SOME ASPECTS OF MINERALOGICAL INVESTIGATIONS ON THE STRUCTURE OF AGED AND UNAGED INDUSTRIAL KAOLINITES

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ABSTRACT

Ageing has become an industrial practice for the improvement of plasticity of clays and bodies both in the slurry and plastic states but no proper explanation exits. Experiments were conducted on Aged and Unaged clays to determine whether chemical bonds were broken at all. Results of X-ray diffraction, Infrared spectroscopy, Differential thermal analysis (D.T.A.) indicate that ageing affects both the mineralogical and structural aspects of clays. It is therefore very likely that ageing is more of a physical phenomenon than chemical activity.

KEYWORDS: *Ageing, Mineralogical investigations, Industrial Kaolinites.*

LITERATURE REVIEW

X-ray Diffraction

Worrall [1] indicates that the irreversible changes associated with ageing are caused by a progressive and irreversible breakdown of aggregated clay particles by the action of water and in some cases, assisted and accelerated by shearing. In X-ray diffraction analysis, it is known that clay minerals exist for the most part only as very fine particles. Therefore, due to the inherent characteristics of the clay minerals, special cameras and special techniques are frequently required for clay mineral work. Many investigators Bragg [2,3] Buerger[4] James[5] Wilson [6] Bragg [7] discussed X-ray methods as applied to clay mineral research. Carroll [9] pointed out that clay mineral reflections occur in the range from 2^{o} to 37^{o} 2θ. Brindley[8] suggested that in many clay mineral studies, it suffices to scan from Bragg angles 2θ 2^{o} to 62^{o} with Cu K α radiation at the rate of 2^{o} per minute.

The first order basal reflections of the Kaolin group of minerals occur in the range of 7.14 A^{o} - 7.20A^{o}

INFRA- RED SPECTROSCOPY

In infra-red spectroscopy, molecular groupings within the crystal often have characteristic vibrations which are accompanied by change in dipole moment. This vibration occurs either due to the displacement of the atoms along their bonds (stretching vibrations) or due to the change in the bond angle (bending vibrations) when radiation of the same frequency as the vibration is passed through the crystal, the radiation is absorbed, so by subjecting a mineral to a range of monochromatic radiation frequencies several absorption bands can be recorded. The important region for studying minerals and crystals is the region 2-25 microns; or as it is more commonly expressed in the frequency range of 400-4000 cm^{-1}

For the kaolinites under study, there is a group of absorption bands between 3750 cm-1 and 3500 cm-1 due to the stretching vibrations of the OH groups.

Farmer and Russel[10] Roy/ and Roy [11] found that the spectra of kaolin mineral of the OH group were much more complex than at first expected. They could hardly explain the presence of multiple absorption bands in terms of X-ray diffraction structure and concluded that there was no simple correlation of OH absorption frequencies with the types of OH groups or the extent of hydrogen bonding in the structure.

In Wolf's studies of the OH stretching vibrations of kaolinites in general, three bands of absorption were recognised 3704, 3663, 3635 cm^{-1} in order of decreasing absorption intensity. The band at 3704 cm^{-1} significantly increased as the angle of incidence increased and Wolf concluded that a majority of the free hydroxyl bonds having a vibrational frequency of 3704 cm^{-1} were oriented perpendicular to the basal plane

Ledoux and white [13] by deuteration of kaolinite confirmed that the absorption of hydroxyl group gave rise to three high frequency bonds at 3697, 3669 and

P. S. Kwawukume

3652 cm^{-1} Van der Mavel and Krohmer [14] found that OH stretching region has four bands at 3693, 3668, 3652 and 3620 cm^{-1} for well-ordered Kaolinite. The less ordered Kaolinite has absorption peaks at 3695, 3667, 3652 (3653) and 3620 cm^{-1} ; fine clay mineral at 3696,3668,3653 and 3621 cm^{-1} and ball clay at 3697, 3652 and 3621 cm^{-1}

From the foregoing, it is clear that there is still some disagreement about the assignment of the absorption bands in this region. However, Farmer and Russell [10] using a grating infra-red spectrophotometer resolved four absorption bands in this region 3750-3500 cm^{-1} To the three highest absorption peaks at 3697,3669 and 3652 cm^{-1} respectively, they assigned the stretching vibration of the inner surface OH groups and to the lowest 3620 cm^{-1} These seem to be generally accepted.

DIFFERENTIAL THERMAL ANALYSIS (D.T.A.)

Differential thermal analysis indicates that the clay minerals when heated, undergo physical or chemical change at a characteristic temperature which involves a change of energy. Usually such changes are manifested by either the absorption or liberation of heat and it is the accurate measurement of this effect which forms the basis of the thermal analysis. Many investigators have used this method to identify clay minerals. The work of Mackenzie [15] Smykatz-Kloss [16] and Grim [17] were relatively outstanding, and agreed on this experimental results. The endothermic reaction for kaolinite usually occurs between 500 °C and 700 °C corresponding to dehydrozylation forming metakaolin, whilst the exothermic reaction occurs at 900 °C to 1000 °C corresponds with crystallization of silicon spinel and/mullite formation.

MATERIALS AND METHODS

The materials used were supreme china clay from E.C. clays, Light blue clay from Watts Blake Bearne Co. Ltd. Fire clay from West Yorkshire clay and Brick clay from London Brick clay. The aged clays were stored in a moist state up to 6 months before testing.

X-RAY DIFFRACTION

Experimental Procedure

Both aged and unaged clays were sieved through 63 micron mesh and pressed into x-ray aluminium sample holder with special care to keep the orientation of the particles at the minimum. This is the unoriented method. For comparison of the interstices of both aged and unaged clays the choice of the cavity of the aluminum holder should be as close as possible when measured. X-ray patterns were obtained-using a Philips X-ray Deffractometer with filtered Cu Kα radiation at 40kv and 20 mA with a scanning speed of 10° 20 per minute. To produce monochromatic X-rays, a material (termed a filter) is selected which transmits the Kα rays and absorbs the Kα. Copper Kα radiation, e.g. can be produced by introducing a sheet of nickel foil into the beam, which effectively blocks the Kα rays.

INFRA- RED SPECTROSCOPY

Experimental procedure

2mg of the sample was accurately weighed out into a small agate mortar using a five figure balance 0.4g of the previously ground and dried potassium bromide was weighed out into the agate motar and the contents were throughly mixed in a mortar with a pestle for 10 minutes..0.2g of this mixture was weighed out into a small container and dried overnight at 110° C. Discs were made by pressing the mixture under vacuum in a 13mm diameter die at a pressure of 8 tons The infra-red absorption spectrum of each sample was then recorded using a pye Unicam Spectrophotometer (Sp1 100). This instrument was able to scan from 400 to 4000 cm-1 which made identification of the clay minerals possible. The intensities of Cu absorption bands at 3700 and 918 Cm^{-1} were determined by the target base line method as shown in fig[1] which is in line with Neal[8] as an alternative crystallinity index.

DIFFERENTIAL THERMAL ANALYSIS

Experimental procedure

A Station Redcroft DTA 673-4 was the instrument used. Both aged and unaged clays were examined in these experiments. .0.1g of the specimen and 0.1g of the inert material (calcined alumina powder) were packed into a separate platinum crucible and adjacently placed in the machine. The furnace temperature was ambient air and the heating was carried out at a rate of 10 degrees per minute and a chart speed of 120mm/h

RESULTS AND DISCUSSION

X-ray discussion data for the clays investigated showed some basic difference in the interplaner distance between aged and unaged china clay and brick clay whilst, ball clay and fire clay showed the same d spacings.

Aged brick clay had 7.20A° d spacing for the 001 reflection whilst unaged brick clay gave 7.14 A° Aged china clay has 7.25 A° whilst unaged china clay is 7.20A° for the same reflection planes. Generally the aged clay showed more well defined reflections than the unaged clays. Tables 1-4 show the x-ray power data for Kaolinite of aged and unaged clays. An attempt was made to calculate the crystallinity index values of all the clays used by infra-red absorption method. There appeared to be a great difference in the crystallinity index values. The IR spectra are shown in figs 2-5 and the crystallinity index values were determined as shown in fig 1. Table 5 has the values for the crystallinity index for both aged and unaged clays.

It could be seen that unaged china clay has the highest value of crystallinity index (1.08) compared with aged china clay (0.78). On the whole, aged clays have lower crystallinity index values than the unaged clays.

The infra-red absorption patterns portrayed higher absorption bands at 3720cm^{-1} in all the unaged clays investigated than the aged clays. According to Neal and Worrall [18] the effect of isomorphous substitution in the octahedral layer would be to cause a decrease in the intensity of both the absorption band at 3720 cm-1 and that at 900cm-1 since the inner and basal hydroxyl groups would be co-ordinated e.g. to magnessium other than Aluminium. These investigators concluded that as the amount of the octahedral substitution increases the amount of disorder increases the ratio of the absorption band at 3700 cm-1 to that of 910 cm-1 (the crystallinity index is the measure of this change).

Also, since the substituent ion is slightly larger than AI, it is reasonable to suppose that the replacement of the latter by Mg could result in local distortion of the kaolinite structure. It could therefore be argued with caution that the plasticity of clays increases due to because of the amount of disorder inherent in a clay.

In the Differential Thermal Analysis (D.T.A.) there appears to be a change in the peak temperatures between the aged and unaged clays. It is a known tendency that a great deal of energy is needed to break bonds holding lattice water, therefore there is an increase in the peak temperature which is also a function of crystallinity. In addition, it is also known that the greater the proportion of kaolinite in the clay the more the peak temperature is affected. In this investigation there appears to be a larger endothermic peak in all the aged clays, in spite of the same weight of material being used.

Dean [20] Robertson Brindley and Mackenziel[15] and smykatz-Kloss[16] have shown that on increasing the amount of reacting material in the sample the endothermic peak shifts to a higher temperature. Table (6) shows peak temperatures higher in all the aged clays investigated than in the unaged clays.

CONCLUSION

The X-ray results show that there is a slight increase in the d spacing of aged Brick and China clays at 001, 002 and 020 basal reflection which indicates an entry of some reacting material into the basal structure after some ageing. However, in the ball clay the 001, 003 and 020 planes have shown no change in the aged or unaged form, except in the 022 plane which recorded a shift of 3.565A^{O} for the unaged to 3.573A^{O} for aged one.

In the fire clay, the only increase in the d spacing was observed at 020 plane which was 4.48A^{O} for unaged and 4.45A^{O} for the aged which is rather surprising because all the other clays have shown a greater d spacing in the aged form. On the whole, one can definitely observe that there is a change taking place in the aged clays.

Crystallinity indexes portrayed by all the clays after ageing showed some decrease. This confirms the fact that ageing has some effect on clays. There is in fact an inverse relationship between crystallinity index and plasticity. The results are from 1.08 to 0.78 for china clay; 0.71 to 0.59 for fire clay 0.62 to 0.53 for ball clay and 0.44 to 0.30 for Brick clay.

Results obtained from D.T.A. confirm Dean [20] Robertson, Brindley and Mackenzie etc assertion that increase in the amount of reacting materials shift endothermic peaks to higher temperatures. These reacting materials could only be introduced while ageing takes place.

From the above results there is no doubt that ageing affects both the mineralogical and structural aspects of clays.

TABLE 1: X-RAY POWDER DATA FOR THE KAOLINITE OF AGED AND UNAGED BRICK CLAY

Aged d(A^{O})	Aged hkl	Unaged d(A^{O})	Unaged hkl
7.20	001	7.41	001
4.44	020	4.47	020
3.56	002	2.245	132, 040
2.287	131,131	2.132	023
2.243	132,040	1.981	203,132
2.132	023	1.546	134
1.546	134	1.386	333
1.386	333	1.375	134

TABLE 2: X-RAY POWDER DATA FOR THE KAOLINITE OF AGED AND UNAGED BALL CLAY

Aged $d(A^{o})$	Aged hkl	Unaged $d(A^{o})$	Unaged hkl
7.25	001	7.25	001
4.461	020	4.461	020
3.573	002	3.565	002
2.38	003	2.38	003
2.49	132,040	2.287	131,131
1.546	134	2.132	023
1.456	330	1.544	134
		1.492	060,331
		1,492	060,331
			331
		1,457	330

TABLE 3: X-RAY POWDER DATA FOR THE KAOLINITE OF AGED AND UNAGED CHINA CLAY

Aged $d(A^{o})$	Aged hkl	Unaged $d(A^{o})$	Unaged hkl
7.254	001	7.196	001
4.18	020	4.44	020
3.586	002	4.35	010
3.376	111	4.171	111
1.223	203,132	3.56	002
1.822	133	3.376	111
1.667	204,133	2.755	022
1.585	134	1.993	203,132
1.490	060,331	1.899	133
	331	1.667	204,133
1.431	005	1.585	134
		1.488	060
			331
			331
		1.453	330
		1.431	005

TABLE 4: X-RAY POWDER DATA FOR THE KAOLINITE OF AGED AND UNAGED FIRE CLAY

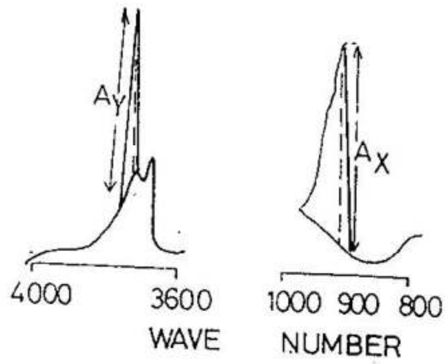
Aged $d(A^{o})$ hkl	Aged hkl	Unaged	Unaged $d(A^{o})$
7.254	001	7.254	001
4.45	020	4.48	020
4.37	110	3.57	002
3.579	002	2.243	132,040
2.338	202,131	2.137	023
2.287	131,131	1.985	203, 132
2.249	132,040	1.661	204,133
2.338	023	1.546	134
1.989	203,132	1.457	330
1.549	134		
1.459	330		
1.291	131,131		

TABLE 5: INFRA-RED CRYSTALLINITY INDEX VALUES

Type of clay	Nature of clay	Crystallinity Index
China clay	Aged	0.78
	Unaged	1.08
Fire clay	Aged	0.57
	Unaged	0.71
Ball clay	Aged	0.53
	Unaged	0.62
Brick clay	Aged	0.30
	Unaged	0.44

TABLE 6: D.T.A. DATA FOR IDENTIFICATION OF AGED & UNAGED CLAYS

Type of clay	Nature of clay	Initial Temp oC	Peak Temp oC
Fire clay	Aged	440	616
	Unaged	411	602
Ball clay	Aged	468	593
	Unaged	468	571
Brick clay	Aged	455	560
	Unaged	450	547
China clay	Aged	311	637
	Unaged	468	625



$$I_C = \frac{A_X}{A_Y}$$

FIG 1. METHOD FOR DETERMING CRYSTALLINITY INDEX I_C BY INFRARED ABSORPTION

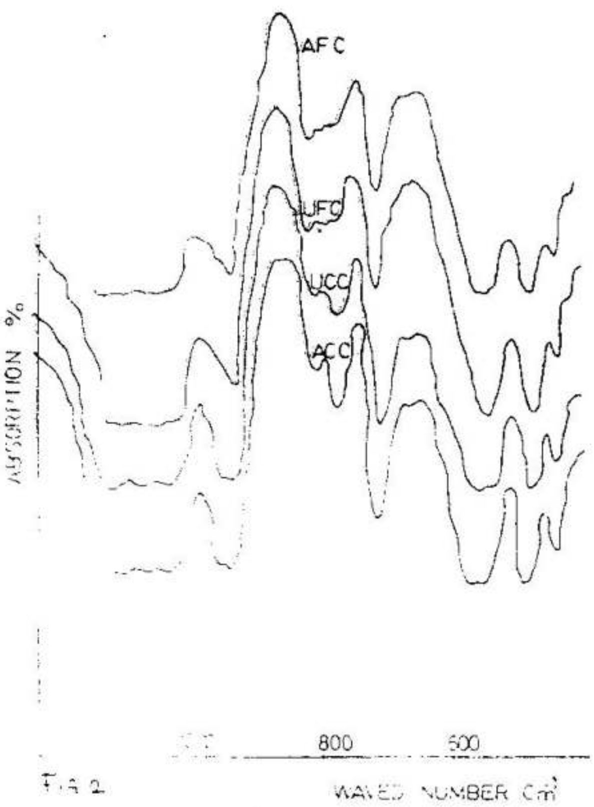


FIG 2

[illegible] Absorption Bands of Aged and Unaged [illegible] China Clays between Frequencies 400 – 1000 cm⁻¹

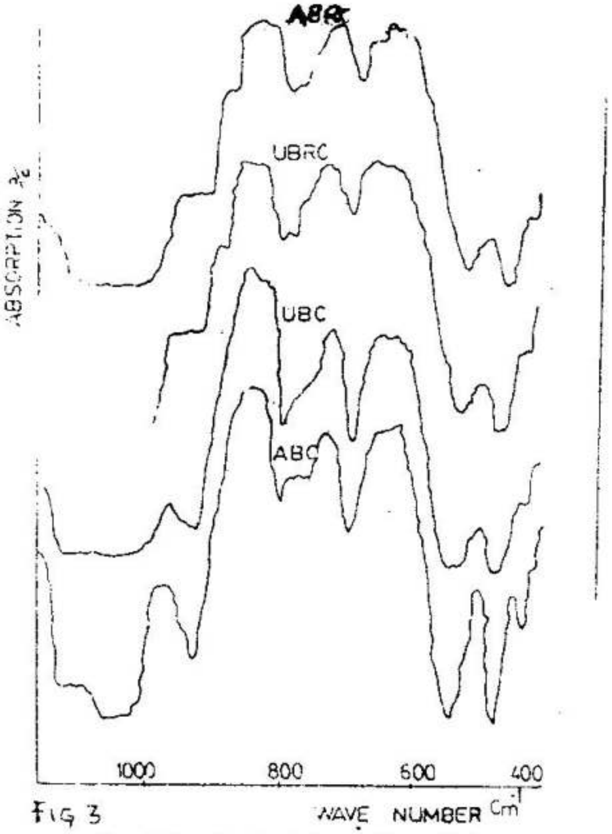


FIG 3

Infrared Absorption Bands Age and Unaged Brick Ball Clays

A Brick C – Aged brick clay ;U BRICK C – Unaged brick clay

ABC Aged ball clay UBC – ball clay

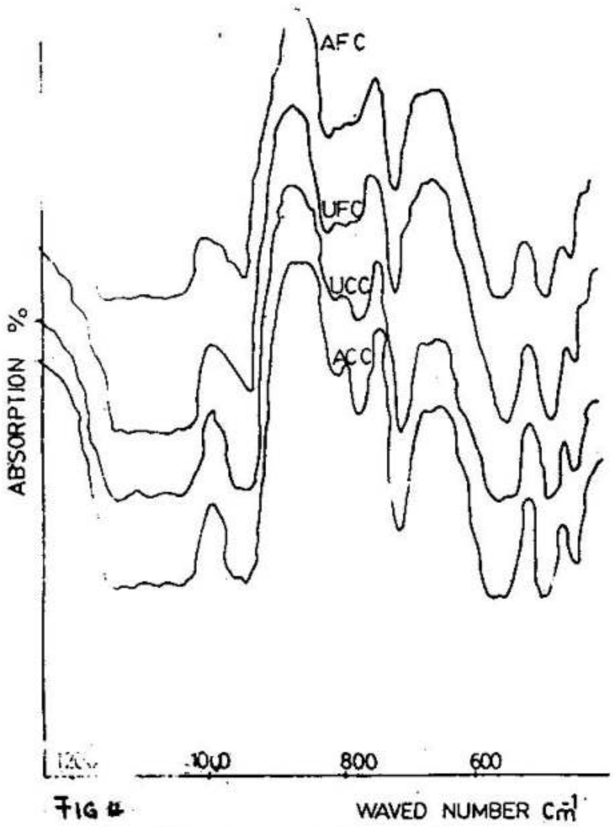


FIG 4

Infrared Absorption Bands of Aged and Unaged Fire and China clays between Frequencies 400 – 1200 cm

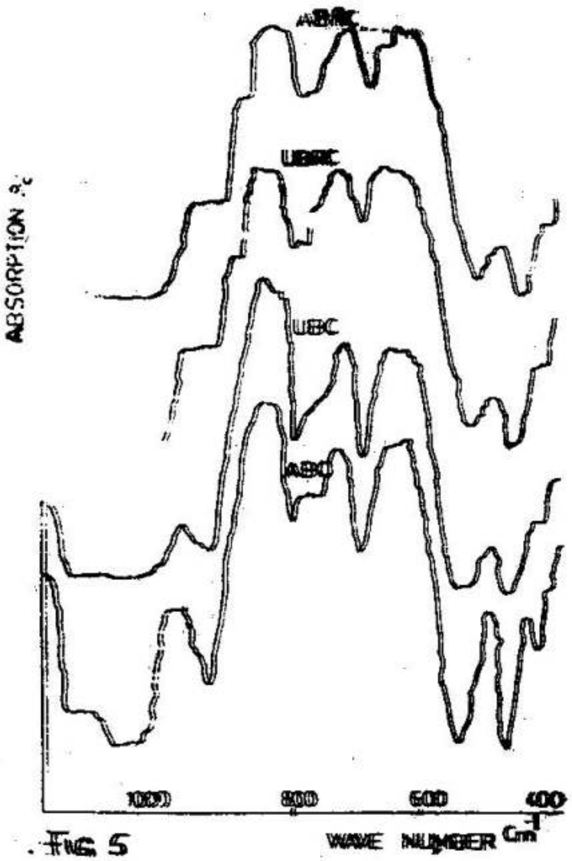


FIG 5

Infrared Absorption Bands Age and Unaged Brick Ball Clays

A Bric- C—Aged brick clay U BRICK C—Unaged brick clay.

ABC Aged ball clay UBC—ball clay.

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