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Toward Sustainable Society with Natural Resources - Frontiers in Earth Resources Technologies and Environmental Conservation -

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Mineralogical Characterization of Di Linh Bentonite, Vietnam: A Methodological Approach of X-ray Diffraction and Transmission Electron Microscopy

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ABSTRACT: Vietnam has decided to establish nuclear power as further energy option. In order to develop a Vietnamese reference bentonite as potential barrier in a final repository for high radioactive waste, a detailed mineralogical investigation of Di Linh bentonite (Lam Dong province), lacustrine clay, was carried out by different methods especially transmission electron microscopy (TEM) linked with energy-dispersive X-ray (EDX). From a sample homogenized from 5 tones of the bentonite, mineral formulae of clay particles was calculated The calculation also focuses on randomly interstratifications of two and three members.

The fraction <2 µm of Di Linh bentonite is composed mainly by montmorillonite ($Ca_{0.06}Mg_{0.03}Na_{0.09}K_{0.03}Al_{1.39}Fe_{0.25}Mg_{0.26}(OH)_2\ Si_{3.96}Al_{0.04}O_{10}$) and regular ordering (R1) illite-smectite interstratifications with K- and charge-deficiency ($Ca_{0.04}Mg_{0.07}Na_{0.18}K_{0.16}Al_{1.76}Fe_{0.08}Mg_{0.16}(OH)_2Si_{3.62}Al_{0.38}O_{10}$). Additionally, Fe-poor kaolinite-smectite-vermiculite interstratifications and trace of Fe-rich chlorite-smectite-vermiculite interstatifications were identified.

TEM-investigations showed analytical proofs of the sedimentary character of smectite formation in the Di Linh deposit. Parent muscovite was weathered in several steps in two different environments: (i) K-leaching and layer-wise alteration into kaolinite; (ii) further edge- controlled alteration of mica into lath-like montmorillonite particles under dissolution of kaolinite layers from former kaolinite-mica intergrowths. Mineralogical composition of the Di Linh bentonite with mainly montmorillonite and illite-rich illite-smectite interstratifications shows that the Di Linh bentonite can be a suitable barrier candidate in final repositories.

KEYWORDS: Bentonite, Transmission electron microscopy, X-ray diffraction, Montmorillonite, Interstratification

1. Material and methodology

Five tons of raw materials (milled < 5 mm) of the Di Linh bentonite (Tam Bo village, Di Linh district, Lam Dong province) from Hiep Phu Joint-Stock Company, HJC (Gia Hiep town, Di Linh district, Lam Dong province) were collected in 2013, homogenized, and used for this study.

Transmission electron microscopy (TEM) investigations were carried out on the < 2 µm fraction using a TECNAI G^2 20 at the VNU University of Science, Vietnam National University, Hanoi. This equipment operated at 200 kV with a LaB_6-cathode and S-TWIN objective and was equipped with an EDAX energy-dispersive X-ray system (EDX) and a FEI Eagle™ 2k CCD TEM camera. About 200 individual clay particles per sample were characterized by morphology, element distribution and electron diffraction (selected particle). The particle morphology was described according to Henning and Störr (1986). The electron diffraction allowed an evaluation of the stack order Zöller (1993). The general procedure to calculate the mineral formula from the EDX-analysis was carried out in according to the procedure of Köster (1977). Kasbohm et al. (2002) adopted to this procedure an Excel-based software tool, which converted results of EDX-analysis (in atom-%) into number of cation per unit cell.

Several methods used to characterize the Di Linh bentonite and to verify the TEM-data include X-ray fluorescence (XRF), differential thermal analysis (DTA), cations exchange capacity (CEC) and especially X-ray diffraction (XRD). The XRD analyses of the bulk samples were performed using a Philips X-ray diffractometer (PW 1710 diffractometer control, PW 1830 generator, PW 3020 vertical goniometer) equipped with a Cu tube (Kα1,2 radiation). The processing of XRD-powder pattern included Rietveld refinement for semi-quantitative determination of essential mineral components by BGMN-software package (Bergmann et al. 1998; Ufer et al. 2004) in cross-checking with the chemical composition of the bulk sample. The oriented specimens of <2 µm fractions were analyzed by SIEMENS Theta/2Theta D5000-goniometer equipped with a Cu tube ($K\alpha_{1,2}$ radiation). XRD patterns of air dried and ethylene glycol-saturated oriented specimens were modeled with the Sybilla© software developed by Chevron™ (Aplin et al. 2006) which is based on the program designed by Drits & Sakharov (1976).

2. Results and discussion

The XRD-powder diffractogram of a bulk sample from the Di Linh bentonite and its semiquantitative evaluation by BGMN-Rietveld refinement showed dominance of IS-ml, quartz, muscovite and ferrihydrite (Table 1). The dioctahedral character of IS-ml and muscovite was proofed by occurrence of their (060)-interference at 0.15 nm. A reverse calculation of chemical formula basing on BGMN-results has shown a good agreement with measured chemical composition by XRF (Table 1). This reverse calculation of chemical composition from BGMN-refinement resulted in a theoretical mass loss by dehydroxylation of 3.18 wt.% as sum of IS-ml (4.6 mg/100 mg), kaolinite (14 mg/100 mg) and chlorite (4.0 mg/100 mg). The thermogravimetric measurement also recorded a mass loss of 3.19% in the interval of 450 - 600°C.

Table 1. Semiquantitative mineralogical composition of Di Linh bentonite by XRD and BGMN-Rietveld refinement in cross-checking with chemical composition

Mineral composition		***Chemical composition***		
Mineral	*wt.%*	*Oxide*	*BGMN**	*XRF*
IS-ml	49%	SiO_2	57.9%	60.3%
Muscovite	9%	Al_2O_3	19.3%	21.3%
Chlorite	6%	$\sum Fe_2O_3$	15.6%	12.1%
Kaolinite	5%	MnO	-	0.1%
Quartz	16%	MgO	2.1%	3.5%
Plagioclase	2%	CaO	0.1%	0.6%
K-Feldspar	<1%	Na_2O	1.6%	1.1%
Anatase	2%	K_2O	1.3%	1.6%
Siderite	<<1%	TiO_2	2.2%	1.1%
Goethite	2%	P_2O_5	-	0.1%
Ferrihydrite	9%			

Note: IS-ml: Illite-smectite interstratifications; (*): chemical composition data were recalculated from BGMN-results

The XRD-patterns of oriented specimens (fraction < 2 µm) of the Di Linh clay showed full expandable IS-ml phases from 1.4 – 1.5 nm to 1.71 nm spacing by ethylene glycol saturation treatment. The fitting process by Sybilla©-software identified two main groups of illite-smectite interstratifications as main clay mineral component of the Di Linh bentonite. IS-ml structures in randomly interstratifications (Reichweite R0) with a smectitic-layer probability of about 90% dominated the fraction < 2 µm with 64%. This IS-ml was characterized by a full K-occupation in interlayer space of illite layers (1.92 per $(OH)_4O_{20}$) and a reduced charge of interlayer space in smectite (0.33 per $(OH)_4O_{20}$). Remarkable octahedral iron content was identified only for the smectitic layers. The second main group of IS-ml was characterized by a R1-ordering with 24%. This illite-rich IS-ml type was composed by 67% of illitic layers with high K-amount in interlayer space (1.90 per $(OH)_4O_{20}$) and also a low interlayer charge for smectitic layers (0.4 per $(OH)_4O_{20}$). The smectitic layers contained notable iron content in the octahedral sheet. Additionally, the approach of Sybilla©-software indicated occurrence of further minor components of clay minerals including kaolinite, illite and chlorite. These five identified clay mineral structures composed the XRD-pattern of EG-saturated and oriented specimen of the bentonite with a misfit of 15.5%. The occurrence of quartz caused mainly the visible differences.

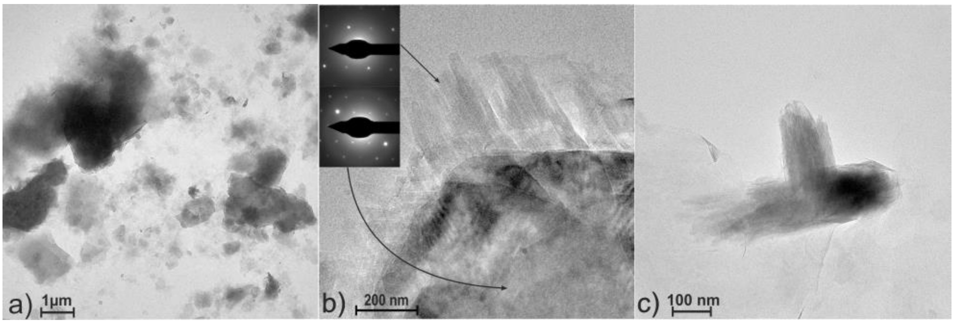

Fig 1. TEM-micrographs of Di Linh bentonite:
a) Illite-smectite interstratifications composed by xenomorphic plates with discrete margins and cloudy aggregates (5.000×); b) Lath-like illite-smectite interstratifications with idiomorphic ends growing at the edges of xenomorphic plates (43.000×) and electron diffraction images of selected areas; c) Goethite (71.000×)

Dioctahedral vermiculite-smectite interstratifications (diVS-ml) were the main clay mineral components (74 frequency-%) in the clay identified by TEM-EDX. Kaolinite-smectite-dioctahedral interstratifications (KSV-ml) and quartz were minor phases with 14 frequency-% and 8 frequency-%, respectively. Furthermore, goethite, anatase and chlorite-smectite-trioctahedral interstratifications were also identified in traces in this sample.

Average mineral formulae of illite-smectite interstratifications in fraction < 2 µm showed a K-deficient composition in illite layers, which was classified as diVS-ml: $Ca_{0.05}Mg_{0.07}Na_{0.11}K_{0.08}$ $Al_{1.39}Fe_{0.41}Mg_{0.19}(OH)_2$ $Si_{3.76}Al_{0.24}O_{10}$. Interlayer space was Na-dominated, octahedral sheet was Fe-rich and smectitic layer probability (%S) is 54%. The diVS-ml phases were characterized in both samples by two morphological forms: (i) xenomorphic plates with discrete margins and (ii) cloudy aggregates, which are composed by < 50 nm broad laths with idiomorphic ends (Fig. 1a). These lath-like particles were found also commonly at the edges of the xenomorphic plates (Fig. 1b). Fe occurred also as discrete phase like goethite (Fig. 1c).

IS-ml identified by TEM-EDX was compared with XRD fitting results of fraction < 2 µm. Sybilla©-modeled components IS R0 and IS R1. These two phases from the Sybilla©-results confirmed the charge deficiency recognized by TEM-EDX. Otherwise, the TEM-EDX-data has shown remarkable differences concerning octahedral iron and %S in comparison to results from XRD-pattern modeling by Sybilla©. The TEM-EDX-based octahedral iron values were higher and the values of %S were lower than those from XRD-pattern modeling by Sybilla©-fitting [octahedral Fe: 0.41 vs. 0.21; %S: 54% vs. 75% (TEM-EDX vs. Sybilla©-fitting)]. Iron could form partially an iron oxide crust surrounding the particles. In this case, TEM-EDX-analyses measured also a certain Fe-amount, which was not part of mineral pattern. The Sybilla©-results for octahedral iron were applied to correct the calculation of mineral formula based on TEM-EDX-data. The lowered Fe-amount reduced also the sum of equivalent charges in the calculation of new mineral formula and caused an increasing of the other element values including Si. In result of this correction and considering the analytical error by TEM-EDX expressed as standard deviation of mean, the new values for %S calculated from corrected TEM-EDX-based mineral formula have shown a good agreement with the data from XRD-pattern modeling (Table 2). All TEM-EDX-data to particles of diVS-ml with a %S lower than 50% were averaged and corrected also by the octahedral Fe-value of Sybilla©-modeling for IS R1-phase. The same procedure has been carried for all of the TEM-EDX-data for diVS-ml particles with a %S higher than 50% as IS R0-phases. In result of this TEM-data processing, %S based on the TEM-EDX-data has shown good agreement with those data concluded from XRD-results (Table 2). A comparison between mineral formulae and morphology of particles indicated mainly the cloudy aggregates as montmorillonite-rich and randomly ordered species of diVS-ml (IS R0) and the xenomorphic plates with discrete edges as regular ordering illite-rich structures (IS R1).

Table 2. Mineral formulae [average, cations per $(OH)_2O_{10}$] of diVS-ml phase of Di Linh bentonite (fraction < 2 µm), corrected TEM-EDX-based by Sybilla©-based XRD-pattern modeling

Sample	Ca	Mg	Na	K	Al	Fe^{3+}	Mg	Ti	Al	Si	XII	n^{VI}	%S TEM	%S XRD
Di Linh	0.05	0.03	0.11	0.08	1.55	0.21	0.24	0.00	0.13	3.87	0.36	2.0	75%	75%
IS R0	0.06	0.03	0.09	0.03	1.49	0.25	0.26	0.00	0.04	3.96	0.30	2.0	91%	90%
IS R1	0.04	0.07	0.18	0.16	1.76	0.08	0.16	0.00	0.38	3.62	0.55	2.0	34%	33%

Notes: IS R0: montmorillonite-rich and randomly ordering illite-smectite interstratifications, values corrected; IS R1: regular ordering illite-smectite interstratifications, values corrected; XII: charge of interlayer space; n^{VI}: number of atoms in octahedral sheet; $\%S^{TEM}$: smectitic layer probability based on TEM-EDX measurement corrected Fe-values; $\%S^{XRD}$: smectitic layer probability based on XRD-pattern modeling by Sybilla©

3. Conclusion

The modeling of XRD-pattern by Sybilla© was a suitable approach to correct measured TEM-EDX-results especially concerning Fe content. The methodological combination of XRD and TEM offers a tool for mineral characterization of very fine and sensitive material like clays.

Pusch & Young (2006) described precipitation of dissolved Si and following cementation of smectite particles as remarkable problem for stability of main properties of a clay barrier for HLW repository. The identified mixture between dominating montmorillonite and remarkable amount of illite-rich illite-smectite interstratifications let expect Di Linh bentonite from mineralogical viewpoint as a suitable barrier material for final HLW repositories. The mentioned illite-rich interstratifications offer a higher Si-buffer in case of possible dissolution processes in the contact zone between nuclear fuel canister and bentonite barrier. Illitic layers from such interstratifications would be altered into montmorillonitic layers absorbing Si that was dissolved before. This process is protecting the barrier performance against precipitation and cementation of smectite particles by dissolved and not incorporated Si.

REFERENCES

Aplin, A. C., Matenaar, I. F., McCarty, D. K., & van der Pluijm, B. A., 2006. Influence of mechanical compaction and clay mineral diagenesis on the microfabric and pore scale properties of deep-water Gulf of Mexico mudstones. *Clays and Clay Minerals, 54*, 500-514.

Bergmann, J., Friedel, P., & Kleeberg, R., 1998. BGMN - a new fundamental parameters based Rietveld program for laboratory X-ray sources, it's use in quantitative analysis and structure investigations. Commission of Powder Diffraction, International Union of Crystallography. *CPD Newslett, 20*, 5-8.

Drits, V. A., & Sakharov, B.A., 1976. *X-ray structural analysis of mixed-layer minerals*. Nauka, Moscow, p. 276. (In Russian).

Henning, K. H., & Störr, M., 1986. *Electron micrographs TEM, SEM of clays and clay minerals*. Schriftenreihe für Geologische Wissenschaften, vol. 25. Akademie-Verlag, Berlin. p. 325.

Kasbohm, J., Tarrah, J., Henning, K.-H., 2002. Transmissionselektronen-mikroskopische Untersuchungen an Feinfraktionen der Ringversuchsprobe "Ton Stoob". In F. Ottner & S. Gier (Hrsg.), Beiträge zur Jahrestagung Wien, 18.-20.9. 2002. *Berichte der DTTG e.V., Band 9*, (pp. 71-84). Deutsche Ton- und Tonmineralgruppe.

Köster, H. M., 1977. Die Berechnung kristallchemischer Strukturformeln von 2:1 - Schichtsilikaten unter Berücksichtigung der gemessenen Zwischenschichtladungen und Kationenaustauschkapazitäten, sowie die Darstellung der Ladungsverteilung in der Struktur mittels Dreieckskoordinaten. *Clay Minerals, 12*, 45-54.

Ufer, K., Roth, G., Kleeberg, R., Stanjek, H., Dohrmann, R., Bergmann, J., 2004. Description of X-ray powder pattern of turbostratically disordered layer structures with a Rietveld compatible approach. *Zeitschrift für Kristallographie, 219,* 519-527.

Zöller, M.H., 1993. Charakterisierung von Illitkristallen durch konvergente Elektronenbeugung. In H. Graf v. Reichenbach (Hrsg.), Hydratation und Dehydratation von Tonmineralen, Beiträge zur Jahrestagung Hannover, 1992. *Berichte der DTTG e.V, Band 2*, (pp. 211-220). Deutsche Ton- und Tonmineralgruppe.

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