

Textural properties of synthetic clay-ferrihydrate associations

R. CELIS, J. CORNEJO AND M. C. HERMOSIN

Instituto de Recursos Naturales y Agrobiología de Sevilla, CSIC, PO Box 1052, E-41080 Sevilla, Spain

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ABSTRACT: Kaolinite-ferrihydrate and montmorillonite-ferrihydrate associations were prepared following a procedure based on the Russell method for the synthesis of ferrihydrate and the texture of the clay-ferrihydrate complexes was studied using different techniques. The textural properties of kaolinite were little affected by the Fe association, showing only a slight increase in the specific surface area measured by nitrogen adsorption and a decrease in the largest pores ($>10 \mu\text{m}$), as measured by mercury porosimetry. In contrast, the nitrogen specific surface area of the montmorillonite complexes was much higher than that of the clay without Fe and the pore structure depended on the amounts of Fe in the complexes. Application of the fractal approach to nitrogen adsorption data indicated that the surface roughness (microporosity) was greater for the complexes prepared from diluted Fe(III) solutions, in agreement with the information obtained from classical interpretation of the adsorption isotherms (shape of the isotherms and t-plots).

The applicability of nitrogen adsorption in the study of the specific surface area of clay minerals has been discussed by many authors (Brooks, 1955; Aylmore & Quirk, 1967; Thomas & Bohor, 1968; Aylmore *et al.*, 1970; Murray & Quirk, 1990). Although some have attributed part of the N surface area of montmorillonite to the penetration of N_2 molecules into the interlamellar spaces of the clay (Thomas & Bohor, 1968), it is more accepted that, provided the outgassing of the sample has been successful and the exchangeable cation is not too large, the N_2 sorption which does occur appears to be essentially between, rather than into, quasi-crystalline regions of montmorillonite (Aylmore *et al.*, 1970; Quirk & Aylmore, 1971). The nature of the exchangeable cation in montmorillonite clays and its effects on the pore matrix formed after sample drying have been reported to be the most important factors affecting the final specific surface areas measured by N_2 adsorption (Aylmore & Quirk, 1967; Rutherford *et al.*, 1997). Clays such as kaolinite which are characterized by a low exchange capacity and relatively coarse particle size show little evidence of the relationship between the N_2 surface area and either the water

content or the nature of the exchangeable cation in the clay.

The recent application of the fractal theory (Mandelbrot, 1982) in studying the pore matrix of solids has been shown to be very useful, because it may describe a pore structure by means of a single parameter, such as its surface fractal dimension, D_s . Recently, assuming a fractal pore-size distribution, Avnir & Jaroniec (1989) and Yin (1991) were able to obtain an adsorption isotherm equation (eqn. 1) which was found to be similar to that obtained by Frenkel-Halsey-Hill (Gregg & Sing, 1982) for multilayer adsorption of gases on a smooth surface (eqn. 2).

$$\log\left(\frac{p_0}{p}\right) = K' \cdot \theta^{(D_s-3)^{-1}} \quad (1)$$

$$\log\left(\frac{p_0}{p}\right) = b \cdot \theta^s \quad (2)$$

In the above expressions, θ represents the surface fractional coverage, p and p_0 are, respectively, the equilibrium and saturation pressures of the adsorbate, s is a 'critical' exponent in the FHH equation (eqn. 2), and D_s is the surface fractal dimension in the Avnir and Jaroniec equation (eqn. 1).

Since the assumptions made to obtain the above equations are quite different, the meaning of the

characteristic parameters, D_s and s , must also be different. Thus, whereas the differences in s values for the adsorption of N_2 on two samples are justified by Halsey (1948) in terms of different strengths of interaction between the adsorbate and the two solids, the corresponding D_s values indicate differences in the surface roughness for the solids studied, provided the adsorbate used is the same.

If the solids studied are truly non-porous, it is reasonable to assume that multilayer adsorption occurs, and hence that differences in the exponents of eqn. 2 are due to different strengths of interaction between the adsorbate and the solids. However, most solids exhibit some porosity and the traditional attempts to rationalize experimental s values in terms of types of interactions should include geometrical considerations as well (Avnir & Jaroniec, 1989).

It has been shown that surface fractal dimensions, D_s , obtained by fitting N_2 adsorption data to eqn. 1 are largely greater for microporous materials than those for non-porous samples (Lefebvre *et al.*, 1992; Celis *et al.*, 1996). However, it seems to be necessary to apply the fractal approach to many other specific problems in order to check the validity and usefulness of the information obtained by applying the fractal approach to nitrogen adsorption data.

In the present paper several techniques have been used to study the changes in porosity of kaolinite and montmorillonite after ferrihydrite association. Special attention has been given to the applicability of the fractal theory to interpret N_2 adsorption data (Avnir & Jaroniec, 1989). The conclusions from assuming a fractal pore-size distribution in the samples were compared with those obtained from classical interpretations of N_2 adsorption isotherms.

MATERIALS AND METHODS

Minerals

Wyoming montmorillonite, SWy-1, and Georgia kaolinite, KGa-2, were supplied by the Clay Mineral Repository of the Clay Minerals Society.

Ferrihydrite was prepared following the procedure of Russell (1979): a solution of 0.06 M $Fe(NO_3)_3$ was boiled for 8 min, dialysed until NO_3^- free, then freeze dried. It was identified by X-ray diffraction (XRD) showing the six diffraction lines corresponding to a well-crystallized ferrihydrite.

Synthesis of clay-ferrihydrite associations

Kaolinite-ferrihydrite and montmorillonite-ferrihydrite associations were prepared by boiling for 8 min suspensions containing 1.4 g of clay and 50 ml of $Fe(NO_3)_3 \cdot 9H_2O$ with 0 (blank), 7.5, 30, 60 and 120 mg Fe/g clay, while constantly stirring. The pH ranged between 1.5 and 3.2, for the suspensions containing 120 and 7.5 mg Fe/g clay, respectively, whereas the pH of the blank clay suspensions was 7.9 for montmorillonite and 6.1 for kaolinite. A blank sample was also prepared by boiling 1.4 g of montmorillonite for 8 min at the same pH as that of the suspension containing 120 mg Fe/g clay (pH 1.5), and it was identified by XRD. All clay-ferrihydrite associations and blanks were washed until NO_3^- free, lyophilized and stored at room temperature until used.

Iron content of the associations

The Fe content in the clay-ferrihydrite associations was determined by oxalate extraction following the procedure of McKeague & Day (1966): 50 mg of sample were treated with a solution of 10 ml of 0.2 M ammonium oxalate/oxalic acid, shaken in complete darkness and centrifuged. The Fe(III) in the supernatant was determined by atomic absorption spectroscopy.

Nitrogen adsorption isotherms

Nitrogen adsorption-desorption isotherms were obtained using a Carlo Erba Sorptomatic 1900 (Fisons Instr., Milan). Samples were outgassed at 80°C and equilibrated under vacuum for 4 h before measuring the N_2 adsorption-desorption isotherms. The BET specific surface areas, S_{BET} , were calculated by applying the BET method (Brunauer *et al.*, 1938) to adsorption data between relative pressures of 0.02 and 0.30. The t-plots (Lippens & de Boer, 1965) were obtained using the standard isotherm proposed by Sing and his co-workers (Gregg & Sing, 1982) from a wide variety of non-porous silicas, and external surface areas, S_t , were calculated from the slope of the linear region of the t-plots (Lippens & de Boer, 1965). Surface fractal dimensions (Mandelbrot, 1982) were calculated from adsorption data assuming the Avnir and Jaroniec equation (eqn. 1), which can be rewritten as follows:

$$V_{\text{ads}} = K \cdot [\log(\frac{p_0}{p})]^{D_s-3} \quad (3)$$

where V_{ads} is the volume of N_2 adsorbed at the relative pressure p/p_0 , K is a characteristic constant, and D_s is the fractal dimension of surface accessible to adsorption. The value for D_s can be obtained from the slope of a plot of $\log(V_{\text{ads}})$ vs. $\log \log(p_0/p)$ in the region of low adsorption potentials (Avnir & Jaroniec, 1989; Yin, 1991; Lefebvre *et al.*, 1992; Celis *et al.*, 1996).

Mercury porosimetry

The distribution of pore radii of clay-ferrihydrate samples from 4×10^4 to 3.7 nm was determined using a Carlo Erba 2000 mercury depression and intrusion porosimeter (Fisons Instr., Milan). Samples were previously dried by heating at 90°C for 24 h and then outgassed at room temperature for 30 min. A value for the surface tension of mercury of 0.48 N m^{-1} and a contact angle on solids of 141.3° were used with the Washburn (1921) equation assuming cylindrical pores in the calculations.

X-ray diffraction and electron microscopy

X-ray diffractograms of the powder samples were obtained with a Siemens D-500 diffractometer (Siemens, Stuttgart) using $\text{Cu-K}\alpha$ radiation. Powder samples were also observed in a JEOL 5400 scanning electron microscope equipped with an X-ray dispersive energy analyser (EDAX).

RESULTS AND DISCUSSION

Iron content of the associations

The amounts of Fe in the clay-ferrihydrate associations were similar for kaolinite and montmorillonite (Table 1). An extraction time of 4 h (McKeague & Day, 1966) was long enough for montmorillonite complexes to become colourless, but kaolinite complexes with the greatest amounts of Fe needed to be shaken for 24 h. A possible explanation for this behaviour is a stronger association of Fe particles in the presence of kaolinite than in the presence of montmorillonite after drying. Greater dispersion of the montmorillonite complex particles in the oxalate extracting solution as well as differences in particle size or crystallinity of the Fe associated in both

TABLE 1. Oxalate extractable Fe (Fe_o) in the clay-ferrihydrate associations with different initial Fe contents (Fe_{ini}) measured after 4 h and 24 h of extraction time.

mg Fe_{ini} /g clay	mg Fe_o /g association	
	Kaolinite	Montmorillonite
0	0.0 ^a (0.0) ^b	0.9 (1.0)
7.5	6.6 (7.5)	8.3 (7.8)
30	23.5 (21.0)	24.9 (26.0)
60	40.2 (25.6)	40.3 (38.8)
120	56.1 (21.3)	54.2 (53.0)

^a Extraction time: 24 h

^b Extraction time: 4 h

clays would also lead to differences in oxalate extractability. Pure ferrihydrate was found to need a long term (24 h) oxalate treatment in order to be completely dissolved, probably due to lower oxalate/Fe ratio as a result of high Fe content in pure ferrihydrate.

X-ray diffraction

X-ray examination of the complexes revealed no diffraction lines corresponding to 6-line ferrihydrate or other crystalline forms of Fe oxides. This can be due not only to small amounts of Fe in the complexes (<15%) but also to the presence of clay minerals which can have a strong influence on Fe oxide formation (Schwertmann, 1979, 1988). Since clays hinder crystallization, it is very likely that the presence of clay has inhibited the growth of crystalline 6-line ferrihydrate, particularly under the influence of low pH during the synthesis of the clay-ferrihydrate complexes (Schwertmann, 1979). Silicon and Al from the clays may have gone into solution inhibiting crystal growth, lowering crystal order or inducing formation of Al-substituted ferrihydrate, which is usually of poorer crystallinity than ferrihydrate formed in the absence of Al (Schwertmann, 1988). Phyllosilicates usually mask the characteristic broad peaks of these poorly-ordered materials, especially when small amounts of Fe are present.

The position (0.72 nm) of the original first-order basal diffraction line of kaolinite was not affected by ferrihydrate association. However, its intensity decreased slightly with the amount of ferrihydrate (Fig. 1). In contrast, a great decrease and broad-

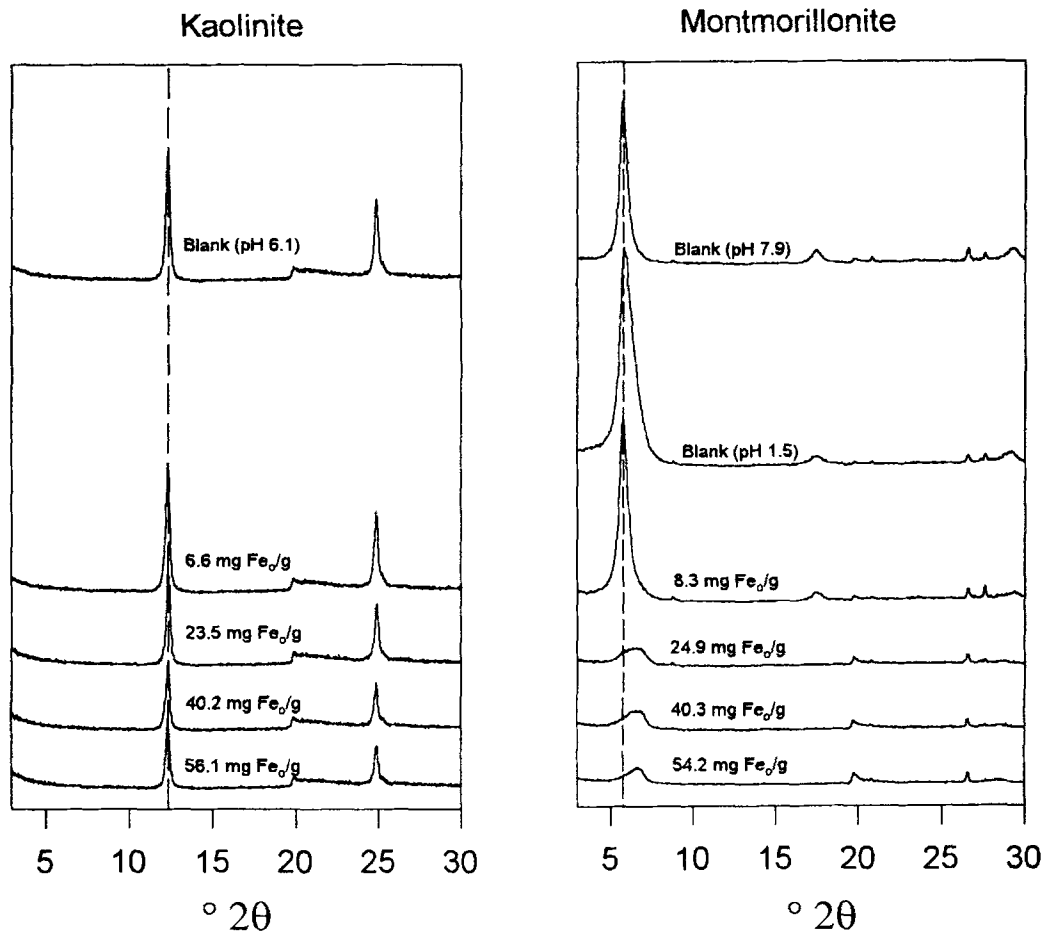


FIG. 1. X-ray diffraction patterns of 001 d -spacings of clay-ferrihydrite associations.

ening of this diffraction line was observed for montmorillonite associated with greater amounts of Fe (Fig. 1). Since the association of ferrihydrite may be influenced by the cation exchange capacity (CEC) of phyllosilicates, the Fe oxide particles may be held on the negatively charged basal surfaces of clays, then more on montmorillonite than on kaolinite. The ferrihydrite association with the negatively charged basal surfaces should make the orientation of the montmorillonite quasi-crystals more difficult during sample drying, resulting in broadening of the basal diffraction. A similar decrease in the intensity (but not the position) of the d_{001} lines in the X-ray diffractogram of montmorillonite by humic acid association was reported by Varadachari *et al.* (1991) and attributed to humic acid interaction with the basal surfaces of the clay, causing disruption in the stacking of the

montmorillonite layers during drying. Although basal spacing values, showing a collapse to 1.0 nm after heating at 200°C (not shown), did not indicate that ferrihydrite was interlayered in the complexes (Barnhisel & Bertsch, 1989), the shift of the 001 d -spacing of montmorillonite to higher angles (lower spacings) observed in Fig. 1 may suggest partial substitution of the original interlayer cations and their water molecules by less hydrated Fe³⁺ monomers or very small poly-[Fe(III)-OH] cations during the synthesis of the complexes. The pH effects can be rejected since a blank sample prepared by keeping montmorillonite for 8 min at 100°C at the same pH as that of the complex containing 120 mg Fe/g montmorillonite (pH 1.5) resulted in the same basal spacing as that of the blank sample prepared at higher pH (Fig. 1). All these changes in the XRD patterns of the mont-

morillonite-ferrihydrate associations are not observed in kaolinite because its low CEC, relatively coarse particle size, and lack of swelling should reduce considerably the negatively charged basal surface exposed in solution for Fe association.

Nitrogen adsorption isotherms

Nitrogen adsorption-desorption isotherms for kaolinite-ferrihydrate and montmorillonite-ferrihydrate associations are shown in Fig. 2. Adsorption isotherms on kaolinite were of type II, according to the Brunauer *et al.* (1940) classification, and were characterized by the absence of an hysteresis loop. This agrees with the presence of large pores (macropores) resulting from the arrangement of the coarse kaolinite particles by drying (Murray & Quirk, 1990; Celis *et al.*, 1996). Little change in the shape of the isotherm was observed after ferrihydrate association with kaolinite. The N_2 adsorption isotherm on montmorillonite was similar to those reported by other authors (Brooks, 1955; Aylmore & Quirk, 1967; Celis *et al.*, 1996). It was of type IV with an hysteresis loop of type H3 (IUPAC, 1985), which agrees with small slit-shaped pores resulting from the arrangement of the thin platelets of montmorillonite during drying (Gregg & Sing, 1982). Adsorption isotherms on montmorillonite-ferrihydrate complexes with small amounts of Fe were similar to that on pure montmorillonite (with a greater degree of hysteresis in the case of the complex with 24.9 mg Fe_o/g); however, those for the complexes with the two greatest amounts of Fe showed a great reduction in hysteresis, thus suggesting a significant reduction in fine pores.

The N_2 specific surface area of montmorillonite is strongly dependent on the water content of the sample during the N_2 adsorption experiment (Brooks, 1955). The weight losses measured for

the montmorillonite-ferrihydrate associations, shown in Table 2, are in agreement with the values reported by Brooks (1955) for Na-Wyoming bentonite which has lost all the water of adsorption and hydration to leave ~5% water of constitution as an integral part of the clay structure. These weight losses (~10%) are nearly the same for the different montmorillonite-ferrihydrate associations studied, so we can compare the values of S_{BET} obtained for the different samples. The N_2 surface area of kaolinite is not strongly dependent on the loss of water of adsorption or hydration (Brooks, 1955). As shown in Table 2, the water losses by outgassing kaolinite-ferrihydrate associations are much less than those for montmorillonite.

The low value of the specific surface area (11 m²/g) measured for montmorillonite without ferrihydrate (blank) compared to that for the crude clay (24.9 m²/g) can be explained if we take into account that the sample treatment previous to obtaining the adsorption isotherm has a strong influence on the sedimentation of montmorillonite quasi-crystals and, therefore, on the pore matrix after sample drying. Regular stacking of montmorillonite lamellae during drying reduces porosity thus resulting in low specific surface area (Srasra *et al.*, 1989; Van Damme & Ben Ohoud, 1990). Thus, by careful preparation of oriented flakes, Greene-Kelly (1964) reduced the N_2 specific surface area of Na-Wyoming bentonite to some 5 m²/g compared with the 40–50 m²/g frequently obtained for this clay. Kaolinite was unaffected by the blank treatment, since the value of 18.4 m²/g for S_{BET} of kaolinite without ferrihydrate (blank) is close to that of 20.1 m²/g corresponding to the crude kaolinite sample.

The BET specific surface areas, S_{BET} , of kaolinite- and montmorillonite-ferrihydrate associations increased with the amounts of ferrihydrate in the

TABLE 2. Weight loss and specific surface areas, S_{BET} and S_t , for clay-ferrihydrate associations.

Fe _o (mg/g)	Kaolinite associations			Montmorillonite associations					
	weight loss (%)	S_{BET} (m ² /g)	S_t (m ² /g)	Fe _o (mg/g)	weight loss (%)	S_{BET} (m ² /g)	S_t (m ² /g)	S_{ext} (m ² /g)	S_{mp}
0.0	0.6	18.4	18.0	1.0	10.0	11.0	10.6	—	—
6.6	0.6	22.1	21.6	8.3	13.0	37.4	38.6	27.8	9.6
23.5	1.4	28.1	27.7	24.9	8.8	50.0	51.3	32.6	17.4
40.2	1.5	31.1	31.6	40.3	9.0	54.5	55.5	—	—
56.1	1.4	34.0	34.0	54.2	8.8	62.1	63.2	—	—

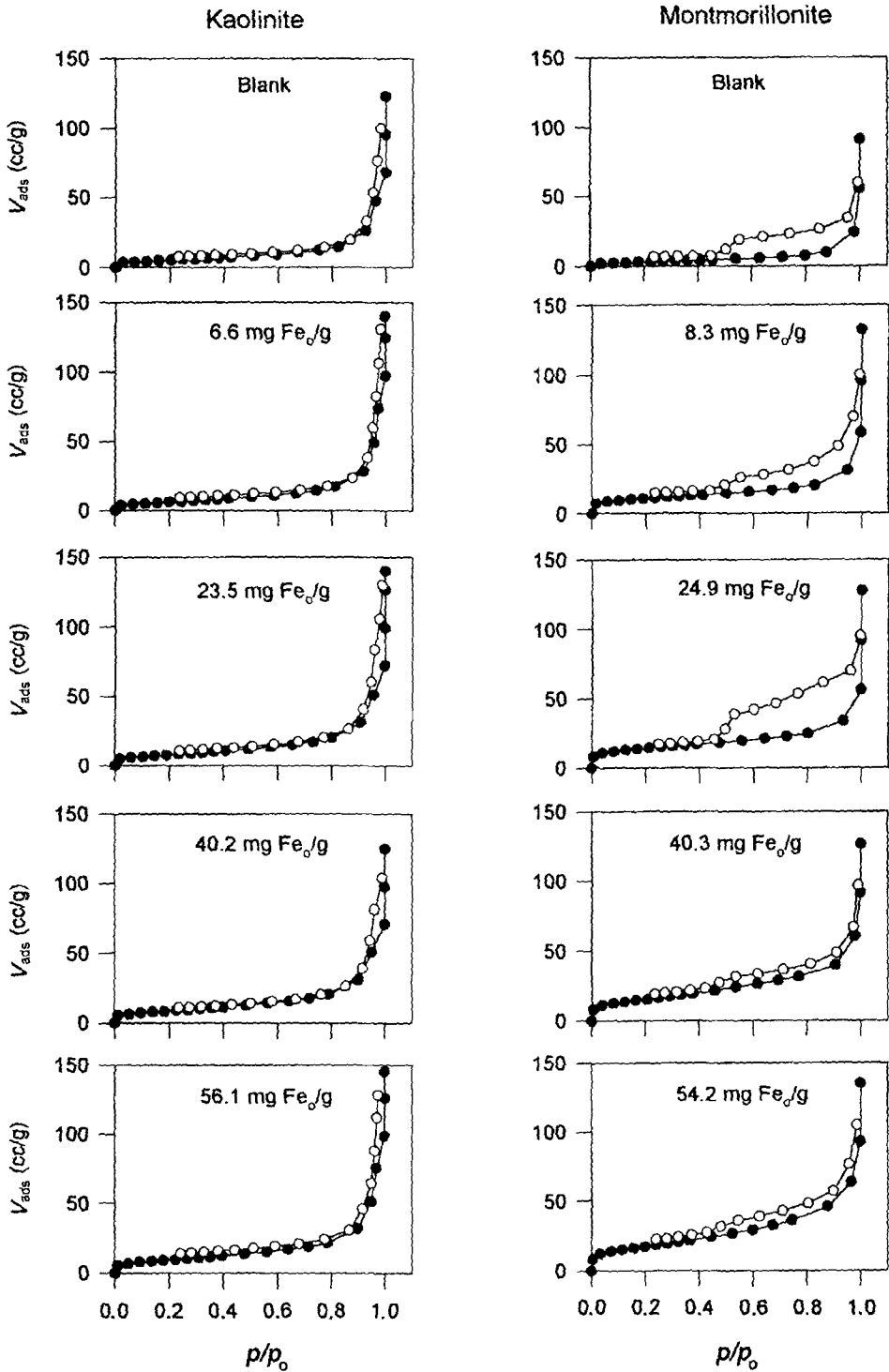


FIG. 2. Nitrogen adsorption-desorption isotherms on clay-ferrihydrite associations.

samples; however, the increase was greater for montmorillonite (Table 2). If we assume clay-ferrhydrite associations to be mechanical mixtures of the two components, the total surface area would be given by the addition of the surface areas of the amount of each component, i.e.

$$S_m = S_c (1 - \theta) + S_f \theta \quad (4)$$

where S_m is the total specific surface area for the mixture, S_c and S_f are the specific surface area for the clay and ferrhydrite samples, respectively, and θ is the proportion of ferrhydrite in the mixture. Pure ferrhydrite, prepared as a reference, had $S_{\text{BET}} = 152 \text{ m}^2/\text{g}$ and its weight loss on outgassing was 7.3%. Although the amount of ferrhydrite in the samples cannot be measured directly, assuming the structural formula $\text{Fe}_2\text{O}_3 \cdot 2\text{FeOOH} \cdot 2.6\text{H}_2\text{O}$ proposed by Russell (1979) from infrared spectroscopy, the Fe content in ferrhydrite is nearly 60%. Thus we can estimate the S_{BET} of the complexes as a function of the Fe content and assuming heterogeneous mixtures of clay and pure ferrhydrite. As can be seen in Fig. 3, experimental S_{BET} values for the kaolinite-ferrhydrite complexes fitted reasonably well to the model of non-interaction between the individual components. On the contrary, the experimental values of S_{BET} for the montmorillonite complexes were much greater than those expected for heterogeneous mixtures of

montmorillonite and ferrhydrite. Although the pronounced difference of S_{BET} for the untreated and subsequent data could be due to preparation effects of the blank sample, it should be noted that the increase in S_{BET} for montmorillonite is linear for Fe contents $\geq 8.3 \text{ mg/g}$ and the observed slope is still larger than calculated for the mixture of pure ferrhydrite and montmorillonite (Fig. 3). This discrepancy could mean that the composition or surface morphology of the Fe phase formed in the presence of montmorillonite is different (higher surface area) from the pure ferrhydrite whereas kaolinite did not influence ferrhydrite formation. In fact, smectites have been shown to retard Fe oxide crystallization to a greater extent than kaolinite (Schwertmann, 1979). Moreover, as mentioned above, the Fe oxide particles may be held on the negatively charged basal surfaces of clays, more on montmorillonite than on kaolinite, making the orientation of the montmorillonite flakes more difficult during sample drying, thus increasing porosity and the specific surface area of the resulting clay-ferrhydrite complexes.

The t-plots (Lippens & de Boer, 1965) of the N_2 adsorption data for all kaolinite-ferrhydrite complexes were typical of mesoporous materials (Fig. 4). They showed a first linear region corresponding to multilayer adsorption on a relatively smooth surface followed by a significant

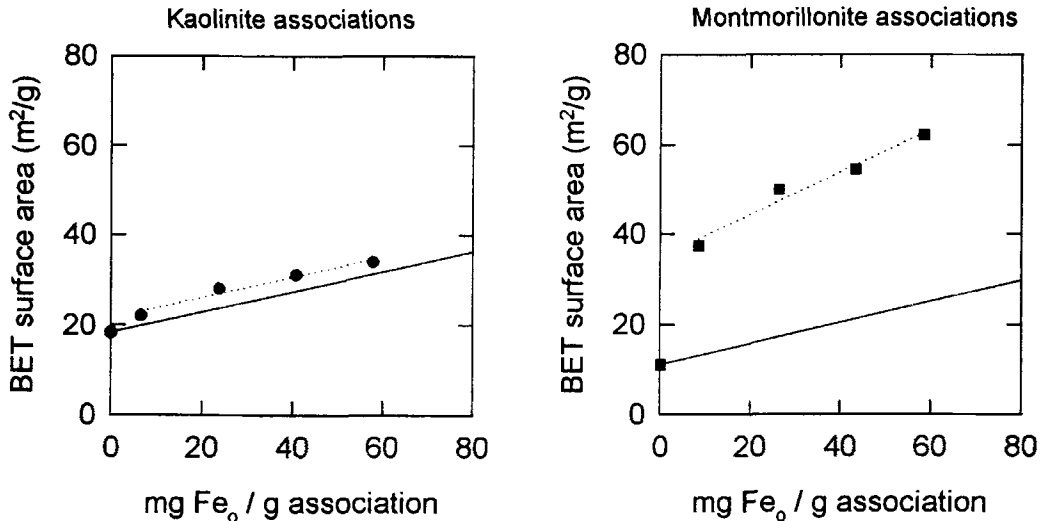


FIG. 3. Values of S_{BET} for the clay-ferrhydrite associations as a function of the Fe content. The Symbols correspond to experimental values whereas solid lines correspond to values calculated assuming mechanical mixtures of clay and ferrhydrite.

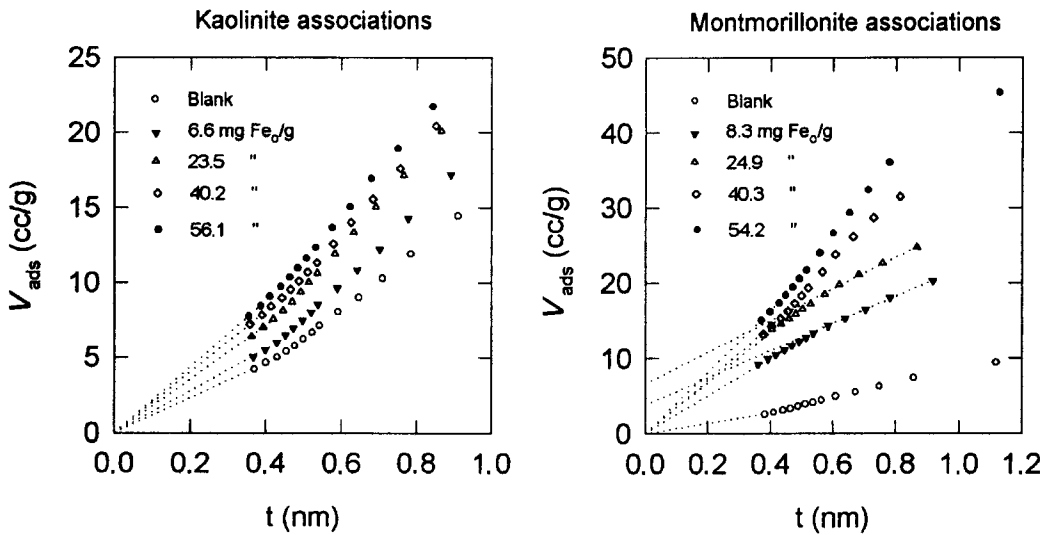


FIG. 4. t -plots of clay-ferrihydrate associations.

increase in the N_2 uptake when capillary condensation began in the mesopores of the sample (Gregg & Sing, 1982). The surface areas derived from the slope of the initial linear region of the t -plots, S_t , were in good agreement with the corresponding S_{BET} (Table 2). The S_t values were always slightly $>S_{BET}$, which has no physical meaning and can be attributed to slight differences between the nature of the surfaces considered and that of the standard used (Gregg & Sing, 1982). The t -plots for montmorillonite-ferrihydrate complexes were dependent on the amounts of ferrihydrate, the t -curves for the complexes with the two lowest doses of Fe showed downward deviations indicative of microporosity (Sing, 1967). For such microporous samples, both the total area, S_t , and the external area, S_{ex} , are calculated from the slopes of the initial steep line and the less steep line after the intersection in the t -plots, respectively. The difference between S_{BET} and S_{ex} may be assumed as micropore surface, S_{mp} . The surface area due to micropores ($S_{BET} - S_{ex}$) were $9.6 \text{ m}^2/\text{g}$ for the complex with $8.3 \text{ mg Fe}_o/\text{g}$ and $17.4 \text{ m}^2/\text{g}$ for the complex with $24.9 \text{ mg Fe}_o/\text{g}$. The micropore volumes, V_{mp} , obtained from the intercept of the first linear region of the t -plots (Fig. 4) were 0.00603 cc/g for the complex with $8.3 \text{ mg Fe}_o/\text{g}$ and 0.0103 cc/g for the complex with $24.9 \text{ mg Fe}_o/\text{g}$. In contrast, t -curves for the complexes with the two highest doses of Fe were typical of mesoporous

materials, with S_t quite similar to S_{BET} , thus resembling those of the kaolinite complexes.

Fractal analysis. Nitrogen adsorption isotherms on the different clay-ferrihydrate associations plotted according to the logarithmic plot of the Avnir & Jaroniec equation (eqn. 3) are shown in Fig. 5. Two regions of linearity were found (above and below $p/p_o = 0.5$). The resulting surface fractal dimensions for each region are shown in Table 3. Although it is not intuitively evident which of the adsorption data ranges best relates to the fractal dimension of the surface, in our case, the changes in D_s values of the associations with increasing amounts of ferrihydrate followed the same tendency for both relative pressure ranges. Most of D_s values in Table 3 are in the range of 2.5–2.75, reported by Lefebvre *et al.* (1992) for a number of widely different samples; however, the changes in D_s values with increasing amounts of ferrihydrate in the montmorillonite associations were quite different from those in the case of kaolinite. Thus, for the two regions, D_s values for the kaolinite associations were low and showed only a small increase with increasing amounts of ferrihydrate (Table 3). In contrast, large D_s values were found for the associations with the smallest amounts of ferrihydrate whereas small D_s values were found for the associations with the largest amounts of ferrihydrate.

The low D_s values shown in Table 3 for the kaolinite-ferrihydrate associations are consistent

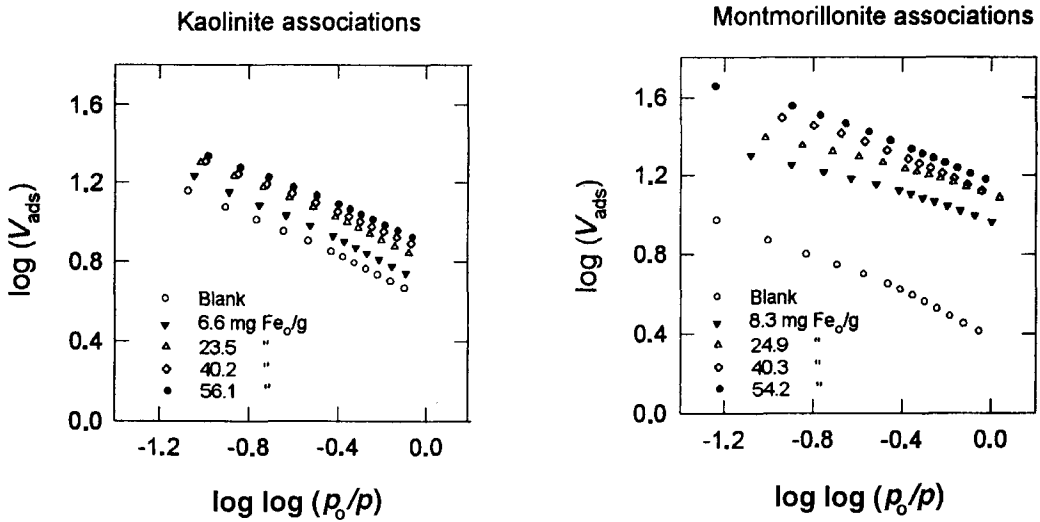


FIG. 5. Nitrogen adsorption isotherms for the clay-ferrihydrate associations plotted according to the Avnir and Jaroniec equation.

with those for meso- or macroporous materials, the slight increase in D_s for the samples with the greatest amounts of ferrihydrate being related to a relatively small increase in the surface roughness. For montmorillonite, the D_s values reported in Table 3 indicated that, whereas the increases in the specific surface areas of the associations with the smallest amounts of ferrihydrate are due to the presence of micropores, in the case of the complexes with the greatest amounts of ferrihydrate the absence of micropores could be indicated by the decrease in the surface fractal dimension calculated for these samples. It is worthwhile to note that these conclusions agree with those obtained from the t-analysis of the adsorption isotherms (Fig. 4) in which the presence of mesoporosity was apparent

for the montmorillonite complexes with the greatest amounts of ferrihydrate as well as for all kaolinite associations.

The presence of greater mesoporosity and the absence of microporosity in the montmorillonite complexes with greater amounts of Fe (40.3 and 54.2 mg Fe/g complex) directly indicated by t-plots and indirectly by D_s values, could be related to the fact that concentrated solutions of Fe^{3+} give rise to the formation of Fe polymers larger than those formed from diluted solutions (Rengasamy & Oades, 1977a). If so, the separation between quasi-crystals in montmorillonite after drying as well as the interaggregate space of Fe particles themselves (Fusi *et al.*, 1993) would be even larger and might fall in the pore-size range of mesopores.

TABLE 3. Surface fractal dimensions, D_s , for the clay-ferrihydrate associations calculated by applying the Avnir & Jaroniec (1989) equation 1 to N_2 adsorption data. Standard errors of the calculated D_s values were ≤ 0.01 in all cases.

Kaolinite associations			Montmorillonite associations		
Fe_0 (mg g ⁻¹)	D_s ($p/p_0 < 0.5$)	D_s ($p/p_0 > 0.5$)	Fe_0 (mg g ⁻¹)	D_s ($p/p_0 < 0.5$)	D_s ($p/p_0 > 0.5$)
0.0	2.44	2.53	1.0	2.41	2.59
6.6	2.44	2.52	8.3	2.62	2.73
23.5	2.46	2.55	24.9	2.65	2.75
40.2	2.53	2.58	40.3	2.51	2.63
56.1	2.51	2.58	54.2	2.52	2.65

It is worth noting in this regard that the amounts of Fe in these complexes were significantly lower than the amounts of Fe initially added to the clay suspension, the rest being lost during washing (Table 1). This could indicate that the external surface of montmorillonite has been completely covered by Fe oxide and perhaps inversion of the surface charge of the clay has taken place. Charge reversal has been reported by other authors to cause changes in flocculation, aggregation, particle size and other properties of Fe and Al oxide coated clays (Rengasamy & Oades, 1977b; Oades, 1984; Arias *et al.*, 1995).

Mercury porosimetry and electron microscopy

Figure 6 shows the evolution of the mercury pore volume of radii smaller and larger than 10 μm with increasing amounts of Fe present in the clay-ferrihydrate complexes. Ferrihydrate association with kaolinite and montmorillonite led to a decrease in the volume of pores $>10 \mu\text{m}$. The volume of pores $<10 \mu\text{m}$ increased slightly for kaolinite, but in the case of montmorillonite it appears that the two greatest amounts of Fe lead to an increase in the volume of pores $<10 \mu\text{m}$. This agrees with the characteristic texture (low microporosity and high mesoporosity) of these complexes observed by N_2 adsorption isotherms.

Scanning electron microscopy studies corroborated the results obtained by mercury porosimetry. The open lamellar morphology of montmorillonite

can be seen in Fig. 7a. In contrast, Fig. 7b and c show the more compact appearance of the montmorillonite complexes with the greater amounts of ferrihydrate. In these samples, it is clear that the effect of ferrihydrate has been to fill the pores partially thereby reducing the macroporosity of the montmorillonite sample. Analysis by EDAX indicated that the distribution of Fe in the associations is quite homogeneous. No regions with preferential accumulations of Fe were found on the clay surface.

In summary, ferrihydrate association with montmorillonite and kaolinite results in aggregates with different textures depending on the clay. Isolated ferrihydrate particles seems to bind only to the external surface of the domains (Aylmore & Quirk, 1967) of kaolinite reducing the volume of largest pores ($>10 \mu\text{m}$) and slightly increasing the specific surface area of the clay. In contrast, ferrihydrate association with montmorillonite causes the pore matrix which results from drying to be very different from that of the clay without ferrihydrate. Different textures were observed for different Fe loadings in montmorillonite. Although ferrihydrate was not interlayered in the complexes, it appears that Fe particles, probably of poorer crystallinity than pure ferrihydrate due to Al substitution, disrupt the stacking of the montmorillonite quasicrystals, as depicted in Fig. 8, which may contribute to the large values of specific surface area measured for the resultant associations. The scheme in Fig. 8 is only a simplification since, as reported by other authors, thin lamellae of montmorillonite are

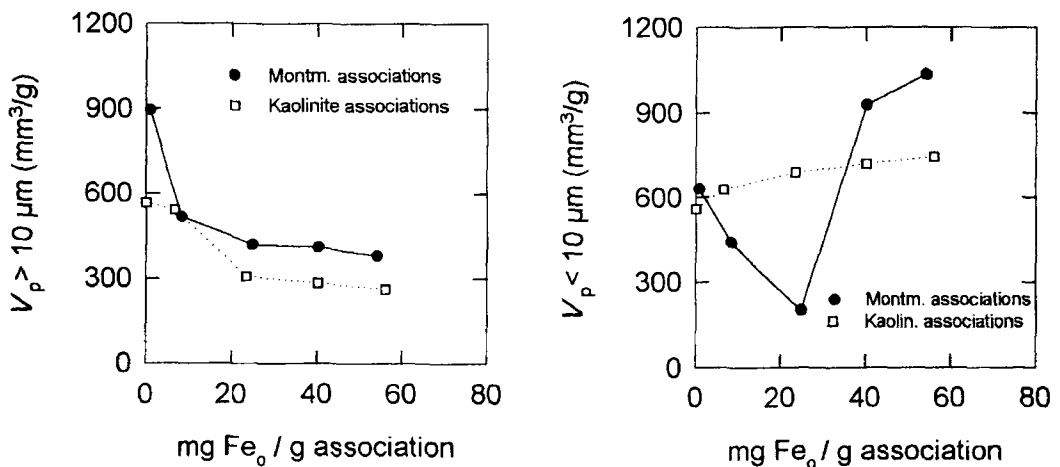


FIG. 6. Mercury pore volume for pore radii smaller and larger than 10 μm for the different clay-ferrihydrate associations.

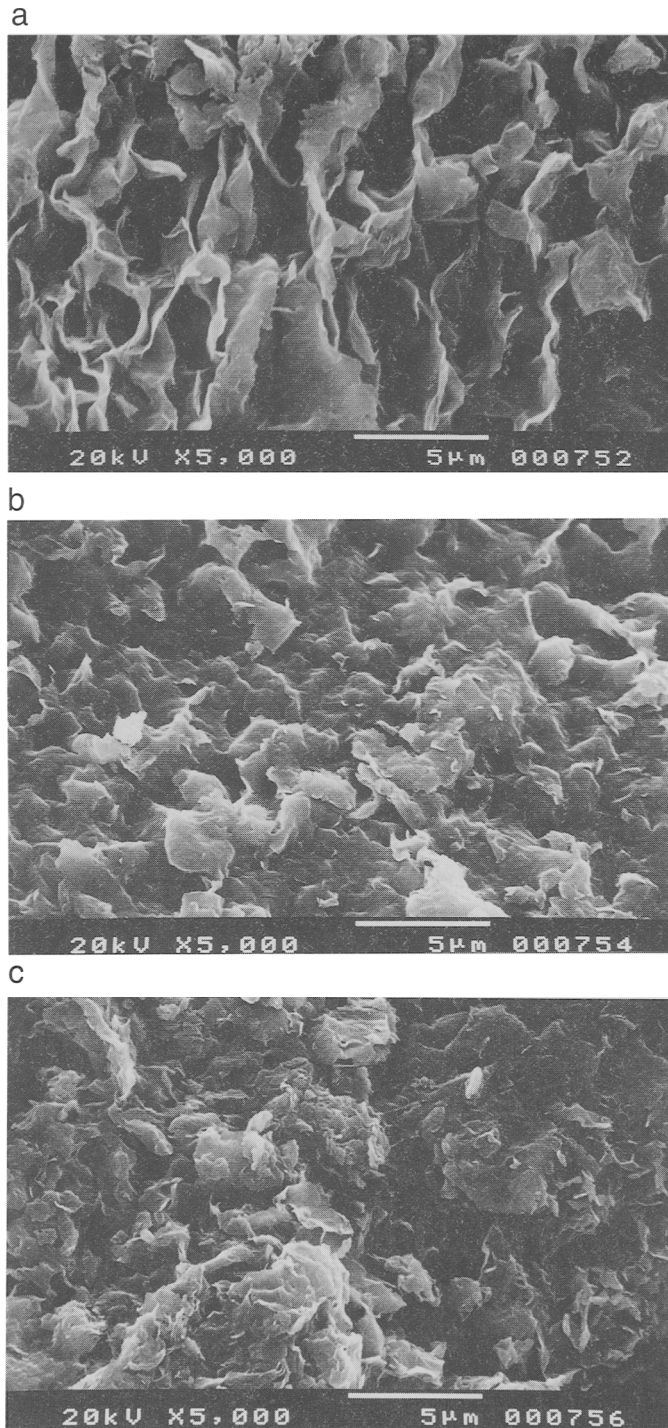


FIG. 7. Scanning electron micrographs of montmorillonite-ferrihydrate associations. (a) 0 mg Fe_o/g (blank), (b) 24.9 mg Fe_o/g, (c) 54.2 mg Fe_o/g.

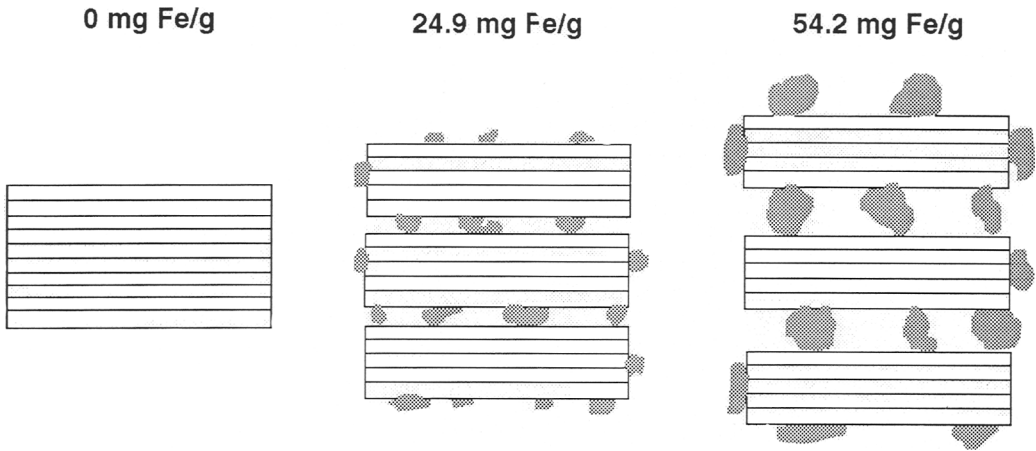


Fig. 8. Scheme of the arrangement of quasi-crystals in montmorillonite-ferrihydrite associations after drying.

subjected to large forces during drying and such forces are responsible for the massive deformation of the thin lamellae, evident in electron micrographs (Fig. 7a), leading to prevalence of cuneiform voids within the remaining microporosity (Greene, 1975; Murray & Quirk, 1990).

CONCLUSIONS

The textural properties of kaolinite show little change in association with ferrihydrite. The specific surface areas of kaolinite-ferrihydrite complexes were in agreement with values which correspond to a mixture of both components. Surface fractal dimensions, D_s , obtained from the N_2 adsorption isotherms following the Avnir & Jaroniec (1989) equation indicated only a small increase in surface roughness for the associations with the greatest amounts of Fe. The macropore volumes obtained by mercury porosimetry also showed small insignificant differences in kaolinite macroporosity by Fe association. The position of the original XRD basal spacing was also unaffected by the presence of ferrihydrite. A slight decrease in intensity was observed.

The ferrihydrite association with montmorillonite leads to important changes in the textural properties of the clay. Iron particles may be held on the negatively charged surfaces of montmorillonite, probably with poorer crystallinity than pure ferrihydrite and making the orientation of montmorillonite quasi-crystals more difficult during

sample drying, thus resulting in high specific surface areas of the resultant aggregates. Greater loadings of Fe on montmorillonite make the texture of the complexes significantly different (low microporosity and high mesoporosity) from that of montmorillonite-ferrihydrite complexes with low amounts of Fe.

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