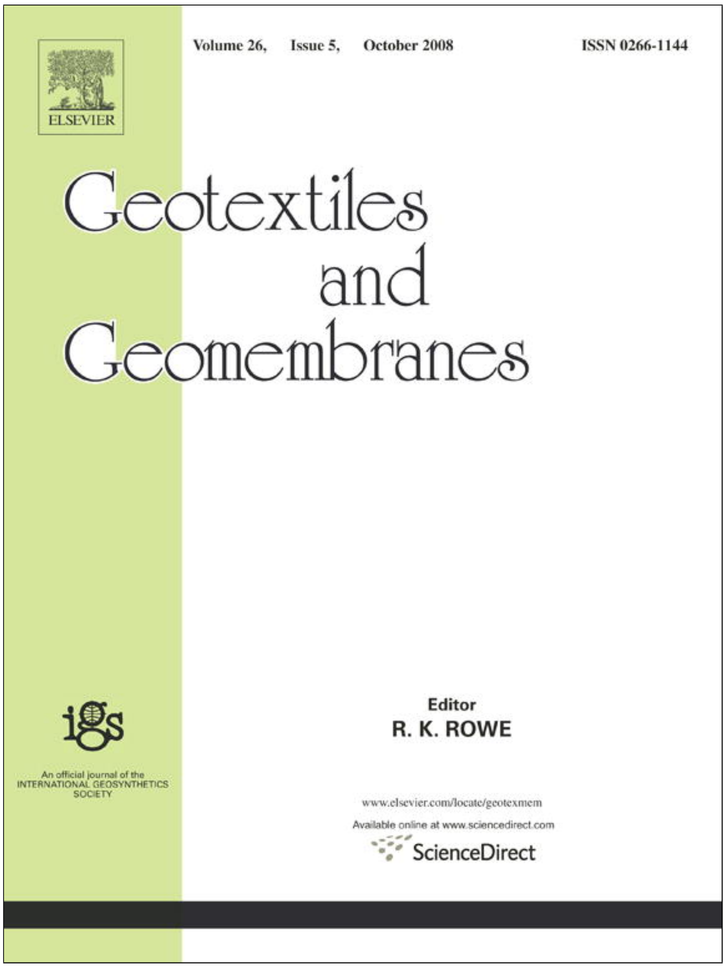
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Technical Note

An investigation into the use of blends of two bentonites for geosynthetic clay liners

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Abstract

Enhancement of geotechnical parameters of Fe-rich bentonite of lower smectite content (L: Lieskovec, Slovakia; 28–56% montmorillonite) by addition of an Al-rich bentonite of higher smectite content (JP: Jelšový potok, Slovakia; 64% montmorillonite) is discussed. The blends of different L and JP contents (L:JP 85:15, 75:25, and 65:35 mass%) were investigated. Addition of more expensive Ca^{2+}-JP to Ca^{2+}-L bentonite caused increase in the geotechnical properties (liquid limit w_L, plasticity limit w_P, water adsorption by Enslin test E_S) compared to raw Ca^{2+}-L samples, but the parameters were still insufficient for sealing purposes of Ca^{2+}-blends. After natrification of the blends with soda ash, the geotechnical parameters markedly improved. Permeability coefficients of all the blends were satisfactorily low, of the order of $10^{-11}\,m\,s^{-1}$. The liquid limit and water absorption values of the blend containing 65 mass% of Na^+-L and 35 mass% of Na^+-JP bentonites meets the requirements on geotechnical parameters of bentonites used in GCLs. Smectite content in the blends is the dominant factor affecting their properties.

Keywords: Geotechnical properties; Water adsorption capacity; Enslin test; Coefficient of permeability; X-ray diffraction; Infrared spectroscopy

1. Introduction

In recent years, the community increasingly focuses on broader uses of raw materials, occurring in relatively sufficient amounts. Among them, bentonites play an important role in the environmental applications. Results presented herein are related to the yet comprehensively unexplored Fe-rich bentonite from Lieskovec deposit (Slovakia).

One of the main problems in the environmental field is the intrusion of toxic contaminants from waste disposal and other sources into the subsoil and underlying ground water supply. Bentonite is commonly used for its low permeability characteristics for (a) a barrier in landfills (Browning, 1998; Bouazza, 2002; Janotka et al., 2002; Malusis et al., 2003; Montes-H et al., 2005; Touze-Foltz et al., 2006), where the adsorption ability, the ion exchange capacity and the swelling behavior of bentonite is important; (b) cut-off walls, where bentonite controls rheological behavior of the slurry and is responsible for the low permeability of the hardened bentonite–cement wall (Loxham and Westrate, 1995; Garvin and Hayles, 1999; Koch, 2002) and (c) nuclear fuel waste disposal sites where bentonites act as buffers to control the spread of radioactive materials into the ground and to protect the integrity of the canister against small rock movements on fractures (Güven, 1990; Cheung, 1994; Lingnau et al., 1996; Choi et al., 2001; McKinley et al., 2006).

Bentonite is being used in combination with geosynthetics to form a composite commonly known as a geosynthetic clay liner (GCL), which has been in use in the landfill construction since 1988 (Koerner, 1999). GCLs are used as a hydraulic barrier and/or contaminant layer for leachate, either in place of a composite layer or in addition to other layers in bottom landfill lining system (e.g., Bouazza, 2002; Southen and Rowe, 2005; Barroso et al., 2006; Bouazza et al., 2007). Bentonite used in GCLs

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is mainly a sodium bentonite, where sodium ions are located in the interlayer space, between clay platelets and on the external surfaces. A fully hydrated sodium bentonite layer has a hydraulic conductivity of approximately 100 times lower than a typical compacted clay liner (CCL). A single GCL of less than 10 mm provides superior hydraulic performance than 1 m of typical compacted clay. The increase in hydraulic conductivity of bentonite is caused either by aggressive leachates containing high amounts of divalent or higher valence cations, especially in landfills subjected to high percolation or in covers also, where the impact of cation exchange can be taken into the consideration. Na^+-bentonite in contact with landfill leachate will exchange its sodium for other cations (such Ca^{2+}, Mg^{2+}, K^+, heavy metals, etc.), which are present in the leachate in abundance. This exchange has a detrimental influence on the GCL hydraulic conductivity (it increases). Laboratory measurements by Ruhl and Daniel (1997) suggest that the influence can be minimized if the first liquid to permeate the GCL is water; these observations need to be investigated further in order to better understand the underlying mechanisms and establish whether this behavior lasts over time (Guyonnet et al., 2001). Thus, the hydraulic conductivity of bentonites is particularly sensitive to changes in the composition of the pore fluid that influences the thickness of the adsorbed layer. High concentrations of monovalent cations (e.g., 0.6 M NaCl) as well as low concentrations of divalent cations (e.g., 0.0125 M $CaCl_2$) can cause a significant increase in hydraulic conductivity provided the test is performed sufficiently long to allow for exchange of adsorbed cations (Shackelford et al., 2000).

Katsumi et al. (2008) concluded that bentonites exhibit remarkable swelling and chemical resistances, respectively, to electrolytic solutions of NaCl and $CaCl_2$ with a molar concentration of $\leqslant 1.0$ M.

The Na^+- to Ca^{2+}-smectite conversion is the most significant chemical transformation of smectite considered to occur during life span of a GCL. Artificially natrificated smectite could be reversibly transformed to origin Ca^{2+}-form with storage time. This cation exchange in MX80 (natural Na^+-bentonite, Wyoming) treated in 1 M solution of calcium chloride has been also confirmed. A simplified method based on volume balance has shown that swelling capacity of this bentonite would be affected after 1000 years of diffusion reaction (Montes-H et al., 2005). Time required establishing completion of cation exchange between the permeant liquid and thin layers of bentonite simulating GCLs is affected by (1) the rate at which adsorbing cation is delivered to the pore space (affected by seepage velocity and influent concentration); (2) the rate of mass transfer between the mobile and immobile liquid phases (controlled primarily by grain size of the bentonite) and (3) the number of sites available for sorption (controlled by CEC and the dry density of the bentonite) (Young Jo et al., 2006). It is shown that for Atterberg limit tests, even using 0.125 M calcium chloride solution full calcium exchange could be not achieved as the amount of liquid added to bring the bentonite to the liquid or plastic limit did not contain sufficient calcium ion for full exchange (Bouazza et al., 2007).

Substantial number of papers oriented to the effects of inorganic salts on the behavior of bentonite were published. However, the test with natrified Lieskovec/Jelšový potok blend have been just commenced and the investigation of Na^+ to Ca^{2+} conversion in terms of estimating the degree of sodium–calcium exchange has been not carried out until now.

The purpose of the present study was to evaluate the geochemical and geotechnical parameters of Ca^{2+}-bentonite vs. Na^+-bentonite from the Lieskovec deposit and of the blends of Fe-rich Lieskovec and Al-rich Jelšový potok bentonites in various ratios to examine the possibility for application of Lieskovec bentonite in GCLs.

2. Materials and methods

2.1. Materials

Raw Ca^{2+}-bentonite samples (Ca^{2+}-L4, Ca^{2+}-L5, Ca^{2+}-L11, Ca^{2+}-L15) from Lieskovec (L) deposit (Central Slovakia) were chosen according to various montmorillonite contents (Andrejkovičová et al., 2006, 2008). The samples were chosen by the previous geological survey. Individual sampling sites are illustrated in Fig. 1.

Ca^{2+}-L4 and Ca^{2+}-L5 (samples with the lowest Fe-rich montmorillonite content of 29% and 31%, respectively) belong to the 30 samples obtained from the Lieskovec deposit, developed from andesitic pyroclastics. Ca^{2+}-L11 and Ca^{2+}-L15 contain the highest amounts of montmorillonite (56% and 50%, respectively), as calculated using the RockJock program (Eberl, 2003), as mentioned later. The specimens were mixed with raw Al-rich Ca^{2+}-bentonite from Jelšový potok, Central Slovakia (Ca^{2+}-JP montmorillonite content 64%), recently used in the mixture with natural zeolite (9:1) as GCL in municipal solid wastes in Slovak and Czech republics. Its parent rocks are rhyolitic pyroclastics. Ca^{2+}-JP serves as an upgrading agent in ratio L:JP as follows: 65:35, 75:25 and 85:15 mass%, respectively. All the samples were air-dried at 60 °C and ground to pass a 0.063 mm sieve. The sodium forms of the mixtures were prepared by natrification with 4% solution of Na_2CO_3 to give consistence with bentonite necessary for liquid limit, air-dried at 60 °C and ground to pass a 0.063 mm sieve. This grain-size is unavoidable condition for manufacturing process (Janotka et al., 2002). The adjusted fineness of both clay and non-clay minerals in the betonites below 0.063 mm and specific surface area (SSA) values are decisive factors influencing the production conditions of bentonites; those with higher SSA are richer on the smectite content and therefore more suitable for GCL application.

The sample name indicates the exchangeable cation and the ratio of two bentonites in mass%. Thus Ca^{2+}-L4/JP-65/35 indicates the blend obtained from 65 mass% of Ca^{2+}-L4 and 35 mass% of JP bentonites.

Fig. 1. Sampling of Lieskovec bentonite (L1–L30) (Andrejkovičová et al., 2006).

2.2. Methods

The characterization and testing methods applied include:

- *The liquid limit* and *plasticity* values were obtained according to STN 72 1014 (Casagrande method) and STN 72 1013 (equivalent to CEN ISO/TC 17892-12:2005 and BS 1377).
- *Water adsorption.* Water adsorption was determined by the Enslin test (STN 72 1029, Standard equivalent to DIN18132 Standard).
- *Free swelling* was obtained as the volume of 2.0 g of a sample in 100 ml of distilled water measured in a graduated cylinder after 120 min of contact. The relative volume change was calculated by comparison to the volume of the dry powder.
- Determination of *permeability coefficient* in a triaxial apparatus is based on the Darcy's law (linear resistance law), which applies generally for steady water flow in soils. It is given as

$$v = k \times i, \tag{1}$$

where v is filtration velocity in $\mathrm{m\,s^{-1}}$, k is coefficient of permeability ($\mathrm{m\,s^{-1}}$), and corresponding flow rate:

$$q = k \times i \times A, \tag{2}$$

where q is quantity ($\mathrm{m^3}$) of fluid flow in a unit time t (s), k is coefficient of permeability ($\mathrm{m\,s^{-1}}$), i is hydraulic gradient, and A is cross sectional area ($\mathrm{m^2}$).

The hydraulic gradient can by expressed as

$$i = \frac{h}{l}, \tag{3}$$

where h is total head difference along the flow path of length or height of the tested sample, l is length or height of the tested sample.

Coefficient of permeability is calculated after modification of relation (1) by applying (2) and (3) to the formula:

$$k = \frac{q \times l}{A \times h \times t} \quad (\mathrm{m\,s^{-1}}) \tag{4}$$

Coefficient of permeability was determined in a triaxial cell apparatus by constant head permeability test, measuring the flow of water through the sample, according to the Manual of Soil Classification and Compaction Tests (Head, 1992) and Slovak technical standard STN 72 1020. The triaxial test determination with a pore pressure apparatus gives substantial control over the hydraulic gradient across the sample. Magnitudes of the gradients were from 30 to 100. The pressure of triaxial cell was 120 kPa and confining pressure was 100 kPa.

- *Total specific surface area* of the samples was determined using ethylene glycol monoethyl ether (EGME) retention. Approximately 0.25 g of a sample was placed in a glass vessel and dried to constant mass over P_2O_5 in an evacuated desiccator for 24–36 h. 0.8 ml of EGME was added to dried samples to form clay/EGME slurries. They were stored in an evacuated desiccator for 30 min and afterwards stored in vacuum over $CaCl_2$ and weighed after 1.5, 3, 4.5, 6 and 7.5 h evacuating intervals. After each weighing, the samples were returned to the desiccator. Surface areas were calculated according to Novák and Èíèel (1970).
- *Powder X-ray diffraction (XRD) profiles* of pressed powder samples were collected on the powdered samples with primary beam monochromatized Co Kα ($\lambda = 1.78897$ Å) radiation using a STOE Stadi P transmission diffractometer (Stoe, Darmstadt, Germany) configured with a linear position sensitive detector.

The diffraction patterns for RockJock analysis were collected in the 2θ range from 4° to 65°, using step of 0.02° 2θ, counting time 2 s per step, on a Philips

PW 1710 diffractometer with Cu Kα ($\lambda = 1.54056\,\text{Å}$) radiation and a secondary beam graphite monochromator PW 1752.

- *RockJock*. Quantitative analysis of bentonites was performed applying the RockJock program (Eberl, 2003). The program fits the sum of stored XRD patterns of pure standard minerals (the calculated pattern) to the measured pattern by varying fraction of each mineral standard pattern, using the Solver function Microsoft excel to minimize a degree of fit parameter between the calculated and measured pattern. Samples for analysis were prepared by adding 0.111 g ZnO (internal standard) to 1.000 g sample. The mixture was ground in a McCrone mill for 5 min with 4 ml of methanol then dried and sieved.
- *Fourier transform infrared (FTIR) spectra* were measured in the 4000–400 cm^{-1} region using KBr pressed-disk technique (1 mg of sample and 200 mg of KBr) on a Nicolet Magna 750 spectrometer with a DTGS detector and a KBr beam splitter. Discs were heated in a furnace overnight at 150 °C to minimize the amount of water adsorbed on KBr and the clay samples.
- *Chemical analyses* of the samples were obtained using standard methods in the geological laboratories GEL (Turèianske Teplice, Slovakia).

3. Results and discussion

Recent information on geotechnical properties of selected Lieskovec bentonite samples (Ca^{2+}-L4, Ca^{2+}-L5, Ca^{2+}-L11, Ca^{2+}-L15) is provided by Andrejkovičová et al. (2008). The permeability coefficients of the order of 10^{-11} m s^{-1} suggest possible suitability of this Ca^{2+}-bentonite for GCLs; however, other geotechnical properties like liquid limit and water adsorption by Enslin test provide insufficient values when compared to industrially made GCL Tatrabent (Janotka et al., 2002). On that account, Na^{+}-forms of L4, L5, L11 and L15 were prepared, and their geotechnical properties are summarized in Table 1. Smectite content of sodium forms is the same like Ca^{2+}-forms and amount of calcite produced in every natrified sample is negligible, less than 1 wt%. Na^{+}-montmorillonite is more hydrophilic than its Ca^{2+} counterpart, which also explains the large uptake of water between the platelets for this clay mineral (Luckham and Rossi, 1999). As expected, higher values of liquid limit, water adsorption by Enslin test and free swelling were obtained for sodium than for calcium forms of bentonites. Na^{+}-bentonites commonly used in GCLs are usually characterized by liquid limits of ~300–500%, water adsorption by Enslin test of ~400–600% and free swell values of 18–28% (Janotka et al., 2002). Liquid limits of the Na^{+}-samples investigated in this work are lower, ranging from 116% to 170% (Table 1). Enslin tests range between 243% and 363% showing that two samples Na^{+}-L11 and Na^{+}-L15 meet the requirements. Indeed, free swelling values of the Na^{+}-forms are at least twice higher than those of the Ca^{2+}-forms; however, even these values are insufficient for GCL applications (Janotka et al., 2002), though permeability coefficients for Ca^{2+}-L4, Ca^{2+}-L5, Ca^{2+}-L11 and Ca^{2+}-L15 are surprisingly low (10^{-11} m s^{-1}). Plasticity limits are comparable for Ca^{2+}- and Na^{+}-counterparts of all L samples but they differ significantly for Ca^{2+}-JP and Na^{+}-JP (54% and 27%, respectively). Based on the properties, four L samples can be divided into two groups: L4 and L5 of low montmorillonite content (31 and 28 mass%, respectively) and rather poor geotechnical properties vs. L11 and L15 of higher montmorillonite content (56 and 51 mass%) and advanced properties. These results demonstrate that the smectite content is the dominant parameter affecting geotechnical parameters within the L series. However, even the samples Na^{+}-L11 and Na^{+}-L15 with the highest montmorillonite

Table 1
Geotechnical properties of Ca^{2+}- and Na^{+}-forms of Lieskovec and Jelšový potok bentonites

Property	Ca^{2+}-JP	Ca^{2+}-L4	Ca^{2+}-L5	Ca^{2+}-L11	Ca^{2+}-L15
Liquid limit, w_L (%)[a]	120	70	64	80	76
Plasticity limit, w_P (%)[a]	54	35	33	48	44
Water adsorption by Enslin test, E_S after 24 h (%)[a]	450	123	127	265	259
Free swell test (%)[a]	8	4	3.5	5	4.5
Permeability coefficient, k ($\times 10^{-11}$ m s^{-1})[a]	0.5	2.7	2.9	2.4	2.1
Specific surface area SSA (m^2 g^{-1})[a]	617	303	289	458	460
Montmorillonite content (%)[a]	64	31	28	56	51
	Na^{+}-JP	Na^{+}-L4	Na^{+}-L5	Na^{+}-L11	Na^{+}-L15
Liquid limit, w_L (%)	338	120	116	170	163
Plasticity limit, w_P (%)	27	35	29	43	42
Water adsorption by Enslin test, E_s after 24 h (%)	795	247	243	363	360
Free swell test (%)	26	9	9	15	11
Permeability coefficient, k ($\times 10^{-11}$ m s^{-1})	0.3	1.3	1.6	0.3	0.9
Specific surface area, SSA (m^2 g^{-1})	472	243	239	290	268

[a] After Andrejkovičová et al. (2008).

content do not satisfy the necessities for GCLs. For comparison, geotechnical properties of Jelšový potok bentonite, which is commercially utilized in GCLs produced in Slovakia, are also provided in Table 1. All the parameters for both Ca^{2+}-JP and Na^{+}-JP are superior to those of the Lieskovec samples (Table 1) because of higher montmorillonite content and lower iron occurrence in the montmorillonite structure in JP. This is clearly confirmed by the results of FTIR and chemical analysis.

Therefore, further investigation was focused on improvement of geotechnical parameters of Lieskovec bentonite via addition of Jelšový potok bentonite into the blends of various ratios. Compositions of different blends and their properties are reported in Table 2.

There is strong evidence in the literature indicating that SSA is one of the most important contributing factors influencing the engineering behavior of fine-grained soils, describing a linear relationship between SSA and liquid limit (e.g., Grabowska-Olszewska, 1970; Ohtsubo et al., 1983; Locat et al., 1984; Smith et al., 1985; Churchman and Burke, 1991, etc.). The EGME sorption on smectite exhibits similar dependence on exchanged cation in the interlayer space like water uptake at certain relative humidity (McNeal, 1964; Carter et al., 1965). SSA depends mostly on smectite content and amount and pore size.

SSA values (Table 1) of Ca^{2+}-forms increase in the order L5, L4, L11, L15, which is the order of increasing montmorillonite content. The same trend was obtained for liquid limits of the samples. The values of SSA are higher for Ca^{2+}- compared to Na^{+}-forms because of superior solvation energy of Ca^{2+}.

Geotechnical properties of Ca^{2+}- and Na^{+}-Lieskovec/Jelšový potok blends (L:JP in ratio 65:35, 75:25, 85:15) are reported in Table 2. The ratios 65:35, 75:25 and 85:15 were chosen to save more quality JP bentonite and to ensure L bentonite consumption.

The parameters improved after adding Ca^{2+}-JP bentonite into Ca^{2+}-L4, Ca^{2+}-L5, Ca^{2+}-L11 and Ca^{2+}-L15 samples compared to Ca^{2+}-L (4, 5, 11, 15) in Table 1. It is a consequence of higher montmorillonite content and lower Fe content in JP bentonite.

Table 2
Geotechnical properties of the Ca^{2+}-bentonite blends

Sample	w_L (%)	w_P (%)	Free swell (%)	E_S (%)	SSA ($m^2\,g^{-1}$)
Ca^{2+}-L4/JP-65/35	99	41	4.5	237	503
Ca^{2+}-L4/JP-75/25	97	39	4	232	490
Ca^{2+}-L4/JP-85/15	90	37	4	227	482
Ca^{2+}-L5/JP-65/35	90	43	4	236	492
Ca^{2+}-L5/JP-75/25	86	40	3.5	213	483
Ca^{2+}-L5/JP-85/15	85	40	3.5	190	463
Ca^{2+}-L11/JP-65/35	109	38	5	352	533
Ca^{2+}-L11/JP-75/25	101	40	4	345	504
Ca^{2+}-L11/JP-85/15	95	40	4	334	489
Ca^{2+}-L15/JP-65/35	102	42	5	353	534
Ca^{2+}-L15/JP-75/25	98	44	4	343	512
Ca^{2+}-L15/JP-85/15	97	39	4	333	494

Smectites are well known for their affinity for water (Stucki, 2006). Structural Fe(III) and Fe(II) both significantly affect the smectite–water interaction. Early studies (reviewed by Stucki, 1988) indicated that the swelling of smectite is influenced by the cationic composition of the mineral layer, and that the presence of octahedral Fe(III) has a modest but generally depressing effect on water retention capacity.

Liquid limits and water adsorption by Enslin test values of all the blends increased compared to native dominantly Ca^{2+}-forms of Lieskovec bentonite, but they are lower than the values for Na^{+}-forms (Table 1).

As expected, specific surface areas of the Ca^{2+}-blends show highest values compared to initial Ca^{2+}- and Na^{+}-L and JP samples and to Na^{+}-blends. It is a consequence of addition of JP bentonite richer on smectite and Ca^{2+} cations and poorer on Fe content (Table 2). Values increase in order $85{:}15<75{:}25<65{:}35$ for all the blends. Na^{+}-blends reveal lower SSAs than Ca^{2+}-equivalents. It is an implication of lower solvation energy of Na^{+} and production of calcite in the natrification procedure.

Addition of JP influenced the free swelling values of the blends. Compared to native Ca^{2+}-L4/L5/L15, free swelling increased for samples with the highest JP content in the mixtures by 11–14%. Addition of JP (64% of smectite) did not affect swelling results of Ca^{2+}-L11/JP-65/35. This can be explained by rather minor increase in smectite content upon addition of JP to Ca^{2+}-L11 containing 56% of smectite.

Though the geochemical properties of the blends containing dominantly L bentonites with 15–35%, JP bentonite improved in comparison with the Ca^{2+}-L samples; however, their parameters were still not suitable for sealing purposes. Liquid and plasticity limits and water absorption values of Ca^{2+}-blends were anticipated to improve upon natrification. As expected, all the geotechnical parameters of Na^{+}-L/JP blends (Table 3) improved in comparison with those of Ca^{2+}-L/JP blends (Table 2, Figs. 2–4).

Main geotechnical properties of bentonite blends exhibit complex dependency on bentonite type (L or JP); blends composition and natrification (main parameters markedly differ for Ca^{2+}- and Na^{+}-forms of individual bentonites).

Figs. 2–4 show mutual dependences between important geochemical and geotechnical parameters of the blends of bentonites in detail. The expected results such as liquid limit and water adsorption values of Na^{+}-L/JP mixtures depend on smectite content and amount of JP mixed with L bentonite are illustrated in Figs. 2 and 3. The higher smectite content in Na^{+}-L bentonite and higher JP content, the higher liquid limit and water absorption is measured. The highest values of w_L and E_S show the blend Na^{+}-L11/JP resulting from high smectite content in L11 (56%). Opposite trend is obvious for Na^{+}-L5/JP blend (Figs. 2 and 3) caused by the lowest smectite content in L5

(28%). The Na$^+$-L/JP blends with 35% of Na$^+$-JP and 65 mass% of Na$^+$-L show the lowest permeability coefficients (Fig. 3). It is deduced that properties of the blends containing 65 mass% of Na$^+$-L and 35 mass% of Na$^+$-JP bentonite are very close to those required for bentonites used in GCL for reliable protection of the environment. Permeability coefficients of these blends are satisfactorily low to create sealing barriers in GCLs suitable for application in the field. Tests with other fluids are the matter of ongoing investigation.

Table 3
Geotechnical properties of Na$^+$-bentonite blends

Sample	w_P (%)	Free swell (%)	SSA (m^2 g^{-1})
Na$^+$-L4/JP-65/35	43	13	346
Na$^+$-L4/JP-75/25	44	12	332
Na$^+$-L4/JP-85/15	41	10	327
Na$^+$-L5/JP-65/35	45	13	333
Na$^+$-L5/JP-75/25	45	8	289
Na$^+$-L5/JP-85/15	41	6	250
Na$^+$-L11/JP-65/35	43	15	409
Na$^+$-L11/JP-75/25	44	13	393
Na$^+$-L11/JP-85/15	40	12	377
Na$^+$-L15/JP-65/35	44	14.5	414
Na$^+$-L15/JP-75/25	45	13	404
Na$^+$-L15/JP-85/15	41	11	397

3.1. X-ray diffraction

Mineralogical composition of the samples and effect of natrification can be seen in the X-ray diffraction patterns of the powders; selected traces are presented in Fig. 5. They provide better understanding of differences in the tested materials. Easily visible differences in mineralogical composition are only minor. The accessory minerals quartz, cristobalite, illite/muscovite and feldspars occur in most samples. Other non-clay minerals identified with RockJock include iron oxides/oxyhydroxides and microcrystalline forms of SiO$_2$. The Ca^{2+}-JP sample contains the lowest amounts of accessory minerals and the highest amount of smectite of all investigated Ca^{2+}-forms (Table 4). This is essential for upgrading geotechnical properties of the blends with L samples.

The effect of natrification is clearly seen when comparing the position of the first basal diffraction (d_{001}) of smectite.

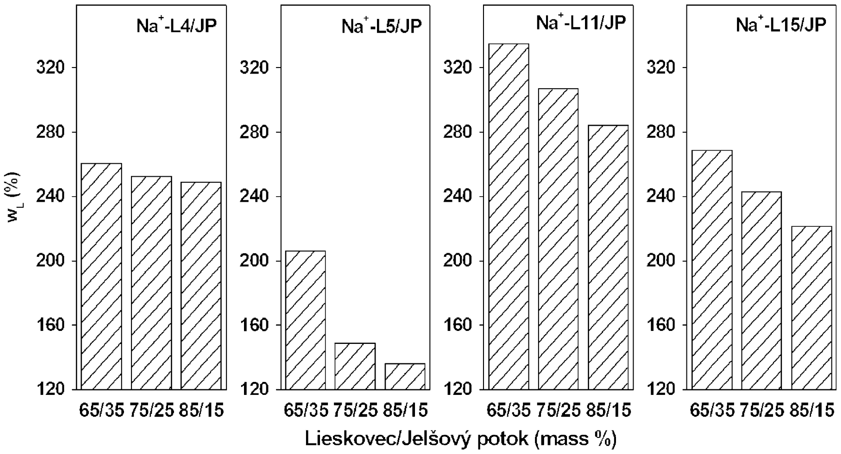

Fig. 2. Effect of blend composition on liquid limit.

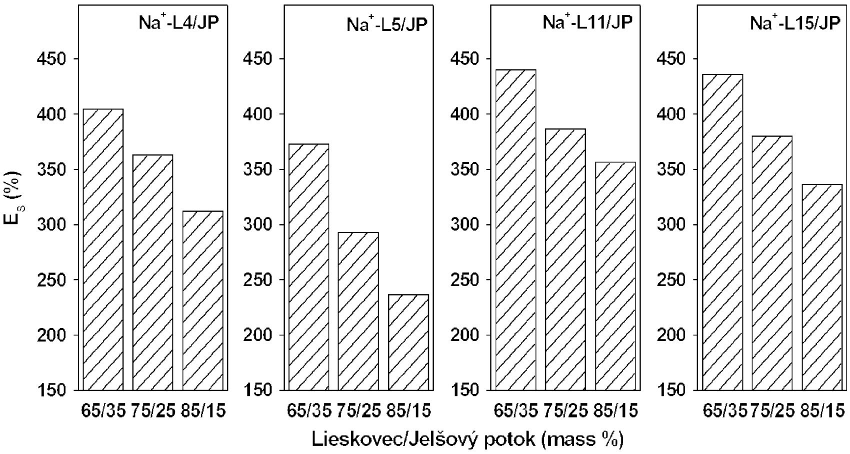

Fig. 3. Effect of blend composition on water adsorption (Enslin test).

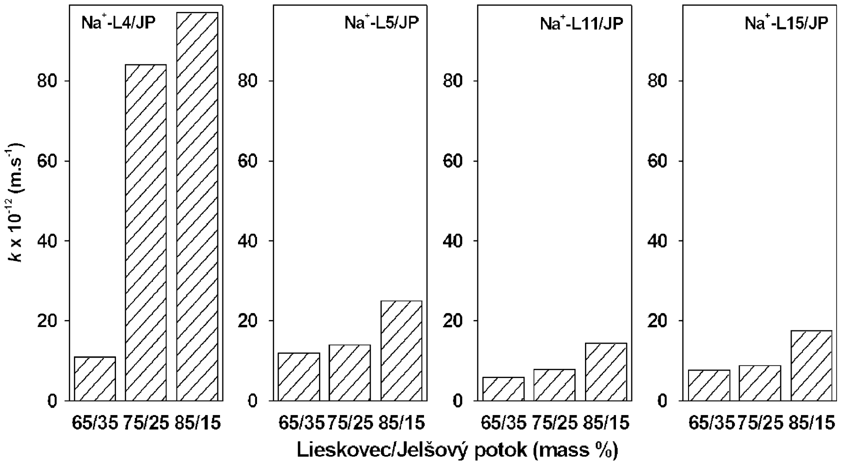

Fig. 4. Effect of blend composition on permeability coefficients.

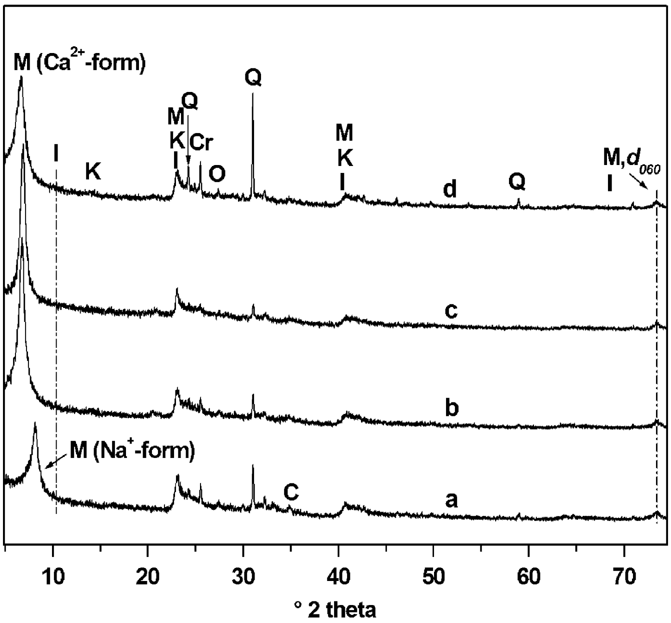

Fig. 5. X-ray diffraction patterns of the Na^+-L15/JP-65/35 (a), Ca^{2+}-L15/JP-65/35 (b), Ca^{2+}-JP (c), and Ca^{2+}-L15 (d) samples. M: montmorillonite, K: kaolinite, Q: quartz, Cr: cristobalite, O: orthoclase, I: illite/muscovite, C: calcite.

It occurs near 8.2° 2θ for the Na^+-saturated blend (Fig. 5, trace a, $d_{001} = 12.4$ Å), while for Ca^{2+}-saturated samples it appears near 6.8° 2θ (Fig. 5, traces b–d, $d_{001} =$ 14.9–15.0 Å). These values are in accordance with the literature data, e.g. Brindley and Brown (1980), proving more extensive hydration of the divalent Ca^{2+} cation. The value $d_{001} = 12.4$ Å for the Na^+-saturated L15/JP-65/35 blend suggests successful Na^+ for Ca^{2+} ion exchange in both montmorillonites present. A weak diffraction of calcite near 35° 2θ appears in the pattern of Na^+-L15/JP-65/35 only. It proves formation of $CaCO_3$ in the natrification process, when Na^+ cations from the added soda ash substitute Ca^{2+} cations in bentonite and these react with CO_3^{2-} anions present to form calcite. Its amount is negligible. Weak d_{001} diffraction peaks of kaolinite at 13.5° 2θ are visible in the X-ray patterns of all samples containing L bentonite. However, characteristic diffractions of kaolinite and illite/muscovite are missing from the pattern of Ca^{2+}-JP (Fig. 5).

Table 4
Mineralogical compositions of raw samples as obtained using the RockJock analysis

	Sample (mass %)				
	Ca^{2+}-JP	Ca^{2+}-L4	Ca^{2+}-L5	Ca^{2+}-L11	Ca^{2+}-L15
Smectite	64	31	28	56	51
Kaolinite	3	9	9	5	8
Illite/muscovite	9	7	13	6	3
Quartz	5	26	28	9	10
Feldspars	9	11	7	8	8
Other non-clay minerals	11	16	15	16	20

3.2. Infrared spectroscopy

IR spectra provide further information on mineralogical composition of the samples and chemistry of the dominating smectite. The adsorption band at 3622 cm^{-1}, assigned to stretching vibrations of structural OH groups of dioctahedral smectite (montmorillonite), occurs in the spectra of all samples (Fig. 6). The characteristic band of stretching vibrations of surface OH groups of kaolinite near 3698 cm^{-1} (Madejová et al., 2002) is clearly visible in spectra a, b and d of Fig. 6, i.e. in all spectra of samples containing L bentonite. X-ray diffraction of the blend Na^+-L15/JP-65/35 does not show occurrence of kaolinite; however, the characteristic kaolinite bands at 3698 and 693 cm^{-1} (Farmer, 1974) appear in the IR spectrum of this blend and confirm presence of kaolinite in this sample. Ca^{2+}-JP bentonite is poorer on this admixture.

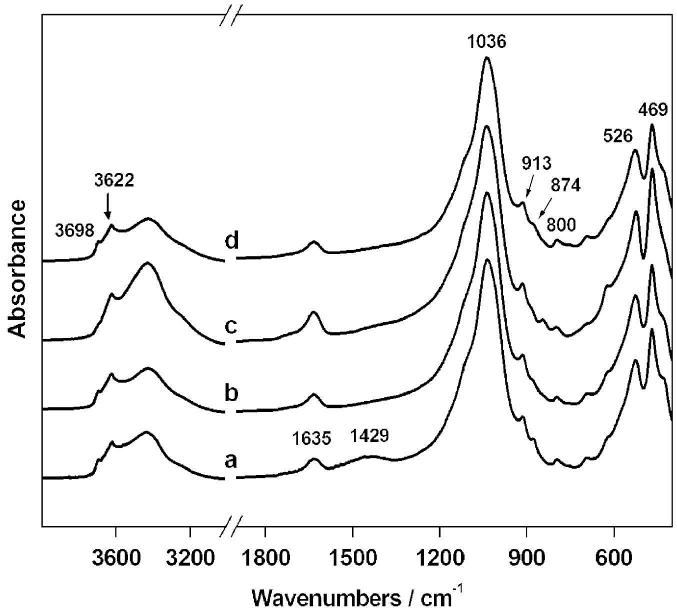

Fig. 6. Infrared spectra of (a) Na^+-L15/JP-65/35, (b) Ca^{2+}-L15/JP-65/35, (c) Ca^{2+}-JP, and (d) Ca^{2+}-L15 samples.

The doublet of quartz at 797 and 779 cm^{-1} is overlapped with the band of microcrystalline SiO_2 in the spectra of all samples. Admixture of calcite identified in the XRD pattern of Na^+-L15/JP-65/35 (Fig. 6, trace a) is recognized also in the IR spectrum. The broad band near 1430 cm^{-1} is ascribed to the stretching vibrations of CO_3^{2-} anions arose from natrification process.

Central atoms in the smectite structure affect the intensity of the components and thus the shape of the absorption bands especially of the OH-bending bands in the 950–800 cm^{-1} region (Fig. 6). Discrete and relatively intense peak at 913 cm^{-1} corresponds to AlAlOH bending vibrations of smectite, the OH bending vibrations of kaolinite and illite/muscovite may contribute to this band. X-ray diffraction shows absence of illite/muscovite and kaolinite in Ca^{2+}-JP sample thus the band at 913 cm^{-1} is attributed dominantly to the AlAlOH bending vibrations of montmorillonite. Therefore, Ca^{2+}-JP bentonite is named as Al-rich. Presence of Fe(III) in the octahedral sheets of L15 is confirmed by AlFeOH band near 880 cm^{-1} visible in the Ca^{2+}-L15 spectrum and Ca^{2+}-L bentonite is Fe-rich. This band is of low intensity in the spectrum of Ca^{2+}-JP, thus confirming low iron content in the structure of montmorillonite present and thereby better quality of the bentonite from Jelšový potok deposit.

One could expect that spectra a and b (Fig. 6) should be comparable, as the blends differ only in the interlayer cations. However, the peak of AlFeOH bending vibration at 874 cm^{-1} appears clearly in spectrum a, but only a shoulder is visible in spectrum b. The reason is that bending vibration of CO_3^{2-} anion, added in the natrification process, also contributes to this band in the spectrum of Na^+-L15/JP-65/35. The AlMgOH vibration near 845 cm^{-1} is not observed in the spectrum of Ca^{2+}-L15, thus proving relatively low Mg content in the octahedral sheets of the main mineral present in Lieskovec bentonite (Andrejkovičová et al., 2006). Spectrum c contains the AlMgOH vibration near 845 cm^{-1} proving higher isomorphous substitution in octahedral sheet in Ca^{2+}-JP resulting in higher layer charge and thus more quality of this bentonite. Higher layer charge and smectite content of Ca^{2+}-JP result in its better geochemical and geotechnical properties compared to L bentonite.

Table 5
Chemical analyses of the samples

	Sample (mass %)				
	Ca^{2+}-JP	Ca^{2+}-L4	Ca^{2+}-L5	Ca^{2+}-L11	Ca^{2+}-L15
SiO_2	65.9	64.5	62.6	64.0	61.3
Al_2O_3	18.6	16.9	17.5	17.7	19.4
Fe_2O_3	2.3	6.3	7.1	6.1	6.5
CaO	1.8	0.6	1.0	1.1	1.0
MgO	2.8	1.2	1.2	1.6	1.6
TiO_2	0.2	1.0	0.9	1.0	0.8
Na_2O	0.7	0.6	0.7	0.4	0.4
K_2O	1.2	1.8	1.7	1.3	1.2

Chemical analyses of the Ca^{2+}-bentonites are shown in Table 5. As expected, Ca^{2+}-JP contains more SiO_2, Al_2O_3, CaO and MgO compared to Ca^{2+}-L samples. Higher Fe(III) content, confirmed by IR spectra, include Lieskovec bentonite. Oxides of Na^+ and K^+ are comparable to Ca^{2+}-JP and Ca^{2+}-L (4, 5, 11, 15). Value of TiO_2 is lowest in Ca^{2+}-JP.

4. Conclusions

FTIR reports that AlAlOH bending vibrations of smectite are typical for Ca^{2+}-JP. Therefore, Ca^{2+}-JP bentonite is Al-rich. The presence of Fe(III) is confirmed by AlFeOH bending vibrations in Ca^{2+}-L bentonites indicating Fe-rich smectite. Differences in the content of iron in the structure of smectite are confirmed by chemical analysis; Fe_2O_3 in Ca^{2+}-JP is 2.3% opposite to 6.1–7.1% occurring in Ca^{2+}-L samples.

Soda ash treatment of the blends of an Al-rich (JP) bentonite of higher smectite content and a Fe-rich (L) bentonite of lower smectite content produces materials of promising geotechnical properties (liquid limit, water adsorption, free swelling and permeability coefficient) for application in GCLs. North part of Lieskovec deposit specified by the samples of L10 to L15 (see Fig. 1) is the most suitable for bentonite blends. This is due to highest smectite content varying between 50% and 56%, respectively. JP bentonite serves as correction constituent improving swelling and sealing properties of the blends with the less expensive L bentonites. The blend containing 65 mass% of Na^+-L and 35 mass% of Na^+-JP bentonite meets the requirements on geotechnical parameters of bentonites used in GCLs. Smectite content in the blends is the dominant factor affecting their properties. Over 10 years experience with GCL Tatrabent of Slovak provenance used at landfills might be the proof of reliability of artificially natrified bentonite, which is mixed together with natural zeolite in weight ratio 9:1. The aim of this investigation was to verify the potential mixing of different calcium bentonites prior to activation and use in GCLs.

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