

Comparison of functions for evaluating the effect of Fe and Al oxides on the particle size distribution of kaolin and quartz

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ABSTRACT: Although it is generally agreed that Fe and Al can act to bind soil particles, their relative efficiencies as aggregants are still disputed. In this work, the aggregating efficiencies of both aged and non-aged Fe and Al oxides precipitated on kaolin or quartz substrates were characterized by comparing their effects on particle size distributions (PSD). To facilitate comparison of PSD data, these were parameterized by fitting them with five different probability density functions (the normal, lognormal, Jaky, fractal and Rosin-Rammler functions). The best fits were given by the Rosin-Rammler function ($R^2 = 0.997$), whose α parameter was used to compare the aggregating efficiency of Fe and Al oxides: in order of decreasing efficiency, non-aged Al > non-aged Fe \approx aged Fe > aged Al-precipitates.

It is widely recognized that Fe and Al compounds favour formation of soil aggregates that are stable to the dispersive action of water and to moderate mechanical stress. Nonetheless, there is little agreement as to the forms of Fe and Al implicated, the mechanisms of their aggregative effect, or which of the two metals is the more efficient stabilizer.

The structural stability of surface soils has frequently been positively correlated with their Fe content (McIntyre, 1956; Arca & Weed, 1966; Kemper & Koch, 1966; Krishna Murti *et al.*, 1977; Colombo & Torrent, 1991; Barral *et al.*, 1992). However, attempts at correlation of stability and Al content have produced contradictory results. For example, Bartoli *et al.* (1988) have positively correlated oxalic acid-oxalate soluble Al with several indices giving some measure of aggregation; but Kemper & Koch (1966), who analysed 519 soil samples from western USA and Canada, found no relationship between Al oxide content and stability, and Benito Rueda & Diaz-Fierros Viqueiria (1989) examined a wide range of soils from the humid temperate region of Spain, concluding that Fe

content was a much more important factor than Al content in the stabilization of soil structure.

In other studies, structural stability and other related soil physical properties, before and after selective extraction of Fe and/or Al oxides, have been compared. Kroth & Page (1947) found that soil aggregates were destroyed by extraction of Al and Fe oxides, suggesting that they are strongly stabilized by both. Arduino *et al.* (1989) have suggested that oxalic acid-ammonium oxalate extractable Fe is a more efficient aggregant (particularly of coarse particles) than crystalline forms such as goethite and hematite. Deshpande *et al.* (1964, 1968) have observed that the crystalline Fe oxides of the clay fraction of red soils exist as discrete, granular particles which have no effect on cementation, and also that an acid treatment extracting mainly Al and only small amounts of Fe and Si had greater effects on physical properties related to aggregation than a dithionite treatment extracting mainly Fe.

The results obtained for natural samples, which suggest that it is Fe oxides that most generally affect aggregate formation and stabilization, contrast with those obtained in experiments using

synthetic precipitates, either added to, or precipitated onto the surface of, whole soil or soil clay particles. These experiments suggest that Al hydroxides are more efficient than those of Fe as regards coating and linking clay particles, which has been attributed to the Al hydroxide particles having planar form while Fe oxide and oxyhydroxide particles have non-planar morphologies (spherical, acicular, etc.) (El-Swaify & Emerson, 1975). It has also been observed that Al oxides are more efficient at reducing swelling and dispersion of clay, thereby improving soil hydraulic conductivity and tensile strength (El-Rayah & Rowell, 1973; Krishna Murti & Richards, 1974). Furthermore, Frenkel & Shainberg (1980) and Goldberg & Glaubig (1987), who examined the effects of added Al and Fe oxides on montmorillonite or kaolinite, have also suggested that Al oxides have the greater flocculant effect.

The aim of this work was clarification of the roles of Fe and Al in the stabilization of aggregates. To do this, we opted to study synthetic systems in which varying amounts of Fe or Al oxide were precipitated on well characterized kaolin or quartz substrates. This approach allowed data for the different oxides and substrates to be obtained under similar controlled conditions which facilitated examination of the effects of oxide crystallinity on aggregation, and also attempts at elucidation of the mechanism of the oxides' aggregative effect.

The degree of aggregation was evaluated from the particle size distributions (PSDs) of samples treated with different doses of Fe or Al oxide. The simplest method of comparing these data, and the one most frequently used in tests of soil aggregate stability, is to select and compare the data for a single particle size interval. However, a large amount of the information inherent in particle size data is lost at the selection stage, such that the results are heavily dependent on the size interval chosen (Schaller & Stockinger, 1953). A more comprehensive method is to fit a mathematical function to the particle size data for each sample, and to compare corresponding function parameters among the samples (Perfect *et al.*, 1993). The suitability of several functions to description of aggregation can be compared in terms of their goodness of fit to the particle size data, the sensitivity of their parameters to changes in PSD due to precipitation of Al or Fe onto the substrate, and their physical implications as regards aggregate formation and fragmentation.

MATERIALS

Substrates

The kaolin (95 wt% kaolinite and 5% micas) has specific surface (S_{EGME}) $46.7 \text{ m}^2 \text{ g}^{-1}$ and CEC $7.0 \text{ cmol}_{(+)}\text{kg}^{-1}$, and the quartz has S_{EGME} $3.1 \text{ m}^2 \text{ g}^{-1}$. For both samples, the particle size-fraction $<0.1 \text{ mm}$ was used: the kaolin comprised 616, 381 and 3 g kg^{-1} of clay ($<0.002 \text{ mm}$), silt ($0.002\text{--}0.05 \text{ mm}$) and sand-sized particles ($0.05\text{--}0.1 \text{ mm}$), respectively, and the quartz 90, 726 and 184 g kg^{-1} , respectively, of the same fractions.

Oxides

Preparation of the Fe and Al oxides has been described previously (Arias *et al.*, 1995). Briefly, they were precipitated in the presence of the substrate by basification of a suspension of this in a solution of the metal ion. The proportions used are roughly equivalent to the addition of 0.5, 1.0, 2.0, 4.5 and 6.5 g of Fe or Al per 100 g of substrate. Non-aged samples (kAl_n and kFe_n with kaolin, and qAl_n and qFe_n with quartz) were obtained directly, by simply oven drying the precipitates at 40°C . Aged samples (kAl_a and kFe_a with kaolin, and qAl_a and qFe_a with quartz) were kept in water at 70°C for 17 days, and then oven dried at 40°C . This ageing process considerably increased the crystallinity of the Al precipitates on both substrates, but increased only that of the Fe oxide on quartz (Arias *et al.*, 1995).

METHODS

Particle size distribution (PSD)

Five grams of sieved ($\leq 2 \text{ mm}$) sample were suspended in 25 ml of distilled water and shaken end-over-end. Then, the particle size-fractions $>0.05 \text{ mm}$ were determined by wet sieving, and those $\leq 0.05 \text{ mm}$ by the Robinson pipette method. The following equivalent spherical diameter intervals (mm) were established: <0.002 , $0.002\text{--}0.02$, $0.02\text{--}0.05$, $0.05\text{--}0.1$, $0.1\text{--}0.25$, $0.25\text{--}0.5$, $0.5\text{--}1$, $1\text{--}2$.

Parameterization of particle size data

The particle size data were fitted by the following probability density functions:

Normal

$$f(X) = [1/\sigma(2\pi)^{1/2}] \exp[-(X-\mu)^2/2\sigma^2]$$

where μ is the arithmetic mean of X (the equivalent spherical diameter) and σ is the corresponding standard deviation.

Log normal

$$F(X) = (1+\operatorname{erf}[(X-\mu)/\sigma\sqrt{2}])/2, X > \mu$$

$$F(X) = (1+\operatorname{erf}[(\mu-X)/\sigma\sqrt{2}])/2, X \leq \mu$$

where μ is the geometric mean of X and σ is the corresponding standard deviation. $F(x)$ is the cumulative distribution function of X , and $\operatorname{erf}[]$ is the error function.

Rosin & Rammler (1933)

$$P(X > x) = 1 - \exp[-(x/\alpha)^\beta]$$

α and β are constants related to the characteristic size and shape of the distribution, respectively. The α value represents the aggregate size corresponding to the 36.78th percentile. A small α denotes a PSD dominated by small aggregates; β , which is analogous to the standard deviation of the normal distribution, decreases as the spread of particle sizes increases.

Jaky (1944)

$$S = \exp\{-1/p^2[\ln(d/d_0)]^2\}$$

S is the cumulative mass of particles with equivalent spherical diameter $< d$, p is a particle-size distribution index characterizing the stretching of the curve, and d_0 is the largest diameter, taken here as 2 mm.

Fractal (Turcotte, 1986; Perfect & Kay, 1991)

$$N_{>x} = k(X)^{-D}$$

where $N_{>x}$ is the cumulative number of aggregates with a characteristic dimension greater than X , k (constant) is $N_{>x}$ at $X = 1$, and D is a scaling factor, the fractal dimension, related to aggregate shape and degree of fragmentation. If aggregates are assumed to be cubes of constant dry density, D is solely a measure of the degree of fragmentation of the aggregates; the larger the value of D , the greater the fragmentation. The fractal dimension, D , was obtained by regressing $\log N_{>x}$ on $\log X$ (X = the arithmetic mean of the limits of the particle size interval). D is equal to the absolute value of the slope. The number of aggregates in each size interval, $N(X)$, was estimated by dividing the weight of each fraction, $W(X)$, by the weight of a single cubic aggregate of length X , according to the following relation (Perfect & Kay, 1991):

$$N(X) = \frac{W(X)}{X^3}$$

Assuming that the density of aggregates is scale invariant, its actual value is not considered, as it has no influence on the value of D .

RESULTS

Particle size distribution (PSD)

Table 1 lists the particle size data for the kaolin based samples. The poorly-crystalline, non-aged Al precipitates (kAl_n) favoured formation of aggregates > 0.1 mm, which constituted 63 wt% of the sample. For doses of added Al > 2.0 wt%, formation of coarse particles occurred simultaneously with redispersion of the clay fraction (< 0.002 mm), producing a bimodal PSD. In contrast, the aged Al precipitates (kAl_a) induced changes in PSD that were relatively small when compared to the blank sample. These changes were largely limited to the particle size-fractions < 0.05 mm, increasing the coarse silt (0.02–0.05 mm) fraction at the expense of the clay (< 0.002 mm) and fine silt (0.002–0.02 mm) fractions for doses $\leq 2.0\%$ Al, and decreasing it for higher doses of Al so that, above 4.5% Al, the finer fractions were once again the largest, having more or less regained their initial levels. The similarly crystalline aged and non-aged Fe precipitates (kFe_a and kFe_n , respectively) both caused large increases in the 0.02–0.05 mm fraction, converting it into the largest fraction, and induced formation of a fraction > 0.1 mm, although this never constituted more than 20 wt% of total aggregates. There was no evidence of redispersion of the clay fraction in the range of Fe doses studied.

The particle size data for the quartz based samples are listed in Table 2. The non-aged Al precipitates (qAl_n) increased the fraction of coarse particles by a proportion that increased with Al dose, but that overall was smaller than for the corresponding kaolin samples. By contrast, the aged Al precipitates (qAl_a) only slightly affected the PSD, decreasing the fractions < 0.02 mm at doses of Al $< 1.0\%$, and increasing them at higher doses. In the case of the Fe-quartz samples (qFe_a and qFe_n), the particle-size data for the samples with added Fe differed little from those of the controls. There was a slight increase in the proportion of sand-sized (0.1–0.25 mm) aggregates, however, which was

TABLE 1. Particle size distribution (wt%) for kaolin (k) samples containing increasing amounts of added Al and Fe, with (kAl_a and kFe_a) and without (kAl_n and kFe_n) ageing of the Al and Fe precipitates.

% Al or Fe φ (mm)	0		0.5		1.0		2.0		4.5		6.5	
	kAl _n	kAl _a	kAl _n	kAl _a	kAl _n	kAl _a	kAl _n	kAl _a	kAl _n	kAl _a	kAl _n	kAl _a
<0.002	43.6	45.1	6.9	26.4	0.9	1.5	1.2	6.9	19.9	61.6	15.7	63.4
0.002–0.02	50.3	50.5	79.5	69.5	42.3	30.7	10.6	89.0	31.4	37.2	17.0	35.2
0.02–0.05	5.7	3.9	12.2	3.6	50.4	67.4	53.6	3.1	1.6	0.9	1.7	1.0
0.05–0.10	0.4	0.4	1.1	0.5	0.7	0.4	1.0	0.6	1.0	0.3	2.3	0.3
0.10–0.25	nd	nd	0.2	nd	0.8	0.1	2.6	0.3	2.0	0.1	4.5	0.1
0.25–0.50	nd	nd	nd	nd	2.6	nd	4.9	nd	4.7	nd	8.9	nd
0.50–1.00	nd	nd	nd	nd	2.0	nd	11.5	nd	10.5	nd	14.8	nd
1.00–2.00	nd	nd	nd	nd	0.3	nd	14.5	nd	28.9	nd	35.1	nd

φ (mm)	kFe _n		kFe _a		kFe _n		kFe _a		kFe _n		kFe _a	
	kFe _n	kFe _a	kFe _n	kFe _a	kFe _n	kFe _a	kFe _n	kFe _a	kFe _n	kFe _a	kFe _n	kFe _a
<0.002	50.9	56.2	38.9	–	1.6	–	1.9	0.9	1.3	1.5	2.3	1.1
0.002–0.02	44.2	40.0	58.5	–	88.5	–	11.0	6.4	8.7	5.8	9.1	6.4
0.02–0.05	4.6	2.8	1.7	–	2.3	–	67.9	85.2	65.1	68.2	60.5	69.5
0.05–0.10	0.3	0.6	0.6	–	4.5	–	7.6	4.7	6.2	3.1	11.4	7.7
0.10–0.25	nd	0.3	0.3	–	1.4	–	8.0	4.7	13.4	3.1	14.6	7.7
0.25–0.50	nd	nd	nd	–	1.1	–	3.4	nd	5.2	nd	2.1	nd
0.50–1.00	nd	nd	nd	–	0.6	–	0.2	nd	0.1	nd	0.1	nd

nd: not detected

–: not determined

TABLE 2. Particle size distribution (wt%) for quartz (q) samples containing increasing amounts of added Al and Fe, with (qAl_n and qFe_a) and without (qAl_n and qFe_n) ageing of the Al and Fe precipitates.

% Al or Fe ϕ (mm)	0		0.5		1.0		2.0		4.5		6.5	
	qAl _n	qAl _a	qAl _n	qAl _a	qAl _n	qAl _a	qAl _n	qAl _a	qAl _n	qAl _a	qAl _n	qAl _a
<0.002	4.2	3.6	1.4	2.1	0.9	1.4	1.2	8.9	1.4	13.6	1.0	16.6
0.002–0.02	22.5	26.8	7.4	9.2	6.8	8.7	16.6	24.3	16.2	21.6	16.5	22.2
0.02–0.05	55.2	49.5	70.5	66.4	70.0	71.6	49.6	46.0	42.9	46.0	42.1	42.6
0.05–0.10	18.1	20.0	18.7	21.7	20.9	18.3	27.4	20.7	32.4	18.5	29.4	16.5
0.10–0.25	nd	nd	2.0	0.6	1.4	nd	5.2	nd	7.0	0.2	11.0	2.1
ϕ (mm)	qFe _n	qFe _a	qFe _n	qFe _a	qFe _n	qFe _a	qFe _n	qFe _a	qFe _n	qFe _a	qFe _n	qFe _a
<0.002	4.2	5.0	1.7	1.3	1.4	1.0	1.3	0.8	1.4	1.6	2.1	0.5
0.002–0.02	23.4	24.7	12.3	14.8	8.8	9.2	7.7	11.0	5.9	8.9	6.1	9.7
0.02–0.05	51.7	53.1	65.4	65.7	59.3	70.2	57.4	65.3	66.6	65.0	63.8	62.7
0.05–0.10	20.8	17.0	20.5	17.9	29.8	17.7	33.1	21.5	25.0	17.5	24.5	18.4
0.10–0.25	nd	nd	0.1	0.3	0.7	1.9	0.6	1.4	1.0	7.0	3.6	8.7

nd: not detected

slightly more marked in the more crystalline qFe_a samples.

Parameterization of particle size data

The probability density function, and thus the parameter(s), best describing the PSD data was selected on the basis of its superior goodness of fit. All five functions evaluated were fitted to the PSD data at the $p \leq 0.01$ level of significance (in all cases, $n = 46$). The Kolmogorov-Smirnov test indicated the mean coefficients of determination (R^2) for the five functions were significantly different from each other at the $p \leq 0.01$ level, except in the case of the normal and lognormal functions. The Rosin-Rammler and Jaky functions had the highest (0.997) and the lowest (0.894) mean R^2 , respectively (Table 3). The normal and lognormal functions gave negative mean particle size when fitted to PSDs skewed towards small particle size, thus limiting the usefulness of these functions.

On the basis of the above observations, the α and β parameters of the Rosin-Rammler function (RR) were used to compare the aggregating effect of Fe and Al on the quartz and kaolin substrates. The constants α and β are respectively related to the characteristic size and shape of the mass-size cumulative probability distribution. These comparisons were contrasted with those for D , from the fractal function, but no meaning of fractal dimension was attached to this parameter (Figs. 1 and 2).

Non-aged, poorly crystalline Al precipitates were the most efficient aggregants (highest α) of both kaolin and quartz; in contrast, the aged, crystalline Al precipitates were poor aggregants, and could even be described as dispersants. Aged and non-aged Fe precipitates had similar, intermediate effects on the aggregation of both kaolin and quartz.

Regardless of substrate, samples containing Fe had higher β than those containing Al. Bearing in mind that a decrease in β reflects an increase in the spread of the PSD, we attribute this observation to the simultaneous occurrence of redispersion of the clay substrate and formation of large aggregates in the Al containing samples.

The value of the parameter D , from the fractal function, was initially close to 4 for the kaolinite samples and close to 2.5 for the quartz samples, but tended to decrease as the dose of added metal increased. For most samples, D and α were inversely related; however, in some kAla samples, notably that containing 4.5% Al, α and D were directly related. The explanation for this exceptional behaviour may be that, at the same time as large aggregates are formed in these samples (increasing α), there is a small amount of dispersion of small particles (which also increases D).

DISCUSSION

The Al and Fe precipitates had different effects on the colloidal properties of the kaolin. Small doses of Al had a flocculant effect, but at $\geq 4.5\%$ Al some redispersion of the clay fraction occurred, whereas Fe oxides caused flocculation of the clay with no redispersion in the range of doses studied. In an earlier paper (Arias *et al.*, 1995), it was noted that aqueous suspensions of kaolin and Al or Fe flocculated in a pH interval that included the PZC of the sample; that, like the PZC, this interval shifted to higher pH as the metal dose increased; and that this interval was displaced towards slightly lower pH for kFe samples. At the pH of the aqueous kaolinite/metal oxide suspensions examined in the present work (*c.* 5), kAl suspensions were dispersed while kFe suspensions were flocculated. The explanation for this differing behaviour may be that Al precipitates have a greater capacity for intimate coating, resulting in

TABLE 3. Coefficients of determination (R^2) for the fits of the five probability density functions to the particle size data (see Tables 1 and 2) (RR = Rosin-Rammler function).

	Fractal	RR	Lognormal	Normal	Jaky
Mean R^2	0.943	0.997	0.991	0.989	0.894
Standard deviation (σ)	0.035	0.007	0.020	0.030	0.080
Minimum	0.865	0.963	0.894	0.792	0.767
Maximum	1.000	1.000	0.999	0.999	0.985

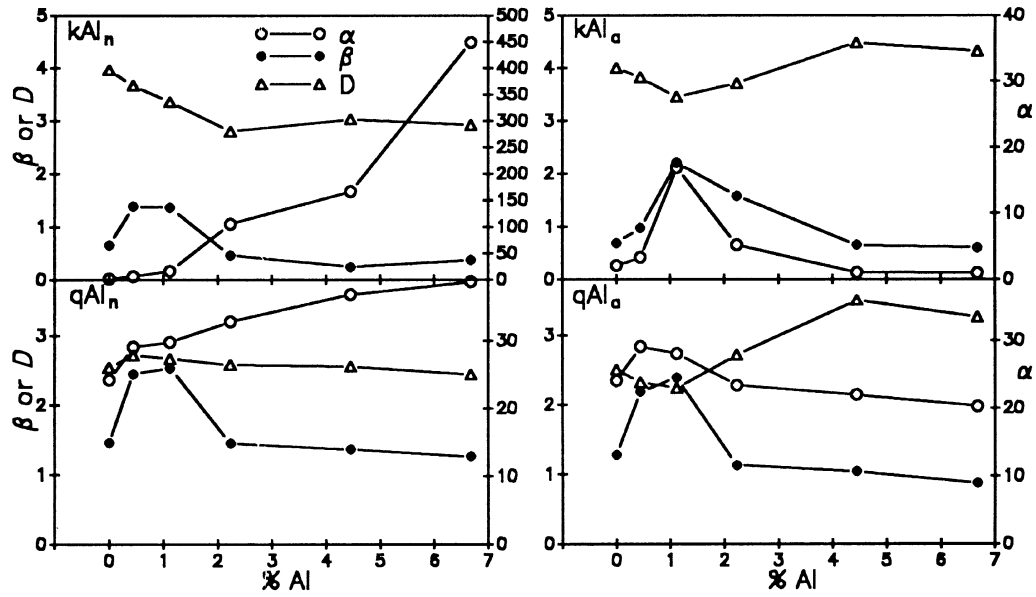


FIG. 1. Comparison of α and β from the Rosin-Rammler (RR) function and D from the fractal function, both of which were fitted to the particle size data for kaolin or quartz samples treated with Al.

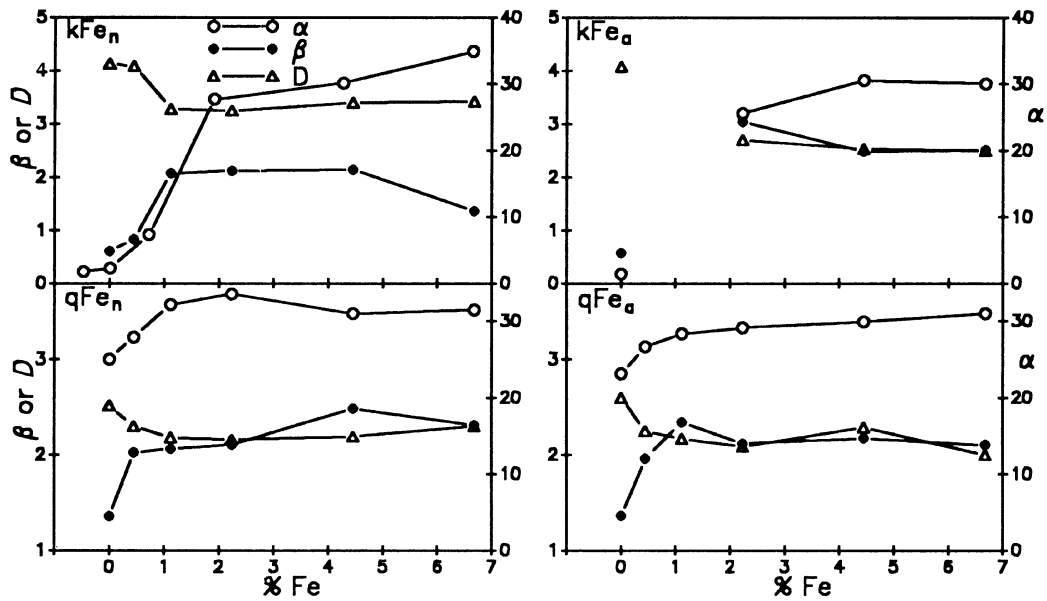


FIG. 2. Comparison of α and β from the Rosin-Rammler (RR) function and D from the fractal function, both of which were fitted to the particle size data for kaolin or quartz samples treated with Fe.

more effective masking of the negative charges of the kaolinite, and, at high doses of Al, possible inversion of the surface charge.

If, as is usual, particle flocculation is considered a step towards formation of stable aggregates, the redispersion of the clay fraction observed at high doses of Al (>2.0%) should hinder formation of stable aggregates. However, the fraction of large aggregates (>0.1 mm) increased with metal dose across the entire range of doses (Table 1). This may be attributable to increased formation of aggregates by cementation at higher doses of metal. However, at variance with this is the observation that non-aged Al precipitates induced formation of larger aggregates (>0.1 mm) than aged Al precipitates, which being more crystalline ought to have favoured cementation. An explanation for this discrepancy may be that redispersion of the clay fraction at high Al doses was so much more acute in aged than in non-aged samples that cementation effects could not overcome repulsion between suspended particles.

For the quartz samples, the effects of the precipitates on the PSD were smaller. The non-aged Al precipitates were again the most powerful aggregants, which, given the low surface reactivity of quartz, was probably almost exclusively due to cementation of the particles with sufficiently continuous coats of precipitate rather than the surface electrical phenomena responsible for flocculation.

Parameterization of the particle size data greatly facilitated comparison of the PSDs for the different samples. The parameter α of the Rosin-Rammler function was specially sensitive to changes in the PSD induced by the metal oxides (compare results for kAl_n in Table 1 and Fig. 1).

The parameter D , from the fractal function, gives a measure of the degree of fragmentation, and so it would be expected to decrease with increasing metal dose. The largest variations in D occurred at low metal doses, which generally decreased the proportion of fine particles. By contrast, D hardly varied at all at high metal doses (see results for kAl_n in Fig. 1 and kFe in Fig. 2), which generally increased the proportion of large aggregates, and increased further when redispersion occurred (kAl_a in Fig. 1).

The value for D is also affected by changes in the spread of the particle size distribution. The results, in particular those for the quartz samples (Figs. 1 and 2), indicate that D changes appreciably

when a new particle size-fraction forms, even if the proportion of substrate in that fraction is very small.

These results are in keeping with the fact that the Rosin-Rammler function is a mass-based distribution function, whereas the fractal function is a number-based distribution function. Thus α is more sensitive to changes in the frequencies of the large particle-size classes (aggregation/dispersion of these particles would cause a large change in the particle mass distribution). Therefore, D appears to be unsuitable as an indicator of variation in aggregative state, but could be useful for monitoring changes in flocculation-dispersion of a colloidal system.

CONCLUSIONS

Addition of Fe or Al oxides to a kaolin or quartz substrate modifies its particle size distribution, generally favouring aggregation, although high doses of Al also caused some simultaneous redispersion of the clay fraction of the substrate.

Particle size distributions (PSDs) for all the substrate-metal samples were well fitted ($p \leq 0.01$) by normal, lognormal, Jaky, fractal and Rosin-Rammler probability density functions. The best fit was given by the Rosin-Rammler function ($R^2 = 0.997$), whose α parameter was thus used to compare the aggregating efficiency of Fe and Al oxides on quartz and kaolin. The order of decreasing aggregating efficiency was non-aged Al > non-aged Fe \approx aged Fe > aged Al precipitates.

The parameter D of the fractal function generally decreases with increasing aggregation efficiency, but is specially sensitive to changes in the distribution of the smaller particles, and is also influenced by the spread of particle sizes.

REFERENCES

- Arca M.N. & Weed S.B. (1966) Soil aggregation and porosity in relation to contents of free iron oxide and clay. *Soil Sci.* **101**, 164–170.
- Arduino E., Barberis E. & Boero V. (1989) Iron oxides and particle aggregation in B horizons of some Italian soils. *Geoderma*, **45**, 319–329.
- Arias M., Barral M.T. & Díaz-Fierros F. (1995) Effects of iron and aluminum oxides on the colloidal and surface properties of kaolin. *Clay Clay Miner.* **43**, 406–416.
- Barral M.T., Arias M. & Díaz-Fierros F. (1992) Estabilidad estructural de suelos desarrolla-

- dos sobre materiales geológicos ricos en hierro. *Proc. III Congreso Nacional de la Ciencia del Suelo*, 57–62, Pamplona, Spain.
- Bartoli F., Philippon R. & Burtin G. (1988) Aggregation in soils with small amounts of swelling clays. I. Aggregate stability. *J. Soil Sci.* **39**, 593–616.
- Benito Rueda E. & Diaz-Fierros Viqueira F. (1989) Estudio de los principales factores que intervienen en la estabilidad estructural de los suelos de Galicia. *An. Edafol. Agrobiol.* **48**, 229–253.
- Colombo C. & Torrent J. (1991) Relationships between aggregation and iron oxides in Terra Rossa soils from southern Italy. *Catena*, **18**, 51–59.
- Deshpande T.L., Greenland D.J. & Quirk J.P. (1964) Influence of iron and aluminium oxides on the charges of soil and clay materials. *Trans. 8th Int. Congr. Soil Sci., Bucharest*, 1213–1225.
- Deshpande T.L., Greenland D.J. & Quirk J.P. (1968) Changes in soil properties associated with the removal of iron and aluminium oxides. *J. Soil Sci.* **19**, 108–122.
- El-Rayah H.M.E. & Rowell D.L. (1973) The influence of iron and aluminium hydroxides on the swelling of Na-montmorillonite and the permeability of a Na-soil. *J. Soil Sci.* **24**, 137–144.
- El-Swaify S.A. & Emerson W.W. (1975) Changes in the physical properties of soil clays due to precipitated aluminium and iron hydroxides: I. Swelling and aggregate stability after drying. *Soil Sci. Soc. Am. Proc.* **39**, 1056–1063.
- Frenkel H. & Shainberg I. (1980) The effect of hydroxy-Al and hydroxy-Fe polymers on montmorillonite particle size. *Soil Sci. Soc. Am. J.* **44**, 626–629.
- Goldberg S. & Glaubig R.A. (1987) Effect of saturating cation, pH and aluminum and iron oxides on the flocculation of kaolinite and montmorillonite. *Clays Clay Miner.* **35**, 220–227.
- Jaky J. (1944) *Soil Mechanics*. Egyetemi Nyomda, Budapest (in Hungarian). Cited in: Probabilistic solutions in geotechnics. *Dev. Geotech. Eng.* **46**, 157.
- Kemper W.D. & Koch E.J. (1966) Aggregate stability of soils from Western United States and Canada. Measurement procedure. Correlations with soil constituents. *ARS, USDA Tech. Bull.* No. 1355.
- Krishna Murti G.S.R. & Richards S.J. (1974) Some effects of sesquioxides on soil structure. *Ind. J. Agron.* **19**, 141–147.
- Krishna Murti G.S.R., Gurcharan S. & Rengasamy P. (1977) The nature of soil clays and the stability of microaggregates. *Aust. J. Soil Res.* **15**, 115–119.
- Kroth E.M. & Page J.B. (1947) Aggregate formation in soils with special reference to cementing substances. *Soil Sci. Soc. Am. Proc.* **11**, 27–34.
- McIntyre D.S. (1956) The effect of free oxide on the structure of some Terra Rossa and Rendzina soils. *J. Soil Sci.* **7**, 302–306.
- Perfect E. & Kay B.D. (1991) Fractal theory applied to soil aggregation. *Soil Sci. Soc. Am. J.* **55**, 1552–1558.
- Perfect E., Kay B.D., Ferguson J.A., Da Silva A.P. & Denholm K.A. (1993) Comparison of functions for characterizing the dry aggregate size distribution of tilled soil. *Soil Tillage Res.* **28**, 123–139.
- Rosin D. & Rammner E. (1933) Laws governing the fineness of powdered coal. *J. Inst. Fuel* **7**, 29–36.
- Schaller F.W. & Stockinger K.R. (1953) A comparison of five methods for expressing aggregation data. *Soil Sci. Soc. Am. Proc.* **17**, 310–313.
- Turcotte D.L. (1986) Fractals and fragmentation. *J. Geophys. Res.* **91**, 1921–1926.