CHAPTER 2 :   EXPERIMENTAL STUDIES

2.1 MATERIALS USED

The clays used in the investigation were taken from a ceramic research company situated at Kapar, near Klang, at the outskirts of Kuala Lumpur.The soil samples were basically used in the manufacture of ceramic tiles and they were in dried and powdered form. The following are brief descriptions of the samples and also the chemicals which are used while conducting the tests.

(a) The clays collected are basically of two types. The first one is "PU3 clay"(Dengkil Clay) and the second one is "PTD clay"(Petaling Tin clay). According to the information furnished by the company,the PTD clay is plastic in nature and the PU3 clay is kaolinitic in nature. Both these clays are known to contain minerals like Silica, Aluminium, sodium, calcium,potassium of varying proportions.The basic properties of clayey soils are usually linked up with the index properties in a civil engg practice.These are liquid limit,plastic limit and shrinkage limit.Plasticity characteristics are at best indicated by these results.These tests and results are described in section 3.3.

(b) It will be known from the index properties that in one soil,the plasticity is quite high and this indicates high swelling and shrinkage.Hence,this soil needs some chemical treatment to bring down the plasticity index and this is done thro' Lime treatment.For the sake of comparison purposes ,this chemical treatment is attempted on both the soils. The chemical used is calcium hydroxide and was used on clay samples in their treated form and the changes in their mineralogical composition were further studied after the concentrations of

calcium hydroxide and temperatures were increased. The treated samples were coated with carbowax(or Poly-ethylene glycol 6000) after circular pellets were prepared with the help of a moulding instrument and then breaking them into two halves. One half was treated with carbowax while the other was left untreated. The fractured surfaces of the untreated and untreated halves were exposed to SEM to study the microstructural changes taking place.X-Ray Diffraction studies were carried out on powdered samples on both the treated and untreated specimens.This has been done to bring out the mineralogical changes.

The tests conducted on the clay samples to study the mineralogical changes are:

(a) X-Ray Diffraction studies(XRD)

(b) Scanning Electron Microscopic studies(SEM)

(c) Atterberg limits(LL,PL,PI,Shrinkage limits)

2.2 METHOD OF MIXING OF CHEMICALS AND THEIR PROPORTIONS

The chemical used for XRD, SEM is calcium hydroxide.The two soil samples-clay and PU3 clay were treated with calcium hydroxide initially of 2%(by weight) concentration and 5%(by weight) concentration. After the addition of the chemicals,they were soaked in water for 10 days and dried in oven at low temperatures(105° c) before obtaining the XRD spectra.Then both the samples were fired up to high temperatures (1000° c) and the same procedure was followed.

2.2.1. Justification of choice of lime percentage:

A range of 1 to 6 % seems to be the practically required range in most cases (see Table 2.1 -- from (16)) . From the fig. (R1), it can be seen that there is no significant improvement of the properties beyond 5 % of lime content. It has been shown and found (2) that a minimum value of about 1% is needed to take care of the soil- base exchange requirements. Hence three intermediate percentage values 2, 3 and 5 % were chosen for the present studies.

2.2.2 Extra cost due to lime treatment:

Lime is a relatively costly material in Malaysia. If the lime requirement is in the range of only 1 to 6 % , maybe on an average about 2 to 3 % for improving the properties of clay to the required level, the extra cost may not be too large.Further more, the additional cost due to addition of lime is to be compared with additional transport costs that may have to be incurred if better quality clay is to be brought from a far off place when the locally available clay does not possess characteristics comparable to those of Kaolinite.

A small extra investment due to a small dose of lime is likely to pay for itself in the long run through reduced rates of rejection and improved quality of finished products.

2.2.3 Choice of curing period:

The improvements in properties of clays due to lime treatment are partly due to pozzolonic reactions that occur in the lime- clay mixture. Pozzolonic reaction is however time- dependent. It is quite well known that the rate of development of such reaction is very fast in the first few days or weeks and relatively slow during subsequent period (asymptotic with time). For example, concrete attains roughly 70% of its 28-day strength in the first 7 days itself. By 14 days, it reaches almost 85% of its strength. Similar tendency is observed also in the case of lime-treated clays. Figs (R 2) and (R 3) reproduced from the reference (66) clearly show that there is practically very little change in properties of lime treated soils after 14 days. It has been shown (16) that curing periods as short as 3 days are sufficient for " full modification" by lime addition. Hence curing of 10 days was considered as adequate.

Clay Type	Clay Mineralogy	ICL Value 1: (%) lime	ICL Value 2: (%) lime
Keuper Marl	Illite, dolomite and quartz minor gypsum and feldspar	1.5	1.0
English China Clay	Very pure, well crystalline Kaolinite, Little quartz	--	1.5
Lower Lias Clay	Diordered kaolinite, illite and Quartz, Minor Calcite and gypsum	6.0	3.0
London Clay	Illite and disordered kaolinite; minor quartz, feldspar and smectite	5.0	3.0

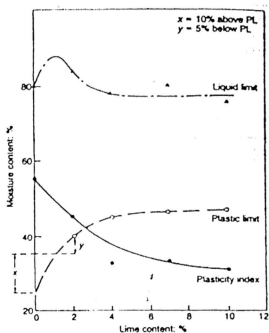Table 2.1: Initial consumption of Lime test results (from reference 16)

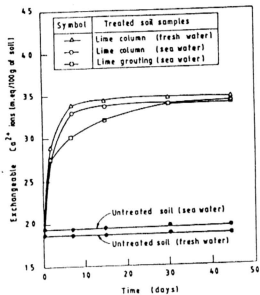Fig. (R1): Effect of addition of lime on properties of London Clay (16)

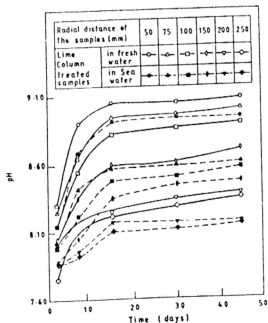Fig. (R2): Variation in Exchangeable Ca^{2+} Ions with Time (66)

Fig. (R3): Variation in pH with Radial Distance and Time (66)

2.3 METHODOLOGY FOR MINERAL IDENTIFICATION

2.3.1 <u>X-Ray Diffraction studies (XRD) :</u>

X-Ray diffraction has been a powerful tool over the last six decades in the analysis of materials. It provides information on the crystal structure, lattice defects, crystallite size etc., X-Ray diffraction works on the principle of Bragg's law which is given by the equation,

$$n\lambda = 2d\sin\theta \qquad \textbf{(2.1)}$$

where , λ = wavelength of x-ray

d = inter-planar distance

θ = angle of incidence

n = Order of reflection (1,2,3....)

Therefore, $n\lambda$ must be less than 2d. For diffraction, the smallest value of n is 1. Therefore the condition of diffraction at any observable angle 2 θ is,

$$\lambda < 2d$$

The following are the diffraction methods commonly employed which are described briefly.
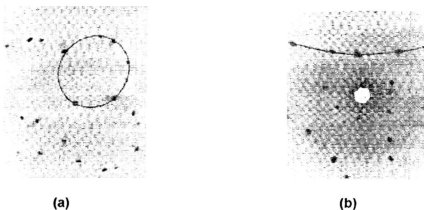
(a) Laue Method (34) :

Laue's method is mainly used for two reasons - determination of crystal orientation and the assessment of crystal quality. In this method, a beam of white radiation was allowed to fall on a fixed single crystal.

The Bragg angle 'θ' was therefore fixed for every set of planes in the crystal, and each set picks out and diffracts that particular wavelength which satisfies the Bragg Law for the particular values of 'd' and 'θ' involved. Each diffracted beam thus has a different wavelength.

There are two variations of the Laue method, depending on the relative positions of source- crystal and film. In each, the film is flat and placed perperdicular to the incident beam.

The film in the Transmission Laue method (original laue method-Fig2.1a) is placed behind the crystal so as to record the beams diffracted in the forward direction. In the other method called back-reflection Laue method(Fig2.1b) , the film is placed between the crystal and X-ray source, the incident beam passing through a hole in the film, and the X-ray source, the incident beam passing through the hole in the film and the beams diffracted in the backward direction are recorded.

In either method, the diffracted beam forms an array of spots on the film as shown in the Fig2.1 (a) and 2.1(b) in the following page.

| (a) | (b) |

Fig(2.1) : An example of (a) Transmission and (b) Back-reflection Laue Method of an aluminium crystal(from "ELEMENTS OF X-RAY DIFFRACTION" by B.D.CULLITY) (34)

The array of spots is commonly called "pattern". The spots are seen to lie on certain curves, as shown by the lines drawn on the figures.. These curves are generally ellipses or hyperbolas for transmission patterns (2.1a) and hyperbolas for back-reflection patterns (2.1b). The positions of the spots on the film, for both the transmission and back reflection method, depend on the orientation of the crystal relative to the incident beam, and the spots themselves become distorted and smeared out if the crystal has been bent or twisted in any way.

(b) Rotating Crystal Method (34):

The main use of the rotating crystal method lies in the determination of unknown crystal structures and because of this reason it is the most powerful tool for the X-ray crystallographer. In this method, a single crystal is mounted with one of its axes, or some important crystollgraphic direction, normal to a monochromatic X-ray beam. A cylindrical

film is placed around it and the crystal is rotated about the chosen direction, the axis of the film coinciding with the axis of rotation of the crystal. As the crystal rotates, a particular set of lattice planes will, for an instant, make the correct Bragg angle for reflection of the monochoromatic incident beam, and at that instant a reflected beam will be formed. Given below is a Fig2.2 showing the method.
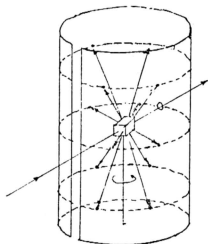
Fig(2.2): Rotating Crystal Method

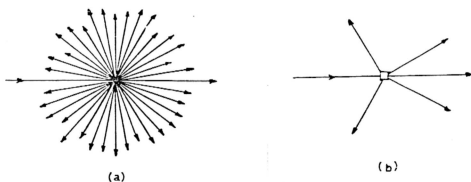(from "ELEMENTS OF X-RAY DIFFRACTION" by B.D.CULLITY) **(34)**

(C) Powder Method **(34)** :

In this method, the crystal to be examined is reduced to a very fine powder and placed in a beam of monochromatic X-rays. Each particle of the powder is a tiny crystal, or assemblage of smaller crystals, oriented at random with respect to the incident beam. Just by chance some of the crystals will be correctly oriented so that their (100) planes, for

example, can reflect the incident beam. Other crystals will be correctly oriented for (110) reflections and so on. The result is that every set of lattice planes will be capable of reflection. This method is specifically suited for determining the lattice parameters with high precision and for identification of phases, whether they occur alone or in mixtures such as polyphase alloys, corrosion products, refractories and rocks.

**Diffraction under non-ideal conditions (34):**

The method mentioned above make use of ideal conditions such as a perfect crystal and an incident beam composed of perfectly parallel and strictly monochromatic radiation.. However, in reality, such conditions do not exist. We can see that only an infinite crystal is really perfect and that small size alone, of an otherwise perfect crystal, can be considered a crystal imperfection. Some examples of diffraction under non-ideal conditions are scattering of incident beam of X-ray by a single atom in all directions in space and the diffraction by a crystal shown in Figs 2.3(a) and (b) below.

(a)   (b)

Fig(2.3): (a) Scattering by an atom and (b) Scattering by a crystal

(from "ELEMENTS OF X-RAY DIFFRACTION" by B.D.CULLITY) (34)

The figure(2.4) below show the comparative X-ray scattering by crystalline solids, amorphous solids, liquids and monatomic gases . The curve of scattered intensity vs 2 θ for a crystalline solid is almost zero everywhere except at certain angles where sharp maxima occur. These are the diffracted beams. Both amorphous solid and liquids have structures characterised ny an almost complete lack of periodicity and a tendency to "Order" slightly which result in one or two broad maxima. Finally, the monatomic gases, where the atoms are arranged perfectly at random and their relative positions change constantly with time. The corresponding scattering curve shows no maxima, merely a regular decrease of intensity with increase in scattering angle.
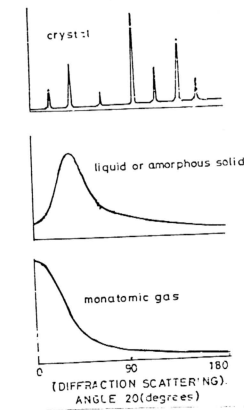
Fig(2.4): Comparative X-ray scattering by crystalline solids, amorphous solids, liquids and monatomic gases(from "ELEMENTS OF X-RAY DIFFRACTION" by B.D.CULLITY) (34):

2.3.2. Scanning Electron Microscope Studies (SEM) (35) :

In this instrument , the primary purpose of the electron beam is to produce an image, and sometimes an electron diffraction pattern of the sample. When electrons strike the sample, X-rays are generated, and a chemical analysis of the electron irradated area is therefore possible if a spectrometer is is attached to the microscope .

The electron focal point on the sample is a scanning electron microscope is atleast ten times smaller than that it is in the microprobe, in order to provide good spatial resolution in the electron image.. As a result, the current in the electron beam hitting the sample is very small, in the order of 10^{-9} amperes or less, and the intensity of the emitted X-rays are very low. Under these circumstances an energy dispersive spectrometer is preferred because it is far more efficient than crystal spectrometer in detecting X-rays from the specimen, as well as being very much faster. In fact , the largest single application of the energy dispersive spectro-meter is as an attachment to the SEM .

Principles of SEM:

(a) Beam diameter :

Normally in the SEM, a current of typically 10^{-11} amp is focused in to a spot of diameter 100 A^0 on the specimen ($1A^0 = 10^{-8}$ cm). The smallest beam diameter that has been achieved with a surface SEM was 25 A^0.

(b) Magnification :

This is controlled by varying the size of area that is scanned on the specimen. Magnification can be varied over a wide range, typically upto 100,000 times or more.

(c) Depth of Focus :

In SEM, the convergence angle must be kept small because of lens aberrations. The SEM has therefore an advantage even at low values of magnification for which optical microscope would be used.

(d) Resolution of SEM :

The resolution of SEM is of two types - low and high resolution. A low resolution image (such as X-ray image, luminescent image or induced - signal image) is one in which the resolution is limited to first order by electron penetration into the solid specimen. On the other hand, a high resolution image is one in which the signal is obtained at the point at which the primary electron enters the specimen.

Types of images :

Images in the SEM are obtained by "looking at" the specimen along the incident beam and with the apparent illumination coming from the signal detector. Images can be classified as follows:

(a) Secondary Electron Image :

This is the most generally useful type of image for studying surface topography. The detector in this case is sensitive to electrons that emerge from the specimen with less then 50 eV energy.

(b) Back scattered electron image:

This is obtained by collecting electrons that leave the specimen with more than 50 eV energy . The appearance of the backscattered electron image will depend on the angle of incidence and on the position and the energy sensitivity of the backscattered electron detector.

(c) High and Low deflection backscattered electron image:

This is obtained by collecting electrons which have been deflected by more than 90 or less than 90 . The resolution of high deflection backscattered electron image is limited to first order by electron penetration. The resolution of low deflection image is better than the high deflection image as it is more senstive to surface topography.

(d) X-ray Image:

This is obtained by collecting characteristic X-rays and is used to display the distribution of chemical elements in the micro-analyzer.