CHAPTER 3: RESULTS AND DISCUSSIONS OF X-RAY DIFFRACTION(XRD) STUDIES, AND INDEX PROPERTIES OF SAMPLE-1(PU3 CLAY- DENGKIL CLAY) AND SAMPLE-2(PTD CLAY-PETALING TIN CLAY)

3.1 Introduction

Clayey materials are extensively used in ceramics. Clayey types of soils are mixed with certain amount of water content so as to make the mixture a plastic mass. Any material which exhibits plasticity characteristics can be conveniently moulded into a desired shape. These moulded specimens at some wet consistancy are dried up and then fired under some controlled conditions.This type of drying and firing makes the specimen very strong and durable under various climatic conditions.Especially,these specimens become very insensitive to water and there is no question of absorption of water under any circumstances.

Ceramics are used for a good variety of industrial purposes such as insulators and are also used as cutlery items.In all these applications,the finished material has to meet certain size and shape requirements. Among all these clayey materials,the kaolinitic clay meets all these stringent requirements of the ceramic industry,and this particular type of soil when mixed with water,is plastic enough so as to be conveniently moulded into any shape. The shrinkage during drying and firing stage is minimum and further there are no cracks developed during the process. Hence,the final finished product meets the requirement of the size and shape without much of difficulty.

Unfortunately,this ideal kaolinitic soil is not found extensively all over the world and the predominant occurance of this clay mineral is reported in a particular province called " Kaoling" in China. In this thesis, an attempt has been made to suggest that certain other types of soils can also be used in ceramic industry using a minimal treatment.

There are a few types of clays which are highly plastic and they undergo large amounts of shrinkage during drying. In addition,these soils suffer from extensive cracking during drying and firing.

In the field of civil engineering,the structures founded on these soils experience large scale foundation failures due to either shrinkage or inadequate shear strength. In such soils, it is quite popular to use lime stabilization and in some of the works reported(as reported in the literature review of this thesis) in the civil engineering discipline, a good coverage of this particular subject are presented by research workers(53) and (54). The use of lime to improve the soil characteristics is a well known technique and a brief literature review is already presented in Chapter-1.

3.2 Materials Studied

The purpose is to study certain characteristics of the two clay minerals which are proposed for a ceramic industry in Malaysia. These are "Dengkil Clay(PU3 Clay)",which is termed as Sample-1 and "Petaling Tin Clay(PTD Clay)" which is termed as Sample-2. In order to get an idea about the plasticity and shrinkage characteristics,the standard type of index properties tests which are popular in civil engineering are carried out. These are Liquid Limit(LL), Plastic Limit(PL) and also shrinkage limit tests. These tests are mentioned in Appendix-A in detail.These are tests detailed in (55).

Basically, "Liquid Limit" is the water content at which the soil behaves like a liquid with negligible shear strength and the "Plastic Limit" is also a water content at which the soil is in the form of a semi-solid and it gains considerable strength.The difference between Liquid Limit and Plastic Limit is the plasticity index and these can be considered as a range of moisture content through which the material behaves like a plastic mass. Infact, this range controls the practical utility of the material in the ceramic industry.

t is already mentioned in the previous section that kaolinite is a material which ideally suits the requirements of ceramic industry. The standard kaolinitic material has the following range of index properties:

Material	**Kaolinite**
Range of Liquid Limit (LL) values	**50% to 60%**
Range of Plastic Limit(PL) values	**25% to 30%**
Range of Plasticity Index(PI) values **= Liquid Limit(LL)-Plastic Limit(PL)**	**20% to 35%**
Range of Shrinkage limit (w_s) values	**25% to 30%**

For this range of plasticity characteristics,if the specimens are moulded at a water content near the Plastic Limit(PL), the shrinkage is minimal during drying. For these two clayey soils from Malaysia,these tests are conducted and the values are presented in table 3.1 in the following page.

Index Property (%)	Sample-1 (DengkilClay)-PU3 Clay	Sample-2 (Petaling Tin Clay)-PTD Clay
Liquid Limit(LL)	82	65
Plastic Limit(PL)	28	31
Plasticity Index(PI) =(LiquidLimit-Plastic Limit)	54	34
Shrinkage Limit (W_S)	19	20

TABLE 3.1:index properties and shrinkage limit values for the two clay samples in untreated condition

3.3 Influence of lime on the plasticity characteristics

It is a standard practise in civil engineering to estimate the plasticity characteristics by conducting these tests-namely, Liquid Limit, Plastic Limit and shrinkage limit. From the results presented in the previous section 3.2,for soil1, plasticity index is 54% and the shrinkage limit is 19%.For soil2,plasticity index is 34% and shrinkage limit is 20%. In comparison with reference materials like kaolinite,the plasticity index value for soil1 is nearly double and for soil2,it is also higher. Further,shrinkage limit values are low and indicate high shrinkage during drying and cracking up in firing stage.

It is proposed that the plasticity index can be conveniently reduced and shrinkage limits can be increased by mixing the soil with lime. Hence,these reference tests are carried out after mixing the soils with lime to an extent of 3% and 5%. In all these cases,soil samples were mixed with the required lime calcium hydroxide in the presence of water and the soil-lime-water mixture was kept for 14 days for the completion of the chemical reaction. From the previous works,the standard reactions taking place are the cationic exchange,flocculation and aggregation (3) and (13). The index properties obtained from these treated samples are presented in table 3.2.

Index Properties (%)	**Sample-1(Dengkil clay)- PU3 Clay 3% of $Ca(OH)_2$**	**Sample-1(Dengkil Clay- PU3 Clay 5% of $Ca(OH)_2$**	**Sample-2(Petaling Tin Clay)-PTD Clay 3% of $Ca(OH)_2$**	**sample-2(Petalin Tin Clay)-PTD Clay 5% of $Ca(OH)_2$**
Liquid Limit(LL)	**61**	**58**	**50**	**44**
Plastic Limit(PL)	**33**	**34**	**34**	**35**
Plasticity Index (PI)=LiquidLimit-Plastic Limit	**28**	**24**	**16**	**9**
Shrinkage Limit(W_S)	**27**	**28**	**28**	**29**

TABLE 3.2: **Index properties and shrinkage limit values for the two clay samples in treated condition**

From the above mentioned results,it is quite clear that in sample1,5% lime treatment has brought down the plasticity index from 58% to 24%. Even 3% lime treatment has brought down the plasticity index to 28%. In sample-2,for the same levels of treatment,the plasticity index values are brought down to 9% and 16% for 5% lime treatment and 3% lime treatment respectively.

Hence ,it is suggested that there is a dramatic improvement in plasticity characteristics. Similarly, there is an increase in shrinkage limit in soil-1 from 19% to 28%(the increase in shrinkage limit is an indication of reduction in shrinkage). For soil-2 also there is an improvement in shrinkage limit from 20% to 29%. This reduction in plasticity is explained as given below.

The penetration of lime in the form of calcium hydroxide can induce two possible changes in the system. This calcium hydroxide has got a tendency to reduce the thickness of the double layer of the clay particles present.This possibly encourage to form clay clusters and crystallites and as a result of which the quantum of rigidly held water is reduced. Any increase in the salt concentration or substitution of divalent cations for monovalent cations results in the decrease of the repulsive force system. Because of these two phenomena,the liquid limit in this type of soil,is expected to get affected by penetration of lime.The significant reduction in the liquid limit does confirm the penetration of lime. In effect,this decreases the plasticity to a comfortable level.

It is known, that the possible base exchange and the associated changes in the fabric arrangements are expected to take place in a short interval of time and these can be considered as immediate effects. However,the possible aggregation and the formation of new compounds as a result of seeping lime are known to take place over a certain time interval (46).Most of the reaction is more or less complete on about 2 week's time.

The above mentioned paragraphs explains that the plasticity characteristics and shrinkage characteristics are favourably altered by mixing them with certain amounts of lime(3% to 5%). Using this technique,even locally available soils can be conveniently used in ceramic industry. The shrinkage limit can be used as a good indicator of volume change.If shrinkage limit is very low,and in cases where this soil is used,the drying reduces the volume significantly.If there is too much of reduction in volume,there will be enormous changes in the sizes of the finished products and there can be considerable scope for the microcracks to be present within the specimen.During the subsequent firing of the specimen in a ceramic industry,there can be damage to the product.Hence,any technique to increase the shrinkage limit is quite welcome.The increase in shrinkage limit from 19% to 29% is a significant improvement and this value is almost equal to the value obtained in kaolinitic clay which is a standard material in ceramic industry.

The mixing of lime with soil causes certain changes in the mineralogy of clay soils. Many soil technologists (56) and (57) and more recently (3) have extensively used X-Ray Diffraction data to bring out the mineralogical changes in this system due to lime treatment.

3.4 X-Ray Diffraction Studies

In order to bring forth the possible formation of the new compounds,x-ray diffraction analysis has been used in this investigation for the identification of crystalline and mineralogical components of clay.

In this method,two parameters can be determined and these are

(a) The spacing between the planes of atoms(lattice planes) in the crystals.

(b) The intensities of x-ray diffractions from the corresponding lattice planes.

These two parameters are known for many crysytalline materials and are available in the form of an index file published by American Society for Testing and Materials(ASTM) and other ceramic companies dealing with clay minerals. Identification of various minerals is normally done by matching the experimentally determined dimensional and diffraction intensity values with those published in the index.

Hence, x-ray diffraction can be conveniently used to identify the reaction products of any chemical stabilization. This method has been used by several investigators to identify the reaction products formed in chemical stabilization methods,as already mentioned in the literature review in Chapter-1.

In this investigation, XRD method has been used for the identification of the reaction products formed both in treated and untreated conditions. The details of the equipment and method are presented in the following section 3.5.

3.5 Details of equipment used and the method adopted

An automatic x-ray diffractometer of Philips make has been used. A schematic diagram of this instrument has been presented in fig A. X-Ray Diffractogrammes have been obtained using CuK(Nickel filters) with an input voltage of 34Kv,24mA. Scan speed of 1°/minute is used for the quantitative estimation of the minerals present and for the identification of new products formed due to seeping of lime and its reaction with soil.

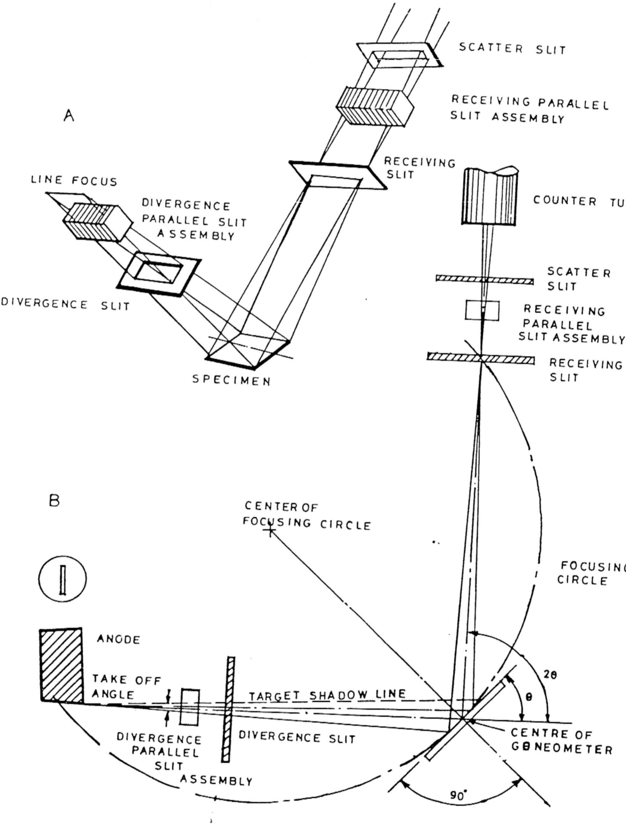

FIG A : SCHEMATIC DIAGRAM OF X-RAY DIFFRACTION

The use of x-ray diffraction depends on the fact,that the intensity of reflections from any crystallographic plane varies directly with the mass of material oriented so that the plane reflects x-rays according to Bragg's relationship,as already discussed in detail in Chapter-2.

X-Ray Diffraction has been used both as a method of assessing fabric and for mineralogical identification. Clay particles have their own characteristic arrangement of atoms forming a basal unit. The regularly spaced atoms diffract a monochromatic beam of x-rays producing several characteristic reflections. From the diffracted intensities as plotted at different angles of 2θ , it is possible to estimate the lattice parameter,d. Since each mineral has its 'd' spacing,it is found convenient to identify the parent mineral and its reaction products formed by noting the angles of 2θ at which the peak reflections are made. This principle has been made use of in this investigation.

It is quite clear that x-ray diffraction can be conveniently used to identify the various minerals present in the soil and also new minerals formed due to lime treatment.The mineralogical analysis of soil is carried out by comparing the obtained XRD patterns with (58) and (59). The XRD patterns of untreated soil indicates the various minerals as given in table 3.3 in the following page.

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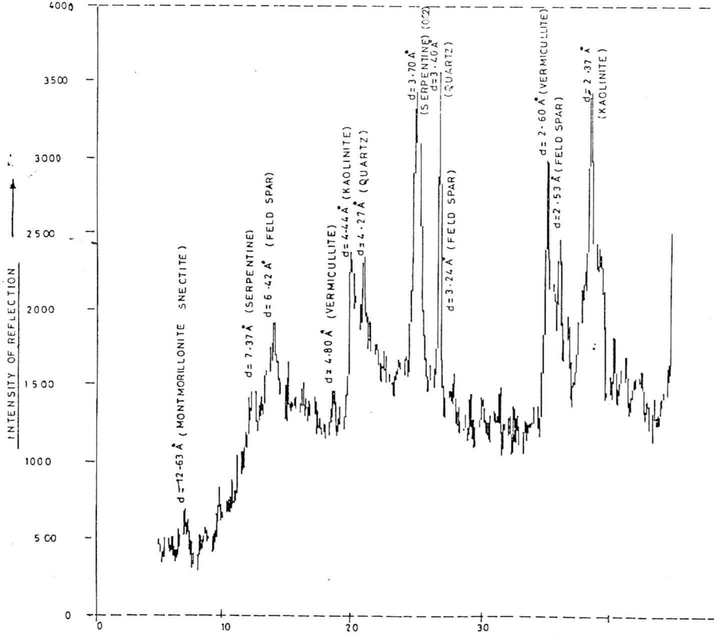
Sl No	Type of minerals	Approx (%)
1	CLAY MINERALS	
a	Montmorillonite	15
b	Serpentine	5-10
c	Vermicullite	10-15
2.	ASSOCIATED MINERALS	
a	Feldspar	10-20

Table 3.3: Minerals present in Soil-1(PU3 CLAY) in untreated condiition

The XRD pattern of untreated samples are shown in Figs 3.1 and 3.6 in the following pages.



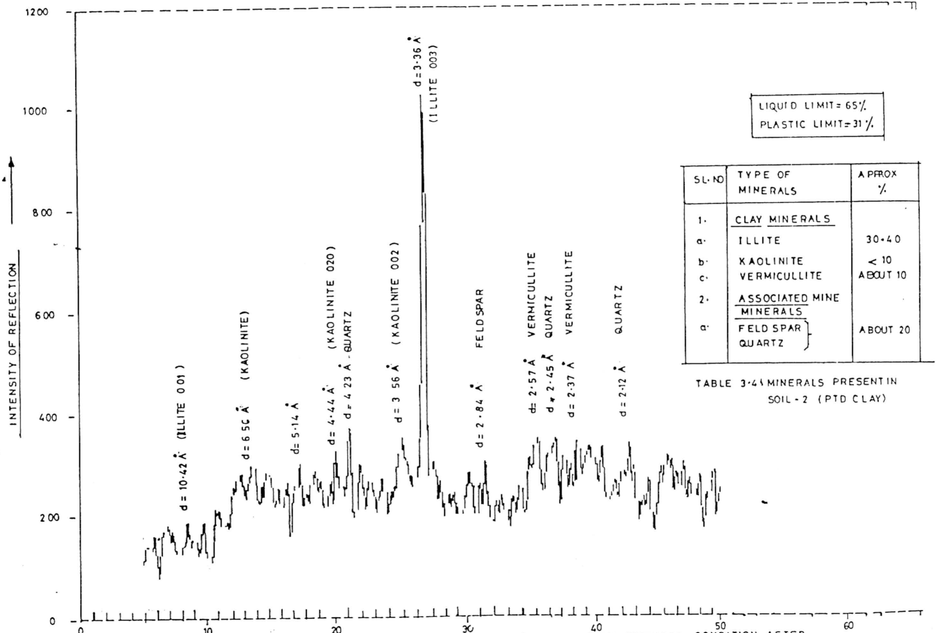
LIQUID LIMIT = 82%
PLASTIC LIMIT = 28%

SL·NO·	TYPE OF MINERALS	APPROX %
1·	CLAY MINERAL	
a·	MONTMORILLONITE	15
b·	SERPENTINE	5-10
c·	VERMICULLITE	10-15
2·	ASSOCIATED MINERALS	
a·	FELD SPAR	10-20

TABLE 3·3: MINERALS PRESENT IN SOIL-1 (PU3CLAY)

CLAY·S.M

FIG 3.1 : X-RAY DIFFRACTOGRAMME OF SOIL-1 (PU3 CLAY IN UNTREATED



LIQUID LIMIT = 65%
PLASTIC LIMIT = 31%

SL·NO	TYPE OF MINERALS	APPROX %
1·	CLAY MINERALS	
a·	ILLITE	30·40
b·	KAOLINITE	< 10
c·	VERMICULLITE	ABOUT 10
2·	ASSOCIATED MINE MINERALS	
a·	FELD SPAR QUARTZ	ABOUT 20

TABLE 3·4 MINERALS PRESENT IN SOIL-2 (PTD CLAY)

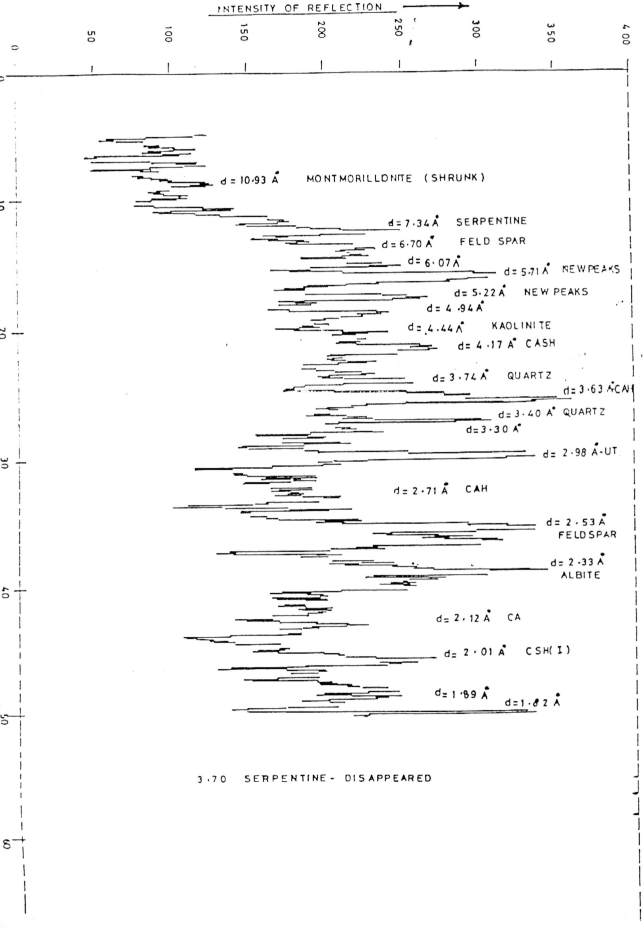
FIG 3.6 X-RAY DIFFRACTOGRAMME OF SOIL-2 (PTD CLAY) IN UNTREATED CONDITION AFTER HEATING TO 105°C

3.6 XRD Studies of treated samples

From the index properties test carried out,it's quite clear that plasticity characteristics have been favourably altered by lime treatment. From the literature review presented,it's quite clear that a good part of the improvement is attributed to the various reaction products formed. These products are in the form of cementation compounds like Unsubstituted Tobermorite (UT), Calcium Aluminate(CA), Calcium Silicate Hydrate(CSH), Calcium Aluminate Hydrate(CAH). Such compounds are reported by several investigators(60) and (61). The XRD patterns obtained from these treated samples are presented in figs 3.3-3.10.Based on this analysis and by comparing with the standard data,it could be seen that in lime treated samples,there are a number of new peaks formed. These are in the form of Calcium Aluminate Silicate Hydrate(CASH), Calcium Aluminate Hydrate(CAH), Calcium Aluminate(CA) etc. Thed presence of new peaks formed are given in Table 3.4 in the following page.

SI No	Type of minerals	Approx (%)
1	CLAY MINERALS	
a	Illite	30-40
b	Kaolinite	<10
c	Vermicullite	ABOUT 10
	ASSOCIATED MINERALS	
a	Feldspar,Quartz etc	ABOUT 20

Table 3.4: Minerals present in soil-2(PTD CLAY) in untreated condition


INTENSITY OF REFLECTION
0
50
100
150
200
250
300
350
4.00
10
20
30
40
50
d = 10·93 Å MONTMORILLONITE (SHRUNK)
d = 7·34 Å SERPENTINE
d = 6·70 Å FELD SPAR
d = 6·07 Å
d = 5·71 Å NEWPEAKS
d = 5·22 Å NEW PEAKS
d = 4·94 Å
d = 4·44 Å KAOLINITE
d = 4·17 Å CASH
d = 3·74 Å QUARTZ
d = 3·63 Å CAH
d = 3·40 Å QUARTZ
d = 3·30 Å
d = 2·98 Å-UT
d = 2·71 Å CAH
d = 2·53 Å FELDSPAR
d = 2·33 Å ALBITE
d = 2·12 Å CA
d = 2·01 Å CSH(I)
d = 1·89 Å
d = 1·82 Å
3·70 SERPENTINE - DISAPPEARED

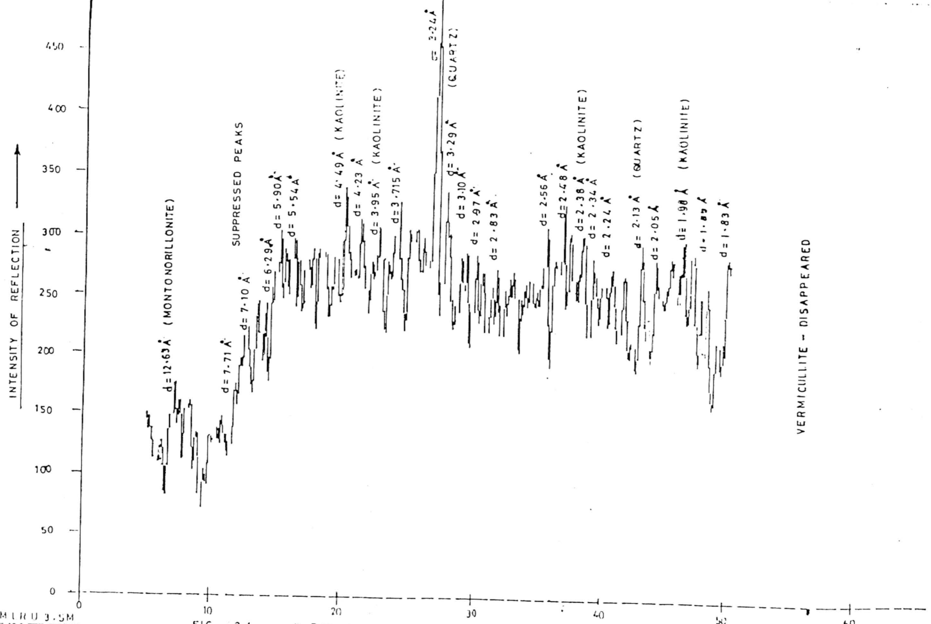


FIG .3.4. X-RAY DIFFCTOGRAMME OF SOIL1 (PU3 CLAY) IN UNTREATED CONDITION AFTER HEATING TO 1000°C

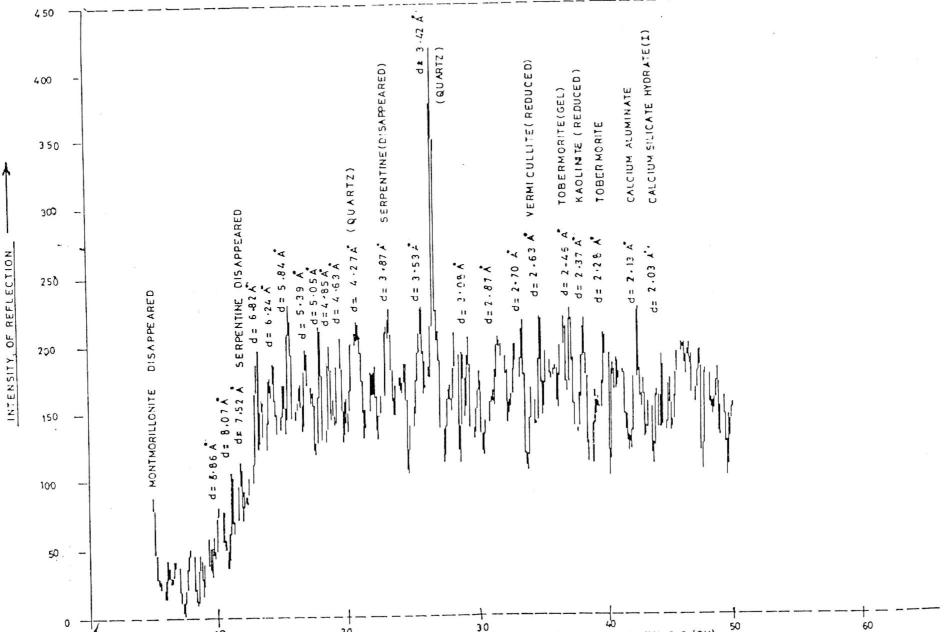
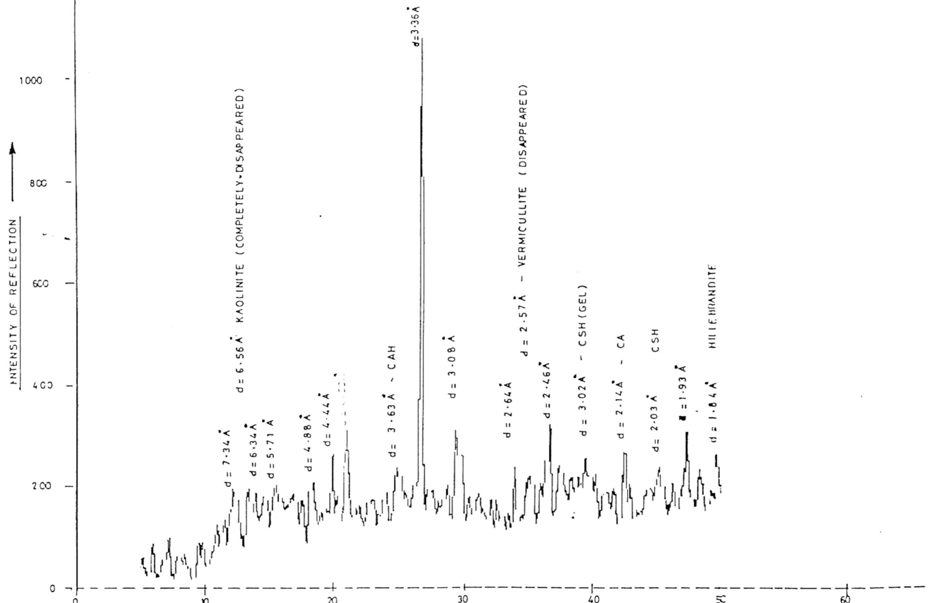


FIG 3.5 :X-RAY DIFFRACTOGRAMME OF SOIL 1 (PU3-CLAY) TREATED WITH 5 $Ca(OH)_2$



5CAPTD·SM

FIG 3.8.: X-RAY DIFFRACTOGRAMME OF SOIL-2 (PTD CLAY) TREATED WITH 5 $Ca(OH)_2$ AFTER HEATING TO 105° C.

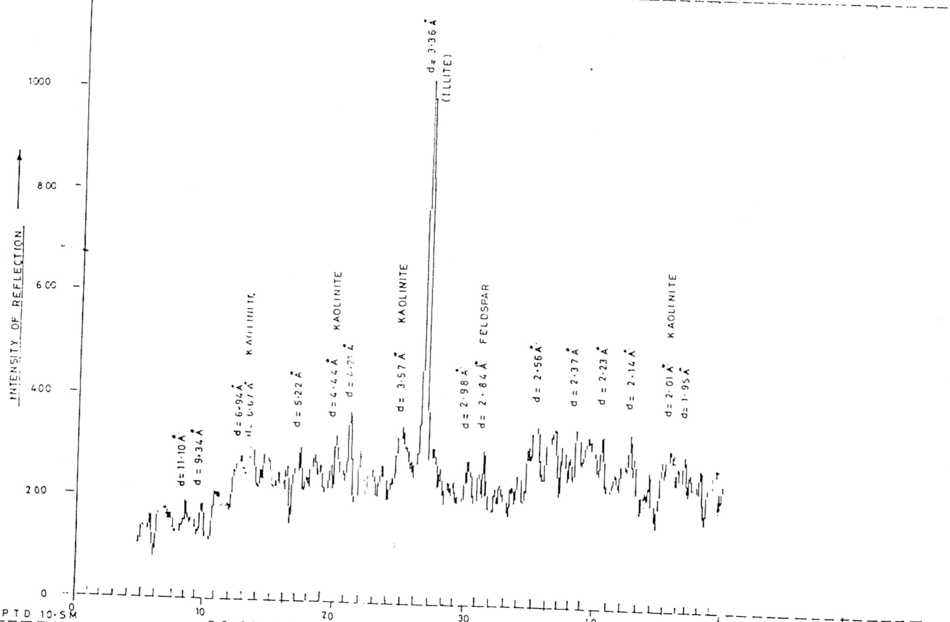


FIG 3.9 : X-RAY DIFFRACTOGRAMME OF SOIL-2 (PTD CLAY) IN UNTREATED CONDITION AFTER HEATING TO 1000°C

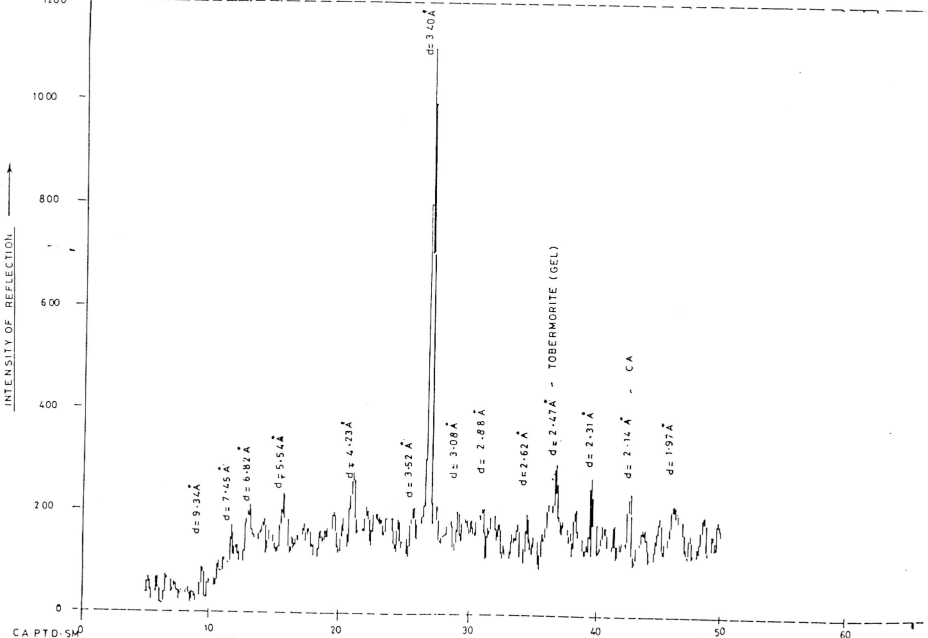
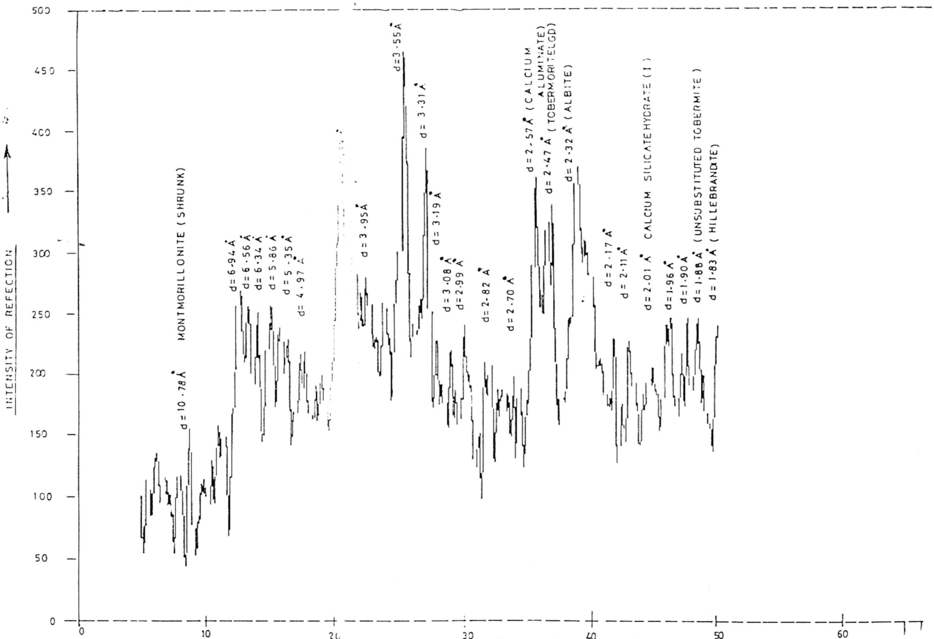


FIG 3.10 : X-RAY DIFFRACTGRAMME OF SOIL-2 (PTD CLAY) TREATED WITH 5% $Ca(OH)_2$
AFTER HEATING TO 1000°C

Besides the formation of new peaks,it is quite significant to note that certain peaks corresponding to clay minerals are either suppressed or have disappeared. The peak corresponding to Montmorillonite at a basal spacing of 12.63 A is very much reduced and in the treated system another shrinking mineral like Vermicullite has completely disappeared. All these do suggest that there is a good possibility for the formation of cementation compounds. These compounds reduce the shrinkage during drying and cracking during firing.

XRD pattern obtained from the sample heated to 1000^{0}c are also presented in Figs. 3.2 and 3.7. Both the X-Ray Diffractogrammes do confirm that the original peaks of clay minerals are completely destroyed and one may not find any clear pattern for the clay minerals. This indirectly suggests that these samples when heated to such elevated temperatures, there is an alteration of the shrinking minerals.The moulds prepared and heated are no more sensitive to water penetration and thereby the durability is very much guaranteed.

Thus,this technique of lime treatment in certain types of soils show a good promise for industrial applications in ceramics. This can be further confirmed through a limited qualitative study using Scanning Electron Microscope(SEM).



2C A PU 3 · SM

FIG 3.2 X-RAY DIFFRACTOGRAMME OF SOIL 1 (PU 3 CLAY) TREATED WITH 2 Ca(OH)$_2$

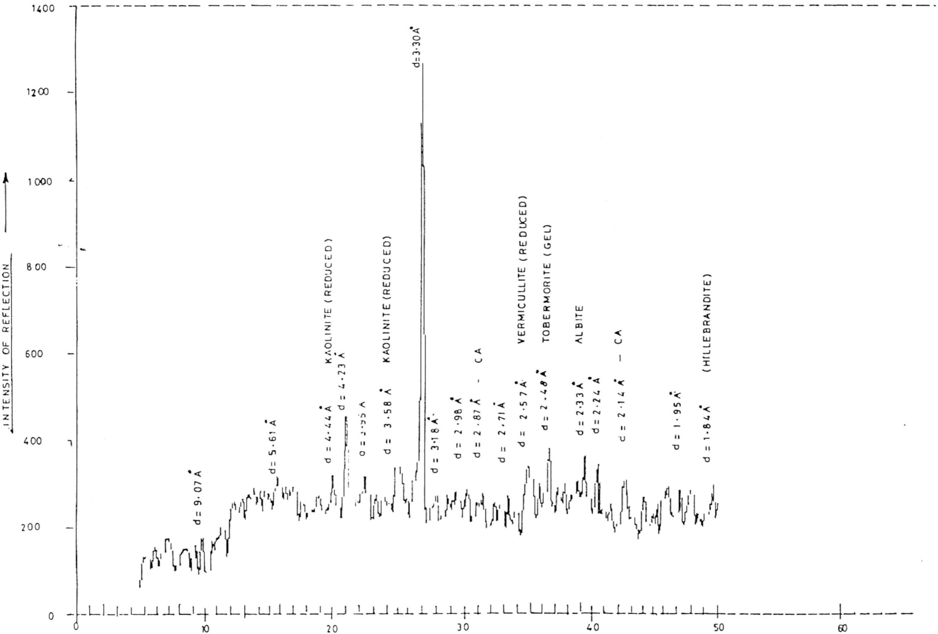


FIG 3.7 X-RAY DIFFRACTOGRAMME OF SOIL-2 (PTD CLAY) TREATED WITH 2% $Ca(OH)_2$ AFTER HEATING TO 105°C