SURFACE FRACTAL DIMENSIONS OF SYNTHETIC CLAY-HYDROUS IRON OXIDE ASSOCIATIONS FROM NITROGEN ADSORPTION ISOTHERMS AND MERCURY POROSIMETRY

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ABSTRACT: Model associations of layer silicates (kaolinite and montmorillonite) and iron oxyhydroxides were obtained by precipitating hydrous iron oxide in clay suspensions at different loading. The porosity of these clay-hydrous iron oxide associations was studied in the macro- and mesopore range by mercury intrusion porosimetry (MIP) and in the micropore region by nitrogen adsorption isotherms, being the fractal geometry applied to the approaches used in porosity studies. Results of nitrogen adsorption isotherms showed that surface area and microporosity of kaolinite and montmorillonite increased upon Fe precipitation, especially for montmorillonite. This process is accompanied by an increase in the surface fractal dimension $Ds(N_2)$ by the presence of hydrous iron oxide coating the clay particles. Results of MIP also showed a decrease in the pore volume by Fe precipitation on montmorillonite due to a decrease in the number of large pores and a development of new medium-size pores. An increase of the fractal dimension $Ds(Hg)$ was also observed.

Pure solid particles can be associated to produce more or less stable associations. Synthetic and natural associations, e.g. drilling mud flocs, catalysts, soil aggregates, etc. normally show a porous structure whose geometry is heterogeneous. Clays, metal oxides or oxyhydroxides and organic matter are normally associated in soils, sediments and particulate matter of surface waters. It is well known that most natural processes occur in heterogeneous environments. The soil aggregates' structure is the porous media in and through which all soil processes take place, and soil structure is closely related with its porosity geometry. Several complementary methods, such as mercury porosimetry, thin-section technique and image analysis, have been used to characterize the heterogeneity of soil structure (Bartoli *et al*., 1992; Young & Crawford, 1991). However, the study of soil structure formation and destruction mechanisms is still an open question and the fractal approach seems to be a potentially useful tool to understand these processes.

Many natural processes are being studied by means of the fractal theory after Mandelbrot's review (1982). Fractals are geometric representations of disordered systems whose structure is described by non-Euclidean dimensions. The association of soil constituents in heterogeneous aggregates causes a disordered state that can be explained by the fractal approach. Very interesting results were obtained by Van Damme *et al*. (1988) applying fractal geometry to granulometric analysis of powders. The application of this theory to the study of the porous structure of soils seems to be very successful because of the ability to describe the porous structure of soils by means of a single parameter; as a fractal dimension. Correlation between this parameter and other soil properties such as soil composition (Burrough,1981), hydraulic conductivity (Shepard, 1993), mass or porosity (Bartoli *et al*., 1991), has been found. A relationship between the surface fractal dimension, Ds, of some natural soils and the mobility of two different herbicides through those soils has also been found by Cox *et al*. (1996).

A simple descriptor of the pore structure of solids is the pore-size distribution, V_p, which can be assumed as a statistical approximation to the roughness of a surface at any magnification. Avnir *et al*. (1984) have calculated Ds values for specific surfaces obtained by adsorption of different size molecules. Thereafter, they have proposed a model

to obtain Ds values in the micropore size range from a single adsorption isotherm (Avnir & Jaroniec, 1989). Mercury intrusion porosimetry (MIP) is being used to study the surface fractality in the range of meso- and macroporosity. Based on the description, by Pfeifer & Avnir (1983), of porous media in fractal terms, Friesen & Mikula (1987) have suggested a fractal model of porous media, applied to determine the fractal dimension of coal particles using the MIP technique. This model has also been applied to show the fractal structure of natural soil surfaces (Bartoli *et al.*, 1991) as well as those altered soils after the addition of several compounds (Bartoli *et al.*, 1992).

A normal procedure to study the formation of soil aggregates is their synthesis by association of inorganic and organic soil colloids under several physical and chemical conditions. Perhaps the simplest example is the association of clays with poorly ordered hydrous iron oxides. The study of this system could be a first step to understand a more complex system like natural soil aggregates.

In the present paper, the nitrogen adsorption isotherm and mercury porosimetry techniques have been applied to study the influence of the precipitation of hydrous iron oxides in the fractal structure of clays. The Avnir & Jaroniec (1989) model has been applied to obtain the surface fractal dimensions of samples studied in the micropore size range ($r_p < 10$ Å). The Ds values in the mesopore (10 Å $< r_p < 250$ Å) and macropore ($r_p > 250$ Å) range were obtained by application of a modification of the Friesen & Mikula (1987) model from mercury porosimetry assuming cylindrical pore shape. A comparison between Ds values and other parameters obtained from pore-size distribution models based on Euclidean geometry is given.

THEORETICAL CONSIDERATIONS

Fractals are mainly used to describe the structures of highly disordered systems, being invariable at any characterization scale used to examine them. These systems are characterized by the self-similarity property indicating that any part of the system looks the same as the whole regardless of the resolution. Self-similarity is a feature which may be a characteristic of a curve, a surface or a three-dimensional system. Mandelbrot (1982) has shown that the geometry of self-similar shapes can be described by a single number, the fractal

dimension D. In fractal geometry it is possible to describe irregular lines, no smooth planes and hazardous volumes existing everywhere in nature by single non-Euclidean dimension D different from the integer 1, 2, 3 values.

Friesen & Mikula (1987) consider that the length, surface area or volume of an object can be given by M_d (d = 1,2,3), and defined as

$$M_d = N_d (r) \cdot m_d$$

where N_d is the number of yardsticks used of size r and mass $m_d \propto r^d$ needed to fill the object.

In Euclidean geometry $N_d (r) \propto r^d$, being M_d, in this case, independent of the size of the yardstick used. On the contrary, when $N_d (r) \propto r^{-D}$ in which $D \neq d$, a fractal object is considered whose M_d is dependent on the yardstick size used.

Mandelbrot's (1982) fractal geometry explains many complex forms found in nature, such as the shapes of coastlines, mountains and clouds which cannot be described by Euclidean geometry. However, the shapes of these examples can easily be explained by the non-integral fractal dimension D, at least between a number of distinct size ranges r_{min} and r_{max}. In this way the increase of surface area $M_2(r)$, obtained when a smaller yardstick r is used, could indicate a greater degree of roughness in this range.

MATERIALS AND METHODS

Synthesis of clay-hydrous iron oxide associations

The three clays, Georgia kaolinite, KGa-2, Wyoming montmorillonite, SWy-1, and Arizona montmorillonite, SAz-1, were purchased from The Clay Mineral Repository. The major exchange cation in SWy-1 was Na (CEC = 76.4 mEq/100 g) whereas the principal exchange cation in SAz-1 was Ca (CEC = 120 mEq/100 g). The CEC of KGa-2 was very low (3 mEq/100 g). Physicochemical properties of these clays have been reported in detail by Van Olphen & Fripiat (1979). One gram of crude clays was added to a solution of 50 ml of 3.75, 7.5 and 15.0 mM $Fe(NO_3)_3 \cdot 9H_2O$. Suspensions were stirred and a sufficient amount of NH_3 was added until the pH reached 7.5. Assuming complete precipitation of the Fe initially added, the Fe content of the associations were 10.5, 21.0 and 42.0 mg Fe/g clay, respectively. The suspensions were centrifuged, washed until nitrate-free and then freeze-dried. In

order to compare the results obtained for the clay-hydrous ferric oxide associations with those corresponding to clays, the original clays were subjected to the above-mentioned treatments, but without the presence of Fe in solution i.e. control samples.

Nitrogen adsorption

Nitrogen adsorption isotherms on clay-iron hydroxide complexes were obtained at 77K using a Sorptomatic 1900 Carlo Erba apparatus. The samples were previously outgassed at 80°C and equilibrated under vacuum for at least 6 h before measuring the adsorption-desorption isotherm. Specific surface areas were calculated using the BET procedure (Brunauer *et al.*, 1938) assuming a cross-sectional area of 16.2 Å^2 for the N_2 molecule. The Horvath & Kawazoe model (1983) was used to calculate the corresponding pore-size distribution. The fractal dimension of the surface accessible to adsorption, $Ds(N_2)$, in the micropore range was obtained assuming the Avnir & Jaroniec (1989) equation,

$$\frac{V_{ads}}{V_m} = K[\ln\left(\frac{p_0}{p}\right)]^{D_s - 3} \tag{1}$$

where V_{ads} is the volume of gas sorbed at a relative pressure P/P_o, V_m is the volume of molecules adsorbed at a monolayer coverage and K is a constant. This equation was obtained by the authors applying fractal considerations to the Dubinin approach (1988) obtaining a similar equation to that of Frenkel-Halsey-Hill (Gregg & Sing, 1982). This equation is also a slightly modified version of that first proposed by De Gennes (1985) for capillary condensation.

Mercury porosimetry

The mercury depression-intrusion porosimetry curves were obtained using a Carlo-Erba Porosimeter 2000 linked to a Macropore unit. The samples were heated at 90°C for 24 h and outgassed *in situ* for 30 min before the measurement. A value for the surface tension of mercury of $\gamma = 0.48$ N/m and a mercury solid contact angle of $\theta = 141.3°$ was assumed to use the Washburn (1921) equation. The surface fractal dimension was calculated by using the cumulative volume, V_{cum} of pores in the meso and macropore range in order to obtain the cumulative surface (S_{cum}) as a function of the

pore radius r_p. The fractal dimension of the surface $Ds(Hg)$ was obtained from the slope of the logarithmic plot of S_{cum} *vs.* r_p, according to the expression,

$$S_{cum} \propto r_p^{2-Ds}$$

This equation is proposed here as another way to obtain the surface fractal dimension, Ds, like that proposed by Pfeifer & Avnir (1983) using the pore-volume relationship ($dV_p/dr_p \propto r_p^{2-Ds}$).

RESULTS AND DISCUSSION

Nitrogen adsorption

Adsorption isotherms of nitrogen on the samples studied belong to type IV of the BDDT (Brunauer *et al.*, 1940) classification except those corresponding with kaolinite which showed a type II character (Fig. 1). The same type of isotherms, as well as high values of specific surface area, were found by Cornejo *et al.* (1984) for ferrihydrite and by Cornejo (1987) for hydrous ferric oxide gels. Table 1 summarizes the specific surface area values, S_{BET}, obtained for crude clays, controls and clay-hydrous iron oxide associations, and Table 2 shows the fractal dimension corresponding with nitrogen adsorption data, $Ds(N_2)$. Tables 1 and 2 show the data corresponding with the untreated samples (crude clays), but the effects of Fe precipitation will be considered by comparison with the control samples, since the control treatment produced, by itself, changes in the surface properties of the crude clays. Contrary to the results reported by Srasra *et al.* (1989), we found a decrease in the surface areas of the smectites under the control treatment. However, these changes were accompanied by a decrease in $Ds(N_2)$ values, also found by Srasra *et al.* (1989)

TABLE 1. Nitrogen specific surface areas, S_{BET}, for the clay-hydrous iron oxide associations studied.

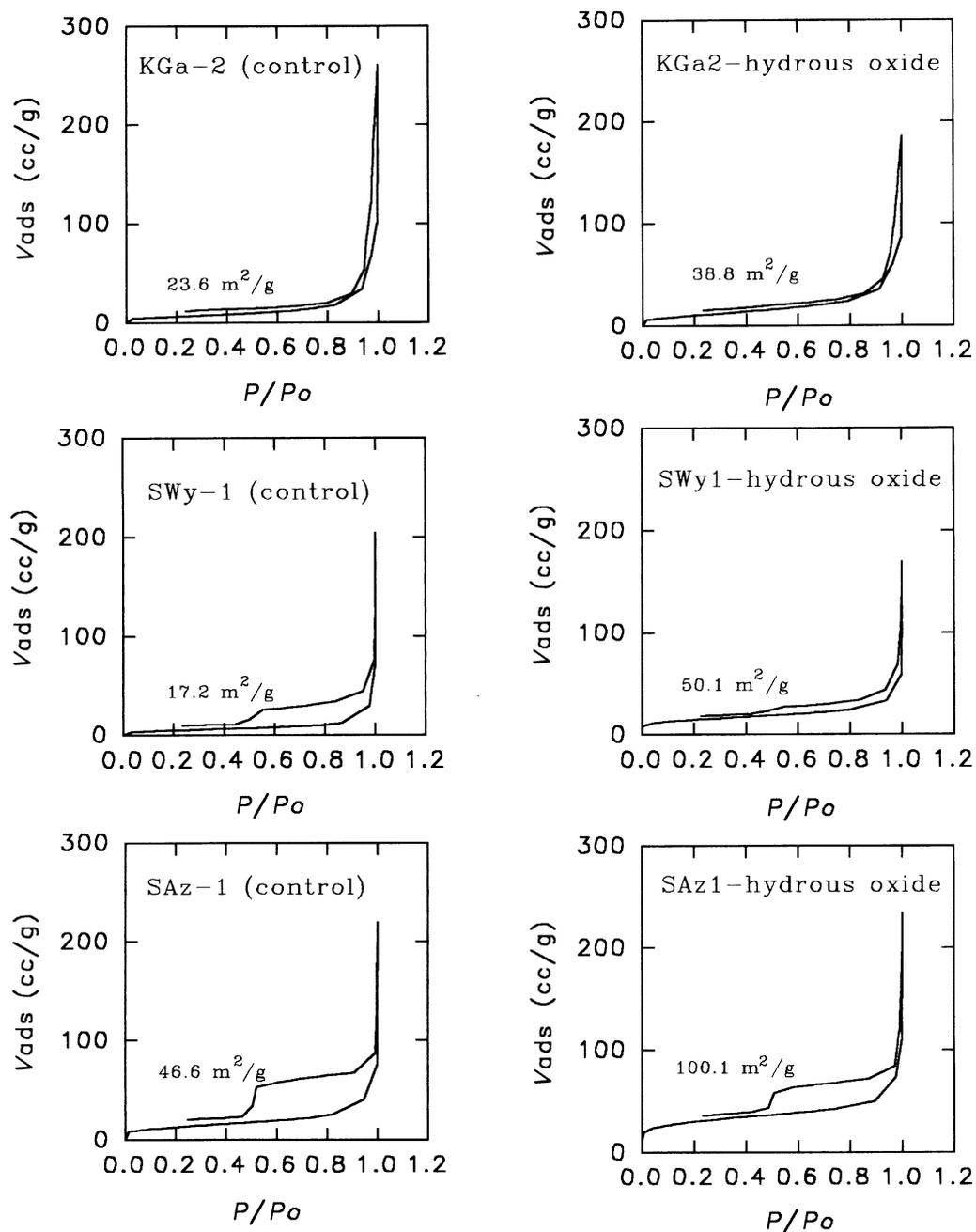|	S_{BET} (m^2/g)		
mg Fe/g clay	KGa-2	SWy-1	SAz-1
Untreated clay	20.1	25.6	74.9
0.0 (control)	23.6	17.2	46.6
10.5	25.1	29.5	68.6
21.0	27.2	39.4	82.3
42.0	38.8	50.1	100.1

FIG. 1. Nitrogen adsorption isotherms for the control clay samples and for the clay-hydrous iron oxide associations with 42.0 mg Fe/g clay.

for their samples. Little change was observed for kaolinite under the control treatment (Tables 1 and 2). These surface changes could be due to some

exchange of the original exchangeable cation by NH_4 in solution which can produce changes in the aggregation of the control sample with respect to

TABLE 2. Surface fractal dimensions, $D_s(N_2)$, calculated from nitrogen adsorption data for the different clay-hydrous iron oxide associations studied.

mg Fe/g clay	$D_s (N_2)$ $10\ \text{Å} < r_k^* < 50\ \text{Å}$		
	KGa-2	SWy-1	SAz-1
Untreated	2.53	2.70	2.78
0 (control)	2.55	2.65	2.71
10.5	2.57	2.71	2.77
21.0	2.58	2.70	2.81
42.0	2.59	2.77	2.83

* Kelvin radius domain corresponding with the interval of relative pressures $0.35 < P/P_o < 0.80$ used for the calculation of $D_s(N_2)$.

the crude clays. This effect is less noticeable in kaolinite because of its low CEC. These data indicate the importance of control treatments in clays to develop surface changes upon chemical treatments.

In agreement with the results obtained by Ben Ohoud & Van Damme (1990) the presence of iron oxide coating the surface of the clays always led to an increase of the surface area S_{BET} as shown in Table 1. The surface area of the clay samples increased after hydrous iron oxide precipitation, SWy-1 showing the greatest increase, almost three times the initial surface area (control sample). The largest surface area was found in SAz-1 because this sample initially had the largest S_{BET} and, hence, higher $D_s(N_2)$ values. However, these higher $D_s(N_2)$ values did not correspond with higher hysteresis cycles in desorption as might have been expected.

The application of the Horvath-Kawazoe (1983) model to obtain the pore-size distribution of these samples indicates that their microporosity increased with the amount of Fe present (Fig. 2). It was also noticed that the increase in microporosity was proportional to the corresponding surface area, S_{BET}, suggesting that microporosity was generated in the outer surface of clay plates through hydrous iron oxide precipitation on it, and it could be related to the CEC of the clays. In fact, as can be seen in Fig. 2, the pore-volume enhancement in the lowest pore size increased with the S_{BET} and CEC of the clay (KGa-2 < SWy-1 < SAz-1).

The validity of the power law of Avnir & Jaroniec (1989) (1) was statistically confirmed

with the samples studied. The values of fractal dimension, $D_s(N_2)$, (Table 2) obtained from the plot of $\ln(V_{ads})$ *vs.* $\ln[\ln(P_o/P)]$ (Fig. 3) in the region of low adsorption potential (Avnir & Jaroniec, 1989) matched closely those obtained by Lefebvre *et al.* (1992) for a wide number of materials (zeolite, quartz, chrysotile, nematile, etc.). Despite the change in the D_s value produced by the control treatment as related to the change in S_{BET} values discussed above, we compared the control samples with the clay-hydrous iron oxide associations. The increase in $D_s(N_2)$ values of the control clays upon Fe precipitation indicated an increase of the roughness of the clay surface. It is interesting to note that $D_s(N_2)$ values agree with conclusions obtained after the Horvath-Kawazoe model was applied. The presence of hydrous iron oxide on clays is responsible for the increasing surface roughness in the micropore range, being more intense in smectite than in kaolinite (Tables 1 and 2) and, as mentioned above, could be related to the CEC of the clays. In fact, although the X-ray diffractograms of the Fe-coated clays were much more poorly defined than those corresponding with the control clays, a slight decrease of the basal spacing values, d_{001}, was detected after the smectites were associated with hydrous iron oxide. Thus, the exchangeable sites on the clay could be the initial points for Fe precipitation and hence the origin of the surface roughness. Taking into account the above results and those found by Cornejo *et al.* (1984) and Cornejo (1987) for poorly crystallized hydrous ferric oxides, it could be suggested that the surface properties of clays are obscured when associated with these compounds.

Mercury porosimetry

Mercury porosimetry is used, after the Friesen & Mikula (1987) work, as a tool to study the fractality of solids. This is based on the relationship between the solid pore entrance size and the pressure needed to intrude the Hg into it, following the Washburn (1921) equation in the meso and macropore range.

Considering the nature of the clay particles used in this study, two types of porous structure can be detected from a porosimetry curve. At low pressures, the mercury intrudes only in the voids between particles or aggregates and at higher pressures, the mercury is forced into the individual particle pores (Fig. 4). The pore volumes of SWy-1,
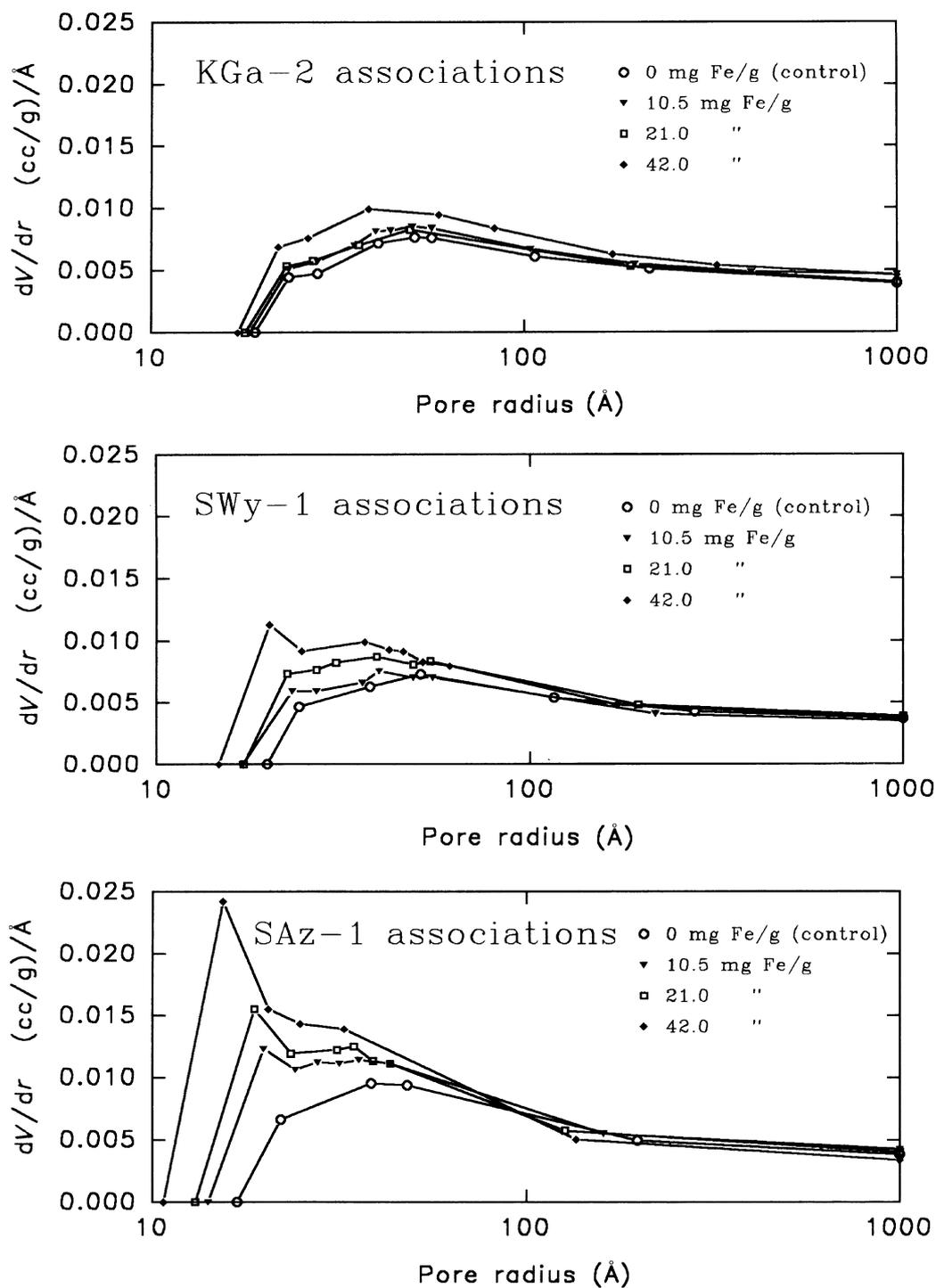
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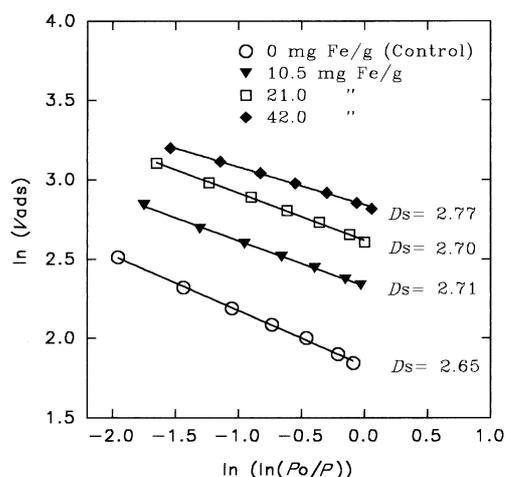FIG. 2. Horvath & Kawazoe pore-size distributions for the different samples studied.

FIG. 3. Nitrogen adsorption isotherms for SWy1-hydrous iron oxide associations plotted according to equation 1.

TABLE 3. Surface fractal dimensions, D_s(Hg), calculated from mercury porosimetry data for the different clay-hydrous iron oxide associations studied.

mg Fe/g clay	D_s (Hg) $300\ \text{Å} < r_p^* < 10^5\ \text{Å}$ KGa-2	SWy-1
Untreated	3.03	–
0 (control)	3.03	2.44
10.5	3.11	2.62
21.0	3.01	2.73
42.0	3.03	2.72

* Pore radius domain calculated from the Washburn (1921) equation used for the calculation of D_s(Hg).

shown in Fig. 4, were found initially to decrease upon hydrous oxide precipitation of 10.5 mg Fe/g clay and 21.0 mg Fe/g clay, and then to increase slightly after 42.0 mg Fe/g clay was precipitated. From the pore-size distribution, also shown in Fig. 4, the method by which these changes in pore volumes were produced can be seen.

The pore-size distribution curve corresponding with untreated SWy-1 showed a maximum for $r_p = 1\ \mu\text{m}$ (not shown); however, this r_p value increased because of the control treatment (Fig. 4a), mainly due to swelling and aggregation of clay particles. The clay-hydrous iron oxide interaction process seems to avoid this effect producing a more homogeneous pore-size distribution (Fig. 4), which agrees with the stabilizer effect that Fe and Al oxides cause in the soil structure shown by Desphande *et al.* (1964), El Rayah & Rowel (1973), Shahmuganathan & Oades (1982) and Goldbetrg & Glaubig (1987). No significant differences were found between the mercury intrusion curves of kaolinite or SAz-1 montmorillonite, before and after Fe oxyhydroxide interaction.

The fractal dimension values corresponding with the meso- and macropore volumes by Hg intrusion porosimetry, D_s(Hg), are given in Table 3 and, as found from S_{BET} data, these values increase upon hydrous iron oxide precipitation. In this case the most important changes were found in the SWy-1 sample. The pore-size distribution of kaolinite in the macropore range could be described in terms of fractal geometry with D_s=3 and with very small change upon Fe precipitation. In the case of the SAz-1 sample a non-fractal pore-size distribution with a maximum $r_p = 1\ \mu\text{m}$ was found, and it was invariable after Fe precipitation (not shown).

In fractal geometry terms, it could be said that the precipitation of Fe in the presence of a SWy-1 clay suspension leads to a higher fractal pore structure (better correlation between ln (S_{cum}) *vs.* ln(r_p)) and with more surface roughness (higher D_s) in the meso- and macropore range when compared with the control clay sample (Fig. 4).

CONCLUSIONS

Iron precipitation on kaolinite and montmorillonite increases the external surface area and the surface fractal dimension in the micropore size range, in agreement with a parallel increase in the micropore volume. The increase in surface area of the Fe-coated clays is related to a high surface roughness in the micropore range. In the case of SWy-1 montmorillonite, this evolution is parallel to that observed for the surface fractal dimension obtained by mercury intrusion porosimetry in the meso- and macropore range, which indicates that Fe association leads to the creation of aggregates with a fractal structure of high D_s value.
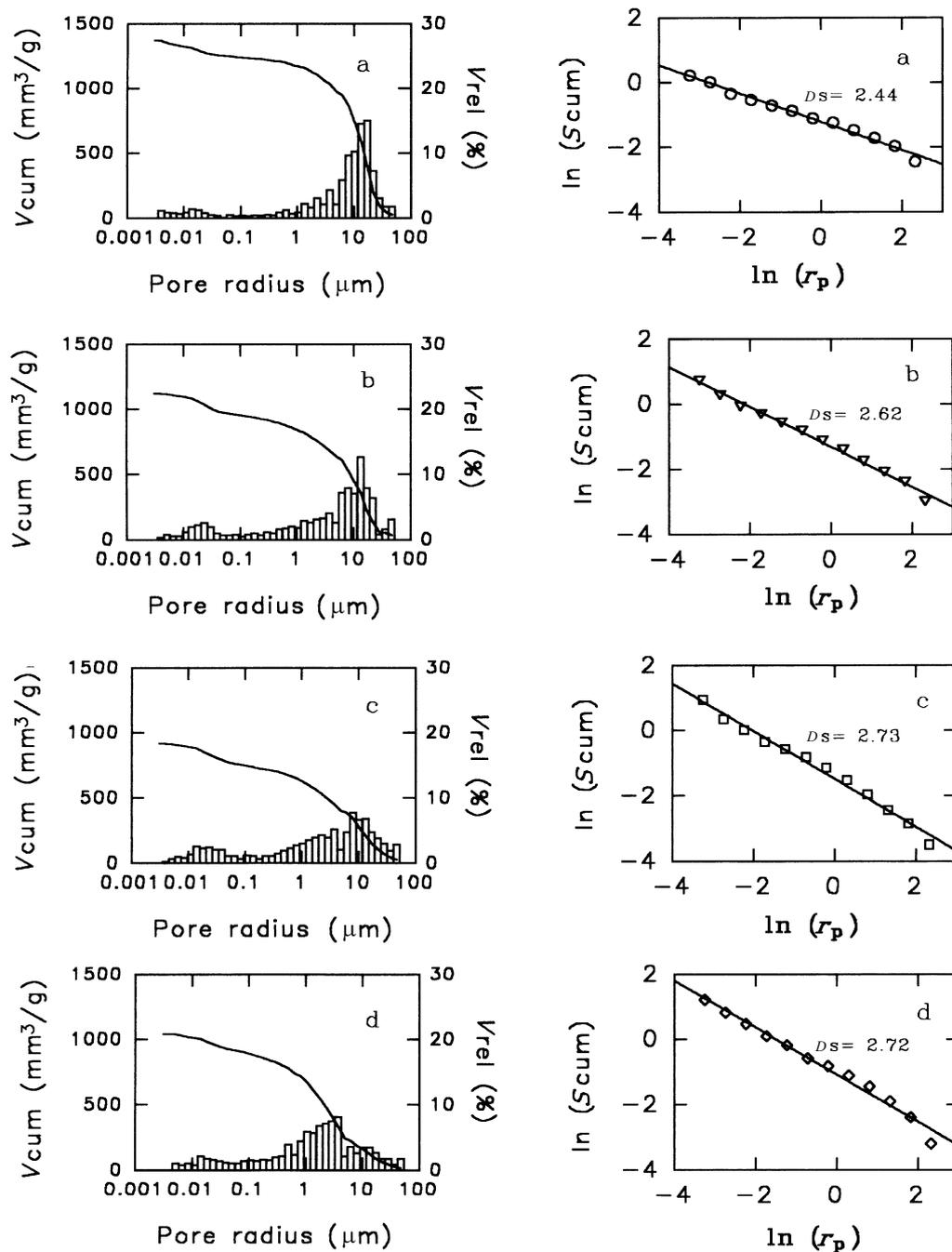
FIG. 4. Mercury pore-size distribution graphs and corresponding plots of ln (S_{cum}) *vs.* ln (r_p) in the range 0.03–10 μm for SWy-1 coated with (a) 0 mg Fe/g clay (control); (b) 10.5 mg/g; (c) 21.0 mg/g; and (d) 42.0 mg/g.

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