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DIELECTRIC DIFFERENTIAL THERMAL ANALYSIS. PART VII. KAOLINS

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Thermodielectric analysis has been used to test some very well-characterized kaolins from Cuban deposits. The samples were analysed by thermal analysis, X-ray diffraction, infrared spectrometry, electron microscopy and chemical analysis.

The dielectrical thermograms show that the most evident effect for the hydrated versions is the water peak. The second dielectric effect, at high temperatures, is related to the cationic conductions. A relation involving the K content of the sample was observed.

Kaolin is usually a fine white clay used in pottery making. It is comprised of clays from the kaolinite group and other minerals, included as impurities, which contribute to its physical and chemical properties.

The structure of kaolinite has been carefully studied [1–5] and its thermal behaviour is also well understood [6, 7]. In the present paper, thermodielectric analysis is used to test some very well-characterized kaolins from Cuban deposits.

Experimental

The tested samples were selected from the "Rio del Callejon" deposit (Youth Island), the "Dumañuecos 2" deposit (Las Tunas Province) and the "El Cobre" deposit (Santiago de Cuba Province), and analysed by thermal analysis (TA), X-ray diffraction (XRD), infrared spectrometry (IR), electron microscopy (EM) and chemical analysis. In all cases, the analysed fractions had a particle size of less than 20 μm, obtained by the classical Stokes law procedure.

Experimental conditions for the MOM 1550 derivatographic studies were: sample weight: 200 mg; reference material: annealed Al_2O_3; sample holders: ceramic crucibles; heating rate: 10 deg/min; furnace atmosphere: air; DTA 1/5; DTG 1/10; TG 200 mg. The conditions for the DRON 2 diffractometer were: goniometer rate:

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Table 1 Sample characterization by XRD, TA, IR and EM

Sample	Locality	Color	XRD	TA	IR	EM
RC–1	Rio Callejon	black	kaolinite and mica	kaolinite, black coal and mica	kaolinite and a little quartz	irregular hexagonal crystals
RC–2	Rio Callejon	white	kaolinite, mica and dickite	kaolinite and mica	kaolinite and a little quartz	regular hexagonal crystals
$R_1 + R_2$	Dumañuecos	white	kaolinite and a little mica	kaolinite and a little mica	kaolinite and vermiculite	kaolinite with no regular hexagonal crystals
R_3	Dumañuecos	white	kaolinite, a little mica and vermiculite	kaolinite and a little mica	kaolinite and vermiculite	kaolinite with no regular hexagonal crystals
R_4	Dumañuecos	white	kaolinite, mica and vermiculite	kaolinite and mica	kaolinite and vermiculite	kaolinite with no regular hexagonal crystals
C_1	Cobre	white	mixed layer of mica and montmorinollite	mixed layer and a little calcite	montmorinollite, mica, trydimite and calcite	mixed layer
C_2	Cobre	white	halloysite and a little chlorite	halloysite, chlorite and gibbsite	halloysite and chlorite	halloysite with tubular forms
C_3	Cobre	white	dickite and a little mixed layer	kaolinite	dickite	well-ordered dickite

Table 2 Chemical analysis of the different kaolins

Sample	SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO_2	MgO	CaO	MnO	Na_2O	K_2O	SO_3	P_2O_5	Loss on ignition
RC–1	60.60	24.35	0.37	0.25	0.80	0.56	0.15	0.1	0.11	2.21	0.5	0.50	9.94
RC–2	49.02	34.41	0.36	0.14	1.47	0.25	0.15	0.01	0.10	1.18	0.5	0.07	11.90
R_1+R_2	50.70	31.68	0.45	0.99	0.67	0.45	0.24	0.02	0.10	0.85	0.88	0.04	12.16
R_3	50.84	32.82	0.13	0.85	0.83	0.23	0.35	0.01	0.1	1.28	1.24	0.05	11.78
R_4	51.82	32.07	0.45	1.02	0.81	0.32	0.15	>0.01	0.1	3.03	1.00	0.05	10.18
C_1	53.73	28.23	0.68		1.49	1.97	0.60		0.26	6.73			6.62
C_2	48.68	30.43	0.98		0.74	2.45	1.43		0.77	0.99			12.50
C_3	47.04	39.33	0.16		0.37	>0.1	0.19		>0.1	>0.1			13.74

1/2 deg/min; radiation: Cu(K_α); angular range: 5–35°; time constant: 2 sec; sensitivity: 1000 imp/sec; voltage: 35 kV; anodic current 20 mA. IR spectra were recorded with a Carl Zeiss IR–71 spectrometer in the range 400–4000 cm^{-1}, with 0.2 mg of sample in KBr. The EM observations were carried out with a JEOL 100 S electron microscope. Thermodielectric thermograms were obtained in the equipment described in Part I of this series [8] with the conditions established in Parts II to VI [9–12]. The results of the characterization are reported in Tables 1 and 2.

Results and discussion

Figures 1–3 present dielectric thermograms of the samples.

The most evident effect is seen for sample C_2, which is fundamentally composed of halloysite, $(Si, Al)_4O_{10}(OH)_8 \cdot 4H_2O$ [3], and which exhibits a very strong water peak [11], clearly related with the existence of water in the tubular halloysite structure. R_3 and R_4, which contain vermiculite, $(Si, Al)_4(O_{10}(OH)_2Mg_{3.35} \cdot 4.5H_2O$ [5], also display a marked water peak, whereas R_1+R_2, which consists only of kaolinite, $Si_2O_5(OH)_4Al_2$ [5], and mica, $(Si_6Al_2)K_2Al_4O_{20}(OH)_4$ [3], is not hydrated. On the other hand, C_1 (a mixed layer comprised of 70% mica and 30% montmorinollite) shows a poorly-developed water peak, and C_3 (comprised fundamentally of dickite, $Si_2O_5(OH)_4Al_2$ [5], a non-hydrated mineral) has no water peak. Samples RC–1 and RC–2 could contain (non-

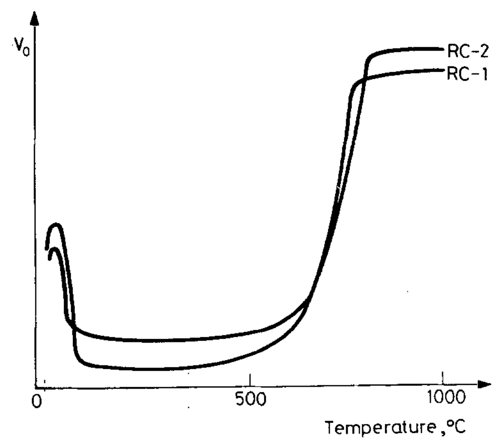

Fig. 1 Dielectric thermograms (output voltage (V_0) *vs.* temperature) of samples RC–1 and RC–2

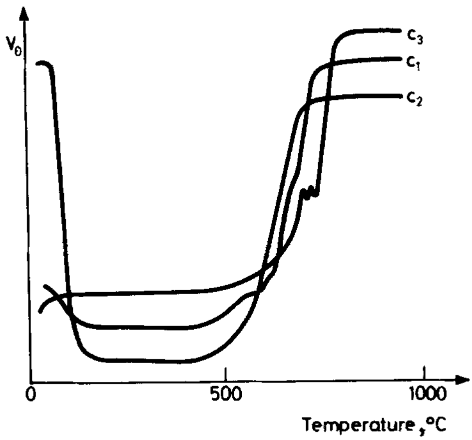

Fig. 2 Dielectric thermograms of samples C_1, C_2 and C_3

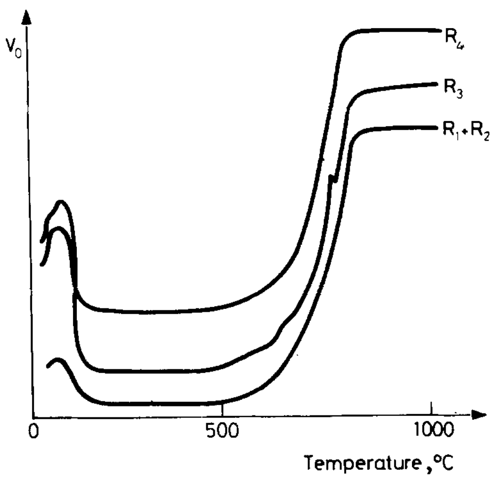

Fig. 3 Dielectric thermograms of samples $R_1 + R_2$, R_3 and R_4

identified) halloysite (halloysite and kaolinite are very similar and are difficult to identify by X-ray diffraction), and it is possible to ascribe the water peak to this.

In connection with the second dielectric effect at high temperatures, which is related with ionic conduction [9, 10, 12], a correlation is observed between the K content in the RC–1, RC–2, $R_1 + R_2$, R_3 and R_4 samples, which contain mica, and the position of the effect, i.e. there is a decrease in the temperature at which the effect starts as the K content rises (Table 2); this can be explained by the presence of K in cationic positions in mica, i.e. as a mobile exchangeable cation for charge balancing in the aluminosilicate structure. C_1, C_2 and C_3 are heterogeneous samples, including mixed layers (C_1 and C_3) in the phases presents in the mineral; mixed layers [13] are alternately disposed layers of montmorillonit and mica (in the present case), where K can be present in cationic or fixed positions [14]. The behaviour of the second effect cannot be discussed here.

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Zusammenfassung — Mittels thermodielektrischer Analyse wurden einige gut charakterisierte Kaoline aus kubanischen Lagerstätten untersucht. Die Proben wurden mittels Thermoanalyse (TA), Röntgendiffraktion (XRD), Infrarotspektroskopie (IR), Elektronenmikroskopie (EM) und Elementaranalyse untersucht. Die Dielektrothermogramme zeigen, daß bei den hydratierten Versionen der augenscheinlichste Effekt der Wasserpeak ist. Der zweite dielektrische Effekt bei höheren Temperaturen wird mit der Kationenleitung in Zusammenhang gebracht, wodurch es möglich wird, Informationen über den K-Gehalt der Proben zu erlangen.

Резюме — Для испытания очень хорошо охарактеризованных каолинов кубинского месторождения был использован термодиэлектрический анализ. Образцы анализировались термическим анализом (ТА), рентгенодиффракционным методом, ИК спектроскопией, электронной микроскопией и химическим анализом. Диэлектрические диаграммы показали, что наиболее доказанным эффектом является пик воды процесса гидратации. Второй диэлектрический эффект, наблюдаемый при высоких температурах, связан с катионной проводимостью, в связи с чем можно наблюдать связь его с содержанием калия в образце.