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Microstructures and physical properties of "backfill" clays: comparison of residual and sedimentary montmorillonite clays

Richard Přikryl[a,*], Tereza Ryndová[a], Jan Boháč[a], Zuzana Weishauptová[b]

[a]Faculty of Science, Charles University, Albertov 6, 128 43 Prague 2, Czech Republic
[b]Institute of Rock Structure and Mechanics, Academy of Sciences of the Czech Republic, Prague, Czech Republic

Abstract

Hydrophysical behaviour of a backfill material produced as a mixture of montmorillonite-rich clays (fine-grained fraction) and ballast material (coarse-grained fraction) is studied. Two different genetic types of clays are evaluated—bentonite, representing the residual weathering type, and sedimentary montmorillonite-rich clay. Hydrophysical properties (liquid and plastic limits, permeability and swelling pressure) were determined for mixtures of mixing ratios from 0% to 100% by weight. The microstructural study focused mainly on pore space and specific surface determination that were employed for the interpretation of the hydrophysical properties. The most favourable results were obtained for activated Ca-bentonite but sedimentary montmorillonite-rich clays yielded good quality backfilling mixtures as well. The transition from fine to coarse-fraction dominated behaviour was established for mixtures containing about 20% of clayey admixture.
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1. Introduction

The isolation of high-level radioactive waste (HLRW) in solid bedrock at great depths (the Swedish concept—see, e.g., SKB, 1998) is based upon the multibarrier principle. Inorganic materials providing mechanical and hydraulic stabilisation of the waste (Lindblom, 1978) represent an important part of the multibarrier system (Savage et al., 1999).

Clays (mainly montmorillonite-rich, in situ weathered volcanic rocks–bentonites) are considered the most suitable material for the external multibarrier system. Bentonites (commonly used as containment liners and an industrial sealing and absorbent material with favourable properties like cation exchange capacity, swelling capacity, etc.—compare Elzea and Murray, 1994 or Kendall, 1996) were tested as an immediate envelope of canisters containing spent nuclear fuel—"buffer zone"—in the form of highly compacted blocks (NAGRA, 1985).

The remaining space of access tunnels and shafts must be filled with a material showing properties similar to buffer. The amount of the material required for backfill at each deposit is enormous—about $1-2$ mil m^3—i.e., at least six times higher than that of buffer (Lopez et al., 1987). The Swedish concept for nuclear waste disposal supposes the use of bentonite/ballast mixtures of different mixing ratios for this zone (SKB, 1995).

* Corresponding author. Tel.: +420-2-2195-1500; fax: +420-2-2195-1496.
E-mail address: prikryl@tao.natur.cuni.cz (R. Přikryl).

This paper aims at evaluating the hydrophysical behaviour of possible backfilling material composed of montmorillonite-rich clays mixed with ballast materials. Two different genetic types of clays are studied—bentonite, representing the residual weathering type, and sedimentary montmorillonite-rich clay. The second type offers an alternative source for backfilling. Its possible application in repositories of HLRW has recently been studied by Přikryl et al. (2001). Physical and hydrophysical properties of the individual constituents and of their mixtures were determined. These included liquid and plasticity limits, permeability and swelling pressure. Experimental results were interpreted in terms of optimum mixing ratio of clay and ballast.

Fig. 2. Grain size distribution curves of studied materials.

2. Experimental material

2.1. Clays

The studied sedimentary clays were collected in the operating Zelená clay quarry (part of Skalná deposit, Cheb basin, western part of the Bohemian Massif, Czech Republic). These upper Miocene sedimentary montmorillonite-illite clays of typical olive green colour (GE type from German "Grün Erde") occur in beds up to 20 m thick. At present, GE clay is occasionally quarried as a sealing material of landfill waste disposal.

Raw Ca-bentonite—R bentonite—was sampled at the Rokle deposit that is the largest bentonite deposit in the Czech Republic. Bentonites from the Rokle deposit include a 25-m-thick formation of basal pyroclastics, forming the periphery of Tertiary alkaline volcanic rocks of the Doupovské Mts., Bohemian Massif (Frańce, 1992). These processed bentonites are used as sealing agents, pet-litter or in foundry sand mixtures, etc. The producer (Keramost, Obrnice, NW Bohemia, Czech Republic) supplied processed bentonite samples—Ca-bentonite partly activated to Na-bentonite—(A bentonite) and milled non-activated Ca-bentonite—(M bentonite).

The mineralogical composition of the studied sedimentary clays and the bentonites was determined by X-ray diffraction (XRD). Dried and powdered samples were examined using the SIEMENS D-5005 equipment (Institute of Inorganic Chemistry, ASCR) with the following measurement conditions: radiation CuKα, secondary monochromator, voltage 40 kV, current 30 mA, in the degree range $2\theta\, 3-80°$ with $0.02°$ steps per 10 s. Analysis of smectites was facilitated by preparation of oriented and glycolated samples (Moore and Reynolds, 1997).
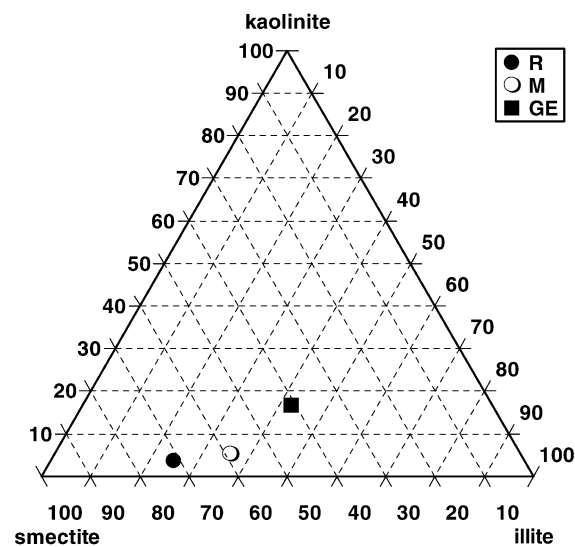

Fig. 1. Proportion of clay minerals in studied montmorillonite-rich clay and bentonites based on XRD measurement interpreted with the help of chemical analyses (in wt.%). R stands for raw bentonite, M stands for milled non-activated bentonite and GE stands for GE clay. Activated bentonite is not expressed.
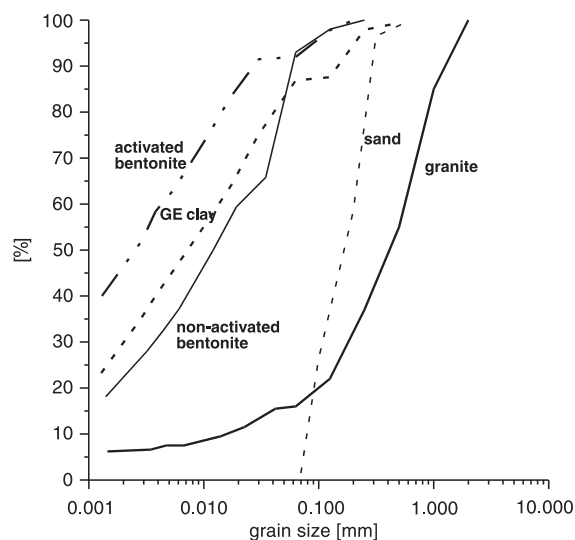
The raw data were processed by the ZDS for Windows program (Ondruš, 1997) employing diffraction pattern database (JCPDS, 1999). Presence and proportion of individual clay minerals was interpreted in detail according to Moore and Reynolds (1997). In order to facilitate determination of mineral quantities, wet chemical analyses of bulk clay samples were performed (Přikryl et al., 2001). The recalculated normative clay mineralogical composition is shown in Fig. 1. Quartz, Fe-oxides, calcite and amorphous phases were found in the studied clays and bentonites, in addition to clay minerals.

2.2. Ballast

Two types of ballast material were selected for the experiments. Fine-grained quartz sand (quarried for the glass industry) was sampled at Střeleč deposit (Bohemian Cretaceous Basin, Czech Republic). Quartz sand represents a pure, non-reactive material with well-sorted (see Fig. 2) and rounded grains.

There were two reasons to use crushed granite as another ballast material. First, its crushing produces angular grains being substantially different from the rounded sand grains. Second, granite comes from an area (Lipnice granite, Dolní Město quarry, Moldanubian pluton, Bohemian Massif, Czech Republic) that has been selected as an HLRW testing site. During construction of the repository, large amounts of the material would be excavated and the spoil may represent a convenient source of backfill ballast.

2.3. Preparation of test specimens

Dried raw GE clay, raw bentonite and granite were milled and sieved to a fraction smaller than 1.6 mm. The processed bentonite was supplied in particles smaller than 0.3 mm and was used without further

Table 1
Content of fine (FC) and coarse (CC) fraction (theoretical and based in grain-size distribution analysis), and basic index and hydromechanical properties of studied mixtures

Mixture	Theoretical FC (%)	Theoretical CC (%)	FC quartz/ granite grains (%)	CC quartz/ granite grains (%)	I_p (%)	e_0	e_f	k (m/s)	Swelling pressure (kPa)
GE100	83	29	83	29	39	1.25	1.61	1.50E−09	248
GE80Q20	66	23	63	22	27	1.07	1.4	4.90E−09	175
GE60Q40	50	17	49	18	21	0.97	1.16	1.40E−08	126
GE40Q60	33	12	37	16	18	0.82	0.87	3.20E−08	98
GE20Q80	17	6	33	13				6.10E−07	
Q100	0	0	0	0				4.80E−05	
GE100	83	29	83	29	39	1.25	1.61	1.5E−09	248
GE80G20	69	24	72	25	36	1.04	1.38	5.8E−09	312
GE60G40	55	18	61	18	29	0.94	1.18	2.5E−08	287
GE40G60	41	13	49	17	20	0.8	0.99	5.9E−08	268
GE20G80	27	7	34	13	8	0.7	0.75	2.5E−07	143
G100	13	2	13	2		0.54	0.52	2.9E−06	
BM100	93	24	93	24	63	1.7	2.02	1.7E−09	106
BM80G20	77	24	67	23	49	1.4	1.7	1.9E−09	117
BM60G40	61	18	60	20	37	1.12	1.25	2.5E−09	95
BM40G60	45	13	50	17	23	0.84	0.94	3.9E−09	62
BM20G80	29	7	32	10	10	0.61	0.63	1.8E−08	
G100	13	2	13	2		0.54	0.52	2.9E−06	
BA100	99	63	99	63	210				734
BA80G20	82	51	87	64	162				586
BA60G40	65	39	74	53	134				399
BA40G60	47	26	57	37	84	0.742	0.88	1.1E−11	262
BA20G80	30	14	40	24	31	0.595	0.71	1.9E−10	137
G100	13	2	13	2		0.54	0.52	2.9E−06	

GE stands for sedimentary montmorillonitic clay, BM for milled bentonite, BA for activated bentonite, G for crushed granite and Q for quartz sand.

modifications. The quartz sand was used in its natural state as obtained from the quarry.

Laboratory specimens were prepared by mixing the appropriate amount of GE clay or bentonite with quartz sand or granite to produce the following mixtures: 100:0, 80:20, 60:40, 40:60, 20:80 and 0:100 (in mass%). Reconstituted specimens were not subject to any standardised compaction effort. The individual constituents were analysed for basic microstructural properties, namely granulometry, porometry and cation exchange capacity.

3. Microstructural properties

3.1. Granulometry

Particle size distributions of all constituents were determined by sieving (for particles over 63 μm−CC fraction) and by hydrometer analysis (for particles smaller than 63 μm−FC fraction). For results, compare Fig. 2 and Table 1.

3.2. Surface area and porosity

Parameters characterising the porous structure of the materials were obtained from the sorption analysis using the SORPTOMATIC 1800 apparatus (Carlo Erba). The samples used were outgassed until they reached a constant weight, at a pressure of $<10^{-6}$ Pa and at the temperature of 333 K.

The specific surface area S_{BET}, which represents predominantly the external surface area of clay particles and the area of meso- and macropores (radii >2 nm), was determined according to the BET method
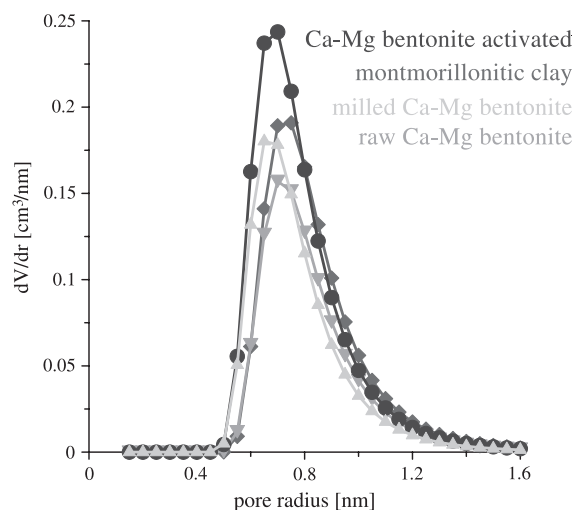

Fig. 3. Micropore size distribution of studied clays and bentonites.

(Brunauer et al., 1938) from the N_2 adsorption isotherm at 77 K.

The microporous structure (pores radii <2 nm) parameters were determined from the CO_2 isotherms at the temperature of 298 K within a pressure range from 0 to 1000 Torr. The isotherms were evaluated according to Dubinin's theory of volume filling. Dubinin's and Medek's equations (Dubinin, 1967; Medek, 1977) were applied in the calculation of the basic texture parameters, i.e., the volume of micropores V_{micro}, the surface area S_{micro} and micropores distribution represented by the most frequent radius r_{mode}.

The results of the porous structure analysis of GE clay and of the R, M and A bentonites are summarised in Table 2. Their micropore size distributions are shown in Fig. 3.

4. Hydromechanical behaviour

4.1. Swelling test

Mechanical properties of the enveloping clays must meet several important criteria to be able to prevent the canisters from sinking, to protect them from shear deformation or to heal rapidly possible fractures (Savage et al., 1999). The last requirement is associated with swelling capacity, an important phenomenon of montmorillonite bearing clays.

Table 2
Porous structure of studied clays and bentonites

	r_{mode} (nm)	V_{micro} (cm³/g)	S_{micro} (m²/g)	S_{BET} (m²/g)
GE clay	0.7259	0.0649	162	153
R bentonite	0.7143	0.0519	132	97
A bentonite	0.6794	0.0773	206	90
M bentonite	0.6712	0.0568	153	123

r_{mode}—the most frequent radius according to micropores distribution, V_{micro}—volume of micropores, S_{micro}—surface area of micropores (pores <2 nm), S_{BET}—surface area of meso- and macropores (pores >2 nm).
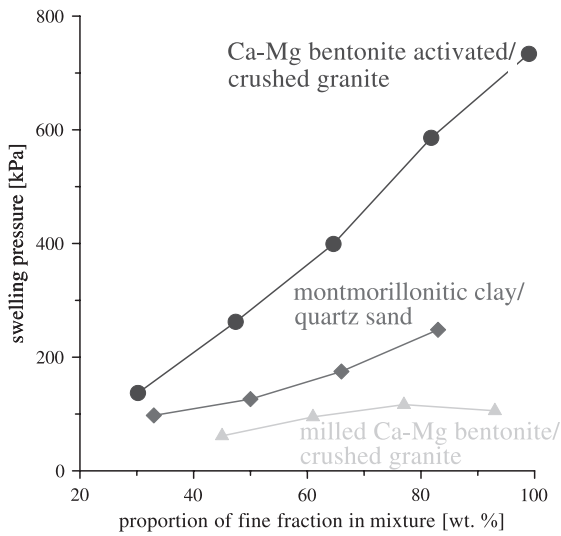
Fig. 4. Swelling pressure of GE clay and its mixtures with ballast. Mixtures are given in wt.%. Data for GE clay and milled bentonite are shown for pure fractions (100 wt.% of clay); data for activated bentonite are shown for mixture containing 40 wt.% of ballast (granite). BM stands for milled non-activated bentonite, BA stands for activated bentonite, GE stands for GE clay, Gr stands for granite and S stands for sand.

The swelling experiments were carried out in the oedometer on specimens of a diameter of 75 mm and a height of 20 mm that were initially consolidated by an axial pressure of about 44 kPa. After flooding the specimens, the axial load was controlled to prevent any change in the height of the specimens. Swelling pressures were computed from the axial load. Results are given in Fig. 4.

4.2. Hydraulic conductivity

The ability to prevent groundwater flow in back-filled tunnels and shafts is a favourable property of the backfill (Savage et al., 1999) and will be one of the decisive factors influencing the application of clays in HLRW repository. Experiments of Pusch et al. (1987) have shown that increasing content of smectite minerals negatively influences (decreases) hydraulic conductivity.

The present experiments were carried out in a triaxial cell on specimens with a diameter of 38 mm and a height of about 80 mm. Reconstituted specimens were prepared from dry constituents at the required mixing ratios and then flooded from bottom to top using a small hydraulic gradient. After flooding, saturation was facilitated by back pressure of 200 kPa. On achieving full saturation, measurement of permeability started in which hydraulic conductivity was determined at constant hydraulic gradients (approx. 26). Highly permeable mixtures and/or constituents ($k>1.0\times10^{-6}$ m/s) were
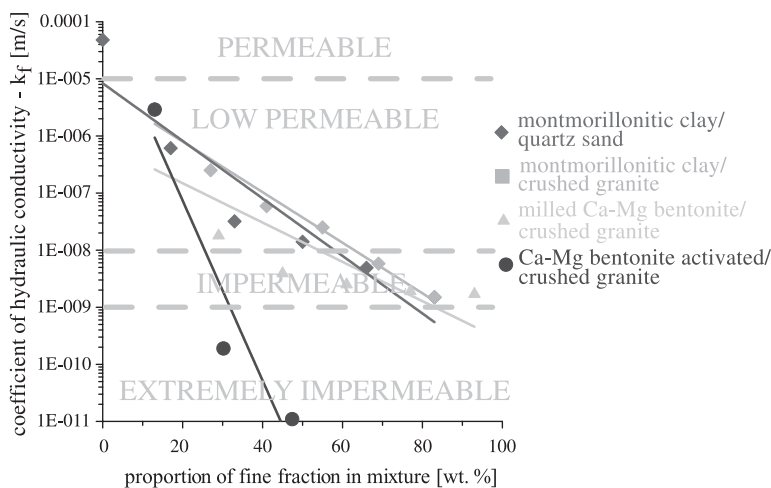

Fig. 5. Hydraulic conductivity of GE clay, non-activated bentonite and their mixtures with ballast. Mixtures are given in wt.%. BM stands for milled non-activated bentonite, BA stands for activated bentonite, GE stands for GE clay, Gr stands for granite and S stands for sand.

tested at hydraulic gradients of 5 to assure laminar flow. Resulting coefficients of permeability, determined with respect to the reference temperature of 10 °C (usual temperature correction), are shown in Fig. 5.

5. Discussion

Experiments on clay/ballast mixtures confirmed the anticipated decrease of hydraulic conductivity with increasing proportion of clay fraction in the mixtures. This is accompanied by an increase of plasticity index and an increase of porosity (void ratio). This contradicts previously published data on soils (Boháč et al., 1998; Thevanayagam and Mohan, 2000) where higher content of clayey fraction lead to decrease of porosity. Increasing e_{fin} with increasing fine fraction content in studied samples is explained by their unique mineralogy—i.e., presence of smectites with high internal microporosity.

Swelling pressure increases from milled bentonite/ granite—GE-clay/sand—GE-clay/—to activated bentonite/granite mixture. The surprisingly low swelling pressure for milled bentonite/granite mixture is probably caused by expansion of raw Ca–Mg bentonite due to temperature increase during processing (milling).

Grading and shape of fragments in ballast material represent another important factor influencing differences among studied mixtures. Uniformity coefficient (C_U) defined as d_{60}/d_{10} reaches 55 for crushed granite. The strong non-uniformity seems to decrease hydraulic conductivity of the mixtures with granite. This is indicated by comparing hydraulic conductivity values for mixtures GE-clay/sand and GE-clay/granite containing 80% of ballast. Sand is, on the other hand, uniformly graded with a very narrow grading curve and $C_U=2$.

Pore space represents a very important factor of fabric of soils. In addition to total porosity, the pore size distribution and surface area of pores are impor-
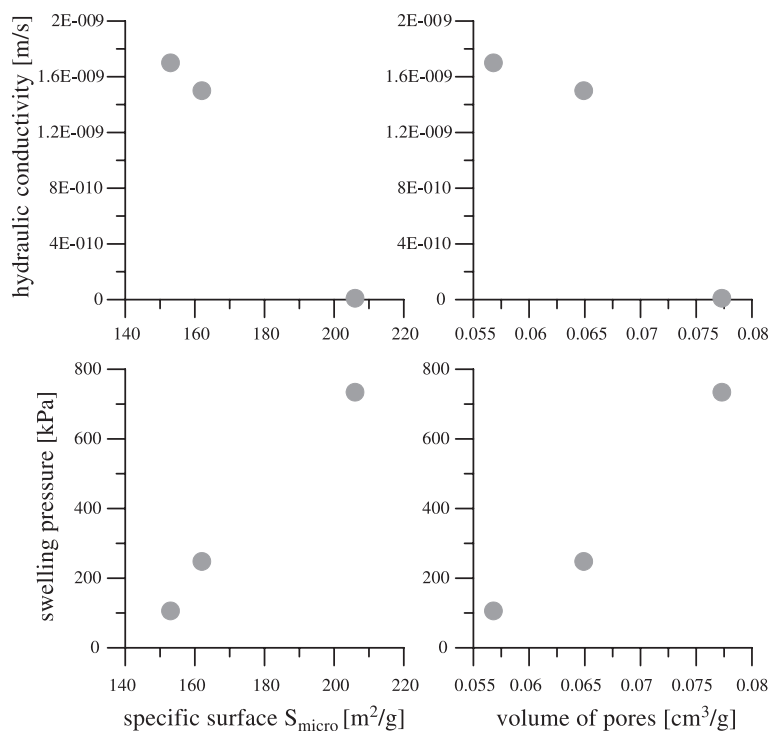

Fig. 6. Correlation between selected hydrophysical properties and micropore characteristics.

tant for the correct interpretation of mechanical and sorption properties. There is a clear correlation between micropore specific surface or pore volume and swelling pressure or hydraulic conductivity (Fig. 6). A higher proportion of micropores (expressed either by their specific surface or volume) means an increase of swelling pressure and decrease of hydraulic conductivity. The high proportion of micropores (pores of size less than 2 nm) is associated with the presence of the swelling clay mineral–montmorillonite and its crystal structure (stacking of trioctahedral and octahedral units). Favourable hydrophysical properties are enhanced by bentonite activation as can be seen from the difference between milled (non-activated) and activated bentonites.

The measured coefficient of permeability and swelling pressure probably present minimal values that may be favourably modified by the in situ processing of the backfill. Compaction will lead to a further decrease of hydraulic conductivity and an increase of swelling pressure. Although the technology of backfill placement has not been specified at yet, heavy compaction can be envisaged.

Generally, mixtures of fine-grained and coarse-grained soils behave as a coarse-grained constituent if the void ratio of the coarse-grained fraction is less than the maximum void ratio ($e_s < e_{s,max}$). On the contrary, when the voids ratio $e_s > e_{s,max}$ the mixture may behave as a fine-grained soil. From this simple assumption a transition void ratio and/or corresponding transition content of fines (particles smaller than 63 µm) can be estimated. The concept was found to work well for mechanical properties, for example strength or stiffness (Thevanayagam and Mohan, 2000; Boháč et al., 1998, 2002). However, it does not seem relevant in the case of hydraulic conductivity that depends more directly on the percentage of fines rather than on any mechanical interaction of particles and/or structural units.

6. Conclusion

Studied mixtures of smectite-rich clays and of ballast show a wide range of hydrophysical properties. Their behaviour is partly explained by microstructural (micropore) properties that seem be the most favourable for activated bentonite. The higher proportion of

fine voids (space between neighbouring TOT units) in bentonite is due to the higher content of smectites in comparison to montmorillonite (GE) clay and due to the activation of raw Ca-bentonite. Ballast can, to a limited extent, contribute to the modification of the hydrophysical properties, as shown for crushed granite with a high non-uniformity of grading curve.

References

Boháč, J., Kárník, J., Kořán, P., Záleský, J., 1998. Behaviour of mechanically stabilized soils. 26th Conference on Building Foundations, CGS, Brno (Czech Republic), pp. 96–99 (in Czech).

Boháč, J., Herle, I., Mašín, D., 2002. Stress and strain dependent stiffness in a numerical model of a tunnel. Proceedings of 2nd International Conference on Soil Structure Interaction in Urban Civil Engineering, Planning and Engineering for the Cities of Tomorrow, ETH Zürich, pp. 264–357.

Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60, 309–324.

Dubinin, M.M., 1967. Adsorption in micropores. J. Colloid Interface Sci. 23, 487.

Elzea, J., Murray, H.H., 1994. Bentonite. In: Carr, D.D. (Ed.), Industrial Minerals and Rocks. Society for Mining, Metallurgy, and Exploration, Littleton, pp. 233–246.

Franče, J., 1992. Bentonites in the eastern part of the Doupovské hory Mts. Sborník geologických věd. Ložisk. Geol. Mineral. 30, 43–90 (in Czech, with English summary).

JCPDS, 1999. Powder Diffraction File, PDF-2 Sets 1–49. International Centre for Diffraction Data, Newtown.

Kendall, T., 1996. Bentonite. Major market review. Ind. Miner. 344, 25–37.

Lindblom, E.E., 1978. Isolation of radioactive waste in Swedish Precambrian bedrock. Bull. IAEG 18, 157–158.

Lopez, R.S., Yong, R.N., Boonsinsuk, P., Card, E.C., White, P., 1987. Development of materials specifications and emplacement procedures for backfilling nuclear fuel waste vaults. Bull. IAEG 36, 43–50.

Medek, J., 1977. Possibility of micropore analysis of coal and coke from the carbon dioxide isotherme. Fuel 56, 131–133.

Moore, D.M., Reynolds, R.C., 1997. X-ray Diffraction and the

Identification and Analysis of Clay Minerals. Oxford Univ. Press, Oxford.

NAGRA, 1985. Project "Gewähr 1985", Feasibility and safety studies for final disposal of radioactive wastes in Switzerland. Nagra, Wettingen.

Ondruš, P., 1997. ZDS-Software for X-ray Powder Diffraction Analysis. ZDS Systems, Prague.

Přikryl, R., Ryndová, T., Vejsada, J., Jelínek, E., Boháč, J., Šebek, O., Hradil, D., Řanda, Z., 2001. Tertiary montmorillonitic clays from the Cheb basin (Czech Republic): alternative backfill material in the nuclear waste disposal. In: Piestrzyński, A. (Ed.), Proceedings of the Joint 6th Biennial SGA-SEG Meeting: Mineral Deposits at the Beginning of the 21st century. A.A. Balkema, Lisse, pp. 1055–1058.

Pusch, R., Börgesson, L., Erlström, M., 1987. Alteration of isolating properties of dense smectite clay in repository environments as examples by seven pre-Quarternary clays. SKB Technical Report TR 87-29. Swedish Nuclear Fuel and Waste Management Company, Stockholm.

Savage, D., Lind, A., Arthur, R.C., 1999. Review of the properties and uses of bentonite as a buffer and backfill material. SKI Report, vol. 99:9. Swedish Nuclear Fuel and Waste Management, Stockholm.

SKB, 1995. Treatment and final disposal of nuclear waste: programme for encapsulation, deep geologic disposal, and research, development and demonstration. SKB RD&D Programme, vol. 95. Swedish Nuclear Fuel and Waste Management, Stockholm.

SKB, 1998. Detailed programme for research and development 1999–2004. Background Report to RD&D Programme, vol. 98. Swedish Nuclear Fuel and Waste Management, Stockholm.

Thevanayagam, S., Mohan, S., 2000. Intergranular state variables and stress-strain behaviour of silty sands. Géotechnique 50 (1), 1–23.