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Research Article

Calcium-Ion Removal from Peat by a Mechanical Filter Cake Washing Process

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This contribution aims to bridge two different fields of science, viz., geoecology and mechanical process engineering. The study reports on the application of mechanical washing processes especially filter cake washing, on calcium-ion removal from peat, which is a natural material that is used in different fields of application such as agriculture, medicine, cosmetics, etc. The interesting properties of peat such as its porous structure and the sorption behavior influence the distribution of liquid inside the bulk and the liquid flow behavior through the porous structure. Experimental results are obtained from filtration tests using differential gas pressure in a filter nutsche. The washing efficiency is determined for different pressures and specific amounts of applied wash liquor. It is found that the water repellent phenomena that occurs when peat has been dried, affects the washing efficiency in a very negative way. The results obtained are compared to the conventional filter cake washing process.

Keywords: Environment, Filtration, Porous media, Solid-liquid separation

Received: April 18, 2007; *accepted:* April 27, 2007

DOI: 10.1002/ceat.200700142

1 Introduction

Filter cake washing is a common process in the field of solid-liquid separation with the aim of remove impurities from the solid bulk. Most products in the chemical, pharmaceutical or biological industries leave the synthetic process as suspensions towards the downstream process, in which the solids have to be separated from the liquid and the impurities have to be removed until the product has reached a certain degree of purity. This purification process is usually integrated in the solid-liquid separation process since the driving forces applied in this process can also be used for transporting diluted impurities out of the bulk. The apparatus used for this purpose can differ from filters, e.g., belt filter, vacuum/hyperbar drum filter, and candle filter to centrifuges, e.g., peeler centrifuge, pusher centrifuge, and screenbowl centrifuge, depending on the desired throughput capacity.

Most common impurities are ionic substances or salts, which are dissociated in liquids. In the human body, calcium ions act together with potassium as regulators of the swelling of cytoplasm. Calcium is also contained in several enzymes and is responsible for their activities. On the other hand, calcium ions are present in spring and river water, mostly in high

concentrations. These ions together with magnesium and carbonate ions are responsible for the water hardness. In many cases, where the presence of the calcium ions is undesired, these have to be removed from the water. This is usually performed in an ionic exchange process using materials which can bound calcium ions onto their surface, and in return, release protons into the water. One example of this type of material is peat.

Peat contains humic acid which can be used to adsorb heavy metal ions [1] and rare elements which are harmful to human health in high concentrations. It is generally used in different fields of application, e.g., waste water purification [2], domestic fuels [3], medicine [4] and cosmetics [5, 6], due to its interesting properties concerning its sorption capacity and fibrous shape.

The idea of this study is to investigate the behavior of peat and a typical example metal ion in an aqueous system during filter cake washing. The experimental studies should provide information on the flow behavior through natural porous media and also the applicability of filter cake washing to purify peat along with its limitations.

2 Theoretical Background

One of the most applicable methods for purifying particulate solids is filter cake washing. It is performed in solid-liquid separation apparatus such as filters and centrifuges. For process design and scientific investigations, experimental studies

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are normally performed using a lab-scale filter nutsche. Important parameters for the filtration are discussed below.

The porosity of a filter cake is defined as the ratio of the pore volume and the total volume¹⁾:

$$\varepsilon = \frac{V_{\text{pores}}}{V_{\text{total}}} \quad (1)$$

The total cake volume consists of the solids and liquid volume. The porosity has a major influence on the permeability of the cake. Particles with a broad size distribution usually build a compact structure in a stable condition, while large particles tend to build a porous structure which is easy to flow by the liquid. The permeability, p_c , is a parameter involved in the filterability of a material. It is inversely proportional to the cake resistance:

$$p_c = \frac{1}{r_c} \quad (2)$$

A well-established correlation to describe the cake building filtration for a single-phase flow is the Darcy equation [7]:

$$v_1 = \frac{1}{A} \cdot \frac{dV_1}{dt} = \frac{p_c \cdot \Delta p}{\eta_l \cdot h_c} \quad (3)$$

According to the correlation, the liquid flow velocity, v_1 , during cake building filtration depends on the cake permeability, p_c , the pressure difference, Δp , as a driving force, the liquid dynamic viscosity, η_l , and the cake height h_c . Gupte [8] proposed a correlation to determine the cake permeability from the filter cake properties such as the Sauter diameter, $x_{1,2}$ [9], and the porosity, ε , Eq. (4):

$$p_c = \frac{1}{5.6} \cdot x_{1,2}^2 \cdot \varepsilon^{5.5} \quad (4)$$

The saturation (S) is a parameter characterizing the moisture content of a bulk of particles, according to:

$$S = \frac{V_1}{V_{\text{pores}}} \quad (5)$$

In industrial applications, the term residual moisture (RM), Eq. (6):

$$RM = \frac{m_l}{m_{s+l}} \quad (6)$$

is more common since it gives the ratio between the liquid mass, m_l , and total mass, m_{s+l} , in the cake. The liquid and solid mass can be measured gravimetrically. The disadvantage of this definition is the disregard of the material density so that a comparison of different products is not always possible.

Concerning the washing process, there are some parameters that are mostly used to characterize the wash efficiency. The concentration ratio, c^* , of the impurity after (c) and before (c_0) washing indicates the degree of purity, Eq. (7):

$$c^* = \frac{c}{c_0} \quad (7)$$

while the wash ratio characterizes the specific amount of wash liquor required to wash the cake, Eq. (8):

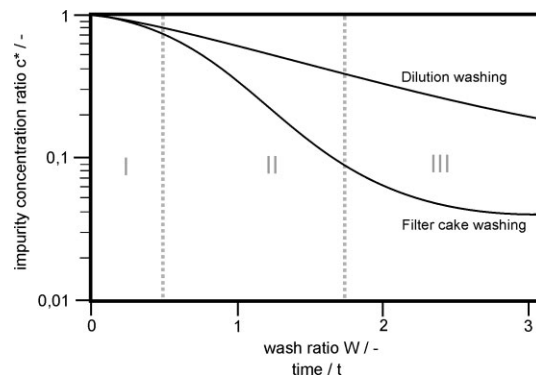


Figure 1. The impurity concentration ratio versus the wash ratio showing typical wash curves.

$$W = \frac{V_{\text{wl}}}{V_{\text{product}}} \quad (8)$$

By plotting the wash results (remaining impurity concentration ratio) as a function of the wash ratio it is possible to compare different wash results in a wash diagram, Fig. 1.

To understand the mechanisms of washing, the wash diagram can be split into three regimes, which are the ideal displacement, dispersion and diffusion regimes. In the first regime (I), the mother liquor is displaced by incoming wash liquor as a piston flow. After a certain wash ratio, the flow of the wash liquor is no longer homogeneous due to dispersion (II). The mechanisms of dispersion have been discussed by Fried and Combarous [10]. The more inhomogeneous is the structure of the cake, the stronger is the dispersion inside the porous structure. After this region, the wash effect disappears in the diffusion regime (III), where the achievable impurity concentration reaches a constant level. Diffusion becomes a limiting factor when an obstruction of the diffusion path is present either due to bulk structure such as complex inner-pore structures or due to surface texture such as roughness or inclusions. Another factor that influences the level of the residual impurity concentration is the interaction between the impurity and the solid products. For adsorbed impurities on the surface of the solid product, the bond between the two components must first be broken to allow further transport of the impurity out of the cake. Thus, adsorption and desorption can also be limiting factors.

In Fig. 1, the general wash curve for dilution washing is also presented in comparison with the wash curve for the filter cake washing. Dilution washing is a method, where the product suspension consisting of solids and the mother liquor, are mixed and stirred with the wash medium in a certain ratio. This can result in very low impurity concentrations, but the process consumes a high amount of wash liquor. Instead of using the wash ratio, one can also utilize the process time. In this way, the kinetics of the washing process can be understood. This is important in industrial processes, especially if the kinetics are a dominating factor in the washing process.

Adsorption is widely used as a separation method of chemical substances distributed in two phases [11]. The adsorbed component accumulates in the solid-liquid interface, especially in the active centers of the solids surface. The equilibrium states can be described physically by different correlations. The

1) List of symbols at the end of the paper.

simplest one is the correlation according to Henry involving a single component adsorption at low concentrations of the adsorbed substance in the liquid. The loading, q , is linearly proportional to the equilibrium concentration, c_{eq} , of the substance in the liquid, Eq. (9):

$$q(c) = k_{\text{H}} \cdot c_{\text{eq}} \quad (9)$$

The proportionality is given by the Henry constant, k_{H} . Langmuir and Freundlich isotherms can also be used for describing a limited loading capacity taking into account the interaction between the adsorptive substances.

3 Materials and Methods

The peat used for the investigations was high-moor or also known as white peat with two origins. The first sample had its origin in northern Germany and the second sample came from Latvia. The characteristics of the two samples are presented in Tab. 1. Peat 2 from Latvia had higher initial moisture content than peat 1 from northern Germany. Also, the darker color of peat 1 indicated the higher degree of decomposition. Due to the humic acid contained in peat, the pH of the water decreases as protons are released from the peat into the water.

Representative SEM images of the product are shown in Fig. 2 and it is obvious that the product has a fibrous and porous structure. The material used in the experiments featured a diverse variation of shape, size and structure. The particle size varied from several μm up to some mm. The bulk or filter cake built from this material had a very voluminous structure with a high total porosity of between 0.89 and 0.99. For the experiments in this study, original material was used to represent the real conditions. Another option would have been to use a pre-screening to obtain uniform-sized fractions. The latter was not performed in this study.

Calcium ions, Ca^{2+} , were used as an artificial impurity since they are well adsorbed by peat and relevant for applications such as water treatment and water softening [12]. The impurity was given as a salt $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (calcium chloride dihydrate) which has a relative high solubility in demineralized water (1000 g/L at 0/C according to Merck). To assure comparability, the standard initial concentration of the salt for each experiment was defined to 0.1 mol/L. Demineralized water was used as the wash liquor. The salt concentration was calculated from conductivity measurements using electrodes. For this purpose, the cake was dried and then mixed with clean water (reslurrying) after the washing experiments.

The experiments were carried out using a lab-scale apparatus known as a wash nutsche, Fig. 3 [13]. It consisted of a filter cell equipped with a full cone nozzle manufactured by Spray-

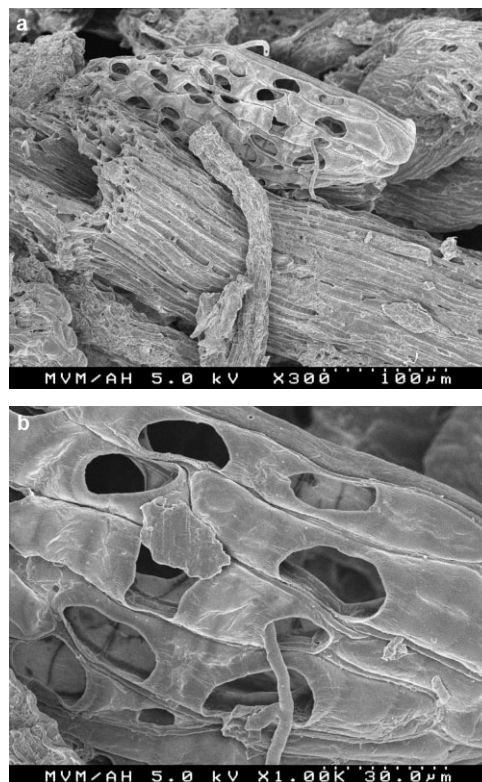


Figure 2. The peat structure revealed using SEM at different magnification factors: (a) 300 x, (b) 1000 x.

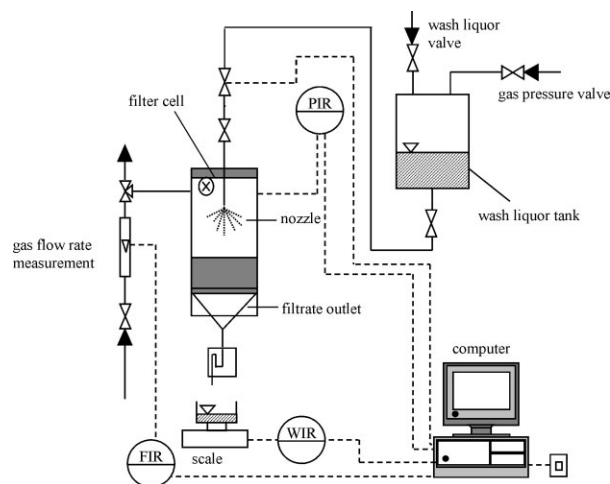


Figure 3. Setup of the wash filter nutsche [13].

Table 1. Product properties of the materials used.

| Peat | Moisture Content (%) | Conductivity (Water + Peat) (mS/cm) | pH (Water + Peat) | $\text{CaCl}_2 + 2\text{H}_2\text{O}$ Concentration (mol/L) | Conductivity ($\text{H}_2\text{O} + \text{CaCl}_2 + \text{Peat}$) (mS/cm) |
|-----------|----------------------|-------------------------------------|-------------------|---|---|
| 1 Germany | 74.9 | 0.022 | 4.1 | 0.1 | 14.4 |
| 2 Latvia | 81.9 | 0.020 | 4.3 | 0.1 | 18.1 |

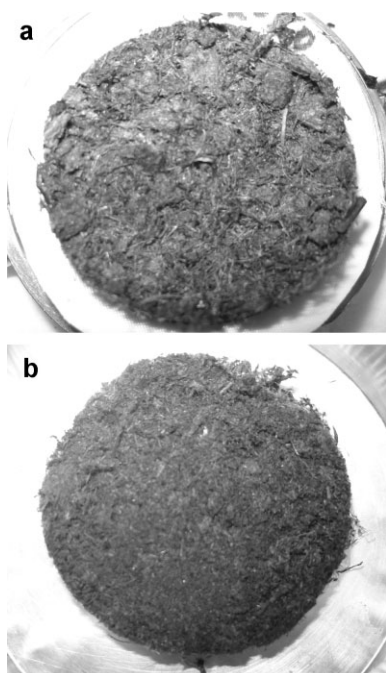


Figure 4. Dewatered filter cake of peat: (a) top view, and (b) the bottom part directly on the filter cloth.

ing Systems Co. IL, U.S.A., for the wash liquor inlet. The cake was built inside the cell on a polymeric filter cloth (50 μm pore size) so that the filtrate could drain out and be collected on a scales while the solids were retained inside of the apparatus. With this setup, the filtration progression could be registered online by a computer. The driving force used was the gas pressure which was varied from 0–2 bar. The filtration area was ca. 20 cm^2 and the initial cake height was kept constant at 20 mm, as standard conditions.

4 Results and Discussion

The filter cake resistance was determined experimentally in flow experiments. The filtrate flow rate was measured at steady-state after a cake building phase. In this phase, a compression of the cake structure occurred due to the loose structure of the fibers. The compression had already been completed in the filtration phase under pressure. The porosity of the cake decreased to 0.68–0.77. The large fluctuation of the porosity was caused by the nonuniformity of the particles. Depending on the experimental sampling procedure, the particle size distribution can vary. Fig. 4 shows the existence of mostly larger particles on the surface of the cake (a), and predominantly smaller particles in the bottom part (b). This always happened although the suspension had been stirred well before sampling. The specific cake resistance was determined to be around $8.8 \cdot 10^{11} \text{ m}^{-2}$ which is rather low compared to spherical particles of the similar size. This shows the good permeability of peat as expected from its porous structure.

The porous structure of the material is not only voluminous but also offers a large surface area for ions to be adsorbed.

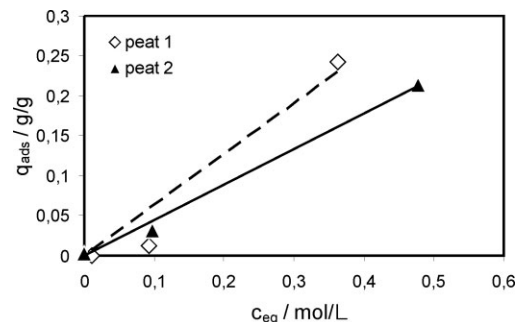


Figure 5. Adsorption behavior of peat 1 (German), and 2 (Latvian).

Batch experiments at lab-scale level were performed at a temperature of $301 \pm 1.1 \text{ K}$ to investigate the adsorption behavior. The results for the adsorption behavior are presented in Fig. 5. This information is important to enable correct determination of the wash efficiency in terms of the initial and final impurity concentrations by dilution of the filter cake after washing and drying. The adsorption behavior was fitted by the linear correlations according to Henry. The constants are listed in Tab. 2. The Henry approximation was not very suitable for describing the adsorption behavior of the German peat (1). Other correlations such as those of Langmuir or Freundlich might be more appropriate for exact calculations. However, this analytical issue was not pursued any further in this work since the focus was on the process instead of the material characterization.

The direct comparison of the wash curves between the German (1) and Latvian (2) peat is shown in Fig. 6. Here the concentration ratio is plotted against the variation of the wash ratio. A reduction of the impurity concentration down to

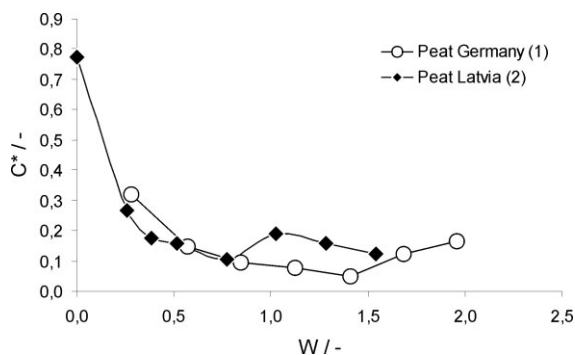


Figure 6. Wash curves for German (1) and Latvian peat (2), both at 0.5 bar filtration pressure, wash rate = 2.85 mL/s, initial cake height = 20 mm.

Table 2. Approximated Henry constants.

| Peat | k_H |
|-----------|--------------|
| 1 Germany | 0.6334 L/mol |
| 2 Latvia | 0.4433 L/mol |

ca. 15% of the initial concentration can be observed for both products. The wash efficiency seems to be similar and independent of the origin of the material. Some differences in the values, especially at high wash ratios, might have been caused by differences in the cake porosity which changed during the experiments. In the experiments, the cake was provided as a suspension to form a cake with a full saturation, $S = 1$. After applying hyper-pressure, the cake height declined due to the compressibility of the cake. Therefore, the porosity of the cake became lower and the structure more compact. Thus, the cake became less permeable according to Eq. (4). At high wash ratios, the wash curve enters the diffusion regime where the impurity removal takes place by means of diffusion. Depending on the structure of the cake and the internal porosity of the particles, the diffusion process can take a considerable length of time. The complicated structure due to irregular particle shape, broad particle size distribution and internal pore structure may hinder the diffusion, and therefore, results in elevated impurity concentration ratios after washing.

4.1 Influence of the Wash Liquor Flow Rate

High wash liquor flow rates normally induce a so-called shock washing where the liquid accumulates on top of the cake. This liquid then flows through the filter cake as a plug flow and carries the impurity out of the porous structure by displacement effects. Fig. 7 shows the wash curves for two wash liquor volumetric rates at 1.91 mL/s and 2.85 mL/s. It appears that washing at the higher wash rate leads to slightly lower final impurity concentrations of the product. However, the difference is very low compared to the wash curve at 1.91 mL/s and the influence was not investigated further.

4.2 Influence of the Filtration Pressure

Besides using higher wash liquor flow rates to enhance the washing and the filtration process, an increase in the pressure difference was also experimentally tested. An increase in filtration pressure leads to higher flow velocities. This could be advantageous for the mass transfer by convection. Fig. 8 shows

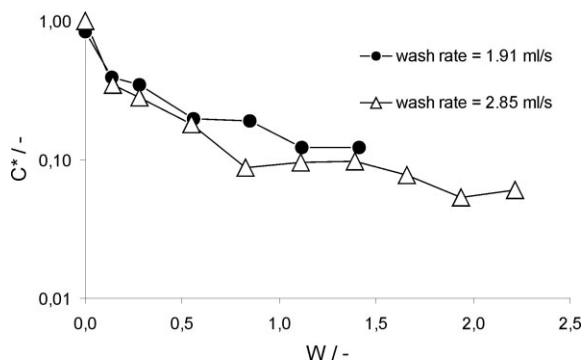


Figure 7. Variation of the wash liquor flow rate, Latvian peat, 0.1 bar filtration pressure, initial cake height = 20 mm.

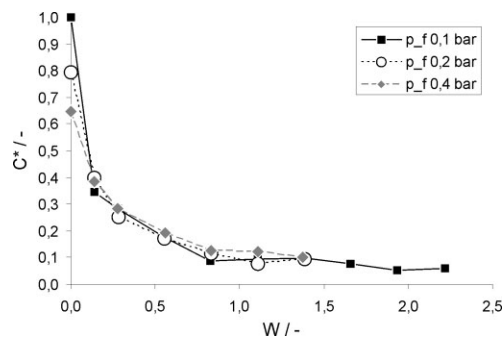


Figure 8. Variation of the filtration pressure, Latvian peat, wash rate = 2.85 mL/s, initial cake height = 20 mm.

the wash curves of the samples washed at different filtration pressures. Similar to the previous results presented in Fig. 7, the filtration pressure did not significantly affect the wash efficiency. Nearly all results from varying the wash liquor and filtrate velocity show the same progression. This indicates the nonsensitive behavior of the product system to changes in convection and flow forces. Due to the porous structure of the particles, the dominating mechanism in the washing process is probably the diffusion of the calcium ions from the inner part of the pores into the primary liquid flow. In this case, longer process times would be necessary to allow thorough or even total removal of the impurity. The surface specific diffusion coefficient was determined by adding non-loaded water to the Ca^{2+} loaded cake of peat. Measurements over a time interval of 24 h delivered a surface specific diffusion coefficient of $2.6 \cdot 10^{-8} \text{ m}^2/\text{s}$.

4.3 Influence of Predrying

The most interesting aspect in this work is the investigation of the influence of the moisture content of the peat on its washing efficiency. When peat had been dried thermally, it showed a hydrophobic behavior. Qualitative tests performed by dropping a definite amount of water droplets on the cake surface showed that the droplet was sucked immediately into the cake when using wet peat, due to the capillary force of the pores, whereas in the experiments using dried peat, the droplet initially remained on the top of the cake for seconds or even minutes. This water repellence has been observed and investigated mainly for soil [14]. Water repellence is believed to correlate with the material composition of the soil such as humic acid, wax, etc., as well as the moisture content of the soil. This affects the infiltration behavior of water into the soil.

Fig. 9 shows the wash results as concentration ratios using peat at different moisture contents. There is a worsening of the concentration ratio up to a factor of five from comparison of the washing of wet peat ($\text{RM} = 0.9$) and thermally dried peat ($\text{RM} = 0.01$). This could be the result of the water repellence after drying. The wash liquor could barely wet all of the particle surfaces and trickled unstably through the cake to the filter cloth. Therefore, there may have been some stagnant areas that were not accessible to the wash liquor. It is possible that impu-

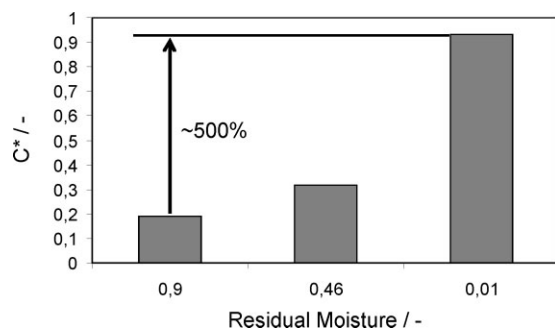


Figure 9. Washing dried Latvian peat at different residual moisture contents, wash rate = 2.85 mL/s, filtration pressure = 0.1 bar.

urities remaining in these areas were not washed out because there was no contact between the wash liquor and the impurities. This would result in a high concentration ratio, as presented in Fig. 9.

In industrial machines, an exact control of the running process sequences is not always viable. Hence, in most cases, the moisture content of the filter cake varies from very low to very high. Fast working machines such as centrifuges are the best examples where a desaturation of the filter cake or even thermal drying due to evaporation often occurs before washing. This means that at first, the particle surface has to be rewetted homogeneously during the washing process to ensure sufficient contact between the mother liquor and wash medium in order to achieve a high degree of purity. In processing synthetic materials such as plastics or polymers, the hydrophobic nature of the materials often causes rewetting and washing problems. In most cases, only a partial rewetting is possible so that the wash liquor is not able to infiltrate through all of the pores. Therefore, similar to the results obtained in this work, the final results when washing pre-dewatered hydrophobic particles were also very poor as reported by Fuchs [15] and Ruslim [16].

The analogy and similarities in material behavior of peat and common particulate matters in the chemical and pharmaceutical industries could be used to optimize processes that are relevant for the products. Advantageous wetting properties are necessary in solids washing to guarantee sufficient contact between the solids surface and the wash liquor so that mass transfer can take place. On the other hand, a good wetting and a homogeneous displacement front of liquid flow in contaminated soil or peat may be undesirable since a high concentration of contaminants would be swept away by rain water into the ground water. In turn, this displacement effect could be utilized as a means of local soil or peat decontamination where a small amount of soil near industrial areas is highly contaminated by ionic compounds or heavy metals. While peat and soil decontamination have been studied thoroughly in the field of ecology and agriculture for years, a more promising field of application may be the high-grade purification of peat for its use in cosmetics. Nevertheless, the specific correlation between the influential parameters and the process results depending on the objectives still demands further investigation. The to-

pics studied in this work are preliminary and will be followed by further studies of other contaminants. The results could have important implications for both ecological and processing/production purposes.

5 Conclusions

This paper deals with experimental investigations on filter cake washing as a unit operation in solid-liquid separation processes using a natural product peat. The purpose is to bridge the fields of geoecology and mechanical process engineering. To be more specific, the applicability of a filter cake washing process was tested on peat which could possibly open new ways for peat decontamination.

Two sorts of peat with different origins were investigated. It was found that the permeability of the cake built by the material was very good in spite of the compressibility of the cake. Calcium ions were used as a model impurity which was adsorbed on the peat surface in liquid suspensions. The adsorption of the impurity limited the wash results since the adsorbed ions could not be removed by means of mechanical flow.

The experimental results showed that a reduction in calcium ion concentration was possible by filter cake washing using a nutsche filter with hyperbar pressure as the driving force of the dewatering and liquid flow. Therefore, the variation of the wash liquor volumetric flow rate and the filtration pressure did not have significant impact on the wash results. The dominating and limiting mechanism was presumably the diffusion of the impurity out of the porous structure of the peat.

A crucial influence factor was the moisture content of the cake before washing. A very low moisture content, for instance after long filtration, evaporation or thermal drying, led to a serious worsening of the wash results compared to the results from washing wet peat. This could probably be the result of poor rewetting behavior since the dry peat was observed to be water repellent. Thus, if the wash water was not able to evenly wet the surface, there could be stagnant areas that were not infiltrated by the liquid. Hence, impurities remaining in these areas could not be washed out. This effect was also observed when washing pre-dewatered cakes of hydrophobic particles. The trickle flow could become unstable especially at low wash liquor flow rates, and the distribution of the wash liquor inside the cake may be inhomogeneous.

Acknowledgements

The collaboration between the Department of Geoecology and Geochemistry of Tomsk Polytechnic University in Russia with the Institute of Mechanical Process Engineering and Mechanics of the University of Karlsruhe in Germany is part of the efforts to establish a sustainable bilateral cooperation between the two universities.

Scientific staff members in this project were partly funded by the German Academic Exchange Service (DAAD). The materials used for the experiments were provided courtesy of the Botanical Garden of the University of Karlsruhe.

Symbols used

| | | |
|---------------|-------------------|---|
| A | [m ²] | filtration area |
| c^* | [–] | concentration ratio |
| c_0 | [mol/L] | initial impurity concentration |
| c_{eq} | [mol/L] | equilibrium concentration |
| h_c | [m] | cake height, (= 1000 mm) |
| h_l | [m] | liquid height |
| k_H | [L/mol] | Henry coefficient |
| m_l | [kg] | liquid mass |
| m_s | [kg] | solid mass |
| p_c | [m ²] | specific permeability |
| Δp | [bar] | pressure difference, (= 10 ⁵ Pa) |
| q | [–] | loading |
| r_c | [m ²] | specific cake resistance |
| RM | [–] | residual moisture |
| S | [–] | saturation |
| t | [s] | time |
| v_l | [m/s] | liquid velocity |
| V_l | [m ³] | liquid volume |
| V_{pores} | [m ³] | pore volume |
| $V_{product}$ | [m ³] | product volume |
| V_{total} | [m ³] | total volume |
| V_{wl} | [m ³] | wash liquor volume |
| W | [–] | wash ratio |
| $x_{1,2}$ | [m] | Sauter diameter |
| ε | [–] | porosity |

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