LITERATURE
Numerous investigators\textsuperscript{5-7} of clays have reported the finding of a kaolinite mineral of lower crystallinity than that of the well crystallized material. Brindley and his colleagues\textsuperscript{4-5} have investigated in detail some examples of rather poorly crystallized kaolinite and have shown that their examples from English fire clays contain fewer reflections than normal kaolinite. According to them the reflections can be indexed as monoclinic or pseudomonoclinic, with a unit cell of the same dimensions as kaolinite but with $\alpha = 90^\circ$. Also, they state that the structure is highly disordered along the $b$ axis with the unit layers randomly displaced by multiples of $\frac{b}{3}$. The arrangement along the $a$-axis is like that of kaolinite. They suggest that there is some randomness in the distribution of aluminium atoms among octahedral positions. The first-order spacings are slightly higher (7.15 to 7.20 Å) for the poorly crystalline than for the well crystallized mineral, suggesting some occasional interlayer water between the kaolin units.

Brindley\textsuperscript{8} suggested mellornite as a name for poorly crystallized kaolinite, and Roberts and Grimshaw\textsuperscript{9} has suggested lavisite for similar material. As there are
probably all gradations from well crystallized kaolinite to that of complete randomness in the b direction and in the population of aluminium position, it appears doubtful that a specific name should be applied. Most kaolin clay contains small amounts of accessory minerals like anatase and rutile, felspar, iron oxides, mica, montmorillonite and quartz, which must be corrected for before it can be established that isomorphous substitution of an element into the kaolinite is occurring. Selective dissolution analysis and separation of kaolinite into narrow size fractions may help to decide how much of a constituent is impurity mineral and how much is substituted into the structure. These methods have certain limitations and recent work has attempted to find confirmation by physical instrumental method.

Al:Si ratios in kaolinites differ from unity by a few percent. Jepson and Rowe\textsuperscript{10} used the electron microscope microprobe analyser (EMMA) to measure Al:Si ratios in many particles from two kaolinites from St. Austell, Cornwall, and from Georgia, U.S.A.; ratios for individual particles varies somewhat, the variance being comprised of counting statistical and instrumental fluctuation and interparticle variation. Although the authors concluded
that variation in particle composition could not be detected in their experiments, they showed that mean Al:Si ratios were significantly different from unity (C.962 ± 0.018) for the 0.9-1.0 μm fractions of the St. Austell clay, but not significantly different from unity for the Georgia kaolinite (0.997 ± 0.019) for the 0.9-1.0 μm fractions. If Al were substituted for Si in the St. Austell clay the Al:Si ratio should have been greater than unity, so this hypothesis was rejected and it was concluded that the kaolinite particles were covered with a surface coating of amorphous silica.

Jepson and Rowse also measured the ratios of the minor components to Si on individual particles and confirmed the conclusion from Mössbauer and ESR measurements that Fe was present within kaolinite particles. Fe:Si ratios showed a wide and significant variation from particle to particles. About 12% of the total Ti in the Georgia (i.e. 0.14% TiO₂) was associated with the kaolinite particles as distinct from individual rutile and/or anatase particles, but the authors considered confirmatory evidence was needed to establish that this represented substitution of Ti into the structure, as was believed by Dolcater et al. Weaver however prompted much evidence that Ti in kaolinite was present as discrete surface oriented form.
Statistically positive K:Si ratios were found for both the St. Austell and Georgia kaolinites, sufficient to require about 1 mica layer per 250 kaolinite layers. Lee et al have shown by HRTEM images that kaolinite can contain micaceous occlusions identified by a 10A lattice spacing defect in the predominantly 7A matrix. A mica concentration of this level is undetectable by x-ray diffraction but is sufficient to account for the K-levels in Jepson and Rowse's kaolinites.

The iron content of kaolinites has been the subject of some discussion (e.g. Angel and Hall, Angel and Vincent, Rengasamy, Herbillon et al, Mestdagh et al, Cutler, Komusinski et al). Meads and Malden showed that several types of ESR signals were obtained from kaolinites, one attributed to Fe$^{3+}$ substituting for octahedral Al, one attributed to trapped holes, and another due to Mn$^{2+}$ and (VO)$^{2+}$. Herbillon et al divided the forms of Fe in kaolinite into that in ancillary oxides, e.g. anatase and rutile, that in micas, and that in the kaolinite structure. Tropical soil kaolinite could contain up to 2% Fe$^{3+}$ but there was increasing disorder as the iron content increased; the structural evidence for disorder has been studied in detail by Plancon and Techoubar. Mestdagh et al further
investigated their relationship and showed that a quantitative treatment of the ESR spectrum at \( g_{\text{eff}} \approx 4 \) provided a method of estimating the structural Fe contents of kaolinites. Well-crystallized kaolinites have a narrow range of Fe\(^{+3} \) contents, but in poorly-crystallized kaolinites, the Fe\(^{+3} \) is partitioned equally into two sites characterized by their ESR spectrum. The difficulty of using selective dissolution analysis to define Fe content of kaolins is emphasized by the work of Komusinski\(^{20} \) et al who showed that dithionite treatment did not totally remove all the "free" Fe oxides and that 9% HCl was sometimes needed; even this did not remove all the free oxides from some samples.

Young and Hecot\(^{23} \) verified the triclinic crystal structure of kaolinite in the following way. On the basis of neutron diffraction studies, the two inner hydroxyl ions in highly ordered kaolinite were recently shown to be differently oriented. One of the inner hydroxyl ion points generally toward a hole in the octahedral sheet and the other toward a hole in the tetrahedral sheet. These orientation and the location of the other atoms in the primitive triclinic unit cell had been determined for a sample of Keokuk kaolinite with improved precision compared with that reported earlier. Rietveld structure refinement was
carried out for the entire crystal structure simultaneously (99 atom positional and 17 other parameters) with each of the two newly collected sets of high-resolution neutron powder diffraction data. The different orientation of the inner-hydroxyl ions were the most marked evidence that the unit cell was not C-centered. The positions of the inner-surface hydrogen atoms provided further evidence in that all differ from a C-centered relationship by six to eight estimated standard deviations in their y coordinates. The cell was therefore, not centered. The space group was P.

Although certain clay deposits contain well-defined microcrystalline particles, most clay minerals occur as particles too small to resolve with the ordinary microscope. Furthermore, a considerable distribution of particle sizes is frequently present. These facts hindered the quantitative development of their colloid chemistry for many years. By the use of the centrifuge and the electron microscope, the experimental limitations have now largely been removed.

The qualitative fractionation of Putnam clay (beidellite) by Bradfield and his study of the properties of the fractions, showed something of the enormous range of particle size present, and stimulated research into more precise methods. The first accurately quantitative
procedure was based on a two layer principle using the tube centrifuge. This method, devised by Marshall\textsuperscript{25-26}, has the advantage that, in addition to giving the distribution of particle sizes, it actually isolates fractions within predetermined size limits. It is thus merely a matter of repetition to accumulate well-defined fractions for study. The range of the method has since been extended downwards by the use of the two layer principle in the Sharples super centrifuge\textsuperscript{27}. The range $2\mu - 10 \mu$m can thus be covered in any number of steps.

Bradfield original procedure was amplified to give roughly quantitative fractionation by Bray\textsuperscript{28}. A mathematical examination of the sedimentation conditions in the Sharples machine has led Houser\textsuperscript{29} and associates to develop a procedure for quantitative fractionation which involves fewer repetitions than that of Bray\textsuperscript{28}.

In case where interest is centered solely upon the distribution of particle sizes, the pipette method is frequently used. Under gravity alone it is not well suited to determinations below 0.5\mu, but it can be combined with a tube centrifuge sedimentation as shown by Steele and Bradfield\textsuperscript{30}. In this way determination down to 50 m\mu have been made.
The use of the electron microscope has greatly simplified the determination of shape and size of clay particles. Two dimensions can be determined directly and the third remains to be found. Since clay particles generally lie flat upon the collodion support, this undetermined third dimension represents the thickness of the plate or lath. It may be deduced by combining sedimentation or ultramicroscopic data with the visible dimensions and some guidance as to its order of magnitude can also be obtained by consideration of electron penetration (Marshall et al).

Electron micrographs of kaolinite were first obtained by Eitel and others. Shaw and Humbert also carried out significant work on electron micrograph of kaolinite. Electron micrographs of well crystallized kaolinite (Fig. 4) show well-formed six-sided flakes, frequently with a prominent elongation in one direction. The elongation is parallel to either (010) or (110). Certain of the edges of the particles are beveled instead of being at right angles to the flake surface. Occasionally the particles appear to be twinned. In poorly crystallized kaolinite, the particles show less distinct six-sided flakes. The edges of the flakes are somewhat ragged and irregular, and the hexagonal outline is only crudely shown (Fig. 4).
Fig. 4 Electron micrograph of Kaolinite.
Lombarid et al. studied the compositional and structural variations in the size fractions of a sedimentary and hydrothermal kaolin. The 16-8-, 8-5-, 5-2-, 2-1-, 1-0.5-, 0.5-0.3-, 0.3-0.1- and 0.1 μm size fractions were centrifuged from a Georgia (USA) sedimentary kaolin and a hydrothermal kaolin from the Sasso mine (Italy) and analyzed by SEM, XRD, IR, DTA and TGA together with the corresponding whole rocks. All size fractions of the Georgia samples consisted dominantly of well crystallized, fine grained kaolinite, associated with minor quantities of smectites. Some halloysite-like elongate particles, were noted by SEM in the intermediate size fractions, minor amounts of quartz were identified in the coarsest size fractions and 1% noncrystalline material and traces of organic material were suspected in the finest size fraction. The crystallinity of the kaolinite as measured by XRD and IR varied moderately with size. IR suggested the nacrite like stacking disorder increased with decreasing size for particles < 5 μm in size.

Hinckley studied the variability in crystallinity values among the kaolin deposits of the coastal plain of Georgia and South Carolina in the following way. Quantitative measurement of the relative degree of crystal perfection among 144 samples of coastal plain kaolin showed that the
deposits were nonhomogeneous with respect to crystallinity and that the hard and soft type could be distinguished at the 0.95 probability level by an analysis of variance. The nonhomogeneity of the deposits and the distinction between the hard and soft types agreed with the result obtained for other properties. Although on the basis of the pulverizing ease there might be a single population with hard and soft end members in terms of origins, the evidence indicated the existence of distinct clay population.

The crystallinity index of kaolinite in relation to other properties of kaolin mass of Karlovy Vary (Czechoslovakia) was studied by Konta. Relative to K-feldspar, the plagioclase grains in the kaolinized granite of Karlovy Vary had weathered to a purer, more readily dispersible kaolinite characterized by a high crystallinity index. For the Karlovy Vary kaolin, increase in bulk density correlated with increased concentration of quartz and/or unweathered K-feldspar and biotite and with an increased crystallinity index for the kaolinite in the < 20\(\mu\)m size fraction.

Plancon et al studied the stacking faults in kaolin group minerals. The study examined nine kaolined samples having a large diversity in defect contents as indicated by Hinckley indexes ranging from 1.44 to 0.18.
The samples were chosen so as to cover this range in as regular a manner as possible.

The types and abundance of the defects were determined by examining the x-ray powder diffraction properties for the 02, 11 and 20, 13 bands. The diffraction intensities were measured by counting for a fixed time in steps of 0.01°2θ. Analysis of these diffraction profiles indicated that (i) the major defect is the existence of a translation between adjacent layers, which is not the usual t (approximately a/3) but is related to that translation by the pseudomirror plane coincident with the long diagonal of the unit cell (2) the existence of a few C-layers among the B layer stacking is a minor defect (3) many of the samples would be accurately modelled only by assuring the existence of two kaolinite phases (4) the existence of only a few C-layers in some samples does not support the idea of a continuous series from kaolinite through disordered intermediates and (5) the Hinckley indexes of several samples depend on the relative proportions of the two types of kaolinites in the mixture.

Grum-Grzhimailo and Makarov studied the surface activity of calcined kaolins with different degrees of
crystallinity. They observed that the surface activity of calcined kaolin depended on the temperature and structural state of the crystals of kaolinite. This dependence permitted more controlled use of kaolin raw material.

Brindley and Robinson\textsuperscript{39-40} studied extensively on the x-ray diffraction for kaolinite. In general the determination of the kaolinite group by x-ray diffraction is simple but the identification of the particular members of the group may be more difficult. The prominent basal reflections at about 7.14 kx (001) and 3.57 kx (002) are usually adequate for identification.

Information on the bonding state of elements in the clay structure, as well as on bond directions, can be obtained from infrared absorption spectroscopy. Various workers studied extensively the infrared absorption spectra of kaolinite and correlated it with different parameters.

Serratosa and Bradley\textsuperscript{41} determined the orientation of -OH bond axes in layer silicates by infrared absorption. Stubican and Roy\textsuperscript{42} studied extensively the infrared spectra of kaolinite and other layer-structure silicates and correlated it with the structural features of these minerals.

Gribina\textsuperscript{43} et al studied spectroscopically the disorder in the structure of kaolinite. Kaolinite from
different regions of USSR with various crystallinities were
examined by x-ray analysis, IR spectroscopy, electron
microscopy and absorption methods. Both the dimensions of
the particles and their specific surfaces were found to be
dependent on the structure. The author utilised IR method
for qualitative and quantitative estimation of the structure
of kaolinite mineral. The experimental quantitative method
for determination of the crystallinity was described on the
basis of peak intensity at 1100 cm⁻¹. The results agree with
those obtained by using x-ray and Hinckley's coefficient.

Miller and Dulton ⁴⁴ studied spectroscopically the
effect of grinding kaolinite with potassium bromide. When
grinding was used in the mixing step in the KBr pressed disc
technique for the IR study of kaolinite, severe changes in
the intensities of some of the -OH stretching bonds occurred
due to an interaction between the KBr and kaolinite. The
variation of this rapid and large effect with storage,
concentration changes and wet grinding were determined.

Ziao-Hui and Jin ⁴⁵ studied the mechanochemical
changes of kaolin during dry grinding by the characteri-
sation of particle size distribution, surface area, SEM, XRD,
IR spectra, DTA, TG and inverse gas chromatography. Amor-
phization, dehydration, alteration of surface property and
aggregation of kaolin were explained from such studies.

Laxmi and Kapoor developed a technique for the identification of kaolinite mineral by infrared spectroscopy. The applicability of IR spectroscopy was demonstrated by the author for the identification of small amount of kaolinite in soil clays. The <2μ size fraction saturated with Na+/K+ cation and evaporated to dryness at room temperature was used for this analysis. The spectral curve for a sample containing both kaolinite and chlorite showed distinct shoulders at 3695, 3660 cm^{-1} and a strong band at 3620 cm^{-1}. The shoulder at the 3660 cm^{-1} band was ascribed to the presence of interlayer H-bonded -OH groups. The 3rd kind of OH group which was directed toward the vacant octahedral site, absorbed near 3620 cm^{-1}. So utilising this technique, the presence of a small amount of kaolinite can be detected in a synthetic mixture of chlorite and kaolinite by comparison the IR spectra.

The effect of pellet pressing on the infrared spectrum of kaolinite was studied by Bell et al. The authors observed that the magnitude of IR spectrum change in the case of kaolinite, depended on the absolute pressure,
pressing time and whether or not a salt matrix was used. Pressing with KBr caused larger differences in IR spectra than pressing neat. The authors further observed that diffusion reflectance IR did not require pressing.

Faglind et al determined quartz and kaolinite minerals in sedimentary rocks by IR spectroscopy. Binary mixture of quartz and kaolinite was analysed by IR spectroscopy using multiple linear regression equation derived from known mixtures.

Foldvar et al studied on the factors influencing the IR spectrometric determination of the crystallinity state of kaolinite. The most important parameters influencing the IR determination of kaolinite crystallinity were found to be the sample preparation method and the interference of accompanying phases. The reliability of measured indexes, deviations, the use of individual indexes and the ways to eliminate errors were discussed by the authors. The method and the type of indexes were outlined for the most suitable determination of kaolinite crystal structure.

Infrared absorption spectra of minerals of the kaolinite-haëloysite series was further studied by Xiuling and KaiHui. The rather similar IR absorption spectra
obtained for samples of kaolinite, fire clay mineral, halloysite and endellite were interpreted as showing a regular change in IR absorption behaviour induced by the progressive increase in disorder and in interlayer water content, which had characterized the following mineral transformation reaction, kaolinite→fireclay mineral→halloysite→endellite. Moreover, heat treated products of the four minerals yielded IR spectra that had showed an increasing structural disorder trend which followed progressive decrease in the thermal dehydroxylation temperature.

The effect of crystallinity or the quantitative determination of kaolinite was studied by Al-Khalissi and Worrabl. IR and x-ray diffraction were used to study the relation between the degree of crystallinity and x-ray diffraction patterns of kaolinites in several different kaolinitic clays. The area under the principal basal peak was found to be affected by the degree of crystallinity of the mineral and the authors deduced a linear relationship between them. This relationship can be utilised in the quantitative determination of disordered kaolinite in clay minerals.

Near infrared reflectance spectra of mixtures of
NIR reflectance spectra for mixtures of ordered kaolinite and ordered dickite had been found to simulate the spectral response of disordered kaolinite. The amount of octahedral vacancy disorder in the nine disordered kaolinite sample was estimated by the authors by comparing the sample spectra to the spectra of reference mixtures. The resulting estimates were observed to be consistent with previously published estimates of vacancy disorder for similar kaolin minerals that were modelled from calculated x-ray diffraction patterns. The ordered kaolinite and dickite samples used in the reference mixtures were carefully selected to avoid undesirable particle size effect that could bias the spectral results.

Johnston et al studied the polarized single crystal Fourier transform infrared microscopy of Ouray dickite and Keokuk kaolinite. Although numerous IR, FTIR and Raman spectra of polycrystalline kaolinite and dickite can be found in literature, the present data represent the first reported single crystal vibrational spectra for clay minerals. The orientation of the crystallographic axes of dickite was determined using a cross-polarising optical microscope fitted with an 550 nm optical retardation plate. Assignment
of the inner hydroxyl group OH, to the 3623 cm\(^{-1}\) band was confirmed and the angle of the OH group to the b-axis was determined to be 47° based upon the measurement of dichoric ratio. The 3702-3710 cm\(^{-1}\) absorption feature appeared to consist of two closely spaced bands having slightly different polarizing behaviour. The inner surface hydroxyl group OH\(_3\) was assigned to the absorption band at 3710 cm\(^{-1}\). The calculated angle of OH\(_3\) group to the b-axis was found to be 22°, which agreed well with the angles determined by x-ray powder diffraction and neutron diffraction. The remaining hydroxyl groups, OH\(_2\) and OH\(_4\) were assigned to the 3656 cm\(^{-1}\) band, the angles of the OH\(_2\) and OH\(_4\) groups to the b-axis was measured at 45°, the polarization behaviour of the -OH deformation bands of dickite at 911, 937 and 952 was found to be similar to that observed in the OH stretching region. Single crystal FTIR spectra of Keokuk kaolinite showed that rotation of electric vector around the c-z axis in the ab plane of kaolinite resulted in a behaviour distinct from dickite. This is related directly to the fact that dickite possesses a glide (space group C\(_c\)) compared to kaolinite which does not (space group C\(_1\)).

Brindley\(^{54}\) et al studied the relationship between structural disorder and other characteristics of kaolinite and dickite. A suite of Georgia kaolinite, ranging from
well ordered to very poorly ordered samples were studied to explore correlation between degree of structural disorder, geological environment, Fe$^{3+}$ content, Fe$^{3+}$ electron paramagnetic resonance (EPR) spectrum, and width. Samples of different locations showed a wide range of disorder which appears to be related to differences in their geological environment. High iron content of the clays correlated strongly with the degree of order. The areas of both the I and E component of the EPR spectrum and the fractional I area correlated inversely with degree of order. Fourier-transmission IR studies of kaolinites and dickite showed that (1) interlayer hydrogen bonding is weaker in dickite than in kaolinite. (2) Frequency of the $\gamma_1$ stretching band of the inner-surface hydroxyls increases sequentially from well ordered kaolinite through the disordered structures to well ordered dickite which is consistent with a model for disorder based on vacancy displacement and (3) the character and temperature dependence of the inner hydroxyl stretching band is not compatible with the crystal structure of kaolinite and dickite.

The interlayer bonding in kaolinite, dickite and nacrite was studied by Giese. The author used a simple electrostatic model to demonstrate that the inner-surface
-OH in kaolinite, dickite and nacrite were responsible for the interlayer bonding in these minerals. The contribution to the interlayer bonding of an individual hydroxyl was observed to be dependent on the orientation of the -OH group relative to the 1:1 layer since this orientation had determined the H-O interlayer distance. Further the author observed if this distance was much greater than the sum of the van der Walls radii, 2.60Å, there would be essentially no bond. As the distance became 2.6Å, the strength of the interlayer bond increased.

Costanzo et al studied the static and dynamic structure of water in hydrated kaolinites. In their work four hydrates with d(001) = 8.4, 8.6 and 10Å (two types) were synthesised by intercalating kaolinite with dimethyl sulfoxide and treating the intercalated clay with fluoride ion. X-ray powder diffraction, infrared spectroscopy, differential scanning calorimetry, thermal gravimetric analysis, and kinetics of dehydration experiments had led to the identification of two types of interlayer water. One type of water (hole water) was observed to be situated in the ditrigonal holes of the silica tetrahedral surface; the second type (associated water) formed a discontinuous layer of mobile water. The 8.4- and 8.6 Å hydrates had only hole
water, whereas the two synthetic 10A-hydrates and halloysite (10A) contain both hole and associated water. The authors concluded that the hole water was probably hydrogen bonded to the basal oxygens of the silica tetrahedra or in the 8A hydrates. When fluorine was exchanged for inner surface hydroxyls, the water molecules could be reoriented and formed stronger hydrogen bonds to the fluorine. Associated water formed water-water hydrogen bonds approximately equal in strength to liquid water but was less strongly bonded to clay surfaces than hole water. At room temperature the hole and associated water in the 10A hydrates did not form an ice-like structure.

Clay minerals possess the property of sorbing certain anions and cations and retaining these in an exchangeable state, i.e., these ions are exchangeable for other anions or cations by treatment with such ions in solution.

Marshall, Mukherjee and Mitra had shown that a single cation might be sorbed by a clay mineral with a wide range of bonding energies, and this could be fundamentally related to the position on the silica-alumina packet at which the cation was sorbed, e.g., whether it would be held between the sheets of the layered minerals or around their edges.
The cation exchange property of kaolinite had been investigated by many authors (Schofield and Samson, Cashen, Flegmann et al, Ferries and Jepson and Bolland et al) and varying views had been expressed about the existence and origin of permanent negative surface charge, distinct from the pH dependent positive and negative charges observed by most experiments. Ferries and Jepson in a very detailed study concluded that cation retention decreased to zero as the electrolyte approached infinite dilution, which indicated that no permanent negative charge was present on the surface. Bolland et al, however, believed that Ferries and Jepson reached this conclusion because they had not taken into account hydrolysis which led to hydroxy-Al species replacing the surface sorbed cation. Most authors seem to accept that kaolinite have a small pH-independent exchange capacity approximately 10-80 μeq g⁻¹ depending on particle size. The surface charge density is in the range 0.11 to 0.15 cm⁻² (Bolland et al) which is about the same as that of smectites. Thus it would be expected that the poorly crystalline kaolinite with a large specific surface would have a larger exchange capacity than the coarse grained samples; the cation exchange capacity as high as 250 μeq g⁻¹, that have been reported by some authors seem too high, implying specific surfaces of the order of
250 m² g⁻¹, which are not observed for kaolinites and Lim et al had concluded that exchange capacities greater than 10 μeq g⁻¹ were caused by impurity.

Zeta potential is another important electrokinetic property of clay minerals which is the most important factor governing the stability of dilute lyophobic sols.

Tuorila studied extensively the effect of various mono and divalent cations on the zeta potential of kaolinite. Muller attempted to formulate a general theory of coagulation based on the zeta potential in absence of disturbing factors. But disturbing factors are specially marked in the case of the clays. One, first noted by Oden concerns the sensitivity to coagulation of particles of different sizes. Oden found that in a polydisperse clay suspension of somewhat indefinite mineralogical nature, the coarser particles were coagulated at lower concentrations of electrolytes than the finer.

A second disturbing factor arises in the coagulation of clays in alkaline solution. Mattson showed than an increased adsorption of the divalent cation was found alongside the usual strong uptake of hydroxyl ions. He therefore suggested that the increased sensitivity was due to the formation of particle-particle linkages through
polyvalent cations. Schematically, one could have,

\[
\text{Clay}-\text{OH} - \text{Ca}-\text{OH-clay}
\]

This explanation was challenged by Tuorila who found a similar effect with a kaolinite clay. He demonstrated, as had Mattson, that the coagulation could occur at abnormally high values of the zeta potential, although this was not invariably the case. In these alkaline solutions no consistent relationship between zeta potential and rate of coagulation was found. Since the effects were particularly marked with bases which form sparingly soluble hydroxides, Tuorila was inclined to regard the increased sensitivity as due to the accumulation of insoluble hydroxide on the surface. The system, then is no longer a pure clay suspension, but a mixture of negatively charged clay with positively charged hydroxide, the latter partially coating the clay particles.

In suspension pure clay minerals show acidity. The work of Bradfield and of Wiegner, Pallmann established the fact that the acidity of clays is not due to substances in true solution. At lower concentration of clay there is a linear relationship between the concentration
of clay and the hydrogen ion activity as calculated from pH measurements. This bends around at higher concentration. This was found from the works of a number of workers who had presented pH titration curves for well characterized clay minerals using divalent bases (Baver, Mitra and Caldwell and Marshall). In general, the changes in slope are more gradual than for monovalent bases and the point of inflexion lies at a lower pH value.

The surface charge of aluminosilicates in aqueous solution was studied by Villu and Olteanu. The surface charge density as a function of pH and ionic strength in KNO₃ solution and the points of zero charge (P.Z.C.) were determined for a neutral (kaolin) and a synthetic aluminosilicate (a catalyst). The isoelectric point was determined by electrophoresis. There are differences between the p.z.c. measured for fast primary equilibrium of the surface with the potential determining ions (H⁺ and OH⁻) and the p.z.c. measured for slow equilibrium. For kaolin, the p.z.c. differences for fast (pH 4) and slow (pH 3) equilibrium are due to adsorption of some ions. For the aluminosilicate catalyst, the p.z.c. difference for fast (pH 4.3) and slow (pH 6) equilibrium are related to approach to equilibrium point (pH 6.21) of Al(OH)₂⁺ and Al(OH)₄⁻.
The role of exchange cations and bound water in the formation of kaolin acidity was studied by Gribina and Tarasevich\textsuperscript{76}. The exchange cations which have a large polarizing ability (Ca\textsuperscript{2+}, Mg\textsuperscript{2+} and especially Cu\textsuperscript{2+}) form aprotic acid centers in kaolinite. The partly dehydrated Ca\textsuperscript{2+} and Mg\textsuperscript{2+} forms of kaolinite have also the protonic acid centers on their surface. The protonic acidity of such centers is associated with the protolytic dissociation of the residual water molecules strongly polarized by the Ca\textsuperscript{2+} and Mg\textsuperscript{2+} ions.

The role of active center concentration in the formation of silicate-dispersion structure was studied by Pavolva\textsuperscript{77} et al. The relation between surface acid properties of natural kaolinite and its cation exchange form and the resulting geometric structure was examined by them. The exchangeable cations affect the concentration of active centres, the number and stability of coagulation contact points and the crystalline structure. A rational basis was proposed by the authors for a method to control the structural properties of inactive and subsequently thermally activated acid centres.

Carroll-Webb and Walter\textsuperscript{78} studied on a surface complex reaction model for the pH-dependence of corundum and kaolinite dissolution rates. Comparison of experimental and theoretical potentiometric titrations of kaolinite at
25°C indicates that the adsorption of H\(^+\) and OH\(^-\) ions to the mineral surface are metal cation specific and that the net adsorption can be modelled in terms of the constituent oxide components. Based on the potentiometric, electrophoretic and dissolution rate data presented, it was concluded that the pH-dependence of the dissolution rates of slightly soluble oxide and silicate minerals was controlled by the adsorption of H\(^+\) and OH\(^-\) ions to specific metal cation on the surface reaction sites.

Assaad and Elnekaw\(y\)\(^7\) studied the relation of physicochemical properties of alkaline metal cations to the exchange selectivity on kaolinite clay. The cation exchange selectivity coefficients were determined at 40°C along with thermodynamic parameters of exchange reactions between the kaolinites. The free energy of exchange reactions correlated linearly with the reciprocal of the distance of the closest approach. The entropy of the adsorbed ions correlated with that of the ions in solution, indicating an ordering both before and after the exchange reaction. The difference in the polarizability of the outgoing and incoming ions controls the effect of entropy on the energy level of the exchange reactions.

The kinetics and mechanism of kaolinite dissolution in H\(_2\)SO\(_4\) solution of several concentrations were studied by
Aglietti et al. A1 was extracted at 130, 150 and 170°C in closed reactors operating at ≤1 MPa. The dissolution curves correspond to the kinetic model of nucleation and growth. The existence of a compensation effect between the pre-exponential factor of the Arrhenius equation and the apparent activation energy of the process was observed. A mathematical expression for the pre-exponential factor of the Arrhenius equation was found to be a function of the acid concentration.

Aglietti et al further studied the kinetic aspects of acid dissolution of kaolinite after mechanochemical treatment of the mineral. The kinetics and mechanisms of acid dissolution of two kaolinites with different degrees of crystallinity were studied by them. These minerals were obtained by mechanochemical treatment of a well-crystallized kaolinite. The parameters obtained through a nucleation and growth model (rate constant, pre-exponential factor and apparent activation energy) were analyzed by them. The reaction rates were found to be strongly dependent on the concentration of superficial defect created through the mechanochemical treatment. Cation exchange capacity was used as a representative parameter to describe the observed increase in reaction rates.
In principle kaolinites should present a comparatively simple surface for water sorption. The particles are relatively large, often 50% or more greater than 0.5 μm and easily measured in the electron microscope. The interlayer spacing is not affected by water sorption (unless the kaolinite has been intercalated) or by varying humidity. The sorption of water should therefore be analogous to that on other oxides and hydroxides.

In detail the sorption properties are not quite so simple although some observers (Martir⁸², Lloyd and Conley⁸³) have calculated that the geometric surface is similar to the surface measured by N₂ sorption. Others (Olivier and Sennett⁸⁴) have found that the N₂ surface is considerably greater than that predicted from particle size measurements. Scanning Electron Microscopic study showed that kaolinite particles consisted of booklets and that some of the additional porosity must be occurring between the leaves of the booklet.

Most kaolinites have cations balancing the surface charge and the effect of cation form on water sorption was investigated by Keenan⁸⁵ et al and Martin⁸² and Jurinak⁸⁶. The results of these investigations calculated in accordance
with the BET equation and expressed as reduced isotherms, impressively demonstrate the concordance of the data. The BET "C" parameter, which relates to the energy of interaction is influenced by the surface cation, as in the monolayer coverage, $\chi_m$. Although the extent of variation of $\chi_m$ with cation varies with investigators, all agree that Li-saturated kaolinite have the smallest monolayer coverage. This was originally explained (Keenan et al) by supposing that Li through its small size was able to fit into the structure so that it no longer influenced hydration of the surface and subsequent work (Martin, Jurinak) tended to confirm this. Greenkelly showed that Li introduced into the cation exchange positions was found to be non-exchangeable after drying by heating at 200°C. It should be noted however, that the effect of surface cation on monolayer coverage observed by later workers was much less marked than in the original publication by Keenan et al.

Recent work has emphasized the arrangement and energy of interaction of water with the surface of kaolinite. Dielectric measurements of kaolinite-water system (Muir, Nelson et al) have shown that loss occurs in two frequency regions. The low frequency loss increasing with decreasing frequency below 1000 Hz is attributed to conduction effects, but the loss maxima in the region 10-100 KHz is believed to
arise from relaxation of dipole rotations. The energy region indicates that the bonding of water molecules is intermediate between that in free water and ice.

Heats of immersion and NMR measurements were made on Georgia kaolinite by Fripiat et al. and the NMR studies were extended to high pressure by Jonas et al. As the surface coverage before immersion is increased, the heat for immersion per unit surface declines steadily to a constant value of 119.5 mJ m\(^{-2}\) at average coverage of 2.6, indicating that the range of surface forces declines rapidly after the second multilayer is completed. In free water, the measurement by NMR of \(T_1\), the spin-lattice relaxation time, has shown that increasing pressure distorts the random hydrogen bond pattern of the structure at atmospheric pressure whereas adjacent to the kaolinite surface this does not occur, the implication being the hydrogen bond pattern is already non-randomized by the adjacent surface. The activation energies for reorientation of the water molecules are lower than in free water and the influence of the surface extends for three to four layers of water (Jonas et al).

The effect of exchange cations on the specific heat of wetting of layered silicates having rigid structures
was studied by Polyakova et al. The heat of wetting of cation exchanged forms of kaolinite, pyrophillite and talc by water was determined microcalorimetrically. The specific surface areas of the silicates were determined by low temperature desorption of Ar. The effect of the cationic form and the characteristic structure on heat of wetting was discussed by the authors.

Gilenti et al studied the water-kaolinite interaction by measurement of complex permittivities. Measurement of conduction (dielectric losses) and real part of permittivity were performed, at variable frequency (10^3-10^7 Hz) and as a function of temperature (27-80°C) in order to study the interaction between vapour and kaolinite. The conduction was found to be increased with frequency and temperature. The use of a conduction model involving proton hops between localized sites proved suitable. The law $\omega^3$ was verified. The real part of the permittivity was found to be decreased with frequency and increased with the water vapour pressure. A simple calculation led to the experimental law

$$\varepsilon' \sim \exp(K \sqrt{P})$$

Blanc and Escouber studied the effect of the nature
of the active sites on the adsorption of water on kaolinite. Water adsorption on kaolinite as observed by the workers, was a specific cooperative adsorption which did not satisfy the fundamental hypothesis of the BET theory. The adsorption on different homoionic samples showed the effect of the hydration energy of the active sites (exchangeable cations) on quantitative adsorption. The corresponding calorimetric curves was found to have a maxima which characterized interaction in the adsorbed phase. A relationship was deduced by the workers between the interactions and the electrical field or polarizability of the fixed cations, which determined the nature of the bond between the surface and the cation. An approximate value was given for the number of moles which composed the primary hydration sheath of the active sites.

Anderson et al. studied the water-ice phase composition of kaolinite/water system. Previous studies indicated that when water-ice phase composition curves are normalized to unit surface area, the unfrozen water content values at given temperature for the kaolinite-water system are higher than those of other soil and soil constituents. The water-ice phase composition curves for this system has been redetermined using an improved isothermal calorimeter and the earlier curves confirmed.
The static-dynamic structure of water in hydrated kaolinites was studied by Lipsicas et al. The authors used NMR measurements of $H_2O$ intercalated into kaolinite and identified two types of interlayer water, one of which was found to be more mobile than the other. This was consistent with the previous works and suggested that the less mobile $H_2O$ is attached to the tetrahedral surface (hole water) and the more mobile water (associated water) is less strongly bonded to the clay surface. Both types of $H_2O$ were found by the workers in a 10-A hydrate while only hole $H_2O$ was observed to be present in 8.4 and 8.6 A hydrates. Motions of both types of water were observed to be slower than bulk water. At a temperature of higher than 260 K an anomaly in the specific heat of water in the 10A hydrates was observed by the workers. This may be associated with a transition involving two dimensional melting.

Dehydroxylation of most kaolinites occurs in normal temperatures above and about 400°C and is accompanied by a weight loss of 14.0% which corresponds with the formula $Al_2Si_2O_5(OH)_4$. Extensive studies by differential thermal analysis (Holdridge and Vaughan) have shown nearly symmetrical endothermic peaks with maximum values near 550-600°C and with a width which diminishes with increased
rate of heating. The exceptionally well-crystallized Keokuk geode kaolinite however, gives a markedly different endothermic peak (Keller et al) which combines a broad peak near 600°C and a sharper, higher peak near 700°C which are not easily resolved into separate reactions. Keller et al considers that the "higher dehydroxylation temperature is the true and characteristic dehydroxylation peak of kaolinite" and that the lower dehydroxylation temperature shown by most "typical" kaolinite may be attributed "to inferior ordering and crystallinity plus some effects from the small crystal size".

X-ray powder diffraction studies normally indicate an almost amorphous product after dehydroxylation but single crystal analysis indicates that some structural order is maintained. Retention of structural order evidently is related to the particular polymorphic form of kaolin minerals, to the degree of crystalline order, and perhaps also to crystal size and other variables. Brindley et al studied the better crystalline polymorph nacrite and Roy et al applied electron diffraction to single crystal of micron size and in both studies some retention of crystallinity was observed. Structural modification of dickite, more particularly of the better structurally ordered forms, have
been observed by Brindley and Wan\textsuperscript{103}, but they observed no similar changes with the Keokuk geode kaolinite, although there were markedly similarities in their DTA curves. Evidently a complex relationship exists between the polymorphic form of kaolin mineral being considered, in state of crystalline order, the particle size and possibly other variables such as water vapour pressure (i.e. without the higher pressure used in hydrothermal studies).

The work of Brindley and Nakahira\textsuperscript{104} using single crystals of kaolinite shows that order persists mainly within the individual structural layers but not between the layers. The progressive disordering of the basal planes was analysed by Mitra\textsuperscript{105} et al. The hk diffractions persist after dehydroxylation but 001 and hkl diffractions usually are not obtained. However, Redetzewski and Schadel\textsuperscript{106} by electron diffraction from dehydroxylated crystals standing on edge succeeded in measuring basal spacings about 6.3\textbf{A} which agrees with estimates made by Brindley\textsuperscript{104} et al, from density considerations. If metakaolin is only slightly less dense than kaolinite, as various authors have found (Ricke and Mauve\textsuperscript{107}, Brown and Gregg\textsuperscript{108}) despite the 14% weight loss due to dehydroxylation then the layers must collapse to about the same extent although in a very regular manner. This argument was not
accepted by Freund who considered that spaces left behind after release of water amounted to 20% by volume. Surface area measurements by BET gas adsorption methods, however, show little change in the available surface of metakaolin (Brown and Gregg, Gastuche et al) which may even decrease slightly.

There is much controversy about the product obtained after dehydroxylation of kaolinite. According to some investigators the residual solid is a mixture of $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ whereas according to other investigators the product is an anhydride of clay having the formula $\text{Al}_2\text{O}_3\cdot2\text{SiO}_2$. Sachsse and Becker showed that the whole of $\text{Al}_2\text{O}_3$ in dehydroxylated kaolin dissolves in dilute hydrochloric acid but firing at higher temperature renders it insoluble. Rinne investigated the nature of dehydroxylated products by x-ray spectroscopy. He obtained no sharpline for quartz, tridymite or cristobalite but only two diffuse bands and termed the product of dehydroxylation metakaolin. Comfero et al obtained similar results and showed that hexagonal shape of kaolinite was preserved above 600°C. Eitel and Kedesdy showed by electron diffraction study that lamellar form of kaolin remains up to 700°C. Planz and Muller Hesse reported the existence of metakaolin from IR study.
Brindley and Nakahira\textsuperscript{104} established the fact that metakaolinite cannot be regarded as oxide mixture. According to them metakaolinite is a two dimensional crystalline phase of composition $\text{Al}_2\text{Si}_2\text{O}_7$, having layer spacing of 6.3Å, consistent with the density. According to Kalinina and Porai-Koshits\textsuperscript{116} metakaolinite in the range 600-850°C contains firm bonds between the component oxides as an inherited structure from kaolinite.

Tscheischwili\textsuperscript{117} et al first proposed a structure of metakolin in which Si-O network remains largely intact. Structure of metakaolinite proposed by Brindley and Nakahira\textsuperscript{104} contains Si-O essentially similar to that in kaolin but aluminium occupies tetrahedral position with lesser number of oxygen atom, with the possibility of increased disturbance in kaolinite lattice. Taylor\textsuperscript{118} concluded from his study of mechanism of dehydroxylation that in kaolinite no oxygen is lost from the acceptor region and the oxygen packing in these regions tends to remain the same as that in the original kaolinite.

Thermodynamic of the various high temperature transformations of kaolinite was studied by Schieltz and Soliman\textsuperscript{119}. Thermodynamic calculation of $\Delta G$ for all
possible transformations of metakaolin at the temperature of the first DTA exothermic peak indicates that the most stable transformation is the one that yields mullite rather than $\gamma$-Al$_2$O$_3$.

Costanzo and Giese$^{120}$ studied the dehydration of synthetic hydrated kaolinites to prepare a model for the dehydration of halloysite. Several hydrates can be synthesized from well crystalline kaolinites. The authors synthesized a 10A hydrate (called Q5-10 hydrate) and 8.6A hydrate and two kinds of partially dehydrated mixed layer hydrates. One kind was a series of unstable material with $d$(001) varying continuously between 10 and 8.6A and the other kind is stable with $d$(001) approximately centered at 7.9A. The 10 and 7.9A phases were observed in halloysite by many workers using x-ray powder diffraction and the 8.6A phase was observed by others in selected area electron diffraction photograph. IR spectra reveal additional similarities between the synthetic hydrates and both halloysite (10A) and partially dehydrated halloysites. Because of these similarities, the synthetic hydrates can be used to develop a model for the dehydration of halloysite (10A). Previous work on the 10 and 8.6A hydrates identified two structural environment for the interlayer water. In one, the water was observed to be keyed into the ditrigonal holes of the silicate
layer (hole water) and the other, the water, is more mobile (associated water). Both types was found by the authors in QS-10 hydrate and halloysite (10A) whereas only hole water was found in the 8.6A hydrate. In the QS-10 hydrate, stronger hydrogen bonding between hole water and the clay makes the hole water more stable than the associated water. The difference in stability is responsible for a two step dehydration process. The first step is the loss of associated water which results in a material with d(001) = 8.6A. This stable hydrate must be heated to temperature \( \sim 200^\circ C \) to drive off the remaining hole water. The less perfect structure of halloysite and its common curvilinear morphology was found to reduce the difference in stability between the hole and associated water so that when halloysite (10A) dehydrates, loss of hole water and associated water overlapped and the d spacings went directly to 7.2-7.9A.

Davies\(^{121}\) studied on the flash dehydroxylation of kaolinite. The effect of furnace atmospheres, composition of kaolinite, specific gravity and the degree of dehydroxylation of the calcined material was examined by the author. As the heating rate or thermal condition of the furnace atmosphere was increased, the extent of void formation increased.
Most calcines had degree of dehydroxylation at ~75% of the specific gravity minimum. The author concluded that the void formation process which occurred when powdered kaolinite was rapidly heated might be controlled by the heating rate and maximization of the process was likely to be achieved when the heat transfer conditions result in calcines which were ~75% dehydroxylated.

A model of non-isothermal firing of a cylindrical kaolin body in the dehydroxylation region was studied by Mazacova et al. A general mathematical model of ceramic body firing in the dehydroxylation region, regarding the process as diffusion involving a chemical reaction and conduction of heat with a source is supplied to, calculation of time, development of concentration and temperature profile during nonisothermal firing of a cylinder body of kaolinite was developed by the authors. The calculated time, development of concentration and temperature profile was verified experimentally at 2-heating rates and a satisfactory agreement was found by them.

Komusinski and Stoch studied the dehydroxylation of kaolinite group minerals by electron spin resonance spectroscopy. Nacrite, dickite, kaolinite and halloysite were heated to 1400°C and investigated by means of ESR at
The results show systematic differences, some of which are related to the crystallinity of the kaolinites and to the mutual orientation of the adjacent layer in polytype modification. The most intense features of the spectra, centered at g values of 4.3 and 3.0 are attributed to Fe$^{3+}$ ion occupying different sites in the structure. Studies of the changes caused in the ESR spectra by thermal treatment led to some general conclusions about structure modification.

De et al studied the dehydration transformation in kaolinite by RDF analysis. Structural changes in kaolinite during dehydration were studied by calculating the radial distribution function (RDF) from the x-ray diffraction intensities. An estimation of the interatomic distances, relative strength of the coupling and the coordination numbers was obtained for the samples at room temperatures and treated at higher temperatures. The results show high stability of the Si-tetrahedral layers compared to the Al-O-(OH) octahedral layer.

Bhattacharjee and Bhattacharya worked on X-ray line broadening study of kaolinite under dynamic heating. X-ray line broadening study of the basal
reflections from two kaolinite samples under dynamic heating condition up to a range of $\sim 400^\circ C$ was carried out in a simple high temperature attachment designed and fabricated for this purpose. The results showed the existence of structural defects in both the samples. Dehydration was observed to be not complete within the range of temperature studied under the condition of heating adopted.

The dehydroxylation entropy of kaolinite was determined calorimetrically by Petzold et al. The standard reaction enthalpy for the conversion of kaolinite into metakaolinite and water was determined in a high temperature flow calorimeter as $230 \pm 21$ KJ/Mole and the standard decomposition enthalpy of metakaolinite was calculated as $-3406 \pm 24$ KJ/Mole. The data was obtained in tests with eight kaolinite samples which were characterized by chemical, mineral phases, thermal and x-ray diffraction analysis.

The exothermic effect at $975^\circ C$ of kaolinite is a subject of discussion. Gerard-Hinne and Maneret discussed that it is caused by recrystallisation of amorphous alumina to spinel like $\gamma$-alumina, or an early formation of mullite. This opinion is contradicted with the fact that distinct
interference lines of mullite commonly are not observed unless metakaolin is heated at least to 1150°C or higher. Richardson\textsuperscript{128} indicated the presence of $\gamma$-$\text{Al}_2\text{O}_3$ from 950 to above 1350°C for kaolinite are dependent on the crystallinity of the original clay minerals. Glass\textsuperscript{129} speaks of metakaolinite as an "amorphous compound" of silica and alumina which persists to the major exothermic peak at 975°C and then collapses to form $\gamma$-$\text{Al}_2\text{O}_3$, amorphous silica and "mullite nuclei". Wahl\textsuperscript{130} investigated the phase changes on heating by continuous x-ray technique and reported the formation of primary mullite at 975°C and secondary mullite at 1200°C.

Levedev\textsuperscript{131} discussed the exothermic effect from the viewpoint of the strongly homopolar bonding of Si-O in the (SiO$_4$) network of kaolinite in contrast with the prevailing ionic bond of the (AlO$_6$) coordinates. After dehydroxylation and destruction of the octahedral structural layer, Levedev\textsuperscript{131} assumed a migration of Al$^{+3}$ ion occurred under the action of electrostatic forces into empty positions previously occupied by hydroxyl groups to characterize the metaphase. At 800-900°C a rearrangement to $\gamma$-$\text{Al}_2\text{O}_3$ interrupted the definite loose connection of these aluminum ions with the tetrahedral network. The unstable oxygen positions at the ruptures have a very
high electron affinity (230,000 Cal/atom) which induced nucleation of aluminium silicates with an energy release causing the exothermic peak in the DTA curves.

A number of works have so far been done on the reconstitution of structural hydroxyl groups with the clay lattice. Following the work of Grim and Bradley\textsuperscript{132} various experiments have shown that some degree of rehydroxylation of dehydroxylated clay minerals may occur under relatively mild condition of hydration, such as exposure to atmospheric moistures or immersion in water over long period, or by passing steam through differential thermal equipment when the sample cools from a temperature above the dehydroxylation range.

The reconstitution of kaolinite group minerals (kaolinite, dickite, nacrite, halloysite) under hydrothermal treatment was examined by Roy and Brindley\textsuperscript{133} and they showed that in all cases some form of kaolinite was developed.

Hurst and Kunkle\textsuperscript{134} studied the dehydroxylation, rehydroxylation and stability of kaolinite. From hydrothermal experiments three pressure temperature time curves have been refined for the system $\text{Al}_2\text{O}_3$-$\text{SiO}_2$-$\text{H}_2\text{O}$ and reversal temperatures established for two of the principal reactions involving kaolinite. The temperature of three isobaric
invariant points enabled the Gibbs free energy of formation of diaspore and pyrophillite to be refined and the stability field of kaolinite to be calculated. The maximal temperatures of stable kaolinite decreases from 296°C and 2kb water pressure to 284°C at water's liquid/vapour pressure and decreases rapidly at low pressures on an isobaric plot of \([H_4SiO_4]\) vs. \(0^\circ K^{-1}\). Kaolinite has a wedge shape stability field which broadens toward lower temperature to include much of the \([H_4SiO_4]\) range of near surface environments. If \([H_4SiO_4]\) is above kaolinite stability field and the temperature is <100°C, halloysite forms rather than pyrophillite, an unknown pedogenic mineral. Pyrophillite forms readily instead of kaolinite above 150°C if \([H_4SiO_4]\) is controlled by cristobalite and noncrystalline silica.

Lutz et al studied experimentally the dehydration and hydrothermal rehydration of kaolinite. The authors found that the optical properties of kaolinite were improved by dehydration at 500-900°C and subsequent hydrothermal treatment at 250-280°C and water vapour pressure 55-65 bar. The dehydrated reaction products were completely transformed into kaolinite during hydrothermal treatment. The specific surface area of the dehydrated and hydrothermally treated kaolin was 5-7 times that of the initial material. The whiteness decreased slightly during
hydrothermal treatment; however, the reflectance of the final product was nearer to the point of achromaticity.

The dehydration and rehydration of clay minerals by infrared absorption spectra was studied by Serratosa. The process of dehydration and rehydration of montmorillonite and nontronite samples had been studied through infrared absorption spectra. The changes observed in the intensity of the bands during dehydration showed the analogy between absorption at 915 cm\(^{-1}\) (montmorillonite) and at 820 cm\(^{-1}\) (nontronite), their origin being deformed vibration of OH groups. During rehydration of the montmorillonite sample, the recovered OH groups occurred in two different forms in accordance with the results of differential thermal analysis.

Hill specially studied the problems of rehydration of fired clay minerals (exposed to 500°C to 1150°C) by treatment with steam for periods up to 96 hours at 200°C. The author found a practical limit of temperature above which no more rehydration appeared to be possible, namely 1000°C for kaolinite, 950°C for illite and 900°C for montmorillonite. Regenerated kaolinite, however, is different from initial material showing formation of hydrargillite in the x-ray powder diagram. An endothermic
effect is observed at 280°C in the DTA curves and this effect is the greatest if kaolinite is fired at 950°C. Hill\textsuperscript{137} concluded that water was resorbed in a "zeolite" like compound as previously presumed by other workers.

Saalfeld\textsuperscript{138} determined a "fire clay like" mineral in rehydroxylated product of calcined kaolinite under a water pressure of 100 atmosphere at 300°C with a relatively good order of the structure in the single crystallites but with considerable disorder in their mutual aggregation of larger particles. If Mg\textsuperscript{2+} ion is present in water, rehydration phases are formed intermediate between kaolinite and serpentine. Roy and Brindley\textsuperscript{133} showed that degree of conversion of metakaolin to kaolinite by hydrothermal treatment varied with temperature, pressure and time.

Dietzel and Dhekne\textsuperscript{139} studied the properties of rehydrated "fire clay like" products of remarkably increased degree of workability in comparison with original kaolinites and higher CEC and specific surface as a consequence of disturbed structure. Thermogravimetric dehydration curves show characteristic distinction of the original kaolin and rehydrated calcined products. Infrared spectra show relative changes in transmissivity minima between 2.7 and 2.8. Intensity of absorption at 2.76 is
distinctly lower than that of 2.72 indicating differences in type of bonding of hydroxyl groups in rehydrated products. Correlation between infrared absorption characteristics with T.G. behaviour and the deuterium uptake in heated clay was shown by Roy.\textsuperscript{140}

Evans and White\textsuperscript{141} investigated the nature of back reaction of rehydration of decomposed clay in steam. According to them the hydrate form is metastable and differs from original clay mineral. The reconstituted -OH groups are less firmly held with the clay lattice.

Metcalfe and Wilcock\textsuperscript{142} studied on the absorptive elastic moduli of kaolinite and porous glass and examined the structure of the adsorbed phase. The change in length of rods of kaolinite and porous vycor glass when exposed to H$_2$O, MeOH, CHCl$_3$, CCl$_4$ and C$_6$H$_6$ vapors at room temperature were examined. Saturated nitrogen surface areas were determined from nitrogen isotherm at 77°K. Differences in the elastic moduli of the absorbent with different absorbates were due to inappropriate application of the Gibbs equation to adsorption at the gas-solid interface for the prediction of the size of forces exerted in the adsorbent.

Rocha\textsuperscript{143} et al observed the rehydration of
metakaolinite can generate kaolinite coexisting evidence from solid state NMR and cognate techniques.

Zyla studied the sorptive properties of clay minerals in detail. Sorption of polar (H$_2$O, MeOH) and nonpolar (n-hexane, Ar) substances on kaolinite, illite and montmorillonite was investigated by the authors. Dependence of the sorptive capacity on the mineral structure and the interlayer space cation was established and the diffusion coefficients for H$_2$O and MeOH vapours were calculated by the author. Preferential absorption of MeOH was demonstrated by the author with higher effective diffusion coefficients as well as by shorter time for attaining diffusion equilibrium. The enhanced absorption was ascribed to the self adjustment of the sorption coefficients.

Many experiments on the kinetics of dehydroxylation have been undertaken with a view to determine the mechanism of dehydroxylation reaction but this objective goes beyond what can be obtained from a kinetic study of a solid state reaction. The results are relevant only to the rate-controlling process, which may not involve the primary mechanism.

Isothermal gravimetric methods are well suited to
these kinetic studies but require much repetitive work. Dynamic methods, such as dynamic gravimetric analysis and differential thermal analysis, offer great convenience by covering both time and temperature variation in a single run (Freeman and Carroll\textsuperscript{145}, Coats and Redfern\textsuperscript{146}, Achar\textsuperscript{147} et al, Sestak\textsuperscript{148} et al) but the difficulties of interpretation are greater than for multiple isothermal runs.

A method of comparing kinetics of isothermal solid state reactions based on the classical equation for analysis of nucleation and growth process had been described by Hancock and Sharp\textsuperscript{149}. In this method plot of ln(1-\(\alpha\)) vs. ln(time), where \(\alpha\) is the fraction reacted, were used to distinguish reaction mechanism. Even non integral slopes obtained for values of the fractions reacted from 0.15 to 0.50 may indicate whether the reaction rate is diffusion or phase boundary controlled.

Sharp and Carter\textsuperscript{150} pointed that it is virtually impossible to distinguish amongst three diffusion mechanism which are

Diffusion in (001) direction, i.e., perpendicular
to the plane should follow the parabolic law.

\[ D_1(\lambda) = \lambda^2 = \frac{k}{x^2} t \]

Two dimensional diffusion into a cylinder of radius 'r' should follow the equation,

\[ D_2(\lambda) = (1 - \lambda) \ln(1 - \lambda) + \lambda = \frac{k}{r^2} t \]

Three dimensional diffusion starting at the exterior of a sphere of radius 'r' is given by,

\[ D_3(\lambda) = (1 - 2\lambda/3) - (1 - \lambda)^{2/3} \]
\[ = \frac{k}{r^2} t \]

where \( \lambda = \frac{\text{fraction of the sample dehydroxylated}}{\text{thickness of plates}} \)

until decomposition is more than 70% complete and a good fit to 100% is desirable.

The dehydroxylation reaction rates of clay minerals vary greatly with the ambient vapour pressure even at low
pressure in the range 0.1-10 Torr. At higher pressure, the reaction proceeds at considerably increased temperatures until eventually the character of the reaction itself changes, as shown by Weber and Roy\textsuperscript{151} for kaolinite. The results, however, belong to the hydrothermal range.

The mechanism involved at low vapour pressure are still not clear but almost certainly involve surface considerations. A simple model which fits experimental results considers that a fraction, $B$, of the surface is covered or blocked by chemisorbed molecules (Brindley\textsuperscript{152,153} et al) and the reaction reaction rate is proportional to the free surface, $(1-B)$, with the empirical relation, $B = mP^n$, the reaction rate $K(P)$ at pressure $P$, is given by

$$K(P) = K_0(1-mP^n)$$

where $K_0$ is the reaction rate in vacuo. Experimental results for kaolinite and serpentine, for a range of temperatures and vapour pressures fits this relationship.

When the vapour pressure is raised to a value such that $mP^n > 1$, the reaction rate is reduced to zero. This is illustrated by the results obtained by Brindley and Millhollen\textsuperscript{154} where a kaolinite sample dehydroxylation in vacuo at 42°C ceased to react when water vapour at 47 Torr was admitted.
The thermobalance showed a gain of weight equivalent to about a monolayer of water molecules. The dehydroxylation was resumed immediately the vacuum was restored and monolayer removed.

Fundamental kinetic studies of dehydroxylation of clay minerals were made by Brindley and Nakahira. The stationary state reached under isothermal conditions in heating kaolinite and other clay minerals and the rate of dehydroxylation depends broadly on crystal shape, size and thickness of samples used for dehydroxylation experiments. The rate is also distinctly different in exterior zones and in cores of the specimens. Such differences are commonly attributed to differences in the composition of the material examined.

Murray and White showed that the isothermal decomposition of clay minerals proceeds according to the first order kinetic law enabling velocity constants to be evaluated at different temperatures. From the velocity constants the Arrhenius parameters have been determined and found to be specific for the different type of clay minerals. Deviation from the Arrhenius plots for the kaolinite and halloysite clay attributed to temperature lag due to high endothermic nature of the decomposition of these clays.
Murray and White\(^{157}\) further considered the kinetic problems associated with the isothermal decomposition of the mixture of clay minerals and a method was advanced for the kinetic analysis of kaolinite and secondary mica clays. Experiments with mixtures of kaolinite and montmorillonite showed that the montmorillonite decomposed more quickly than when used alone. This was shown to be caused by an effect of sample weight on velocity constant and appeared to be a general phenomenon associated with these decomposition.

Birch Holt\(^{158}\) et al stated that the rate of dehydroxylation of clay minerals may be controlled by reaction at the interface between decomposed and undecomposed minerals and diffusion through the decomposed phases and only in rare instances are mineral decomposition reaction homogeneous.

Differential thermal analysis (DTA) and differential thermogravimetric analysis of single, binary and ternary system containing the clay minerals kaolinite, illite, nontronite and montmorillonite was carried out by Rai\(^{159}\) et al. For single systems both the techniques found to be equally useful, while DTA enabled a semiquantitative estimation of the heat values, DTGA enabled a relatively more accurate estimation of the weight losses due to desorption or
dehydroxylation. In binary and ternary systems, this always found to yield precise information.

The kinetics of dehydration of clay was studied by Shlykov and Sbornik\textsuperscript{160} at 600-900°C. In the process of dehydration under isothermal conditions at all stages of equilibrium the reaction was found to be of first order provided the composition of the gas phase in the pores of the specimen practically had remained constant. When the gases from the surrounding medium began to diffuse into pores of the specimen an accelerated dehydration was observed. Activation energy (F) of the process of dehydration of clay minerals was found to be significantly lower than at lower temperature intervals. The value of \( E \) calculated was 12-23 K cal/Mole as compared with the value obtained by other investigators.

Lesker\textsuperscript{161} et al studied the kinetics and mechanism of dehydroxylation of kaolinite by DTA. The energy of activation of dehydroxylation of kaolinite decreased as grain size shortened. The degree of kaolinite decomposition during dehydroxylation increased as the kaolinite particle size decreased at the maximum dehydroxylation rate. No effect of the degree of disorder of the structure of kaolinite on the kinetics of dehydroxylation was detected as the degree of structural disorder increased.
Toussaint et al carried out study on the kinetics of dehydroxylation of kaolinite by thermogravimetry. The following diffusion process must be taken into consideration.

I. Gross diffusion of water vapour from the clay surface towards the gas phase.

II. Inner diffusion of water molecules, nucleated in the lattice, outwards from the crystal.

(I) can be estimated by working at relatively low temperature (430°C). When this condition is fulfilled, the orders of the rate process with respect to the solid phase is unity but no definite order exists with respect to their vapour phase. This is explained by the existence of a water film operating as a diffusion barrier at the reaction interface.

Dehydroxylation occurs by removal of constitutional water from a complete octahedral layer and not by random nucleation in the lattice.

Criado et al studied the kaolinite dehydroxylation and explained why different investigators had ascribed both first order kinetics and diffusion mechanism to this reaction. The fact that activation energy reported
by these workers agreed well in spite of the different kinetics assumed when performing the calculations, was also explained. From a comparison of the results obtained by isothermal and non-isothermal methods, it was concluded that the reacted fractions \( \alpha \lesssim 0.6 \), and kaolinite dehydroxylation was controlled by a diffusion process. A reaction mechanism explaining this behaviour was proposed.

Horvath et al. performed thermoanalytical study of high temperature dehydration of kaolinite. The activation energy, frequency factor, activation entropy, activation enthalpy for dehydroxylation of kaolinite were estimated by the authors from thermogravimetric analysis. The activation energy of the process increased with increasing water partial pressure in the environment. The activation parameters was found to exhibit a compensation kinetic effect. According to this linear relation, the calculated isokinetic dehydroxylation temperature was \((679 \pm 1)^\circ K\).

The significance of structural factors in dehydroxylation of kaolinite polytypes was studied by Stoch. The relations between the perfection of the structure, the size of the crystals and the course of dehydroxylation of kaolinite polytypes as revealed by DTA and DTG curves were discussed by the author. The dehydroxylation of kaolinite was found to be a peculiar type of homogeneous, intercrystalline thermal dissociation and the kinetics of the process was further found to be dependent on
the nature of water vapour from the structure and its pressure in the structural domain.

Havarda et al determined the rate constant of kaolinite dehydroxylation. A method was developed and conditions established by the authors for the determination of kaolinite dehydroxylation rate. The temperature dependence of the rate constants was determined experimentally by the authors. According to them the dehydroxylation of kaolinite can be considered as first order chemical reaction if the body thickness is 1 mm; the bodies were pre-ignited at 573°K and rapid changes in temperature are assured both on heating and cooling the body.

Prasad and Bishnu carried out thermogravimetric and differential thermal analysis methods to determine the dehydroxylation kinetics of five kaolinite clays. In all cases the reactions were found to obey first order kinetics and good agreements between both methods were obtained by the authors. From a comparison of the activation energies it was concluded by them that the samples were of different degrees of crystallinity.

The kinetics of dehydroxylation of kaolinite and halloysite by thermal analysis was studied by Stoch and Waclawska. The rate of the dehydroxylation reaction was
found to be influenced by particle size of these minerals and the order of stacking of the layers in their structures, and the Arrhenius activation energy "E" and the order of reaction "n" decreased with the increase in specific surface area of the mineral. Further it was observed by the authors that an increase in the degree of disorder of the kaolinite lattice diminished the value of E and it also influenced the n values for fractions linear than 1

Stoch and Waclawska further studied the dehydroxylation kinetics of dickite by thermal analysis which was found to be a 2-stage process. The authors concluded that the higher temperature of dickite dehydroxylation than that of kaolinite was the result of the different arrangement of the layers in its structures. A disturbance in the order of stacking of the layers in the dickite structure was found to cause a lowering in the temperature of dehydroxylation and reduction of the activation energy of the process, which caused in turn the appearance of an additional peak or band at 580°C in the DTA and DTG curves.

The kinetics of kaolinite dehydroxylation was further studied by Gabrara and Eddleston. The accuracy of the various methods determining the value for the kinetic
parameter and their sensitivity in detecting the mechanism of reaction was investigated by the authors. Kaolinite from well-known sources were used by the authors to study the influence of crystallinity on the values of kinetic parameters. The statistical significance of various mathematical methods for the assessment of the data obtained from non-isothermal gravimetry was determined by the authors by comparison with experimental and theoretical data by using a computer programme developed for this purpose. The authors concluded that the kinetic parameters could be used to predict the degree of crystallinity of kaolinite and it also confirmed other findings that the dehydroxylation of kaolinite was a second order reaction.

Xinjian and Lianghe measured 171 studied the kinetics of dehydration of kaolinite. The dehydration of kaolinite of a certain size distribution was studied by the authors. At a certain temperature loss of water was observed by the authors from the clay lattice. The authors further observed that heating rate had an effect on the reaction order.

Slade et al. 172 studied on the flash calcination of kaolinite. Physical transformation of powdered kaolinite associated with rapid dehydroxylation during flash calcination was followed by the authors using pycnometry, TG, DTA, XRD
Anthony and Garn studied the kinetics of kaolinite dehydroxylation in the following way. When kaolinite is heated under pressures of self-generated water vapour from 0.4 to 3.2 atm, the dehydroxylation is best described by a nucleation and growth equation with exponent \( m \) varying from 1.10 to 2.16 as the pressure is increased. The temperature coefficient of the rate constant expressed as an apparent activation energy varies from 62.4 to 260 KCal/mole. The water vapour evolved in a self-generated atmosphere and the sample holder was automatically swept into a gas chromatograph at fixed intervals. The measurement is specific for water.

Liang and Li studied on the effect of structure on the dehydration activation energy of kaolinites. The activation energy for dehydration of kaolinite from two different samples was determined by the authors as 35.2 and 88.0 KCal/mol by DTA. They concluded that the difference in the activation energy resulted from the difference in crystal structure (i.e., crystal cell parameters). The authors further observed that the surface modification by acid washing or magnetic separation affected the activation energy insignificantly.
The kinetics of kaolinite dehydration and its dependence on mechanochemical activation was studied by Klevtsov et al. The authors observed that mechanochemical activation caused two processes to occur, the structural disordering of laminar crystals and the formation of more dense aggregates from particle. Further they observed that the activation energy of the dehydration decreased if the first order had predominated and vice versa.

The authors concluded that therefore to study and compare the kinetics of dehydration of different kaolinite, the properties of the initial sample should be taken into account are structural defects, particle size, particle packing into aggregates and size and dimension of the aggregates.

Killingley and Day studied the dehydroxylation kinetics of kaolinite and montmorillonite from Queensland tertiary oil shale deposits. Water released during clay dehydroxylation was measured by the authors in a small reactor coupled to a mass spectrometer. Dehydroxylation of Rundle montmorillonite and Nagoorin kaolinite was found to occur at 250-700°C and 280-600°C respectively. The low temperature of montmorillonite decomposition suggested Fe substitution for Al in the crystal lattice (nontronite structure). The montmorillonite dehydroxylation kinetics
best fit a diffusion controlled reaction in a sphere to \( \sim 80\% \) reaction. Kaolinite dehydroxylation was found to be best represented by second order kinetics (to \( \geq 90\% \) of reaction). Activation energies for the dehydroxylation reaction were determined by the authors as 145 ± 15 and 99 ± 8 KJ/Mol for kaolinite.

Horvath studied the kinetics and compensation effect in kaolinite dehydroxylation. Activation parameters \((E, A, \Delta H^* \text{ and } \Delta S^*)\) and the effect of various factors involved in kaolinite dehydroxylation reaction were studied by the author using isothermal TG measurements. Thermal decomposition of kaolinite was found to be diffusion controlled for degree of dissociation \(0 < \approx 0.65-0.70\) and the rate of water release in dehydroxylation obeyed the expression for diffusion in a spherical particles and/or the rate equation of the 2nd order reaction, depending upon the kaolinite nature. The activation energies (140-300 KJ/Mol) was found to increase with increasing of partial water pressure in the reaction environment and increasing of structural disorder (natural or induced by grinding). The author further observed that the activation parameters showed a compensation behaviour, \(E = 51.1 + 12.961 \log A\) and \(\Delta H^* = 220.0 + 0.680 (\Delta S^*)\). The isokinetic
temperature \( \beta = (679 + 2)°K \) derived from the relation were also found to be in good agreement with the temperature range of the isothermal measurement.

The effect of compaction on the kinetics of thermal dehydroxylation of fire clay was observed by Mitra\textsuperscript{178} et al. Kinetics of thermal dehydroxylation of fireclay which is mainly disordered kaolinite have been studied by the authors as a function of compaction of the loose aggregates. Kinetic parameters have been correlated with the pressure of pelletisation and also the disorderness inherent in the crystal structure.

The electrical conductivity of kaolinite increases to a maximum at around 350°C, then diminishes but increases again above 420°C when dehydroxylation occurs (Fripiat and Toussaint\textsuperscript{179}; Nakahira\textsuperscript{160}; Weiss and Hartl\textsuperscript{181}). Parallel infrared measurements show related changes in the -OH stretching frequencies. An interchange of protons and deuterons occurs readily in kaolinite at 300°C, which is a clear evidence for proton delocalization at temperatures below the dehydroxylation range (White\textsuperscript{182} et al).

Schipalov\textsuperscript{183} et al studied the dielectric constant of dehydrated kaolins of different chemical composition. The
authors examined the change in the dielectric constant of dehydrated kaolin in relation to calcination temperature of 600-1200°C. The effect of $\text{R}_2\text{O}$, $\text{Fe}_2\text{O}_3$ and $\text{SiO}_2$ addition on the change of dielectric constant and fired product was also studied by the authors.

Abd-El Nour et al. studied the effect of firing temperature on the dielectric properties of kaolinitic clay. The dielectric constant and loss of kaolinitic clay were measured by the authors in the low frequency region for firing temperature of 600-1400°C. The measurements were taken by them at different temperatures and different pressures. The dielectric loss was found to decrease with increasing frequency, while both the dielectric constant and loss increased with increasing pressure and firing temperature.

The reactivity of the surface hydroxyl groups of kaolinite was studied by Darmovzal. A modified method was described by the authors for determining the surface reactive hydroxyls in kaolinite by $50\text{Cl}_2$ treatment. Kaolins from different sources was found to contain different numbers of reactive hydroxyls even after calcination; this being dependent on the degree of crystallinity of the
kaolinite in the non-calcined kaolins. The content of reactive hydroxyls was found to decrease with increasing calcination temperature. At 200-250°C the Si-OH groups in certain impurities or in SiO₂ gel on kaolin surface were dehydroxylated. At a temperature higher than 250°C the Al-OH groups of kaolinite were found to be dehydroxylated. A pronounced decrease in concentration of reactive hydroxyl occurred at high degree of hydroxylation of Al-OH groups. After the disappearance of the later only about one third of the initially present active hydroxyls was found to remain. The authors concluded that the reactive hydroxyls of kaolinite (concentrated in edge faces of particles) consisted thereof Al-OH groups which were prone to dehydroxylation as well as Si-OH groups which were thermally stable, thus representing the reactive hydroxyls of metakaolinite and the reactive hydroxyls could have influenced the protonic acidity of kaolinite but they were not protonic sites. The protonic acidity of kaolinite was found to increase with the degree of dehydroxylation; metakaolinite being a strong protonic acid in nonaqueous solution. The reaction of Si-OH groups of metakaolinite was found to cause an even further increase of protonic acidity and the molecule of water chemisorbed on Al together with the exchangeable proton neutralising the charge on an oxygen atom
connecting Al and Si atoms, could be regarded as protonic sites of kaolinite. Thermogravimetric results confirmed the existence of two types of water sorption centers in metakaolinite at 400-525°C.

Prabhakaram studied the effect of exchangeable cations of kaolinite between 950-1000°C by DTA methods. According to him the exothermic peak in this temperature range was due to the rapid formation of a spinel as postulated by Brindley and co-workers and the exothermic peak observed above 1000°C for kaolinite was due to the rapid formation of mullite. He concluded from his work that cations do not affect the formation of mullite but the formation of cristobalite phase is greatly affected.

Lach and Sauman studied on the development of kaolinite microstructure and its conversion to mullite. Kaolinite microstructure in Zettlitzer kaolin was observed by the authors at 1400°C. At 110-400°C, no changes of porosity or crystal form of kaolin was found by them. At 500-800°C, it was observed that the porosity increased and formation of microstructure through pseudomorphosis of kaolinite took place. At 900-1000°C, which was described by the authors as transition range, disintegration of pseudomorphosis took place and sintering started and 1100°C,
rapid decrease of porosity with intensive sintering was observed.

The thermal transformation of kaolinite and autigorite was studied in detail by Tahour. X-ray diffraction analysis was utilized by the author to investigate the thermal transformation of kaolinite and autigorite. The results showed that kaolinite began to be affected by heating at 400°C, but autigorite showed a detectable effect at 500°C. Kaolinite altered to meta-kaolinite which was transformed into spinel, mullite and amorphous silica. Autigorite did not pass into meta-autigorite phase but transformed quantitatively into enstatite and olivine. The difference in the octahedral compositions of the two minerals was held responsible by the author for this behaviour.

The effect of exchangeable cations on kaolinite during the heat treatment was observed by Mackenzie and significant difference in the rate of mullite formation and a simple size/charge ratio was observed for alkali and alkaline earth cation. The author also studied the firing atmosphere on the formation of mullite from kaolinite and found that the reaction was enhanced by water vapour and vacuum and to
lesser extent by nitrogen and hydrogen but is retarded by oxygen and carbon monoxide.

Mackenzie\textsuperscript{190} also studied the kinetics of mullite formation from dehydroxylated synthetic kaolinite by IR spectroscopy method. The higher temperature IR data indicated that there was little or no difference in the cation coordination of the phases intermediate to metakaolinite and mullite, but principal coordination change occurred during the later stages of mullite formation.

Duncan\textsuperscript{191} et al studied the kinetics of mullite formation of kaolinite and halloysite by x-ray diffraction analysis and found the reaction to be nucleation controlled.

Flank\textsuperscript{192} studied on the behaviour of kaolinite pellets at elevated temperature and observations made by him, like the following. Pellets undergo two sharp contractions of roughly comparable magnitude at 450-550°C and 70-980°C respectively. Isothermal heating-soaking to confirm that both reactions are kinetically controlled. Water vapour inhibits the low temperature contractions, promote shrinkage at the high temperature. The low temperature reaction is attributed to dehydroxylation; dehydroxylation occurs at the high temperature. Bonding
energy changes measured by x-ray fluorescence shifts were significant for Si but not for Al, at < 950°C suggesting that high temperature energy release was associated with segregation or crystallisation of SiO₂ rather than an Al-containing phase.

Perera and Attot¹⁹³ studied mullite morphology in fired kaolinite/halloysite clays. The mullite morphology in fired kaolinite and halloysite clays, having platy and spheroidal particles, respectively, was investigated by the authors for different firing temperatures and soak times. The mullite from halloysite was found to be finer than that from kaolinite at all firing temperatures and soak times and was found to be affected by the original clay morphology, and by the alkali content, which affected the properties of the liquid phase on firing and thereby the grain-growth kinetics.

Toma¹⁹⁴ et al performed structural investigation on mullite phase in fired clay minerals. The formation of the mullite phase in fired Egyptian bentonite and kaolinite clay minerals was detected by the authors using TEM and diffraction techniques. The dimension and orientation of
the mullite needles was found to be depended on the type and degree of crystallinity of the clay samples. The analysis of the electron diffraction patterns proved that the mullite crystallites had a polycrystalline structure.

Mackenzie et al. investigated on the outstanding problems in the kaolinite-mullite reaction sequence using silicon-29 and aluminium-27 solid state nuclear magnetic resonance. Structural models previously for metakaolinite were examined by the authors in the light of the most recent published experimental data and new informations obtained by solid state high resolution 29 Si and 27 Al NMR. A new model for metakaolinite consisting of anhydrous regions of distorted Al-O tetrahedra containing randomly distributed isolated residual tetrahedral symmetry, was proposed by the authors. Such a structure which can readily be formed from kaolinite by the removal of hydroxyls in certain sequences accounts for the lack of a well-defined x-ray pattern and the persistence of 210% residual hydroxyls in metakaolinite and is consistent with the most recent diffraction data, bond length and the new 29 Si and 27 Al NMR data.
Brown et al. further continued investigation on the outstanding problems in the kaolinite-mullite reaction sequence as a continuation of the previous work using $^{29}$Si and $^{27}$Al solid state NMR during the high temperature transformation of metakaolinite. The solid state $^{29}$Si and $^{27}$Al NMR spectra of kaolinite fired at 800$^\circ$C to 1450$^\circ$C were interpreted by the authors in light of a newly proposed metakaolinite structure and complementary x-ray diffraction results. Removal of the final residual hydroxyl radicals was found to trigger the separation of a considerable amount of amorphous free silica and the formation of poorly crystalline mullite and spinel phase. Mullite and spinel was found to form in tandem, the former originating in the vicinity of Al-O units of regular octahedral and tetrahedral symmetry randomly distributed throughout the metakaolinite structure. The authors further observed that the initially formed mullite was Al$_2$O$_3$ rich but at higher temperatures it progressively gained silica and approached to the conventional 3Al$_2$O$_3$·2SiO$_2$ composition. The spinel phase was found to contain insufficient Si to be detected by $^{29}$Si NMR but had $^{27}$Al NMR spectrum consistent with $\gamma$-Al$_2$O$_3$. On further heating, the spinel was found to be converted to mullite by reaction with some of the amorphous SiO$_2$, the balance of which eventually became cristobalite.
Lin et al also worked on mullite. The authors synthesised mullite by reaction sintering of kaolin-alumina mixtures and analysed its microstructure by various physical instrumental methods.