

# EXTRACTION OF POTASSIUM FROM THE CLAY FRACTION OF A BENTONITE

ALEXANDER ČUMAKOV, KLÁRA HRNČIAROVÁ, PETER KOMADEL

*Institute of Inorganic Chemistry,  
Slovak Academy of Sciences,  
Dúbravská cesta 9, 842 36 Bratislava, Slovakia  
E-mail: uachcumo@savba.sk*

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*Electro-ultrafiltration (EUF) method was employed at 20, 40 and 80 °C for investigation of potassium extraction from a K<sup>+</sup>-saturated <2 μm fraction of a bentonite. Up to 85% of total potassium present in the sample was extracted. At least three different sites of K<sup>+</sup> desorption were found on bentonite particles dispersed in water. EUF analyses of duration of 30 - 40 minutes were optimal for adequate information on K<sup>+</sup> sites. Experiments at 20 °C and voltages 50-350 V caused desorption of K<sup>+</sup> from the external surface of particles, which terminated after extraction of about 9 mg K/g clay, i.e. 22% of total potassium present. Increase in voltage to 400 V applied at 20 °C caused onset of K<sup>+</sup> desorption from the weaker interlayer sites, observed also at 40 °C and 50 - 150 V. These sites are supposed to occur mainly in swelling interlayers of smaller quasicrystals, close to the layers of lower negative charge. At 200 V started K<sup>+</sup> desorption from the stronger interlayer sites, occurring probably predominantly in the less swelling interlayers of bigger particles, next to highly charged layers. As expected, no sharp border appears between the weaker and stronger interlayer sites, they cover combined 63% of total potassium present in the investigated material.*

## INTRODUCTION

Smectites are clay minerals with layered structure. Their layers are formed by two tetrahedral sheets linked with an octahedral sheet. The octahedral sites of montmorillonites, the most common dioctahedral smectite, are occupied mainly by Al(III) but partly replaced by Fe(III) and Mg(II), while the tetrahedra contain normally Si(IV) and Al(III) as central atoms. Unequivalent substitution in the octahedra and/or tetrahedra generates a negative charge on the layers, which is balanced by hydrated exchangeable cations in the interlayers, typically by Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> or K<sup>+</sup>. Small exchangeable cations, such as Li<sup>+</sup> or Cu<sup>2+</sup>, become trapped in the layers upon heating at 110 - 300 °C [1-5]. Potassium or ammonium can get fixed in the montmorillonite structure relatively easily upon wetting/drying cycles [6 - 8]. This is due to the size and dehydration properties of these ions [9]. The fixation of K<sup>+</sup> is a frequently observed diagenetic reaction in sediments [6]. The retention of potassium by expanding soil clay minerals is important to agriculture because it affects the availability of one of the substantial nutrients. The ability of smectites to retain K<sup>+</sup> increases with the total layer charge [10, 11], however, both none [10] and good [11] correlation was found in different studies between the amount of K<sup>+</sup> retained and tetrahedral charge. K<sup>+</sup> ions occur in illites in three different positions [12], i.e.

- external surface exchange sites,
- interlayer sites near the edges of the clay particles,
- interlayer sites away from the edges of the particles.

This is important for ion-exchange reactions on these minerals and thus for plant nutrition. K<sup>+</sup> ions bound to soil illites, illite/smectites or vermiculites in various positions differ in the bond strength and thus they are differently available for plants.

Recent extraction methods use salts of various inorganic and organic acids [13]. The main uncertainty connected with the extraction methods is that two or even more fractions of potassium can be extracted simultaneously [14] and thus the soil analysis gets inaccurate [15]. One possibility to overcome this problem is to apply electrochemical instead of chemical extraction methods. The most promising results were obtained with electro-ultrafiltration (EUF), which is a combination of electrodialysis and ultrafiltration [16]. When developing EUF, the primary aim was to create a reliable method to differentiate between the fractions of nutrients present in soils, which are partly available and partly unavailable for the plants. However, the available fraction of any nutrient consists of more sub-fractions, which differ in their mobility. Figure 1 shows the main part of an EUF apparatus [17, 18]. Platinum net electrodes are covered by micropore filters on the side facing compartment *A* and split the main vessel into three compartments - *A*, *B* and *C*. The clay or soil suspension from which ions are to be extracted is placed into the central compartment *A*. Its content can be stirred and/or heated up to 80 °C during the experiment. The separation of the ions present in the analysed suspension is forced by applying vacuum in both *B* and *C* side compartments, while employing a high direct electric field (up to 400 V or 90 V cm<sup>-1</sup>) in *A*. The liquid is passing continuously through the ultrafilters from *A* to *B* and *C* carrying along the ions that have been

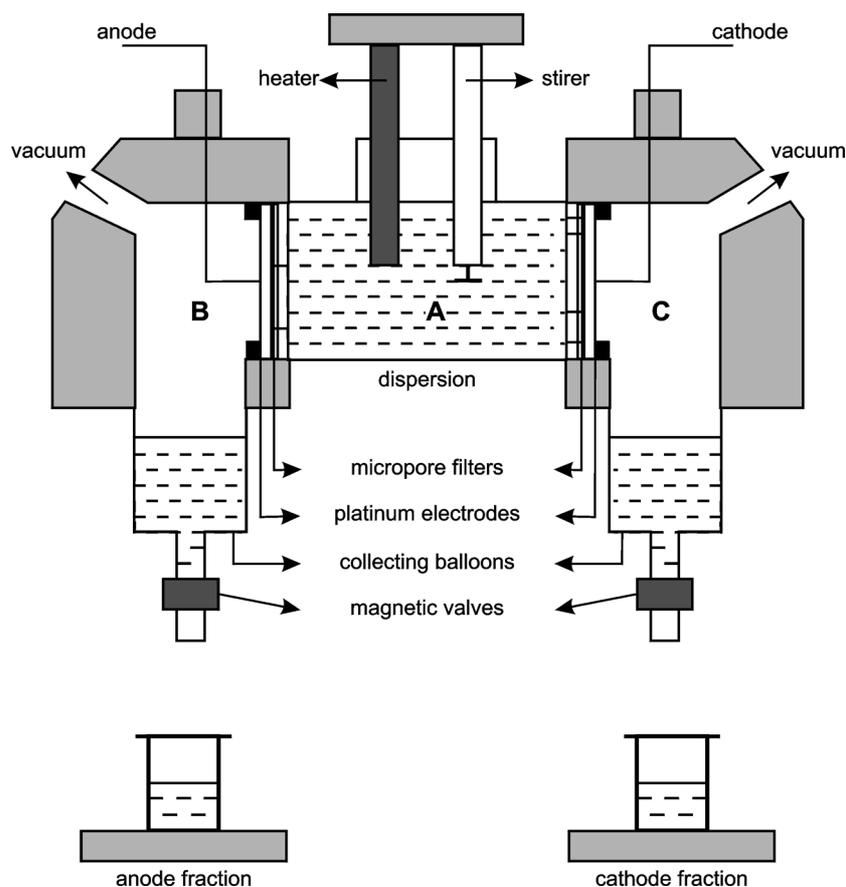


Figure 1. EUF apparatus.

attracted by the electrodes. The effluents from *B* and *C* are collected into flasks which are exchanged usually in 5 minute intervals. Solvent is added automatically to the cell *A* to maintain the volume of the liquid constant. Available variations in the electric field, temperature and time of the extraction provide sufficient basis to separate the solutions obtained from the soil suspensions into several fractions, which can be subsequently analysed for the ions present [17, 18].

The kinetics and rate equations for a quantitative description of  $K^+$  desorption from soils in the course of an EUF experiment were discussed in detail in [18, 19]. It was suggested to use the rate equation for extraction of  $K^+$  from soils in the form

$$\frac{t}{d} = \frac{t_{0.5}}{d_m} + \frac{1}{d_m} t \quad (1)$$

where  $t$  is the time and  $t_{0.5}$  is the half-time of extraction of  $K^+$ ,  $d$  is the cumulative quantity of  $K^+$  extracted at time  $t$  and  $d_m$  is the theoretically extractable amount of  $K^+$ . The values  $t/d$  are plotted versus  $t$ ,  $d_m$  is calculated

from the slope and  $t_{0.5}$  from the intercept of the linear line obtained.

Analyses of soils showed that the desorption maximum was always equal or very close to the exchangeable  $K^+$  content in different soils and no fractionation of exchangeable  $K^+$  was possible by applying different field strengths at room temperature [19]. The principal advantage of the EUF apparatus shown in figure 1 is that simultaneous modification of the electric field and temperature in compartment *A* allows to affect the rate of extraction of variously bound  $K^+$  in the sample. Appropriate experimental conditions for extractions at 20 and 80 °C permitted to obtain information on all  $K^+$  present in the analysed materials [15, 20]. However, important disadvantages in the EUF experiments at 80 °C include deformation (frequently with cracks) of the ultrafilters and fast evaporation of water from the compartment *A*.

The aim of this work was to find suitable conditions for EUF experiments to differentiate between the fractions of  $K^+$  ions present in a  $K^+$ -saturated clay fraction of a bentonite, to extract and quantify these fractions and thus to obtain information on the present sites for  $K^+$  adsorption/desorption.

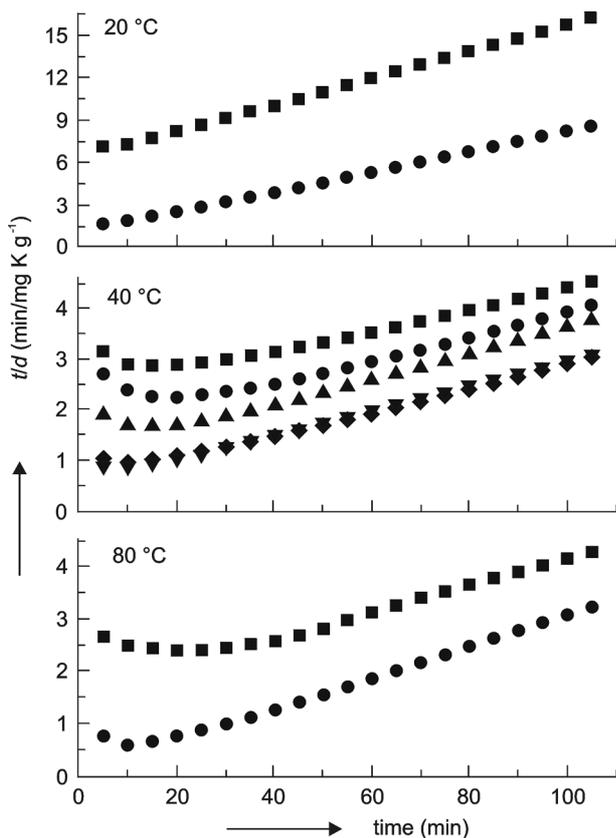


Figure 2. EUF desorption of  $K^+$  from the clay fraction of bentonite:  $t/d$  (time of desorption/desorbed amount of  $K^+$ ) vs.  $t$  dependencies at various temperatures and voltages.  
 a)  $T = 20\text{ }^\circ\text{C}$ , ■ - 50 V, ● - 400 V; b)  $T = 40\text{ }^\circ\text{C}$ , ■ - 50 V, ● - 100 V, ▲ - 150 V, ▼ - 200 V, ◆ - 400 V; c)  $T = 80\text{ }^\circ\text{C}$ , ■ - 50 V, ● - 400 V.

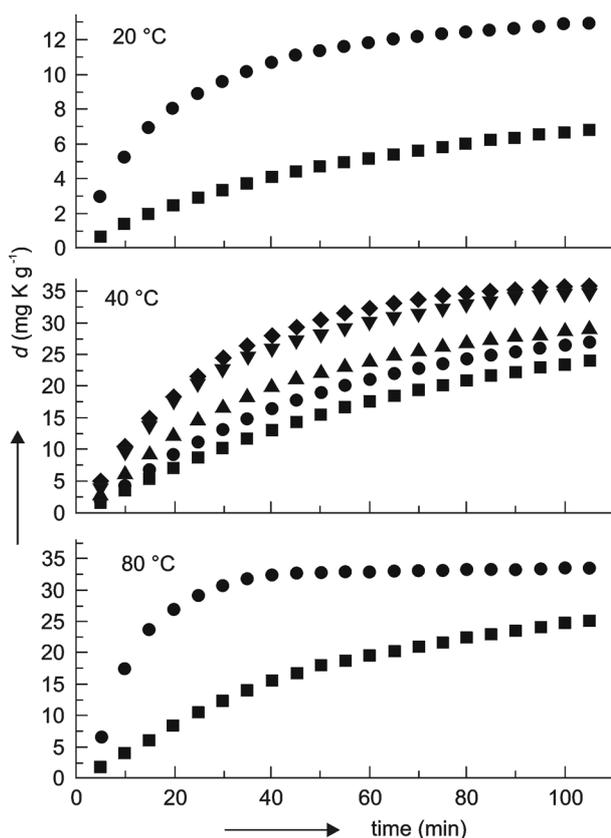


Figure 3. Total EUF desorption of  $K^+$  from the clay fraction of bentonite at various temperatures and voltages.  
 a)  $T = 20\text{ }^\circ\text{C}$ , ■ - 50 V, ● - 400 V; b)  $T = 40\text{ }^\circ\text{C}$ , ■ - 50 V, ● - 100 V, ▲ - 150 V, ▼ - 200 V, ◆ - 400 V; c)  $T = 80\text{ }^\circ\text{C}$ , ■ - 50 V, ● - 400 V.

## EXPERIMENTAL PART

### Material

$K^+$ -saturated clay fraction was prepared from the bentonite from Jelšový Potok deposit in the Kremnica Mountains (Slovakia). The coarse ore was size fractionated to  $<2\text{ }\mu\text{m}$ , potassium saturated with KCl, washed free of chloride with water, centrifuged, dried at  $60\text{ }^\circ\text{C}$  and ground to pass a  $<0.2\text{ mm}$  sieve. Montmorillonite was the only mineral identified by X-ray diffraction and infrared spectroscopy. This montmorillonite is of inhomogeneous layer charge distribution, covering the charges of  $0.25 - 0.36\text{ e}^-/\text{O}_{10}(\text{OH})_2$ , which were found for other montmorillonites as well [21]. Heterogeneity in the charge contributes to the distribution of the bond strength of  $K^+$  ions. Chemical analysis showed 0.16 and 4.18 wt % potassium content in the  $<2\text{ }\mu\text{m}$  fraction before and after the  $K^+$ -saturation, respectively.

### Methods

A modified EUF 724 apparatus (Vogel, Giessen, Germany) was used. The modification allows to collect effluents from the compartments B and C at any time, the total time of extraction is unlimited and no additional solvent is added to cell A (figure 1). The EUF extractions of  $K^+$  were performed at 20, 40 and  $80\text{ }^\circ\text{C}$ , voltages 50 - 400 V and times up to 105 minutes. 100 mg (for the EUF experiments at  $80\text{ }^\circ\text{C}$  and voltages 300 - 400 V) or 500 mg (all other experiments) of the clay mineral were dispersed in 70 ml  $\text{H}_2\text{O}$ .

$K^+$  content in the solutions was examined by atomic emission spectroscopy (AAS 3, Carl Zeiss Jena, Germany). All EUF experiments were performed at least in duplicates, selected runs were repeated up to five times. Deviations in the amounts of  $K^+$  desorbed from the mean values were always  $<5\%$ .

## RESULTS AND DISCUSSION

EUf data for the extractions performed at 20, 40 and 80 °C are presented in figures 2-4. The experiments at 20 and 80 °C were described in detail elsewhere [20], therefore only the data obtained at these temperatures using the lowest (50 V) and the highest (400 V) voltages are displayed in figures 2 and 3 for comparative reasons. Most of the  $t/d$  vs. time dependencies obtained at 20 °C [20] could be considered visually linear (figure 2), in agreement with the first experiments describing this method [18, 19]. The linear shape of the  $t/d$  vs. time dependence at the highest possible voltage of 400 V clearly showed that 105 minutes of EUf desorption at 20 °C were insufficient to remove all K<sup>+</sup> ions from this type of sites. This conclusion was supported by the total K<sup>+</sup> desorption curve at 400 V (figure 3), showing that increasing EUf extraction time  $t$  over 105 minutes would induce further K<sup>+</sup> desorption. This means that 12 mg K/g of sample, extracted at room temperature and 400 V within 105 minutes, does not cover all K<sup>+</sup> bound to a single type of sites. However, longer EUf experiments would be difficult due to the much decreased filtration rate through the anode filter covered by the negatively charged clay mineral particles and additional desorption of K<sup>+</sup> is very low. Application of higher vacuum causes cracks in the ultrafilters. These results led to EUf desorption experiments at higher temperatures.

The  $t/d$  vs. time lines obtained from the data measured at 40 °C were curvilinear, more resembling those obtained at 80 °C than those at 20 °C (figure 2). At lower voltages (50 - 150 V) the  $t/d$  values first decreased and later increased with increasing time, thus producing a minimum near 15 minutes. This feature clearly indicates that K<sup>+</sup> was desorbed at 40 °C from more sites in the montmorillonite structure [18]. Further increase in voltage (range of 200 - 400 V) had minor effect and the curves overlapped (figure 2). Similarly overlapped the curves showing the total amount of K<sup>+</sup> desorbed (figure 3). The shape of these curves suggests that potassium is desorbed at 40 °C independently on the voltage applied in the range 200 - 400 V. In other words, both the rate of desorption and the total amount of desorbed K<sup>+</sup> after 105 minutes is the same, about 36 mg K g<sup>-1</sup> of clay. This is about 85% of the total amount of K<sup>+</sup> present in the sample. EUf desorption experiments at 80 °C did not lead to any higher amount of desorbed K<sup>+</sup> at 200 - 400 V, however, the desorption was faster than at 40 °C. This means that about 15% of total potassium present in this material is fixed in substances which can retain potassium in high direct electric field up to 80 °C. No accessory minerals were identified by X-ray diffraction in the sample, thus admixtures can include only minor amounts of crystalline minerals containing potassium, such as feldspars, which are frequently present in bentonites. Alternatively, K<sup>+</sup> ions can be more strongly held in bigger montmorillonite particles than in the smaller ones and/or partly trapped in non-swelling (illitic) inter-

layers. Quasicrystals of various size occur in the fine fractions of bentonites and illite/montmorillonite mixed layer minerals are very common in nature and many bentonites contain these minerals with low content of non-swelling interlayers rather than pure montmorillonites with 100% of swelling interlayers [22, 23]. Application of EUf need not to be sufficient to remove all K<sup>+</sup> from the illitic interlayers. 80 °C is the upper temperature limit for EUf experiments using this apparatus. Longer desorption times than 105 minutes would be inconvenient for two reasons: slow filtration rates due to montmorillonite coverage of the microfilter on the anode and frequently appearing cracks of the microfilters when applying higher vacuum to increase the filtration rate.

Total desorption curves at single temperature and voltage did not provide sufficient information on the number of various sites for K<sup>+</sup> desorption. On the other hand, in several cases a voltage increase by 50 V caused only a negligible change in K<sup>+</sup> desorption curve and both curves overlapped (figure 3). More facts can be gained using the EUf data obtained at different temperatures and voltages and selecting those parts of these curves where maximal desorption has not been reached. Comparison of the series measured (figure 3) led to selection of 30 - 40 minutes as the most suitable times. Total desorption of K<sup>+</sup> from one gram of clay within 30 - 40 minutes at different temperatures and voltages are shown in figure 4. More parts can be distinguished on these dependencies thus showing the desorption of K<sup>+</sup> from different sites. EUf experiments at 20 °C using the voltages range 50 - 350 V caused desorption of K<sup>+</sup> from the weakest sites present, i.e. probably mostly from the sites on the surface of the particles (surface (*s*) sites). The dependencies obtained for all three selected times were parallel in this voltage range. Their regular increase was slightly slowed down at 200 V, then increased again and terminated at 300 V after the desorption of about 9 mg K g<sup>-1</sup> clay, which is about 22% of total potassium present. Two parts of the desorption dependencies (50 - 200 and 200 - 300 V) in this region suggest that the surface sites can be divided into two groups, which are similar but not fully equivalent in the strength of K<sup>+</sup> bonding (figure 4). EUf is unable to strictly distinguish between them. A sensitivity limit to distinguish between alike sites in montmorillonite structure is known from previous investigations using other experimental methods, such as Mössbauer or infrared spectroscopy. Fe(III) signals in Mössbauer spectra of smectites are frequently fitted with only two doublets characterising two groups of similar sites, which differ slightly due to some differences in the second nearest environment of the Fe atoms. At least comparable if not superior fits were achieved using distributions of the parameters of the doublets, thus proving that rather a continuous distribution of the mutual effect of the atoms present in the structure on the Fe(III) sites occurs.[24]. Similarly, variations in the neighbourhood of atoms involved in various vibrations observed in the IR spectra of

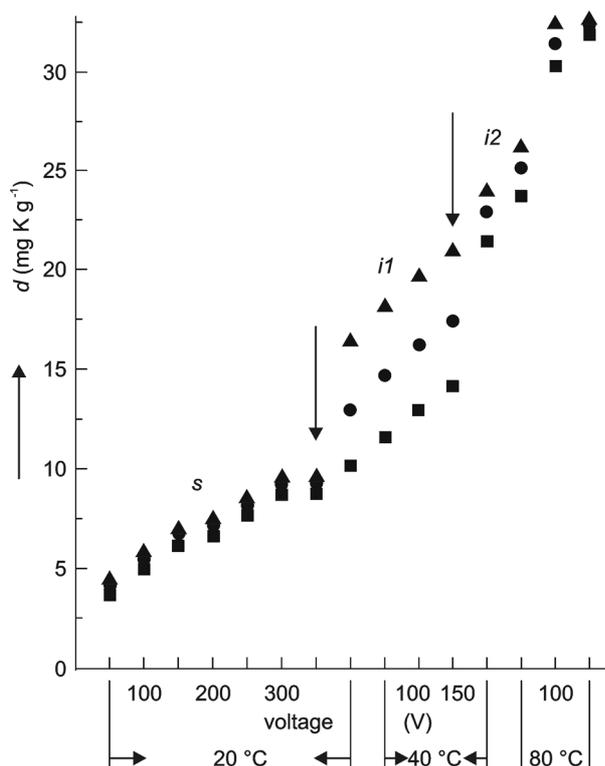


Figure 4. Total EUF desorption of  $K^+$  from the clay fraction of bentonite within 30 - 40 minutes at different temperatures and voltages; *s* - surface sites; *i1* and *i2*- weaker and stronger interlayer sites, respectively.

■ - 30 min, ● - 35 min, ▲ - 40 min.

smectites cause bands broadening rather than appearance of separated bands [25]. Consequently, it is thought that desorption of  $K^+$  from montmorillonite under the same EUF conditions covers desorption from a set of similar rather than same  $K^+$  sites.

Increasing the voltage applied at 20 °C from 350 to 400 V, substantial increase in the amount of desorbed  $K^+$  occurred, indicating the onset of desorption from the next weakest (interlayer, *i1*) sites (figure 4).  $K^+$  desorption shown in this part of the desorption dependencies was strongly dependent on both the length and the voltage applied in EUF experiments, thus revealing that both these parameters affected the desorption substantially. The 30 - 40 min. desorption curves were roughly linear and parallel in the 20 °C / 400 V - 40 °C / 150 V region, however, the distance between them was much bigger than in the 20 °C / 50 - 350 V region, thus proving time-sensitive  $K^+$  desorption from the *i1* sites. Increased voltage from 150 to 200 V at 40 °C caused accelerated desorption in all three sets of EUF extraction experiments shown in figure 4, thus exhibiting onset of  $K^+$  desorption from another type of sites, retaining  $K^+$  more toughly as the *i1* sites. It is supposed that these sites are also

interlayer sites (*i2*), occurring in the less swelling interlayers, probably close to highly charged layers, and/or in the bigger particles. Distribution of layer charge on Jelšovský Potok montmorillonite is heterogeneous [21] and the layers of the highest negative charge could possibly trap  $K^+$  effectively. Moreover, application of a high direct electric field and vacuum causes limited swelling of the montmorillonite interlayers in the mineral particles stacked to the filter on the anode, thus hindering the availability of  $K^+$  for desorption. The data for various durations of EUF extraction do not overlap but lie apart (figure 4), proving that there is no sharp difference in the energy needed for desorption of  $K^+$  from *i1* and *i2* sites. This was expected because neither continuously changing size of the particles or charge of the layers, nor limited swelling can create a sharp border between *i1* and *i2* sites. Possible inclusion of some of *i1* and *i2* sites into any of these groups is more likely.  $K^+$  ions got partly desorbed from *i2* sites using 200 V at 40 °C, higher levels of desorption were achieved at 80 °C. Total desorption of  $K^+$  at 80 °C / 150 V was roughly time independent for the 30 - 40 minutes EUF experiments (figure 4), reaching about 35 mg of desorbed  $K^+$  per one gram of clay, which was the maximal desorption achieved in this study. Some of the layers of the highest negative charge could possibly trap  $K^+$  so strongly that it remained retained even after EUF desorption for 105 minutes at 80 °C, mainly if the layers did not swell. An in situ X-ray diffraction study of clay mineral layers collected on the anode filter in high electric field would be needed to test this hypothesis.

## CONCLUSIONS

Up to 85% of total  $K^+$  present in the K-saturated clay fraction of Jelšovský Potok bentonite were extracted by the EUF procedure. The remaining 15% are supposed to be bound in non-clay admixtures and/or in the biggest quasicrystals containing highly charged, possibly illitic interlayers. At least three different sites of  $K^+$  desorption occur on bentonite particles dispersed in water. The weakest  $K^+$  sites, occurring probably on the external surface of particles, cover about 9 mg K/g clay, i.e. 22% of total potassium present. The interlayer montmorillonite sites can be roughly divided into two groups without any sharp border between them. In the 30-40 minutes EUF experiments, desorption of  $K^+$  from the weaker interlayer sites started at 20 °C and 400 V and was observed also at 40 °C and 50 - 150 V. These sites are supposed to occur dominantly in smaller particles and in the swelling interlayers, close to the layers of lower negative charge.  $K^+$  desorption from the stronger interlayer sites, occurring probably mostly in the bigger quasicrystals and/or in the less swelling interlayers next to highly charged layers, started at 40 °C and 200 V.

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EXTRAKCIA DRASLÍKA  
Z ILOVEJ FRAKCIE BENTONITU

ALEXANDER ČUMAKOV,  
KLÁRA HRNČIAROVÁ, PETER KOMADEL

Ústav anorganickej chémie,  
Slovenská akadémia vied,  
Dúbravská cesta 9, 842 36 Bratislava, Slovensko  
E-mail: uachcumo@savba.sk

Metóda elektroultrafiltrácie (EUF) pri 20, 40 a 80 °C sa využila na sledovanie extrakcie draslíka z jemnej frakcie bentonitu po výmene vymeniteľných kationov K<sup>+</sup>-iónmi. Vyextrahovalo sa do 85 % celkového prítomného draslíka. Našli sa najmenej tri skupiny miest na časticach bentonitu dispergovaných vo vode, z ktorých sa K<sup>+</sup> desorboval. Trvanie EUF analýz v rozmedzí 30 až 40 minút bolo optimálne pre poskytnutie relevantných informácií o miestach desorpcie draslíka. Experimenty pri 20 °C a napätiach 50 - 350 V spôsobili desorpciu K<sup>+</sup> z povrchu častíc, ktorá skončila po extrakcii približne 9 mg K g<sup>-1</sup> ílu, teda 22 % celkového obsahu draslíka. Zvýšenie napätia na 400 V pri 20 °C spôsobilo začiatok desorpcie K<sup>+</sup> zo slabších sorpčných miest v medzivrstviach montmorillonitu, ktorá prebiehala aj pri 40 °C a 50 - 150 V. Predpokladá sa, že tieto miesta sa vyskytujú v napučiavajúcich medzivrstviach v blízkosti vrstiev s nižším záporným nábojom, prítomných pravdepodobne prevažne v menších časticach. Pri 200 V začala desorpcia K<sup>+</sup> zo silnejších miest v medzivrství, ktoré sa pravdepodobne nachádzajú prevažne vo väčších časticach v medzivrstviach s obmedzeným napučiavaním za daných experimentálnych podmienok, v blízkosti vrstiev s vyšším negatívnym nábojom. Podľa očakávania neexistuje ostrá hranica medzi slabšími a silnejšími sorpčnými miestami v medzivrství, spolu viažu 63% celkového draslíka prítomného v skúmanej jemnej frakcii bentonitu.