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INFLUENCE OF ASSOCIATED COMPONENTS OF KAOLIN ON THE DEGREE OF DISORDER OF KAOLINITE AS DETERMINED BY XRD

[1]EMILIO GALÁN, [1]PATRICIA APARICIO, [1]ISABEL GONZÁLEZ and [2]ANGEL LA IGLESIA

[1]Departamento de Cristalografía, Mineralogía y Q. Agrícola, Facultad de Química, Univ. Sevilla apartado 553, Sevilla 41071, Spain
[2]Instituto de Geología Económica, C.S.I.C. Univ. Compluetense, Madrid, Spain

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Abstract: The determination of the structural order of kaolinite in mixtures of amorphous phases and minerals has been performed by the application of a so-called "expert system" and by means of the calculation of the "crystallinity indices", determined from the corresponding X-ray diffraction diagrams. From the statistical study of the results obtained, it has been shown that the measure of the Stoch index is not affected by the presence of associated components like those studied (quartz, feldspar, iron hydroxide, silica and alumina gels), while this is not true for the Range & Weiss index in a general manner. For the other indices the reproducibility varies as a function of the crystallinity of the kaolinite and the components present and their particle-size distribution. In commercial kaolins, where the percentage of quartz varies between 5 - 10 % and the presence of iron hydroxide gels is less than 5 % the Stoch index can be used independently of the crystallinity. For raw kaolins, with percentages of kaolinite around 75 % and in the presence of quartz, feldspars and gels, the only indices which are not influenced by these minerals and gels are those of Stoch and Hughes & Brown, independently of the crystallinity of the kaolinite. Further it has been determined that the percentage of well ordered kaolinite as determined by the expert system is not reproducible for kaolinites of high crystallinity in the presence of minerals and amorphous material such as those studied.

Key words: kaolinite, degree of disorder, crystallinity indices, XRD.

Introduction

The grade of structural order of the kaolinite is a very useful parameter for the kaolin industry and of great importance in genetic considerations (Murray & Lyons 1956; Galán et al. 1977; Yvon et al. 1980; Brindley et al. 1986; Köster & Brandl 1991; Velho & Gomes 1991). For this reason it has for a long time been attempted to find a rapid and simply determined value of the order-disorder in kaolinites. For this, various relations have been used denominated "crystallinity indices", obtained from diagrams of X-rays diffraction, from differential thermal analysis curves or infrared spectra. Of these the most widely used have been the indices calculated by X-ray diffraction, which are based on the variations observed in two groups of reflections: **1** - The 02*l* and 11*l* sequence (20° - 33° °2Θ using Cu Kα radiation) which is sensitive to arbitrary and special interlayer displacements (of type b/3) and **2** - the 13*l* and 20*l* sequence (35° - 40° °2Θ) affected by arbitrary displacements (Cases et al. 1982).

For their part, Plancon & Zacharie (1990) have proposed "an expert system" which runs on a compatible PC and describes the structural defects of kaolinite based on measures directly obtained from the diffraction profile. The first structural parameter to be determined is the number of different phases in the sample because this determines the outcome of the analysis. For a bi-phased system the system established the percentage of the low-defect phase (% wcp), while for single phase samples, the system fixed the amount of the C layers (W_C), the variation of interlayer translations about the mean values (δ), the proportion of translation defects (p), and the mean number of layers (M).

The fundamental objective of the present work lies in getting to know the influence of the associated* components of the kaolin in the determination by X-ray diffraction of certain indices of crystallinity of the kaolinite, with the aim of selecting those least influenced by the presence of the other phases and comparing them in systematic studies of commercial kaolins. In the same way we aim to determine the effect

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*In accordance with Brown (1980, p. 361) the term "associated minerals" is used for all those components of clay rocks which occur in intimate association with the clay minerals (phyllosilicates).

which is provided by these same contaminants in the application of the expert system.

Materials and methods

Materials

For this work three kaolins of distinct structural order have been used, according to the criteria proposed by Murray & Lyons (1956):

a - *Georgia Kaolin* (USA). This is a Cretaceous kaolin from Warren County, which has been characterized and used amply in numerous investigations. It corresponds to the standard KGa-2 (Van Olphen & Fripiat 1979), of medium crystallinity, a polytype intermediate between T and pM.

b - *Guadalajara Kaolin* (Spain). This a Cretaceous kaolin (Albian) which comes from Poveda de la Sierra, belonging to the type denominated Cordillera Iberica (Galán & Martín Vivaldi 1973; Galán 1976). The kaolinite of this sedimentary kaolin is very well ordered, close to the triclinic polytype (T) (Galán et al. 1977; La Iglesia 1993).

c - *Pontevedra Kaolin* (Spain). This is a kaolin from the Plioquaternary deposits of La Guardia, which has been described and studied by Galán & Martín Pozas (1971), Galán (1973, 1974, 1975), and Caramés et al. (1983). The kaolinite of this kaolin is of a low order, polytype pM, and contains halloysite.

Using these kaolins we have studied the influence exercised by the following mineral and amorphous phases: quartz, feldspar, commercial silica gel (Riedel-De Haen, reference No. 3712), iron hydroxide gel (obtained in the laboratory) and commercial alumina gel (Panreac, reference No. 17100).

Methods

The kaolins and selected associates were characterized by X-ray diffraction (powder method); chemical analysis, which was carried out by atomic absorption spectrometry (Al, Fe, Ti, and Mg), emission spectrometry (Na and K) and spectrophotometry of UV-V (Si); and granulometric analysis, which was carried out by a microanalyser by absorption of X-rays (Sedigraph 5100).

Table 1: Mixtures of kaolinite and associated components.

Binary mixtures				
	Georgia Kaolin<4 μm	Georgia Kaolin<2 μm	Guadalajara Kaolin<4 μm	Pontevedra Kaolin<4 μm
Iron hydroxide gel <50 μm				
5,10,15 & 20%	x	x	-	-
Iron hydroxide gel <10 μm				
5 & 10%	x	x	x	x
15 & 20%	x	x	-	-
Silica gel < 50 μm				
5%	-	-	x	x
10%	x	x	x	x
20, 30 & 40%	x	x	-	-
Silica-iron gel (2:1)				
10, 20, 30, 40 & 50%	x	x	-	-
Alumina gel < 50 μm				
10, 20, 30, 40 & 50%	x	x	-	-
Quartz < 50 μm				
5, 10, 15, 20 & 30%	x	x	-	-
Quartz < 10 μm				
5, 10 & 20%	x	x	x	x
15 & 30%	x	x	-	-
Feldspar < 50 μm				
5, 10, 15 & 20%	x	x	-	-
Feldspar < 10 μm				
5 & 10%	x	x	x	x
15 & 20%	x	x	-	-
Multiphasic mixtures				
	Georgia Kaolin < 10 μm		Guadalajara Kaolin < 10 μm	Pontevedra Kaolin < 10 μm
Fraction <10 μm of: quartz (10%), feldspar (5%), iron hydroxide gel (5%) and silica gel (5%)	x		x	x

- : Not realised

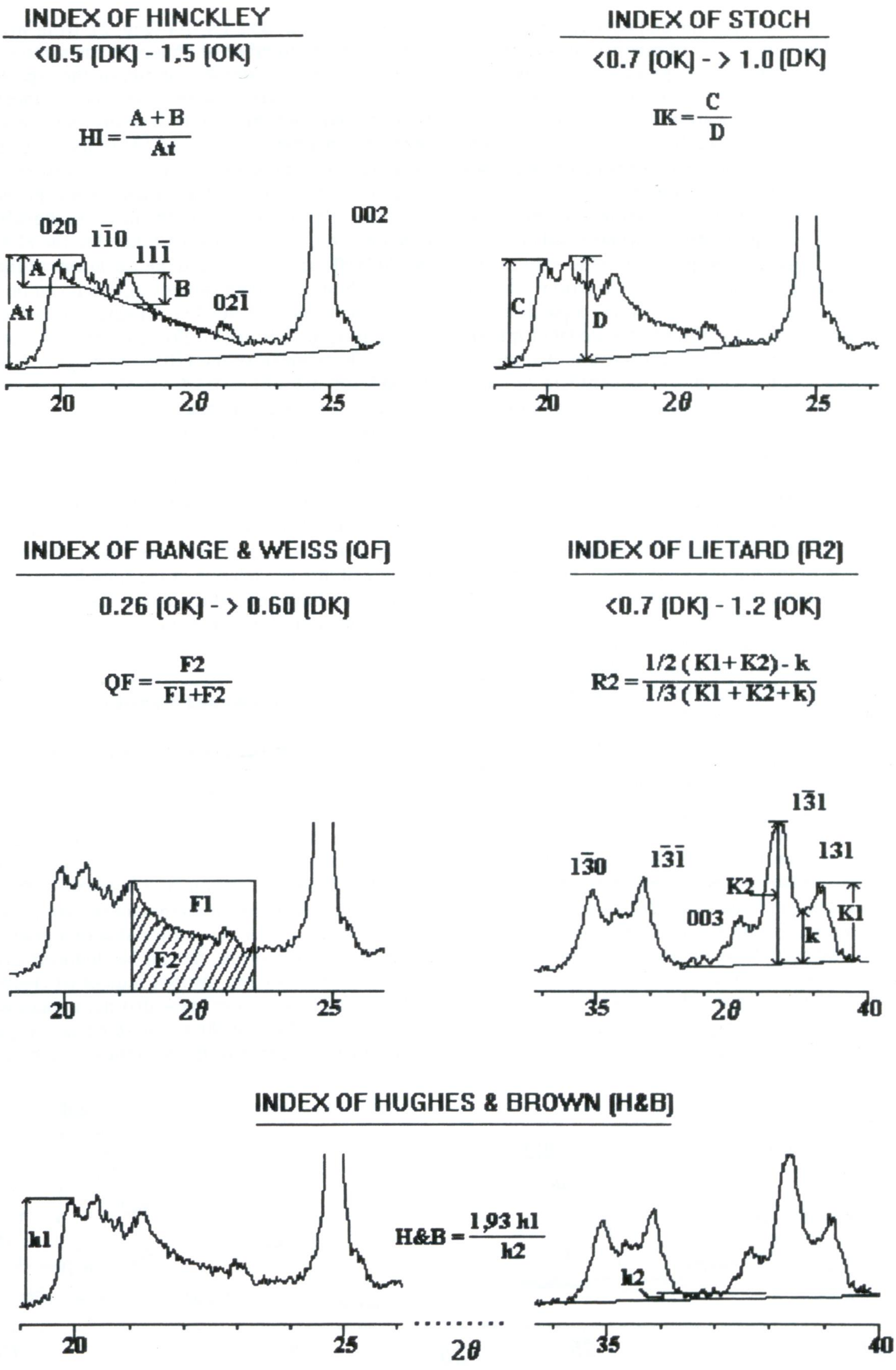


Fig. 1. Crystallinity indices measured, and ranges according to data of Stoch (1974), Cases et al. (1982), Gomes (1987).

All the materials were ground and sieved (sieve dimension 50 μm). Then two types of mixtures of kaolin and associated components were prepared: 2-phase and multiphasic mixtures (Tab. 1). In the 2-phase mixtures made with the Georgia Kaolin we used the fractions <2 μm and <4 μm of the kaolin and fractions <10 μm and <50 μm of the associated components; while for those made with the Guadalajara and Pontevedra kaolins we only employed the fraction <4 μm of the kaolin (because no appreciable differences had been observed between mixtures prepared with the <2 μm and <4 μm in the Georgia Kaolin) and the fraction <10 μm of the associated components (to obtain a particle-size closer to that of kaolin). Finally we prepared multiphasic mixtures using a constant 75 % proportion of kaolinite and the phases which occur most frequently in kaolins.

The determination of the structural order of kaolinite before and after mixing it with other phases was carried out from X-ray diffraction data (indices of crystallinity and expert system). We used a Philips diffractometer, model PW 1130/90, equipped with an automatic slit, Cuα radiation and Ni filter, and working at 20 mA and 40 KV. A lateral sample holder to avoid as far as possible the orientation of the minerals was used. The interval of exploration was from 19° to 40° °2Θ. The analysis of each sample was carried out fivefold.

We selected the crystallinity indices (Fig. 1) of Hinckley (HI, Hinckley 1963) and Range & Weiss (QF, Range & Weiss 1969) as being those which are most used since their definition; the Stoch index (IK, Stoch 1974) because it is measured in the same zone as the Hinckley index, with the advantage of being less sensitive to the presence of quartz; the Lietard index (R2, Lietard 1977) because it is only sensitive to the presence of arbitrary defects (according to Cases et al. 1982), and finally the Hughes and Brown index (H&B, Hughes & Brown 1979) the one which has been definitely specified for kaolinites present in soils, where the other indices can not be determined. For the calculation of HI, IK, QF, and H&B (Fig. 1) we used the sequence of reflections 02*l* and 11*l* (20° - 33° °2Θ) and for the calculation of R2 and H&B we used the sequence 13*l* and 20*l* (35° - 40° °2Θ).

The application of the expert system also is based on a series of measures carried out on the sequences of reflections 02*l*, 11*l*, and 13*l*, 20*l* (Fig. 2), from which one can obtain the number of phases in the sample, and in the case where the sample is uniphasic the expert system allows the following parameters: the proportion of C layers ($\mathbf{W_C}$), which directly depends on the narrowing of the distance between 131 and 1$\bar{3}$1 reflections (m8); the proportions of translation defects (**p**), whose evaluation is based on the change in the measurements proposed by Hinckley (1963); the mean of the layers in the diffracting domains (**M**), which is directly related to the HWHM of the 002 reflections (m7); and the variations of the translations about the mean values (δ), which can be related to the weakening of the 131 reflection relative to the 1$\bar{3}$1 reflection (m9, m11). For a bi-phased system the ratio of the intensity of the 1$\bar{1}$0 to the height of the background (or m2/m6) is used for the determination of % wcp by the expert system.

The reliability of the crystallinity indices used has been established using the standard deviation value (σ_{n-1}). Finally, with the values obtained for distinct indices and the expert system, we carried out a study based on an application of the test-t of Student, "comparison of a mean with a standard", with the object of determining reproducibility in each one of the samples.

Fig. 3 is a flowsheet which shows the way followed in the carrying out of the each stage of the work.

Results and discussion

Characterization of the materials

In the mineralogical analysis carried out with the *Georgia Kaolin* only the presence of kaolinite is detected (Fig. 4); the chemical analysis is very close to the theoretical composition of kaolinite, with a noteworthy high content of TiO_2 as a fundamental impurity (Tab. 2). The granulometric analysis shows that more than 95 % of the material is below 4 μm. The order- disorder grade of this kaolinite is medium-low, as can be deduced from the values obtained for the distinct indices of crystallinity (Tab. 3). The reliability of these distinct indices is good, given the low values for the standard deviation (Tab. 4), except for the Hughes & Brown index. The results ob-

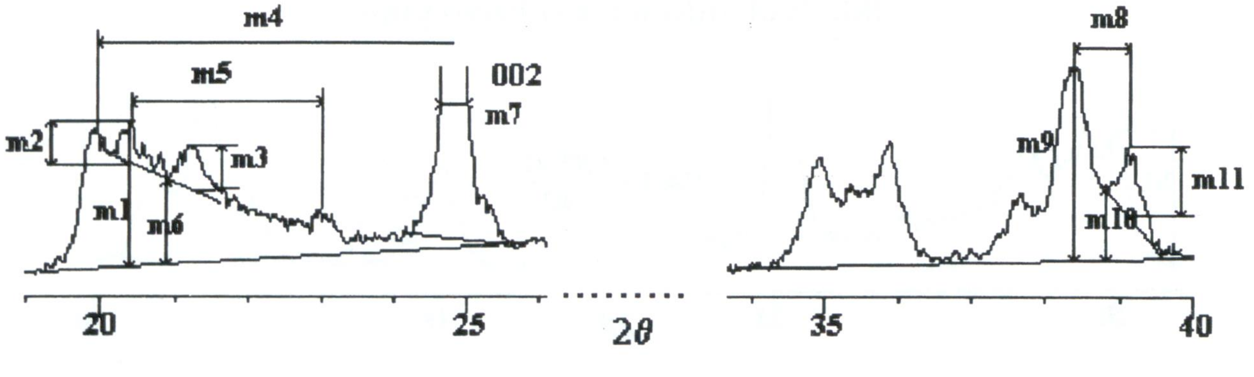


Fig. 2. Measures proposed by Plancon & Zacharie (1990) to apply the "expert system".

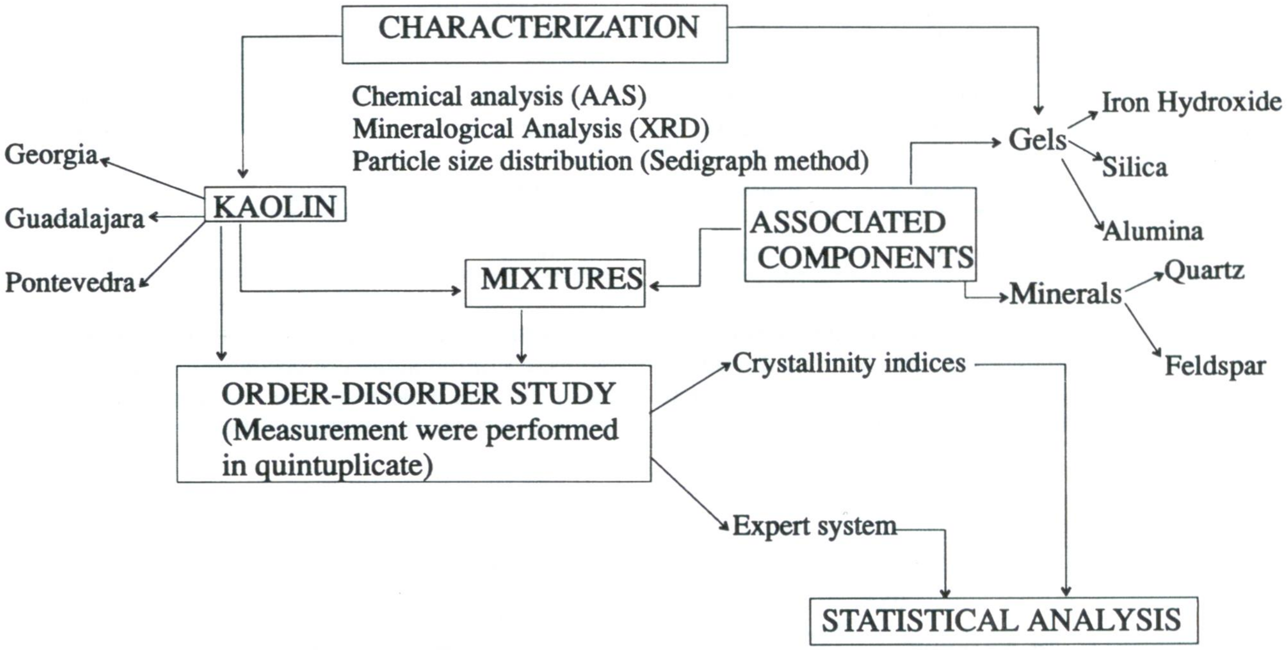


Fig. 3. Work Plan.

tained using the "expert system" due to Placon & Zacharie (1990) indicate that the fraction <2 μm of the Georgia Kaolin is bi-phased with a medium value of % wcp of 11 %, while in the fraction <4 μm the % wcp varies between 0 and less than 10 %. For the <4 μm the utilization of the "expert system" is complicated by the fact that the percentage of the well crystallised phase is less than 10 % and when this occurs as the authors of the program indicate, it is very difficult to detect this phase.

The *Guadalajara Kaolin* is composed principally of kaolinite with small percentages of quartz (<5 %) and

Table 2: Chemical analyses (%).

Sample	SiO_2	Al_2O_3	Ti_2O	Fe_2O_3	MgO	Na_2O	K_2O	LOI	TOTAL
Georgia Kaolin	46	39	1.2	0.43	0.06	0.10	0.16	13.6	100.5
Georgia Kaolin <4 μm	46	39	1.2	0.43	0.05	0.10	0.14	13.7	100.6
Georgia Kaolin <2 μm	46	39	1.2	0.43	0.03	0.10	0.15	13.7	100.6
Guadalajara Kaolin	48	37	0.1	0.52	0.08	0.16	0.24	13.3	99.4
Guadalajara Kaolin <4 μm	47	39	0.1	0.60	0.11	0.16	0.24	13.7	100.9
Pontevedra Kaolin	51	35	0.7	1.52	0.16	0.16	0.96	11.0	100.5
Pontevedra Kaolin <4 μm	45	37	0.7	1.52	0.13	0.20	1.78	13.1	99.4
Feldspar	67	20	-	0.11	0.02	4.03	8.65	-	99.8

Table 3: Crystallinity indices for kaolins.

	HI	IK	R2	QF	H&B
Georgia Kaolin					
<4 μm	0.54	1.02	0.68	0.58	25
<2 μm	0.63	0.97	0.70	0.60	26
Guadalajara Kaolin					
<4 μm	0.89	0.80	0.83	0.51	99
Pontevedra Kaolin					
<4 μm	0.30	1.18	0.55	0.72	15

Table 4: Standard deviation for crystallinity indices.

	$(\sigma_{n-1})_{HI}$	$(\sigma_{n-1})_{IK}$	$(\sigma_{n-1})_{R2}$	$(\sigma_{n-1})_{QF}$	$(\sigma_{n-1})_{H\&B}$
Georgia Kaolin					
<4 μm	0.02775	0.02509	0.03502	0.02191	3.4162
<2 μm	0.01923	0.02236	0.04775	0.01220	6.5480
Guadalajara Kaolin					
<4 μm	0.03434	0.04301	0.03578	0.01893	38.7777
Pontevedra Kaolin					
<4 μm	0.0343	0.053	0.06426	0.06426	1.95310

mica (traces) (Fig. 4), and so its chemical composition (Tab. 2) is somewhat different from that of a theoretical kaolinite. The results of the granulometric analysis indicate that 96 % of the sample is below 10 μm. In this case the kaolinite shows a high grade of order, as is proved by the values of the indices of crystallinity (Tab. 3), where there are two phases in the <4 μm fraction, with a % wcp of 26 %. The reliability of the indices utilized is good

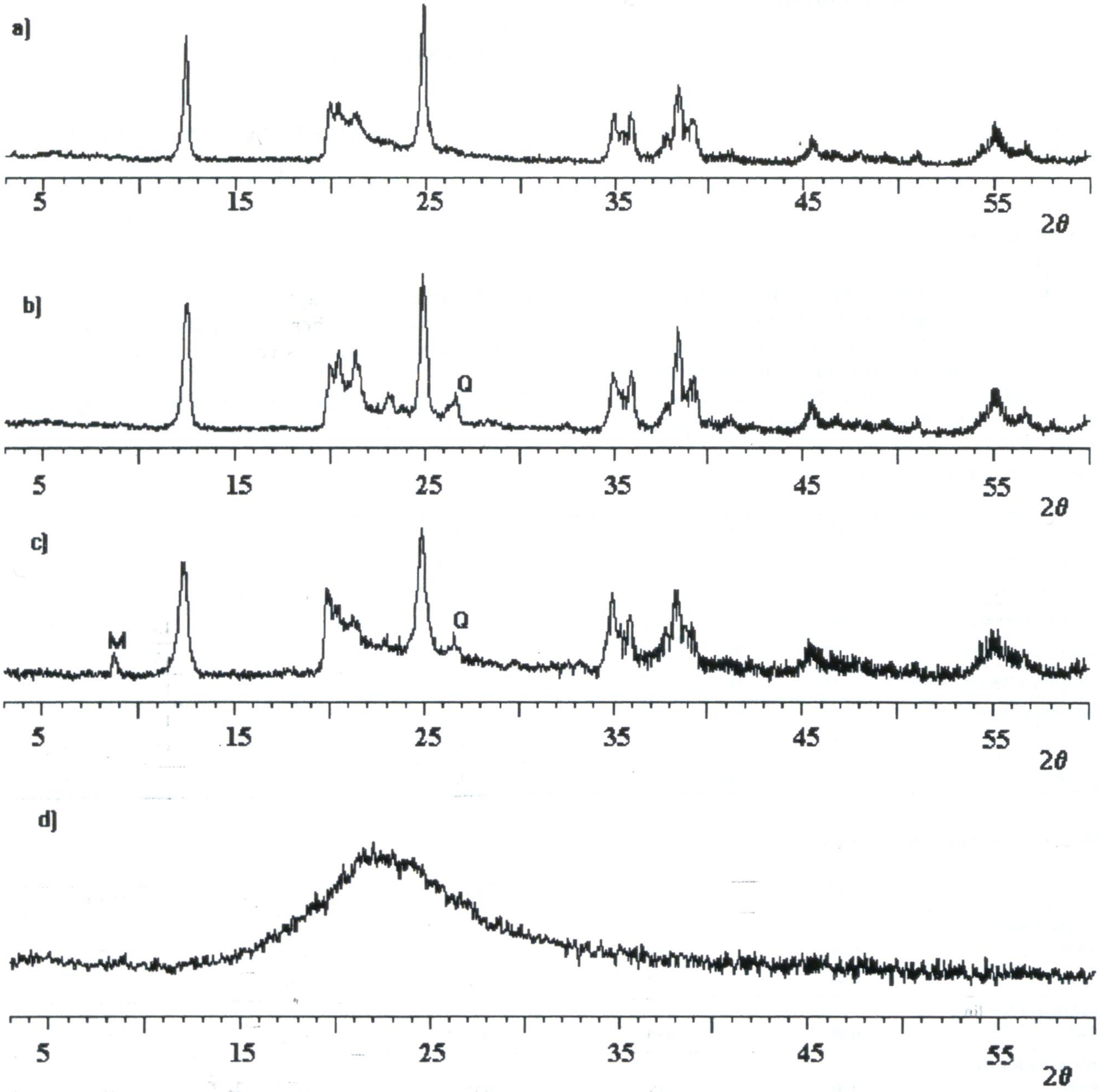


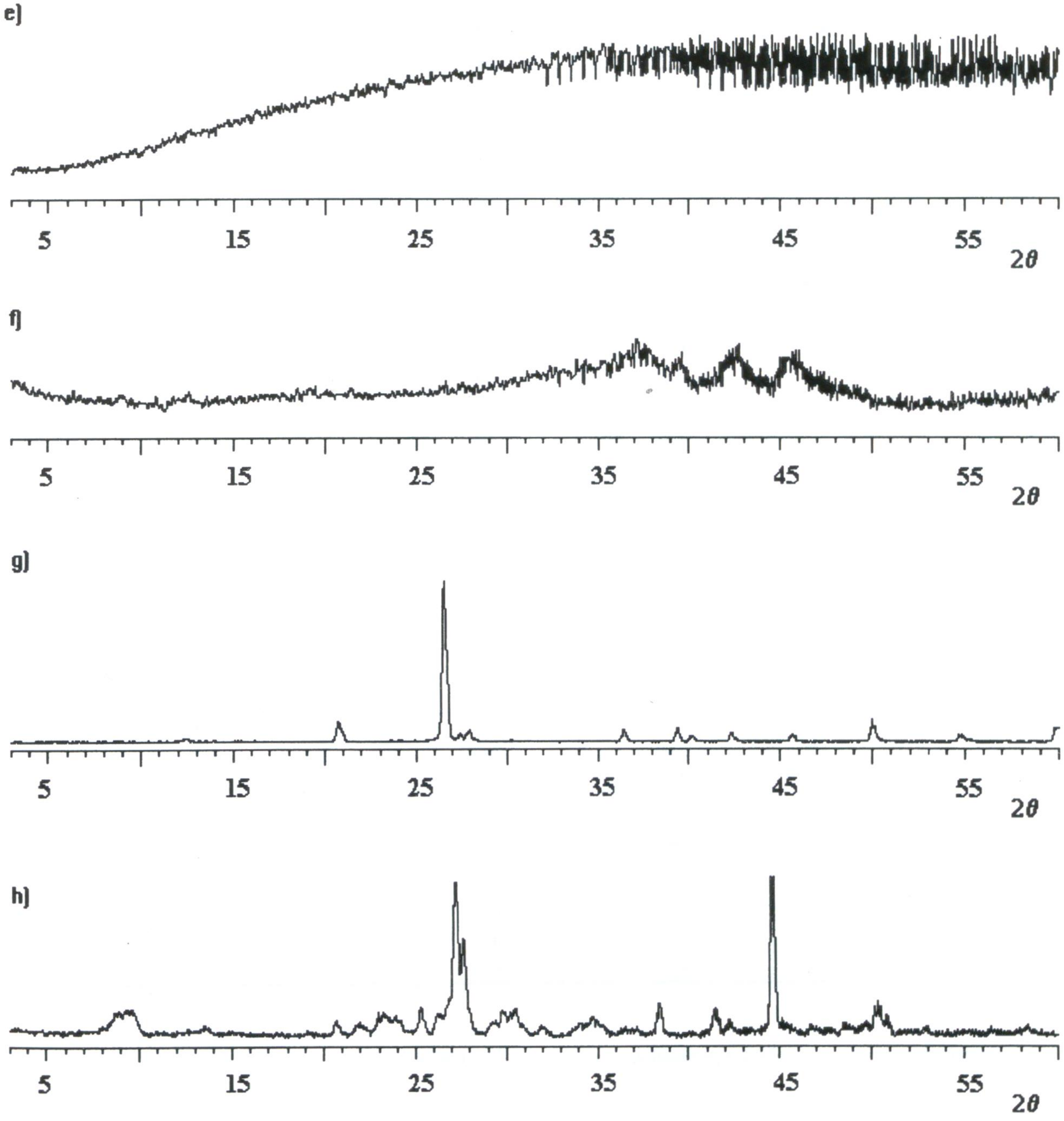
Fig. 4. X-ray diffraction patterns of the phases utilized: **a** - Georgia Kaolin <4 μm, **b** - Guadalajara Kaolin <4 μm, **c** - Pontevedra Kaolin <4 μm, **d** - silica gel <50 μm, **e** - iron hydroxide gel <10 μm, **f** - alumina gel < 50 μm, **g** - quartz < 50 μm and **h** - feldspar < 50 μm. **Q** - quartz; **M** - mica.

given the low values of the standard deviation (Tab. 4), except in the case of the Hughes & Brown index.

The results obtained for the chemical analysis of the *Pontevedra Kaolin* (Tab. 2) correspond in its mineralogical composition, because this is a kaolin with high percentages of quartz (35 % for the raw kaolin and 5 % for the fraction $<4\ \mu m$) and mica (5 % for the kaolin and 10 % for the fraction $<4\ \mu m$). The pattern of diffraction and the high iron content (Tab. 2), suggest the possible presence of amorphous gels (Fig. 4). The granulometric analysis indicates a larger grain size than in the other kaolins due to the presence of quartz, with only 67 % of particles $<4\ \mu m$. The kaolinite is very disordered, as can be deduced from the value of its indices of crystallinity (Tab. 3). The reliability of the indices employed is good given the low values of the standard deviation (Tab. 4), except for the case of the Hughes & Brown index. The kaolinite is formed out of a single disordered phase (% wcp = 0) with a percentage of defects of translation (p) equal to 35 %, the percentage of C layers $W_C = 0.24$, and the mean of the layers in the diffracting region $M = 24$ and $\delta = 0.04$.

The particle-size distribution of the *silica gel* presents a content of 81 % $<4\ \mu m$. X-ray diffraction shows a single band between 15° and 30° °2Θ (Fig. 4).

The *iron hydroxide gel* has 97 % of particles less than $50\ \mu m$ with a 27 % $<4\ \mu m$. A part of this gel was ground to obtain 94 % of the particles below $10\ \mu m$ and 85 % less than $4\ \mu m$. The diffraction diagram shows an increase of the background, especially beyond 2Θ equal to 20° (Fig. 4).



Continuation of Fig. 4

Table 5: Index of Hinckley (HI) in binary mixtures. Reproducibility.

	Georgia Kaolin < 4μm	Georgia Kaolin < 2μm	Guadalajara Kaolin < 4μm	Pontevedra Kaolin < 4μm
Iron hydroxide gel < 50μm				
5%	0.60	0.59	-	-
10%	0.57	0.59	-	-
15%	0.60	0.66	-	-
20%	0.60	0.59	-	-
Iron hydroxide gel < 10μm				
5%	0.53	0.60	1.04	0.37
10%	0.65	0.61	1.04	0.34
15%	0.55	0.67	-	-
20%	0.70	0.59	-	-
Silica gel < 50μm				
5%	-	-	0.93	0.36
10%	0.60	0.59	0.97	0.36
20%	0.57	0.57	-	-
30%	0.56	0.57	-	-
40%	0.59	0.59	-	-
Silica-iron gel (2:1)				
10%	0.56	0.64	-	-
20%	0.51	0.62	-	-
30%	0.63	0.64	-	-
40%	0.62	0.63	-	-
50%	0.69	0.62	-	-
Alumina gel < 50μm				
10%	0.59	0.61	-	-
20%	0.61	0.61	-	-
30%	0.59	0.59	-	-
40%	0.61	0.68	-	-
50%	0.59	0.66	-	-
Quartz < 50μm				
5%	0.62	0.53	-	-
10%	0.56	0.59	-	-
15%	n.d.	n.d.	-	-
20%	n.d.	n.d.	-	-
30%	n.d.	n.d.	-	-
Quartz < 10μm				
5%	0.56	0.54	1.01	0.42
10%	0.51	0.55	0.99	0.31
15%	0.56	0.58	-	-
20%	0.61	0.55	0.97	n.d.
30%	n.d.	n.d.	-	-
Feldspar < 50μm				
5%	0.58	0.62	-	-
10%	0.63	0.58	-	-
15%	0.68	0.61	-	-
20%	0.75	0.65	-	-
Feldspar < 10μm				
5%	0.56	0.58	1.03	0.56
10%	0.57	0.62	1.03	0.60
15%	0.59	0.63	-	-
20%	0.69	0.67	-	-

n.d.: Undeterminable __ : Not reproducible - : Not realised

Table 6: Index of Stoch (IK) in binary mixtures. Reproducibility.

		Georgia Kaolin <4μm	Georgia Kaolin <2μm	Guadalajara Kaolin <4μm	Pontevedra Kaolin <4μm
Iron hydroxide gel < 50μm					
	5%	1.01	1.02	-	-
	10%	1.02	1.01	-	-
	15%	1.05	1.01	-	-
	20%	1.01	1.03	-	-
Iron hydroxide gel < 10μm					
	5%	0.98	1.02	0.73	1.16
	10%	1.03	0.98	0.76	1.15
	15%	1.04	0.96	-	-
	20%	0.98	0.93	-	-
Silica gel < 50μm					
	5%	-	-	0.78	1.22
	10%	1.00	0.97	0.82	1.20
	20%	0.99	0.99	-	-
	30%	1.05	1.00	-	-
	40%	0.99	0.99	-	-
Silica-iron gel (2:1)					
	10%	1.02	1.03	-	-
	20%	1.07	1.00	-	-
	30%	1.03	0.98	-	-
	40%	0.96	0.98	-	-
	50%	1.01	0.90	-	-
Alumina gel <50μm					
	10%	1.01	0.99	-	-
	20%	1.00	0.98	-	-
	30%	1.00	0.98	-	-
	40%	1.01	0.98	-	-
	50%	1.02	1.00	-	-
Quartz < 50μm					
	5%	0.97	0.99	-	-
	10%	1.00	1.00	-	-
	15%	1.00	1.00	-	-
	20%	0.98	1.00	-	-
	30%	0.99	0.93	-	-
Quartz <10μm					
	5%	0.99	0.98	0.78	1.22
	10%	0.96	0.96	0.79	1.24
	15%	0.98	0.96	-	-
	20%	0.98	0.94	0.79	1.15
	30%	0.92	0.93	-	-
Feldspar <50μm					
	5%	0.95	0.95	-	-
	10%	0.95	1.00	-	-
	15%	0.95	1.00	-	-
	20%	0.99	1.00	-	-
Feldspar <10μm					
	5%	0.98	0.97	0.77	1.19
	10%	1.01	0.96	0.74	1.22
	15%	0.98	0.96	-	-
	20%	0.92	0.98	-	-

___ : Not reproducible - : Not realised

Table 7: Index of Lietard (R2) in binary mixtures. Reproducibility.

	Georgia Kaolin $< 4\mu m$	Georgia Kaolin $< 2\mu m$	Guadalajara Kaolin $< 4\mu m$	Pontevedra Kaolin $< 4\mu m$
Iron hydroxide gel $< 50\mu m$				
5%	0.74	0.69	-	-
10%	0.68	0.69	-	-
15%	0.76	0.69	-	-
20%	0.78	0.73	-	-
Iron hydroxide gel $< 10\mu m$				
5%	0.61	0.68	0.81	0.56
10%	0.74	0.58	$\underline{0.93}$	0.58
15%	0.71	0.71	-	-
20%	0.75	0.76	-	-
Silica gel $< 50\mu m$				
5%	-	-	0.86	0.49
10%	0.70	0.71	0.84	0.53
20%	0.65	0.69	-	-
30%	0.69	0.66	-	-
40%	0.68	$\underline{0.64}$	-	-
Silica-iron gel (2:1)				
10%	0.65	0.70	-	-
20%	0.68	0.71	-	-
30%	0.68	0.74	-	-
40%	0.73	0.72	-	-
50%	0.76	$\underline{0.77}$	-	-
Alumina gel $< 50\mu m$				
10%	0.71	0.69	-	-
20%	0.69	0.70	-	-
30%	0.69	0.72	-	-
40%	0.72	0.74	-	-
50%	0.70	0.73	-	-
Quartz $< 50\mu m$				
5%	0.66	0.68	-	-
10%	0.66	0.69	-	-
15%	$\underline{0.74}$	0.67	-	-
20%	$\underline{0.73}$	$\underline{0.73}$	-	-
30%	$\underline{0.79}$	$\underline{0.79}$	-	-
Quartz $< 10\mu m$				
5%	0.66	0.67	$\underline{0.86}$	0.53
10%	0.68	0.69	$\underline{0.87}$	0.60
15%	0.70	0.69	-	-
20%	0.71	0.74	$\underline{0.90}$	0.64
30%	0.75	0.79	-	-
Feldspar $< 50\mu m$				
5%	0.69	0.65	-	-
10%	0.73	0.65	-	-
15%	$\underline{0.66}$	$\underline{0.66}$	-	-
20%	$\underline{0.68}$	$\underline{0.64}$	-	-
Feldspar $< 10\mu m$				
5%	0.70	0.70	0.86	$\underline{0.80}$
10%	0.67	0.74	$\underline{0.91}$	$\underline{0.85}$
15%	0.65	0.69	-	-
20%	0.69	0.70	-	-

$\underline{\quad}$: Not reproducible - : Not realised

Table 8: Index of Range & Weiss (QF) in binary mixtures. Reproducibility.

		Georgia Kaolin < 4μm	Georgia Kaolin < 2μm	Guadalajara Kaolin < 4μm	Pontevedra Kaolin < 4μm
Iron hydroxide gel < 50μm					
	5%	0.60	0.64	-	-
	10%	0.66	0.68	-	-
	15%	0.72	0.71	-	-
	20%	0.75	0.76	-	-
Iron hydroxide gel < 10μm					
	5%	0.65	0.60	0.57	0.77
	10%	0.69	0.75	0.62	0.83
	15%	0.75	0.78	-	-
	20%	0.80	0.84	-	-
Silica gel < 50μm					
	5%	-	-	0.56	0.74
	10%	0.60	0.66	0.57	0.75
	20%	0.68	0.67	-	-
	30%	0.69	0.67	-	-
	40%	0.76	0.74	-	-
Silica-iron gel (2:1)					
	10%	0.65	0.66	-	-
	20%	0.70	0.71	-	-
	30%	0.74	0.74	-	-
	40%	0.76	0.80	-	-
	50%	0.82	0.83	-	-
Alumina gel < 50μm					
	10%	0.58	0.59	-	-
	20%	0.59	0.60	-	-
	30%	0.60	0.60	-	-
	40%	0.58	0.63	-	-
	50%	0.60	0.65	-	-
Quartz < 50μm					
	5%	0.60	0.58	-	-
	10%	0.58	0.58	-	-
	15%	n.d.	n.d.	-	-
	20%	n.d.	n.d.	-	-
	30%	n.d.	n.d.	-	-
Quartz <10μm					
	5%	0.62	0.58	0.54	0.73
	10%	0.63	0.57	0.55	0.70
	15%	0.64	0.56	-	
	20%	0.63	0.56	0.55	n.d.
	30%	n.d.	n.d.	-	-
Feldspar < 50μm					
	5%	0.61	0.60	-	-
	10%	0.63	0.60	-	-
	15%	0.58	0.59	-	-
	20%	0.55	0.60	-	-
Feldspar < 10μm					
	5%	0.66	0.66	0.53	0.78
	10%	0.66	0.68	0.55	0.75
	15%	0.68	0.65	-	-
	20%	0.70	0.66	-	-

n.d.: Undetermined ___ : Not reproducible - : Not realised

Table 9: Index of Hughes & Brown (H&B) in binary mixtures. Reproducibility.

	Georgia Kaolin < 4μm	Georgia Kaolin < 2μm	Guadalajara Kaolin < 4μm	Pontevedra Kaolin < 4μm
Iron hydroxide gel < 50μm				
5%	29	$\underline{18}$	-	-
10%	29	$\underline{19}$	-	-
15%	24	$\underline{15}$	-	-
20%	23	$\underline{15}$	-	-
Iron hydroxide gel < 10μm				
5%	20	26	56	$\underline{13}$
10%	22	$\underline{21}$	$\underline{37}$	$\underline{12}$
15%	$\underline{19}$	$\underline{16}$	-	-
20%	$\underline{16}$	$\underline{16}$	-	-
Silica gel < 50μm				
5%	-	-	$\underline{94}$	16
10%	29	30	$\underline{96}$	17
20%	$\underline{33}$	35	-	-
30%	$\underline{37}$	32	-	-
40%	$\underline{45}$	$\underline{37}$	-	-
Silica-iron gel (2:1)				
10%	26	24	-	-
20%	27	24	-	-
30%	27	25	-	-
40%	24	27	-	-
50%	$\underline{29}$	$\underline{16}$	-	-
Alumina gel				
10%	$\underline{23}$	$\underline{19}$	-	-
20%	$\underline{18}$	$\underline{18}$	-	-
30%	$\underline{13}$	$\underline{13}$	-	-
40%	$\underline{13}$	$\underline{14}$	-	-
50%	$\underline{11}$	$\underline{10}$	-	-
Quartz < 50μm				
5%	$\underline{17}$	23	-	-
10%	$\underline{20}$	21	-	-
15%	$\underline{16}$	21	-	-
20%	$\underline{21}$	23	-	-
30%	$\underline{19}$	$\underline{19}$	-	-
Quartz < 10μm				
5%	28	27	53	15
10%	31	27	$\underline{97}$	15
15%	34	28	-	-
20%	31	32	$\underline{90}$	15
30%	31	24	-	-
Feldspar < 50μm				
5%	35	22	-	-
10%	27	21	-	-
15%	20	$\underline{20}$	-	-
20%	$\underline{20}$	$\underline{19}$	-	-
Feldspar < 10μm				
5%	25	27	$\underline{43}$	$\underline{19}$
10%	33	$\underline{21}$	$\underline{43}$	$\underline{22}$
15%	22	$\underline{21}$	-	-
20%	$\underline{17}$	$\underline{18}$	-	-

__ : Not reproducible   - : Not realised

The *alumina gel* has a particle-size distribution which is characterized by the presence of a maximum between 10 μm and 50 μm, with 34 % of the particles below 1 μm. In the diffraction diagram there are some very diffuse maxima at 37°, 42° and 47° °2Θ (Fig. 4).

The *quartz* selected is composed exclusively of this mineral and was previously ground in a ball mill to obtain a size <50 μm (90 %). Part of the quartz was ground again to obtain a size <10 μm (99 %) (Fig. 4).

The *feldspar* used is composed of 70 % potassium feldspar, 27 % of sodium feldspar and 5 % of quartz. The chemical analysis (Tab. 2) corresponds to this mineralogical composition. The mineral was ground in an agate mortar to obtain a mean size of <50 μm. Later a part of this mineral was ground again to obtain 88 % of particles lower than 10 μm (Fig. 4).

Reliability of the method

The reliability of the indices utilized in this work is in general good, although one notes a progressive increase in the standard deviation of the Hughes & Brown index as the crystallinity of the kaolinite increases, for which reason this index is more reliable for kaolins of a high grade of structural disorder. It can be indicated furthermore that the reproducibility of the method is good and the indices of crystallinity are independent.

Reproducibility of the indices selected for mixtures

a) In binary mixtures

Hinckley Index

The presence of iron hydroxide and silica gels affects the reproducibility of the Hinckley index in mixtures with the kaolins of Guadalajara and Pontevedra, but has had no effect with the Georgia Kaolin (Tab. 5). In the first this is due to kaolin of high structural order which is very much affected by any reflection or band which modifies the appearance of the pattern in the zone in which the index is measured (Fig. 5a); and in the case of the Pontevedra Kaolin, because such hydroxides of iron, together with those from the kaolin, significantly affect the measure of the index.

For the Georgia Kaolin, the effect due to the quartz is less when its particle-size is <10 μm because it has been obtained by successive millings, giving rise to lower crystallinity and less intense reflections, consequently less interference with the kaolinite reflections. In the figure 5b we show the effect due to the 100 reflection of quartz in the kaolinite reflections used for the calculation of this index. As the Pontevedra Kaolin shows quartz in its initial composition this index appears to be considerably more affected by the mixtures realized with this kaolin than with the others. The influence of the quartz in the Hinckley index has already been shown by Stoch (1974) and Gomes (1987).

The same effects seems to happen with the presence of feldspars, which affect to the reproducibility of the Hinckley index for the kaolinite very well ordered and in the case of Pontevedra Kaolin because kaolinite presents a band 02*l*, 11*l*, which is easily affected by any reflection corresponding to other minerals. In this case feldspar presents $\bar{2}01$, 111 and $1\bar{3}0$ reflections in that region.

Stoch Index

In our experiment as carried out, this index is not affected by the presence of other mineral phases or amor-

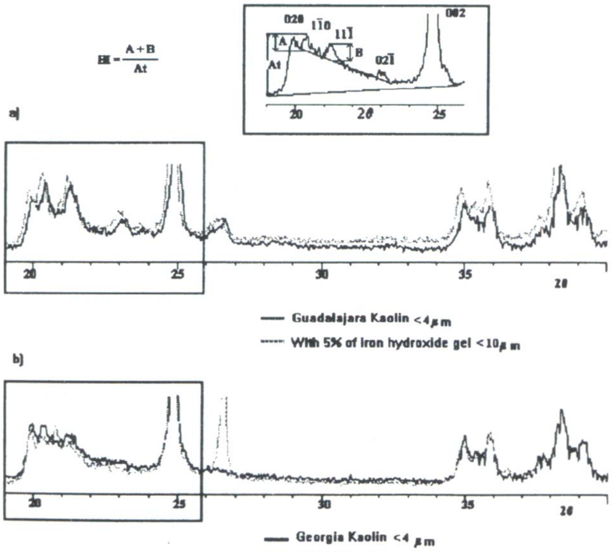


Fig. 5. Influence of distinct phases in the measurement of the index of Hinckley: **a** - Guadalajara Kaolin <4 μm with 5 % of iron hydroxide gel <10 μm. **b** - Georgia Kaolin <4 μm with 10 % of quartz <10 μm.

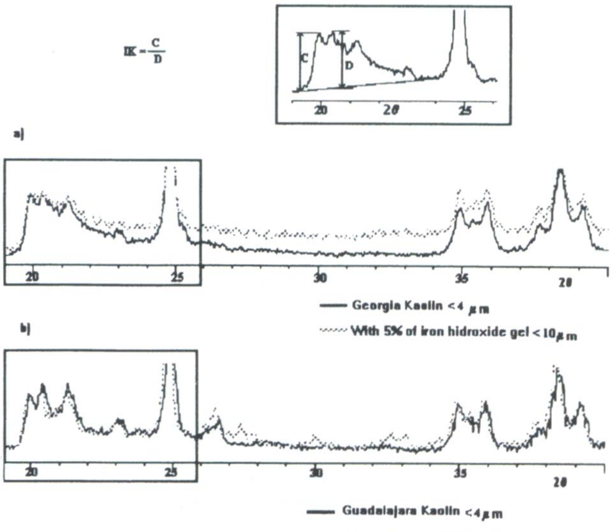


Fig. 6. Influence of distinct phases in the measurement of the index of Stoch: **a** - Georgia Kaolin <4 μm with 5 % of iron hydroxide gel <10 μm. **b** - Guadalajara Kaolin <4 μm with 10 % of feldspar <10 μm.

phous material (Tab. 6), because their effects do not modify the reflections used in the calculation (Fig. 6).

Stoch (1974) indicated that this index classified kaolinites in a similar form to that of Hinckley, with the advantage of being less influence by the presence of quartz.

Lietard Index

The presence of the amorphous phases studied does not significantly affect the measure of the Lietard index in these kaolins (Tab. 7), except in the case where there is more than 5 % of iron hydroxide gel in the mixture with the kaolin from Guadalajara. This effect is due to the fact that treating a kaolin with a high grade of order, and with well defined reflections, is influenced by the effect of iron hydroxide gel on the background.

In Fig. 7a one can observe the reflections $1\bar{3}1$ and 131 of the kaolinite of Pontevedra have increased in intensity as an effect of the presence of iron hydroxide gel, but this latter has been proportional in both reflections so that the Lietard index is not affected.

On the other hand, quartz provokes a variation of this index for the Guadalajara Kaolin (Tab. 7). Further, the presence of feldspar (reflection 240) gives a variations of the $1\bar{3}1$ reflection of the kaolinite and causes the reproducibility of this index to vary (Fig. 7b). It should be noted that the influence of these minerals diminishes using the fraction <10 μm, due to the reduction of crystallinity.

Range & Weiss Index

In the experiment carried out it has been determined that the Range & Weiss index is not advisable in the presence of amorphous phases due to the fact that its measure is based on a relation between areas which is very much affected by the presence of amorphous material (except for alumina gel) which varies the background of the zone measured (Tab. 8). In Fig. 8a we compare the variation caused in the pattern of kaolin from Guadalajara by the presence of iron hydroxide gel. The presence of silica gel affects more the greater is the crystallinity of the kaolinite.

Also the presence of quartz affects more the greater is the crystallinity of the kaolinite (Tab. 8), and it should be noted that quartz of smaller particle-size has less influence due in this case to the loss of crystallinity. Cases et al. (1982) and Gomes (1987) have also come to the same conclusions in relation to the presence of quartz.

The utilization of this index is not advisable in the presence of feldspar, and in Fig. 8b we show the effect caused on the kaolin pattern by the presence of a sequence of reflections of feldspar ($\bar{2}01$, 111 an $1\bar{3}0$).

Hughes & Brown Index

This index is mainly affected by the presence of the iron hydroxide gel, which modifies the basis of the profile and in particular influences on the determination of h1 and principally of h2 (see Fig. 9). Consequently it does not seem advisable to measure the crystallinity of kaolinites in soils by this means, since usually in these materials there is a considerable quantity of iron gel, even though the authors defined precisely this index for soils (Hughes & Brown 1979). The presence of the silica has a larger effect the larger is the crystallinity of the kaolinite. Furthermore, the presence of alumina gel also

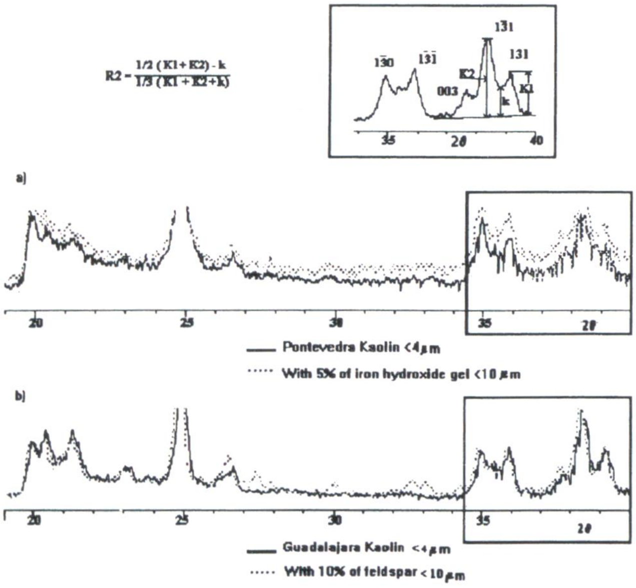


Fig. 7. Influence of distinct phases in the measurement of the index of Lietard: **a** - Pontevedra Kaolin <4 μm with 5 % of iron hydroxide gel <10 μm. **b** - Guadalajara Kaolin <4 μm with 10 % of feldspar <10 μm.

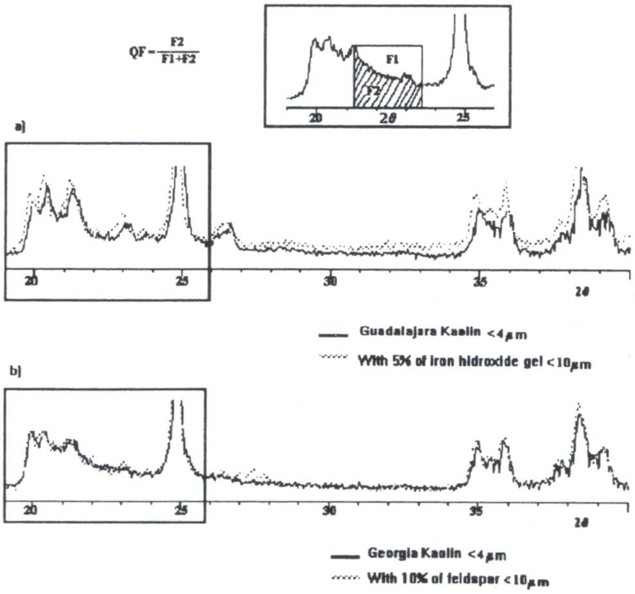


Fig. 8. Influence of distinct phases in the measurement of the index of Range & Weiss: **a** - Guadalajara Kaolin <4 μm with 5 % of iron hydroxide gel <10 μm. **b** - Georgia Kaolin <4 μm with 10 % of feldspar <10 μm.

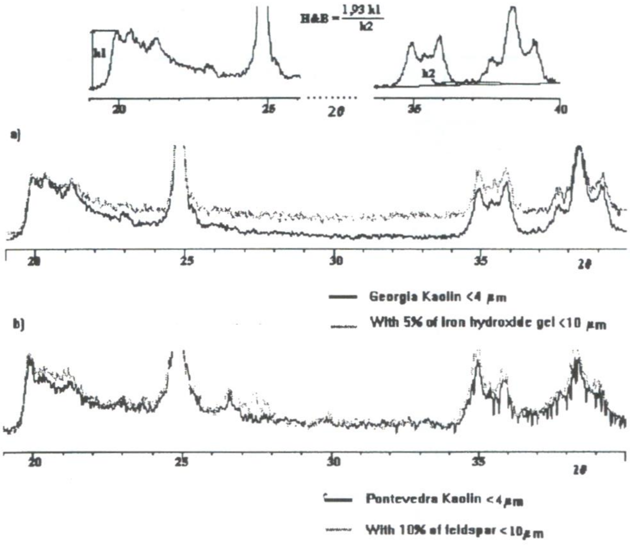


Fig. 9. Influence of distinct phases in the measurement of the index of Hughes & Brown: **a** - Georgia Kaolin <4 μm with 5 % of iron hydroxide gel <10 μm. **b** - Pontevedra Kaolin <4 μm with 10 % of feldspar <10 μm.

affects its measurement since one of the bands of the gel utilized coincides with the zone of measurement of h2.

We ought to bring out that comparing the results obtained with mixtures using the two fractions of the Georgia Kaolin, one notices a behavior which may be called "arbitrary" (Tab. 9). Probably this is due to the measurement of h2 not being objective and giving rise to errors.

The quartz <10 μm only affects the kaolinite of a larger structural order. The presence of feldspars affects to kaolins in general feldspar produces a distortion of the zone of measurement of h2 independently of the crystallinity of the kaolinite (Fig. 9b).

By the way of *summary* we may indicate the index of Range & Weiss is not advisable. On the other hand according to the mineralogical composition of the kaolin apart from the Stoch index, the other indices of crystallinity which may be used are:

If the kaolinite is of a large structural order and in presence of amorphous silica, one can also use those of Hinckley and Lietard.

If the kaolinite is of medium order and in the presence of gels, one can use the Hinckley and Lietard indices indistinctly, while in the presence of quartz and feldspar the Lietard index can be used.

If the sample is of a high degree of structural disorder in the presence of quartz or gels of silica one can employ either the Lietard or the Hughes & Brown indices; while in the presence of iron hydroxide gel one prefers the Lietard index.

b) In multiphasic mixtures

The statistical study of the data obtained (Tab. 10) using multiphasic mixtures indicates that IK is the only index reproducible for the mixture of any kaolins and H&B is reproducible for the Georgia and Pontevedra kaolins, that is to say those of low-medium degree of crystallinity.

Influence of the components associated in the use of the expert system

When the % wcp is less than 10 %, according to Plancon & Zacharie (1990) it is difficult to detect the presence of a well crystallised phase. This is what happens with the majority of the mixtures used with Georgia Kaolin, for which reason it has not been possible to carry out the statistical study of these mixtures.

The mixtures with Guadalajara Kaolin are affected by the presence of the iron hydroxide, quartz and feldspar (Tab. 11). In this case we have a well crystallised kaolin (that is to say with clearly defined reflections), for which the effect of the iron hydroxide is shown by a band of reflections which distorts the measures utilized for applying the expert system. The presence of the mineral phases for their part modifies the reflections of the kaolinite in the two bands studied. It may be indicated that in using this system of mixtures the presence of the well crystallized kaolinite is concealed.

The mixtures with Pontevedra Kaolin (monophasic) are not affected by the presence of the other phases, except as concerns the percentage of type C layer. The presence of a single disordered phase is indicated and the parameters characterizing the disordered kaolinitic phase are reproduced in all samples.

Table 10: Indices of crystallinity in multiphasic mixtures. Reproducibility.

	%wcp	HI	IK	R2	QF	H&B
Georgia Kaolin						
Not mixed (<10μm)	11.2	0.59	0.97	0.72	0.64	39
experimental	0	0.71	0.98	0.84	0.74	31
Guadalajara Kaolin						
Not mixed (<10μm)	23.1	0.94	0.82	0.90	0.55	84
experimental	19.9	1.03	0.81	0.99	0.66	31
Pontevedra Kaolin						
Not mixed (<10μm)	0	0.59	1.22	0.78	0.73	27
experimental	0	0.67	1.16	0.87	0.77	23

___ : Not reproducible

Table 11: Expert system in binary mixtures. Reproducibility.

	Guadalajara Kaolin $<4\mu m$	Pontevedra Kaolin $<4\mu m$			
	% wcp	Wc	p	M	δ
Not mixed kaolin	26	0.24	0.35	24	0.04
With iron hydroxide gel $< 10\mu m$					
5%	32	0.01	0.34	25	0.04
10%	31	0.04	0.33	25	0.03
With silica gel $< 10\mu m$					
5%	27	0.06	0.33	25	0.04
10%	27	0.03	0.35	23	0.05
Quartz $<10\mu m$					
5%	25	0.01	0.33	25	0.04
10%	18	0.01	0.33	25	0.03
20%	14	0.00	0.30	25	0.02
Feldspar $<10\mu m$					
5%	31	0.03	0.33	25	0.04
10%	30	0.07	0.34	25	0.04

___ : Not reproducible

Conclusions

From the results obtained and previously discussed one may deduce that the Stoch index for kaolinites is not affected by the presence of the associated components; on the contrary the Range & Weiss index should not be used. On the other hand, the reproducibility of the Hinckley, Lietard and Hughes & Brown indices vary according to the structural grade of the kaolinite and the components present and their particle-size.

One may note that in commercial kaolins, where the percentage of quartz varies between 5 - 10 % and the presence of iron hydroxide gels is less than 5 %, the Stoch index can be used independently of the crystallinity of the kaolinite, while the indices of Hinckley and Lietard can be used except in kaolins of high crystallinity. If the percentage of kaolinite in a raw kaolin is around 75 %, and in presence of quartz, feldspar and gels, the only indices which are not influenced by these minerals and gels are those of Stoch and Hughes & Brown, independently of the crystallinity of the kaolinite.

With regard to the expert system employed it must be indicated that this should not be used for kaolinites of a medium grade of order-disorder (type Georgia KGa-2), because the presence of the well-ordered phase is hardly noticeable. It should be emphasized that the "expert system" is not reproducible in mixtures with kaolinite of high crystallinity but is effective in mixtures with disordered kaolinite.

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5. SYMPOSIUM ON INDUSTRIAL MINERALS IN NEUBRANDENBURG, GERMANY

March 22 - 23, 1995
Neubrandenburg, Germany

Themes

- use of mineral ressources and saving of environment
- characterization and application of building material for restoring of waste deposits/contamined grounds
- innovative products by industrial mineral processing

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Address for further contacts:

DURTEC GmbH
Ihlenfelder Strasse 153
D-17034 Neubrandenburg
Tel: 0049395 / 4525434
Fax: 0049395 / 4525433