Kaolin from Djebel Debbagh Mine, Guelma, Algeria

A. Boulmokh, Y. Berredjem, K. Guerfi and A. Gheid
Laboratory of Water Treatment and Valorisation of the Industrial Waste (L.T.E).
Department of Chemistry, Faculty of Science, University Badji Mokhtar, BP.12-23000 Annaba, Algeria

Abstract: Clay, in regard to its origin is unique. The kaolin of the mine of Djebel Debagh (Guelma, Algeria) has a hydrothermal geological formation. It presents it self a fragile and crumbly material, of whitish color. The characterization has for objective to situate to what family belongs this clay of the kaolin group (kaolinite, nacrite, dickite and halloysite). The elementary analysis showed the mineral to be composed mainly of aluminium, oxygen and silicon, with a low content of iron. The dehydrated state of the mineral was confirmed by XRD analysis; the basal spacing reflections indicate a sharp peak at 7.35 Å of d001 and the absence of a peak at 10Å form, which indicative of hydrated kaolin. Dimethyl Sulfoxide (DMSO), intercalate into the kaolin mineral and increases the basal pacing d001 from 7.35 Å to approximately 11.39 Å. The specific surface area measured by BET_{N2} of the mineral was very large ($56.45m^2.g^{-1}$). SEM studies indicated that the sample of kaolin was no uniform in content, containing a lot of tubular material, as well as large undesirable particle agglomerates. Others analysis methods (IR, TGA, DTA) were used investigations for the characterization and identification of kaolin.

Key words: Kaolin, characterization, TGA, intercalation, X-ray diffraction, FTIR

INTRODUCTION

The exploitation of the white kaolin by the Chinese in the industry of ceramics goes back to the first millennium (Grim, 1968). Various layers of this ore were thereafter discovered. We distinguish four types of minerals: kaolinite most abundant, the dickite (1888), nacrite (1807), halloysite (1826) which belongs to the kaolin group. These minerals of the group of kaolin have mainly three different origins (Caillère *et al.*, 1982), by heritage where the inherited minerals are obtained by deterioration and transport, also by degradation major transformations (Hurst and Kunkle, 1985). These are 1:1 phyllosilicates, characterized by a 1:1 dioctahedral structure, with the chemical composition $Al_2Si_2O_5(OH)_4$. Kaolinite is interesting as a mineral precursor due to its unique asymmetric layered structure with $(SiO)_6$ macrorings on one side and aluminol groups on the other side. This asymmetry creates large superposed dipoles in the lamellar structure, resulting in a large cohesive energy (Bailey, 1988a). Their chemical composition is almost uniform: 46.54% of SiO_2, 39.50% of Al_2O_3, 13.96% of H_2O; corresponding to the general formula $Al_2Si_2O_5(OH)_4$ for the first three minerals and halloysite $Al_2Si_2O_5(OH)_4.2H_2O$. Small quantities of iron, titanium, potassium and magnesium can be also (Deer *et al.*, 1971). Berthier discovered the mineral whose chemical composition belongs to the group of kaolin but differs by incorporation from water between the layers and called this mineral halloysite. Hofmann *et al.* (1934), Ross and Kerr (1934) established its chemical composition for the hydrated form $Al_2Si_2O_5(OH)_4.2H_2O$ and the basal distance d001 of this ore increases by 7Å with 10Å. To differentiate these two situations, the metahalloysite term was introduced (Mehmel, 1935) for the dehydrated form and by using the halloysite term for the hydrated form (Churchman *et al.*, 1972). This nomenclature was accepted by Keller and Johns (1976), Brindley (1980). The intercalation of Dimethyl Sulfoxide (DMSO) into clay minerals has been used to separate the chlorite fractions from the kaolin minerals (Churchman, 1990). The reason DMSO is so successful at separating the clay minerals is that the kaolins expand from 7.2 to 11.2 Å. This expansion of the kaolin minerals by DMSO followed by deintercalation results in an increase in the stacking disorder of the kaolin. Intercalation of DMSO into kaolinite provides a method for the incorporation of other alkali and alkaline metal salts into the kaolin by replacement of the DMSO (Lahav, 1990).

In this present research our investigations will concern the chemical composition in order to evaluate the concentrations out of silica, alumina, water and the elements such as: potassium, magnesium… etc. Granulometry is used to determine particle and their

---

Corresponding Author: A. Boulmokh, Department of Chemistry, Faculty of Science, University Badji Mokhtar, BP.12-23000 Annaba, Algeria

distribution size of this clay. The Differential Thermal Analysis (DTA) and Gravimetric the Thermique analysis (TGA) make it possible to characterize the type of clay (Caillère *et al.*, 1982). By the study of adsorption-desorption of nitrogen we determine specific surface BET, the type of the isotherm and dimensions of the pores. X-rays diffraction which is a means of identification of crystallographic texture is studied; the infrared analysis constitutes a tool for characterization of the crystallinity of clays by the observation of the relative intensities of the bands of vibrations of hydroxyls of structure (Cruz-Cumplido, 1982 and Brindley, 1986). Electronic Scan Microscopy (SEM) is also put at contribution to know the morphology of the kaolin.

MATERIALS AND METHODS

The kaolin was used as clay in this study and obtained from the town of Guelma (Djebel Debagh) in Algeria. The type of kaolin is much rarer than other clay minerals (Papke, 1971). Details about the physicochemical proprieties were determined elsewhere (Boulmokh *et al.*, 2004).The sample was characterized by BET, SEM, X-ray diffraction, thermogravimetric and FTIR spectroscopic analyses. The chemical compositions of the kaolin was found to be as follows: 43.82% SiO_2, 36.90% Al_2O_3, 0.20%,Fe_2O_3, 0.02% MnO, 0.03%, MgO 0.23%, CaO, 18.51% loss on ignition.

Specific surface area: Nitrogen adsorption measurements were performed at 78.20 K using an ASAP-2010 volumetric adsorption analyzer (Micromeritcs, Norcross, GA). Prior the adsorption measurements, each sample was degassed at 473 K for at least 2 h until a pressure of 10^{-4} Pa was attained. The BET specific surface area (Sing *et al.*, 1985) was calculated from adsorption data in a relative pressure range from 0.05 to 0.23. The total pore volume was obtained according to the single point method (Jaroniec *et al.*, 1996). The α_s-plot method (Jaroniec and Kaneko, 1997) was employed to assess the porosity of the samples and estimate the volume and surface area of mesopores. The sample kaolin has a specific surface area of 56.45m^2.g^{-1} with an average diameter of the pores of 121.4Å. The curves of adsorption and desorption has a low hysteresis characteristic of the porosity of the solid.

The DMSO intercalate was prepared following a slightly modified version of the procedure reported by Costanzo *et al.* (1984). Two grams of kaolin was stirred with 50 mL of anhydrous dimethylsulphoxide for 7 days. The excess solution was removed by centrifugation and isolated in powder form after washings with dioxane to remove excess. The intercalated kaolin was kept in a desiccator before thermoanalytical and XRD.

Thermogravimetric Analysis (TGA): was performed using a TGA 2050 Thermogravimitric analyser TA instruments. Analysis was performed over the temperature range 30-600°C using a heating rate of 10°C min^{-1}, the sample weights examined were between 10 and 20 mg. Argon gas flowed over the open crucibles containing the sample as the analysis was performed. The percentage weight losses incurred during the heating cycle were estimated using the associated software.

X-rays diffraction: Powder patterns were performed on INEL XGR 2500 with a detector CPS 120 diffractometer using a generator voltage of 50 kV and a current of 240 mA. The radiation applied was CuKá from a long, fine focus Cu tube. The samples were measured with relative humidity in step-scan mode with steps of 0.03° 2è and a counting time of 1s. Particles morphology was observed by Electronic Scan Microscopy (SEM) using a JEOL 6400F with field affect instrument. The spectra FTIR was obtained by using Perkin Elmer FTIR recorded in ATR modulate with crystal ZnSe.

RESULTS AND DISCUSSION

Figure 1 shows curves thermogravimetric that an endothermic peak clearly accentuated at the temperatures 500-520°C corresponded to the disordered kaolin. Also this endothermic peak has a dissymmetry and this form was used to distinguish kaolinite from the halloysite (Caillère *et al.*, 1982) for which the downward branch presents a slope more marked than the increasing branch. The loss in weight found by thermogravimetric analysis confirms the preceding results. Two losses in, one at low temperature (2%) corresponding at the beginning of the hygroscopic water, which is related on the smoothness of the grains and the degree of deterioration of the sample. The other starting from 420°C indicate the decomposition
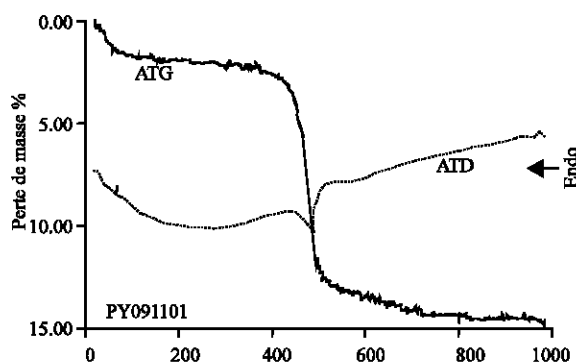

Fig. 1: DTA and TGA curves of the kaolin

of the octahedral layer. It is relatively constant and corresponds to a loss 14.5%. The slope of the curve of loss in weight varied with the state of crystallinity (Caillère *et al.*, 1982).

The main feature of the TGA thermogram of kaolin is a major endotherm near 520°C attributed to the loss of water due to the crystal lattice dehydroxylation with formation of metahalloysite. This endotherm usually corresponds to ca. 18% weight loss in the TGA (Fig. 2a). As shown in Fig. 2b, the kaolin-DMSO intercalate exhibits three weight losses in the TGA accompanied by three endotherms centered at ca. 70, 225 and 500°C. The first is due to the removal of molecular water adsorbed on the external surface and the second is attributed to the loss of DMSO from the interlamellar space of kaolin. The third one is due to the dehydroxylation step of kaolin.

Many works were devoted to the crystallographic structure of the various families of minerals (Brindley and Brown 1980; Bailey, 1990, 1988b). The minerals of this group consist of layers including/understanding an octahedral layer and a tetrahedral layer whose basal distance varies between 7.1 Å and 7.3 Å, in this last layer each SiO_4 tetrahedron is related to the tetrahedrons close by three to its tops, thus creating a plane surface of oxygen atoms (Drits and Tchoubar, 1990). These minerals (halloysite, kaolinite, dickite and nacrite) are different according to layers (Brown *et al.*, 1989) then (Drits and Tchoubar, 1990). The identification of our kaolin sample is founded in the position of peak in particular d001 observed on the diffractogram.

The principal's peaks of this spectrum DRX, with peak d001 to 7.35 Å, peak d02, 11 to 4.42 Å, d002 at 3.58 Å and d003 at 2.36 Å are those of the métahalloysite according to Brindley (1980). In addition, we note that the majority of the peaks are broad and dissymmetrical (Fig. 3). Peak d001 of maximum asymmetry is a measurement of the degree of crystalline disorder. Also the peaks 1.98 Å and 1.64 Å confirm this attribution (Cases *et al.*, 1982).

Figure 3 shows the X-ray diffraction patterns of kaolin and their DMSO intercalates. X-ray diffraction shows that the kaolin was intercalated to the 100% level. Also kaolin show a shift of the d001 reflection from 7.35 Å to 11.39 Å. The significance of this broad band is that the intercalated kaolin was now showing a certain degree of amorphicity. The kaolin expands from 7.35 to 11.39 Å. This is an increase of 4.04 Å. The size of the S=O group is 3.38 Å and if the DMSO is parallel to the siloxane surface then there is an imbalance of 0.66 Å. The question arises as to how this gap may be filled. In the model of the DMSO-kaolin intercalate presented by Thompson and Cuff (1985) one of the methyl groups is pointing directly into
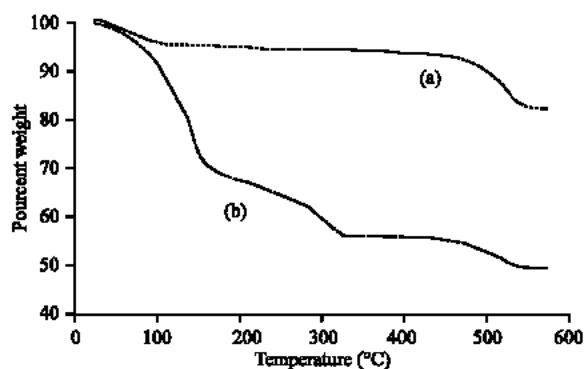

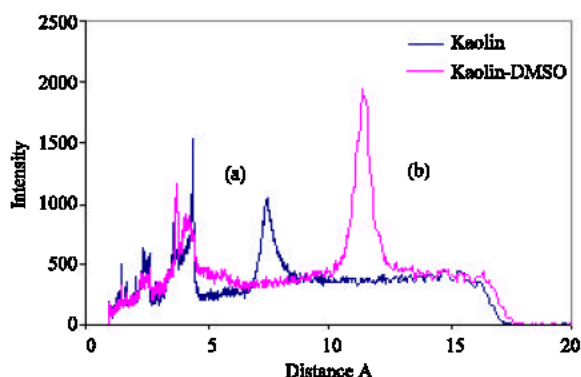Fig. 2: TGA curves for (a) kaolin and (b) kaolin-DMSO

Fig. 3: X-ray diffraction of (a) kaolin and (b) DMSO intercalated kaolin (0 - 20 Å)

the ditrigonal cavity with the second methyl group pointing away from this surface (Thompson and Cuff, 1985). The oxygen of the S = O group is pointing toward two or three of the inner-surface hydroxyls. This model, however, is based on an absence of water in the intercalate and also depends on the presence of nonpolymeric DMSO.

The sample kaolin was subjected to electron microscopy and to particle size analysis. SEM studies indicated that the sample was uniform in content, containing a lot of tubular material, as well as large undesirable particle agglomerates. Despite the longest individual tubules being only 3-5 μm, the average median particle size of the simple was determined to be 30μm, confirming the presence of large aggregates. The sample kaolin was passed through a 100 μm sieve, yielding 80% approx product. Figure 4 shows a SEM of a typical sieved sample, illustrating the high tubular content with the presence of occasional aggregates. The detailed appearance of some typical tubules is shown in Fig. 4 (A-01: Magnification ×75000) whose length is quite variable, but whose outer diameter is more consistent at 0.2 μm.
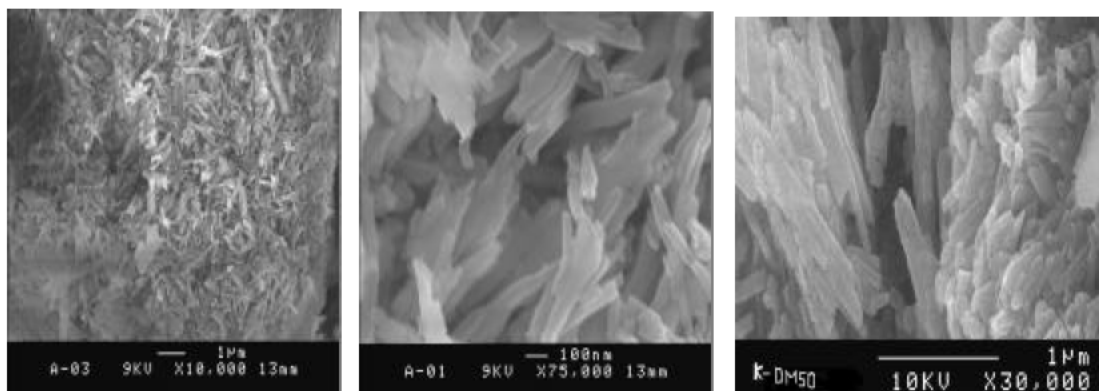
Fig. 4: SEM of the kaolin and intercalated kaolin

Table 1: Attribution bands vibrations the Spectrum IR of kaolin

ν (cm^{-1})	(ν) observed in literature	Assignment of Kaolin bands	References
3695	3695	νOH interfeuillet	Ledoux and White, 1964a
3674	3670	νOH surface of grains	Ledoux and White, 1965a
3647	3650	νOH interfeuillet	Ledoux and White, 1964a
3623	3620	νOH intern with feuillet	Ledoux and White, 1964a
3470-3486	3400-3540	νOH H2O	Srasra *et al.*, 1994
1645		δAlOH hydratation	Srasra *et al.*, 1994
1120	1096	νSiO	Percival *et al.*, 1974
1007	1010	νSi-O-Si	Farmer, 1974
912	912-915	δAl-OH-Al external With layer	Pros and Dameme, 1987
789	789	Al-OH	Percival *et al.*, 1974
750	757	Al-OH	Farmer, 1974
686	700.1	Al-OH	Farmer, 1974

Fig. 5: Infrared spectra of (a) kaolin and (b) hydrated kaolin-DMSO complex

The infrared Spectroscopy constitutes for the mineralogists a tool for characterization of the crystallinity of clays by the observation of the relative intensities of the bands of vibrations of hydroxyls of structure (Cruz-Cumplido *et al.*, 1982; Brindley *et al.*, 1986). On Fig. 5, we note that the vibrations characteristic of clays are separate in two groups (Farmer, 1974). The first group corresponds to the bands of vibrations of elongation of hydroxyls between 3750 and 3400 cm^{-1}. The second group of vibrations corresponds to the network between 1300 and 600 cm^{-1} (mode of elongation between 1300-1000 cm^{-1} and mode of deformations between 800-600 cm^{-1}) and to the vibrations of hydroxyls which are located between 950-900 cm^{-1}. The positions in frequency and attributions of the peaks of the kaolin sample are given in Table 1.

Attributions bands of the spectra given in Table 1 presented previously were compared with those raised in literature. Kaolin characterized by a diagnostic, signature O-H stretching pattern consisting of four bands at 3695, 3674, 3647 and 3623 cm^{-1} (Fig. 5a). The attribution of these bands has been the subject of extensive study
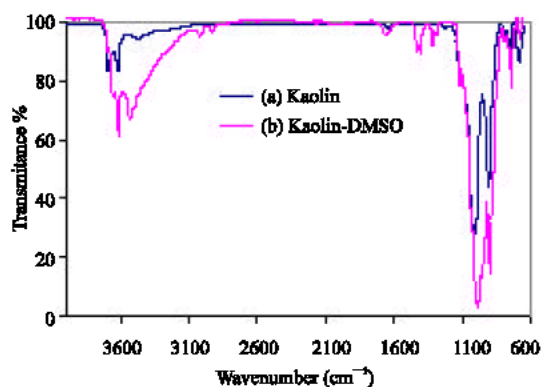
(Cruz-Cumplido *et al.*, 1982; Brindley *et al.*, 1986; Johnston *et al.*, 1984; Prost *et al.*, 1989). The band at 3621 cm^{-1} has been unambiguously assigned to the stretching frequency of the internal hydroxyl group of kaolin (Ledoux and White, 1964). This hydroxyl group is believed to be oriented almost parallel to the direction of the d00l layers, pointing in the direction of the unoccupied octahedral hole (Bish, 1993). The inner-surface hydroxyl groups associated with the remaining bands (3695, 3674 and 3647 cm^{-1}) are believed to make an angle of 60-73° with the (001) plane (Bish, 1993). The inner hydroxyl stretching band at 3623 cm^{-1} is not usually influenced very much by interlamellar modification reactions since it is removed from the interlamellar surface. In contrast, the three inner surface hydroxyl stretching bands are very much influenced by interlamellar modifications (Ledoux and White, 1966; Sugahara *et al.*, 1989) as it can be readily observed for Kao-DMSO (Fig. 5b).The presence of broad band of low

centered intensity with 3489 cm^{-1} corresponds to the vibrations valence of the water hydration of the sample: two bands vibrations of deformation hydroxyls group at 927 cm^{-1} and the other at 912 cm^{-1} The band of deformation low frequency due to the external OH is connected to the vibrations of elongation of high frequencies in particular that which is to 3623 cm^{-1}.

The interesting feature of the infrared spectrum of intercalated DMSO is the appearance of sharp peaks in the regions of 3633, 3620 and 3520 cm^{-1} and decreased intensity of the peak at about 3680 cm^{-1}. Intercalation of the kaolin with DMSO has caused the rearrangement of the orientation of the kaolin hydroxyls such that different hydroxyl deformation modes are observed. In particular, the band at 896 cm^{-1} is attributed to the hydroxyl deformation of the inner-surface hydroxyl groups which are hydrogen bonded to the S = O group of the DMSO. The spectra of the hydroxyl deformation region of the kaolin intercalated with DMSO shows basically two bands at 976 and 896 cm^{-1} with a minor band at 947 cm^{-1}. The FTIR spectra of C-H stretching region of the DMSO intercalated kaolin is shown in Fig. 5b, two bands at 3009 and 2916 cm^{-1}. These bands are attributed to the antisymmetric C-H stretching modes. The in-plane methyl bending region the IR spectrum of this region for the DMSO intercalated kaolin is complex with bands observed at 1405, 1401 and 1314 cm^{-1}. This number of bands indicates at least seven different types of H-C-H bending vibrations. The complexity of the C-H bending region supports the concept of different molecular arrangements of the DMSO molecules in the intercalate (Johnston *et al.*, 1984).

CONCLUSION

This research demonstrates that more one analytical technique should be employed to acquire the composition and structure picture of the constituents of the clay simple. The chemical composition of the sample gave percentages of silica and of aluminium respectively 43.82 and 36.90%, the loss on the ignition is 18.51%. These values approach those found in literature. The curve of DTA presents a dissymmetrical endothermic peak at 520°C, characteristic of metahalloysite. The TGA confirmed the preceding results with two weight losses; the first is due to the removal of molecular water adsorbed on the external surface and the second is attributed to the loss the dehydroxylation step of kaolin. Specific surface area of simple kaolin is 56.44 m2.g-1. X-rays diffraction revealed principal peak at 7.35Å (d001) and a peak at 4.42 Å (d02, 11). Further confirmation of the dehydrated state was the presence of the d002 basal reflection at

3.58Å characteristic of the métahalloysite; also the width and the dissymmetry of the peaks confirm this attribution. The peak (001) of maximum asymmetry gives a measurement of the degree of the crystalline disorder of this clay. Other peaks do not belong to the métahalloysite, are allotted to the impurities which sample contains. DMSO intercalated to the 100% level, also kaolin show a shift of the d001 reflection from 7.35 to 11.39 Å; the significance of this broad band is that the intercalated kaolin was now showing a certain degree of amorphicity. The FTIR spectra confirm structural changes during intercalated DMSO with sharp peaks in the regions of 3633, 3620 and 3520 cm^{-1} and decreased intensity of the peak at about 3680 cm^{-1}. SEM show kaolin used is largely microtubular and relatively uniform with occasional aggregates. The results of this study confirm that this kaolin is métahalloysite.

REFERENCES

Bailley, S.W., 1988a. Hydrous Phyllosilicates, American Mineralogical Society, Washington, DC.

Bailley, S.W., 1988b. Hydrous Phyllosilicates exclusive of Micas Rev. Minerals, pp: 19- 698.

Bailey, S.W., 1990. Halloysite a critical assessment. In: Farmer, V.C. and Y. Tardy, Ed., Proceedings of the 9th International Clay Conference, Strasbourg, 1989. Sciences Géologiques, Mémoire, 86: 89-98.

Bish, D.L., 1993. Reetviet refinement of kaolinite structure at 1.5K.Clays and Clay Minerals), 41: 738 -744.

Brindley, G.W., 1980. Order-Disorder in the Clay Mineral Structures. In: Brindley, G.W. and G. Brown, (Eds.), Crystal Structures of Clay Minerals and Their X-ray Identification. Mineralogical Society, London, pp: 125-196.

Brindley, G.W. and G. Brown, 1980. Crystal Structure of Clay Minerals and their X-ray Identificationmineralogical Society, London. Kaolinite Science, 143: 244 -246.

Brindley, G.W., C. Kao, J.L. Harrison, M. Lipsicas and R. Raythathe, 1986. Relation beteween Structure Desorder and other characteristics of kaolonites and dickites. Clays and Clay Minerals, 34: 239-249.

Brown, A.S., V.A. Drits, A. Plançon and C. Tchoubar, 1989. Stacking faults in kaolin group mineralsinthe light of real structural features. Clays and Clay Minerals, 37: 297-307

Boulmokh, A., Y. Berredjem, K. Guerfi and A.E.K. Gheid, 2004. J. Soc. Alger. Chim., 14: 155 -165.

Caillère, S., S. Hénin and M. Rautureau, 1982. Minéralogie des argiles. Masson.

Caillère, S., S. Hénin and M. Rautureau, 1982. Minéralogie des argiles. Masson.

Cases, J.M., O. Lietard, J. Yvon and J.F. Delon, 1982. Etude des propriétés Cristallochimiques morphologiques superficielles de kaolonites désordonnées Bull. Minérals, 105: 439- 455.

Churchman, G.J., 1990. Relevance of Different Intercalation Tests for Distinguishing Halloysite from Kaolinite in Soils. Clays and Clay Minerals, 38: 591-599.

Churchman, G.J., L.P. Albridge and R.M. Carr, 1972. The relationship between the hydrated and dehydrated states of an halloysite.Clays and Clay Minerals, 20: 241-246.

Costanzo, P.M., R.F. Giese and M. Lipsicas, 1984. Static and dynamic Structure of Water in Hydrated Kaolinites PT.1. The Static Structure. Clays Clay Minerals, 32: 419 - 428.

Cruz-Cumplido, M., S. Cheik and J.J. Fripiat, 1982. Spectre infrarouge des hydroxyles, cristallinité et énergie de cohésion des kaolins Bull.Minérals, 105: 493 - 498.

Deer, W.A., R.A. Howie and J. Zussman, 1971. Rock-Forming Minerals.

Drits, V.A. and C. Tchoubar, 1990. X-ray diffraction by disordered lamellar structures: theory and application to microdivided silicates and carbons Springer Verlag Berlin, pp: 371.

Farmer, V.C., 1974. The infrared Spectra of mineral. Mineralogical Society, London, pp: 331-363.

Grim, R.E., 1968. Clay Mineralogy: Mc Graw-Hill, New York, pp: 596.

Hofmann, U., K. Endell and D. Wilm, 1934. Röntgenographische und kolloidchemische Untersuchungun über Ton. Angewandte Chemie, (in German), 47: 539 -547.

Hurst, V.J. and A.C. Kunkle, 1985. Deshydroxylation rehydroxylation, stabilite of kaolinite: Clays and Clay Minerals, 33: 1-14.

Jaroniec, M., T.J. Pinnavaia and M.F. Thorpe, 1996. Nanoporous Materials, Plenum, New York.

Jaroniec, M. and K. Kaneko, 1997. Physicochemical Foundations for Characterization of Adsorbents by Using High-Resolution Comparative Plots. Langmuir, 13: 6589-6596.

Johnston, C.T., G. Sposito, D.F. Bocian, R.R. Birge, 1984. Vibrational Spectroscopic Study of the Interlamellar Kaolinite-Dimethyl Sulfoxide Complex J. Phys. Chem., 88: 5959-5964.

Keller, W.D. and W.D. Johns, 1976. Endellite Will reduce ambiguity and comfusion in nomenclature of halloysite. Clays and Clay Minerals, pp: 24-149.

Lahav, N., 1990. Preparation of stable suspensions of delaminated kaolinite by combined dimethylsulfoxide-ammonium fluoride treatment Clays and Clay Minerals, 38: 219-22.

Ledoux, R. and J.L. White, 1964. Infrared studies of the hydroxyl groups OH expended.

Ledoux, R. and J.L.White, 1965. Infrared Studies of the Hydroxyl Groups in intercalated kaolinite complex 13th, Nat. Con. Clays and Clay Minerals, pp: 289-315.

Ledoux, R.L. and J.L. White, 1966. Infrared studies of hydrogen bonding interaction between kaolinite surfaces and intercalated potassium acetate, hydrazine, formamide and urea. J. Colloid Interface Sci., 21: 137-152.

Mehmel, M., 1935. Uber die struktur von Halloysit und metahalloysit Z. Kritallogr., 90: 35-43.

Papke, K.G., 1971. Halloysite deposits in the Terraced Hills, Washoe County, Nevada: Clays and Clay Minerals, 19: 71-74.

Percival, H.J., J.F. Dancan and P.K. Foster, 1974. Interpretation of the kaolinite-mullite reaction sequence from Infrared absorption spectra. J. Am. Ceramic Soc., 57: 57-61.

Prost, R. and A.E. Damême, 1987. Huard..Infrared study of srtuctural OH in kaolinite, dikite and nacrite at 300 to 5 K. Proceedings of the International Clay Conference, Denver.

Prost, R., A. Dameme, E. Huard, J. Driard and J.P. Leydecker, 1989. Infrared Study of Structural OH in Kaolinite, Dickite, Nacrite and Poorly Crystalline Kaolinite at 5 to 600 K Clays and Clay Minerals, 37: 464-468.

Ross, C.S and P.F.Kerr, 1934 Halloysite and alophane. U.s.Geol. Surv. Prof., pp: 151-185.

Sing, K.S.W., D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol and T. Siemieniewska, 1985. Pure Applied Chem., pp: 57- 603.

Srasra, E., F. Bergaya and J.J. Fripiat, 1994. Infrared Spectroscopy Study of Tetrahedral and Octahedral Substitutions in an Interstratified Illite-Smectite. Clay Clays and Clay Minerals, 42: 237-241.

Sugahara, Y., S. Satokawa, K. Yoshioka, K. Kuroda and C. Kato, 1989. Kaolinite-Pyridine Intercalation Compound derived from Hydrated Kaolinite Clays Clay Minerals, 37: 143 -150.

Thompson, J.G. and C. Cuff, 1985. Crystal Structure of Kaolinite: Dimethylsulfoxide Intercalate. Clays and Clay Minerals, 33: 490-500.