Short Communications

THERMODIELECTRICAL ANALYSIS

VI. Bentonites

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The paper presents an application of thermodielectrical analysis in a geological material of industrial interest (bentonites). Thermodielectrical curves show noticeable differences in dependence of the cationic content and chemical nature of the cations, and also, with the cation position in the lattice.

The term bentonite was first applied by Knight to a particular, highly colloidal, plastic clay found near Fort Benton in the cretaceous beds of Wyoming [1]. This clay is formed by the alteration of volcanic ash in situ and is largely composed of smectite clay minerals (montmorillonite, beidellite, nontronite, etc.).

DTA curves of smectitic minerals are quite different due to substitutions in the lattice. The dioctahedral minerals present two zones thermally active, the first between 100 and 300° where there occurs the loss of adsorbed water and the water associated with exchangeable cations, and a second zone between 500 and 1000° where the dehydroxylation, collapse and structural change of the mineral [2–5] take place.

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Experimental

Materials

The tested samples were selected from "Managua" deposit (Havana City province) and "La Tagua" manifestation (Guantanamo province) situated in the occidental and oriental region of Cuba, respectively.

Methods

X-ray diffraction, thermal analysis, infrared spectroscopy, electron microscopy and thermodielectric analysis were carried out. A DRON–2.0 diffractometer, MOM–1500 derivatograph, IR–71 Carl Zeiss spectrophotometer, JEM–100 s JEOL electronic microscope and scanning thermodielectric equipment [6] were applied. Also chemical analysis and cation exchange capacity were fulfilled.

Experimental conditions of the thermal analysis were the following: Sample weight: 800 mg, reference material: aluminium oxide annealed; thermocouples: Pt/Pt (10%)–Rh, sample holders: ceramic crucibles, heating rate: 10 deg/min, furnace atmosphere: air, without any current or turbulence, TG sensitivity: 200 mg.

In the case of X-ray diffraction, patterns were recorded using a goniometer rate of 1/2 deg/mm (2θ), soiler: 1.5° Cu(K$_\alpha$) radiation, angular range: 5–35° (2θ), time constant: 2 sec, sensibility: 1000 imp/sec, voltage: 35 kV and anodic current: 20 mA. X-ray intensities were recorded on strip chart recorder at 200 mm/h.

IR spectra in the range 400–4000 cm^{-1} were recorded with 0.2 mg sample weight in KBr pellets. The observations by electronic microscopy were carried out on samples dispersed in butyl alcohol. Thermodielectric curves were carried under the same conditions described in [6]. Clay fractions (<2.0 µm) were obtained using the classical levigation procedure. Clay specimens for XRD were prepared by applying the clay on glass slides (oriented aggregates (OA)) using a filter-membrane peel technique [7]. The amount was then dried in air and later saturated with ethylene glycol employing a vacuum pump [8]. Finally, the OA were heated to 600° for 1 hour. In the case of Managua samples it was necessary to saturate with LiCl [9], to differentiate between montmorillonite, beidellite or interstratified mineral.

The results obtained by XRD, and by derivatograph (DA), infrared spectroscopy (IR) and electron microscopy (EM) are presented in Table 1 also, chemical analysis and cation exchange capacity are presented in Tables 2, 3 and 4.

Table 1 X-ray diffraction, DA, IR and EM results of the tested samples (fraction < 2.0 μm)

Sample	Locality	Results			
		XRD	DA	IR	EM
M-1	Managua	Random of interstratification of beidellite and montmorillonite with beidellite predominantly* small amounts of kaolinite, quartz and goethite.	Interstratification beidellite and montmorillonite (peak 550 °C very broad), kaolinite, hisingerite (exothermic peaks at 830 and 970 °C.	Smectitic mineral beidellite type—(Al, Mg)-OH band—at 835–845 cm^{-1} very short, small amounts of quartz kaolinite and calcite.	Smectitic mineral and some particles of kaolinite.
M-2	Managua	Similar to M-1 also it contains hematite.	Similar to M-1, also it contains small amounts of calcite.	Similar to M-1 but it contains more—goethite and calcite than M-1.	Similar to M-1.
M-3	Managua	Similar to M-1.	Similar to M-1.	Similar to M-1.	Similar to M-1.
T-2	La Tagua	Dioctahedral smectite (montmorillonite (d060) = 1.50 A (10)).	Montmorillonite and small quantities of calcite.	Montmorillonite—(Al—OH band at ~910 cm^{-1} very well defined) small amounts of calcite and quartz.	Montmorillonite.
T-8	La Tagua	Dioctahedral smectite (montmorillonite (d060) = 1.50 A (10)).	Montmorillonite.	Similar to T-2 but it shows 910 cm^{-1} band more intense.	Montmorillonite.

* Interstratified mineral corresponds to dioctahedral series (d060 = 1.51 A calculated by the Rich method (10)). The diffractogram saturated with LiCl shows an irregular series of basal orders.

Table 2 Chemical analysis of "La Tagua" and "Managua" samples

Locality	Sample number	SiO_2, %	Al_2O_3, %	TiO_2, %	Fe_2O_3, %	FeO, %	MgO, %	CaO, %	Na_2O, %	K_2O, %	MnO, %	SO_3, %	CO_2, %	LDI, %	Total
La Tagua	T-2	55.68	18.91	0.30	3.58	0.25	3.84	1.30	0.40	0.89	0.1	0.5	1.00	15.08	100.23
La Tagua	T-8	51.88	22.04	0.42	4.82	0.08	4.20	0.78	0.10	0.14	0.1	0.5	1.00	15.63	100.09
Managua	M-1	48.54	21.45	0.93	9.33	0.06	2.18	2.12	0.1	0.24	0.06	0.5	0.25	14.35	99.57
Managua	M-2	49.92	21.70	0.92	8.94	0.06	2.35	2.14	0.1	0.18	0.08	0.5	0.20	13.54	99.97
Managua	M-3	49.60	19.90	0.81	8.95	0.06	2.41	2.17	0.1	0.30	0.05	0.5	0.75	14.50	99.40

Table 3 Cation exchange capacity results (meg/100 g) of "Managua" (M–1 to M–3) and "La Tagua" (T–2 and T–8) samples

Sample number	Ca^{2+}	Mg^{2+}	Na^+	K^+	$\sum Ca^{2+}, Mg^{2+}, Na^+, K^+$
M–1	63.07	16.06	0.086	0.012	79.21
M–2	45.43	15.69	0.057	0.012	61.17
M–3	64.68	17.32	0.053	0.021	82.09
T–2	19.94	25.72	0.01	0.12	45.79
T–8	26.24	28.96	0.01	0.07	55.31

Table 4 Cationic contents of calcium and magnesium total, exchangeable and non-exchangeable (in percent)

Sample number	Ca^{2+} (total)	Ca^{2+} (exch.)	Ca^{2+} (non-exch.)	Mg^{2+} (total)	Mg^{2+} (exch.)	Mg^{2+} (non-exch.)·
T–2	0.92	0.40	0.52*	2.31	0.31	2.00
T–8	0.55	0.52	0.03	2.52	0.35	2.17
M–1	1.50	1.26	0.24	1.31	0.19	1.11
M–2	1.52	0.91	0.61*	1.41	0.19	1.22
M–3	1.54	1.29	0.25	1.44	0.21	1.23

* Small amounts of calcite ($CaCO_3$).

** Non exchangeable positions are structural positions.

Results and discussion

Dielectric curves are presented in Fig. 1. Thermodielectric curves show two noticeable effects (it was discussed in connection with zeolites [11]). The first is related with the polarization of cations and water (temp. 100–200°), and the second is related to ohmic conductivity which is a function of the cationic transport in the aluminosilicate lattice (temp. > 550°). Both effects are related to the cationic content and chemical nature of the cations, and also, to the cation position in the lattice.

Samples M–1, M–2 and M–3 are characterized by cation exchange capacities between 61 and 82 meq/100 g (see Table 3) with Ca^{2+} as the principal exchangeable cation in relation to exchangeable Mg^{2+} (TAble 4). Also, in samples T–1 and T–2 the amount of exchangeable Ca^{2+} and Mg^{2+} is similar, however, the Mg^{2+} is fundamentally in structural position (non-exchangeable). The higher content of Ca^{2+} in exchangeable position explains why the first peak in M samples (M–1, M–2, M–3) is more intensive than those T samples (T–2, T–8), due to the mobility of

exchangeable cation Ca^{2+}. This result can be also supported by the very well known fact that in smectitic minerals, the hydration capacity is related to exchangeable Ca^{2+} contents [1]. On the other hand the second peak position is related to cationic conduction as was stated elsehwere [11]. Figure 1 shows that the temperature for the second peak is higher for T samples than for M samples. This fact can be directly correlated to the higher exchangeable cationic contents in M samples.
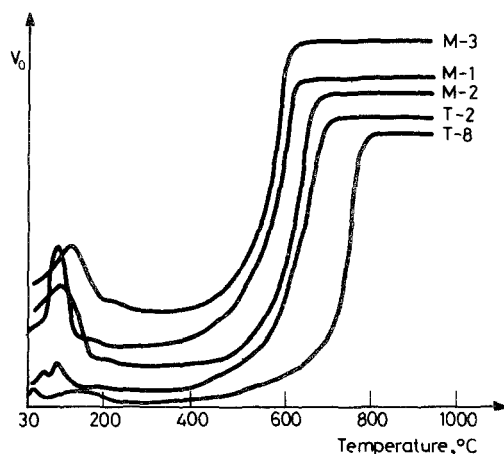

Fig. 1 Dielectrical curve of Bentonites from "Managua" (M–1, M–2 and M–3) and "La Tagua" (T–1 and T–2) deposits

T–2 has an anomalous behaviour, which can be explained by taking into account the lower aluminium contents of T–2 compared to T–8. For aluminium is the element which ties exchangeable cations to the aluminosilicate structure, due to the negative charge excess generated by aluminium in aluminosilicate crystal lattice of smectite type mineral, and therefore cationic conduction is higher.

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