THE USE OF CLAY PARTICLE MORPHOLOGY STUDIES TO CHARACTERIZE INDUSTRIAL CLAY DEPOSITS: EXAMPLES FROM BRAZIL

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(Received 19 January 1993; revised 22 June 1993)

ABSTRACT: The use of transmission electron microscopy in association with other methods is described for the characterization of Brazilian industrial clays, especially kaolinitic-halloysitic clays. Examples are presented from: (a) tubular 7 Å-halloysites and the characterization of mixtures with ordered and disordered kaolinites in residual china clays; (b) tubular kaolinitic clay from Piedade, São Paulo; (c) platey 10 Å-halloysite from Poços de Caldas, Minas Gerais; (d) rolled forms similar to 10 Å-tubular halloysite formed by repeated K Ac intercalation in well ordered kaolinite; (e) use of particle shape and size of kaolinite crystals in the São Simão, São Paulo ball clays as orientation for good sanitaryware ball clays; (f) characterization of gibbsite crystals in high alumina gibbsite/kaolinite clays; (g) antigorite as a clay mineral; (h) electron optical studies of thermal phase transformations involving tubular kaolinite, halloysites, antigorite, chrysotile, talc and pyrophyllite mono crystals.

Brazil is a major producer of industrial clays, (Souza Santos, 1989, 1992). It is the world’s sixth largest producer of bentonite and the eighth largest for china clays and also has major resources and production of talc, pyrophyllite, vermiculite, chrysotile asbestos and bauxite (Virta, 1992). This paper presents a concise review of the use of the crystal particle shapes for the characterization of industrial Brazilian clays. In these studies, transmission electron microscopy (TEM) has been extensively used to characterize the particle shapes of clay minerals, particularly the kaolin group, and to help to identify the distribution of clay mineral species in natural and industrially processed clays. Some special problems in characterizing the mineralogical compositions and technological properties of some industrial Brazilian clays are highlighted.

Particle shape in residual china clays

Industrially processed residual china clays derived from the weathering of pegmatites and granites are found in northern and southeastern Brazil, especially in the States of Minas Gerais and São Paulo. The X-ray diffraction (XRD) powder patterns of these clays show them to be b-ordered or well-crystallized kaolinite, though sometimes they are b-disordered kaolinite. Examination by TEM of these china clays using the conventional preparation technique (drying a drop of water dispersion on the grid) shows the presence of long tubular and platey particles with the long tubes very predominant. Such observations led to the hypothesis made by Visconti (1956) that the tubes were of a tubular kaolinite.

An extensive search was made to find a residual china clay containing only tubular particles without platey crystals when examined in the TEM. Such a sample was found as a white vein in a pegmatite in Sta. Helena County, Minas Gerais. Analysis by XRD showed it...
to be 7 Å-halloysite and not kaolinite; however, the 7 Å basal reflections were sharp and not bands, as in a regular tubular halloysite; also the tubes were longer and thicker in diameter than the usual short and small diameter halloysite tubes.

Consequently, Brindley et al. (1963) proposed that four different kind of X-ray powder diffraction patterns could be recognized for kaolinites and 7 Å-halloysites; these patterns are illustrated in Fig. 1 as A, B, C, D. Type A is for well-ordered, well-formed (euhedral) kaolinite crystals. Type B is b-axis disordered kaolinite, always composed of platey crystals; both A and B are readily oriented on the basal plane. Type D is a well-formed tubular 7 Å-halloysite with probably no preferred basal plane orientation. Type C is 7 Å-halloysite composed only of curled or rolled forms of flat crystals that are longer and thicker than type D tubes; they have a strong tendency to basal plane orientation. Type C resembles types B and D in that the 02,11 band is diffuse in the range 20–30° 2θ (Cu-Kα radiation). The 20,13 band between 34 and 40° 2θ, is less continuous than in Fig. 1D, but is less well resolved into separate reflections than Fig. 1B. The basal reflections show about the same intensities as the peak of the 02,11 band. They are slightly enhanced compared to the basal reflections in Fig. 1D, but are not enhanced much further even by intentional orientation procedures. This last observation, together with the breadth of the 001 reflection and frequently some asymmetry in the profile, suggest curved layers akin to those in type D halloysites. Various

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**Fig. 1.** X-ray powder diffraction patterns of four types of monomineralic kaolin minerals. (a) Well-ordered, well-formed (euhedral) crystals, enhanced basal reflections. (b) Platey crystals with b-axis disordered sequence, enhanced basal reflections (disordered kaolinite). (c) Crystals with layer sequence partially disordered with respect to both a and b-axes, little enhancement of basal reflections, rolled forms (7 Å-halloysite). (d) Crystals with highly disordered layer sequence, no enhancement of basal reflections, tubular forms (7 Å-halloysite). Back-filled rotating sample holder. Cu-Kα radiation; 1° 2θ/min.
mixtures of type A well-ordered kaolinite with types C and D halloysites were studied by X-ray powder diffraction in order to verify the effects on the diffraction patterns.

Figure 2 shows data for mixture of a type A well-ordered Brazilian kaolinite and a type D well-formed tubular 7 Å-halloysite. Additions of 5% and 10% kaolinite produce scarcely noticeable changes in the diffraction pattern, but with 20% and 25% kaolinite (Fig. 2C) the composite diffraction pattern resembles that of the type C halloysite of Fig. 1; with 40% kaolinite, the diffraction characteristics of kaolinite are clearly seen and in the absence of very careful examination, especially by TEM, the mixture would be identified as a slightly disordered kaolinite, approaching type A rather than type B: i.e. 60% of type D halloysite is almost completely masked by 40% type A kaolinite, if only X-ray powder diffraction is used for characterization of this mixture.

Figure 3 shows data for the same kaolinite with a second halloysite, this time a type C Brazilian halloysite composed of long rolled forms (it contains a mica impurity); 100% kaolinite is Fig. 2A; with 5% addition of kaolinite, Fig. 3E, there is little change in the XRD pattern of type C halloysite, but with 10% addition of kaolinite, Fig. 3D, the pattern begins

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**Fig. 2.** X-ray powder diffraction patterns of mixtures of type A kaolinite (Minas Gerais, Brazil) and type D halloysite (Utah, USA) in the weight proportions indicated.
to resemble type B in Fig. 1. With additions of 20% and 25% kaolinite, Fig. 3C, the mixture would be identified as a kaolinite with some degree of b-axis disorder, probably nearer to type B than to type A. With 40% kaolinite in the mixture, it would be recognized as approximating to a well ordered kaolinite and 60% halloysite would be overlooked, unless very careful XRD or TEM examinations were made. So, in mixtures with well ordered kaolinite, as much as 75% type C halloysite could be overlooked, if only X-ray powder diffraction is used. This is the case for the southeastern china clays of Brazil which are constituted predominantly by type C halloysite with small amounts of kaolinite (Souza Santos et al., 1964); type C halloysite is the clay mineral that Visconti (1956) considered as a tubular kaolinite. Figure 4 is a TEM photograph of a residual china clay from decomposed granite from Mar de Espanha, Minas Gerais; it shows a predominance of rolled forms over kaolinite plates, but its X-ray powder diffraction pattern is of a type A kaolinite. These data show that TEM is always necessary in parallel with X-ray powder diffraction to characterize the presence (or absence) of 7 Å tubular halloysite in the study of china clays and particularly in soils where kaolinites often have a very small particle size.

**Tubular kaolinite from Piedade, São Paulo**

During a systematic study of halloysitic clays in São Paulo, a white vein clay was discovered that was macroscopically fibrous (asbestiform); XRD analysis showed it had a
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Fig. 4. Transmission electron micrograph of typical residual china clay from Mar de Espanha, Minas Gerais, containing a large proportion of rolled forms of type C halloysite in relation to kaolinite plates. This sample has an X-ray powder diffraction pattern of type A kaolinite.

10.2 Å basal spacing that expanded on treatment with ethylene glycol to 10.6 Å. From TEM analysis the sample was found to consist of long tubular crystals; the first characterization was as a 10 Å halloysite, constituted by very long tubes several centimeters in length. However, the strongly marked tendency of the clay to produce basal plane orientation, the evidence for some degree of regularity indicated by both X-ray (fibre diagram) and electron diffraction data and the very intense basal reflections in the XRD powder patterns lead to classification of the kaolin mineral as a special tubular 7 Å/10 Å-kaolinite (Souza Santos et al., 1965). This special fibrous or tubular kaolinite behaves as a kaolinite when intercalated with potassium acetate (Wiewora & Brindley, 1969). The tubular crystals of the Piedade clay are shown in Fig. 5 and the XRD pattern in Fig. 6.

A similar fibrous kaolinite was described by Hughes & Brown (1977). These examples show that the tubular shape of crystals cannot be used as a specific criterion to identify 7 Å-halloysite in china clays.

Platey or tubular halloysite from Minas Gerais

In a white vein in a gibbsitic bauxite deposit from Poços de Caldas County, Minas Gerais, a 10 Å kaolin mineral was found; it was characterized as a 10 Å halloysite by XRD methods; however, by TEM it was observed to be constituted by thin platey crystals of irregular profile (Souza Santos et al., 1966). If the sample was air-dried before examination of TEM, the platey crystals rolled into tubes and resembled type C tubular 7 Å-halloysite. A wet sample of the platey 10 Å-halloysite from Poços de Caldas is shown in Fig. 7. A similar tubular halloysite was described by Kunze & Bradley (1963).

To date, several other halloysite morphologies have been identified, depending on their geological origin: toroid, spherical and others (Birrell et al., 1955; Sudo, 1977; Kirkman, 1977).
Fig. 5. Transmission electron micrograph of tubular kaolinite crystals from Piedade, São Paulo, Brazil.

Fig. 6. X-ray powder diffraction patterns of Piedade clay (H = 7 Å reflection; E = 10 Å reflection; EGH = ethylene glycol complex): (a) Wet clay without prior drying in a cavity-type holder; 001E more intense than 001H. (b) Air-dried clay on glass slide H (7 Å) reflections only. (c) Sample (b) saturated with ethylene glycol, 001H approximately the same as in (a); 001EGH is not to be confused with 001H (a).
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Fl6.7. Transmission electron micrograph of wet 10 Å-halloysite clay from Poços de Caldas, Minas Gerais: the crystals are very thin and flaky, often showing fractures. After drying in air they change to rolled forms and curly flaky masses.

The variety of crystal shapes again demonstrates the necessity of using the TEM to characterize the presence of 7 Å-halloysite in mixture with kaolinite in clays and soils.

Repeated intercalation of potassium acetate

The intercalation of potassium acetate plus water increases or expands the 7 Å spacing of kaolinite 14 Å, and then after washing with water, the basal spacing returns to 7 Å. However, after repeating the intercalations plus washing more than 30 times for a residual china clay composed of type A well ordered kaolinite from Junco County, State of Paraíba (Northeast Brazil), the basal spacing did not return to 7 Å but to 10 Å. The 10 Å crystals are rolled forms of the original hexagonal platey crystals of well ordered kaolinite (Souza Santos & Souza Santos, 1978). They are very similar to 10 Å-tubular halloysite, except that they show an additional 8 Å reflection (which is attributed to hole water). After drying at 70°C, the 8 Å reflection disappears and the 10 Å reflection contracts to 7 Å. By TEM, the clay now resembles a tubular 7 Å-halloysite and is also very similar to the type C 7 Å-halloysite. Figure 8 shows rolled forms after 40 intercalations of potassium acetate and water for euhedral crystals of kaolinite.

Mode of occurrence of the type C 7 Å-halloysite

The presence of significant amounts of long tubular type C 7 Å-halloysite is characteristic of deposits of residual china clays from decomposed pegmatites and granites in the States of São Paulo and Minas Gerais and in the processed china clays produced from them. Residual china clays formed in the State of São Paulo that do not contain halloysite are the exceptions (Wilson & Souza Santos, 1981). This raises the question as to whether the halloysite was
formed simultaneously or not with the kaolinite during the weathering of the pegmatite or granite. Examination by TEM of bulk samples of these china clays after dispersion in water, always showed the presence of both kaolinite and halloysite. However, after drying the bulk clays and examining them by scanning electron microscopy, it was observed that the bulk residual china clays are full of open pores. The internal surfaces of the pores are lined with tubular halloysite which cannot be separated from kaolinite during industrial processing. This observation suggests that repeated interaction of the kaolinite with salts present in surface water for long periods during weathering could result in the formation of type C halloysite in these kaolinitic residual china clays.

**Particle shape in São Simão “ball clay”**

There is no ball clay in Brazil similar to the English ball clays that are used in casting slips for sanitaryware and other whitewares. The only plastic clay found in Brazil that has been used with success for sanitaryware is a sedimentary kaolinitic grey clay from São Simão County, State of São Paulo. It has the low thixotropy and high mechanical strength needed for casting slips.

An extensive study has been under way for a long time to evaluate Brazilian sedimentary plastic white burning clays for use in casting slips for sanitaryware. Each potentially useful clay is examined by TEM to investigate the shapes of the clay particles: in the São Simão clay the kaolinite is present both as large hexagonal thin crystals and small hexagonal crystals, both of well ordered kaolinite. These crystal morphologies and sizes could give rise to the face-to-edge interactions that are supposed to exist in good low-thixotropy ball clays, in which the kaolinite crystals have the edges covered by smectite platelets. In the São Simão clay, TEM analysis has revealed that edges of the large thin kaolinite plates are covered by the small kaolinite plates, so presenting only negative surfaces which repel each
Other, thereby preventing the formation of the thixotropic “house-of-cards” structure. All the other plastic clays so far examined that have been rejected by their highly thixotropic slips are composed of very small, often irregular, kaolinite plates. The particle shapes and sizes found in the São Simão ball clay are being used to define good ball clays for sanitaryware.

**High alumina clays**

Brazil has many sedimentary deposits of refractory plastic gibbsite clays but no diaspore or boehmite clay has yet been found. These gibbsite clays are mainly used for fabrication of high alumina fireclay refractories. They were also evaluated for use in sanitaryware manufacture but it was found that >3 wt% of gibbsite increased their thixotropy beyond the limit for good casting slips.

In TEM analysis of the clays it was difficult to differentiate gibbsite and kaolinite crystals because they have similar sizes and shapes. However, heating the clays at 350°C to dehydroxylate the gibbsite caused a change in the texture of the gibbsite crystals and the pseudomorphs can then be easily identified.

**Antigorite clay**

The serpentine clay mineral antigorite usually occurs as a massive rock. However, a white clay deposit in Castro County, State of Paraná, was shown to be composed of very pure clay-sized platey antigorite crystals, with very irregular and peculiar outlines (Brindley & Souza Santos, 1971); this deposit was first identified as talc. The antigorite clay is being used for cordierite production. The 45·4 Å a parameter of the antigorite can be seen in Fig. 9.

Talc also occurs as a white clay deposit in Campo Largo County, State of Paraná; the shapes of the crystals of the talc clay vary considerably (Souza Santos et al., 1990).
Thermal transformations of some Brazilian clay minerals

Electron optical observations (TEM and selected area electron diffraction) have been used extensively in association with XRD and DTA to study the thermal transformations of some selected Brazilian clay minerals, and to establish topotactical crystallographic relationships between the phases formed and the consequent morphological changes. These studies were recently reviewed by Souza Santos (1989).

Changes in particle crystal shapes and in crystal structure (studied by selected area electron diffraction) during heating were studied using the following clay samples: tubular kaolinite from Piedade County, São Paulo (Campos et al., 1976; Lopes & Souza Santos, 1987); types C and D halloysites from several regions of Minas Gerais and São Paulo (Campos & Souza Santos, 1978); chrysotile asbestos from Uruaçu County, State of Goiás (Souza Santos & Yada, 1979); clay antigorite from Castro County, Paraná (Souza Santos & Yada, 1983); elongated platey massive talc (Souza Santos & Yada, 1988) and pyrophyllite from Diamantina County, Minas Gerais (Salvatori & Souza Santos, 1987).

Pyroexpansible macrocrystals of pyrophyllite from Ibitiara County, State of Bahia, were described by Duailibi Filho (1982). They can be exfoliated into large white crystals with very low bulk density that can have the same uses as exfoliated vermiculite; the pyroexpansibility is not shown by small size. The macrocrystals of Ibitiara pyrophyllite enabled Lee & Guggenheim (1981) to make the refinement of the 1Tc pyrophyllite crystalline structure.

It is interesting to compare the high-temperature phases formed from Al and Mg clay minerals: kaolinite, 7 Å-halloysite and pyrophyllite with chrysotile, antigorite and talc. In all cases it is possible to establish topotactical relationships between the original crystals and the crystalline phases up to 1400°C. The most obvious difference between the reaction sequences of kaolinite-halloysite and pyrophyllite on the one hand and serpentines and talc on the other is the formation of the intermediate metaphases in the former before the high-temperature reactions for both groups. Thus, by comparing high-temperature reactions, kaolinite/halloysite-mullite, pyrophyllite-mullite, serpentines-forsterite, and talc-enstatite, great differences can be observed, especially by electron optical means.

Figures 10 to 15 are examples of the phase transformation that can be observed in clay mineral crystals after being fired at high temperatures after the dehydroxylation reactions (Souza Santos & Yada, 1979, 1983, 1988).

Nickel clays

Brazil is the 10th world producer of Fe-Ni alloy and Ni using Ni clays as ores from three large deposits (Goiás, Minas Gerais and São Paulo). High nickel containing clay minerals from these deposits were described by Brindley & Souza Santos (1975a,b) and by Brindley & Whan (1975). Souza Santos et al. (1978) described their crystal shape using TEM. Smectites from these deposits were used by Vieira Coelho & Poncelet (1991) to prepare pillared Al and Ga complexes as precursors of Ni containing clay catalysts.

CONCLUSIONS

It has been shown that TEM associated with selected area diffraction, XRD, thermal methods of analysis and elemental chemical analysis has proved to be an invaluable research method for characterization of several special Brazilian clays as well for
Fig. 10. Transmission electron micrograph of a carbon replica of Piedade clay after firing at 1200°C; observe mullite elongated crystals inside the pseudomorphs, frequently making 120° angles between them.

Fig. 11. Transmission electron micrographs. (A) After firing at 900°C the walls of the original chrysotile fibril unit present a scalloped appearance, wavy sites corresponding to an individual patch. The circled area is enlarged in (B): lattice image of (020) planes of forsterite (5.12 Å fringes system), almost perpendicular (about 85°) to the fibril length.
FI6.12. Lattice image in a patch structure after firing at 800°C, showing fringe systems of 3.9 Å, 5.1 Å and 5.9 Å corresponding to the (021), (020) and (001) planes of forsterite, respectively. The 5.9 Å fringe system makes a 67° angle with the original fibril length.

FI6.13. Lattice image of antigorite fired at 800°C, showing the fringe system of 3.9 Å, 5.1 Å and 5.9 Å (2 × 2.99 Å) corresponding to the (021), (020) and (001) planes, respectively, of forsterite. The 5.1 Å fringe system, which is the c-axis direction in forsterite, is parallel to the antigorite b-axis.
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Fig. 14. Transmission electron micrograph of a long thin lath of talc fired at 900°C. Note enstatite crystallite inside the lath in three orientations making 60° angles with each other (short arrow).

Fig. 15. Talc lath fired at 1100°C. Lattice image of one enstatite crystallite showing 4.4 Å fringes corresponding to the enstatite 020 reflection.

correlation with industrial uses. Combined with selected area diffraction, not only changes in particle shape and crystalline structure can be followed, but also topotactical orientations of the new formed crystalline phases in relation to the original clay minerals.
ACKNOWLEDGMENTS

This paper was aided by a grant from FAPESP EQ-92/0412-9. The author is grateful for the collaboration of Prof Helena Souza Santos, Institute of Physics of the University of São Paulo for the electron optical data presented in this paper.

REFERENCES


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