B kaolin.

Electrodewatering experiments were performed with both batches of kaolin. Later on kaolin batch B will be preferred.

### 3.2.2 Electrodewatering of kaolin

#### *3.2.2.1 Recovered water, current density and temperature profile*

Two different batches of kaolin (batch A and batch B) were used in the electrodewatering tests. In both cases, deionized water was mixed with solid kaolin to make sludge with 62 wt% of solids, also referred to as 62% dryness. Both batches of kaolin were used as received from the supplier. Two-hour tests were performed at 70 kPa. The voltage was turned on (50 V) after the first hour. The mass of water recovered by filtration as a function of time is shown in Figure 3.3.

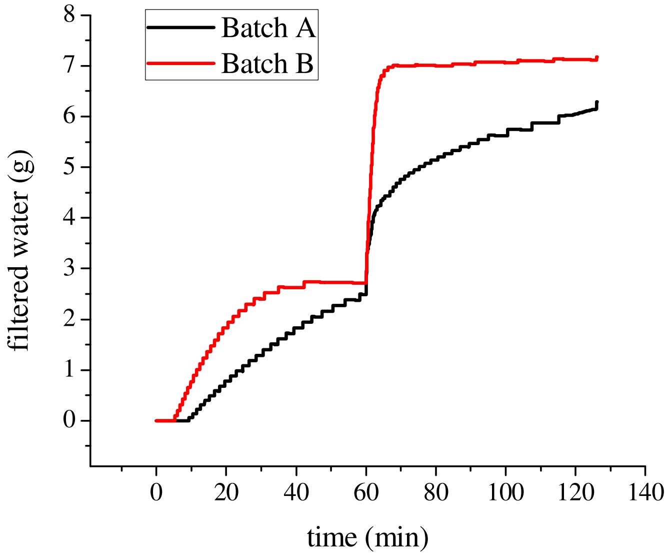

**Figure 3.3** Electrodewatering profile of kaolin – batch A and batch B. The initial dryness is 62 wt% and the applied pressure is 70 kPa. The voltage (50 V) was turned on after one hour of conditioning. Deionized water was used as electrolyte.

For both batch A and batch B, there is a gradual increase of the amount of recovered water in the first 60 minutes (designated step 1 or pressure induced dewatering). When the voltage is turned on (designated step 2 or voltage induced dewatering), there is a rapid increase in dewatering, as it is shown by the steep slope of the mass *vs.* time curve of Figure 3.3. The slope is steeper for batch B than batch A. After 10 minutes, the electrodewatering process is practically finished for batch B, whereas for batch A, the amount of recovered water increases slowly and continuously during the 60 minutes of the step 2 dewatering. The total amount of water removed is higher for batch B (7.17 g) than for batch A (6.29 g), which corresponds to 20.4 and 17.6% increase in dryness, respectively.

The evolution of the current density during the electrodewatering processes of kaolin batch A and B are shown in Figures 3.4 and 3.5, respectively.

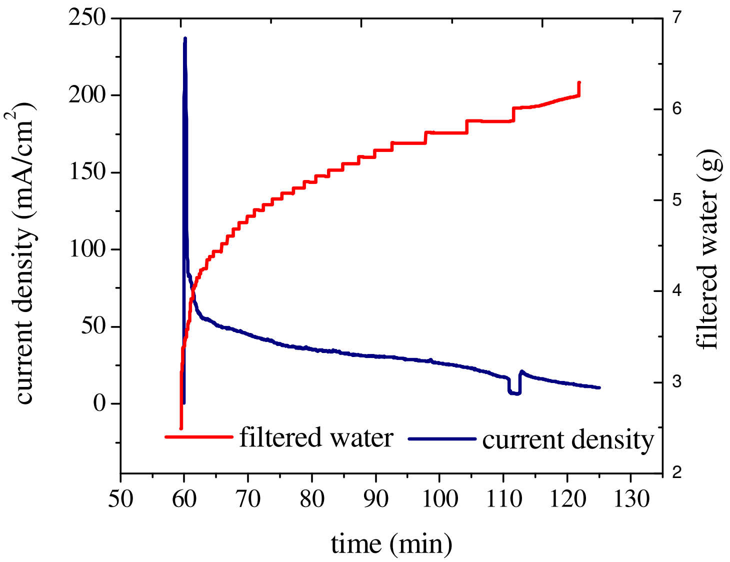

**Figure 3.4** Evolution of the current density with time for electrodewatering of sludge composed of kaolin batch A and deionized water at 62% dryness. The mass of recovered water is represented for reference. The pressure (70 kPa) was applied during all the experiment.

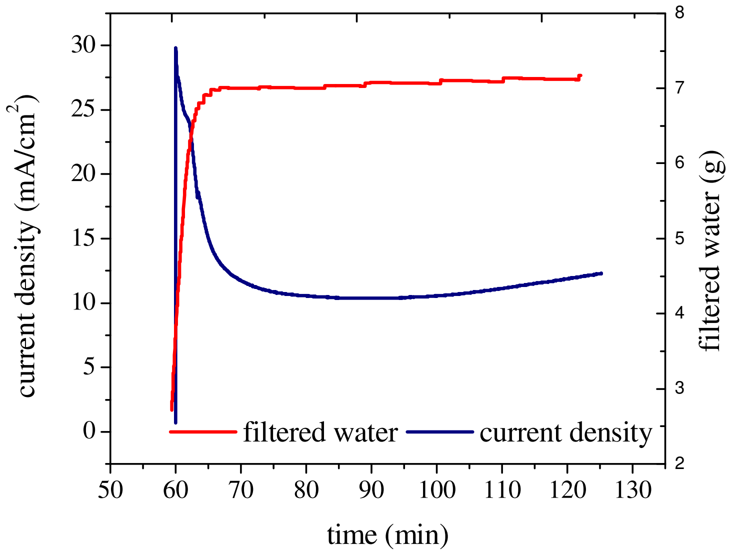

**Figure 3.5** Evolution of the current density with time for electrodewatering of sludge composed of kaolin batch B and deionized water at 62% dryness. The mass of recovered water is represented for reference. The pressure (70 kPa) was applied during all the experiment.

Batch A and batch B have similar current density profile. Indeed, they both present an initial sharp peak followed by a rapid decay. After the initial peak, the current density stabilizes and remains practically constant, batch B, or decreases slightly in the case of batch A. A sudden depression of the current density (around 115 minutes) is observed for batch A, which could be the result of the formation of a gas layer around the anode that increases the resistance of the sludge cake. Further mechanical compression of the sludge re-establishes the electric contact and the current density goes up again.

The rapid increase in dewatering observed for batch B in the first 10 minutes coincides with the period for which the current density is higher. The maximum value observed for current density is about 8 times higher for batch A than for batch B (237 and 30 mA/cm$^2$, respectively). This can be the result of the higher sodium content of batch A (Table 3.1), which is about 13 times more concentrated in sodium atom than batch B. As a consequence of higher current density combined with lower dewatering, the removal of water from kaolin batch A requires more energy than batch B (2.8 *vs.* 0.9 kWh/kg of extracted water, respectively). For these calculations and for all the other energy calculations throughout chapter 3, only the water extracted by the combined action of pressure and voltage was considered (second step of the electrodewatering experiment).

The temperature of the sludge (Figure 3.6) rises constantly upon application of an electric field as a consequence of ohmic heating effect. The maximum temperature was 50.3$^{o}$C for batch B and a similar phenomenon was observed for batch A.

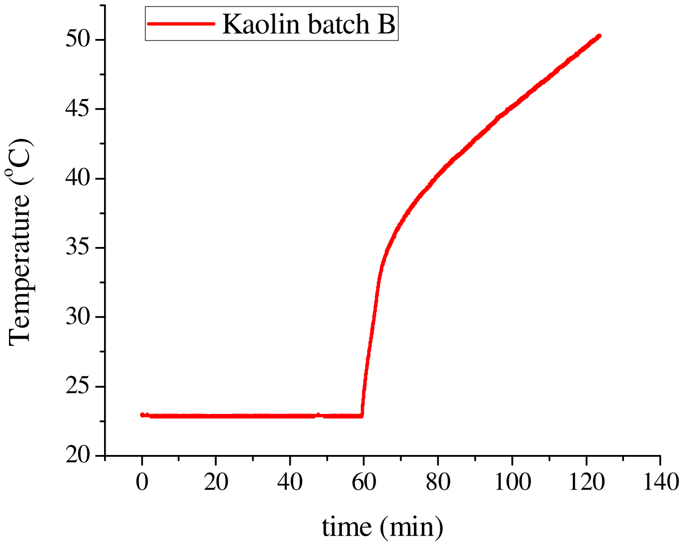

**Figure 3.6** Evolution of the sludge temperature with time during electrodewatering of kaolin batch B at 62% initial dryness. The pressure (70 kPa) was applied during all the experiment.

#### *3.2.2.2 Reproducibility experiments*

Although there are differences in the electrodewatering of kaolin according to its source, it is of importance to know if different tests under the same experimental conditions are reproducible within each batch. A set of experiments was performed with kaolin batch A (six tests) and kaolin batch B (three tests) with deionized water at 62% initial dryness. The pressure (70 kPa) was applied during all the experiments. The results are summarized in Table 3.2.

**Table 3.2** Set of experiments performed with kaolin batch A and kaolin batch B with deionized water at 62% initial dryness; results shown are average ± standard deviation of six (batch A) and three (batch B) independent experiments.

| Parameter | Batch A | Batch B |
|---|---|---|
| Total filtered water (g) | 6.1±0.3 | 7.1±0.2 |
| Final wt% solid | 72.7±0.8 | 74.7±0.5 |
| Increase in dryness (%) | 17±1 | 20.4±0.8 |
| Step 1 filtrate (g) | 2.57±0.08 | 2.6±0.1 |
| Step 2 filtrate (g) | 3.6±0.4 | 4.5±0.1 |
| 10-minute filtrate after voltage is turned on (g) | 2.1±0.2 | 4.3±0.1 |
| Maximum current density (mA/cm$^2$) | 225±37 | 29±2 |
| 60-minute energy consumption (kWh/kg) | 3.0±0.2 | 0.95±0.04 |
| 10-minute energy consumption (kWh/kg) | 1.5±0.3 | 0.29±0.01 |

The variability observed within the same batch of kaolin is not large and accounts for less than 5% of the total filtered water. Kaolin batch B dewaters on average 20% more than batch A, using a bit less than three times the energy required for batch A. The amount of water extracted in the pressure induced step (step 1) is the same for both batches A and B, within the experimental error. In the second step, the dewatering is more efficient for batch B, where more water is extracted from the sludge. Electrodewatering of batch B is also faster and in fact the process is practically complete 10 minutes after the voltage is turned on. At this point, about 96% of the total water extracted in step 2 has already been removed from the sludge, using less than one third of total energy consumed. Further studies on the electrodewatering of kaolin were performed with batch B because this batch was available in higher quantities.

### 3.2.2.3 *Effect of voltage*

The effect of voltage on electrodewatering was analyzed by performing a series of experiments at different voltages with freshly prepared sludge composed of kaolin batch B and deionized water at 62% dryness. Pressure was held constant at 78 kPa, during two hours, and the voltage was turned on after one hour of conditioning. The results are summarized in Figure 3.7 and Table 3.3.

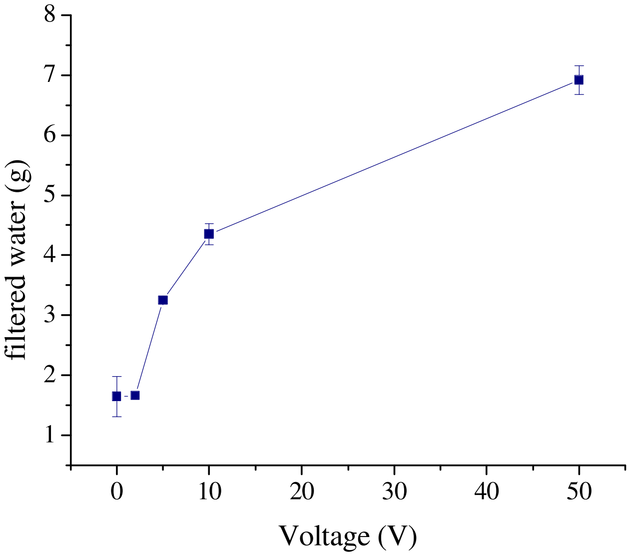

**Figure 3.7** Effect of the voltage on electrodewatering of kaolin batch B with deionized water sludge at 62% initial dryness. The pressure was held constant to 78 kPa during all the experiment and the voltage was not applied before the end of the first hour. In each case, a new sample was used.

**Table 3.3** Summary of results for electrodewatering of kaolin batch B with deionized water at 62% initial dryness. The pressure was held constant at 78 kPa during all the measurements. The voltage was not applied before the end of the first hour of measurement. Results shown are average ± standard deviation for the number of independent experiments referred to in the second column.

| **Voltage (V)** | **Total # of experiments** | **Final wt% solid** | **Increase in dryness (%)** | **Recovered water (g)** | **Maximum temperature (°C)** | **Total energy (kWh/kg)** |
|---|---|---|---|---|---|---|
| 0 | 11 | 64.5±0.5 | 4.0±0.8 | 1.7 ± 0.3 | 23.2±0.9** | --- |
| 2 | 1 | 64.5 | 4 | 1.7 | 24.1 | n.d.*** |
| 5 | 3 | 67.1±0.1 | 8.1±0.2 | 3.25 ± 0.06 | 23.2±0.1* | $(3.9\pm0.5)\times10^{-2}$ |
| 10 | 3 | 69.0±0.3 | 11.2±0.5 | 4.4 ± 0.2 | 24±1 | $(6.0\pm0.2)\times10^{-2}$ |
| 50 | 4 | 73.9±0.5 | 19.1±0.8 | 6.9 ± 0.2 | 56.7±0.6* | 1.1±0.1* |

*data for 2 experiments only; **data for 8 experiments only; ***no water extracted in electrofiltration step (step 2)

As shown in Fig. 3.7 and Table 3.3, the amount of filtered water increases with increasing voltage. The same result has already been obtained in the literature [9 , 10]. Electrodewatering at 2 V do not yield to any increase in the amount of recovered water when compared to 0 V (pressure only). Thus, there is a minimum onset voltage required to force the flow of interstitial water. This minimum voltage for the studied sludge should be between 2 and 5 volts.

The increase in voltage and consequent increase in final dryness is accompanied by an increase in the energy spent to extract the water molecules. In all experiments, except at 50 V, the temperature of the sludge was constant at ~23°C during all the duration of the experiment. The temperature of the sludge increases to 57 °C when 50 V was applied.

The same type of experiment was performed on kaolin although the voltage was increased step by step from 0 to 50 V. As shown in Figure 3.8 (a) and in Table 3.4, water is extracted from the sludge every time the voltage is increased. For comparison, the results of an experiment where 50 V was directly applied to the sludge are also presented in Figure 3.8 (b).

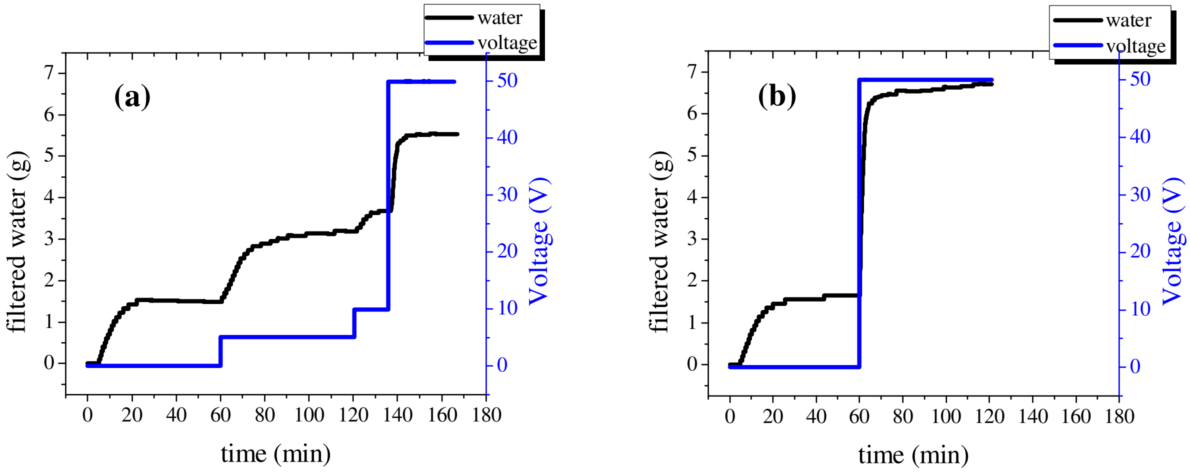

**Figure 3.8** (a) Effect of successive voltage increase on electrodewatering of kaolin batch B with NaCl $10^{-3}$ M as the electrolyte (62% initial dryness). The pressure was held constant at 78 kPa during all the experiment. (b) Electrodewatering at constant voltage of a sludge having the same characteristics as in (a). In both cases, conditioning of the sludge was performed for one hour prior to the application of voltage.

**Table 3.4** Amount of recovered water as a function of successive increase of voltage for electrodewatering of kaolin batch B with NaCl $10^{-3}$ M as the electrolyte (62% initial dryness). The pressure was held constant at 78 kPa during all the experiment.

| Voltage (V) | Duration of impulse (min) | Filtered water (g) | Accumulated water (g) |
|---|---|---|---|
| 0 | 60 | 1.5 | 1.5 |
| 5 | 60 | 1.7 | 3.2 |
| 10 | 15 | 0.5 | 3.7 |
| 50 | 35 | 1.8 | 5.5 |

As seen in Figure 3.8, there is a 25 % increase of the amount of water recovered from the sludge when the higher voltage (50 V) is applied directly compared to a situation where it is applied step wisely (5 V, followed by 10 V and then 50 V). For this reason, in all the subsequent experiments, the application of constant voltage (50 V) was preferred.

### 3.2.3 Effect of metal cations in electrodewatering

#### *3.2.3.1 Monovalent cations*

Monovalent cations of alkali metals were found to have an influence on electrodewatering, the extent of which depends both on the nature and concentration of the cations. The electrodewatering tests were performed on kaolin sludge prepared by mixing solid kaolin with solutions of known concentrations of the chloride salt of the cation of interest. The extracted water is shown in Figure 3.9 as a function of the concentration of the added salt.

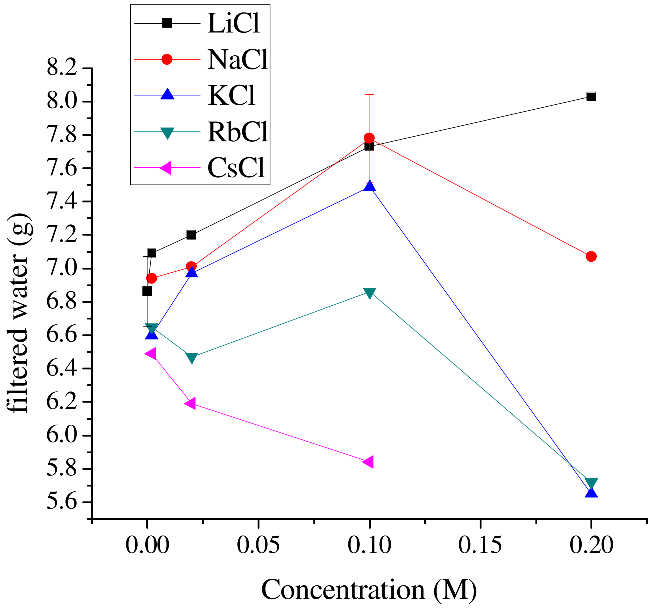

**Figure 3.9** Effect of the addition of chloride salts of alkali metal cations on the total filtered water recovered from electrodewatering of kaolin sludge with 62% initial dryness. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa.

Inspection of Figure 3.9 shows that the amount of filtered water removed from the sludge by the combined use of pressure and electric potential difference increases from CsCl, RbCl, KCl, NaCl to LiCl at all concentrations. In general, for each salt there is an increase in dewatering up to 0.1M and then dewatering decreases when the concentration of salt is increased further. In the case of CsCl, an increase in the salt concentration results in a detrimental effect on the amount of extracted water.

When kaolin sludge is prepared with deionized water, on average (6.9±0.2) g of water are recovered. This corresponds to an increase in dryness of (18.9±0.7)% (previous results are the average ± standard deviation of 13 independent experiments). The increase in dryness for NaCl 0.1 M, concentration at which this salt has its best performance, is (22.0±0.9)% (for 8 independent experiments), while it is 22.9% for LiCl 0.2 M. At the other end of the spectrum, CsCl 0.1 M presents an increase in dewatering of 16.7%, lower than for pure deionized water. Data for all experiments is presented in tables A1.1 to A1.5 in the appendix.

Increasing the concentration of added salts results in an increase of total energy spent and increase in temperature, regardless of the effect of salt on the dewatering properties. When water is used as the electrolyte, the total energy spent is 0.9±0.1 kWh per kg of water extracted and the maximum temperature is (52±5)$^{o}$C. In comparison, for LiCl 0.2 M, the maximum temperature achieved is 110$^{o}$C, and total energy spent is 2.1 kWh/kg of water removed. The complete set of data for LiCl is shown in Figure 3.10.

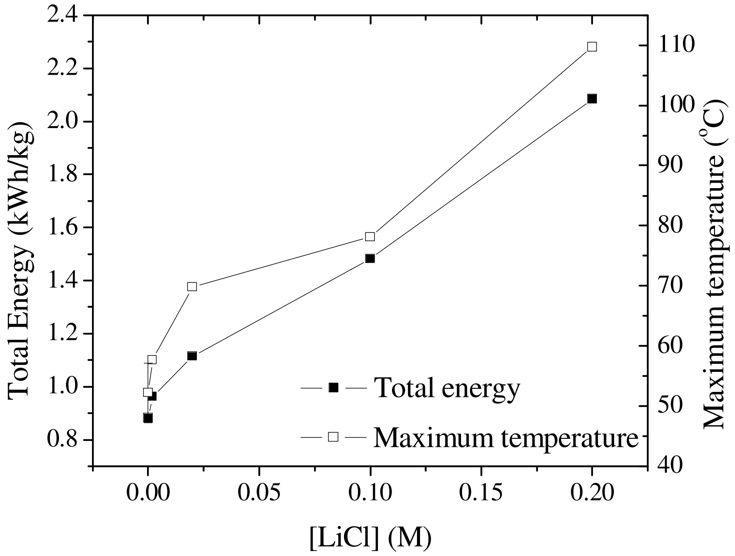

**Figure 3.10** Variation of the total energy spent and maximum temperature achieved in electrodewatering of kaolin sludge in the presence of LiCl as a function of the salt concentration. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa.

All alkali metals show a similar behavior in terms of the variation of energy consumed per kilogram of extracted water and the variation of maximum temperature with concentration. For example, the variation of the maximum temperature achieved and the energy spent as a function of the concentration of CsCl is shown in Figure 3.11. The trend observed in Figure 3.11 is similar to that observed for LiCl in Figure 3.10, even if the addition of CsCl does not result in any improvement of the electrodewatering process compared to pure water. Therefore, aiming at an increase of the current density by increasing the ionic strength of the electrolyte may not result in any improvement of electrodewatering. This is further illustrated in Figure 3.12, where it is seen that the current density for a sludge prepared with CsCl 0.1 M is always higher than for a sludge prepared with deionized water. Nevertheless, the use of CsCl 0.1 M as electrolyte results in a 15% reduction in the amount of filtered water compared to a sludge prepared with deionized water.

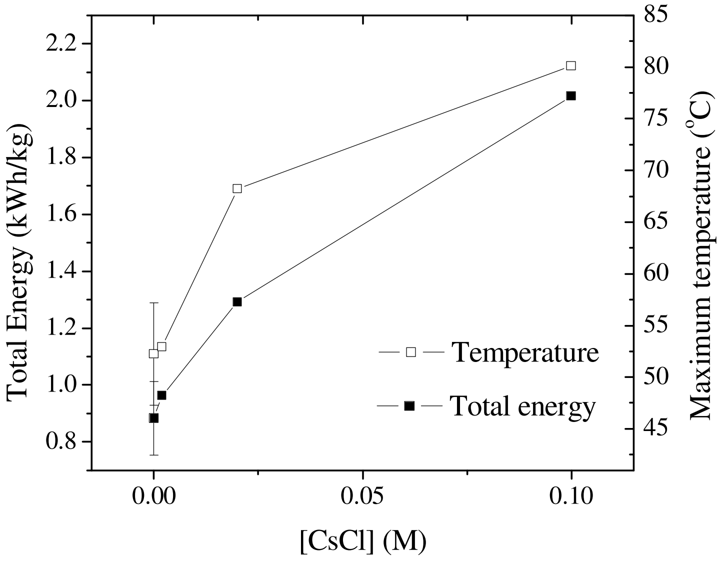

**Figure 3.11** Variation of the total energy spent and maximum temperature achieved in electrodewatering of kaolin sludge in the presence of CsCl as a function of the salt concentration. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa.

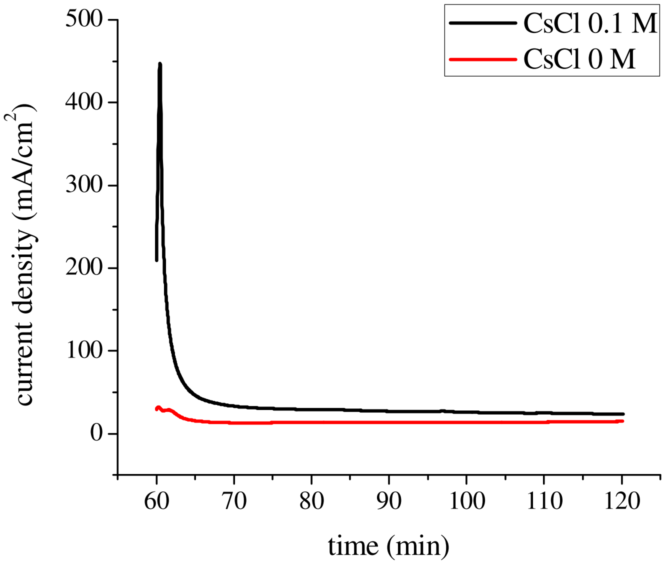

**Figure 3.12** Evolution of the current density with time for electrodewatering of a sludge composed of kaolin and CsCl at 62% dryness. The pressure (70 kPa) was applied during all the experiment.

### *3.2.3.2 Mono-, di- and trivalent cations*

#### *3.2.3.2.1 <u>Electrodewatering experiments</u>*

Sodium, calcium and cerium chloride were used as electrolytes at different concentrations in the electrodewatering of kaolin. Each salt influences the dewatering differently depending on their concentrations and charge. The recovered water is shown as a function of the concentration of added salt in Figure 3.13.

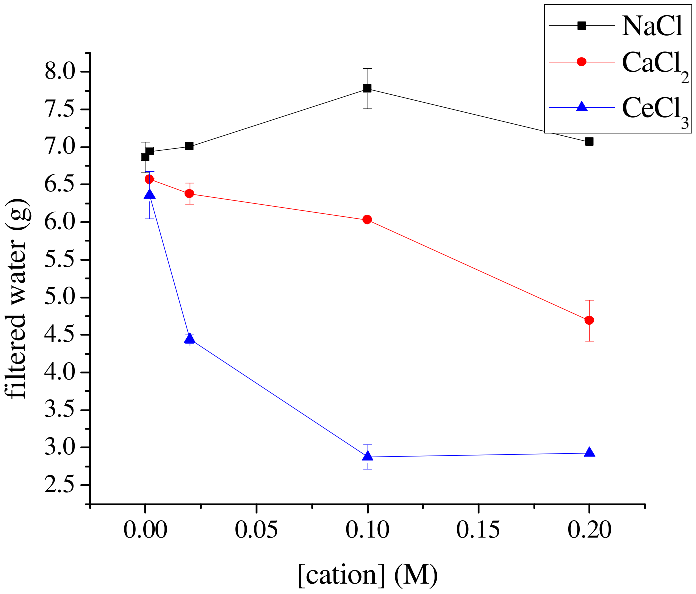

**Figure 3.13** Effect of the addition of sodium, calcium and cerium on the total filtered water recovered from electrodewatering of kaolin sludge with 62% initial dryness. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa.

The behavior of NaCl was described previously and is characterized by an increase in dewatering as the concentration is increased from 0.0 to 0.1 M, after which the dewatering decreases. In the case of calcium and cerium chloride, there is a continuous decrease of the amount of filtered water as the salt concentration is increased. This decrease is more pronounced for cerium chloride than it is for calcium chloride. The effect observed must be due to the different charge on each cation, and high valence cations are detrimental for electrodewatering of kaolin. Thus, the performance in electrodewatering follows the trend: $Na^+ > Ca^{2+} > Ce^{3+}$.

The maximum temperature and total energy spent are represented in Figures 3.14 and 3.15, respectively, as a function of the concentration for each salt. More details are provided in table A1.6 in the appendix. In general, the maximum temperature and the total energy spent increase with a concentration increase of the added salt.

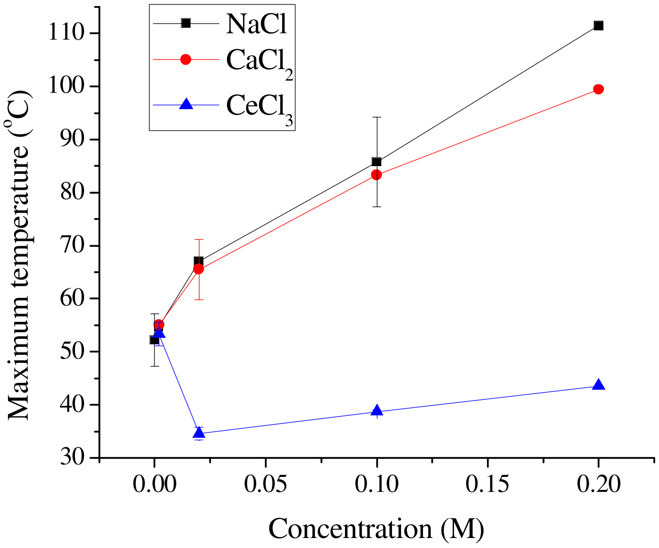

**Figure 3.14** Maximum temperature in electrodewatering of kaolin sludge 62% initial dryness as a function of the salt concentration. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa.

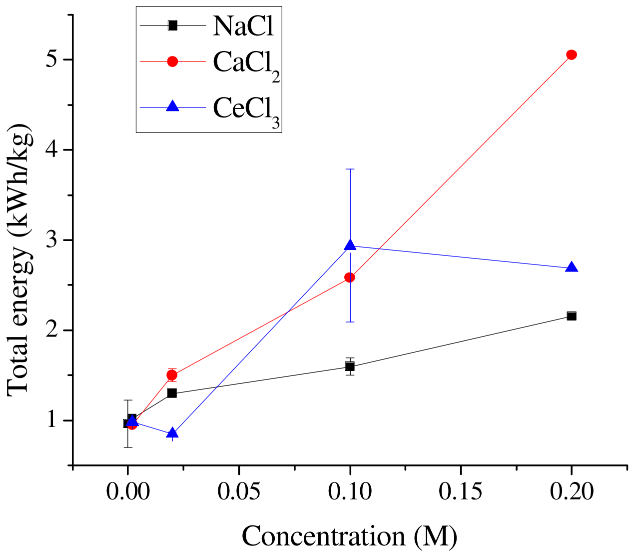

**Figure 3.15** Total energy spent in electrodewatering of kaolin sludge 62% initial dryness as a function of the salt concentration. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa.

#### *3.2.3.2.2 Zeta-potential measurements*

To further investigate the different behavior of each salt, the zeta-potential of kaolin 0.05 g/L suspensions was measured at 0.002 M of added electrolyte. Results are summarized in Table 3.5.

**Table 3.5** Zeta-potential measurements for kaolin 0.05g/L suspension in electrolyte 0.002 M.

| **Salt (0.002M)** | **Zeta-potential (mV)** |
|---|---|
| NaCl | -30±8 |
| $CaCl_2$ | -15±2 |
| $CeCl_3$ | 19±3 |

The zeta potential is more negative for NaCl suspensions than for $CaCl_2$, and it is positive for $CeCl_3$. In general, an increase in the zeta-potential value results in an increase of the electroosmotic flow (equations 1.10 and 1.12) measured at the cathode. Therefore, it is expected that the electroosmotic flow and as consequence the dewatering of the sludge will be higher in the presence of NaCl than in the presence of $CaCl_2$ or $CeCl_3$. The zeta potential values correlate well with the amount of water recovered at the cathode, which vary along the series $Na^+ > Ca^{2+} > Ce^{3+}$.

#### *3.2.3.3 Other +2 and +3 cations*

In order to verify that the decrease in dewatering observed with calcium and cerium chloride was not specific to these elements but was a consequent of their charge, a few other plus two and plus three cations were tested. As shown in Figures 3.16 and 3.17, magnesium sulfate, copper sulfate, calcium nitrate and aluminum sulfate all show the same behavior characterized by a decrease of the amount of filtered water as the salt concentration in the electrolyte is increased from 0.0 to 0.2 M. This behavior is similar to the one shown by $CaCl_2$ and $CeCl_3$. Therefore, the valence state of the added metal cation is indeed an important factor affecting (adversely) the electrodewatering of kaolin.

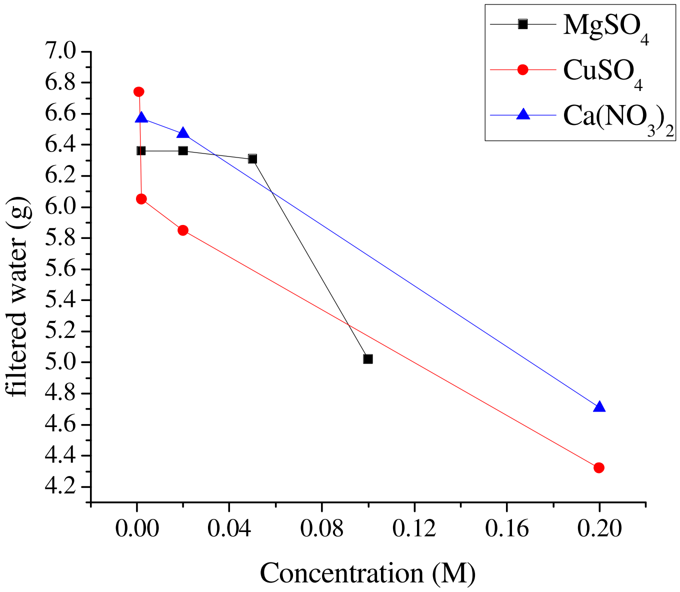

**Figure 3.16** Electrodewatering profile as a function of the salt concentration for kaolin sludge with $MgSO_4$, $CuSO_4$ and $Ca(NO_3)_2$ with initial 62% dryness. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa.

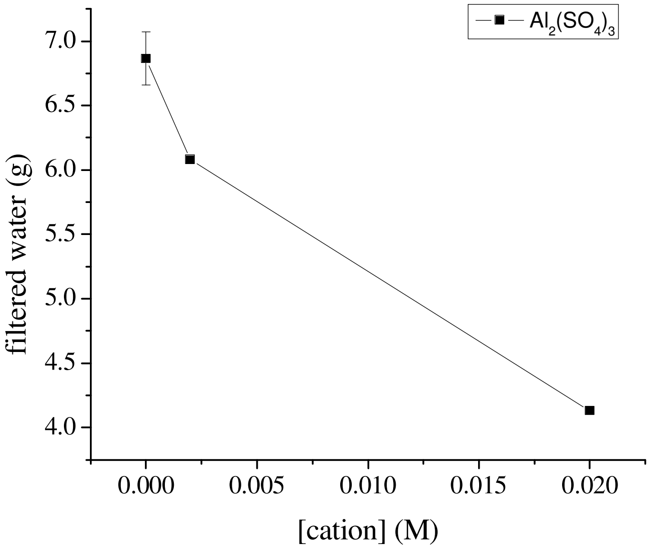

**Figure 3.17** Electrodewatering profile as a function of the salt concentration for kaolin sludge with $Al_2(SO_4)_3$ 62% initial dryness. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa.

In general, the maximum temperature and the total energy spent increase with an increase in the concentration of the added salt. This is the case for $MgSO_4$ and $Ca(NO_3)_2$ (data are not available for $CuSO_4$) and the profiles of the maximum temperature and total energy spent *vs.* the salt concentration do not differ significantly from that of LiCl and CsCl shown in Figures 3.10 and 3.11, respectively. In contrast, the variation of the maximum temperature and total energy spent decreases as the $Al_2(SO_4)_3$ salt concentration is increased (see Figure 3.18). Again, an increase in current density (as a result of increasing the ionic strength) is not critical to increase the amount of water extracted from the sludge. Instead, the nature of the added cation is the determining factor.

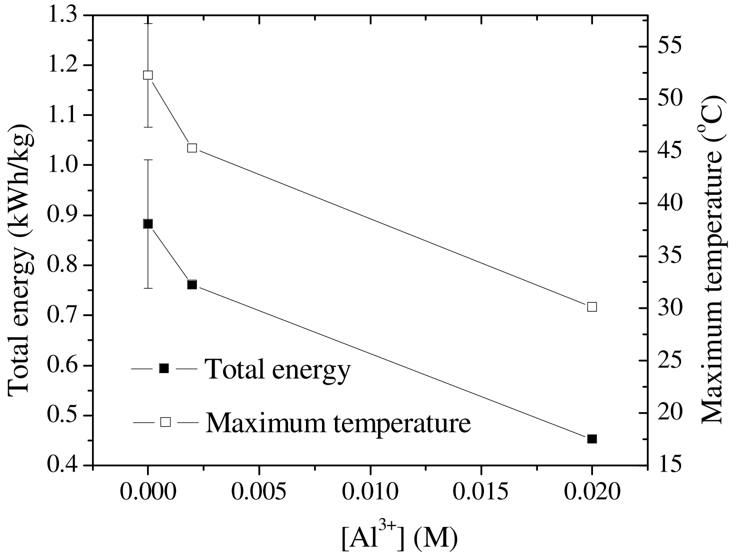

**Figure 3.18** Variation of total energy spent and maximum temperature achieved in electrodewatering of kaolin sludge in the presence of $Al_2(SO_4)_3$ as a function of the salt concentration. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa.

### 3.2.4 Effect of anions and pH in electrodewatering

Different sodium salts were tested at 0.1 M, concentration at which NaCl has the best electrodewatering performance, to verify any differences in behavior due to the different anions. Sodium chlorate, sulfate, nitrate, hydrogen carbonate, and hydroxide were tested. The amount of filtered water recovered at the end of each experiment is represented in Figure 3.19, as well as the initial pH of the starting electrolyte. Table A1.8 contains further details.

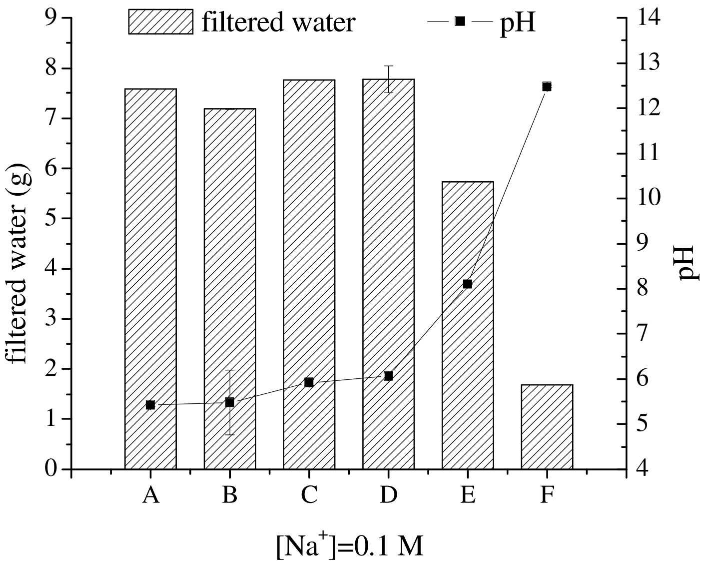

**Figure 3.19** Total filtered water recovered from electrodewatering of kaolin sludge at 62% initial dryness, in the presence of different sodium salts at 0.1 M. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa. A= $NaClO_3$, B=$Na_2SO_4$, C=$NaNO_3$, D=NaCl, E=$NaHCO_3$, F=NaOH. The initial pH of the electrolyte solution is also shown.

The initial pH of 0.1 M solutions of $NaClO_3$, $Na_2SO_4$, $NaNO_3$ and NaCl are similar (5.43-6.07). In contrast, $NaHCO_3$ and NaOH 0.1 M solutions have more basic pH, 8.11 and 12.48, respectively. Within the experimental error of the determination (±0.3 g), the amount of filtered water recovered in the experiments with $NaClO_3$, $NaNO_3$ and NaCl is approximately the same and equal to 7.7 g. In the case of $Na_2SO_4$, slightly less water is removed, (7.185±0.007) g. When the kaolin sludge is prepared with one of the two more basic solutions ($NaHCO_3$ and NaOH 0.1 M), the extent of the electrodewatering is reduced. In the case of NaOH, for example, only 1.7 g of water is recovered, which represents only 22% of the water obtained when NaCl 0.1 M is used. Moreover, NaOH 0.1 M liquefied the sludge. Apparently very high pH is detrimental for electrodewatering.

To make sure the differences observed previously are due to the different anions and not to the different pH's, only the solutions of chlorate, sulfate, nitrate and chloride sodium salt can be compared directly. The total filtered water is then, within experimental error, approximately the same for the chloride, nitrate and chlorate and slightly less for the sulfate: filtered water $Cl^-$ , $NO_3^-$, $ClO_3^-$ > $SO_4^{2-}$. On this limited set of anions, we can conclude that 1:1 electrolytes are better for electrodewatering than 1:2 electrolytes and that both monovalent cations and anions should be preferred for electrodewatering. There are no major differences among these anions in terms of energy consumption and maximum temperature.

NaCl and $Na_2SO_4$ are further compared in Figure 3.20 (full details in Table A1.9).

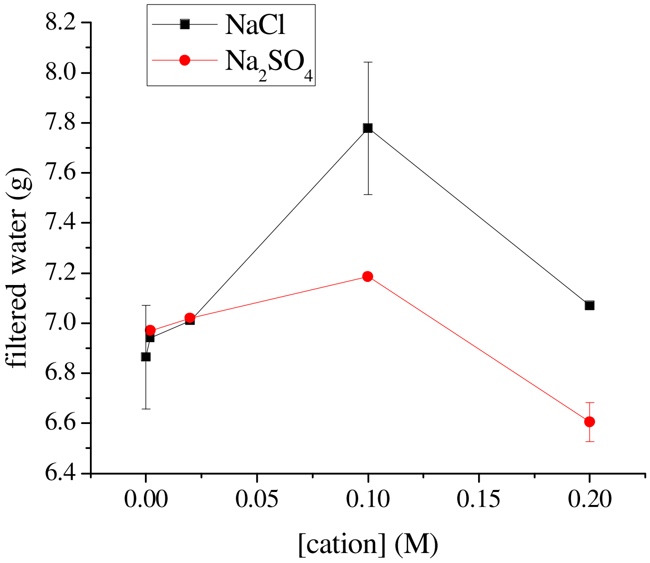

**Figure 3.20** Electrodewatering profile as a function of the salt concentration for kaolin sludge with initial 62% dryness. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa.

As seen in Figure 3.20, sodium chloride and sodium sulfate show the same electrodewatering profile, this is, there is an increase in filtered water up to 0.1 M of $Na^+$, followed by a decrease. At 0.1 M $Na^+$ there is 8.2% more filtered water with NaCl than with $Na_2SO_4$. No major differences are observed in terms of energy consumption or maximum temperature.

The pH dependency of electrodewatering of kaolin was further investigated by using HCl at different concentrations (0.002, 0.02 and 0.1 M) and different pH's. The amount of filtered water versus the HCl concentration is shown in Figure 3.21. Table A1.8 contains further details.

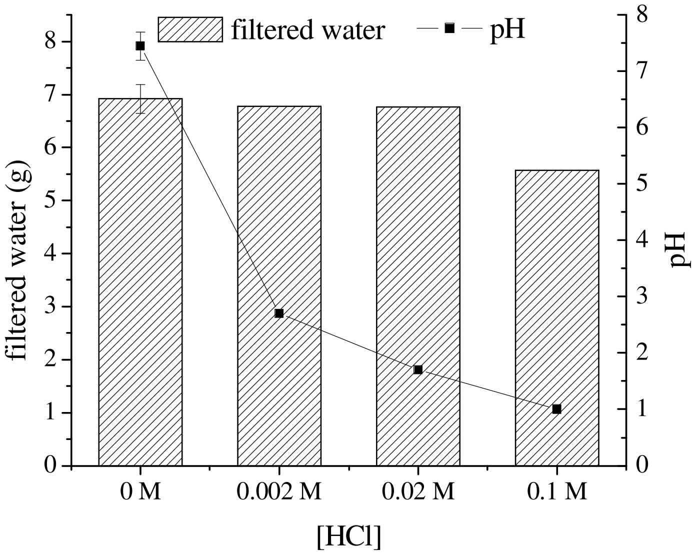

**Figure 3.21** Total filtered water recovered from electrodewatering of kaolin sludge at 62% initial dryness in the presence of different concentrations of HCl. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa. The initial pH of the electrolyte is shown.

Electrodewatering is similar in the range 0-0.02 M of HCl and is independent of pH in the range 1.5 to 7. However, when the pH is too low (pH 1), there is a negative effect on the amount of water removed. To maximize electrodewatering, pH should be between 2 and 7.

### 3.2.5 Water evaporation

The increase in the sludge temperature observed as a consequence of ohmic heating is responsible for the evaporation of water, resulting in dryer sludge cakes. This is demonstrated in Figure 3.21, for the electrodewatering of kaolin in the presence of NaCl.

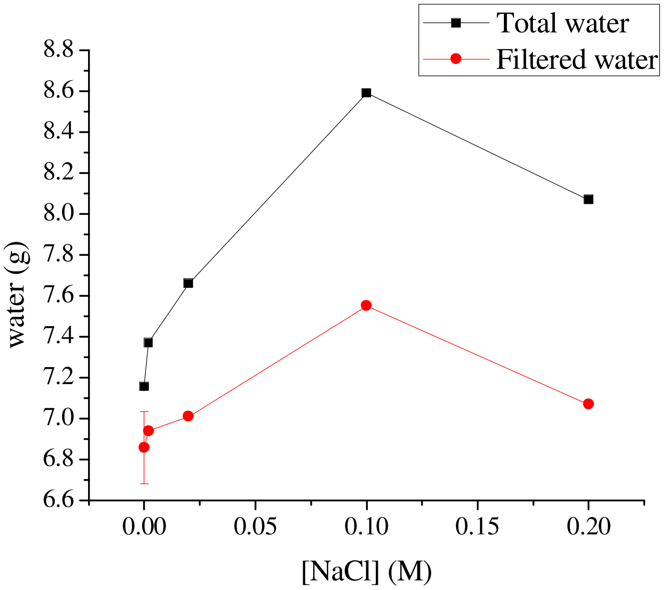

**Figure 3.22** Filtered water and total water loss (filtered plus evaporated) from the sludge in electrodewatering of kaolin in the presence of various concentrations of NaCl. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa. The initial dryness was 62%.

In the absence of NaCl, the evaporated water represents only (4±2)% of the total water loss. In contrast, the percentage of water evaporated increases with increasing NaCl concentration, reaching 11-12% at the highest concentrations used (0.1 and 0.2 M). The relation between the maximum temperature and the total evaporated water is shown in Figure 3.23 (further details in table A1.10).

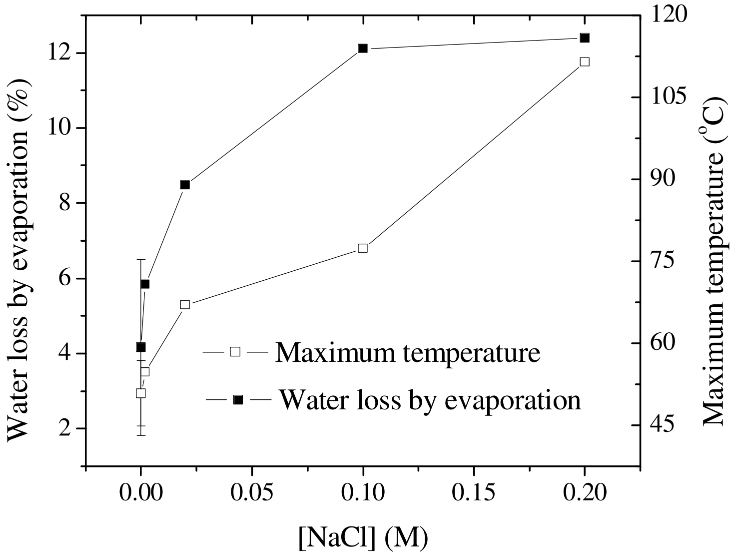

**Figure 3. 23** Variation of the percent of water loss by evaporation and the maximum temperature reached by the cake as a function of the salt concentration. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa. The initial dryness was 62%.

As shown in Fig. 3.23, an increase in the cake maximum temperature results in an increase of evaporated water. Water loss by evaporation is more significant in media with higher ionic strength. In one experiment with $Na_2SO_4$ 1 M plus NaCl 0.1 M, 18% of total water removed was due to evaporation (6.41 g of total water removed, 3.7 kWh/kg energy spent and the temperature reached was 119°C). In comparison, in the presence of NaCl 0.1M, evaporated water represents 12% of total water removed. The percentage of water evaporated decreases further as the ionic strength of the electrolyte is diminished and represents only (4±2)% when deionized water is used.

## 3.3 Discussion

The electrodewatering of kaolin sludge was evaluated according to different parameters, namely, the source of kaolin, the voltage intensity, and the presence of several electrolytes at different concentrations.

Two batches of kaolin were analyzed, one presenting more dewatering (batch B) than the other one (batch A). The main difference between the two batches that could account for the discrepancy in dewatering is the pH: batch A presents higher pH than batch B (see Table 3.1). Several authors have measured the zeta-potential of kaolin suspensions as a function of pH [1, 2, 9]. All reported a decrease of the absolute value of zeta-potential with a decrease of pH. The isoelectric point of kaolin is at pH 2-4. This means that the coefficient of electroosmotic conductivity, which is directly proportional to the zeta-potential (see Equation 1.10) should decrease with a decrease of the pH. A similar behavior is expected for electrodewatering. However, the opposite is observed with batch A and B of kaolin, where the batch with the lower pH (batch B) shows the highest dewatering. This can be understood by the flocculation of kaolin at lower pH, which facilitates the pressure-driven drainage of water. The flocculation also explains why water is more rapidly removed (faster kinetics) from batch B in both steps 1 and 2 of the dewatering process. The flocculation of batch B kaolin was observed with 50 g/L suspensions in deionized water, whereas batch A suspensions are more stable (Table 3.1). Therefore, high pH favors the dispersion of kaolin particles and decreases the amount of water that can be extracted from the sludge. Also, this explains the low dewatering properties of kaolin batch B in the presence of more basic electrolytes, such as $NaHCO_3$, or NaOH 0.1 M (Figure 3.19).

The electrodewatering of the more dispersed kaolin (batch A) requires three times more energy than batch B. Ten minutes after turning on the voltage, batch B has already lost about 96% of the total water lost in step 2 electrodewatering. Moreover, the energy spent over these first 10 minutes is only 30% of total energy consumed in the process. This means that both the nature/composition of the sludge and the operation time are crucial for the energetic performances of the process. As a consequence, the direct comparison of the obtained results with the ones published in the literature is not straightforward since all the experimental conditions are not always mentioned. Differences in electrodewatering and in zeta-potential between different batches of kaolin have already been mentioned in the literature [2, 10].

In the following, only kaolin batch B results will be discussed, since it was the one available in large amount in the laboratory.

The effect of voltage on dewatering was analyzed at 0, 2, 5, 10 and 50 V. An increase in voltage provides sludge cakes with higher solid content. The increase in dryness induced by the increase in voltage is accompanied by an increase in energy consumption (Table 3.3). There is only a certain amount of water that can be removed at each voltage, and most notably, a minimum voltage is required to initiate a significant electroosmotic flow. More than 2 V are required for water to be drained out of the sludge after the initial 60 minute pressure induced dewatering. The existence of a threshold voltage has already been mentioned in the literature [11]. The interstitial water is bond to sludge particles by capillary forces. The stronger the interactions between the water and the sludge particles, the more difficult it is to remove the water, and higher voltages are required. This is why there is a limit amount of water that can be removed at each voltage.

Cations (and anions) influence the electrodewatering differently according to their intrinsic properties and concentration in solution. The effect of alkali metal cations (monovalent cations) was studied in section 3.2.3.1, using the chloride salts of these cations. The effectiveness in electrodewatering was found to be higher for $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. They all differ in electronegativity, ionic radius, hydrated radius and hydrated number. These characteristics are given in Table 3.6.

**Table 3.6** Ionic and hydrated radii, hydration number and electronegativity for alkali metal cations.

| **Cation** | **Ionic radii [12] (pm)** | **Hydrated radii [13] (pm)** | **Hydration number [12]** | **Electronegativity** |
|---|---|---|---|---|
| **$Li^+$** | 60 | 340 | 25.3 | 0.98 |
| **$Na^+$** | 96 | 276 | 16.6 | 0.93 |
| **$K^+$** | 133 | 232 | 10.5 | 0.82 |
| **$Rb^+$** | 148 | 228 | 10.0 | 0.82 |
| **$Cs^+$** | 169 | 228 | 9.90 | 0.79 |

The smaller cations are the ones with larger hydrated radii (or hydration number). When an electric field is applied, the cations will move towards the cathode dragging along their hydration shell, in a process called electromigration (Chapter 1 section 1.2.2). The influence of hydrated radius on electrodewatering is shown in Figure 3.24 for the electrodewatering of kaolin in the presence of 0.002 M of added cation.

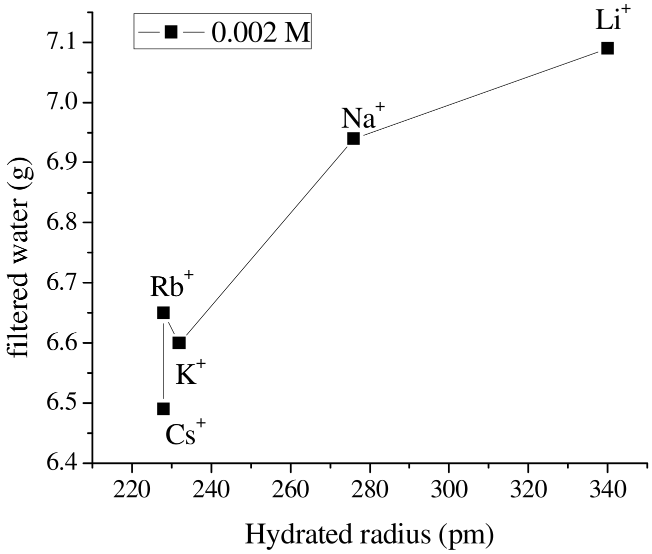

**Figure 3.24** Relation between hydrated radius and amount of recovered water for electrodewatering of kaolin sludge. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa. The initial dryness was 62%. The chloride salts of the alkali metal cations were used at 0.002 M.

As seen in Figure 3.24, the amount of filtered water increases in the presence of cations with larger hydrated radius. Because of their large hydration shells, small cations, such as Li$^+$, are more efficient to transport water molecules to the cathode and thus more efficient to remove them from the sludge cake. As a result, the solid content of the cake is increased. This explains the trend observed for electrodewatering with the monovalent cations of alkali metals.

Published measurements [8] show that the zeta-potential decreases in the series[1]: Li$^+$ > Na$^+$ > K$^+$ > (Rb$^+$) > Cs$^+$. This means that the zeta-potential decreases with decreasing electronegativity (Table 3.6) or increasing polarizability. From the previous series, the coefficient of electroosmotic conductivity (and hence the electrodewatering or the amount of recovered water) may be assumed to increase in the same way, that is, Li$^+$ > Na$^+$ > K$^+$ > Rb$^+$ >

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[1] Measurements of zeta-potential were only made for concentrations higher than 0.1M for each salt. RbCl suspensions with kaolin were not measured. Its position on the series of zeta-potential is assumed from its electronegativity in respect to K$^+$ and Cs$^+$.

$Cs^+$, which corresponds exactly the experimentally observed series. The increase in dewatering in the presence of these monovalent cations, especially the ones with larger hydrated radius, is thus explained by the changes in electromigration and electroosmosis, according to the Smoluchowski theory. However, the same theory cannot explain successfully the variation of the electrodewatering properties as the concentration of a given salt is varied, except perhaps for CsCl.

In accordance with the Smoluchowski theory, an increase in ionic strength, as a result of the addition of a salt to a suspension, compresses the electric double layer (equation 1.12). In fact, the thickness of the double layer changes from about 102-103 nm in very dilute solutions to values lower than 1 nm in concentrated ones [11]. As a result of the compression of the electric double layer in a response to the increase in electrolyte concentration, the zeta-potential decreases and so does the electroosmotic flow. As a consequence, an increase in salt concentration should decrease the amount of water recovered in electrodewatering. That is the case of CsCl (Figure 3.9) but it is not the case for the remaining cations. For instance, increasing the concentration of NaCl from 0.0 to 0.1M increases the amount of recovered water. Any further increase in the NaCl concentration results then in a pronounced decrease in dewatering. Accordingly, to account for the increase in electrodewatering, one would expect the absolute value of the zeta-potential to increase for NaCl concentrations varying from 0.0 to 0.1 M. Indeed, recent measurements of zeta-potential of kaolin suspensions do show that the absolute value of the zeta-potential increases in the presence of NaCl up to 0.1 M [14]. However, the results of the electrodewatering experiments and most importantly the published measurements of zeta-potential with varying NaCl concentrations [14] are not in agreement with the classical Smoluchowski theory that predicts that a decrease of the zeta-potential value should be observed when the ionic strength of the electrolyte is increased. The differences in experimental data from what would be expected from the theory can be due to the fact that the kaolin particles may have both positive and negative charges at the surface, depending on the pH of the solution.

Changing the charge on the metal cation also influences the dewatering properties and an increase in valence results in a decrease in dewatering. In general, electrodewatering is higher in the series: $Na^+ > Ca^{2+} > Ce^{3+}$. The hydration radius is higher for $Na^+$ than it is for $Ca^{2+}$ or $Ce^{3+}$

(Table 3.7), so more water is dragged by the electromigration of $Na^+$ cation, thus explaining the higher dewatering observed in the presence of monovalent salts versus di- or trivalent ones.

**Table 3.7** Ionic and hydrated radii, hydration number and electronegativity for $Na^+$, $Ca^{2+}$ and $Ce^{3+}$.

| Cation | Ionic radii (pm) | Hydrated radii (pm) | Hydration number | Electronegativity |
|---|---|---|---|---|
| **$Na^+$** | 96 [13] | 276 [13] | 16.6 [13] | 0.93 |
| **$Ca^{2+}$** | 126 [15] | 253 [16] | 9.0 [16] | 1.00 |
| **$Ce^{3+}$** | 115 [16] | --- | 9.00 [17] | 1.12 |

As shown in Table 3.5, the zeta-potential of kaolin (0.05 g/L suspension in electrolyte 0.002 M) varies with the valence of the alkali metal cation. At a given concentration, it is more negative for NaCl suspensions than for $CaCl_2$ and positive for $CeCl_3$. As a consequence, the electroosmotic flow is higher for $Na^+$ than for $Ca^{2+}$, and so dewatering is higher for a sludge treated with NaCl. Because of the positive zeta-potential value of kaolin in presence of $CeCl_3$, the electroosmotic flow takes place towards the anode, resulting in less water recovered at the cathode.

The differences in zeta-potential observed in the alkali metal cations series and between cations of different charges are a consequence of the strength of interaction between metal cations and the surface of kaolin. In general, cations that interact strongly with the kaolin surface are able to shield more effectively the negative charge of the kaolin particles and by doing this the zeta-potential becomes less negative, as if the surface charge had changed. From the literature, the clay-cation bond increases linearly with increasing polarizability: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ [7]. The strong interaction between Cs and kaolin explains why cesium is the worst dewatering agent in the alkali metal cations series. Electromigration is diminished because of the strong adsorption of Cs to kaolin. Also, it decreases the zeta-potential and reduces the electroosmotic flow. It will be shown in chapter 6 that this effect is not limited to cesium and that cations with higher valence (like $Ca^{2+}$ and $Ce^{3+}$) interact more strongly with the kaolin surface, and hence are among the poor electrodewatering agents for kaolin.

In electrodewatering, the presence of chloride can result in the evolution of $Cl_2$ gas (equation 1.4). In order to verify if chloride could be replaced by other anions without reducing the effectiveness in dewatering, several sodium salts were tested. There was no difference in using chloride, nitrate or chlorate, but the use of sulfate decreased slightly the amount of recovered water. Anions can interact with the positive edges of the kaolin platelets, changing the surface charge and the zeta-potential. This is why differences can be observed between the different anions.

In section 3.2.4 it was shown that to maximize electrodewatering, the pH of starting solutions should be between 2 and 7. For pH's above 7, the suspension gets fully dispersed and electrodewatering is more difficult, as a consequence of inferior drainage properties, even if the absolute value of the zeta potential is higher [1, 2, 12]. Furthermore, at high pH, charges at the edges of kaolin particles could be negative, which prevents the already mentioned edge-to-face interactions responsible for partial flocculation at lower pH's. In the presence of HCl, no differences in dewatering were observed in the range HCl 0-0.02 M. Smaller value of pH decreases the amount of recovered water (Figure 3.21) as a result of further decrease of the zeta-potential. From equation 3.3, $-SiO^-$ surface groups become protonated at this low pH value and the decrease in surface charge results in diminishing the zeta-potential.

In general, with an increase in electrolyte concentration, the maximum temperature reached by the sludge increases, which leads to a concomitant increase of the amount of water lost by evaporation, which can account to 18% of the total water removed. Evaporation of water as a consequence of the ohmic heating of the sludge is extremely important on the overall efficiency of electrodewatering of wastewater sludge (Chapter 5).

Regardless of the effect of the added electrolyte, the energy consumed during the electrodewatering of kaolin increases with an increase of the salt concentration.

## 3.4 Conclusions

The electrodewatering of kaolin sludge depends on the nature of added salt and its concentration. Monovalent cations are better for dewatering (1-1 electrolytes, for example NaCl, should be preferred) than di- or trivalent cations. Smoluchowski theory and zeta-potential measurements explained very well the behavior of the different alkali metal cations and between mono-, di- and trivalent cations. However, this theory fails to explain the dewatering profile, or the variation of filtered water with concentration, for the monovalent cations. Changes in zeta-potential values result from variation of the interaction between the metal cations and the kaolin surface. High valence metal cations, which interact strongly with kaolin, will have a greater impact on zeta-potential, thus influencing the electrodewatering greatly. In chapter 6, the uptake of metal by the kaolin particles will be measured to better understand the behavior of metal cations with different charges.

Kaolin sludge allowed a better understanding of the effect of metal cations in electrodewatering. However, kaolin is a poor model for municipal sludge, mostly because about 20% of water can be removed by the application of pressure only. This is not the case of municipal sludge where negligible amounts of water can be removed by pressure only. This is why in the following chapter a better model was developed by mixing kaolin with xanthan gum.

## 3.5 References

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# Chapter 4 – Electrodewatering of kaolin plus xanthan gum

## 4.1 Introduction

Xanthan gum is a polysaccharide produced by the bacterium *Xanthomonas campestris*, which is a plant-pathogen [1]. Xanthan gum is nowadays produced at an industrial level from fermentation of glucose in the presence of the above mentioned bacteria [1]. Most of its applications are found in the food industry [2], where it is used as an additive in common commercial products such as salad dressings, beverages, dairy and bakery products, just to name a few. It also finds applications in the pharmaceutical, agricultural, petroleum (oil drilling) and even paper industries [2, 3]. Xanthan gum widespread use is due to its thickening and emulsion- and suspension-stabilizing properties [1]. It is very resistant to changes in pH, temperature, and salinity. Moreover, it is very resistant to mechanical degradation and it is biodegradable. All these properties make xanthan gum attractive in many fields.

Chemically, xanthan gum is a polymer with a main chain composed of β-D-glucose (with the same structure as cellulose). Trisaccharide side chains are grafted on every other glucose of the main chain. Side chains are composed of three units, namely two D-mannoses and one D-glucuronic acid unit that is placed between the two D-mannoses. Figure 4.1 shows the chemical structure of the repeating unit of xanthan gum.

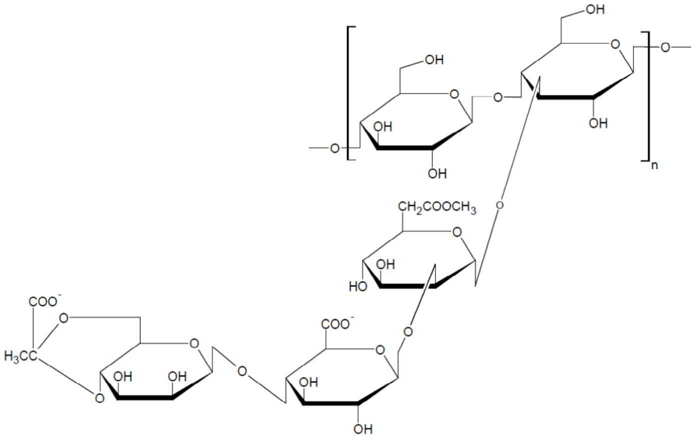

**Figure 4.1** Chemical structure of the repeating unit in xanthan gum [1-3].

Approximately half of the terminal mannose units have a pyruvic acid residue, and in general the mannose directly bonded to the glucose backbone has an acetyl group substitute. The presence of two ionizable acid groups, the pyruvic acid on the terminal mannose unit and the acetic acid on the glucuronic acid, both increase the solubility of xanthan gum in water. Most of the times, the negative charges are balanced by the presence of $Na^+$, $K^+$ or $Ca^{2+}$.

Xanthan gum may interact with suspended particles of kaolin in different ways. Kaolin particles are shaped as platelets with a negative charge at the face of those platelets and a positive charge (or mostly positive) at the edges. One possible way of xanthan gum molecules to interact with kaolin particles is by electrostatic forces, either attractive to the positive charges at the edges of kaolin, or repulsive to negative charges on the faces of kaolin. Hydrogen bonding with the hydroxyl groups on the kaolin surface is also a possibility [4]. The strength of the interaction, as a result of different pH and ionic force conditions, is going to rule the stability of the kaolin plus xanthan gum suspensions, and thus the electrodewatering properties.

## 4.2 Results

### 4.2.1 Recovered water, current density and temperature profile

The addition of xanthan gum changes the electrodewatering properties of kaolin, even if kaolin is present in large excess (about 13:1). The recovered water versus time curve is shown in Figure 4.2. Electrodewatering of pure kaolin is also shown for comparison. One of the most remarkable differences is that no dewatering occurs in kaolin plus xanthan gum at the beginning of the experiment (first 60 minutes) when only the pressure is applied. After the application of voltage (50 V), the amount of recovered water rises slowly to reach 2.8 g after 120 minutes of experiment.

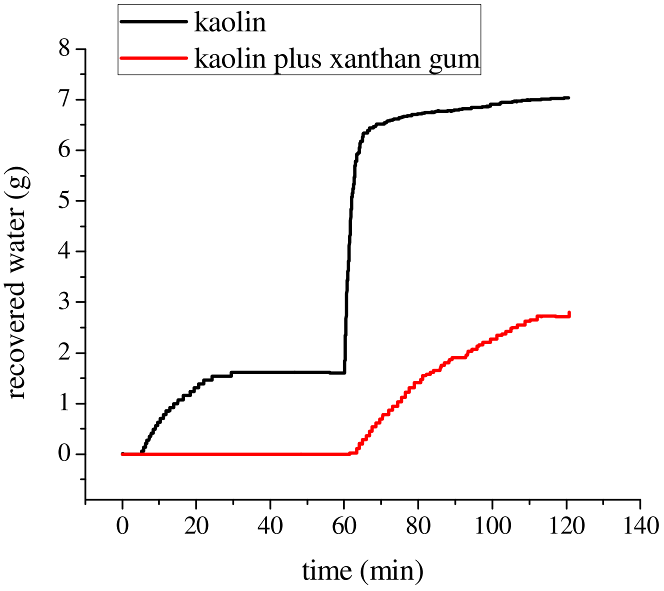

**Figure 4.2** Electrodewatering profile of kaolin plus xanthan gum sludge at 62% initial dryness and 77 kPa. Voltage (50 V) was applied after one hour of conditioning. Deionized water was used as electrolyte. Dewatering of pure kaolin sludge is shown for comparison.

Kaolin plus xanthan gum is more difficult to dewater than kaolin alone, and about 2.5 times less water is recovered when xanthan gum is added to the sludge. The current density and the temperature profile for the electrodewatering of kaolin plus xanthan gum are shown in Figures 4.3 and 4.4, respectively.

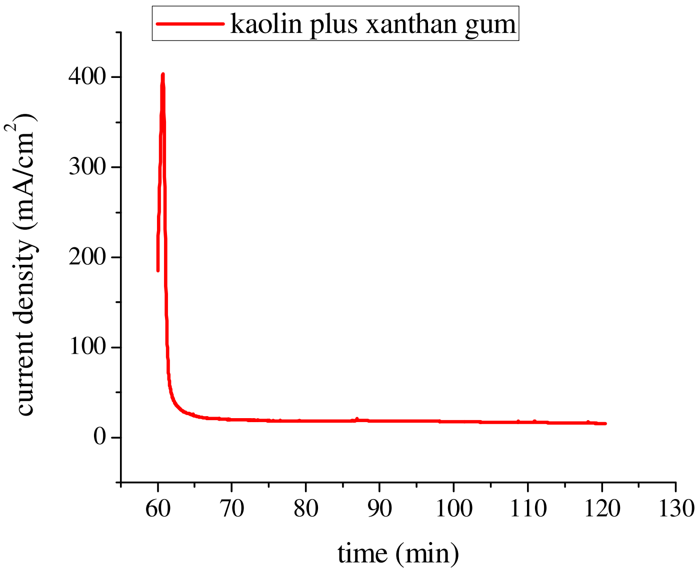

**Figure 4.3** Variation of the current density with time in the electrodewatering of kaolin plus xanthan gum sludge at 62% initial dryness and 77 kPa. The voltage (50 V) was applied after one hour of conditioning. Deionized water was used as electrolyte.

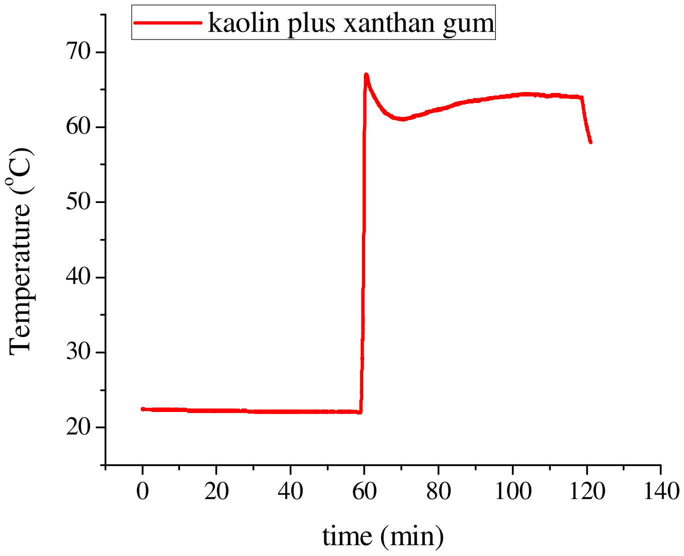

**Figure 4.4** Temperature profile in the electrodewatering of kaolin plus xanthan gum sludge at 62% initial dryness and 77 kPa. The voltage (50 V) was turned on after one hour of conditioning. Deionized water was used as used as electrolyte.

As shown in Figure 4.3, there is a sharp increase of the current density when the voltage is turned on. This is followed by a rapid decrease to a constant value of ~16 mA/cm$^2$ for the remaining of the experiment. The temperature (Figure 4.4) also increases very rapidly when the voltage is turned on, reaching a maximum value of 67.1$^{\circ}$C.

### 4.2.2 Reproducibility experiments

The reproducibility of electrodewatering of kaolin plus xanthan gum sludge was evaluated by performing five independent experiments under the same conditions. The results are summarized in Table 4.1. On average, (2.7±0.3) g of water is removed from a sludge made of kaolin plus xanthan gum. The water removed by filtration is equal to (2.3±0.3) g whereas the water lost by evaporation is (0.4±0.1) g. The errors shown are the standard deviations. These errors are of the same order of magnitude as the ones observed previously for the experiments with kaolin alone. The maximum temperature is (73±5)°C and the total energy consumed in the process is (2.9±0.1) kWh/kg of water extracted.

**Table 4.1** Electrodewatering of kaolin plus xanthan gum sludge at 62% initial dryness. All experiments were performed at 77 kPa and the voltage (50 V) was applied 1 h after the beginning of the experiment. Kaolin is also shown for comparison.

| Parameter | Kaolin batch B | Kaolin batch B plus xanthan gum |
|---|---|---|
| **Total # of experiments** | 4 | 5 |
| **Duration of experiment (h)** | 2 | 1.5 |
| **Initial wt% solid** | 62.05±0.01 | 62.04±0.01 |
| **Filtered water (g)** | 6.9±0.2 | 2.3±0.3 |
| **Evaporated water (g)** | 0.3±0.2 | 0.4±0.1 |
| **Total water (g)** | 7.16±0.01 | 2.7±0.3 |
| **Final wt% solid*** | 74.38±0.03 | 66.2±0.6 |
| **Increase in dryness (%)*** | 19.88±0.04 | 6.7±0.9 |
| **Maximum temperature ($^o$C)** | 51±6 | 73±5 |
| **Total energy (kWh/kg)**** | 0.81±0.02 | 2.9±0.1 |

*calculated with total water loss; **energy consumed per kilogram of water extracted by electrofiltration and by evaporation

The presence of xanthan gum in kaolin sludge influences negatively the final dryness. About 2.5 times less water is removed from the sludge that contains the xantham gum compared to the kaolin sludge. On average, the amount of evaporated water is the same in both cases. However, because less water is removed from the sludge that contains the xanthan gum, the evaporated water represents about (15±3)% of total water molecules that are removed. The total energy consumption per kilogram of water extracted in the sludge that contains xanthan gum is 3.5 times higher than in pure kaolin. The maximum temperature reached in the sludge that contains the xanthan gum, (73±5)°C, is higher than with pure kaolin (51±6)°C.

### 4.2.3 Effect of metal cations in electrodewatering

#### *4.2.3.1 Monovalent cations*

The influence of alkali metal cations on the electrodewatering of kaolin plus xanthan gum was tested. The results for the total amount of water removed, that is, the sum of the evaporated water and the water recovered at the cathode, are shown in Figure 4.5 with respect to the concentration of the added alkali metal cations. Further details are given in table A1.11.

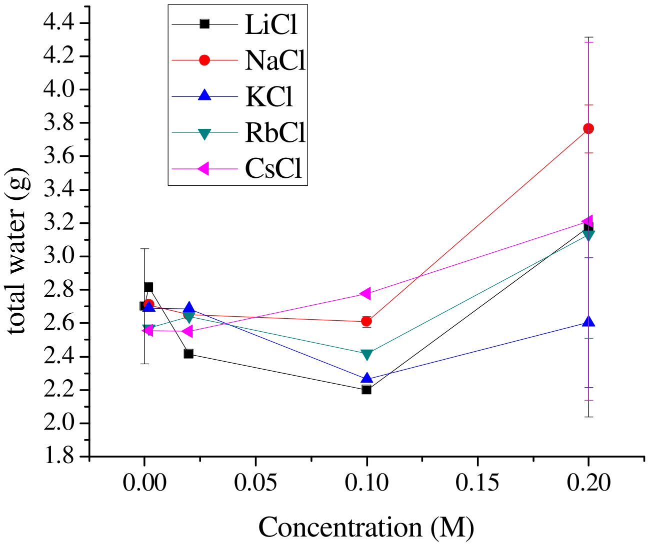

**Figure 4.5** Effect of the concentration of chloride salts of alkali metal cations on the total water removed during the electrodewatering of kaolin plus xanthan gum sludge with 62% initial dryness at 77 kPa. The voltage (50 V) was turned on after 30 minutes of conditioning.

All monovalent cations except CsCl behave similarly during the electrodewatering of kaolin plus xanthan gum. The amount of water extracted decreases slightly when the concentration of added salt is increased from 0.0 to 0.1 M. This effect is more evident for LiCl. For concentrations higher than 0.1 M, the amount of extracted water increases slightly. In the case of CsCl, in general, the extracted water increases with increase in concentration. The total amount of extracted water does not differ significantly between the different cations at the same concentration. For example at 0.002 M, the amount of recovered water is 2.8, 2.7, 2.7, 2.6, and

2.6 g for Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$, respectively. For Li$^+$ and Cs$^+$ 0.2M, total water removed was (3±1) g in both cases.

The typical variation showing the maximum temperature and the energy profiles as a function of the concentration of alkali metal salt are shown in Figure 4.6 for KCl. Data for all the alkali metals are shown in Table A1.11 in the appendix. An increase in the concentration of KCl results in an increase of the cake maximum temperature and the energy consumed per kilogram of extracted water.

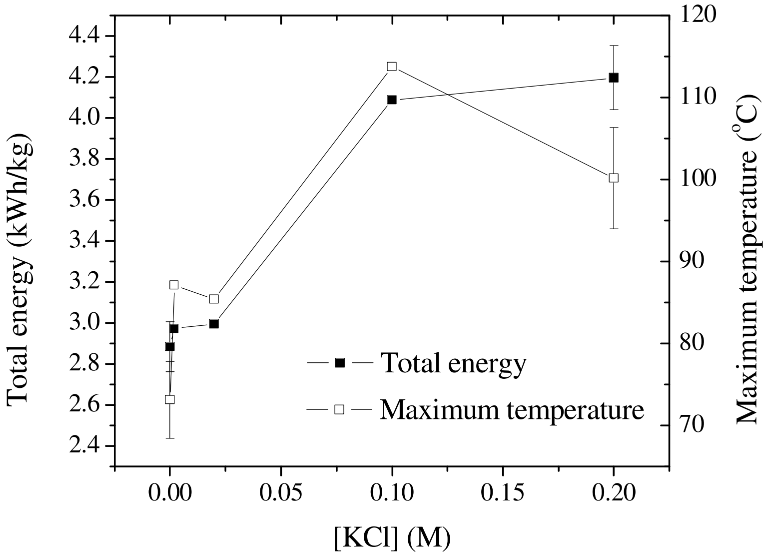

**Figure 4.6** Variation of total energy spent and maximum temperature in electrodewatering of kaolin plus xanthan gum sludge as a function of potassium chloride concentration at 62% initial dryness and 77 kPa. The voltage (50 V) was turned on after 30 minutes of conditioning.

### *4.2.3.2 Mono-, di- and trivalent cations*

Kaolin plus xanthan gum sludge was tested in electrodewatering with sodium, calcium and cerium chloride at different concentrations. The total amount of water removed, this is the sum of the filtered water plus the evaporated one, depends on the charge of the metal cation and its concentration (Figure 4.7; further details in Table A1.12).

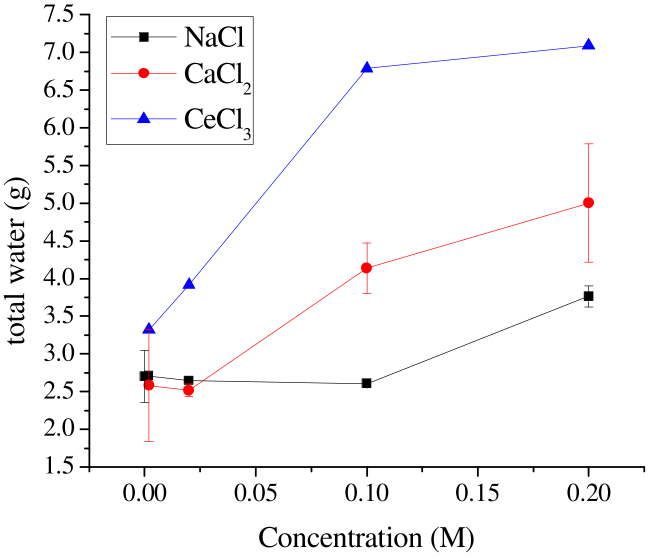

**Figure 4.7** Effect of the concentration of chloride salts on the total water removed during the electrodewatering of kaolin plus xanthan gum sludge with 62% initial dryness at 77 kPa. The voltage (50 V) was turned on after 30 minutes of conditioning.

In this case, the total amount of extracted water, which corresponds to higher final dryness of sludge, is favored by the presence of high valence cations. Thus, the total water removed increases in the following order: $Na^+ < Ca^{2+} < Ce^{3+}$. This is different and opposed from what was observed previously with pure kaolin (Chapter 3 section 3.2.3.2), where electrodewatering increases along the series $Na^+ > Ca^{2+} > Ce^{3+}$, instead. In general, an increase in temperature results in an increase of evaporated water (Figure 4.8). For $CeCl_3$ 0.1 M, about 40% of the total extracted water is lost by evaporation (maximum temperature is 92°C). In comparison, at $CeCl_3$ 0 M, water evaporation represents only (15±3)% and the maximum temperature is (73±5)°C.

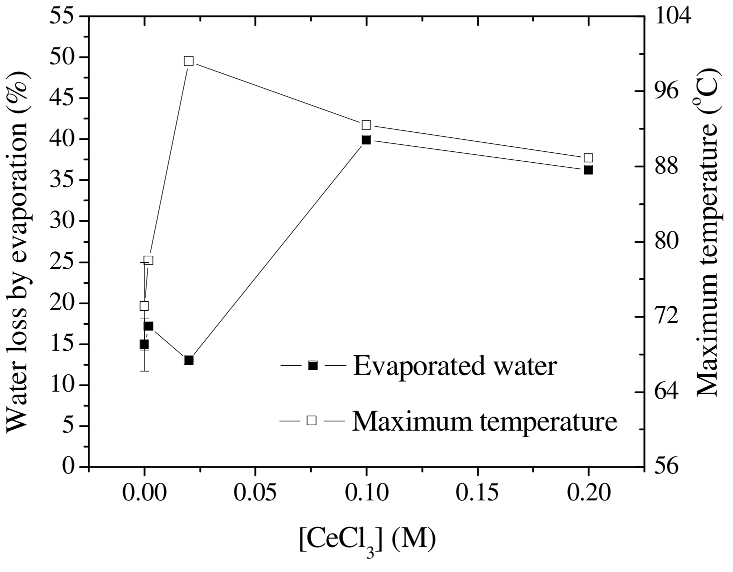

**Figure 4.8** Percentage of water loss by evaporation and its relation to the maximum temperature in the electrodewatering of kaolin plus xanthan gum in the presence of different amounts of $CeCl_3$

Compared to blank experiments, the energy consumption per kilogram of extracted water does not change significantly as the concentration of NaCl and $CaCl_2$ is increased. However, for $CeCl_3$ (see Figure 4.9; full details in Table A1.12 in the appendix), there is a significant decrease of the energy consumption per kilogram of extracted water at the highest concentrations. This decrease is a direct consequence of the larger amount of water that is lost through evaporation for the highest concentration of $CeCl_3$. Indeed, if no water had been lost by evaporation, energy consumption would be practically constant around 2.9-3.1 kWh/kg of extracted water, for the all tested concentrations of $CeCl_3$.

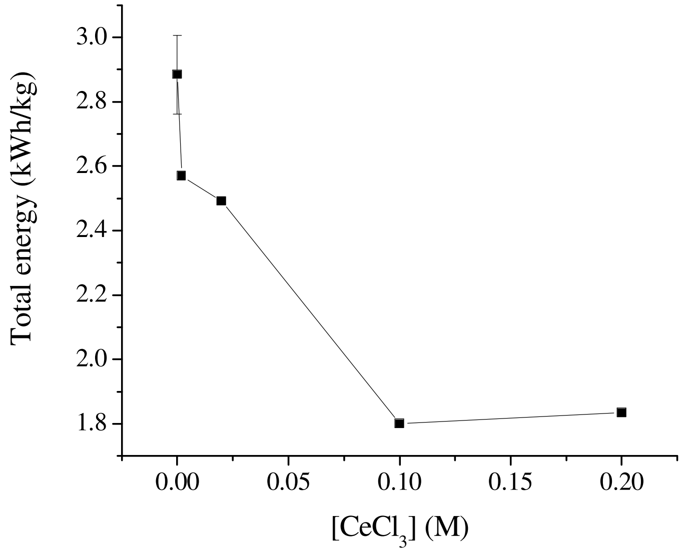

**Figure 4.9** Variation of the total energy spent in electrodewatering of kaolin plus xanthan gum sludge as a function of $CeCl_3$ concentration at 62% initial dryness and 77 kPa. The voltage (50 V) was turned on after 30 minutes of conditioning.

#### *4.2.3.3 Other +2 and +3 cations*

The electrodewatering of kaolin plus xanthan gum sludge was further studied with other plus 2 and plus 3 cations. Calcium nitrate, ruthenium (III) chloride, iron (III) chloride and aluminum chloride were tested. The total water removed from the sludge as a function of the concentration of added salts is given in Figure 4.10. Further details are provided in Table A1.13.

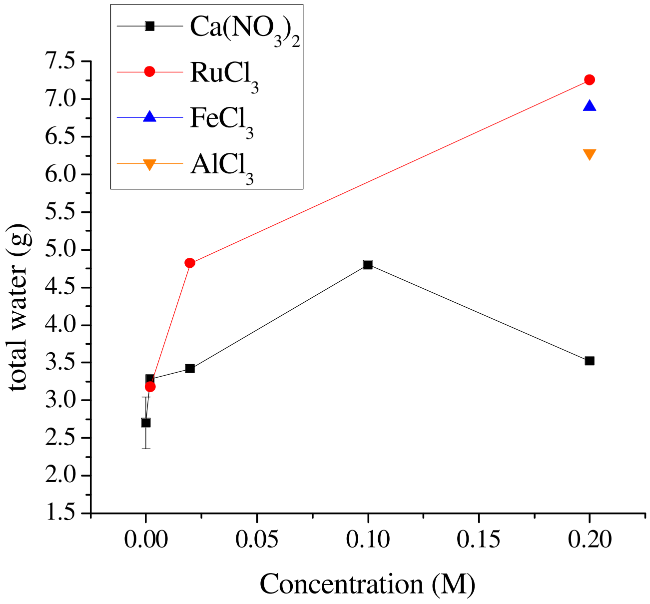

**Figure 4.10** Effect of +2 and +3 cations on the total water extracted from kaolin plus xanthan gum sludge at 62% initial dryness and 77 kPa. The voltage (50 V) was turned on after 30 minutes of conditioning.

As shown in Figure 4.10, the total water extracted from the sludge increases steadily from 0.0 to 0.1 M in the case of calcium nitrate and ruthenium chloride. At highest concentration (0.2 M), the total amount of water extracted for $Ca(NO_3)_2$, $RuCl_3$, $FeCl_3$ and $AlCl_3$ is larger than with pure water. This behavior is similar to the one observed previously with $CeCl_3$ (see Figure 4.7). The effect of +3 cations is best at 0.2 M. Within the experimental error, the effect of all the +3 cations that were tested should be considered equivalent. Table 4.2 shows some experimental data for the comparison of + 3 cations.

**Table 4.2** Comparison of the behavior of plus 3 cations at 0.2 M in the electrodewatering of kaolin plus xanthan gum sludge.

| **Cation** | **Total water loss (g)** | **Water loss by evaporation (%)** | **Maximum temperature ($^o$C)** | **Total energy (kWh/kg)** | **Electronegativity** |
|---|---|---|---|---|---|
| **$Al^{3+}$** | 6.3 | 32 | 88 | 2.1 | 1.61 |
| **$Ce^{3+}$** | 7.1 | 36 | 89 | 1.8 | 1.12 |
| **$Fe^{3+}$** | 6.9 | 16 | 95 | 2.1 | 1.83 |
| **$Ru^{3+}$** | 7.3 | 32 | 89 | 2.2 | 2.2 |

As seen in Table 4.2, $Al^{3+}$, $Ce^{3+}$, and $Ru^{3+}$ behave very similarly to one another: the percentage of water loss by evaporation and the maximum temperature are approximately identical. Only $Fe^{3+}$ shows a reduction of the amount of water lost by evaporation (one half) although the sludge cake reaches higher temperature. The sludge prepared with $FeCl_3$ 0.2 M shows another peculiarity: unlike the other salts studied here, water molecules can be removed from the sludge prepared with $FeCl_3$ by the application of pressure alone during the first 30 minutes of conditioning. Indeed 0.5 g of water was thus removed from the sludge by simply applying pressure, representing a bit more than 7% of the total water lost. The energy spent per kilogram of extracted water increases in the series: $Ce^{3+} < Al^{3+}$, $Ru^{3+} < Fe^{3+}$, and the electronegativity, increases in the series: $Ce^{3+} < Al^{3+} < Ru^{3+} < Fe^{3+}$

Figure 4.11 shows the variation of maximum temperature and total energy consumption as a function of the concentration of $RuCl_3$. A similar behavior was observed for $CeCl_3$ (Figures 4.8 and 4.9). As seen in Figure 4.11, the maximum temperature increases, and the total energy consumed per kilogram of water extracted decreases, in the range 0.0 to 0.1 M. The decrease in energy consumed is again a consequence of the increase in evaporated water caused by the increase in temperature.

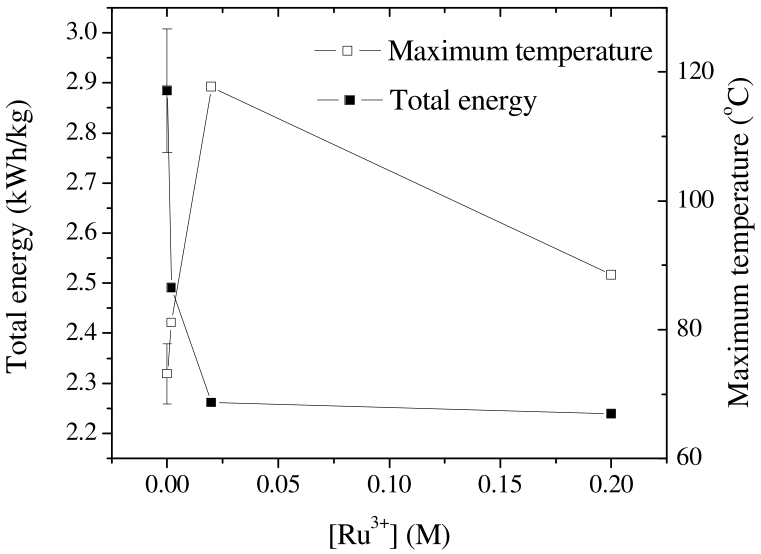

**Figure 4.11** Variation of the total energy spent and maximum temperature in electrodewatering of kaolin plus xanthan gum sludge as a function of ruthenium (III) chloride concentration at 62% initial dryness and 77 kPa. The voltage (50 V) was turned on after 30 minutes of conditioning.

### 4.2.4 Effect of anions and pH in electrodewatering of kaolin plus xanthan gum

The effect of changing the chloride anion by other anions was tested with sodium salts at a fixed concentration (0.1 M). The results for the total amount of water (the sum of filtered and evaporated water) extracted from the kaolin plus xantham gum sludge as a function of the nature of the anion are shown in Figure 4.12. Further information is presented in table A1.14.

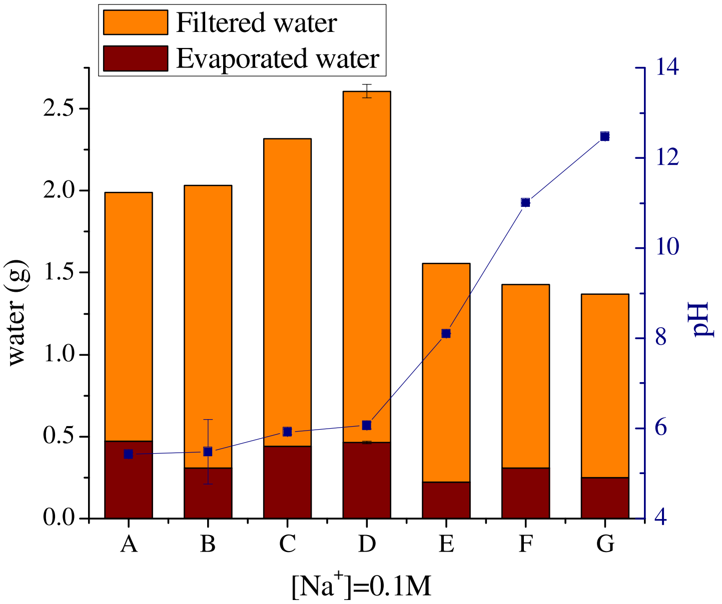

**Figure 4.12** Filtered and evaporated water extracted from kaolin plus xanthan gum sludge at 62% initial dryness and 77 kPa in the presence of different sodium salts at 0.1 M. The voltage (50 V) was turned on after 30 minutes of conditioning. A= $NaClO_3$, B=$Na_2SO_4$, C=$NaNO_3$, D=NaCl, E=$NaHCO_3$, F=$Na_2CO_3$, G=NaOH. The pH of the starting electrolyte solution is also shown.

As shown in Figure 4.12, $NaClO_3$, $Na_2SO_4$, $NaNO_3$, and NaCl, all have similar pH around 5.43-6.07, which means that any difference in final dryness of the cake must be due only to the different anions. The total amount of water removed from the sludge decreases in the series: $Cl^- > NO_3^- > ClO_3^-, SO_4^{2-}$, varying from (2.61±0.03) to 2.0 g, for NaCl and $Na_2SO_4$, respectively. There are no major differences among these anions in terms of energy consumption and maximum temperature (data shown in table A1.14 in the appendix).

As it can be inferred from the results of Figure 4.12, basic electrolytes such as $NaHCO_3$ 0.1 M, $Na_2CO_3$ 0.05 M, and NaOH 0.1 M are detrimental for dewatering. All these electrolytes have pH higher than 8.

The effect of low pH (below 7) on the total amount of extracted water was verified by using solutions of HCl in the range 0.0 - 0.2 M. The results for the amounts of filtered and evaporated water are shown in Figure 4.13.

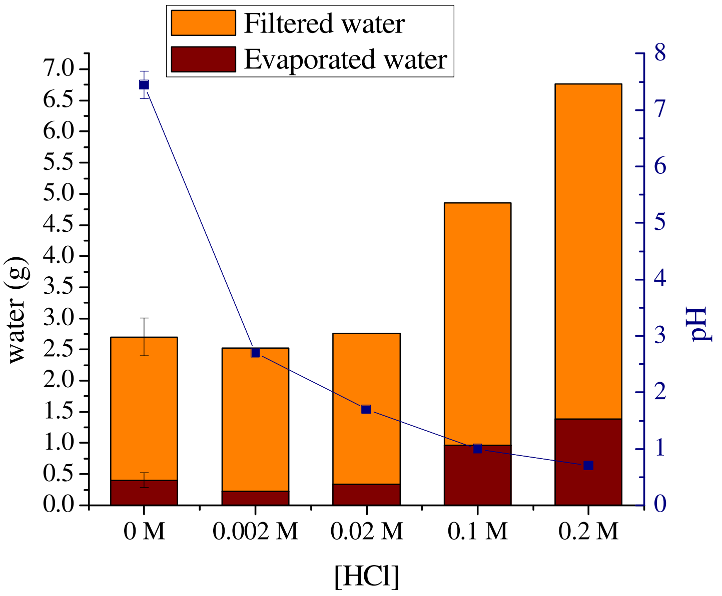

**Figure 4.13** Filtered and evaporated water extracted from kaolin plus xanthan gum sludge at 62% initial dryness and 77 kPa as a function of HCl concentration. The voltage (50 V) was turned on after 30 minutes of conditioning. The pH of the starting electrolyte solution is also shown.

As shown in Figure 4.13, the amount of recovered water (filtered plus evaporated water) remains practically unchanged when HCl solutions from 0.0 (pH 7.4) to 0.02 M (pH 1.7) are used. Therefore there is a range of pH, roughly from 2 to 7, where the electrodewatering is not affected. However, a further decrease in pH (0.1M (pH 1) and 0.2 M (pH 0.7)) results in a dramatic increase of the electrodewatering. The increase observed is in fact comparable to the increase registered upon the addition of plus +3 cations. As an example, 6.8 g of water is extracted in the presence of HCl 0.2 M and 6.3-7.3 g of water is extracted when plus 3 cations are used (see Figure 4.10).

The variation of the maximum temperature and the total energy consumed as a function of the concentration of HCl are both shown in Figure 4.14.The total energy consumption per kilogram of water extracted, decreases as the HCl concentration is increased. Likewise, the maximum temperature increases as the HCl concentration is increased. The same behavior was observed previously with +3 cations. The water extracted by evaporation can represent up to 21% of total water lost.

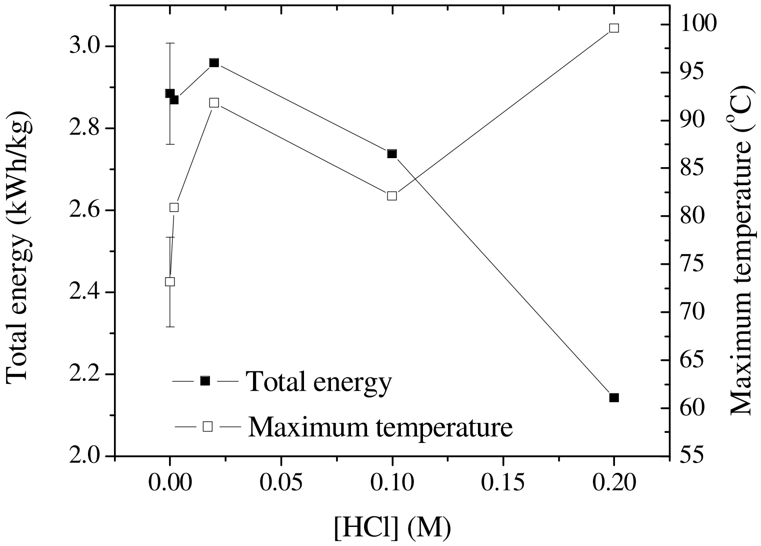

**Figure 4.14** Variation of total energy spent and maximum temperature in electrodewatering of kaolin plus xanthan gum sludge as a function of HCl concentration at 62% initial dryness and 77 kPa. The voltage (50 V) was turned on after 30 minutes of conditioning.

## 4.3 Discussion

The presence of xanthan gum in kaolin sludge decreases the amount of water that can be removed during the electrodewatering process: about 2.5 less water is recovered upon the addition of less than 10% of xanthan gum to kaolin. Particularly, no dewatering occurs in the first step of dewatering that consists of applying pressure (Figure 4.2). This behavior is identical to that observed in municipal sludge (Chapters 5 and 7). Xanthan gum is thus helping further disperse the kaolin particles, mostly because of electrostatic repulsion between the negatively charged xanthan gum particles and the kaolin particles, even if the later are positively charged at the edges.

If the reduction in dewatering is due to an increase in the dispersion of the particles of kaolin, then it is hypothesized that an increase in pH would result in a further decrease in dewatering, because the kaolin particles will then become even more negative, as a result of deprotonation at the edges (Chapter 3 Equation 3.2). Experimentally this is what is observed by the addition of a basic electrolyte, such as NaOH 0.1 M (measured pH 12.48±0.03). At this high pH, the kaolin surface charge is negative both at the edges and at the faces of the particles, and thus the sludge is fully dispersed because of the electrostatic repulsion to the negative xanthan gum particles. As a consequence, a decrease in dewatering occurs (Figure 4.12). On the other side of the pH scale, the opposite effect should occur and an increase in dewatering is indeed observed as a result of the partially flocculation of the sludge (Figure 4.13). More than 2.5 times water is extracted when using HCl 0.2 M compared to HCl 0 M. At this very low pH several phenomena may take place, such as the protonation of the aluminol and silanol kaolin groups, and as result hydrogen bonding can occur between kaolin and xanthan gum particles [4]. Furthermore, xanthan gum acid groups can also be protonated, reducing the electrostatic repulsion mentioned above. In general, the electrodewatering of kaolin and xanthan gum seems to be regulated by the interaction of kaolin and xanthan gum. From this interaction can result a fully dispersed sludge (at high pH) very difficult to dewater, or a partially or a fully flocculated sludge (at low pH) that dewaters as easily as if no xanthan gum was present.

The action of monovalent cations of alkali metals does not differ much from one another, except the case of CsCl which has a slightly different behavior (Figure 4.5). For all the other alkali metal cations, up to 0.1 M of added salt, the total water loss decreases slightly and then there is an increase at 0.2 M. As discussed elsewhere, the absolute value of the zeta-potential increases for concentration up to 0.1 M and then decreases at higher concentrations [5]. As a consequence, up to 0.1 M, there is an increasing repulsive interaction between negatively charged xanthan gum and kaolin particles. Thus, the system is more dispersed than in the absence of salt and hence less dewatering is observed. At 0.2 M, the absolute value of the zeta potential decreases and so the interaction between xanthan gum and kaolin particles get stronger, allowing partial flocculation and higher dewatering.

CsCl was previously shown to behave in accordance with Smoluchowski theory (Chapter 3 section 3.3), and an increase in salt concentration results in a decrease of the absolute value of zeta-potential as a result of the strong interaction with the kaolin surface. In the presence of xanthan gum, the addition of CsCl resulted in an increase in dewatering as the salt concentration is increased. Because the $Cs^+$ anion is making the surface of kaolin more positive, the interaction with the xanthan gum becomes less repulsive and partial coagulation may occur. As a result, more water is removed from the sludge.

Electrodewatering is favored in the presence of high valence cations and increases in the series $Na^+ < Ca^{2+} < Ce^{3+}$. This is the opposite of what was observed during the dewatering of kaolin sludge alone (Chapter 3 section 3.2.3.2). Again the observed effect must be due to the aggregation of the kaolin plus xanthan gum particles in the presence of high valence cations. In fact, several authors have observed that the presence of hydrolysable cations (such as $Ca^{2+}$ and $Ce^{3+}$) increase the adsorption of polysaccharides [6] thus favoring the flocculation of the sludge and consequently providing higher dewatering. High valence metal cations are decreasing the surface charge of kaolin, in the same way as discussed for the $Cs^+$ anion. This effect is due to the preferential uptake of $Ca^{2+}$ and $Ce^{3+}$ by kaolin when compared to $Na^+$ (Chapter 6). The effect of partial flocculation in the presence of +2 or +3 cation is very well illustrated by kaolin plus xanthan gum sludge in the presence of $FeCl_3$. In that later case, the application of pressure alone enabled the removal of 7% of the total water lost during electrodewatering. This would not happen if the sludge were fully dispersed as in the absence of the electrolyte.

The counterions have a moderate effect in electrodewatering and it is not very different from the effect observed previously with kaolin (Chapter 3 section 3.2.4). The electrodewatering decreases in the series $Cl^- > NO_3^- > ClO_3^-$, $SO_4^{2-}$, and about 23% less water is lost when using $SO_4^{2-}$ when compared to $Cl^-$ (Figure 4.12).

The energy consumption per kilogram of water extracted is highly dependent on the nature of the added electrolyte. In general, the addition of electrolyte results in a decrease in energy spent. This decrease is more significant for high valence metal cations. Furthermore, comparing different +3 cations, more energy is consumed for the more electronegative cations. The temperature of the cake can reach values as high as 100°C. Ohmic heating has a positive effect on electrodewatering by increasing sludge cake temperature. Increase of the cake temperature gives rise to evaporation of water that can represent up to 40% of total water extracted, as it is the case for $CeCl_3$ 0.1M. Therefore, the importance of ohmic heating of the sludge should not be disregarded in electrodewatering. The viscosity of water also goes down with increasing temperature which facilitates the dewatering as well [7].

## 4.4 Conclusions

The kaolin plus xanthan gum sludge is more difficult to dewater compared to pure kaolin sludge. In particular, the application of pressure at the beginning of the process no longer enables dewatering, as it was the case of for pure kaolin. Xanthan gum is helping dispersing the kaolin particles and keeping them in solution, and hence preventing dewatering by the sole application of pressure.

Electrodewatering is favored in the presence of high valence cations as a result of partial flocculation of the kaolin - xanthan gum sludge. High valence cations are bridging kaolin and xanthan gum particles allowing the formation of aggregates [6]. As a result of higher degree of flocculation, dewatering is facilitated and it was shown to increase in the series $Na^+ < Ca^{2+} < Ce^{3+}$. In some cases, such as in the presence of $Fe^{3+}$, water molecules can be extracted by the application of pressure alone. To unequivocally prove that the metal cations are acting on the flocculation/coagulation of xanthan gum and kaolin particles, measurements of turbidity and/or measurements of the adsorption of xanthan gum on kaolin surface should be performed. However, this is out of the range of the present study.

Alkali metal cations ($Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$) have a similar effect on electrodewatering, and different anions have only a mild effect $Cl^- > NO_3^- > ClO_3^-$, $SO_4^{2-}$.

As it will be shown later on, the behavior of kaolin plus xanthan gum sludge is very similar to the one shown by municipal sludge (Chapters 6 and 7).

## 4.5 References

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# Chapter 5 – Electrodewatering of Municipal Sludge

## 5.1 Introduction

The municipal sludge is a by-product of wastewater treatment. Although its composition can vary greatly, it its very compressible and its water content is high. Therefore, municipal sludges are very difficult to dewater by recurring to mechanical methods (Chapter 1). The suspended solids in the water of municipal sludge also include microorganisms and extracellular material, such as polysaccharides, organic acids, proteins and lipids [1]. Due to the presence of ionizable groups (for example carboxylic acid groups in biomolecules), sludge particles are negatively charged. As a consequence, high valence cations induce flocculation by reducing the repulsive forces between adjacent particles.

Upon the application of an electric field to a compressed sludge cake, water is removed at the cathode as a result of the electroosmotic flow, which is directly proportional to the zeta-potential (equations 1.10 and 1.12). However very high absolute value of zeta-potential may be detrimental to electrodewatering as a result of the formation of a more stable suspension [2]. Electrophoresis may also be important, especially because the migration of negatively charged particles towards the anode will reduce the clogging at the cathode, thus reducing the resistance to filtration [3]. In this context, the electrodewatering of municipal sludge was studied, focusing on the effect of different metal cations on the overall dryness of the sludge cake. Importance was also given to the energy performance of the process so as to evaluate its feasibility when compared to an industrial thermal drying process where water evaporation requires 1.2 kWh of energy per kilogram of extracted water [4].

## 5.2 Results

### 5.2.1 Recovered water, current density and temperature profile (INRS laboratory cell 2)

The electrodewatering of sewage sludge from La Prairie, Qc, Canada, municipality was tested in INRS-laboratory cell number 2 to allow a direct comparison with the kaolin sludge and the kaolin plus xanthan gum sludge. La Prairie sludge has a measured initial dryness of (15.10±0.07)%. The evolution with time of the amount of water recovered at the cathode during an electrodewatering experiment is shown in Figure 5.1. A two-hour experiment was performed at 78 kPa. Voltage was turned on after the first hour.

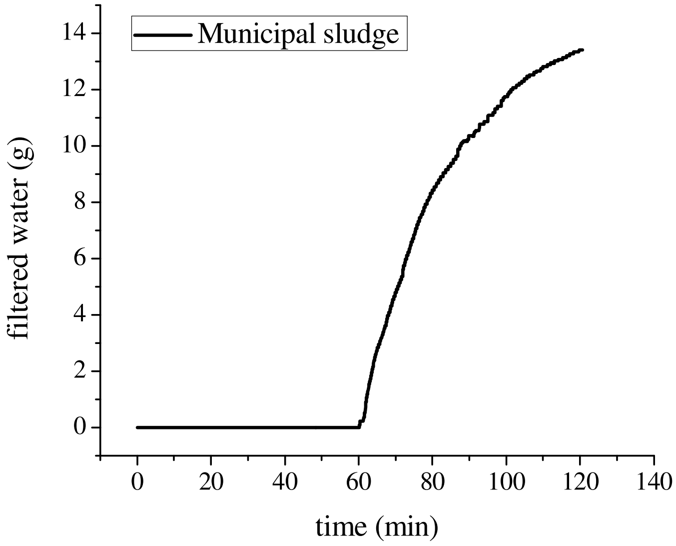

**Figure 5.1** Variation of recovered water by filtration with time for the electrodewatering of La Prairie municipal sludge at initial (15.10±0.07)% dryness and at 78 kPa. The voltage (50 V) was turned on after one hour of conditioning.

As it can be seen in Fig. 5.1, no dewatering occurs in the first 60 minutes, when only pressure is applied. At the end of the measurement, which was stopped after 120 minutes, a total of 13.4 g of water has been removed from the sludge. This corresponds to a final dryness of 24%. In that case, electrodewatering was able to increase the solids content of the sludge by

60%. The electrodewatering profile of municipal sludge is very similar with the one of kaolin plus xanthan gum (Figure 4.2).

The variation of the current density with time is shown in Figure 5.2. When the voltage is turned on, the current density increases very sharply and then it gradually decreases with time. Some spikes are observed during this decay. At the end of the experiment, the total energy consumed was 0.446 kWh/kg of extracted water.

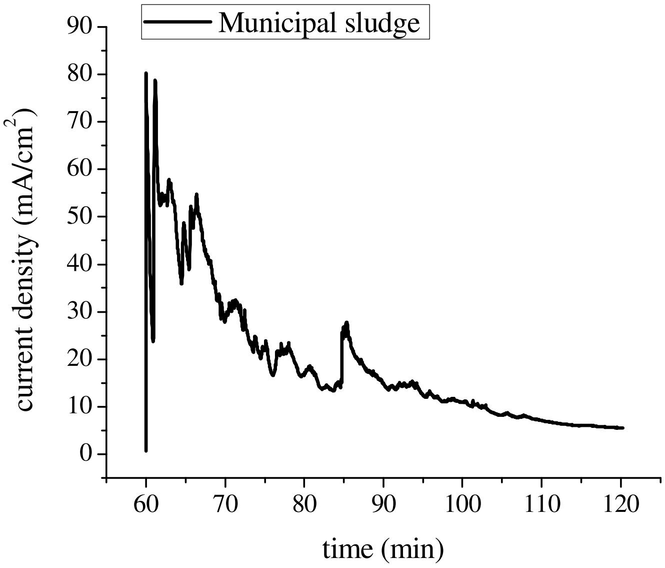

**Figure 5.2** Variation of the current density with time for the electrodewatering of La Prairie municipal sludge at initial (15.10±0.07)% dryness and at 78 kPa. The voltage (50 V) was turned on after one hour of conditioning.

The variation of temperature with time is presented in Figure 5.3. The temperature of the sludge cake increases sharply in the first 12.5 minutes after the voltage is turned on, reaching 69.6$^o$C. Then, there is a gradual decrease of the temperature following that initial sharp increase.

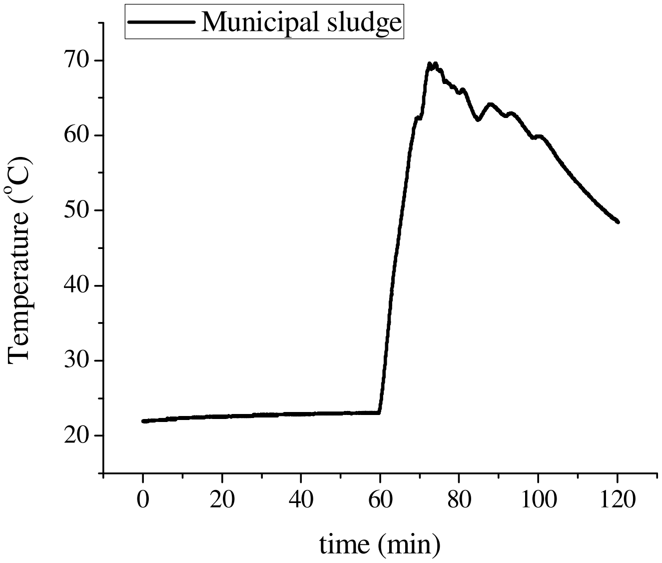

**Figure 5.3** Variation of temperature with time for the electrodewatering of La Prairie municipal sludge at initial (15.10±0.07)% dryness and at 78 kPa. The voltage (50 V) was turned on after one hour of conditioning.

### 5.2.2 Recovered water, current density and temperature profile. Reproducibility experiments (Ovivo laboratory cell)

The tests with the Ovivo cell lasted only 8 minutes. According to our industrial partner, the increase in dryness observed in longer tests (> 8 minutes) does not compensate the extra energy input required to remove these extra water molecules. So generally, tests performed in the Ovivo's laboratory do not exceed 8 minutes. Optimization of the tests is made for 50 V and (116±4) kPa pressure. Also, the current intensity is limited to 6.1 A (the voltage is adjusted automatically to a value that does not allow the current to increase above 6.1 A, that corresponds to 50 mA/cm$^2$). Ovivo cell allows the recording of the variation of voltage, current, filtered water and sludge thickness with time. The filtered water collected at the cathode from the dewatering of La Prairie municipal sludge is shown in Figure 5.4.

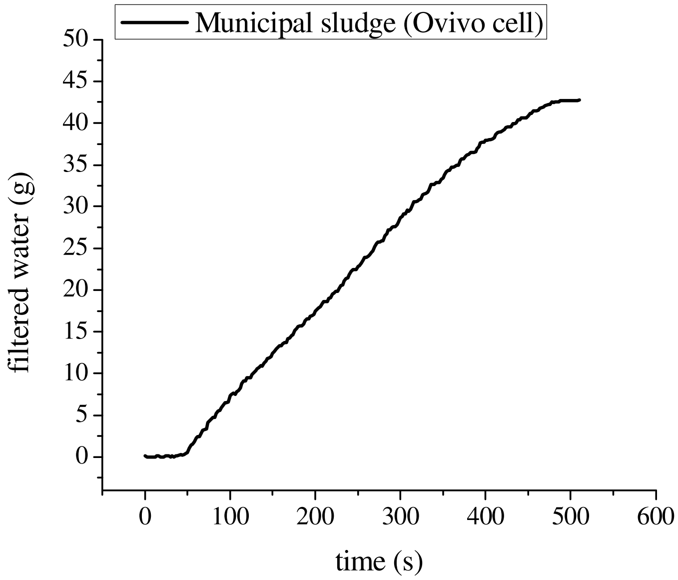

**Figure 5.4** Variation of recovered water with time for the electrodewatering of La Prairie municipal sludge at initial (14.4±0.6)% dryness. Test performed with Ovivo dewatering cell; pressure – (116±4) kPa – and voltage (50 V) were applied for 8 minutes.

A total of 42.8 g of water is recovered. The evaporated water (estimated from the measurement of final dryness) reached 9.2 g, which represents about 18% of the total water lost. The dewatering starts in less than one minute after application of voltage.

The variation of current density with time is shown in Figure 5.5. There is an initial sharp increase in current density followed by a slow decrease. A second maximum is observed at ~ 300 s. The total energy consumption is 0.270 kWh/kg of water extracted.

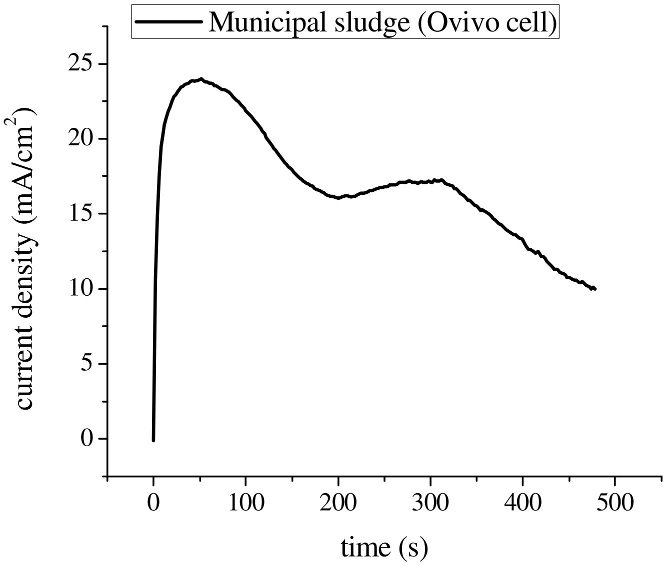

**Figure 5.5** Variation of current density with time for the electrodewatering of La Prairie municipal sludge at initial (14.4±0.6)% dryness. Test performed with Ovivo dewatering cell; pressure – (116±4) kPa – and voltage (50 V) were applied for 8 minutes.

The sludge thickness (Figure 5.6) decreases with time as a result of the removal of water. The initial compression of sludge leads to a thickness decrease from 44.4 to 12.4 mm. Then, the thickness of the sludge decreases steadily with time. The final sludge thickness is 7.8 mm, which represents a reduction of about 37% of its initial volume.

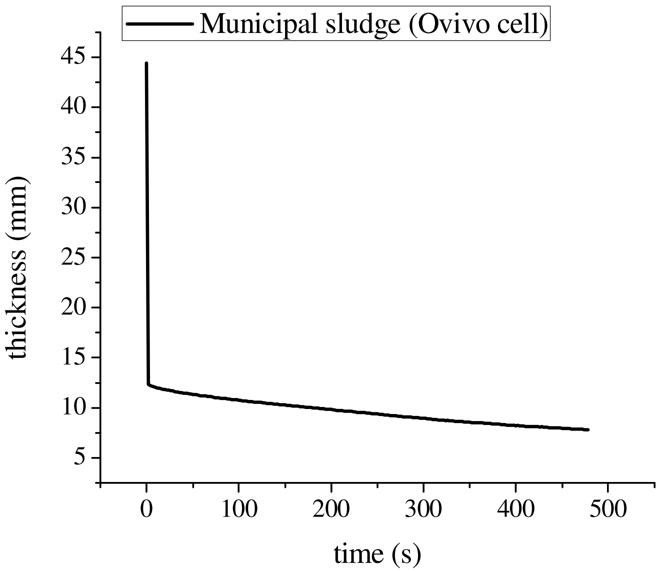

**Figure 5.6** Variation of sludge thickness with time for the electrodewatering of La Prairie municipal sludge at initial (14.4±0.6)% dryness. Test performed with Ovivo dewatering cell; pressure – (116±4) kPa – and voltage (50 V) were applied for 8 minutes.

The reproducibility of the results for the electrodewatering of municipal sludge was tested by taking measurements during nine different days over a period of four months. The results are summarized in Table 5.1.

**Table 5. 1** Results of electrodewatering experiments with a municipal sludge from La Prairie These measurements are the average of 9 different experiments that were realized over a period of 4 months. In each case, 8-minute experiments were performed at 50 V and (116±4) kPa, using Ovivo cell. Results shown are average ± standard deviation.

| Initial dryness (%) | Final dryness (%) | Water loss by evaporation (%) | Total energy (kWh/kg) |
|---|---|---|---|
| 14.3±0.3 | 26±3 | 18±3 | 0.29±0.02 |

The error for the final dryness presented in Table 5.1 is about 12% of the average value. This is higher than the error found for the synthetic sludges prepared with kaolin (Table 4.1) where this error is lower than 1%. This difference was assumed to be a result of the higher variability in the municipal sludge composition when compared to the synthetic ones, whose composition is fully controlled during their preparation.

### 5.2.3 Effect of metal cations in electrodewatering

#### *5.2.3.1 Monovalent cations*

The effect of the addition of alkali metal cations was tested by adding an aqueous solution of the corresponding chloride salt to the sludge. The addition was made on the side of the sludge that stays in contact with the anode. The increase in dryness, given by Equation 5.1, is shown in Figure 5.7 for each alkali metal cation (at a concentration of 4.4 mmol) and for deionized water (blank experiment). All details are presented in table A1.15.

$$Increase\ in\ dryness\ (\%) = \frac{Final\ dryness - Initial\ dryness}{Initial\ dryness} \times 100 \text{ (Equation 5.1)}$$

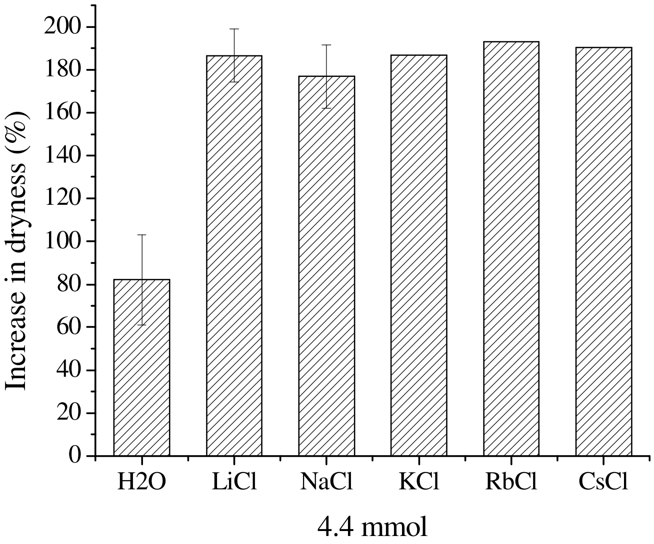

**Figure 5.7** Increase in dryness caused by the addition of water (blank experiments) and alkali metal cations solution (at 4.4 mmol) to La Prairie municipal sludge. The initial dryness was

(14.3±0.3)%. Tests performed with Ovivo dewatering cell; pressure – (116±4) kPa – and voltage (50 V) were applied for 8 minutes.

As seen in Fig. 5.7, all alkali metal cations have a similar effect in the electrodewatering of municipal sludge. The increase in dryness induced by the alkali metal cations is close to a factor of two compared to deionized water. The water lost by evaporation represents approximately 20 % of the total water lost. The use of alkali metal cations as electrodewatering agents resulted in an increase of dryness without a significant increase in the energy consumed (Figure 5.8) when compared with the blank experiments.

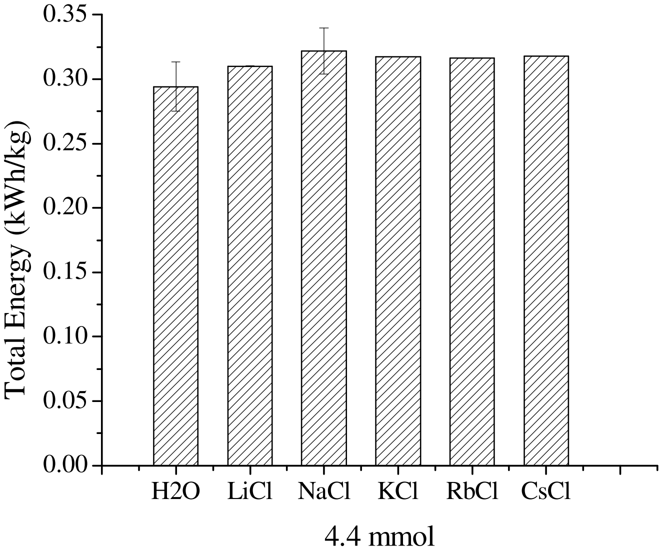

**Figure 5.8** Variation of the total energy consumption per kilogram of water extracted in the electrodewatering of municipal sludge in the presence of 4.4 mmol of alkali metal cations. Initial dryness was (14.3±0.3)%. Tests performed with Ovivo dewatering cell; pressure – (116±4) kPa – and voltage (50 V) were applied for 8 minutes.

### *5.2.3.2 Mono-, di-, and trivalent cations*

Several electrodewatering experiments were performed to verify the effect of added sodium, calcium and cerium chloride on the final dryness of municipal sludge. The results are presented in Figure 5.9. Further details are presented in table A1.16.

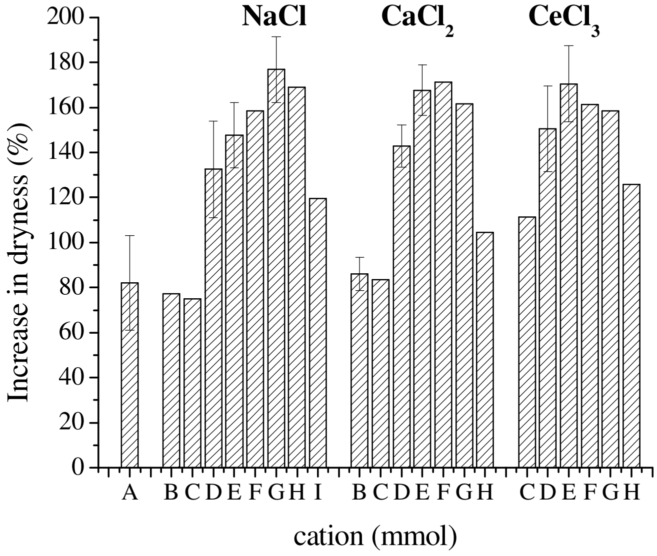

**Figure 5.9** Increase in dryness caused by the addition of NaCl, $CaCl_2$ and $CeCl_3$ to La Prairie municipal sludge. Initial dryness was (14.3±0.3)%. Tests performed with Ovivo dewatering cell; pressure – (116±4) kPa – and voltage (50 V) were applied for 8 minutes. A – 0 mmol, B – 0.3 mmol, C – 0.43 mmol, D – 1.5 mmol, E – 2.2 mmol, F – 3 mmol, G – 4.4 mmol, H – 7.5 mmol, I – 13 mmol

In general, dewatering increases with the concentration of added salt up to a maximum value, which is dependent on the nature of the cation. Indeed, there is a specific concentration range where the performance of each cation is at its best. That range is 4.4-7.5, 2.2-4.4, and 1.5-4.4 mmol of added cation for $Na^+$, $Ca^{2+}$ and $Ce^{3+}$, respectively. A further increase in the concentration is detrimental for dewatering.

The energy consumed in the electrodewatering process is presented in Figure 5.10. The energy spent increases with an increase in concentration for both $Ca^{2+}$ and $Ce^{3+}$, but not for $Na^{+}$. In this case, the energy consumed is constant, within the experimental error, for all the range of tested concentrations.

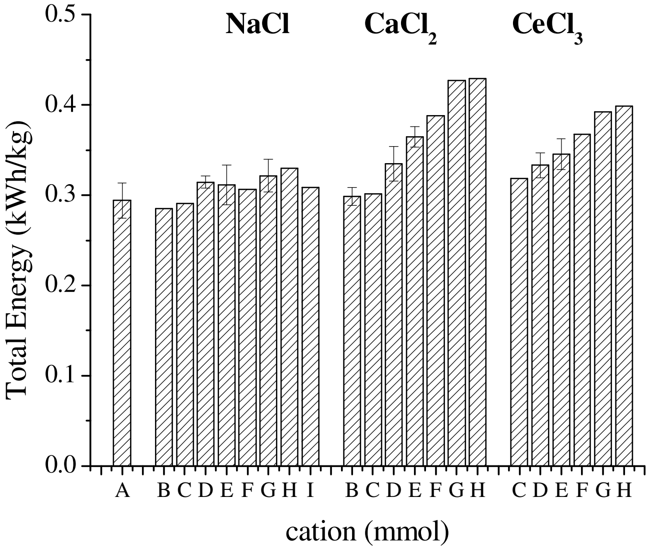

**Figure 5.10** Variation of total energy consumption per kilogram of extracted water caused by the addition of NaCl, $CaCl_2$ or $CeCl_3$ solution to La Prairie municipal sludge. Initial dryness was (14.3±0.3)%. Tests performed with Ovivo dewatering cell; pressure – (116±4) kPa – and voltage (50 V) were applied for 8 minutes. A – 0 mmol, B – 0.3 mmol, C – 0.43 mmol, D – 1.5 mmol, E – 2.2 mmol, F – 3 mmol, G – 4.4 mmol, H – 7.5 mmol, I – 13 mmol

In the range of optimal concentration, the energy spent is about 0.32, 0.36-0.43, and 0.33-0.39 kWh/kg for $Na^{+}$, $Ca^{2+}$ and $Ce^{3+}$, respectively. Energetically speaking, sodium salts seem to be more efficient in electrodewatering of the municipal sludge. Water loss by evaporation is always lower than 25% of total water loss, for all salts and at all concentrations.

The highest dryness reached with each salt is given in Table 5.2. The experiments with added deionized water (blanks) are also shown for comparison.

**Table 5.2** Concentrations at which highest dewatering is achieved for each cation. Water is shown for comparison. Tests performed with Ovivo dewatering cell; pressure – (116±4) kPa – and voltage (50 V) were applied for 8 minutes. Initial dryness was (14.3±0.3)%.

| **Electrolyte** | **mmol cation** | **Final dryness (%)** | **Increase in dryness (%)** | **Total energy per kg of extracted water (kWh/kg)** | **Volume variation (%)** |
|---|---|---|---|---|---|
| $H_2O$ | --- | 26±3 | 82±21 | 0.29±0.02 | -(47±8) |
| NaCl | 4.4 | 42 | 193 | 0.33 | -70 |
| $CaCl_2$ | 2.2 | 41 | 186 | 0.35 | -67 |
| $CeCl_3$ | 2.2 | 41 | 190 | 0.34 | -68 |

The highest final dryness is not significantly different for $Na^+$, $Ca^{2+}$ or $Ce^{3+}$. However, in the case of sodium, the amount of salt required to achieve this performance is higher by a factor of two of the one required by either calcium or cerium cations. Therefore, the electrodewatering performances per cation decreases in the series: $Ce^{3+}$, $Ca^{2+} > Na^+$. In Table 5.2, the total energy spent is not significantly different and neither is the variation of volume, when comparing the different metal cations.

### *5.2.3.3 Other +2 and +3 cations*

The range at which +2 and +3 metal cation performances in electrodewatering is the best is 2.2-4.4 and 1.5-4.4 mmol for $Ca^{2+}$ and $Ce^{3+}$, respectively. Other +2 and +3 cations were tested at 2.2 and 1.5 mmol of added cation. The results are shown in Figure 5.11. Further details are presented in Tables A.16 and A1.17.

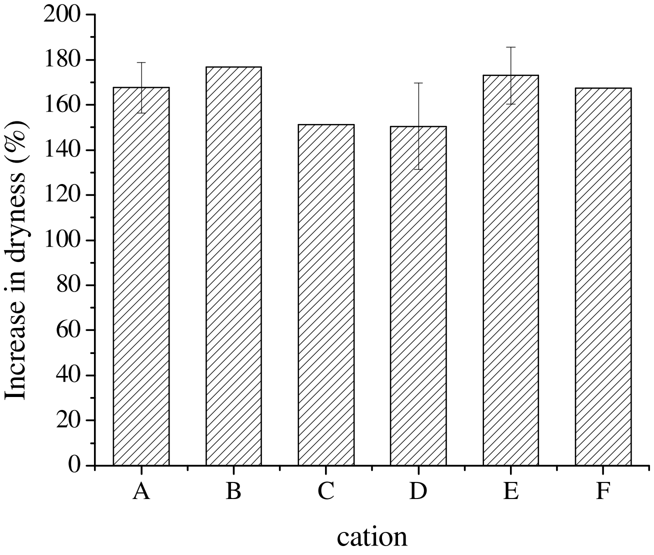

**Figure 5.11** Increase in dryness caused by the addition of +2 and +3 metal cations solution to La Prairie municipal sludge. Initial dryness was (14.3±0.3)%. Tests performed with Ovivo dewatering cell; pressure – (116±4) kPa – and voltage (50 V) were applied for 8 minutes. A – $CaCl_2$ 2.2 mmol, B – $Ca(NO_3)_2$ 2.2 mmol, C – $Cu(SO_4)_2$ 2.2 mmol, D – $CeCl_3$ 1.5 mmol, E – $FeCl_3$ 1.5 mmol, F – $AlCl_3$ 1.5 mmol

There are no significant differences among +2 or +3 cations in the electrodewatering of municipal sludge. Also, the energy consumption is practically the same for all salts (Figure 5.12). All tested +2 and +3 cations have a similar effect in electrodewatering of municipal sludge.

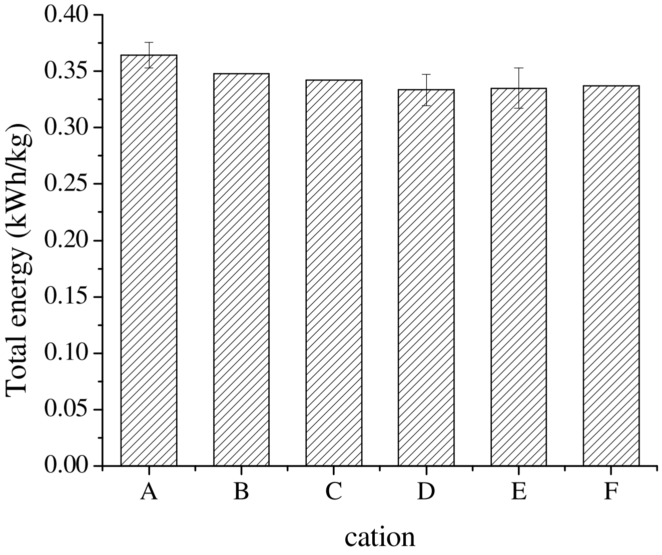

**Figure 5.12** Variation of total energy consumption caused by the addition of +2 and +3 metal cations solution to La Prairie municipal sludge. Initial dryness was (14.3±0.3)%. Tests performed with Ovivo dewatering cell; pressure – (116±4) kPa – and voltage (50 V) were applied for 8 minutes. A – $CaCl_2$ 2.2 mmol, B – $Ca(NO_3)_2$ 2.2 mmol, C – $Cu(SO_4)_2$ 2.2 mmol, D – $CeCl_3$ 1.5 mmol, E – $FeCl_3$ 1.5 mmol, F – $AlCl_3$ 1.5 mmol

### 5.2.4 Effect of anions and pH in the electrodewatering

Different sodium salts were tested in electrodewatering of municipal sludge at 4.4 mmol of added cation. The increase in dryness observed during these experiments is shown in Figure 5.13. Further details are given in table A1.18

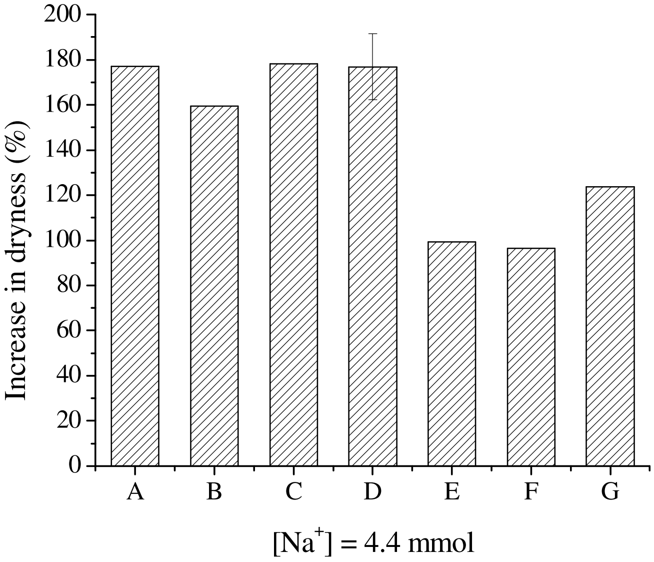

**Figure 5.13** Increase in dryness caused by the addition of different sodium salts solution to La Prairie municipal sludge. Initial dryness was (14.3±0.3)%. Tests performed with Ovivo dewatering cell; pressure – (116±4) kPa – and voltage (50 V) were applied for 8 minutes. A= $NaClO_3$, B=$Na_2SO_4$, C=$NaNO_3$, D=NaCl, E=$NaHCO_3$, F=$Na_2CO_3$, G=NaOH

Within experimental error, the increase of dryness for $ClO_3^-$, $SO_4^{2-}$ , $NO_3^-$ and $Cl^-$ is the same (~175%). In comparison, $OH^-$, $HCO_3^-$ and $CO_3^{2-}$ do not show any significant increase in dryness compared to deionized water. It is hypothesized that this effect is due to the high pH effect. A similar effect has already been observed in the dewatering of kaolin plus xanthan gum sludge (Chapter 4 section 4.2.4). The energy spent in these experiments is practically the same for all salts (figure 5.14).

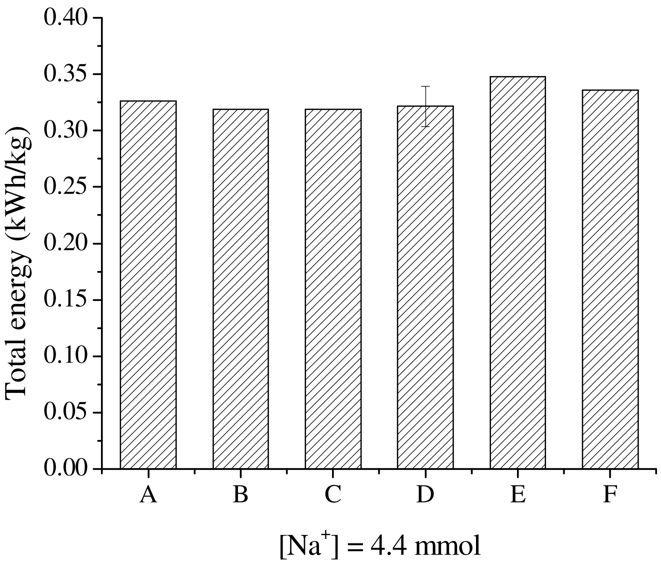

**Figure 5.14** Variation in the total energy consumed during the dewatering of municipal sludge upon addition of different sodium salts solutions. Initial dryness was (14.3±0.3)%. Tests performed with Ovivo dewatering cell; pressure – (116±4) kPa – and voltage (50 V) were applied for 8 minutes. A= $NaClO_3$, B=$Na_2SO_4$, C=$NaNO_3$, D=NaCl, E=$NaHCO_3$, F=$Na_2CO_3$. No available data for NaOH.

The effect on electrodewatering of the addition of HCl solution is given in Table 5.3. The increase in dryness reaches 166 % at 4.4 mmol HCl. This effect is similar to the one presented by the addition of other electrolytes with other plus one cations at the same concentration (see Fig. 5.7). As comparison, NaCl induces an increase in dryness of (177±15)%.

**Table 5.3** Effect of the addition of HCl 4.4 mmol on the electrodewatering of municipal sludge from La Prairie. Tests performed with Ovivo dewatering cell; pressure – (116±4) kPa – and voltage (50 V) were applied for 8 minutes.

| Electrolyte | Final wt% solid | Increase in dryness (%) | Total water loss (g) | Water loss by evaporation (%) | Total energy (kWh/kg) |
|---|---|---|---|---|---|
| HCl 4.4 mmol | 38 | 166 | 91 | 21 | 0.32 |

## 5.3 Results discussion

The electrodewatering profile of a municipal sludge (Figure 5.1) resembles that of kaolin plus xanthan gum sludge. Two main features are common: (i) no water is extracted in the compression step, and (ii) dewatering increases progressively with time over a 60 minutes period following the application of voltage. This is not case for the kaolin sludge where the electrodewatering process is practically finished 10 minutes after the application of voltage.

For the municipal sludge, the current density (Figure 5.2) decreases after the first initial burst. Some spikes are observed over time which can be due to the formation of an insulating gas layer immediately beneath the anode that reduces momentarily the current [5]. However, when the gas escapes – because of the continuous application of pressure – and the sludge is further compressed, the anode is again in good contact with the sludge and the current goes up again. The temperature of the sludge (Figure 5.3) increases with time to reach a maximum. It then decreases slowly. The temperature increase favors the evaporation of water and facilitates the removal of water from the sludge because of the consequent decrease in viscosity [6]. Again, the time variations of the current density and temperature of municipal sludge are very similar with the ones observed for kaolin plus xanthan gum sludge.

The initial dryness of municipal sludge collected at La Prairie varies from 13.8 to 14.8%, over a four-month period during which nine samples were taken and tested. The final solids content after 8 minutes of electrodewatering is (26±3)%. The standard deviation found is comparable to values found by other authors in similar tests [7]. Due to the difference in initial dryness between the various samples, the electrodewatering results are better represented by the increase in dryness (Equation 5.1) rather than by the total amount of extracted water or the final dryness, as it was the case for kaolin and kaolin plus xanthan gum sludges. Therefore, the increase in dryness achieved by the application of an electrical field combined with pressure is (82±21)%. This corresponds to a volume reduction of (47±8)%. The energy consumption per kilogram of extracted water is (0.29±0.02) kWh/kg. This represents about four times less energy when compared to a thermal drying process.

In order to improve the electrodewatering of municipal sludge, different metal cations were studied as additives. Aqueous solutions of the various salts were added to the side of the sludge in contact with the anode, immediately before the beginning of the test. This was done to take advantage of electromigration taking place upon application of the electric field. Thus, cations of the added salts could migrate through the sludge towards the cathode dragging along with them the water molecules of their solvation shell and also influencing the electroosmotic flow.

Tests performed with NaCl, $CaCl_2$ and $CeCl_3$ (Figure 5.9) over a range of concentrations showed that these salts behave similarly during the electrodewatering of municipal sludge. The dryness increases with the concentration of the added salt up to a maximum. Further increase in concentration causes a decrease of the dryness. The optimal concentration interval is 4.4-7.5, 2.2-4.4, and 1.5-4.4 mmol for NaCl, $CaCl_2$ and $CeCl_3$, respectively. In these ranges of concentration, there is a factor of two in the increase of dryness of municipal sludge compared to deionized water. The solids content at the end of the experiment can be almost a factor of 3 higher than the initial values. Also, the energy spent to dewater the municipal sludge is about 0.32, 0.36-0.43, and 0.33-0.39 kWh/kg, for $Na^+$, $Ca^{2+}$ and $Ce^{3+}$, respectively. In the case of NaCl, increasing the salt concentration does not influence significantly the energy consumed. Precipitation of $Ca(OH)_2$ and $Ce(OH)_3$ on the cathode side due to high pH resulting from water electrolysis (equation 1.2) can be the reason why there is an increase in the energy spent when the concentrations of $Ca^{2+}$ and $Ce^{3+}$ are increased. The introduction of metal cations leads to a decrease in volume that can be as high as 70% relative to the starting material. This will have a positive impact on the transport and the disposal of sludge.

From the results presented before, we can conclude that dewatering of municipal sludge is better in the presence of $Ce^{3+}$, $Ca^{2+} > Na^+$. Also, as seen in Table 5.1, it takes twice as much $Na^+$ cation than $Ca^{2+}$ or $Ce^{3+}$ to achieve the same final dryness. This effect is suggesting that the addition of cations is also acting on the agglomeration of the sludge particles to facilitate the removal of water molecules. High valence cations are better coagulating agents and hence higher amount of $Na^+$ is needed to produce the same effects as lower concentrations of $Ca^{2+}$ or $Ce^{3+}$. The agglomeration effect caused by the presence of metal cations is related to the affinity of each cation with the surface of the sludge particles. The stronger the interaction between the cation and the surface of the sludge particle the more efficient that cation will be to shield the negative surface charge of the particles, therefore promoting coagulation. In chapter 6, it will be shown that interactions with sludge particles surface increases in the series: $Na^+$, $Ca^{2+} < Ce^{3+}$, which then explains the better electrodewatering performances shown by plus 2 and plus 3 cations. The same behavior was observed during the electrodewatering of kaolin plus xanthan gum.

Testing of other monovalent metal cations at the same concentration show there is no difference in performance among the cations of alkali metals: $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$. A similar phenomenon was observed in the electrodewatering of kaolin plus xanthan gum sludge. The effect of the counter ion is only significant if it induces a change in the pH of the electrolyte. Thus, very similar final solid contents were observed for $ClO_3^-$, $SO_4^{2-}$, $NO_3^-$ and $Cl^-$. In the case of $OH^-$, $HCO_3^-$ and $CO_3^{2-}$, the final dryness of the municipal sludge was only 75% of that reached by the previous series. This effect is related to the electrolyte being at a pH higher than 12.

## 5.4 Conclusions

The electrodewatering behavior of a municipal sludge is very similar to the one observed in kaolin plus xanthan gum sludge. In both cases, no dewatering occurs with the application of pressure only and the different metal cations tested in this study have a similar effect. Higher valence metal cations show a higher increase in dryness: $Ce^{3+}$, $Ca^{2+} > Na^+$. No significant differences were observed among other +1 or +2 or even +3 cations. The counterions do not influence significantly the electrodewatering as long as the pH of the solution remains lower than 7.

The addition of metal cations to a municipal sludge improves its dewatering and the final solid content may increase by a factor of 3 when compared with initial values or a factor of 2 when compared to deionized water. In the optimal conditions, the energy spent per kilogram of water extracted is about four times lower than in thermal drying. Another important aspect is that electrodewatering is accompanied by a decrease of the volume of the sludge cake that can be reduced by up to 70% compared to the initial volume. The increase in dryness (with consequent volume reduction) and the lower energy consumption are the main advantages of the electrodewatering process of municipal sludge that motivates the research around this topic.

## 5.5 References

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# Chapter 6 – Adsorption of Metal Cations

## 6.1 Introduction

Kaolin is composed of particles of alternate alumina and silica layers. In general, these particles are hexagonal in shape and have a diameter of 0.5-1.0 μm and are 0.1 μm thick [1]. From a global point of view, the charge of the kaolin particles is pH dependent. On the flat surfaces, the surface charge is always negative, whereas at the edges of the particles, the surface charge is positive for acidic pH's and negative for basic pH's (Chapter 3). Kaolin particles will interact with metal cations according to their nature and concentration. For cations with the same valence, the higher the ionic radius (which results in a higher polarizability) the stronger will be the adsorption of that cation to the surface of kaolin. Therefore, the relative adsorption affinity varies along the series [2]:

$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$.

Multivalent cations interact strongly with kaolin surface as it can be seen by the changes of zeta-potential in presence of +2 or +3 cations, where a concentration increase leads to a decrease of the zeta-potential and even a change of its sign [3, 4].

The municipal sludge particles are also negatively charged at their surfaces due to the presence of ionizable groups (such as carboxyl and hydroxyl groups) that are part of the biomolecules naturally present in the sludge. This means that adsorption of cations can also occur, and in fact, multivalent metal cations haven been used in the flocculation of municipal sludge to improve its dewaterability [5].

The interaction of Li, Na, Ca and Ce cations with kaolin and municipal sludge particles was studied. Kaolin or municipal sludge was suspended in an electrolyte solution (Li, Na, Ca, Ce or deionized water). After stirring, the solids were filtered out and the remaining solutions were analyzed for the metal content by ICP-AES method. The adsorption of a metal cation to the surface of the solid (kaolin or municipal sludge) is given by the difference between the concentration of the starting electrolyte and the concentration of that metal cation in the filtrate.

The experiments thus performed are referred to as "one-batch" experiments in the sections below. The interaction of metal cations with the kaolin surface was further investigated by measuring the metal content of the filtrates obtained from the electrodewatering experiments performed in Chapters 3 and 4.

## 6.2 Results

### 6.2.1 Kaolin one-batch adsorption experiments

#### *6.2.1.1 Adsorption of metal cations*

The $Li^+$, $Na^+$, $Ca^{2+}$ and $Ce^{3+}$ content of kaolin (50 g/L) suspensions in deionized water was measured (kaolin batch B was used throughout all experiments). Suspensions were stirred overnight at room temperature. The following day, the supernatant was filtered (45 µm filter porosity) and the metal content was measured by ICP. The results are shown in Table 6.1.

**Table 6.1** $Li^+$, $Na^+$, $Ca^{2+}$ and $Ce^{3+}$ content in of kaolin (50 g/L) suspensions in deionized water. Values shown are average ± standard deviation.

| Cation | $M^{n+}$ (mg) | mg $M^{n+}$/kg kaolin |
|---|---|---|
| $Li^+$ | Not detected | |
| $Na^+$ | $(1130\pm5)\times10^{-3}$ | $452\pm2$ |
| $Ca^{2+}$ | $(15.0\pm0.3)\times10^{-3}$ | $6.0\pm0.1$ |
| $Ce^{3+}$ | Not detected | |

The ICP measurements give the amount of metal cations that were washed out from the kaolin particles to the solution (deionized water). As shown in Table 6.1, kaolin is a source for both sodium and calcium ions, whereas neither lithium nor cerium was detected.

The adsorption of metal cations to kaolin surface was first studied with calcium. $CaCl_2$ at 0.002 M was mixed with kaolin so as to prepare 50, 100 and 150 g/L suspensions of kaolin. After overnight stirring, the kaolin was filtered out and the calcium content in the remaining solution was measured by ICP. The adsorption was determined as mentioned before (Section 6.1). The results are shown in Figure 6.1 (full details in Table A2.1).

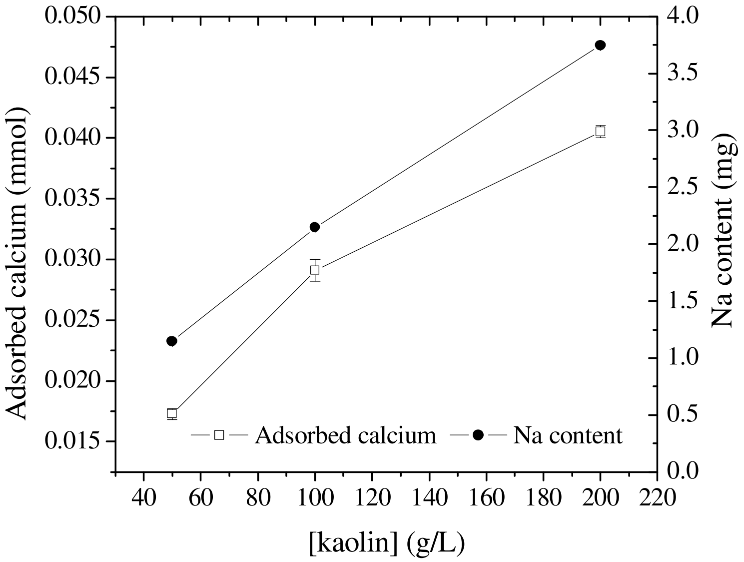

**Figure 6.1** Adsorbed calcium as a function of the concentration of kaolin. $CaCl_2$ 0.002 M was used as starting solution. Sodium content is also shown.

At the same $CaCl_2$ concentration (Figure 6.1), an increase in the amount of kaolin results in an increase of adsorbed $Ca^{2+}$. At the same time, the sodium content increases linearly with an increase in the kaolin concentration. This increase is expected because of the naturally occurring sodium in the kaolin used, as seen in Table 6.1.

The adsorption of different metal cations ($Li^+$, $Na^+$, $Ca^{2+}$ and $Ce^{3+}$) was studied at a fixed concentration (0.002 M) using a suspension of kaolin (50 g/L). The results are presented in Figure 6.2.

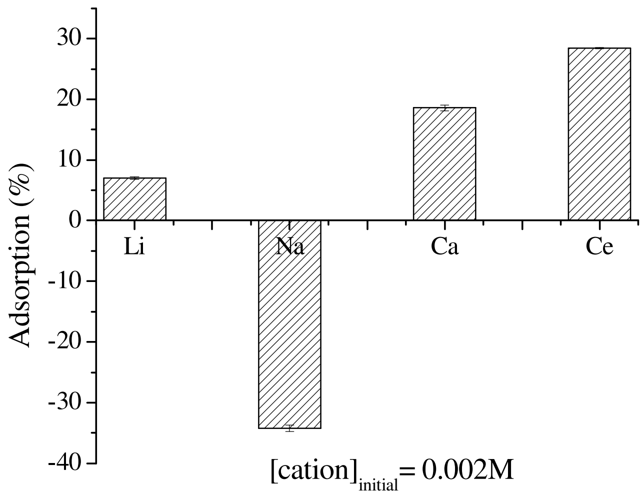

**Figure 6.2** Metal cation adsorption as a function of the nature of cation (0.002 M). In all cases, a 50 g/L kaolin suspension was used, that was stirred overnight prior to ICP analysis.

As shown in Fig. 6.2, the adsorption is different depending on the nature of the metal cation as a result of different interactions with the kaolin surface. The experiments performed with LiCl, $CaCl_2$ and $CeCl_3$ show that an increase in the charge of the metal cation results in an increase of adsorption. Sodium (NaCl) is an exception because of the high sodium content of the kaolin used (there is on average (452±2) mg of sodium per kilogram of kaolin).

#### *6.2.1.2 Adsorption of $H^+$*

Kaolin was mixed with LiCl 0.002 M at two different starting pH's: 6.8±0.1 and 3.13±0.08. In that later case, the pH was adjusted with HCl solution. The pH's of the solution and its Li content were measured before and after the addition of kaolin. The results are shown in Table 6.2.

**Table 6.2** pH and Li content for suspensions of kaolin in LiCl 0.002 M at initial neutral and acid pH, before (a) and after (b) addition of kaolin (50 g/L suspension).

| (a) | | (b) | |
|---|---|---|---|
| **pH** | **[Li] / ppm** | **pH** | **[Li] / ppm** |
| 6.8±0.1 | 14.641±0.006 | 5.83±0.08 | 13.61±0.02 |
| 3.13±0.08 | 14.76±0.06 | 4.39±0.03 | 14.5±0.1 |

After the addition of kaolin (second column of Table 6.2), the pH of the suspension changes: it decreases from 6.8 ± 0.1 to 5.83 ± 0.08 when the initial pH is neutral and it increases from 3.13 ± 0.08 to 4.39 ± 0.03 when the initial pH is acidic. This increase in pH could be indicating an adsorption of protons to the kaolin surface, upon preparation of the kaolin suspension. On the other hand, the decrease of the pH observed could be the result of desorption of $H^+$ initially present on the kaolin surface. When the initial pH is neutral, the concentration of $Li^+$ in solution decreases upon the addition of kaolin. In the second case, when the initial pH is acidic, the concentration of $Li^+$ remains unchanged. Upon adsorption of $H^+$, the adsorption of $Li^+$ no longer occurs. This suggests that $H^+$ and $Li^+$ are competing for the same adsorption centers in the kaolin.

### 6.2.2 Municipal sludge one-batch adsorption experiments

The $Li^+$, $Na^+$, $Ca^{2+}$ and $Ce^{3+}$ content of municipal sludge (50 g/L suspension) in deionized water was measured. The suspensions were stirred for one hour at room temperature. The supernatant was then filtered (45 µm filter porosity) and the metal content was measured by ICP. The results are shown in Table 6.3.

**Table 6.3** $Li^+$, $Na^+$, $Ca^{2+}$ and $Ce^{3+}$ content of municipal sludge (50g/L suspension) in deionized water. Values shown are average ± standard deviation.

| **Cation** | **$M^{n+}$ (mg)** | **mg $M^{n+}$/kg municipal sludge** |
|---|---|---|
| $Li^+$ | Not detected | |
| $Na^+$ | 1.034±0.002 | 414.4±0.9 |
| $Ca^{2+}$ | 1.065±0.005 | 426±2 |
| $Ce^{3+}$ | Not detected | |

As shown in Table 6.2, municipal sludge is a source of both sodium and calcium ions, whereas neither lithium nor cerium was detected.

The adsorption of $Li^+$, $Na^+$, $Ca^{2+}$, and $Ce^{3+}$ was measured municipal sludge suspensions (50 g/L). The results are shown in Figure 6.3.

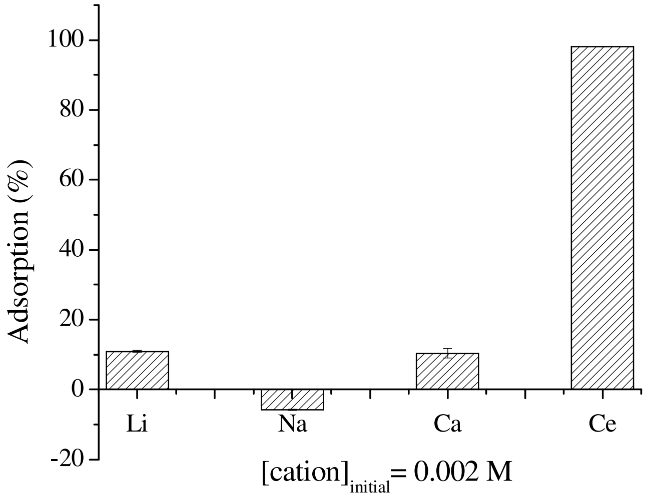

**Figure 6.3** Metal cation adsorption as a function of the nature of cation (0.002 M). In all cases, 50 g/L municipal sludge suspensions were used and stirred for one hour prior to ICP analysis.

The metal cations (Figure 6.3) with the higher charge are the ones that are more adsorbed.

### 6.2.3 Determination of the metal content in the filtrates from the electrodewatering of kaolin sludge

In the electrodewatering of kaolin, it is possible to distinguish two different steps (chapter 3 section 3.2.2). At the beginning, dewatering is observed upon the application of pressure alone. Then, dewatering occurs when the voltage is turned on. The two filtrates (filtrate 1 from the pressure step, and filtrate 2 from the pressure plus voltage step) were both analyzed for the metal content for experiments with kaolin mixed with different electrolytes (LiCl, NaCl, $CaCl_2$ and $CeCl_3$) in the concentration range 0-0.2 M. The results for experiments at 0 and 0.002 M are shown in Tables 6.4 and 6.5, respectively. All other concentrations are shown in table A2.4 in the appendix.

**Table 6.4** Metal content of filtrates from electrodewatering of kaolin sludge at 62% initial dryness (blank experiments). The sludge was prepared with deionized water.

|  | **Filtrate 1** | **Filtrate 2** |
|---|---|---|
| **Cation** | **mg $M^{n+}$ / kg filtrate** | **mg $M^{n+}$ / kg filtrate** |
| $Li^+$ | Not detected |  |
| $Na^+$ | 343±2 | 805±8 |
| $Ca^{2+}$ | 38.9±0.3 | 19.0±0.2 |
| $Ce^{3+}$ | Not detected |  |

**Table 6.5** Metal content of the filtrates recovered from electrodewatering experiments of kaolin in the presence of different electrolytes. The metal contents of the starting electrolytes solutions are also given for reference.

| Electrolyte | Initial solution<br>mg $M^{n+}$/ kg solution | Filtrate 1<br>mg $M^{n+}$/ kg filtrate | Filtrate 2<br>mg $M^{n+}$/ kg filtrate |
|---|---|---|---|
| LiCl 0.002M | 14.40±0.07 | 9.52±0.05 | 15.26±0.06 |
| NaCl 0.002M | 48.1±0.1 | 401.8±0.7 | 1031±9 |
| $CaCl_2$ 0.002M | 74.4±0.4 | 41.1±0.4 | 26.7±0.1 |
| $CeCl_3$ 0.002M | 278±5 | 0.94±0.01 | 0.12±0.01 |

$Li^+$ and $Ce^{3+}$ are not present in the filtrates obtained from the electrodewatering of sludge composed of kaolin and deionized water (Table 6.4). However, sodium and calcium are present in both filtrates. The sodium content increases from (343±2) to (805±8) mg/kg of filtrate by turning on the voltage, whereas the calcium content decreases from (38.9±0.3) to (19.0±0.2) mg/kg of filtrate.

As shown in Table 6.5, filtrates 1 and 2 are generally less concentrated in lithium, calcium and cerium chloride than the initial solutions, with the exception of filtrate 2 in the LiCl experiment. In the case of sodium, the opposite is observed, and there is an increase in the sodium concentration consistent with the residual sodium present in kaolin sludge (Table 6.4). Furthermore, in the presence of LiCl, $CaCl_2$ and $CeCl_3$, the amount of sodium in filtrate 1 increases, as if the cations of these salts were able to replace sodium (shown in Table 6.6). This effect is more pronounced for the highest concentrations of salt and the concentrations of sodium can almost double the value found when deionized water is used as an electrolyte. For example, in the presence of $CeCl_3$ 0.2 M, the sodium content of filtrate 1 is (614±3) mg/kg filtrate. When water is used as electrolyte the sodium content is about 1.8 times less, this is, (343±2) mg/kg filtrate.

**Table 6.6** Sodium content of filtrate 1 for the dewatering of kaolin sludge with different electrolytes at 0-0.2 M.

| Electrolyte | Filtrate 1<br>mg Na / kg filtrate |
|---|---|
| Water | 343±2 |
| LiCl 0.002M | 351±3 |
| LiCl 0.02M | 471±2 |
| LiCl 0.1M | 532±2 |
| LiCl 0.2M | 591±3 |
| $CaCl_2$ 0.002M | Not measured |
| $CaCl_2$ 0.02M | 566.6±0.3 |
| $CaCl_2$ 0.1M | 608±2 |
| $CaCl_2$ 0.2M | 664±3 |
| $CeCl_3$ 0.002M | 390±2 |
| $CeCl_3$ 0.02M | 540.8±0.9 |
| $CeCl_3$ 0.1M | 576±2 |
| $CeCl_3$ 0.2M | 614±3 |

### 6.2.4 Determination of metal content in filtrates from electrodewatering of kaolin plus xanthan gum sludge

The filtrates obtained from the electrodewatering of kaolin plus xanthan gum were analyzed for their metal content. There was undissolved material in all experiments that was filtered out from solution prior to ICP analysis. The results are shown in Tables 6.7 and 6.8.

**Table 6.7** Metal content of filtrates from electrodewatering of kaolin plus xanthan gum sludge at 62% initial dryness (blank experiments). The sludge was prepared with deionized water.

| **Cation** | **mg $M^{n+}$ / kg filtrate** |
|---|---|
| $Li^+$ | Not detected |
| $Na^+$ | 11781±24 |
| $Ca^{2+}$ | 86±2 |
| $Ce^{3+}$ | Not detected |

**Table 6.8** Metal content of the filtrates recovered from electrodewatering experiments of kaolin in the presence of different electrolytes. The metal contents of the starting electrolytes solutions are also presented for reference.

| **Electrolyte** | **Initial solution** mg M/ kg solution | **Filtrate** mg $M^{n+}$/ kg filtrate | **Filtrate** mg $Na^+$ / kg filtrate |
|---|---|---|---|
| LiCl 0.002M | 14.40±0.07 | 3.09±0.01 | 11878±49 |
| LiCl 0.02M | 134.1±0.6 | 168.4±0.3 | 12587±60 |
| LiCl 0.1M | 661.0±0.4 | 965±1 | 11513±9 |
| LiCl 0.2M | 1338±9 | 1973±3 | 12111±15 |
| $CaCl_2$ 0.002M | 74.4±0.4 | 2.08±0.06 | 9514±38 |
| $CaCl_2$ 0.2M | 7395±33 | 345.3±0.8 | 17358±21 |
| $CeCl_3$ 0.2M | 24049±12 | 1389±5 | Not measured |

As shown in Table 6.7, both sodium and calcium are present in the filtrates obtained from electrodewatering of kaolin plus xanthan gum sludge prepared with deionized water, Moreover, the sodium content is higher (about 15 times more) than the one obtained from the electrodewatering of kaolin alone (Table 6.4). The very high sodium content of all filtrates precludes any further analysis of the electrodewatering experiments where NaCl was intentionally added. No lithium or cerium is present in the kaolin plus xanthan gum sludge (Table 6.7).

As shown in Table 6.8, the concentration of lithium generally increases in the filtrate, whereas the concentrations of calcium and cerium decrease with respect to their values in the starting electrolyte.

## 6.3 Results discussion

A suspension of kaolin in deionized water was analyzed by ICP for its Li, Na, Ca and Ce content. It was found that sodium and calcium are both present in solution and the concentration of sodium is about 75 times higher than the concentration of calcium. These cations originate from kaolin but it is not possible to distinguish between cations that were present to compensate the negative charge of kaolin from those that may come from impurities mixed with the kaolin.

The first studies of adsorption were focused on calcium, to verify the evolution of adsorption as a function of concentration of kaolin. An increase in the concentration of kaolin in the range 50-200 g/L results in an increase of the adsorption of calcium (Figure 6.1). At 50 g/L, about 18% of the initial calcium ions present in the solution are adsorbed on the surface of kaolin. The adsorption increases to 44% when kaolin concentration increases to 200 g/L, consistent with the idea that an increase in the concentration of kaolin leads to an increase in the amount of active sites that can adsorb calcium ions. The sodium content increases with the concentration of kaolin, as expected, since sodium in naturally present in the kaolin used.

The adsorption of metal cations was also studied with respect to the nature of the cation. The studies were performed at 0.002 M and 50 g/L of kaolin. Figure 6.2 shows that the adsorption increases along the series: $Ce^{3+} > Ca^{2+} > Li^{+}$. Furthermore, about 2.3 times more $Ca^{2+}$ and 3.6 times more $Ce^{3+}$ are adsorbed compared to $Li^{+}$. The relation between metal cation charge and the adsorption on kaolin is plotted in Figure 6.4.

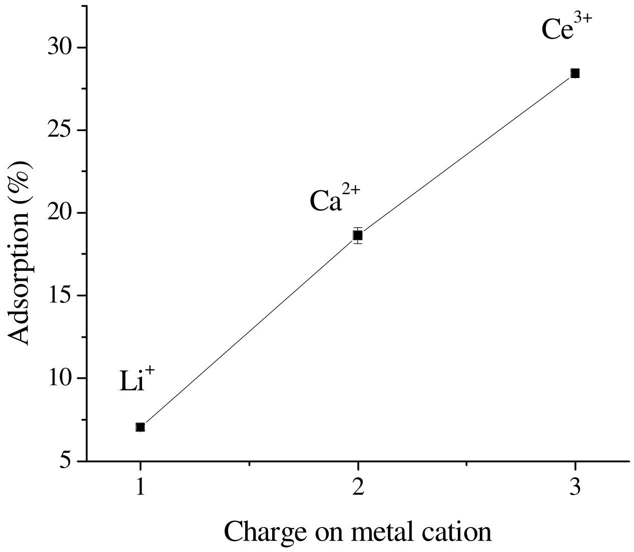

**Figure 6.4** Relation between the adsorption on kaolin of a metal cation and its intrinsic charge.

Figure 6.4 shows that there is an almost linear relation between the charge of the metal cation charge and its adsorption on kaolin.

The sodium is a particular case due to the fact that it is already present in large quantities in kaolin. Because of this, the addition of NaCl 0.002 M to a kaolin suspension (50 g/L) results in a final concentration of $Na^+$ higher than 0.002 M which explains the negative variation (-34%) observed in Figure 6.2. Nonetheless, the figure obtained by adding the concentration of the initial electrolyte to the concentration of sodium naturally present in kaolin is higher than the measured concentration. Hence, 14% of the sodium initial present in the 0.002 M solution binds to the kaolin surface. The later value is consistent with the assumption that the affinity with kaolin increases with increase ionic radius: $Li^+ < Na^+$, as a consequence of the increase in polarizability (the amount of lithium adsorbed is 7%). Overall, the adsorption to kaolin increases in the series: $Li^+ < Na^+, Ca^{2+} < Ce^{3+}$. The position of sodium relative to calcium may seem irrelevant to the charge on each metal but it is more of a consequence of the fact that sodium is present in large amounts in the kaolin.

The adsorption of lithium ion was also studied at acidic pH (Table 6.2). Acidification of the initial LiCl 0.002 M solution to pH 3 reduces the adsorption of Li from 7 to 2%. The final pH of the suspension is less acidic than the initial pH of the same solution, which seems to indicate that protons are being adsorbed to the surface of kaolin as well. It is speculated that these adsorbed protons would decrease the adsorption of lithium ions, possibly because of a reduction of negative surface charges that are being shielded by the newly adsorbed protons.

About the same amounts of sodium and calcium were found in a suspension of municipal sludge in deionized water (Table 6.3). Neither lithium nor cerium was present in solution. Once again, adsorption is favored for cations with the higher charge. For example, $Ce^{3+}$ is about 9.8 times more adsorbed than $Li^{+}$. In the case of sodium and calcium, due to their residual concentration, the variation in final concentration is -6 and 10%, respectively. As explained before for sodium and kaolin, the adsorption of sodium and calcium is around 40 and 37%, respectively. Overall, adsorption of metal cations to municipal sludge occurs along a series similar to the one observed for kaolin ($Li^{+} < Na^{+}$, $Ca^{2+} < Ce^{3+}$) and differences lie mostly on the extent at which the adsorption occurs for each individual metal cation.

The metal contents of the filtrates obtained from electrodewatering of kaolin mixed with different metal cations were measured by ICP (Tables 6.4 and 6.5). The two filtrates obtained in the electrodewatering of kaolin mixed with deionized water (blank experiments) show the presence of sodium and calcium, but not that of lithium and cerium, in accordance with the results obtained in the one batch experiments. Furthermore, the concentration of sodium practically doubles from filtrate 1 to filtrate 2, whereas that of calcium roughly decreases by half. Upon turning on the voltage, electrokinetic phenomena take place, and so does electromigration. The effect of electromigration is easily observed for sodium since its concentration increases significantly upon the application of voltage. This is not the case of calcium and the difference may be due to different solubility of sodium and calcium in basic medium. As a consequence of water electrolysis, a pH gradient is formed throughout the sludge cake and higher pH's are found near the cathode. When sodium and calcium reach the cathode as a consequence of the electrical potential difference imposed on the sludge cake, they will reach a region of very high pH (pH's close to 12 have been reported for the water recovered at the cathode [6]). At this high pH, calcium may precipitate on the sludge cake as hydroxide ($Ca(OH)_2$ is slightly soluble with $pK_{ps}$ of 5.33 [7]). In comparison, sodium hydroxide is very soluble and the precipitation of NaOH is less important. This could then justify the decrease in the calcium content as opposed to sodium.

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The measurements of metal contents of the filtrates obtained in electrodewatering of kaolin with LiCl, NaCl, $CaCl_2$ and $CeCl_3$ also show the preferential adsorption of high valence metal cations, already observed for the one batch experiments. In the case of lithium, calcium and cerium ions at 0.002 M, their concentration decreases in filtrate 1 (relative to the initial concentration), which indicates that they are being adsorbed on the kaolin particles. Moreover, the decrease observed is more pronounced in the series: $Li^+ < Ca^{2+} << Ce^{3+}$, indicating once again that the high valence cations are preferentially adsorbed. The application of voltage results in an increase in the concentration of lithium with respect to the added electrolyte. At the same time the concentrations of calcium and cerium are even lower in filtrate 2 than in filtrate 1. The higher concentration of $Li^+$ in filtrate 2 relative to the initial solution is once again a consequence of electromigration. For calcium and cerium, their precipitation as hydroxides close to the cathode is responsible for the further decrease in concentrations observed for filtrate 2 ($pK_{ps}$ for cerium hydroxide is as high as 24 [8]). In the case of sodium, filtrate 1 and filtrate 2 are more concentrated than the initial NaCl 0.002 M, because of the high residual concentration of sodium already present in kaolin. In general, the adsorption increases in the series $Na^+ < Li^+ < Ca^{2+} << Ce^{3+}$. In that series, the relative position of lithium and sodium ions is a consequence of the fact that sodium is present in high concentrations in kaolin. $Li^+$, $Ca^{2+}$ and $Ce^{3+}$ are also able to replace sodium in kaolin (Table 6.6) and the effect is more pronounced for high valence cations at the highest concentrations. The preferential adsorption of high valence cations justifies why an increase in concentration of these cations leads to a decrease of the zeta-potential and a decrease in electrodewatering.

The analysis of filtrates from electrodewatering of kaolin and xanthan gum (Tables 6.7 and 6.8) is not straightforward because filtrates had residual material which was not soluble and was therefore, filtered out of solution prior to ICP measurements. This could mean that the analysis did not include cations that are trapped in the undissolved material. However, the same trends were observed as in kaolin sludge dewatering experiments, that is, an increase in the concentration of lithium ions and a decrease of that of calcium and cerium compared to that of the electrolyte. The high concentration of sodium in all filtrates that were analyzed, including the blanks, invalidates the analysis of the electrodewatering of kaolin plus xanthan gum in the presence of different sodium concentrations. This high concentration of sodium originates from the xantham gum itself (35 mg of sodium are present in one gram of xanthan gum). Furthermore, this high concentration of sodium was shown to have an influence on the determination of calcium and cerium (Chapter 2 section 2.2.4). This results in an overestimation of the calcium and an underestimation of the cerium content, which means that the values presented in Tables 6.7 and 6.8 should be considered only in terms of orders of magnitude and not of real analytical values.

## 6.4 Conclusions

In general, the adsorption of metal cation on both kaolin and municipal sludge was found to increase along the series $Li^+ < Na^+$, $Ca^{2+} < Ce^{3+}$. The adsorption of high valence cations leads to a decrease of the thickness of electric double layer, as a result of the smaller hydration radius. Consequently, the absolute value of the zeta-potential decreases and so does the electroosmotic flow which has a negative impact on electrodewatering. This is what it is observed in the electrodewatering of kaolin. Furthermore, a decrease in the thickness of the electric double layer may also result in the coagulation of the sludge particles, increasing therefore the mechanical dewaterability of that sludge. This must be the predominant effect observed in the electrodewatering of municipal sludge, and the reason why $Ce^{3+}$ and $Ca^{2+}$ have a more positive effect than that of $Li^+$ or $Na^+$.

## 6.5 References

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# Chapter 7 – Conclusion

Three different electrodewatering systems were tested in this work, namely municipal, kaolin plus xanthan gum and kaolin sludges. Their electrodewatering profiles are shown in Figure 7.1. The dewatering of municipal sludge and kaolin plus xanthan gum occurs only when the voltage is applied. In both cases also, the amount of water extracted increases gradually over a 60 minutes period after the voltage is turned on. This behavior is different from that observed in the case of kaolin, where the electrodewatering is practically finished in the first 10 minutes following the application of voltage. Furthermore, kaolin dewaters during the first step (application of pressure only), a phenomenon not observed with municipal or kaolin plus xanthan gum sludges.

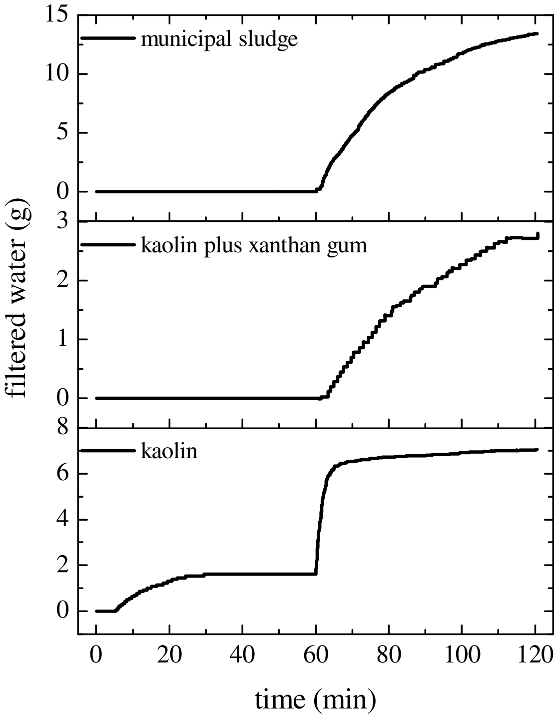

**Figure 7.1** Variation of the extracted water with time for electrodewatering of municipal sludge (78 kPa), kaolin plus xanthan gum (77 kPa) and kaolin (77 kPa); the voltage (50 V) was applied.

During electrodewatering of kaolin, about 20% of the total water extracted is due to the application of pressure, which makes this system different from the municipal sludge. Further comparison between the three different sludge types is made in Table 7.1.

**Table 7.1** Electrodewatering properties of kaolin, kaolin plus xanthan gum and municipal sludge.

| **Parameter** | **Kaolin** | **Municipal sludge** | **Kaolin plus xanthan gum** |
|---|---|---|---|
| Composition | Inorganic clay $Al_2(OH)_4Si_2O_5$ | Mixture of organic, biological and inorganic material | Mixture of inorganic clay plus organic solid |
| Initial dryness (%) | 62.03±0.02 | 14.3±0.3 | 62.04±0.01 |
| *Final dryness (%) | 74.38±0.03 | 26±3 | 66.2±0.6 |
| *Increase in dryness (%) | 18.9±0.7 | 82±21 | 6.7±0.9 |
| *Water loss by pressure (%) | 20±2 | No dewatering | No dewatering |
| *Water loss by electrodewatering (%) | 76±3 | 82±3 | 85±3 |
| *Water loss by evaporation (%) | 4±2 | 18±3 | 15±3 |
| Cation effect on dewatering (size) | $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ | $Li^+= Na^+= K^+= Rb^+= Cs^+$ | $Li^+= Na^+= K^+= Rb^+=Cs^+$ |
| Cation effect on dewatering (charge) | $Na^+ > Ca^{+2} > Ce^{+3}$ | $Ce^{3+}, Ca^{2+} > Na^+$ | $Ce^{3+} > Ca^{2+} > Na^+$ |
| Anion effect on dewatering | $Cl^-, NO_3^-, ClO_3^- > SO_4^{2-}$ | $Cl^-, NO_3^-, ClO_3^-, SO_4^{2-}$ | $Cl^- > NO_3^- > ClO_3^-, SO_4^{2-}$ |
| Metal adsorption (one-batch experiments) | $Li^+ < Na^+, Ca^{2+} < Ce^{3+}$ | $Li^+ < Na^+, Ca^{2+} < Ce^{3+}$ | Not tested |

* sludge prepared with deionized water

In the presence of small monovalent cations, such as $Li^+$ or $Na^+$, the electrodewatering of kaolin is increased, while high valence cations, such as $Ca^{2+}$ or $Ce^{3+}$, reduce electrodewatering as a consequence of their higher adsorption on kaolin surfaces. Adsorption of these cations leads to a decrease of the zeta-potential – and even a charge reversal – that will result in a more limited electroosmotic flow.

The addition of xanthan gum to kaolin results in a decrease of extracted water, consistent with the formation of a more dispersed sludge. In fact, by adding xanthan gum to kaolin, the electrodewatering properties of the sludge thus obtained resembles more closely those of the municipal sludge. In both cases, about 15% of the extracted water is due to evaporation and the addition of high valence cations increases the electrodewatering performances. In the case of municipal sludge, the addition of metal cations may even triple the solid content of the end product and cause a volume reduction that can be as high as 70% of its initial value. In optimized conditions, about four times less energy is required to extract a given amount of water when compared to a thermal drying process. As a consequence, the addition of a salt solution prior to the beginning of the electrodewatering process is an attractive method to treat municipal sludge residues. This is a simple approach which does not impose any major technical modifications to the equipment in order to be implemented. The scaling-up of the process should not, therefore, constitute a problem. Apart from the effectiveness of the metal cation in question, other considerations (environmental and economical) must be taken into account in order to choose the electrolyte to use at an industrial scale. However, this work has clearly shown that for better performances, high charge cations should be preferred.

The use of a synthetic model for municipal sludge, most notably the mixture of kaolin plus xanthan gum, has enabled a systematic study of the effect of metal cations in electrodewatering. A treatment procedure can now be envisaged following the results obtained with this model compound that were already confirmed in laboratory-scale experiments with municipal sludge. The synthetic sludge may also be used as a tool in more fundamental studies, such as the measurement of zeta-potential in order to predict the values with municipal sludge which is a less reliable system due to its natural variability in composition. Furthermore, comprehensive studies on the impact of other additives that affect electrodewatering, such as polymers and polyelectrolytes, may be accomplished using once again the synthetic model originally developed in this work.

## A1. Data from the electrodewatering experiments

**Table A1.1** Effect of the addition of LiCl on the electrodewatering properties of kaolin sludge with 62% initial dryness. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa. The total energy spent in the process per kilogram of water extracted only takes in consideration the water removed from the sludge after voltage was turned on.

| [LiCl] (M) | Total # of experiments | Final wt% solid | Increase in dryness (%) | mass of water recovered (g) | Maximum temperature ($^o$C) | Total energy (kWh/kg) |
|---|---|---|---|---|---|---|
| 0 | 13 | 73.8±0.4 | 18.9±0.7 | 6.9±0.2 | 52±5 | 0.9±0.1* |
| 0.002 | 1 | 74.3 | 19.7 | 7.1 | 58 | 1.0 |
| 0.02 | 1 | 74.4 | 20.0 | 7.2 | 70 | 1.1 |
| 0.1 | 1 | 75.6 | 21.8 | 7.7 | 78 | 1.5 |
| 0.2 | 1 | 76.2 | 22.9 | 8.0 | 110 | 2.1 |

*data for 9 experiments only

**Table A1.2** Effect of the addition of NaCl on the electrodewatering properties of kaolin sludge with 62% initial dryness. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa. The total energy spent in the process per kilogram of water extracted only takes in consideration the water removed from the sludge after voltage was turned on.

| [NaCl] (M) | Total # of experiments | Final wt% solid | Increase in dryness (%) | mass of water recovered (g) | Maximum temperature ($^o$C) | Total energy (kWh/kg) |
|---|---|---|---|---|---|---|
| 0 | 13 | 73.8±0.4 | 18.9±0.7 | 6.9±0.2 | 52±5 | 0.9±0.1* |
| 0.002 | 1 | 73.9 | 19.2 | 6.9 | 55 | 1.0 |
| 0.02 | 1 | 74.1 | 19.4 | 7.0 | 67 | 1.3 |
| 0.1 | 8 | 75.7±0.6 | 22.0±0.9 | 7.8±0.3 | 86±9 | 1.60±0.09 |
| 0.2 | 1 | 74.2 | 20.0 | 7.1 | 111 | 2.2 |

*data for 9 experiments only

**Table A1.3** Effect of the addition of KCl on the electrodewatering properties of kaolin sludge with 62% initial dryness. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa. The total energy spent in the process per kilogram of water extracted only takes in consideration the water removed from the sludge after voltage was turned on.

| [KCl] (M) | Total # of experiments | Final wt% solid | Increase in dryness (%) | mass of water recovered (g) | Maximum temperature (°C) | Total energy (kWh/kg) |
|---|---|---|---|---|---|---|
| 0 | 13 | 73.8±0.4 | 18.9±0.7 | 6.9±0.2 | 52±5 | 0.9±0.1* |
| 0.002 | 1 | 73.3 | 18.1 | 6.6 | 53 | n.m. |
| 0.02 | 1 | 74.0 | 19.3 | 7.0 | 61 | n.m. |
| 0.1 | 1 | 75.1 | 21.0 | 7.5 | 88 | n.m. |
| 0.2 | 1 | 71.4 | 15.1 | 5.7 | 102 | 2.6 |

*data for 9 experiments only

**Table A1.4** Effect of the addition of RbCl on the electrodewatering properties of kaolin sludge with 62% initial dryness. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa. The total energy spent in the process per kilogram of water extracted only takes in consideration the water removed from the sludge after voltage was turned on.

| [RbCl] (M) | Total # of experiments | Final wt% solid | Increase in dryness (%) | mass of water recovered (g) | Maximum temperature (°C) | Total energy (kWh/kg) |
|---|---|---|---|---|---|---|
| 0 | 13 | 73.8±0.4 | 18.9±0.7 | 6.9±0.2 | 52±5 | 0.9±0.1* |
| 0.002 | 1 | 73.3 | 18.2 | 6.7 | 62 | 1.1 |
| 0.02 | 1 | 73.0 | 17.6 | 6.5 | 65 | 0.9 |
| 0.1 | 1 | 73.8 | 18.9 | 6.9 | 90 | 1.9 |
| 0.2 | 1 | 71.5 | 15.3 | 5.7 | 98 | 2.6 |

*data for experiments only

**Table A1.5** Effect of the addition of CsCl on the electrodewatering properties of kaolin sludge with 62% initial dryness. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa. The total energy spent in the process per kilogram of water extracted only takes in consideration the water removed from the sludge after voltage was turned on.

| [CsCl] (M) | Total # of experiments | Final wt% solid | Increase in dryness (%) | mass of water recovered (g) | Maximum temperature ($^oC$) | Total energy (kWh/kg) |
|---|---|---|---|---|---|---|
| 0 | 13 | 73.8±0.4 | 18.9±0.7 | 6.9±0.2 | 52±5 | 0.9±0.1* |
| 0.002 | 1 | 73.0 | 17.7 | 6.5 | 53 | 1.0 |
| 0.02 | 1 | 72.4 | 15.7 | 6.2 | 68 | 1.3 |
| 0.1 | 1 | 71.8 | 16.7 | 5.8 | 80 | 2.0 |

*data for 9 experiments only

**Table A1.6** Effect of the addition of NaCl, $CaCl_2$ and $CeCl_3$ on the electrodewatering properties of kaolin sludge with 62% initial dryness. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa. The total energy spent in the process per kilogram of water extracted only takes in consideration the water removed from the sludge after voltage was turned on.

| Electrolyte | Total # of experiments | Final wt% solid | Increase in dryness (%) | mass of water recovered (g) | Maximum temperature (°C) | Total energy (kWh/kg) |
|---|---|---|---|---|---|---|
| Water | 13 | 73.8±0.4 | 18.9±0.7 | 6.9±0.2 | 52±5 | 0.9±0.1* |
| NaCl 0.002M | 1 | 73.9 | 19.2 | 6.9 | 55 | 1.0 |
| NaCl 0.02M | 1 | 74.1 | 19.4 | 7.0 | 67 | 1.3 |
| NaCl 0.1M | 8 | 75.7±0.6 | 22.0±0.9 | 7.8±0.3 | 86±9 | 1.60±0.09 |
| NaCl 0.2M | 1 | 74.2 | 20.0 | 7.1 | 111 | 2.2 |
| $CaCl_2$ 0.002M | 2 | 73.20±0.01 | 17.96±0.04 | 6.57±0.01 | 55.0±0.1 | 0.9 |
| $CaCl_2$ 0.02M | 2 | 72.8±0.3 | 17.4±0.4 | 6.4±0.1 | 66±6 | 1.50±0.07 |
| $CaCl_2$ 0.1M | 1 | 72.1 | 16.2 | 6.03 | 83 | 2.6 |
| $CaCl_2$ 0.2M | 2 | 69.6±0.5 | 12.2±0.8 | 4.7±0.3 | 99 | 5.1 |
| $CeCl_3$ 0.002M | 2 | 72.8±0.6 | 17±1 | 6.4±0.3 | 53±2 | 0.98±0.02 |
| $CeCl_3$ 0.02M | 2 | 69.2±0.1 | 11.5±0.2 | 4.45±0.06 | 35±1 | 0.85±0.02 |
| $CeCl_3$ 0.1M | 2 | 66.5±0.3 | 7.1±0.4 | 2.9±0.2 | 38.8±0.4 | 2.9±0.9 |
| $CeCl_3$ 0.2M | 1 | 66.6 | 7.3 | 2.9 | 44 | 2.7 |

*data for 9 experiments only

**Table A1.7** Effect of the addition of different electrolytes on the electrodewatering properties of kaolin sludge with 62% initial dryness. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa. The total energy spent in the process per kilogram of water extracted only takes in consideration the water removed from the sludge after voltage was turned on.

| Electrolyte | Final wt% solid | Increase in dryness (%) | mass of water recovered (g) | Maximum temperature ($^{o}$C) | Total energy (kWh/kg) |
|---|---|---|---|---|---|
| $MgSO_4$ 0.002M | 72.7 | 17.3 | 6.4 | 57 | 1.0 |
| $MgSO_4$ 0.02M | 72.8 | 17.3 | 6.4 | n.m. | 1.3 |
| $MgSO_4$ 0.05M | 72.7 | 17.1 | 6.3 | 70 | 1.5 |
| $MgSO_4$ 0.1M | 70.2 | 13.2 | 5.0 | n.m. | n.m. |
| $CuSO_4$ 0.001M | 73.5 | 18.5 | 6.7 | n.m. | n.m. |
| $CuSO_4$ 0.002M | 73.5 | 16.3 | 6.1 | n.m. | n.m. |
| $CuSO_4$ 0.02M | 72.2 | 15.7 | 5.9 | n.m. | n.m. |
| $CuSO_4$ 0.2M | 71.8 | 11.1 | 4.3 | n.m. | n.m. |
| $Ca(NO_3)_2$ 0.002M | 73.2 | 18.0 | 6.6 | 60 | 1.0 |
| $Ca(NO_3)_2$ 0.02M | 73.0 | 17.6 | 6.5 | 65 | 1.4 |
| $Ca(NO_3)_2$ 0.2M | 69.7 | 12.3 | 4.7 | n.m. | 3.2 |
| $Ca(SO_4)_2$ 0.002M | 73.5 | 18.5 | 6.7 | n.m | n.m. |
| $Al_2(SO_4)_3$ 0.001M | 72.3 | 16.4 | 6.1 | 45 | 0.8 |
| $Al_2(SO_4)_3$ 0.01M | 68.5 | 10.6 | 4.1 | 30 | 0.5 |

**Table A1.8** Effect of the addition of different electrolytes on the electrodewatering properties of kaolin sludge with 62% initial dryness. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa. The total energy spent in the process per kilogram of water extracted only takes in consideration the water removed from the sludge after voltage was turned on.

| Electrolyte | Total # of experiments | Final wt% solid | Increase in dryness (%) | mass of water recovered (g) | Maximum temperature ($^{o}$C) | Total energy (kWh/kg) |
|---|---|---|---|---|---|---|
| Water | 13 | 73.8±0.4 | 18.9±0.7 | 6.9±0.2 | 52±5 | 0.9±0.1* |
| NaCl 0.1M | 8 | 75.7±0.6 | 22.0±0.9 | 7.8±0.3 | 86±9 | 1.60±0.09 |
| $Na_2SO_4$ 0.05M | 2 | 74.45±0.01 | 19.97±0.02 | 7.185±0.007 | 84±5 | 1.4±0.1 |
| $NaClO_3$ 0.1M | 1 | 75.3 | 21.3 | 7.6 | 77 | 1.6 |
| $NaHCO_3$ 0.1M | 1 | 71.6 | 15.3 | 5.7 | 62 | 1.7 |
| $NaNO_3$ 0.1M | 1 | 75.7 | 22.0 | 7.8 | 82 | 1.6 |
| NaOH 0.1M | 1 | 75.3 | 4.1 | 1.7 | 93 | 5.0 |
| HCl 0.002M | 1 | 73.6 | 18.6 | 6.8 | 48 | 0.8 |
| HCl 0.02M | 1 | 73.6 | 18.6 | 6.8 | n.m. | 1.3 |
| HCl 0.1M | 1 | 71.2 | 14.8 | 5.6 | 48 | 1.4 |

*data for 9 experiments only

**Table A1.9** Effect of the addition of different electrolytes on the electrodewatering properties of kaolin sludge with 62% initial dryness. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa. The total energy spent in the process per kilogram of water extracted only takes in consideration the water removed from the sludge after voltage was turned on.

| Electrolyte | Total # of experiments | Final wt% solid | Increase in dryness (%) | mass of water recovered (g) | Maximum temperature (°C) | Total energy (kWh/kg) |
|---|---|---|---|---|---|---|
| Water | 13 | 73.8±0.4 | 18.9±0.7 | 6.9±0.2 | 52±5 | 0.9±0.1 |
| NaCl 0.002M | 1 | 73.9 | 19.2 | 6.9 | 55 | 1.0 |
| NaCl 0.02M | 1 | 74.1 | 19.4 | 7.0 | 67 | 1.3 |
| NaCl 0.1M | 8 | 75.7±0.6 | 22.0±0.9 | 7.8±0.3 | 86±9 | 1.60±0.09 |
| NaCl 0.2M | 1 | 74.2 | 20.0 | 7.1 | 111 | 2.2 |
| $Na_2SO_4$ 0.001M | 1 | 74.0 | 19.3 | 7.0 | n.m. | 0.9 |
| $Na_2SO_4$ 0.01M | 1 | 74.1 | 19.4 | 7.0 | 55 | 0.9 |
| $Na_2SO_4$ 0.05M | 2 | 74.45±0.01 | 19.97±0.02 | 7.185±0.007 | 84±5 | 1.4±0.1 |
| $Na_2SO_4$ 0.1M | 2 | 73.3±0.2 | 18.1±0.2 | 6.61±0.08 | 105±7 | 2.08±0.02 |

**Table A1.10** Effect of the addition of NaCl on the electrodewatering properties of kaolin sludge with 62% initial dryness. Two hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa. The total energy spent in the process per kilogram of water extracted only takes in consideration the water removed from the sludge after voltage was turned on.

| [NaCl] (M) | Total # of experiments | Evaporated water (g) | Filtered water (g) | Total water (g) | %water lost by evaporation | Maximum temperature (°C) | Total energy* (kWh/kg) |
|---|---|---|---|---|---|---|---|
| 0 | 4 | 0.3±0.2 | 6.9±0.2 | 7.16±0.01 | 4±2 | 51±6 | 0.81±0.02 |
| 0.002 | 1 | 0.4 | 6.9 | 7.3 | 6 | 55 | 0.9 |
| 0.02 | 1 | 0.7 | 7.0 | 7.7 | 8 | 67 | 1.2 |
| 0.1 | 1 | 1.0 | 7.6 | 8.6 | 12 | 77 | 1.4 |
| 0.2 | 1 | 1.0 | 7.1 | 8.1 | 12 | 111 | 1.8 |

*Total energy consumed per kilogram of water extracted in electrodewatering step (filtered plus evaporated water)

**Table A1.11** Effect of the addition of different electrolytes on the electrodewatering properties of kaolin plus xanthan gum sludge with 62% initial dryness. 1.5 hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa. The total energy spent in the process per kilogram of water extracted was calculated having in consideration the water extracted both by filtration and evaporation after voltage was turned on.

| Electrolyte | Total # of experiments | Final wt% solid | Increase in dryness (%) | Total water loss (g) | Maximum temperature ($^{o}$C) | Total energy (kWh/kg) |
|---|---|---|---|---|---|---|
| Water | 5 | 66.2±0.6 | 6.7±0.9 | 2.7±0.3 | 73±5 | 2.9±0.1 |
| LiCl 0.002M | 1 | 66.4 | 7.0 | 2.8 | 85 | 2.8 |
| LiCl 0.02M | 1 | 65.7 | 5.9 | 2.4 | 88 | 3.2 |
| LiCl 0.1M | 1 | 65.4 | 5.4 | 2.2 | 102 | 3.1 |
| LiCl 0.2M | 2 | 67±2 | 8±3 | 3±1 | 100±2 | 3.5522±0.0001 |
| NaCl 0.002M | 1 | 66.2 | 6.70 | 2.7* | 70 | 3.1 |
| NaCl 0.02M | 1 | 66.1 | 6.54 | 2.7* | 85 | 3.0 |
| NaCl 0.1M | 2 | 66.04±0.04 | 6.43±0.09 | 2.61±0.03 | 99±13 | 3.2±0.6 |
| NaCl 0.2M | 2 | 68.0±0.3 | 9.6±0.4 | 3.8±0.1 | 113±4 | 3.34±0.05 |
| KCl 0.002M | 1 | 66.2 | 6.7 | 2.7 | 87 | 3.0 |
| KCl 0.02M | 1 | 66.2 | 6.6 | 2.7 | 85 | 3.0 |
| KCl 0.1M | 1 | 65.5 | 5.5 | 2.3 | 114 | 4.1 |
| KCl 0.2M | 2 | 66.0±0.6 | 6±1 | 2.6±0.4 | 100±6 | 4.2±0.2 |

*Only water extracted by filtration

**Table A1.11** ***(cont.)***

| Electrolyte | Total # of experiments | Final wt% solid | Increase in dryness (%) | Total water loss (g) | Maximum temperature ($^{o}$C) | Total energy (kWh/kg) |
|---|---|---|---|---|---|---|
| RbCl 0.002M | 1 | 66.0 | 6.3 | 2.6 | 89 | 3.0 |
| RbCl 0.02M | 1 | 66.1 | 6.5 | 2.6 | 97 | 3.0 |
| RbCl 0.1M | 1 | 65.7 | 5.9 | 2.4 | 100 | 3.6 |
| RbCl 0.2M | 2 | 67±1 | 8±2 | 3.1±0.6 | 111±8 | 3.8±0.2 |
| CsCl 0.002M | 1 | 65.9 | 6.3 | 2.6 | 87 | 2.8 |
| CsCl 0.02M | 1 | 65.9 | 6.3 | 2.6 | 82 | 3.4 |
| CsCl 0.1M | 1 | 66.3 | 6.9 | 2.8 | 115 | 3.6 |
| CsCl 0.2 M | 2 | 67±2 | 8±3 | 3±1 | 111±8 | 3.8±0.2 |

**Table A1.12** Effect of the addition of different electrolytes on the electrodewatering properties of kaolin plus xanthan gum sludge with 62% initial dryness. 1.5 hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa. The total energy spent in the process per kilogram of water extracted was calculated having in consideration the water extracted both by filtration and evaporation after voltage was turned on.

| Electrolyte | # Exp | Final wt% solid | Increase in dryness (%) | Total water loss (g) | Water loss by evaporation (%) | Maximum temperature (°C) | Total energy (kWh/kg) |
|---|---|---|---|---|---|---|---|
| Water | 5 | 66.2±0.6 | 6.7±0.9 | 2.7±0.3 | 15±3 | 73±5 | 2.9±0.1 |
| NaCl 0.002M | 1 | 66.2 | 6.70 | 2.7 | n.m. | 70 | 3.1 |
| NaCl 0.02M | 1 | 66.1 | 6.54 | 2.7 | n.m. | 85 | 3.0 |
| NaCl 0.1M | 2 | 66.04±0.04 | 6.43±0.09 | 2.61±0.03 | 17.8±0.5 | 99±13 | 3.2±0.6 |
| NaCl 0.2M | 2 | 68.0±0.3 | 9.6±0.4 | 3.8±0.1 | 19±5 | 113±4 | 3.34±0.05 |
| $CaCl_2$ 0.002M | 2 | 66±1 | 6±2 | 2.6±0.7 | 15±1 | 74±15 | 2.7±0.5 |
| $CaCl_2$ 0.02M | 2 | 65.9±0.2 | 6.2±0.2 | 2.52±0.08 | 15±3 | 93±4 | 2.9±0.4 |
| $CaCl_2$ 0.1M | 2 | 68.6±0.6 | 11±1 | 4.1±0.3 | 14±3 | 90±8 | 2.5±0.2 |
| $CaCl_2$ 0.2M | 2 | 70±1 | 13±2 | 5.0±0.8 | 23±3 | 98±3 | 2.70±0.02 |
| $CeCl_3$ 0.002M | 1 | 67.2 | 8.4 | 3.3 | 17 | 78 | 2.6 |
| $CeCl_3$ 0.02M | 1 | 68.2 | 10.0 | 3.9 | 13 | 99 | 2.5 |
| $CeCl_3$ 0.1M | 1 | 73.6 | 18.7 | 6.8 | 40 | 92 | 1.8 |
| $CeCl_3$ 0.2M | 1 | 74.2 | 19.7 | 7.1 | 36 | 89 | 1.8 |

**Table A1.13** Effect of the addition of different electrolytes on the electrodewatering properties of kaolin plus xanthan gum sludge with 62% initial dryness. 1.5 hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa. The total energy spent in the process per kilogram of water extracted was calculated having in consideration the water extracted both by filtration and evaporation after voltage was turned on.

| Electrolyte | Total # of experiments | Final wt% solid | Increase in dryness (%) | Total water loss (g) | Water loss by evaporation (%) | Maximum temperature ($^oC$) | Total energy (kWh/kg) |
|---|---|---|---|---|---|---|---|
| Water | 5 | 66.2±0.6 | 6.7±0.9 | 2.7±0.3 | 15±3 | 73±5 | 2.9±0.1 |
| $Ca(NO_3)_2$ 0.002M | 1 | 67.2 | 8.2 | 3.3 | 17 | 88 | 2.6 |
| $Ca(NO_3)_2$ 0.02M | 1 | 67.4 | 8.6 | 3.4 | 25 | 83 | 2.4 |
| $Ca(NO_3)_2$ 0.1M | 1 | 69.8 | 12.5 | 4.8 | 29 | 109 | 2.0 |
| $Ca(NO_3)_2$ 0.2M | 1 | 67.6 | 8.9 | 3.5 | 19 | 94 | 2.8 |
| $RuCl_3$ 0.002M | 1 | 67.0 | 8.0 | 3.2 | 16 | 81 | 2.5 |
| $RuCl_3$ 0.02M | 1 | 69.8 | 12.6 | 4.8 | 12 | 118 | 2.3 |
| $RuCl_3$ 0.2M | 1 | 74.6 | 20.2 | 7.3 | 32 | 89 | 2.2 |
| $FeCl_3$ 0.2M | 1 | 73.8 | 19.0 | 6.9 | 16 | 95 | 2.1 |
| $AlCl_3$ 0.2M | 1 | 72.6 | 17.1 | 6.3 | 32 | 88 | 2.1 |

**Table A1.14** Effect of the addition of different electrolytes on the electrodewatering properties of kaolin plus xanthan gum sludge with 62% initial dryness. 1.5 hour-experiments were performed; in the last 60 minutes, the potential was turned on (50 V). The pressure was kept at 77 kPa. The total energy spent in the process per kilogram of water extracted was calculated having in consideration the water extracted both by filtration and evaporation after voltage was turned on.

| Electrolyte | # Exp | Final wt% solid | Increase in dryness (%) | Total water loss (g) | Water loss by evaporation (%) | Maximum temperature (°C) | Total energy (kWh/kg) |
|---|---|---|---|---|---|---|---|
| Water | 5 | 66.2±0.6 | 6.7±0.9 | 2.7±0.3 | 15±3 | 73±5 | 2.9±0.1 |
| $Na_2SO_4$ 0.05M | 1 | 65.1 | 4.94 | 2.0 | 15 | 91 | 3.8 |
| $Na_2SO_4$ 0.1M | 1 | 64.8 | 4.46 | 1.8 | 27 | 113 | 4.6 |
| $NaClO_3$ 0.1M | 1 | 65.0 | 4.84 | 2.0 | 24 | 81 | 3.7 |
| $NaNO_3$ 0.1M | 1 | 65.6 | 5.67 | 2.3 | 19 | 117 | 3.5 |
| NaCl 0.1M | 2 | 66.04±0.04 | 6.43±0.09 | 2.61±0.03 | 17.8±0.5 | 99±13 | 3.2±0.6 |
| $NaHCO_3$ 0.1M | 1 | 64.4 | 3.74 | 1.6 | 14 | 59 | 4.0 |
| $Na_2CO_3$ 0.05 M | 1 | 64.2 | 3.42 | 1.4 | 22 | 61 | 4.3 |
| $Na_2CO_3$ 0.1 M | 1 | 63.5 | 2.26 | 1.0 | 22 | 53 | 5.2 |
| NaOH 0.1M | 1 | 64.1 | 3.28 | 1.4 | 18 | 65 | 5.1 |
| HCl 0.002M | 1 | 65.9 | 6.2 | 2.5 | 9 | 81 | 2.9 |
| HCl 0.02M | 1 | 66.3 | 6.8 | 2.8 | 12 | 92 | 3.0 |
| HCl 0.1M | 1 | 69.9 | 12.7 | 4.9 | 20 | 82 | 2.7 |
| HCl 0.2M | 1 | 73.6 | 18.6 | 6.8 | 21 | 100 | 2.1 |

**Table A1.15** Effect of the addition of different electrolytes on the electrodewatering properties of municipal sludge with (14.3±0.3)% measured initial dryness. Eight-minute experiments were performed at (116±4) kPa and 50 V. The total energy spent in the process per kilogram of water extracted was calculated having in consideration the water extracted both by filtration and evaporation.

| Electrolyte (4.4 mmol) | Total # of experiments | Final wt% solid | Increase in dryness (%) | Total water loss (g) | Water loss by evaporation (%) | Total energy (kWh/kg) |
|---|---|---|---|---|---|---|
| Water | 12 | 26±3 | 82±21 | 66±9 | 18±3 | 0.29±0.02 |
| HCl | 1 | 38 | 166 | 91 | 21 | 0.32 |
| LiCl | 2 | 41±2 | 187±12 | 93±1 | 20.1±0.7 | 0.3100± 0.0004 |
| NaCl | 5 | 39±2 | 177±15 | 96±5 | 20±1 | 0.32±0.02 |
| KCl | 1 | 41 | 187 | 94 | 21 | 0.32 |
| RbCl | 1 | 42 | 193 | 95 | 21 | 0.32 |
| CsCl | 1 | 41 | 190 | 94 | 21 | 0.32 |

**Table A1.16** Effect of the addition of different electrolytes on the electrodewatering properties of municipal sludge with (14.3±0.3)% measured initial dryness. Eight-minute experiments were performed at (116±4) kPa and 50 V. The total energy spent in the process per kilogram of water extracted was calculated having in consideration the water extracted both by filtration and evaporation.

| Electrolyte | Total # of experiments | Final wt% solid | Increase in dryness (%) | Total water loss (g) | Water loss by evaporation (%) | Total energy (kWh/kg) |
|---|---|---|---|---|---|---|
| Water | 12 | 26±3 | 82±21 | 66±9 | 18±3 | 0.29±0.02 |
| NaCl<br>0.3 mmol | 1 | 26 | 77 | 72 | 14 | 0.29 |
| NaCl<br>0.43 mmol | 1 | 25 | 75 | 72 | 14 | 0.29 |
| NaCl<br>1.5 mmol | 4 | 33±3 | 133±21 | 84±6 | 19±3 | 0.314±0.007 |
| NaCl<br>2.2 mmol | 4 | 35±2 | 148±14 | 89±5 | 19±3 | 0.31±0.02 |
| NaCl<br>3 mmol | 1 | 37 | 158 | 103 | 20 | 0.31 |
| NaCl<br>4.4 mmol | 5 | 39±2 | 177±15 | 96±5 | 20±1 | 0.32±0.02 |
| NaCl<br>7.5 mmol | 1 | 39 | 169 | 96 | 19 | 0.33 |
| NaCl<br>13 mmol | 1 | 32 | 120 | 80 | 16 | 0.31 |
| $CaCl_2$<br>0.3 mmol | 2 | 27±1 | 86±7 | 68±3 | 17.2±0.1 | 0.299±0.010 |
| $CaCl_2$<br>0.44 mmol | 1 | 27 | 84 | 67 | 17 | 0.30 |
| $CaCl_2$<br>1.5 mmol | 2 | 34.5±0.4 | 143±9 | 84.12±0.07 | 21±3 | 0.33±0.02 |
| $CaCl_2$<br>2.2 mmol | 5 | 38±1 | 168±11 | 92±2 | 24±1 | 0.36±0.01 |
| $CaCl_2$<br>3 mmol | 1 | 39 | 171 | 91 | 25 | 0.39 |
| $CaCl_2$<br>4.4 mmol | 1 | 38 | 162 | 94 | 24 | 0.43 |
| $CaCl_2$<br>7.6 mmol | 1 | 30 | 104 | 77 | 24 | 0.43 |

**Table A1.16** ***(cont.)***

| Electrolyte | Total # of experiments | Final wt% solid | Increase in dryness (%) | Total water loss (g) | Water loss by evaporation (%) | Total energy (kWh/kg) |
|---|---|---|---|---|---|---|
| $CeCl_3$ 0.43 mmol | 1 | 30 | 111 | 82 | 17 | 0.32 |
| $CeCl_3$ 1.5 mmol | 9 | 36±2 | 150±19 | 88±5 | 20±3 | 0.33±0.01 |
| $CeCl_3$ 2.2 mmol | 3 | 38±3 | 170±17 | 92±3 | 21±1 | 0.35±0.02 |
| $CeCl_3$ 3 mmol | 1 | 38 | 161 | 94 | 22 | 0.37 |
| $CeCl_3$ 4.3 mmol | 1 | 37 | 158 | 93 | 21 | 0.39 |
| $CeCl_3$ 7.5 mmol | 1 | 33 | 126 | 88 | 21 | 0.40 |

**Table A1.17** Effect of the addition of different electrolytes on the electrodewatering properties of municipal sludge with (14.3±0.3)% measured initial dryness. Eight-minute experiments were performed at (116±4) kPa and 50 V. The total energy spent in the process per kilogram of water extracted was calculated having in consideration the water extracted both by filtration and evaporation.

| Electrolyte | Total # of experiments | Final wt% solid | Increase in dryness (%) | Total water loss (g) | Water loss by evaporation (%) | Total energy (kWh/kg) |
|---|---|---|---|---|---|---|
| Water | 12 | 26±3 | 82±21 | 66±9 | 18±3 | 0.29±0.02 |
| $Ca(NO_3)_2$ 0.3 mmol | 2 | 26±2 | 87±13 | 66±8 | 16.5±0.7 | 0.2918±0.0003 |
| $Ca(NO_3)_2$ 0.43 mmol | 1 | 25 | 79 | 60 | 16 | 0.29 |
| $Ca(NO_3)_2$ 1.5 mmol | 1 | 34 | 148 | 88 | 19 | 0.33 |
| $Ca(NO_3)_2$ 2.2 mmol | 1 | 38 | 177 | 93 | 23 | 0.35 |
| $Ca(NO_3)_2$ 3 mmol | 1 | 38 | 177 | 92 | 27 | 0.39 |
| $Ca(NO_3)_2$ 4.4 mmol | 2 | 39.4±0.8 | 186±6 | 100±6 | 27±1 | 0.409±0.010 |
| $Ca(NO_3)_2$ 7.6 mmol | 1 | 30 | 120 | 81 | 25 | 0.40 |
| $CuSO_4$ 2.2 mmol | 1 | 36 | 151 | 90 | 23 | 0.34 |
| $AlCl_3$ 1.5 mmol | 1 | 38 | 167 | 91 | 21 | 0.34 |
| $FeCl_3$ 1.5 mmol | 5 | 39±2 | 173±13 | 92±2 | 23±2 | 0.33±0.02 |

**Table A1.18** Effect of the addition of different electrolytes on the electrodewatering properties of municipal sludge with (14.3±0.3)% measured initial dryness. Eight-minute experiments were performed at (116±4) kPa and 50 V. The total energy spent in the process per kilogram of water extracted was calculated having in consideration the water extracted both by filtration and evaporation.

| Electrolyte | Total # of experiments | Final wt% solid | Increase in dryness (%) | Total water loss (g) | Water loss by evaporation (%) | Total energy (kWh/kg) |
|---|---|---|---|---|---|---|
| Water | 12 | 26±3 | 82±21 | 66±9 | 18±3 | 0.29±0.02 |
| HCl<br>4.4 mmol | 1 | 38 | 166 | 91 | 21 | 0.32 |
| *$Na_2CO_3$<br>4.4 mmol | 1 | 28 | 96 | 72 | 19 | 0.34 |
| $Na_2SO_4$<br>4.4 mmol | 1 | 37 | 160 | 92 | 18 | 0.32 |
| $NaClO_3$<br>4.4 mmol | 1 | 40 | 177 | 91 | 23 | 0.33 |
| *$NaHCO_3$<br>4.4 mmol | 1 | 29 | 99 | 75 | 23 | 0.35 |
| $NaNO_3$<br>4.4 mmol | 1 | 40 | 178 | 94 | 20 | 0.32 |
| *NaOH<br>4.4 mmol | 1 | 32 | 124 | 79 | 18 | n.m |
| NaCl<br>4.4 mmol | 5 | 39±2 | 177±15 | 96±5 | 20±1 | 0.32±0.02 |

*Basic pH (starting solution)

# A2. Data from ICP-AES experiments

**Table A2. 1** Adsorption of calcium in function of concentration of kaolin; the solid kaolin was mixed with $CaCl_2$ 0.002 M at different concentrations of kaolin (50, 100 and 200 g/L); the resulting suspensions were stirred overnight; the supernatants were then filtered and analyzed by ICP for calcium and sodium content; the results shown are average ± standard deviation.

| [kaolin] (g/L) | Adsorbed calcium (μmol) | % Adsorbed calcium | mg Na |
|---|---|---|---|
| 50 | 16.4±0.4 | 17.7±0.4 | 1.456±0.001 |
| 50 | 17.5±0.3 | 18.9±0.4 | 1.399±0.003 |
| 50 | 17.3±0.5 | 18.6±0.5 | 1.145±0.002 |
| 100 | 29.1±0.9 | 31±1 | 2.147±0.004 |
| 200 | 40.5±0.5 | 43.7±0.5 | 3.746±0.004 |

**Table A2. 2** Adsorption of lithium, sodium, calcium and cerium to kaolin at 50 g/L; solid kaolin (50 g/L) was mixed with the metal cations (0.002 M); the suspensions were stirred overnight; the supernatants were then filtered and analyzed by ICP for metal content; the results shown are average ± standard deviation. NaCl-0 indicates that the residual amount of sodium present in kaolin was taken into account in the determination of the final number of moles of sodium in solution; two duplicates were performed (i and ii).

| Salt | $M^{n+}$ (μmol) present in starting electrolyte | $M^{n+}$ (μmol) left in solution after mixing with kaolin | Variation (%) |
|---|---|---|---|
| LiCl | 105.47±0.05 | 98.0±0.2 | 7.0±0.2 |
| NaCl | 102.0±0.5 | 137.0±0.7 | -34.2±0.6 |
| NaCl-0 i | 102.0±0.5 | 72.0±0.5 | 29.1±0.6 |
| NaCl-0 ii | 102.0±0.5 | 88.0±0.8 | 14.0±0.7 |
| $CaCl_2$ | 92.7±00.4 | 76.0±0.2 | 17.7±0.4 |
| $CaCl_2$ | 92.7±0.4 | 75.0±0.5 | 18.8±0.4 |
| $CaCl_2$ | 92.7±0.4 | 75.0±0.6 | 18.6±0.5 |
| $CeCl_3$ | 93.5±0.2 | 67.00±0.08 | 28.4±0.1 |

**Table A2. 3** Adsorption of lithium, sodium, calcium and cerium to municipal sludge 50 g/L; municipal sludge was collected at La Prairie, Qc, Canada on May 11 2011; the starting electrolyte was 0.002 M in metal cation content; the suspensions were stirred for one hour after which the supernatants were filtered and analyzed by ICP; the results shown are average ± standard deviation. NaCl-0 or $CaCl_2$-0 indicates that the residual amount of sodium/calcium present in municipal sludge was taken into account in the determination of the final number of moles.

| Salt | $M^{n+}$ (µmol) present in starting electrolyte | $M^{n+}$ (µmol) left in solution after mixing with municipal sludge | Variation (%) |
|---|---|---|---|
| LiCl | 97.86±0.06 | 87.0±0.3 | 10.9±0.3 |
| NaCl | 97.3±0.5 | 103.0±0.5 | -5.8±0.2 |
| NaCl-0 | 97.3±0.5 | 58.0±0.4 | 40.4±0.2 |
| $CaCl_2$ | 99.6±0.4 | 89±1 | 10±1 |
| $CaCl_2$-0 | 99.6±0.4 | 63±1 | 37±1 |
| $CeCl_3$ | 101.3±0.4 | 2.00±0.01 | 98.13±0.02 |

**Table A2. 4** Metal content of the filtrates recovered from the electrodewatering experiments with kaolin in the presence of different electrolytes. The metal contents of the starting electrolytes solutions are also presented for reference.

| Electrolyte | mg $M^{n+}$/ kg initial solution | mg $M^{n+}$/ kg filtrate 1 | mg $M^{n+}$/ kg filtrate 2 |
|---|---|---|---|
| LiCl 0.002M | 14.40±0.07 | 9.52±0.05 | 15.26±0.06 |
| LiCl 0.02M | 134.1±0.6 | 105.7±0.2 | 170.7±1.0 |
| LiCl 0.1M | 661.0±0.4 | 622±1 | 744.6±0.7 |
| LiCl 0.2M | 1338±9 | 1313±2 | 1293±3 |
| NaCl 0.002M | 48.1±0.1 | 401.8±0.7 | 1031±9 |
| NaCl 0.02M | 452±2 | 751.3±0.8 | 3181±7 |
| NaCl 0.1M | 2268±11 | 2391±2 | 30115±325 |
| NaCl 0.2M | 4643±10 | 4708±31 | 23524±30 |
| $CaCl_2$ 0.002M | 74.4±0.4 | 41.1±0.4 | 26.7±0.1 |
| $CaCl_2$ 0.02M | 782±8 | 436±3 | 47.3±0.5 |
| $CaCl_2$ 0.1M | 3786±13 | 3408±8 | 1278±6 |
| $CaCl_2$ 0.2M | 7395±33 | 7625±51 | 2399±27 |
| $CeCl_3$ 0.002M | 278±5 | 0.94±0.01 | 0.12±0.01 |
| $CeCl_3$ 0.02M | 2572±11 | 891±3 | 435±3 |
| $CeCl_3$ 0.1M | 13174±51 | 10945±23 | 10687±60 |
| $CeCl_3$ 0.2M | 24049±12 | 23572±21 | 20127±49 |

# A3. Résumé

L'électro-déshydratation est une technologie qui combine l'application d'une pression (effet mécanique) et d'un courant électrique (phénomènes électrocinétiques) au travers une boue afin d'en extraire les molécules d'eau [1-11]. Parce que ce projet de recherche a été mené en étroite collaboration avec Ovivo, les effets de l'ajout de sels ont été étudiés sur des boues d'épuration en provenance de l'usine de filtration des eaux de La Prairie, Québec, et des boues synthétiques composées de kaolin et de kaolin additionné de gomme de xanthane. L'effet de la nature, de la taille, de la charge et de la concentration des cations et des anions ont été étudiés sur les trois types de boues. L'effet du pH a été également étudié. Les résultats sont expliqués en se basant sur l'adsorption sélective des cations à la superficie des particules en suspension.

## Électro-déshydratation du kaolin

Dans un premier temps, des boues synthétiques ont été préparées en mélangeant du kaolin et un électrolyte composé d'une solution aqueuse d'un sel dont la nature et la concentration (de 0.0 à 0.2 M) ont été variées. Le profil d'électro-déshydratation est illustré sur la Figure 1 pour une boue préparée avec du kaolin et de l'eau déionisée, dont la siccité initiale est de 62%.

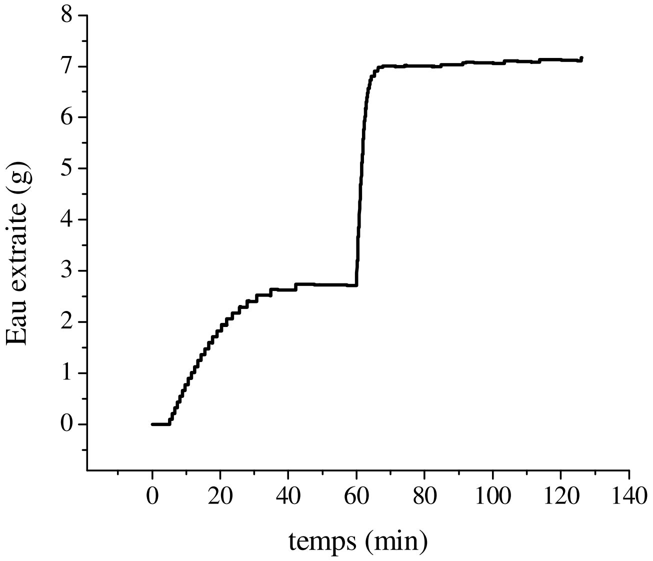

**Figure 1 –** Électro-déshydratation du kaolin mélangé avec de l'eau déionisée. La siccité initiale de la boue est de 62% et la pression appliquée est de 70 kPa. Le voltage est appliqué à t = 60 minutes.

Après deux heures de traitement, 7.17 g d'eau ont été extraites du kaolin, ce qui correspond à une siccité finale de 74% et donc une augmentation de 20% par rapport à la siccité initiale.

En général l'addition de sels de cations monovalents, MCl, avec M = $Li^+$, $Na^+$, $K^+$ et $Rb^+$ à des concentrations inférieures à 0.1 M, entraîne une augmentation de la quantité d'eau extraite (voir Figure 2). Dans le cas de CsCl, la quantité d'eau extraite diminue constamment avec une augmentation de la concentration.

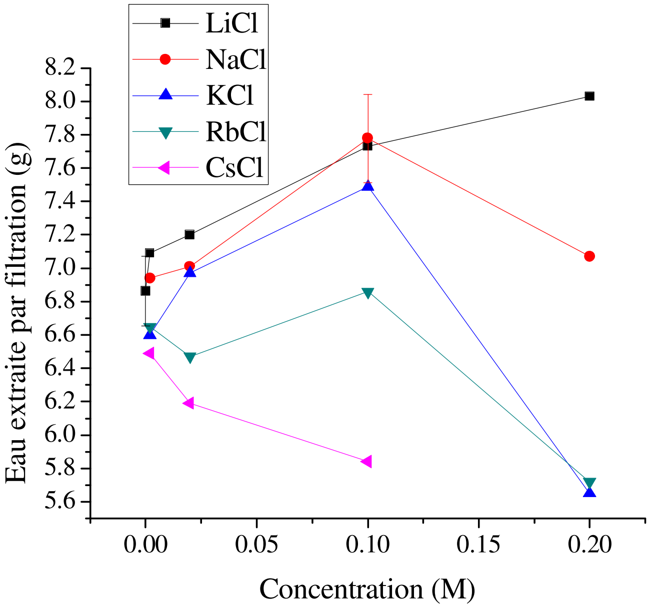

**Figure 2 –** Effet de l'addition de sels de cations monovalents sur l'électro-déshydratation du kaolin (siccité initiale de 62%). Les essais ont une durée de deux heures; la pression appliquée est de 77 kPa; le voltage (50 V) est appliqué à t = 60 minutes.

Selon les données de la Figure 2, pour une concentration donnée, la quantité d'eau extraite augmente lorsque le rayon d'hydratation des cations croît: $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. Cet ordre est à l'opposé de l'affinité des cations pour la surface du kaolin : $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ [12]. Conséquemment, la déshydratation est favorisée par la présence de cations qui ne s'adsorbent pas à la surface du kaolin.

L'effet d'addition de cations avec charges différentes est illustré dans la Figure 3.

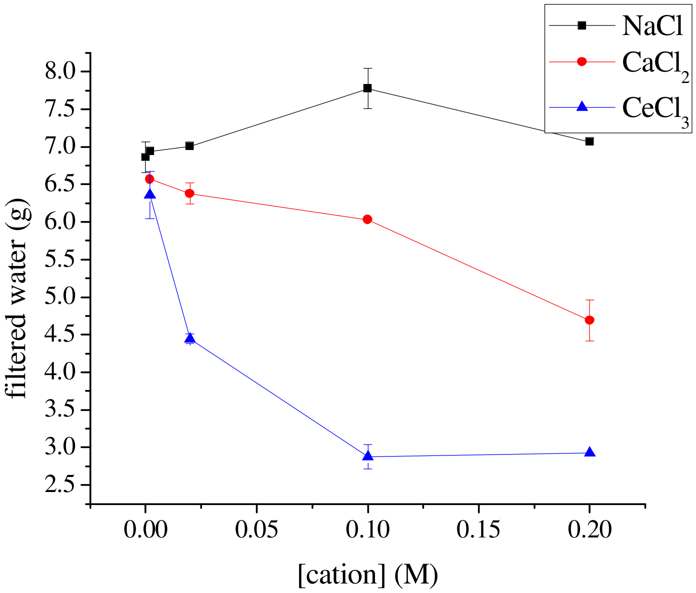

**Figure 3 –** Effet de l'addition de NaCl, $CaCl_2$ et $CeCl_3$sur l'électro-déshydratation du kaolin (siccité initiale de 62%). Les essais ont une durée de deux heures; la pression appliquée est de 77 kPa;  le voltage (50 V) est appliqué à t = 60 minutes.

Comme il est montré à la Figure 3, une augmentation de la charge du cation des sels de chlorure (NaCl, $CaCl_2$ et $CeCl_3$) cause une réduction du volume d'eau extraite : $Na^+ > Ca^{2+} > Ce^{3+}$. L'adsorption de ces cations à la surface du kaolin est d'autant plus importante que les cations sont plus chargés: $Na^+ < Ca^{2+} < Ce^{3+}$. Une fois de plus, l'électro-déshydratation est favorisée par la présence de cations qui ne s'adsorbent pas à la surface du kaolin.

L'électro-déshydratation dépend aussi du pH, qui doit idéalement être situé entre 2 et 7 (voir Figure 4). Dès lors, on ne note pas de différences dans la quantité d'eau qu'il est possible d'extraire avec les différents sels de sodium (NaCl, $NaNO_3$, $NaClO_3$, $Na_2SO_4$, $NaHCO_3$, NaOH, $Na_2CO_3$) en autant que la dissociation de ceux-ci n'a pas d'effet sur le pH de l'électrolyte, ce qui est le cas de NaCl, $NaNO_3$, $NaClO_3$ et $Na_2SO_4$. En revanche, les sels de $NaHCO_3$, NaOH et $Na_2CO_3$ qui, dans la gamme de concentration étudiée rendent l'électrolyte basique (pH>8), entraîne une diminution notable de la quantité d'eau extraite.

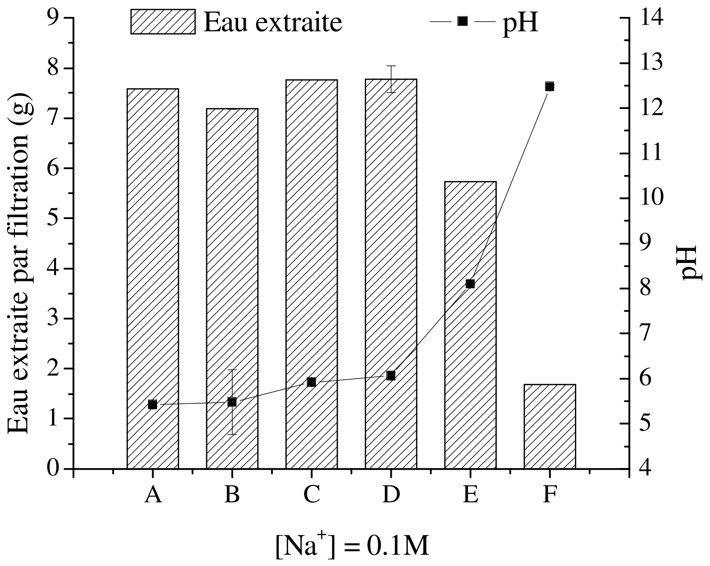

**Figure 4 –** Quantité d'eau extraite en fonction de la nature du sel de sodium (0.1M) lors de l'électro-déshydratation du kaolin (siccité initiale de 62%). Les essais ont une durée de deux heures; la pression appliquée est de 77 kPa; le voltage (50 V) est appliqué à t = 60 minutes. A= $NaClO_3$, B=$Na_2SO_4$, C=$NaNO_3$, D=NaCl, E=$NaHCO_3$, F=NaOH. Le pH initial de l'électrolyte est indiqué.

L'énergie consommée lors de l'électro-déshydratation du kaolin mélangé à de l'eau déionisée est de 0.9±0.1 kWh/kg d'eau extraite. Cependant, 96% de l'eau est extraite durant les premières 10 minutes de l'expérience et l'énergie consommée durant cette période est de 0.20±0.02 kWh/kg d'eau extraite, ce qui représente seulement 20% de l'énergie consommée lorsque le test est prolongé sur une période d'une heure.

L'addition de sels au kaolin entraîne une augmentation de la quantité d'eau extraite. Cependant, cette accroissement de la siccité va de pair avec une augmentation de l'énergie consommée. Par exemple, une addition de LiCl 0.2 M au kaolin permet d'augmenter la quantité d'eau extraite, qui passe de 6.9 g (sans sel ajouté) à 8.0 g. De même, la consommation énergétique est de 1.1 et 2.1 kWh par kilogramme d'eau extraite pour des expériences d'une durée respective de 10 et de 60 minutes.

## Électro-déshydratation du kaolin plus gomme de xanthane

L’addition d’une petite quantité de gomme de xanthane (4.4 wt%) à du kaolin a pour effet de changer les propriétés de déshydratation du milieu (voir Figure 5). Par exemple, une boue composée de kaolin et de gomme xanthane ne se déshydrate pas sous l’effet de la pression, au contraire de qui se passe avec la boue de kaolin. La gomme de xanthane aide à la dispersion des particules de kaolin, ce qui rend la déshydratation plus difficile. De plus, la masse totale d’eau extraite du mélange kaolin plus gomme de xanthane est de 2.7 g, comparativement à 7.2 g pour le kaolin seul, soit une diminution d’un facteur 2.6.

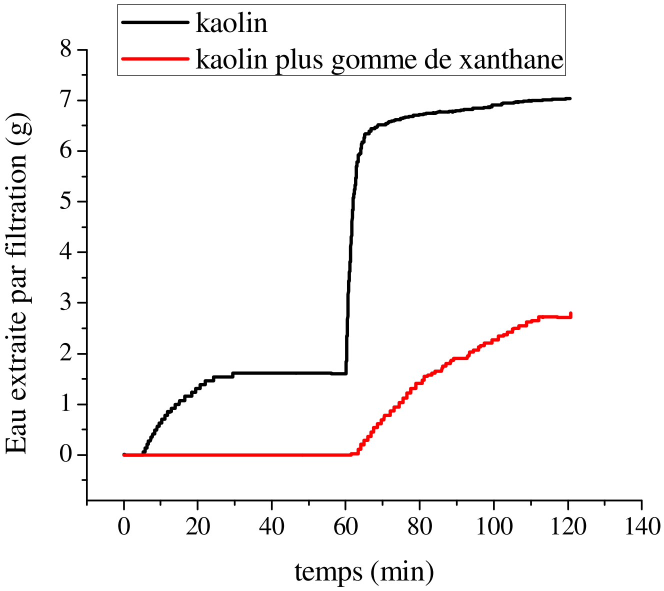

**Figure 5 –** Comparaison entre les profils d’électro-déshydratation du kaolin et du kaolin plus gomme de xanthane (les deux avec une siccité initiale de 62%). Les essais ont une durée de deux heures; la pression appliquée est de 77 kPa; le voltage (50 V) est appliqué à t = 60 minutes.

L’effet d’additionner des sels de chlorure ayant des cations de différentes charges est illustré dans les Figures 6 et 7.

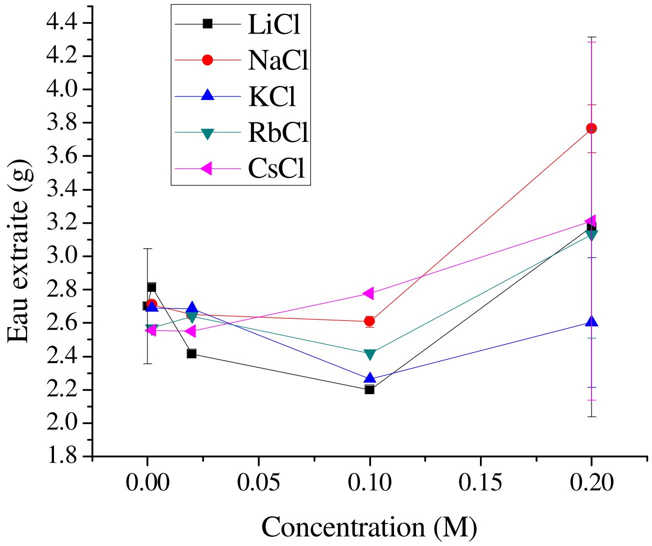

**Figure 6 –** Effet de l'addition de sels de cations monovalents sur l'électro-déshydratation du kaolin plus gomme de xanthane (siccité initiale de 62%). Les essais ont une durée d'une heure et demie; la pression appliquée est de 77 kPa; le voltage (50 V) est appliqué à t = 30 minutes. La quantité totale d'eau extraite est donnée par la somme des masses d'eau récupérée perdue par filtration et perdue par évaporation.

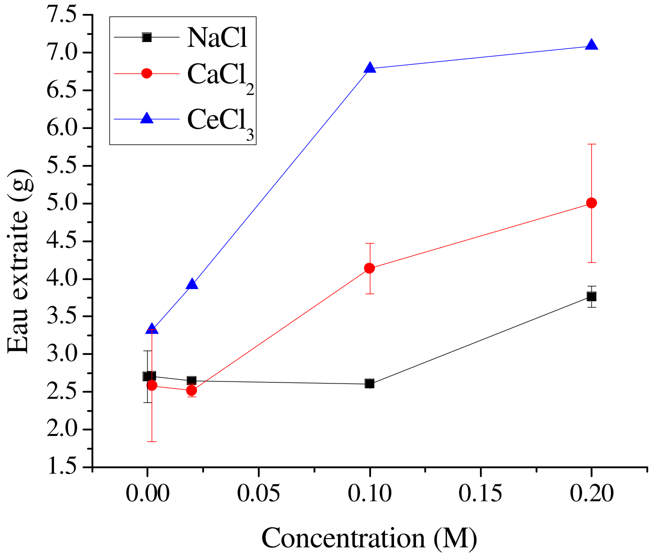

**Figure 7 –** Effet de l'addition de NaCl, $CaCl_2$ et $CeCl_3$ sur l'électro-déshydratation du kaolin plus gomme de xanthane (siccité initiale de 62%). Les essais ont une durée d'une heure et demie; la pression appliquée est de 77 kPa; le voltage (50 V) est appliqué à t = 30 minutes. La quantité totale d'eau extraite est donnée par la somme des masses d'eau récupérée perdue par filtration et perdue par évaporation.

Tous les sels de cations monovalents (MCl, avec M=$Li^+$, $Na^+$, $K^+$, $Rb^+$, and $Cs^+$) présentent un effet similaire: $Li^+=Na^+=K^+=Rb^+=Cs^+$ (Figure 6). En revanche, la déshydratation est plus importante dans le cas où on ajoute des cations ayant une charge plus importante: $Na^+ < Ca^{2+} < Ce^{3+}$ (Figure 7). Dans ce cas, la quantité d'eau extraite augmente avec la concentration de sels (de 0 à 0.2 M). La siccité finale est de 74.2% pour un sel de $CeCl_3$ (0.2 M) alors qu'elle n'est 66.2% avec de l'eau déionisée. La présence de cations comme le $Ce^{3+}$, qui s'adsorbe plus facilement à la surface du kaolin, favorise l'agrégation entre les particules de kaolin et de gomme de xanthane, ce qui entraîne un accroissement de l'électro-déshydratation de la boue.

Le remplacement de l'anion chlorure par autres anions a été investigué avec le NaCl (voir Figure 8). La quantité d'eau extraite diminue selon la série : $Cl^- > NO_3^- > ClO_3^-$, $SO_4^{2-} >> HCO_3^- > CO_3^{2-} > OH^-$. L'électro-déshydratation du kaolin plus gomme de xanthane est favorisée aux pH's plus acides. L'évaporation d'eau, qui survient parce que la température de la boue augmente, peut représenter plus de 20% de toute l'eau extraite. L'énergie consommée par kilogramme d'eau extraite est de 2.9±0.1 kWh.

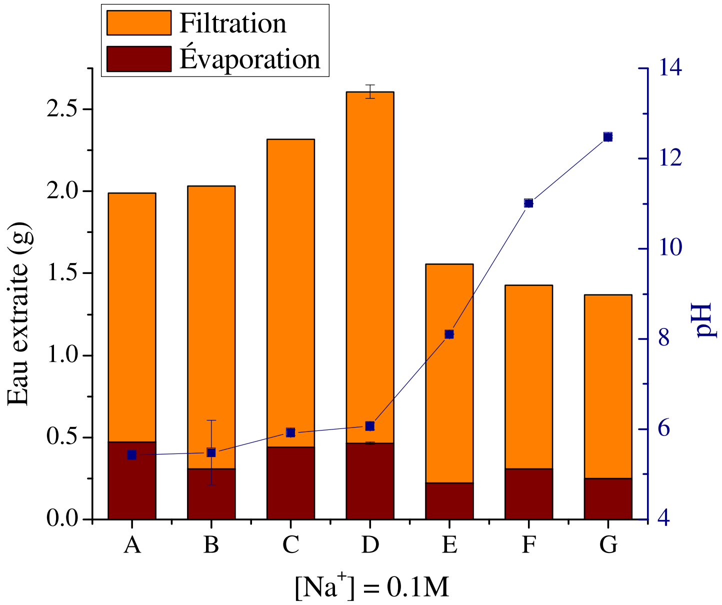

**Figure 8 –** Quantité d'eau extraite en fonction de la nature du sel de sodium (0.1 M) lors de l'électro-déshydratation du kaolin plus gomme de xanthane (siccité initiale de 62%). Les essais ont une durée d'une heure et demie; la pression appliquée est de 77 kPa; le voltage (50 V) est appliqué à t = 30 minutes. A= $NaClO_3$, B=$Na_2SO_4$, C=$NaNO_3$, D=NaCl, E=$NaHCO_3$, F=$Na_2CO_3$, G=NaOH. Le pH initial de l'électrolyte est indiqué.

## Électro-déshydratation des boues municipales

La boue municipale de la station d'épuration de La Prairie, Québec, a été testée. Cette boue a une siccité initiale de 14.3%. La siccité finale de la boue double (siccité finale de 26±3 %) quand de l'eau déionisée est utilisée et le volume final de la boue est réduit par un facteur 2. Vingt pourcent de toute l'eau extraite est perdue par évaporation. L'énergie consommée est de 0.29 kWh par kilogramme d'eau extraite, ce qui représente quatre fois moins d'énergie en comparaison avec une méthode de séchage thermique [4].

L'effet de différents cations sur l'électro-déshydratation de la boue municipale est représenté dans les Figures 9 et 10.

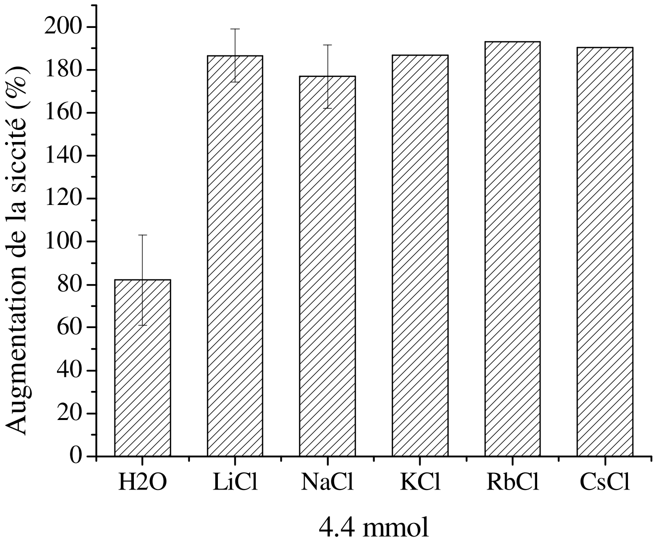

**Figure 9 –** Augmentation de la siccité résultant de l'addition des différents électrolytes à la boue municipale de La Prairie (siccité initiale de 14.3%). Les essais ont une durée de huit minutes; la pression est de 116 kPa; le voltage est de 50 V.

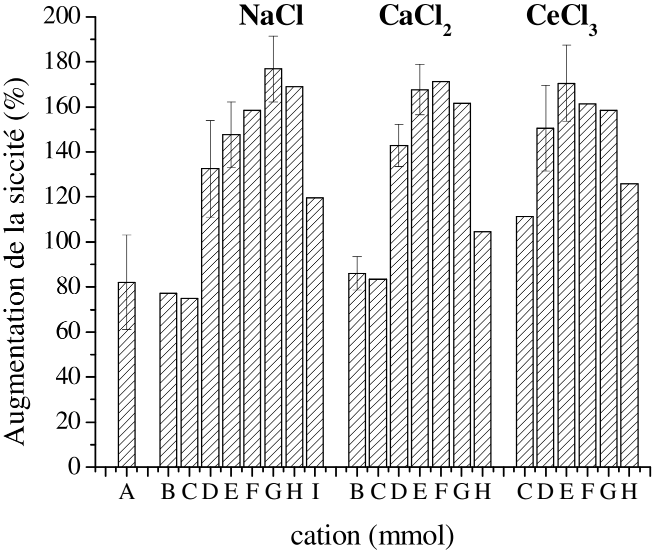

**Figure 10 –** Augmentation de la siccité résultant de l'addition des différents électrolytes à la boue municipale de La Prairie (siccité initiale de 14.3%). Les essais ont une durée de huit minutes; la pression est de 116 kPa; le voltage est de 50V. A – 0 mmol, B – 0.3 mmol, C – 0.43 mmol, D – 1.5 mmol, E – 2.2 mmol, F – 3 mmol, G – 4.4 mmol, H – 7.5 mmol, I – 13 mmol

Tous les cations monovalents (voir Figure 9) présentent un effet similaire entre eux : $Li^+=Na^+=K^+=Rb^+=Cs^+$. Les cations +2 et +3 sont plus efficaces dans la déshydratation des boues municipales que les cations +1 : $Ce^{3+}$, $Ca^{2+}$ > $Na^+$ (Figure 10). La quantité d'eau extraite augmente avec la concentration de sels ajoutés jusqu'à un maximum avant de diminuer. La concentration à laquelle la déshydratation est maximale dépend de la nature du sel et est respectivement égale à 4.4-7.5, 2.2-4.4 et 1.5-4.4 mmol pour le NaCl, $CaCl_2$ et $CeCl_3$. Par exemple, en additionnant 4.4 mmol de NaCl, la siccité finale de la boue atteint 42%, ce qui représente une augmentation d'un facteur 3 par rapport à la siccité initiale. Dans ces conditions, la déshydratation de la boue est aussi accompagnée d'une réduction du volume de 70%.

La consommation énergétique du processus d'électro-déshydratation est montrée dans la Figure 11.

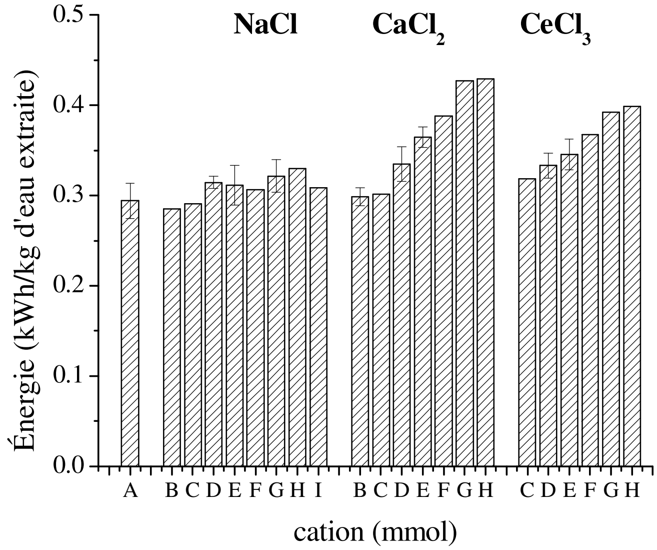

**Figure 11 –** Variation de l'énergie consommée par kilogramme d'eau extraite pour divers sels ajoutés lors de l'électro-déshydratation de la boue municipal de La Prairie (siccité initiale de 14.3%). Les essais ont une durée de huit minutes; la pression est de 116 kPa; le voltage est de 50V. A – 0 mmol, B – 0.3 mmol, C – 0.43 mmol, D – 1.5 mmol, E – 2.2 mmol, F – 3 mmol, G – 4.4 mmol, H – 7.5 mmol, I – 13 mmol

Dans le cas de NaCl, la consommation énergétique est pratiquement constante et indépendante de la concentration. Par ailleurs, l'addition de $CaCl_2$ ou de $CeCl_3$ cause une augmentation de l'énergie consommée au fur et à mesure que la concentration de sel augmente. Dans les conditions optimales, la consommation énergétique est de 0.32, 0.36-0.43 et 0.33-0.39 kWh/kg pour le $Na^+$, le $Ca^{2+}$ et le $Ce^{3+}$, respectivement, très proche de celle déterminé lorsque de l'eau déionisée est utilisée. La consommation énergétique demeure donc largement inférieure à ce qu'elle est lorsque les mêmes boues sont séchées par des procédés thermiques. L'électro-déshydratation est donc une méthode commode pour le traitement des boues municipales et peut être optimisé à travers de l'ajout de sels.

## Comparaison entre les boues synthétiques et les boues municipales

Finalement, la Figure 12 illustre une comparaison entre les profils d'électro-déshydratation des trois boues qui ont été testées dans cette étude.

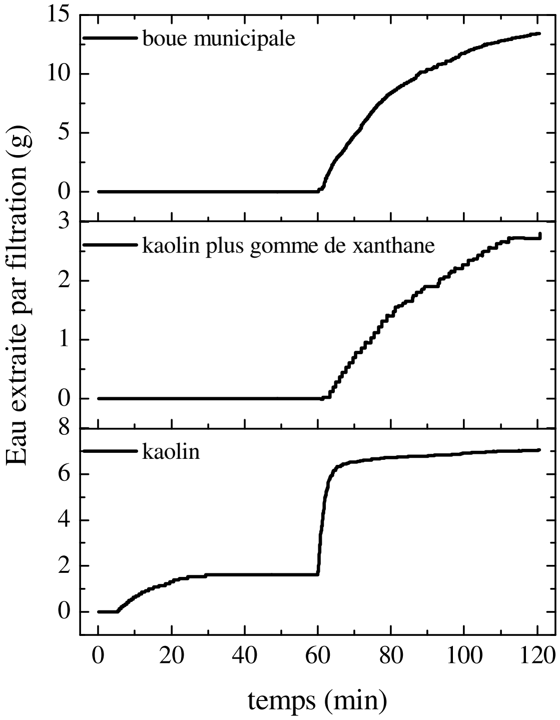

**Figure 12 –** Profils d'électro-déshydratation de la boue municipale (78 kPa), kaolin plus gomme de xanthane (77 kPa) and kaolin (77 kPa); Le voltage (50 V) est appliqué à t =60 minutes.

Lors de l'électro-déshydratation, la boue synthétique composé de kaolin plus gomme de xanthane et la boue municipale ont des caractéristiques très proches. Cette boue synthétique peut être donc utilisée en lieu et place de la boue municipale lors d'étude plus fondamentale des processus qui régissent l'électro-déshydratation.

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