PHYSICO-CHEMICAL AND MINERALOGICAL STUDIES ON SOME PLASTIC KAOLINITIC CLAYS

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.........to my elder brother who was given a few days in this earth by
THE ALMIGHTY !

DECLARATION

I hereby declare that this thesis is a bonafide record of the work done by me and that no part of the thesis has been presented earlier for any Degree, Diploma or similar title of any other University.

Kshama

(Kshama V. Das)

December 1992

Thiruvananthapuram

CERTIFICATE

This is to certify that the thesis bound herewith is an authentic record of the research carried out by **Kshama V. Das, M.Sc.** under our supervision in partial fulfilment of the requirements for the **Degree of Doctor of Philosophy in Chemistry** of the University of Kerala and further that no part thereof has been presented before for any other Degree.

Nair
(Prof. Dr. C.G.R. Nair)

Lalithambika
(Dr. (Mrs.) M. Lalithambika)

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ABSTRACT

Among the best-known and widely used important industrial minerals, ball clays are of much value since they can be used in various ceramic industries. One of the essential features of ball clays is their fine grain size compared to those of other clays which is the main reason for its plasticity and so it is used to enhance the binding property. They can be added to other clays to give strength to the moulded shape and yet maintain the white colour after firing. In countries like UK, USA, Japan and Germany specially formulated ball clays are available for specific industries like sanitaryware, high tension and low tension insulators, porcelainware etc. These have been prepared by different blending techniques to make the product with tailor-made properties. In India we are using the naturally available materials with no significant processing operations as far as ball clays are concerned. It is with a view to get an idea about the preparation of tailor-made ball clay material that this detailed study of different types of ball clays was undertaken.

In Kerala, the occurrence of 1.7 million tons of economically viable ball clay has been identified so far of which the major source is the Tertiary sedimentary sequence in the Quilon District, especially the Padappakkara reserve which comprises around 1.3 million tons. The origin of these kaolinite horizons has been discussed in detail in the second chapter. It mainly pertains to the diagenesis of kaolinite group of minerals (from feldspathic rocks) and associated iron sulphide

minerals - which exist as an impurity in the matrix- with respect to the interrelationship between sandstone and clay beds of Tertiary deposits (Warkalla formation) in Kerala. Industrially these minerals find use as binding agents because of the high plastic nature once the ferruginous impurities are removed. By sedimentation method using suitable dispersing agent the denser impurities can be removed to a certain extent.

The amount of the kaolinite mineral in a clay material is of considerable importance since it is responsible for many of the properties of the material. The quantitative determination of kaolinite in clay- by considering that the degree of crystallinity may have effect on the measurements - has been done by many investigators for more than forty years. Moreover, the crystallinity of kaolinite is a parameter of great structural, geochemical and industrial significance. Besides the grey variety of ball clay from Padappakkara six other samples from different locations of the world were collected for the studies; namely Payyangadi (Kerala), Bikaneer (Rajasthan), Bimadole (Andhra Pradesh), Than (Gujarat), Westerwald (Germany) and Inagakikibushi (Japan). < 1 micron fraction of each sample was separated by sedimentation method obeying Stoke's law. These fractions already collected were concentrated in the clay content by removing organic matter, carbonates and iron oxides and the crystallinity indices of the purified kaolinitic materials were measured from X-ray diffraction and Infrared absorption patterns (Hinckley's and Worral's crystallinity measurements techniques). The lattice parameters have also been computed from the XRD data using the program LCLSQ least square refinement technique.

'The next chapter deals with the plasticity of ball clays. The samples from Padappakkara is found to be the best plastic among all the other samples already mentioned. Plasticity is a composite property which depends on the total characteristics of the particular clay material. Hence a detailed investigation on the physical, chemical and mineralogical properties of all these samples has been carried out and finally a regression analysis was also done to correlate the plasticity parameter with other three properties as silica content, base exchange capacity and particle size. The effect of humic acid content on plasticity was also studied in this context by removing the organic matter in two methods, (1) by the oxidative decomposition with 30% H_2O_2 (2) by extraction with NaOH. An attempt has also been made to correlate the zeta potentials of the samples with other properties.

While doing the effect of grinding on the plasticity of Padappakkara clays, it was seen that in the XRD patterns of the ground samples, new mineralogical phases were being introduced in the matrix. So the grinding study on kaolinite was extended with another two clays, the plastic clay from Bikaneer, Rajasthan, and one kaolinitic clay sample from Thonnakkal, Trivandrum District. The change in plasticity, particle size and shape, cation exchange capacity and mineralogy with grinding have been investigated. It was alpha alumina or corundum found to form during grinding of ball clay from Padappakkara and has been attributed to the presence of gibbsite as an impurity. Mineralogically, no considerable change was observed in the case of the other two clays. However, the formation of alpha alumina in the former case is worthwhile as this proves to be a method for making a high temperature phase by wet grinding.

The last chapters are mainly concerned with the changes taking place during their sintering. The aim of this study is to determine the relationships between raw material characteristics on the phase composition and the physical properties of the fired samples. On the basis of these relationships, some additives have been incorporated in the mix to modify the properties of the fired product of the blends. The first set of blends was prepared using Bikaneer clay by mixing it with different percentages of alumino silicate gel prepared from Zeolite 3A. The gel addition upto 10% can be used as a technique for improving fired strength. The second set of blends was prepared with a view to improve the properties of Padappakkara clay so that it can be used as a substitute of the ball clay from Bikaneer which has been widely used for making high tension insulators. Accordingly the final blended mix was tested in M/s. Bharat Heavy Electricals Ltd. and the results were found to be satisfactory. Thus the ball clay from Padappakkara which otherwise could not have been used as a binding clay, inspite of its high plasticity was modified by a blending procedure to get an industrially valuable product.

LIST OF PUBLICATIONS

1. Kshama V. Das, Sathy Chandrasekhar, M. Lalithambika, A.D. Damodaran and C.G.R. Nair (1991)
   Study on the plasticity of a ball clay from South Kerala
   Trans. Ind. Ceram. Soc., Vol. 49, pp.12-15.

2. K.V. Das, B.V. Mohan, M. Lalithambika and C.G.R. Nair (1991)
   Grinding studies on kaolinites
   Interceram, Vol. 40(1) pp.11-14.

3. V. Das Kshama, B.V. Mohan, M. Lalithambika and C.G.R. Nair (1992)
   Sintering studies on plastic clays
   Accepted in Ceramic International.

4. V. Das Kshama, B.V. Mohan, Gracey Thomas, Sathy Chandrasekhar, M. Lalithambika and C.G.R. Nair (1992)
   Plastic clays from South India - Mineralogy and Geochemistry
   Communicated to Clays and Clay Minerals.

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Perfection is attained by slow
degrees: it requires the hand of time.
—Voltaire

CHAPTER 1

INTRODUCTION : CLAYS - AN OVERVIEW

1.1 GENERAL

The rise of the industrial age has accelerated the demand for minerals and simultaneously the world has dug up and consumed more of its mineral resources. A glance at the history of development of leading industrial nations reveals that their rise has coincided with the optimum utilization of their mineral resources. Among the minerals which are most important for industry, ceramic materials especially clay minerals claim a unique position in the field of material science.

The term clay as opposed to clay mineral indicates a mixture of clay minerals with a variable amount and type of non-clay mineral material. They are the product of the decomposition and alteration of feldspathic rocks through a process called kaolinisation (Ceramic Industry, 1992).

K-Feldspar Kaolinisation Kaolinite

$$K_2O \cdot Al_2O_3 \cdot 6\ SiO_2 \xrightarrow[\substack{-\ K_2CO_3 \\ -\ 4\ SiO_2}]{\substack{CO_2 \\ 2\ H_2O}} Al_2O_3 \cdot 2\ SiO_2 \cdot 2\ H_2O$$

Clay is an admixture of particles of different sizes and widely differing physical, chemical and mineralogical properties. The non-plastic portion consists of altered and unaltered rock particles of which the most common and abundant substances are quartz, micas, feldspars, iron oxides and calcium and magnesium carbonates. Organic matter is normally present in greater or lesser amounts, and frequently plays an important role in determining the property of clay particles. The essential constituents of clays are hydrated silicates of aluminium of which there are several, but the most important and widespread are the kaolinite group $(Si_2O_5)\ Al_2(OH)_4$ and the montmorillonite group $(Mg, Ca)O\ .\ Al_2(Si_2O_5)_2\ (OH)_2$.

A ceramic may be defined as the product obtained by the heat treatment of inorganic material (Singer, Singer, 1963). The term 'ceramics' is derived from the Greek word 'Keramikos' which originally meant the horn of an animal and later began to signify burnt stuff (Thomas Chirayath, 1969). In ancient times, probably the main items that came under ceramics were the commonest pottery articles made from clays.

1.2 CLASSIFICATION OF CLAYS

Clays may be designated as residual or sedimentary according to their geologic history. Residual clays are those occurring in the same location as originally formed by weathering . The most important residual clays in the world are English China clays and North Carolina kaolins. Sedimentary clays are transported and are deposited through air, water etc. Clays are divided for commercial purposes into china clay (kaolin), ball clay, fire clay and tile clay. China clays or kaolins are mainly residual clays formed in situ, by the break down of primary minerals. The word 'kaolin' is a chinese word meaning high hill (William Lee,1961).

They are white burning and can be used in the manufacture of crockery, sanitaryware, earthenware, stoneware, high grade tiles, porcelain, textiles, paper, rubber, paints, ultramarine blue, insecticides, abrasives, cosmetics, pharmaceuticals etc. (Project Report, RRL, Trivandrum, 1984). Clays which are plastic or 'sticky' yet burn white, are termed ball clays. They can be used in whitewares to increase the green strength of the body. Fire clays are refractory which have a high fusion point. This type of clay seams vary considerably in composition and properties and there is no progressive relationship to geological age. Fire clays are the most extensively used refractory material and the nature of the minerals present in them and their influence on the property of the fired bricks have been the subject of much research for many years. Tile clays depend for their value on the physical properties rather than their chemical composition. They are suitable for making roofing tiles, terra-cotta and coarse eathernware (brownware).

1.3 CLAY MINERALS

Classification

In most layer lattice structures, the silica units are arranged in the form of hexagonal rings and the sheet is constructed of such symmetrical rings surrounded by six similar ones, each of which share two corners. This silica sheet is mixed with one or more gibbsite layers composed of Al atoms and hydroxyl groups.

Clay minerals can be classified into two major groups (1) the kaolins, and (2) the montmorillonites. The kaolin group includes kaolinite, nacrite, dickite, halloysite and allophane. Of all these, the most important is kaolinite, since it is the principal constituent of china clay, ball clay, fire clay and many brick clays. The montmorillonite group consists of montmorillonite, nontronite, beidellite, hectorite and saponite. In addition to these two groups there are the mica group, illite group, chlorite group, palygorskite group and vermiculites (Worrall, 1975).

1.3.1 Single layer group

All the kaolin minerals contain one silica layer and one gibbsite layer and are therefore sometimes called single layer group or 1:1 layer minerals.

In the silica layer each silicon atom is surrounded by four oxygen atoms, the oxygens being at the corners of a regular tetrahedron with a net charge of minus four. The fourth oxygen in each tetrahedron is joined to only one silicon, and so has one valency unsatisfied. It is through these valency unsatisfied oxygens that the silica layer can join via cations to gibbsite layer structures. The basic 'building block' of the gibbsite layer is an aluminium atom surrounded by six hydroxyl groups in a regular octahedral structure. Since every OH group receives half a valency share from two trivalent aluminium atoms, the hydroxyl groups are all valency satisfied in the layer. The dimensions of the hexagonal rings in the silica and gibbsite sheets are very similar and it is possible for the two sheets to condense together. This occurs by elimination of two hydroxyl groups, their places being taken by the valency unsatisfied oxygen in the silica layer in fixed position and give a constant basal spacing of 7.2 Å. This leads to electrical neutrality as $(Al_2(OH)_4)^{2+}$ $(Si_2O_5)^{2-}$ (Ryan, 1978).

1.3.2 Double layer group

When a gibbsite layer is condensed between two hexagonal silica units a double-layer structure is formed which is capable of indefinite extension in two dimensions by covalent/ionic linkages. The ideal formula of this unit is $Al_2(Si_2O_5)_2$ $(OH)_2$ i.e. the pyrophyllite structure. This group of minerals is indicated as 2:1 layer minerals. Montmorillonite group of minerals come under this group. In addition to the montmorillonite minerals, micas, hydromicas, chlorites and vermiculites are all slight variants of the same basic structures.

1.3.3 Mixed layer structures

Many layer-silicate minerals which occur in nature are composed of mixed layers of more than one type. Some are known which consist of units of mica, chlorite, vermiculite, hydrous mica and montmorillonite.

1.4 GLOBAL STATUS

Availability and use trend

Common clays are found everywhere in the world but high grade clays are more restricted. Their chief distribution is as follows (Mead et al., 1981., Table 1).

Table 1

Type of clay	Foremost localities
China clays (high grade kaolins)	England, Czechoslovakia, Germany
China clays (paper clays)	France, China, England, Germany, Czechoslovakia, United States
Ball clays	England, Germany
Fire clays	Germany, England, Belgium, United States

The estimated world production of kaolin in 1986 was 21.6 million tonnes, about 5.5% higher than that in 1985. Production from 58 countries was reported (Indian Minerals Year Book, Vol.2, 1989, Table 2). The USA continued to be the leading producer followed by USSR, UK, South Korea, Hong Kong, Brazil, India and Czechoslovakia. These eight countries together accounted for 79% production.

Table 2

World production of kaolin from 1984 to 1986
(by Principal Countries)

(in tonnes)

Country	1984	1985	1986
World (Total)	19,900	20,400	21,600
GDR (Marketable)	175	175	175
FRG	370	342	477
USA	7,214	7,070	7,755
UK	2,809	2,870	2,913
USSR	2,800	2,900	3,000
Korea	671	612	790
Hong Kong	700	758	710
Brazil	590	655	650
India	—	—	4,300
Czechoslovakia	540	548	546

1.4.1 England

In British Isles, the kaolin deposits of economic importance are those where a large mass of igneous rock has been altered by hydrothermal action, as in Cornwall and Devon (WBB Co., 1973). Large deposits of ball clays occur in the south western countries of England and they are widely used in the British Isles particularly in the white-ware industry. The three important clay producing areas are in Dorset, North Devon and South Devon. The ball clays of Devon have been in general use since the latter half of the 17th century and since the middle of the 19th century have been exported to countries throughout Europe and to the United States. They are now marketed extensively throughout the world and owe their continuing popularity to their unique and consistent combination of physical properties. The areas in which clay is worked are confined to the valley of the Bovey and Teign, near Newton Abbot, a depression near Terrington in North Devon, near Wareham and Corfe Castle in the Isle of Purbeck and also near Wimbourne Dorset (Worrall, 1982).

1.4.2 America

The annual production of clays in the United States ranges from 60 to 65 million tons, valued at about $ 1500 millions (Mead et al, 1981). In 1978, clays were produced in all states of Latin America except Hawaii, Rhode Island and Vermont. The leading 56 firms supplied about one-half of the total output and nearly 600 firms the remainder. Together these firms operated a total of 1,179 mines (U.S. Dept. of Interior, 1983). Estimated value of all marketable clay produced in 1978 was 694 million tons of which ball clay constitutes around 958 thousand tons. Total quantity of clays sold or used by domestic producers in 1978 increased 4% in tonnage and rose 20% in total value. Demand for the various clays from a 1977 base is expected to return to its annual rates of increases between 2% and 6% through 1985. This continued growth of the energy intensive clay-based industries could be impeded severely by persistent energy problems and lowered construction rates. Average prices for most clays are expected to rise slowly, reflecting higher quality requirements for the speciality clays and increasing costs associated with land acquisitions, land rehabilitation and environmental and energy factors. Greater recovery of byproducts and coproducts should occur as processing technology improves and as problems of solid waste disposal become increasingly acute. Further enhancement of the U.S. position as a major world supplier of high-quality clays is assured by the possession of more than adequate resources of all major types of clay coupled with the clay processing technology necessary to provide large quantities of consistent quality clays over extended periods. The aluminium companies were acquiring kaolin, the principal high alumina clay.

1.4.3 Japan

Japan produces negligible amounts of kaolin formed in the paleozoic and Mesozoic eras (Geological Survey of Japan, 1969). In the prefectures of Aichi, Gifu and Mie in Central Japan, lagoonal deposits mainly consist of the alteration of gravel beds, sand beds, silt beds and kaolin clay beds, often intercalating lignite measures

(Matsuzawa, 1960). The kaolin clay beds are, for example chiefly made up of kaolinite presenting the colours of light brown and light ashbrown with an admixture of carbonaceous materials and high in plasticity as in the case of clays from Kibushi deposit. Gairome clay consists mainly of kaolinite with small quantities of unweathered feldspar. Kaolin deposits derived from vitric tuff are scattered all over central and northeast Japan.

1.4.4 Germany

The total amount of kaolin (marketable) production in West Germany was 175 tonnes in 1986. According to IBM, FRG produced 477 tonnes kaolin simultaneously. The processed clays from the Westerwald deposits of West Gerrmany is well known for the manufacture of various ceramic products.

1.4.5 China

The Peoples Republic of China is moderately prominent in ceramics and their raw materials but statistical data are very sketchy. Good clay deposits for general use are found in most of the provinces of China, and improved technology has extended resources further. Chinese clays and porcelain from Chingtechen in Fuliang District of Kiangsi Province have long been world famous. Chingtechen's yearly production of porcelain clays may be between 300,000 and 500,000 tons (Wang, 1978). Quality of porcelain clays is not as good elsewhere. However Hopeph province produces several hundred thousand tons yearly and Shanting and Kaingsu provinces each produces possibly 100,000 tons.

PRC's output of kaolin and fire clays for industrial and brick use may be between 1 million and 1.5 million tons yearly. Although industrial demand has been rising, some surpluses are still available for export. Leoning is the leading producing Province, with annual output of approximately a half million tons, coming mainly from Fu Hsein and Penksi Hsien. Hopeph province ranks next, with yearly output of several hundred thousand tons derived primarily from Tangshan. Other lesser producing Provinces include Kiangsi, Szechnan, Shanting, Kwangtunej, Kiangsu, Fukieu and Kwanghing.

1.4.6 India

The literature survey shows that an attempt for characterising the clays of India started as early as 1953 (Krishnaswamy, 1979; Guha, 1982). Geological Survey of India in collaboration with the Central Glass and Ceramic Research Institute, Calcutta, carried out the clay mapping of the country. Identified ball clay resources of India is estimated to be around 5.26 million tonnes of which Kerala has got around 1.67 million tonnes. The China clay deposits of Kundara in Kerala is world famous as a valuable source of raw material. Potential source of ball clays occurs in Rajasthan near the villages of Litaria, Khajwana, Gunga and Rel Chandawatan in Jodhpur District and also Madh Kletri and near Kelyatji.

Occurrences of ball clays had been reported from near Udaipur, Bhagagela, Bhagat Talavdi and Than in Saurashtra and at Quilon in Kerala. A small deposit of white plastic clay resembling 'ball clays' are found in Nagaland from Teliamura to Ampi Bazar Khowai. Other similar occurrences are near Jogindranagar and between Ranir Bazar and Agartala.

As per the report of Indian Bureau of Mines (Indian Minerals Year Book, Vol. 1,, 1989) the production of ball clays in India is as follows:

Table 3

Production of ball clay, 1986

	No. of mines	Quantity (tonnes)	Value (Rs.)
India	59	Total 279,562 (Public Sector 60,380 Private Sector, 182,014)	1,60,13,000
Kerala	2	739	-
Cannanore	1	175	
Quilon	1	564	

In 1987, the ball clay production in Kerala is estimated to be 497 tonnes.

According to the Kerala State Geological Department, a reserve of 0.71 million tons of ball clays occur in Patuvam, Karivallur, Eripuram and Payyangadi areas (Krishnaswami, 1971). In Kerala a potential deposit of ball clays can be seen at an interval of 50 to 60 metres along the steep bank of Ashtamudi lake in Padappakkara. Two layers of plastic clays were observed in this section separated by lignitic clays. According to the information obtained from the locals the lower layer continues to a depth of about 6 m below the ground level in the quarry. An investigation on the physical, chemical and mineralogical characteristics of the clays from this deposit was carried out which will be described in detail in the coming Chapters.

1.5 BALL CLAYS - A REVIEW

Ball clays are plastic sedimentary deposits that were laid down in the Eocene and Oligocene periods in lakes and swamps. According to Scott the name 'Ball clay' is derived from the original method of production which consisted of cutting out the clay in open pit into cubes or balls (Scott, 1929). Sedimentary or secondary clays are those that have been transported by water, ice or wind and redeposited, and alteration usually occurring during the transportation process.

Ball clays impart high green strength and good workability to whiteware bodies. The primary mineral phase is kaolinite. Along with other dominant and accessory mineral they also contain varying amounts of carbonaceous matter which occur in different physical forms. They have no definite chemical composition and in that respect they do not differ greatly from china clays. However it often contains a large proportion of silica and is more plastic. If the so-called 'siliceous' ball clays are included, the maximum SiO_2 content rises to 80% and the minimum Al_2O_3 content falls to 15% (Worrall, 1982). The following table illustrates the wide variation in chemical composition of ball clays.

Table 4

Oxide	Range of variation
SiO_2	40-60
Al_2O_3	25-40
Fe_2O_3	0.25-4.0
Na_2O	0-0.75
K_2O	0.5-4.0

Ball clays have more than 85% of the particles, finer than 1 μ. A linear dry shrinkage of about 12% is often regarded as a permissible maximum for ball clay (Guha, 1982). As high shrinkage and high strength go hand in hand, it is normal for ball clays to exhibit high strength; most of the clays range between 125 and 250 psi in tensile strength and between 150 and 500 psi modulus of rupture.

Ball clays are variously described as "blue", "black" or "ivory" according to their colour (Worrall, 1982); the blueness or blackness is caused by the presence of much organic matter whereas ivory clays owe their colour to the presence of iron oxide. The colour of an unfired ball clay however is not necessarily any guide to its fired colour. The fired colour ranges from white to buff and PCE is generally below cone 33 ($1743^{o}C$).

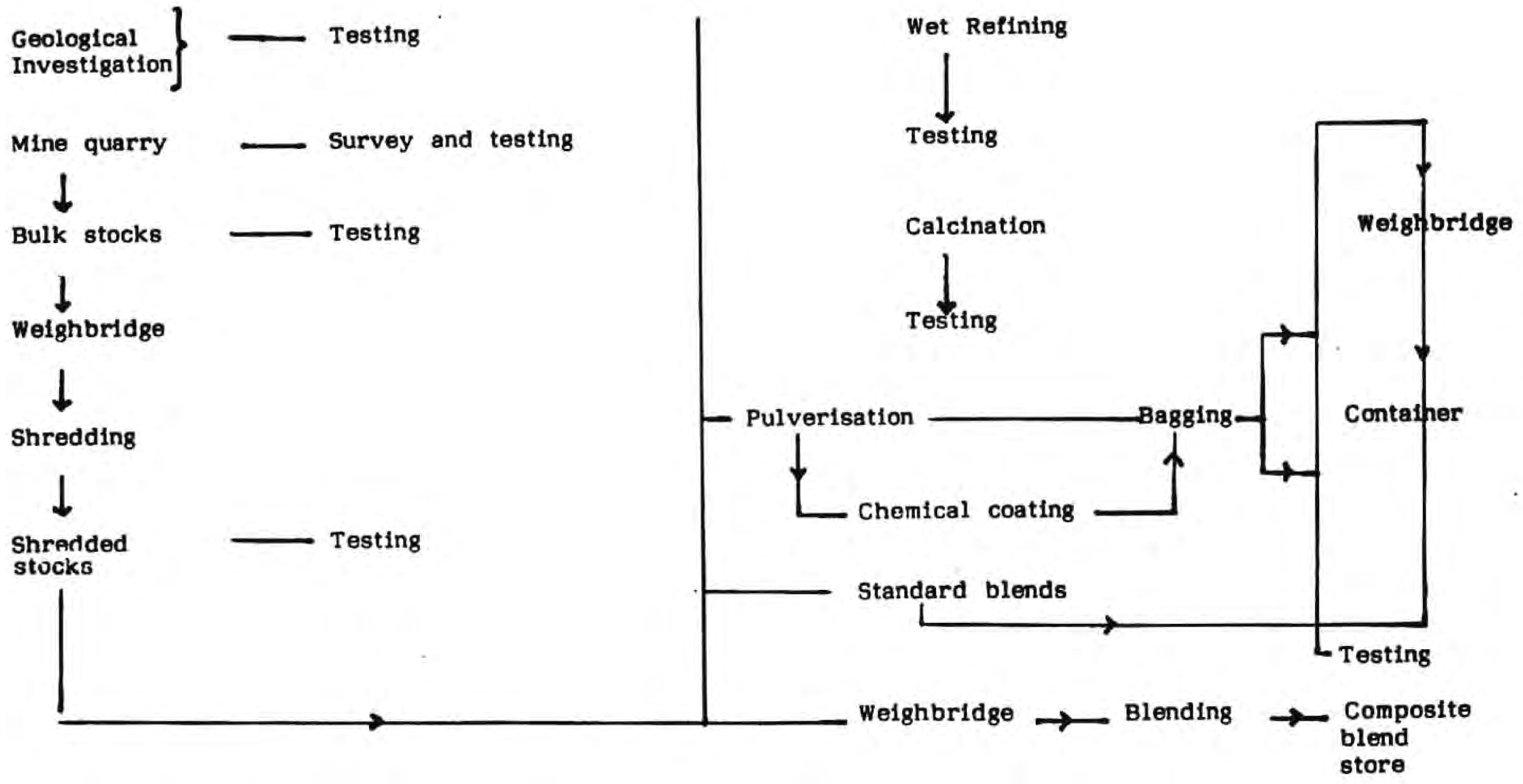
1.5.1 Extraction

The method adopted for extracting sedimentary clays - ball clays depends on the depth of the clay seam, the hardness of the clay, the depth of overburden and the inclination of the seam to the horizontal. Ball clays are mined either by open-pit or underground methods.

For open-pit or open cast working, the overburden of soil is removed by mechanical excavators or bull dozers and then the underlying clay is dug out by means of pnuematic shovels and loaded onto lorries by means of an elevator. When underground mining is employed, the workings seldom extend to more than 120 ft below ground, the clay being hauled directly to the surface by mechanical excavator. Today however underground mining is carried out by the adit method, in which the main tunnel is driven to follow the dip of the clay seam to a horizontal distance underground which is usually of the order of 900 to 1000 metres (WBB & Co., 1973). Clay extraction takes place from levels which are driven at right angles to main tunnel. The clay is either won by using a mining machine or by hand-operated compressed air spades, and then winched to the surface in small rail-trucks. Using the adit method clay is extracted from vertical depths of 150 to 200 metres. Recently underground working has become increasingly uneconomic and this activity is now being reduced. However, it is still necessary for certain seams to be won in this way, as insufficient quantities are available from the open cast workings.

Table 5

Flow Diagram



Throughout the extraction process, the type and quality of the clay is ascertained by a pit selector, in cooperation with the works quality control laboratory.

The first stage in processing the bulk clay is known as shredding. Clays of various seams are shredded together in predetermined proportions to produce standard clay blends of an easily landleable, easily dispersible size.

As with most naturally occurring minerals, property variations is not uncommon in ball clays. Because of their fine particle size, associated natural contaminants and to some extent their relatively low selling price it was not until recently that economically viable methods for their purification and refining were developed. Even today therefore strict selection procedures at the pit face, with frequent sampling and testing of the clays throughout the production system are essential. A typical production and quality control system is illustrated in the flow diagram.

1.5.2 Mineralogy and chemistry

Many of the properties of clays and other ceramic materials are dependants on the nature and amounts of the various minerals in them so that their identification, determination and estimation are of very great importance. The conditions in which the minerals originate are determined by the concentration of the components, temperature, pressure and the interactions of minerals with country rocks (Milovski & Kononov, 1985). The phasal transition of a substance from its liquid form into hard form is a particularly widespread means of mineral formation.

The chemical analysis of clay or other ceramic material is usually expressed in terms of percentage. Composition of the constituent oxides is referred to as ultimate analysis. But the clay does not occur naturally in the form of oxides which needs further mineralogical analysis. The type of a mineral may depend on the mode occurrence or the nature of the locality or the environment. Accordingly they can be summarised as

1. Those dependent on the chemical nature of the mineral.
2. Those dependent on the external crystallographic features of the mineral i.e. the microscopic studies.
3. Those dependent on the internal atomic or ionic arrangements within the crystal lattice; this group includes X-ray, infrared and electron diffraction analysis.
4. Those dependent on some physical or chemical change within a mineral which can be measured under controlled conditions, such as differential thermal analysis (i.e. the measurement of heat changes which occur during reaction).

The technical properties of clays are principally determined by their mineralogical composition and particle size distribution. The most important feature is the type of phyllosilicate minerals in a clay (Heinrich Kromer, 1981). Phyllosilicates affect the plasticity and binding abilities because of their fine particle size and surface properties. . While kaolinite controls the refractoriness, illite, mica, montmorillonitic minerals and chlorites promote sintering. Dry strength depends partly on particle size, but the presence of montmorillonite minerals is still more important. Illite, feldspar and fine grained carbonates influence the vitrification. Coarse grained carbonates lead to bursting ("lime splits"). Feldspar and iron minerals are still more effective for vitrification even if present only in small quantities. Iron minerals, titanium and lime control the development of the fired colour. Quartz opens the structure of a body and thus it facilitates drying processes. On the other hand it can cause difficulties during the firing process because of its phase transformation which affect volume changes.

The dominant minerals present in ball clays are kaolinite, a micaceous mineral and quartz. Minor amounts of other minerals, in addition to carbonaceous material are often found in association with these major components. These minerals can include tourmaline, feldspar, chlorite, montmorillonite, interstratified clay minerals, various titanium compounds such as anatase, ilmenite (occasionally rutile) and various iron minerals such as siderite (also called chalybite), pyrite, marcasite, ilmenite and haematite. For general descriptive purposes, ball clays can be regarded as an idealised ternary system consisting of kaolinite, mica and quartz.

The surest way of mineral identification is by X-ray diffraction studies and differential thermal analysis. The internal structure of minerals could be identified by following the X-ray diffraction technique. The calculation pertaining to the analysis of the X-ray data are performed by following the Bragg's equation

$$n\lambda = 2\,d\,\sin\theta$$

where

n - order of reflection

λ - wavelength of the incident radiation

d - distance between the planes

θ - angle of diffraction

The DTA is based on the measurement of heat evolution/absorption when a material undergoes physical and chemical changes. As every clay mineral has its own thermal properties, it is possible to identify the mineral by carrying out the DTA studies. The temperatures are recorded using thermocouples in reference to the standard inert materials.

Chemical characterisation is invariably required for the proper utilization of the particular raw material. It is an essential step in establishing the nature of mineral but the chemical composition of silicates is so complex that a satisfactory systematic classification was not formulated until the spacial arrangement of the atoms was revealed by X-ray diffraction studies. Establishing the chemical constitution of a clay mineral remains as important today as ever it was in spite of its mineralogical description.

Unlike many fields of analysis where the percentage of a given element present is recorded, the ceramic analyst reports the percentage of the oxides. This convention not only saves calculating or even determining the oxygen content of the sample but also represents a truer picture of the constitution of the material.

Table 6

Chemical analysis

by

Classical methods

Estimation of SiO_2		Estimation of Na_2O, K_2O by	Estimation of Al_2O_3, Fe_2O_3, TiO_2,
Volumetric (silica fluoride) method	Gravimetric (single baking) method includes the precipitation of silica and then its removal by hydrofluorization	flame photometry. Sample solution is prepared by taking it in 1:1 HCl after removing silica with ($HF + HClO_4$)	CaO and MgO by spectrophotometry. Sample solution is prepared by the fusion of sample with potassium pyrosulphate after removing silica by hydrofluorization. The melt is taken in 3% H_2SO_4.

1.5.3 Physical properties

Many properties of ceramic raw materials are related to their composition with equal importance to the particle size and the shape of the minerals and also the way in which they are agglomerated to each other. In ceramic bodies though the treatment and processing during manufacture produces many changes in the appearance, colour, hardness and other physical properties, the original arrangement of the grains exists and can be traced in the final product. The important physical properties of the clays are enlisted below.

(a) Particle size distribution analysis

The information obtained on particle size distribution analysis of clay samples is very valuable. Usually this was done with the aid of sedigraph. If most of it remains on 18 mesh, the material is unlikely to contain much clay particles. In case there is a small residue on 18 mesh and high residues on 60, 100 and 200 mesh sieves, the material is usually suitable for coarser ceramic products and on grinding may be good for the manufacture of fine ceramics. A material with less than 3% residue on 200 mesh and 5% on 350 mesh is very fine grained and is suitable for fine ceramicware.

(b) Plastic properties

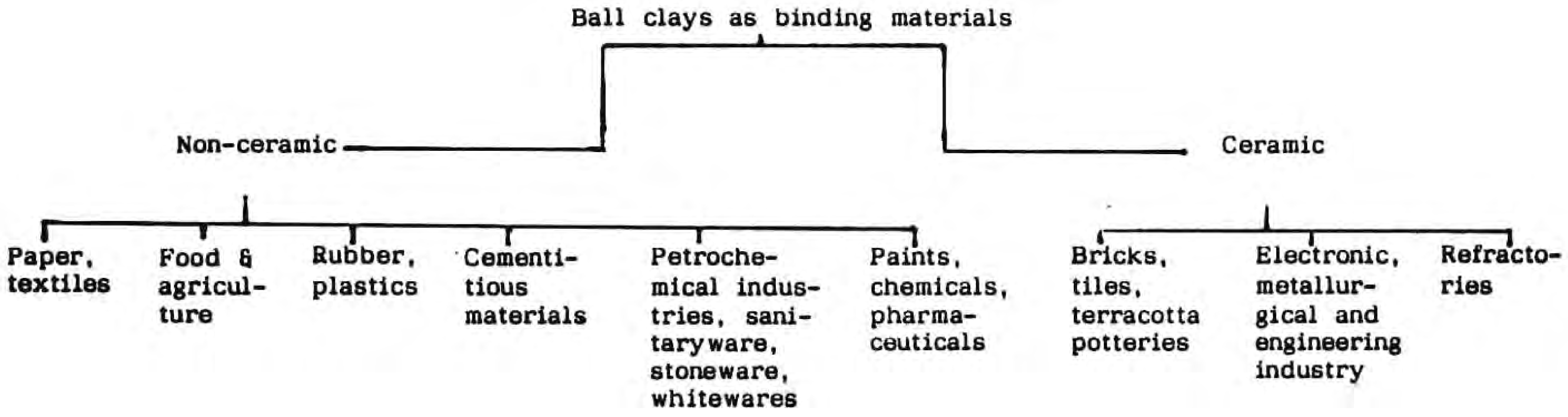
These properties such as water of plasticity, Atterberg number, base exchange capacity and pH values are highly interrelated and their combined effect determines the workability and moulding characteristics of a clay. The percentage of water required by a clay sample to develop its optimum plasticity is termed as water of plasticity. The plasticity of natural clays depends on the nature of the fine fractions as seen from montmorillonite in kaolinite which has a significant effect on this property. The Atterberg number is an index of the plasticity of a clay. The larger the Atterberg number the higher will be the plasticity. The base exchange capacity (BEC) of a clay is a measure of the exchangeable cation present in a clay. It is found that minerals of high BEC value have high plasticity.

(c) Fired properties

The important fired properties of clay which are of interest in ceramic industry are fired colour, fired shrinkage, water absorption, fired strength and pyrometric cone equivalent (PCE). The colour of a burnt clay has no constant connection with its colour before firing though in some cases it is possible to predict roughly its fired colour. The colour mainly depends on the amount of iron present and the firing conditions namely the oxidising and reducing atmosphere. Clays of low iron content will be white or pale cream when fired. As the iron content increases the colour varies from primrose, yellow through buff, red, brown, grey, blue or black whilst in some cases it may be melted on account of the irregular distribution of the iron compound present. Fired shrinkage and water absorption are interrelated properties. Higher the shrinkage lower will be the water absorption. The shrinkage when fired at high temperatures is mainly the result of reactions which occur within and between the minerals present. The reactions are of two types, (a) crystallisation where amorphous components undergo an internal rearrangement to form mineral types, (b) liquid formation arising by the action of fluxing agent as clay body to form low melting eutectics. Both reactions reduce the volume of the ceramic material mainly by decreasing the proportions of void space thereby reducing the porosity of the sample which is measured as the percentage of water absorption. The amount of shrinkage is dependent on the fineness of the particles too. Finely grained material shrink more than coarser grains.

1.5.4 Applications

Table 7



Ball clays are almost invariably used for the manufacture of bricks, tiles, terracotta, stoneware and sewer pipes. The variety of ball clay used for such applications are mostly of carbonaceous and red burning type. Facing bricks which are generally considered to be somewhat higher in quality can also be made from about the same type of material, but with less detrimental components and high kaolinitic content. A certain percentage of ball clay is added to get sufficient plasticity to porcelain and dinnerware bodies. Clays satisfactory for the manufacture of refractories are dominantly composed of kaolinite both sedimentary and residual. In recent years there has been much development of plastic refractories. Such material is applied in the plastic state where it is to be used and then burned into place to provide a monolithic unit.

Clay mineral analyses provide information on the source area and possible post-depositional changes which can lead even to the formation of petroleum products. This involves the consideration of whether or not the clay minerals experienced diagenetic changes on passing from one environment to another and hence whether any clay mineral composition is characteristic of a particular environment.

CHAPTER II

DIAGENESIS OF THE PLASTIC KAOLINITE CLAY MINERALS FROM THE WARKALLA FORMATION, PADAPPAKKARA - ITS GEOCHEMICAL AND INDUSTRIAL SIGNIFICANCE

2.1 GENERAL

The Cenozoic sediments in Kerala are generally restricted to the narrow stretch along the coastal tract of South India. The Tertiary basin which spreads (though unconformably) from Kanyakumari to Manjeshwaram, is essentially made up of three distinct formations (Fig. 1) (Raghava Rao, 1975). Extending as a narrow belt along the major part of the Kerala coast, the onland part contains essentially Neogene and Quaternary sediments. The Tertiary comprises a series of variegated sandstones and clays with lenticular seams of lignite (Warkalla formation $\backsim$ 80 m thick). These are underlain by more compact sands and clays with fragments and thin beds of limestone called Quilon formation with $\backsim$ 70 m depth (Kumar et al., 1933). And below this is a thick sequence of sediments called the Vaikom beds (Soman, 1980 and Raghava Rao, 1975).

The Warkalla formation well exposed in the Padappakkara region of Quilon district comprises a number of mine faces along the steep bank of Ashtamudi lake ($8^{o}59'$ N: 76^{o} 39' E), (Fig. 2). This is a continental and deltaic formation (Ghosh, 1986 and Menon, 1967) with a series of variegated sandstones and clay beds with lignitic intercalation. Although this sedimentary deposit has been identified a few

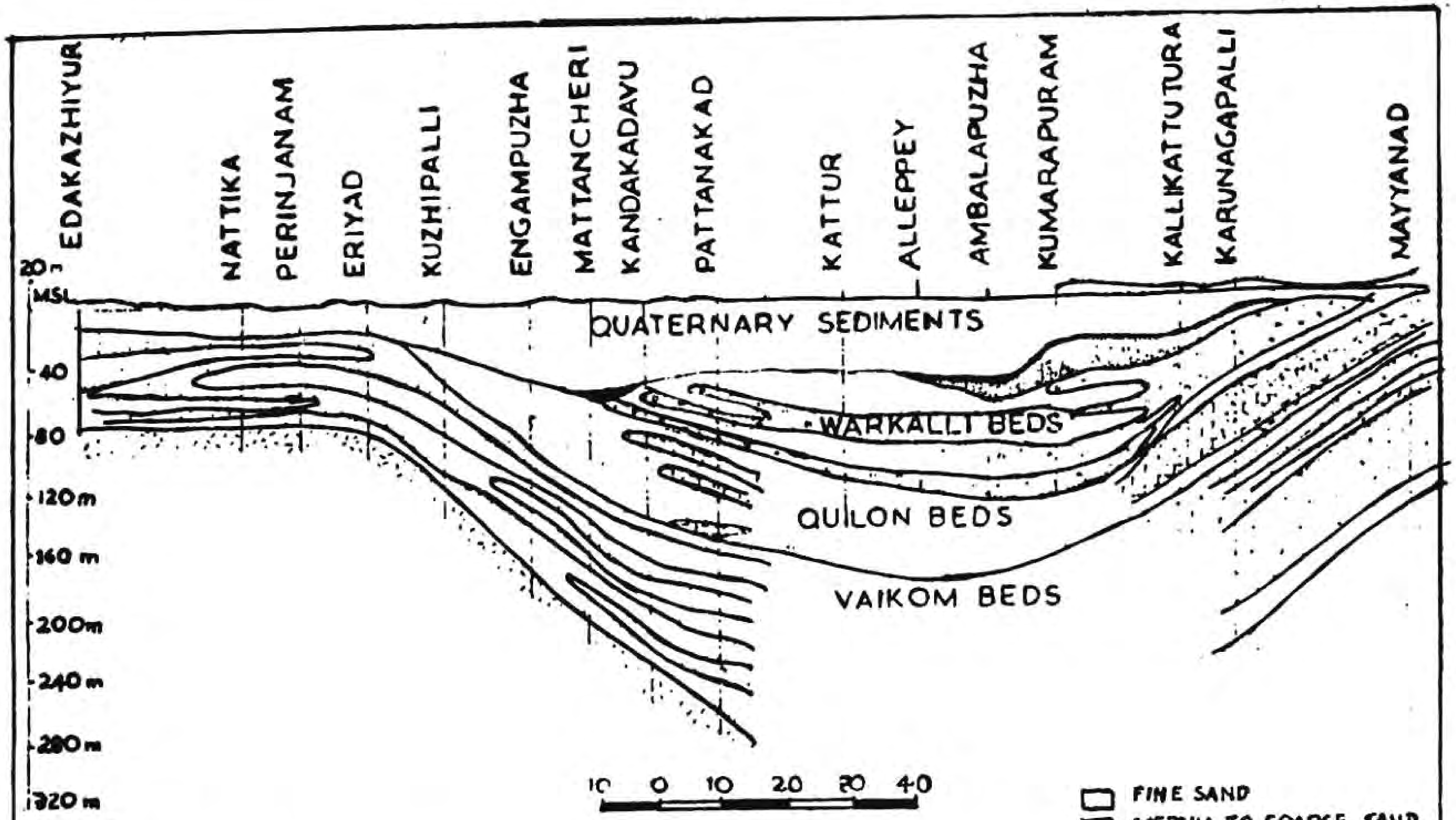


Fig.1.

SUBSURFACE GEOLOGICAL SECTION ALONG THE COASTAL — BELT OF KERALA BASED ON BOREHOLE DATA

(AFTER RAGHAVA RAO 1975)

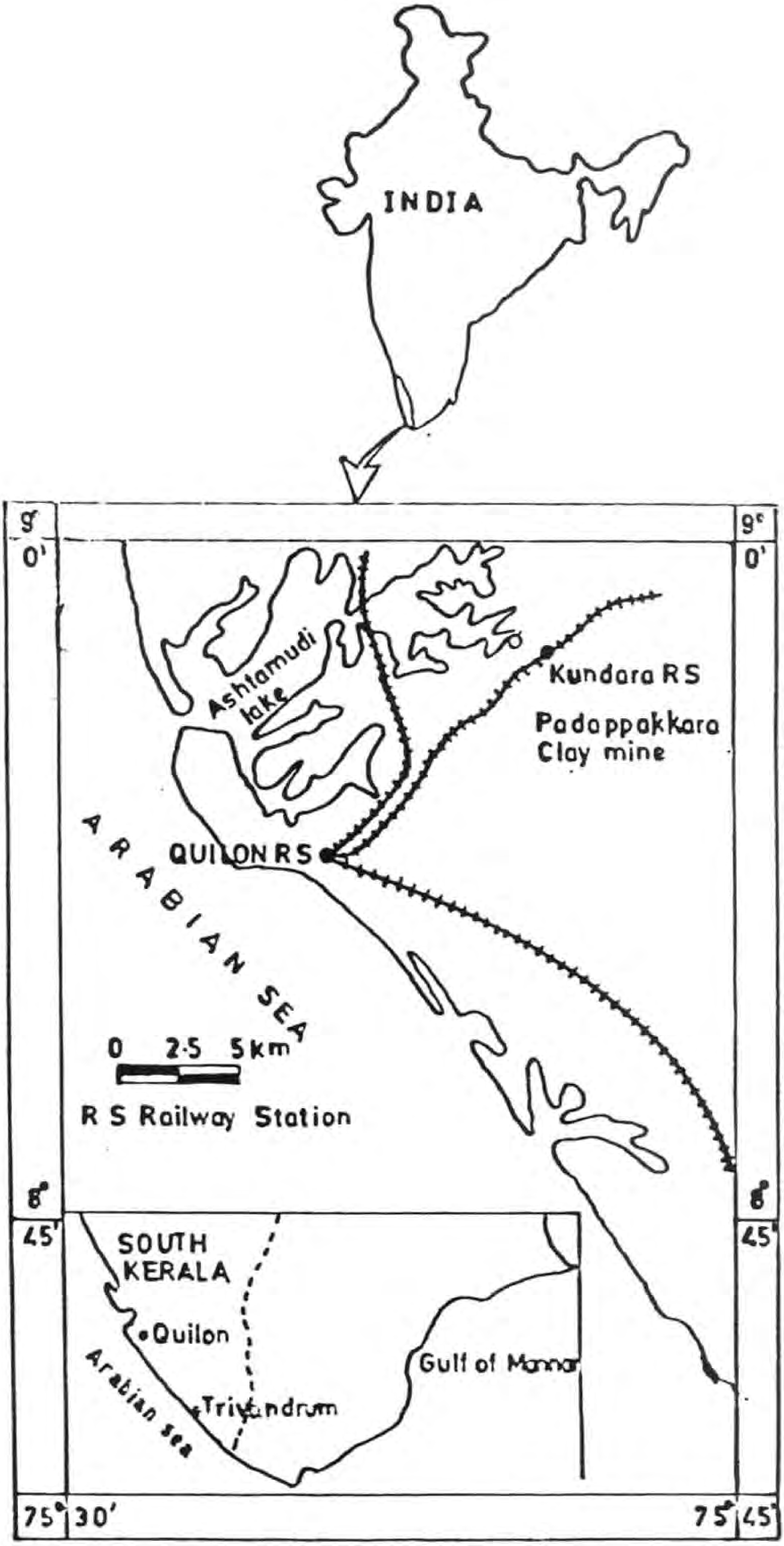


FIG. 2. MAP SHOWING THE LOCATION OF STUDY AREA

decades back, the exploitation of the raw material for commercial purposes has begun recently. The nature of the ferruginous impurities found in this deposit, the physical properties and industrial application of the prominent ball clay seams have been explained.

2.2 SEDIMENTATION AND GENESIS AS GEOCHEMICAL PROCESSES - AN INTRODUCTION

Sedimentation and diagenesis are the geochemical processes of greatest importance to mankind, since they provide us with our basic economic resources, soils and clays.

The key reactions in the geochemistry of sedimentation are the chemical breakdown of some minerals and the formation of others. Some hypotheses assumed the hydrolysis of aluminosilicates with the formation of colloidal silicic acid and aluminium hydroxide which later reacted to give clay minerals. During the initial attack some silicate minerals go into ionic solution. Aluminium and silicon attract OH $ions_{-}$ strongly and aggregate to form clusters of colloidal size. These colloidal aggregates, on ageing will be oriented into definite crystal lattices and thus formation of clay minerals takes place (Mason et al., 1991). The most stable alkali metal ions and alkaline earths will remain in the solution.

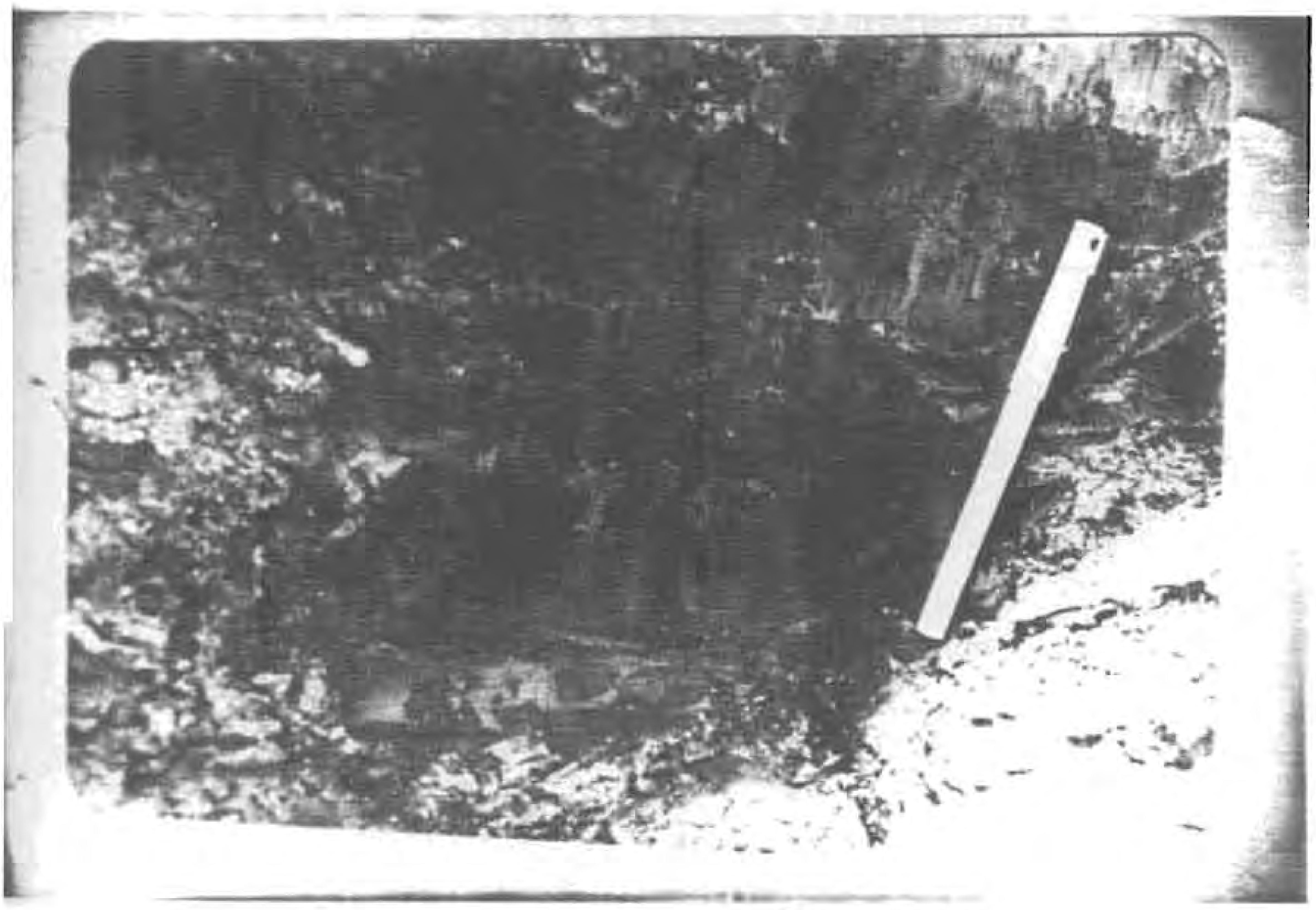
As far as genesis of clays is concerned, kaolinisation is one of the most important neoformations in nature (Millot, 1970). According to Singer and Muller (1983) the term diagenesis refers to all changes which take place in a freshly deposited sediment until it reaches the stages of metamorphism. Diagenesis comprises all those changes occurring in a sediment near the earth's surface at low temperature and pressure and without crustal movement being directly involved. It contains the history of the sediment immediately after its deposition and with increasing temperature and pressure it passes into lithification and metamorphism. According to Richard and Brian (1924) the important diagenetic proceses are solution, deposition, replacement, recrystallisation, segregation, compaction and cementation.

2.3 STRATIGRAPHY AND GEOCHEMISTRY

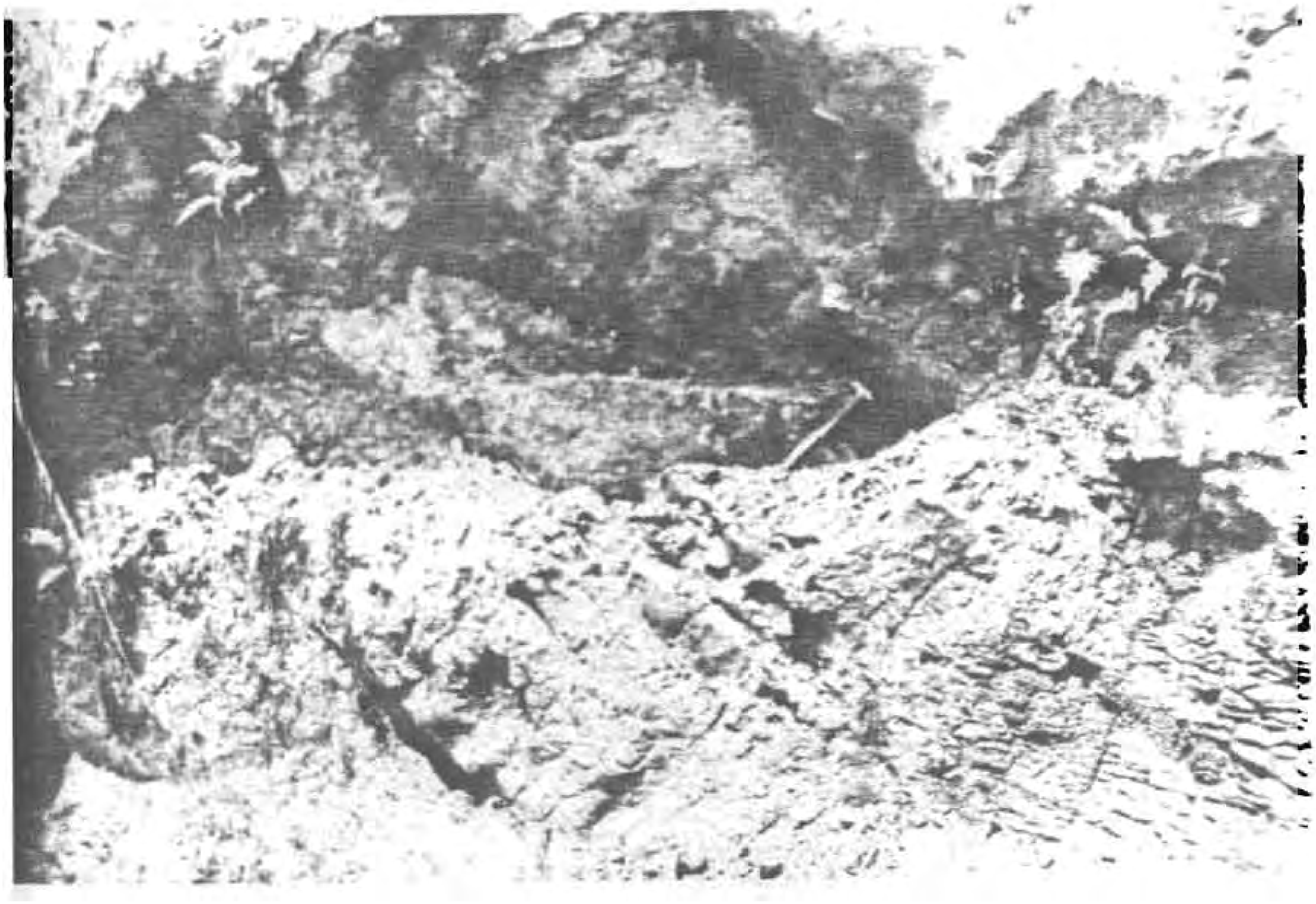
The lithologic succession of the Padappakkara belt can be divisible into different groups. The upper variegated sandstones overlain by the lateritic burden are characterised by their pink (PS1), red (RS2) and yellow (YS3) colours in the mottled area (Fig. 3 a,b). Just below the laterite is a partially altered kaolinite bed which forms the first part of the sandstone. Second layer is a hard cemented red coloured deposit of around 60 cm thick with clay material on either side. The yellow coloured part of the sandstone (∼ 40 cm thick) is seen under the hard cemented layer. A generalised stratigraphic sequence of the clay and sandstone layers in the profiles is as shown in Table 1. A thick layer of lignite deposit can also be seen between the lower part of the sandstone and a thin layer of brown clay (BC). Underlying the brown clay is the plastic kaolinitic bed which has a thickness of ∼ 4 metres. In the field two colour variants of this clay can be seen, namely the grey (G) and black (B) varieties. Embedded in the clay matrix are the sulphide nodules which vary in size from a few mm to a few cm.

The distribution of the extractable iron oxide - by the

Fig. 3: The vertical section of the cliff showing lateritic overburden current bedded sandstones and the ball clays



(a)



(b).

Table 1: General characteristics

Sample	Thickness (m)	General appearance	pH	Slaking nature
Laterite	12	-	-	--
Pink sandstone PS1	0.5	Off-white coloured lumps with red patches	7.05	Not slaking easily
Red sandstone RS2	0.6	Aggregates stained with ferric oxide	6.05	Slaking very easily
Yellow sandstone YS3	0.4	Buff coloured lumps	8.3	Slaking easily
Brown clay BC	0.2	Brown lumps with yellowish red patches	3.55	Slaking very easily
Gray ball clay G	2	Gray lumps contaminated with nodular ferrous sulphide	4.7	Not slaking easily
Black variety B	2	Black lumps with ferrous sulphide impurities	3.7	Not slaking easily

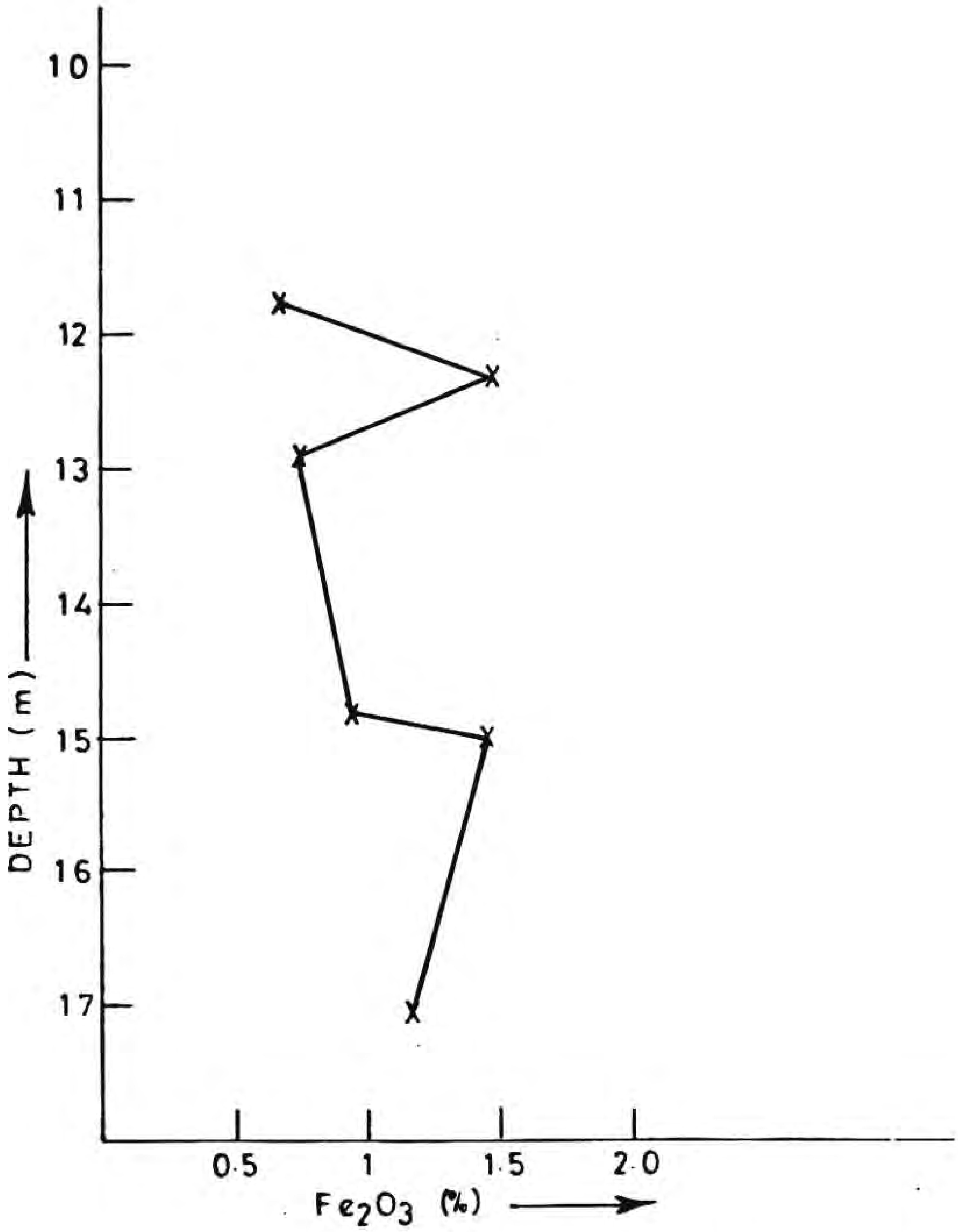


Fig. 4. Concentration of Fe (as Fe_2O_3) in the CBD extract for samples as a function of depth from the top of of the deposit.

repeated citrate - bicarbonate-dithionite (CBD) method (Jackson, 1973 and Worral, 1983 - Appendix) from each sample (which has already been washed with distilled water and passed through 350 mesh (B.S. sieve) showed an increasing trend (Fig. 4) from top to bottom. Sample 2 was an exception as it has a higher concentration of red pigment of iron oxide. The lateritic horizon and the sandstones are cemented by red pigment and kaolinite. The origin of the red pigment in the sandstones is problematic, because they have undergone intense weathering. It is possible that the red pigment formed diagenetically and was overprinted by subsequent weathering cycles. In a primary deposit where kaolinite is formed by the weathering of feldspathic gneiss, iron in clays below the laterite and sandstone should show a decreasing trend. Because the opposite is observed here, the iron distribution is assumed to have a sedimentary origin.

The loss on ignition (LOI) at 1050^{o} varies from 12-24%. The maximum is observed in grey and black ball clays. The results of the elemental analyses of the ignited samples are given in Table 2. Sample RS2 was originally brick brown in colour and contains high percentages of iron. The percentage of trace elements such as Cu, Ni, Cr and Mn in the samples did not show any regular trends (Fig. 5). The morphology of the representative sample from each layer can be seen from Fig. 6.

Nodules with metallic lusture are found in the gray and black clay beds as inclusions which are identified as ferrous sulphide.

Table 2: Chemical Assay of the Samples

Constituents (wt %)	PS1	RS2	YS3	BC	G	B
SiO_2	65.19	50.29	56.28	64.48	52.21	62.92
Al_2O_3	25.30	4.037	18.24	17.57	35.45	25.43
Fe_2O_3	3.28	40.26	14.92	12.12	4.21	4.87
TiO_2	2.25	0.945	5.819	1.92	2.89	1.11
Na_2O	0.365	0.071	0.076	0.082	0.089	0.089
K_2O	0.036	0.032	0.041	0	0.032	0.016
CaO	1.05	3.21	3.07	2.373	2.95	3.4
MgO	1.75	1.16	1.11	1.22	2.12	1.23
LOI	14.86	11.82	13.38	14.39	20.4	24.94

PS1	Pink sandstone
RS2	Red sandstone
YS3	Yellow sandstone
BC	Brown clay
G	Grey clay
B	Black clay

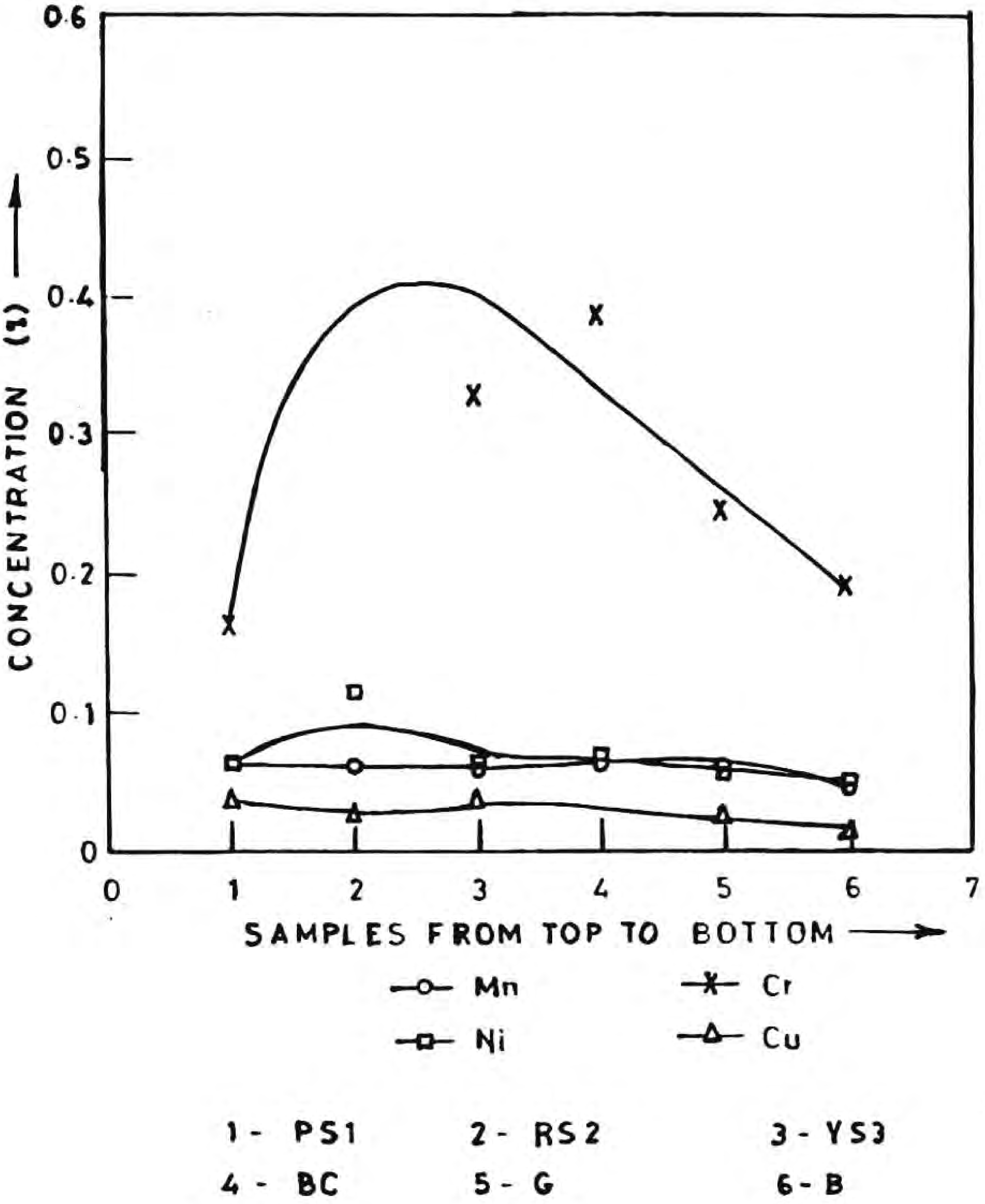


Fig.5. Trace Analysis

Fig. 6: SEM pictures of the representative samples taken from different layers

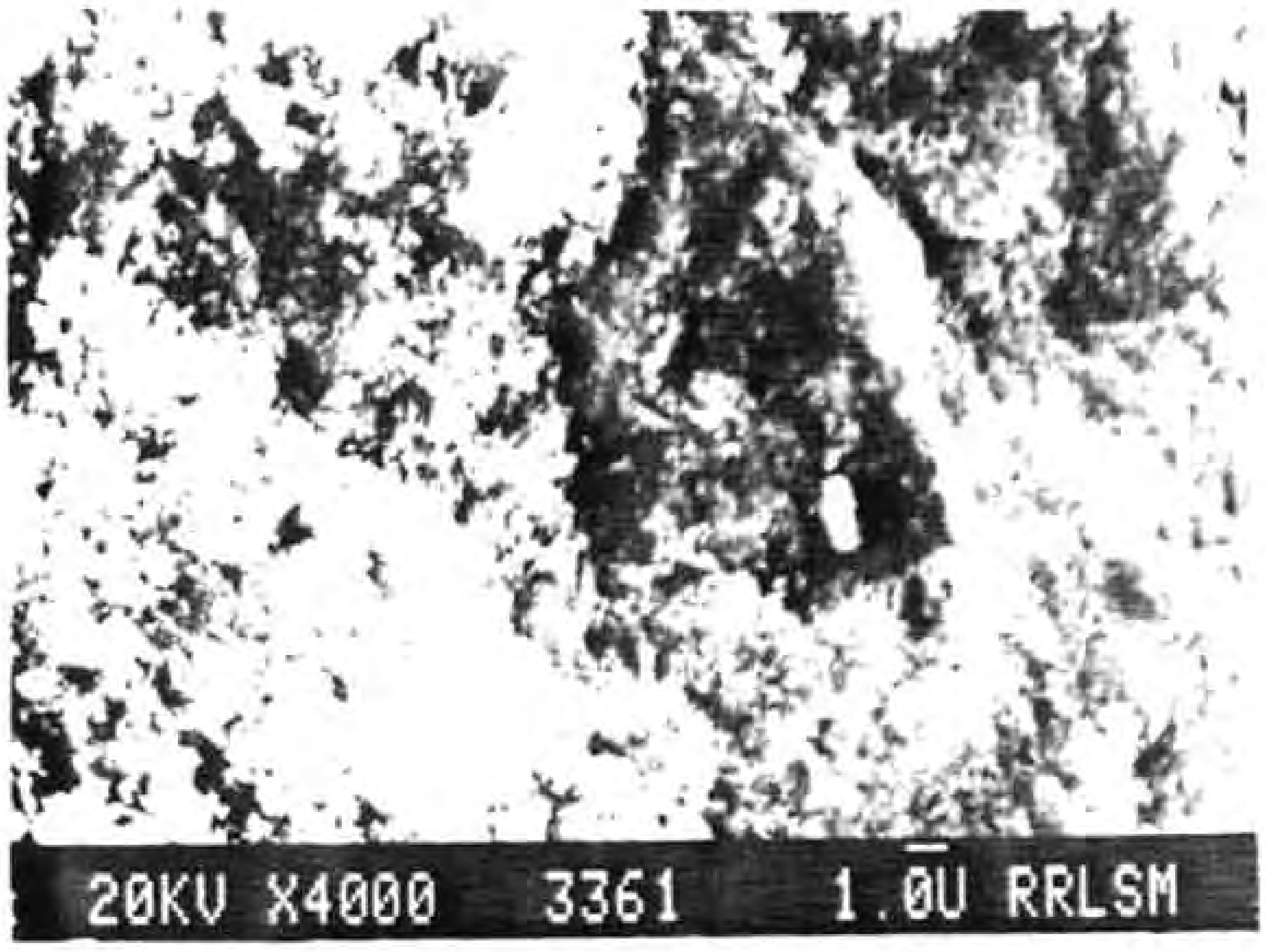


Fig. 6.1: Sample PS1

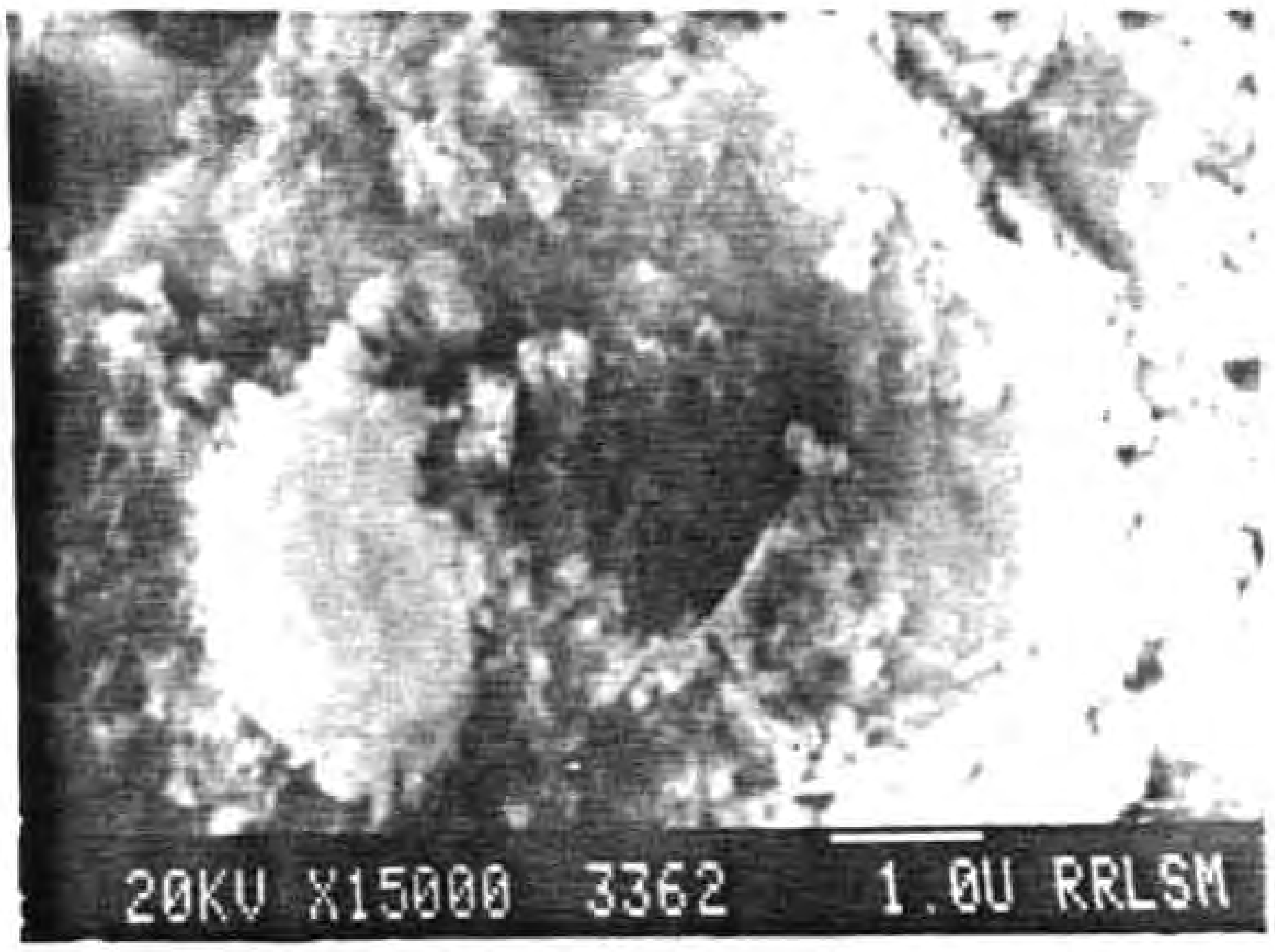


Fig. 6.2: An enlarged picture of RS2

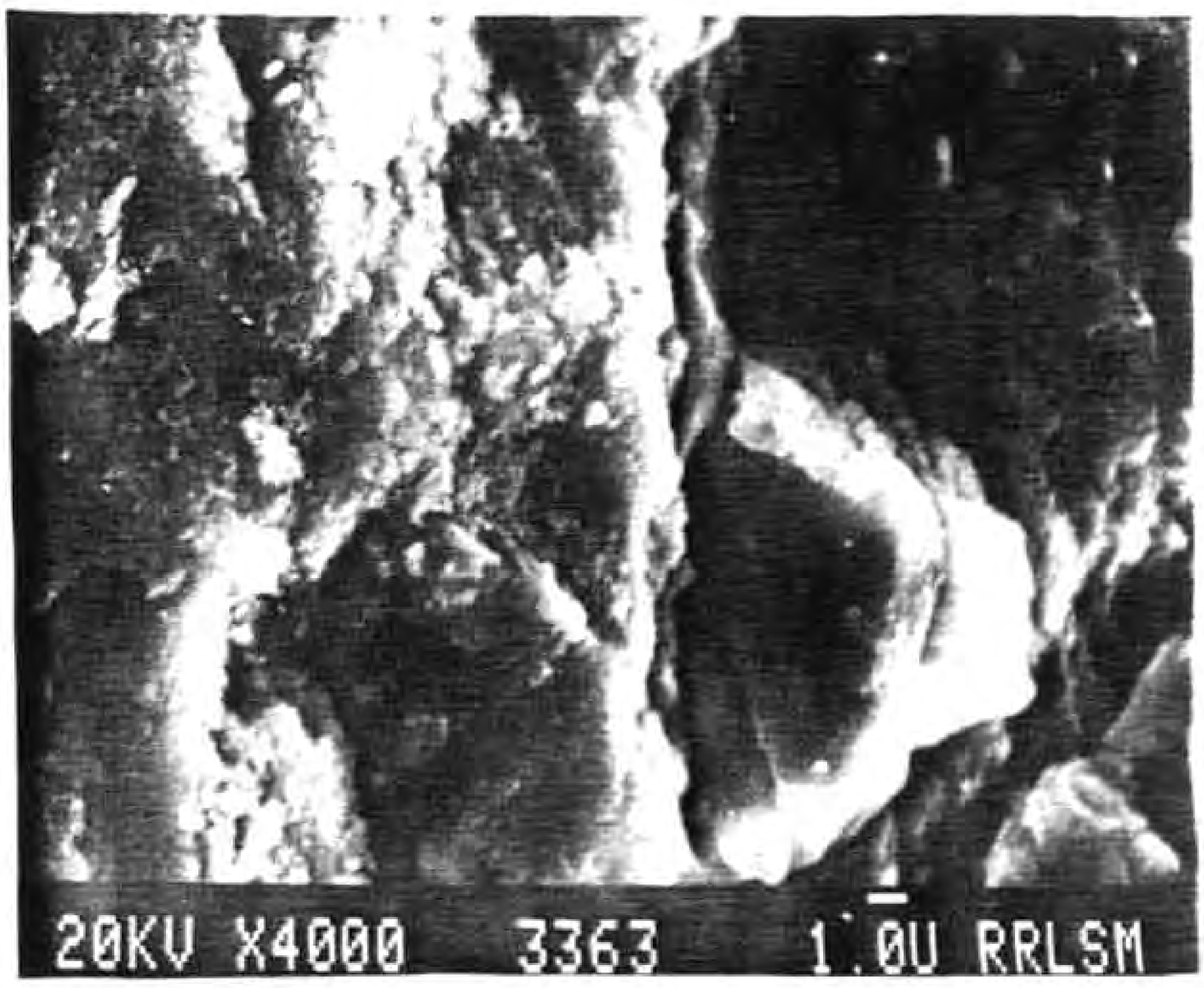


Fig. 6.3: Sample YS3

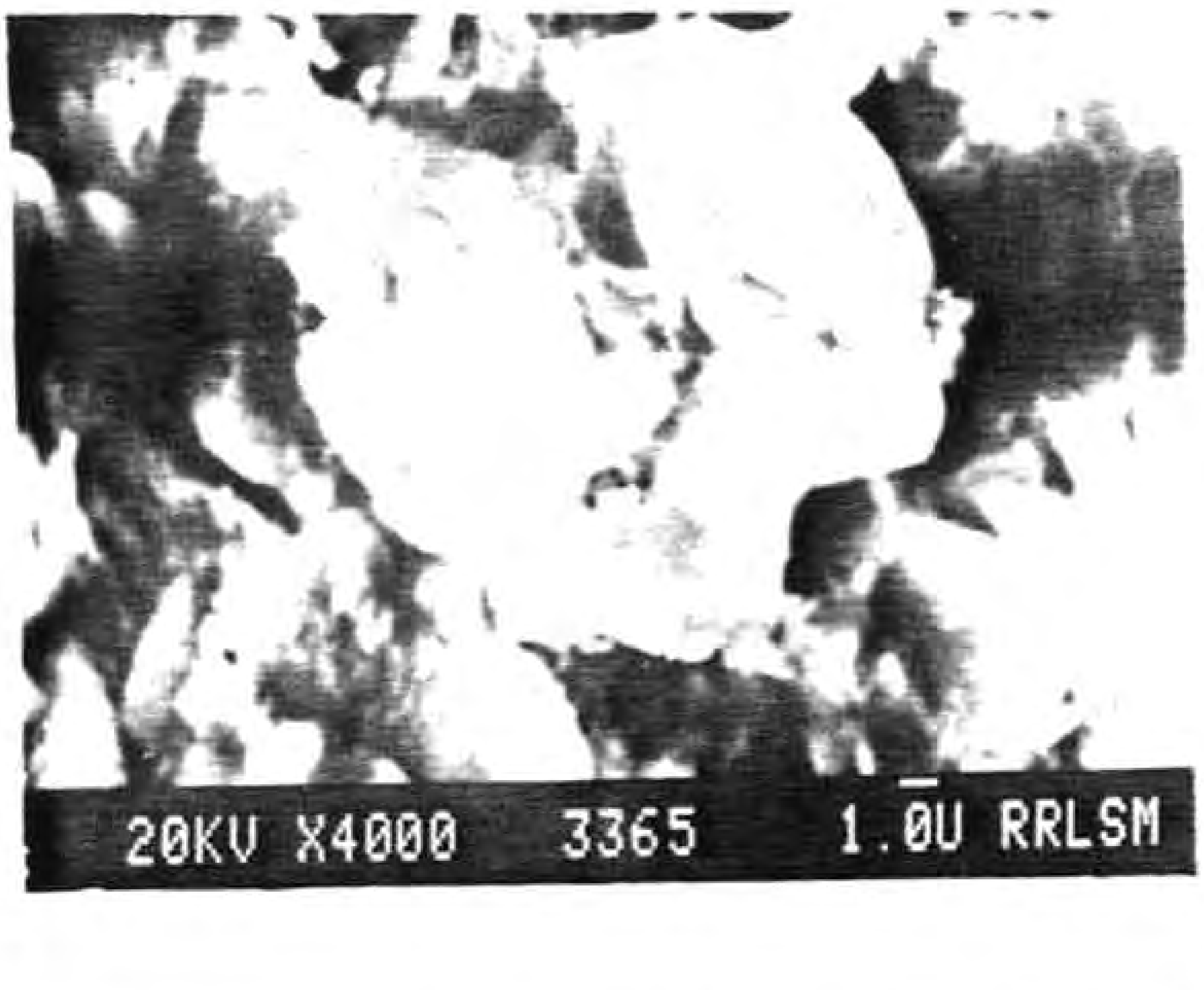


Fig. 6.4: Sample BC - A quartz grain with clay particle

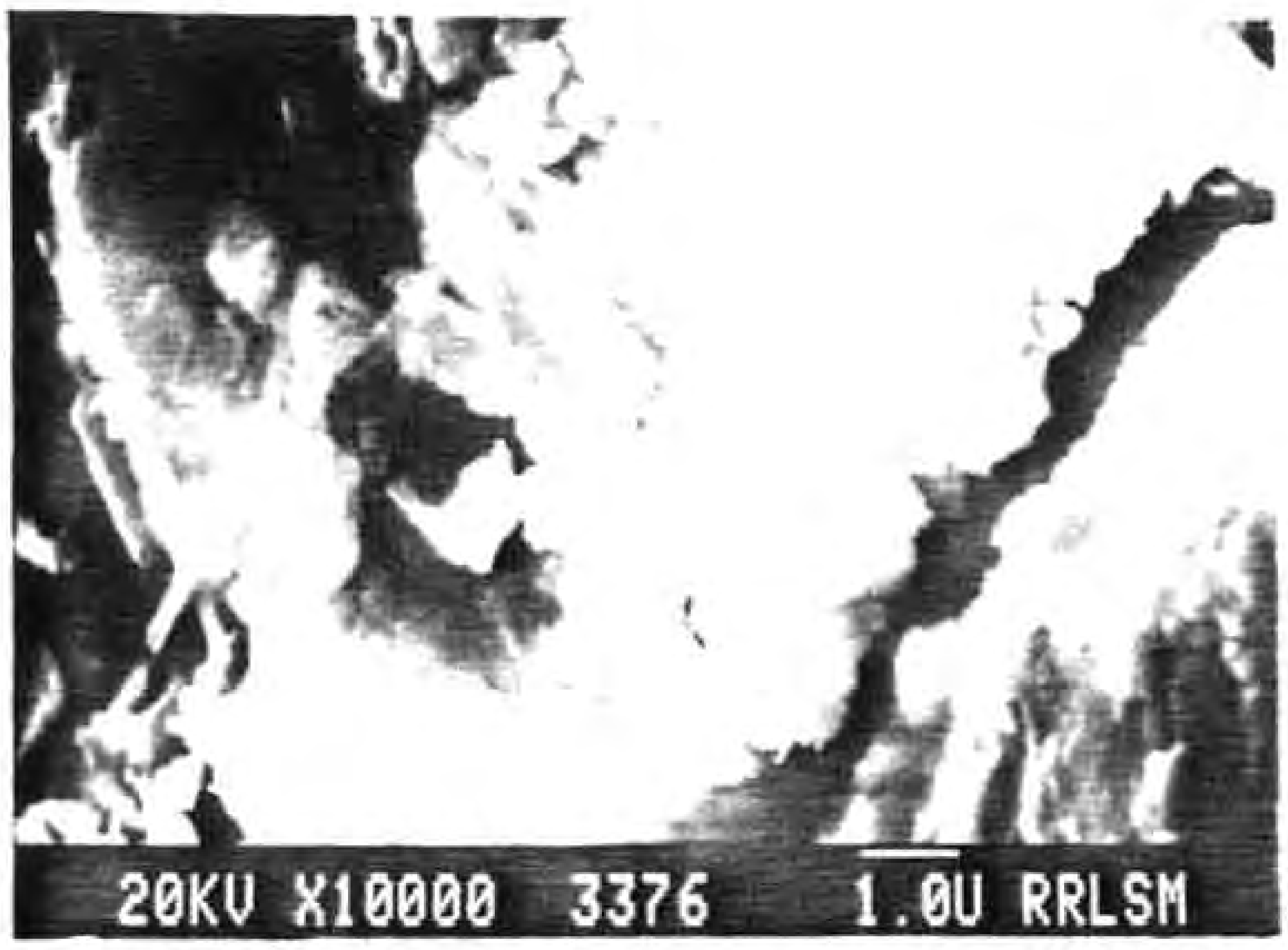


Fig. 6.5: Sample G, clay mineral with regular morphology

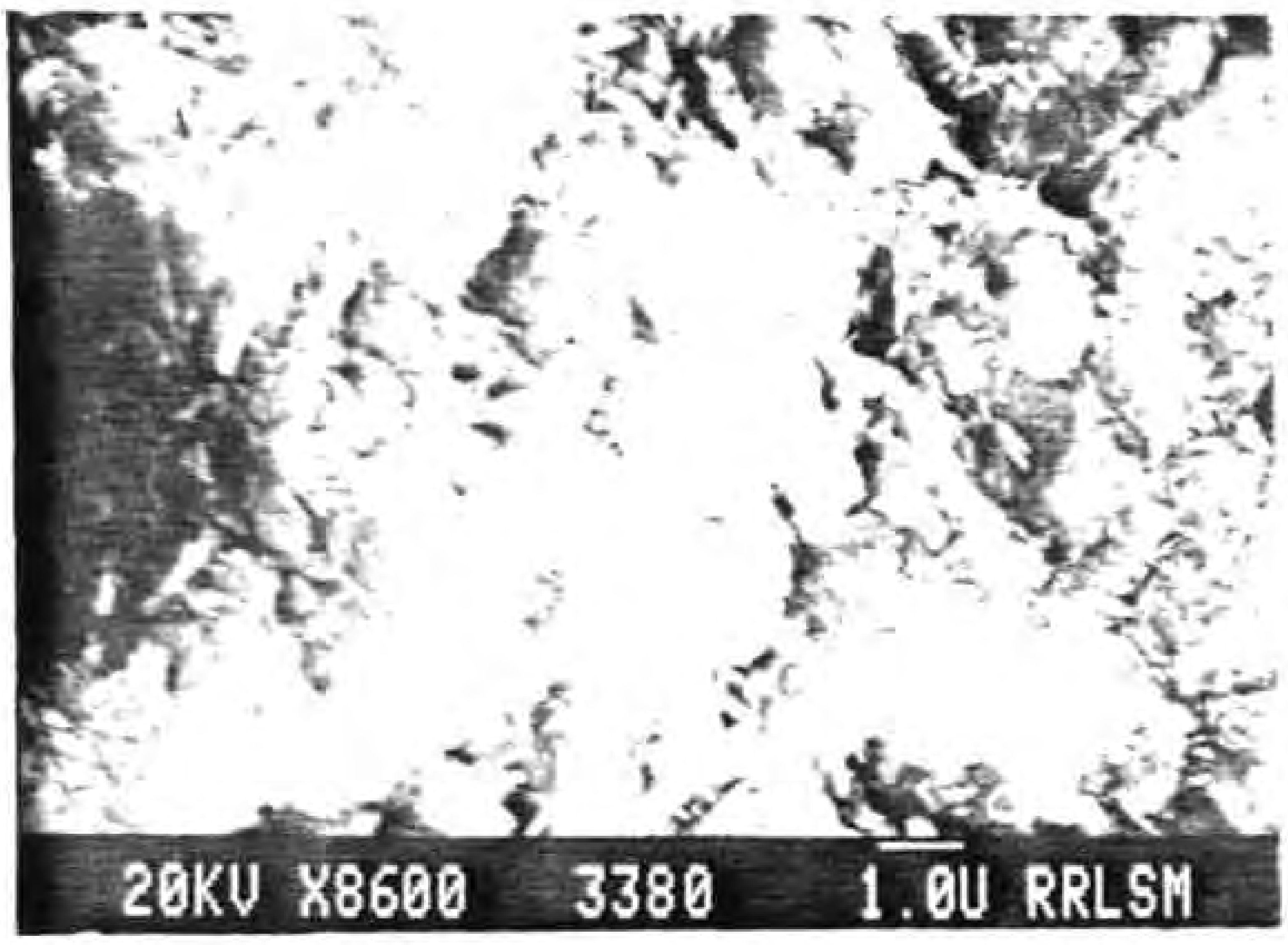
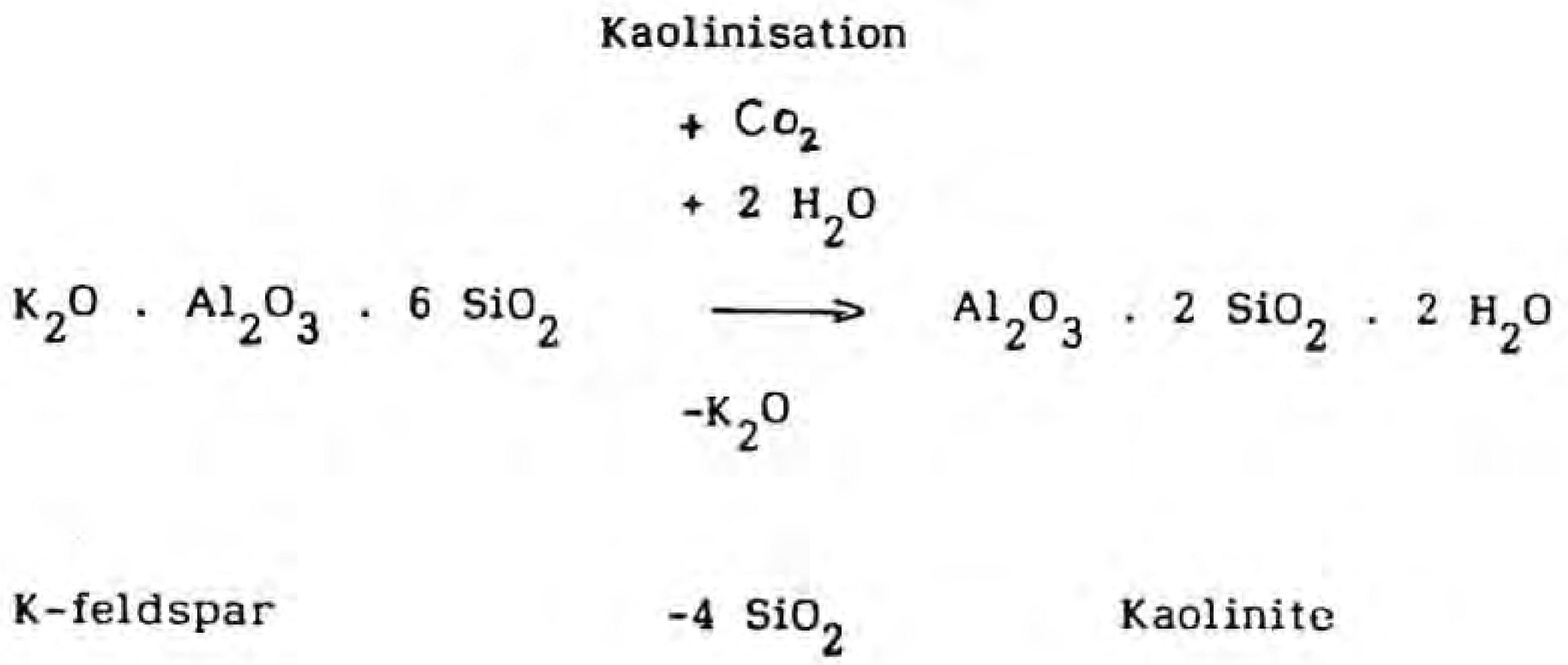


Fig. 6.6: Sample B, clay particles with a leaf-like morphology

2.4 MINERALOGY AND CHEMISTRY

The enrichment of kaolinite in continental argillaceous sediments has been ascribed to upward leaching of ground water (Singer and Muller, 1983). In Padappakkara, it is believed that this upward leaching causes pores in feldspathic particles (Fig. 7).
The conventional micrographic features (Fig. 8) and the X-ray patterns (Fig. 9) illustrate the alteration of sub-cubic feldspathic particles into kaolinite. Kaolinite which is being formed as a result of this type of diagenesis is responsible for pore-filling phenomenon (Fig. 8(a)). The alteration of feldspathic gneiss into kaolinite is described (Ryan, 1978) as follows.



$$\underset{\text{K-feldspar}}{K_2O \cdot Al_2O_3 \cdot 6\ SiO_2} \xrightarrow[-K_2O \quad -4\ SiO_2]{\text{Kaolinisation} \quad +\ Co_2 \quad +\ 2\ H_2O} \underset{\text{Kaolinite}}{Al_2O_3 \cdot 2\ SiO_2 \cdot 2\ H_2O}$$

During kaolinisation, the precipitated silica will be leached out as spherical particles (Fig. $8(b)_2$). These particles, by the percolation of pore solution are transformed to crystalline quartz which can be detected from X-ray diffraction studies (Fig. 9). However, crystalline quartz present originally in the matrix may also contribute to this.

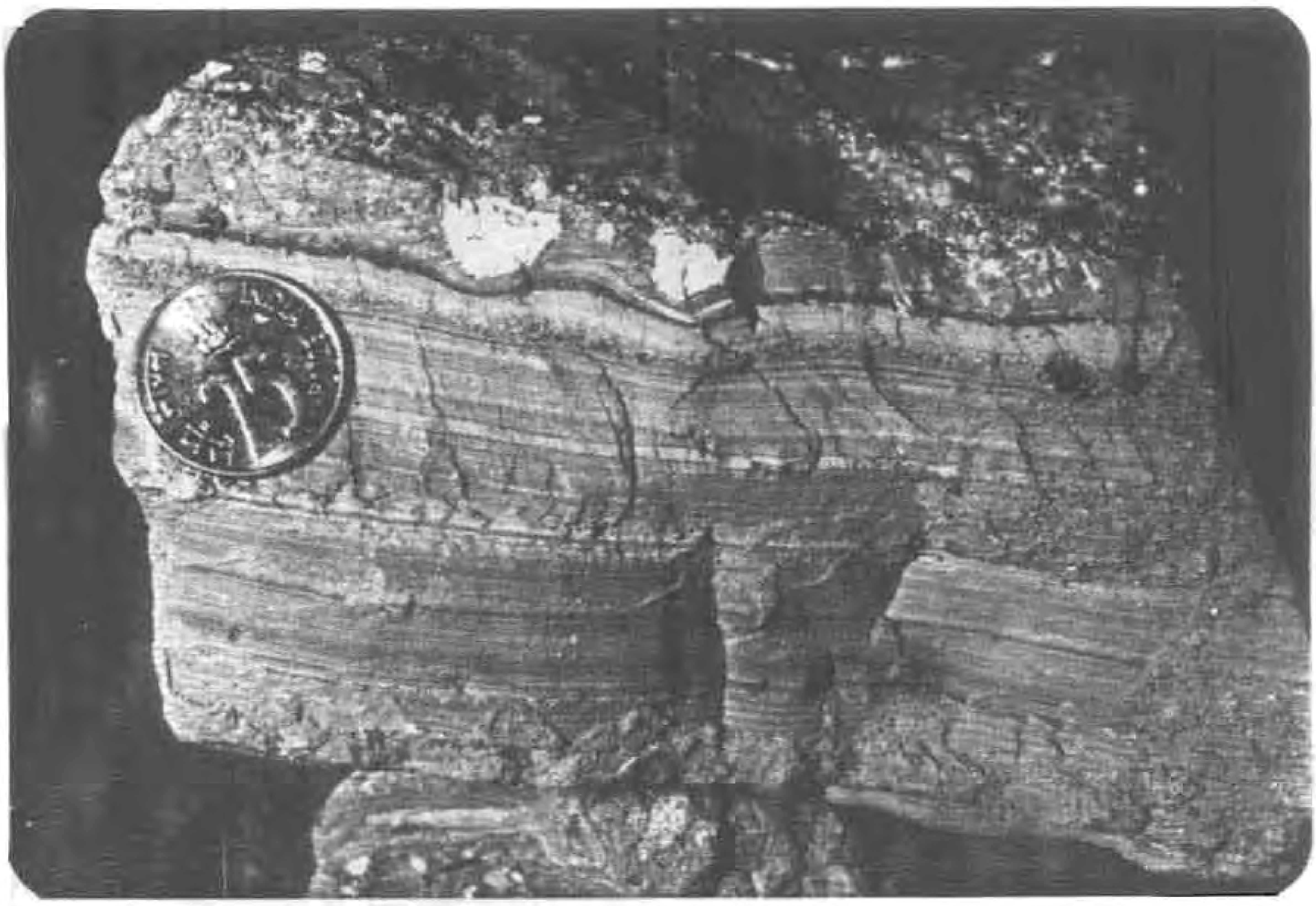
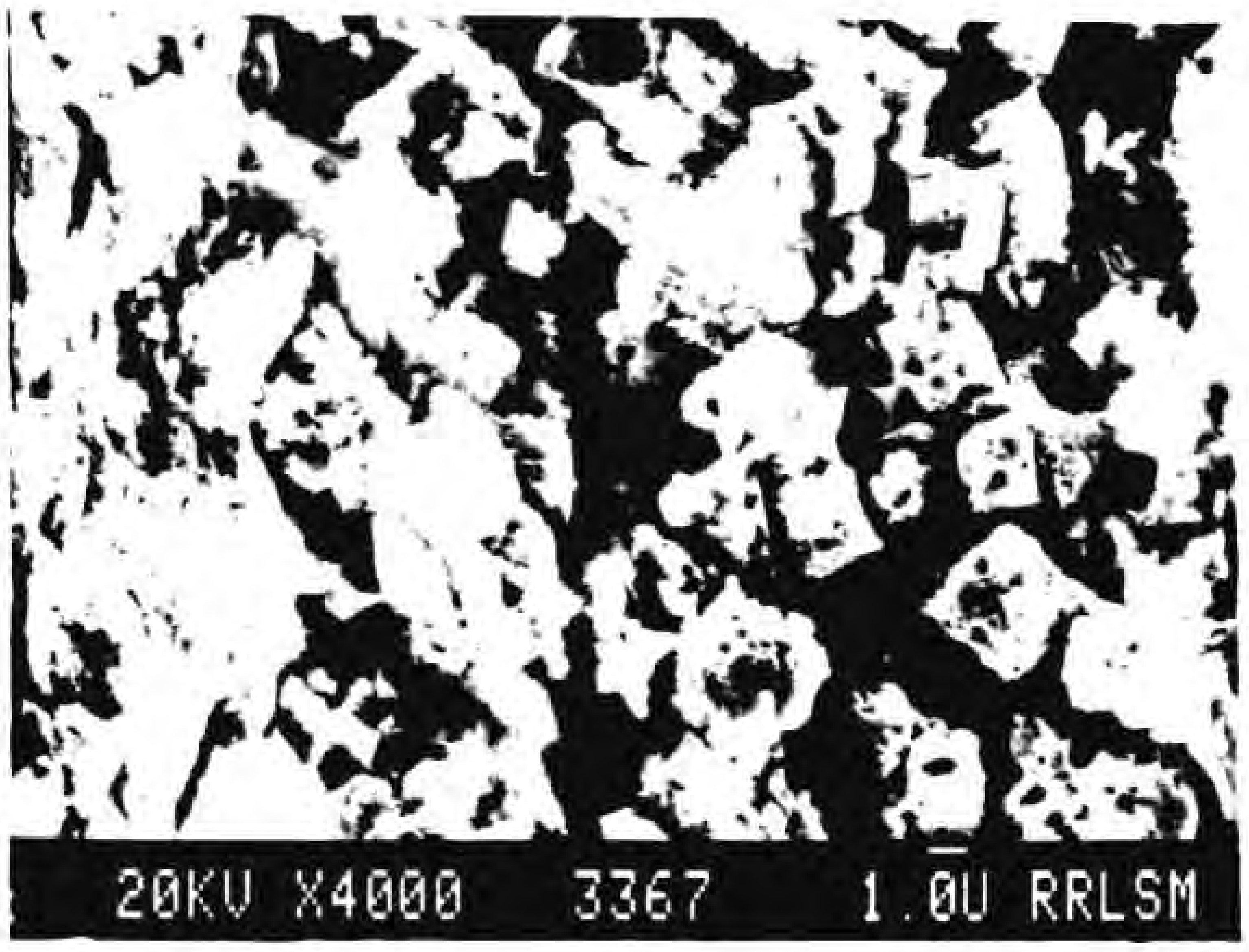


Fig. 7: Feldspathic sample collected from the sandstone

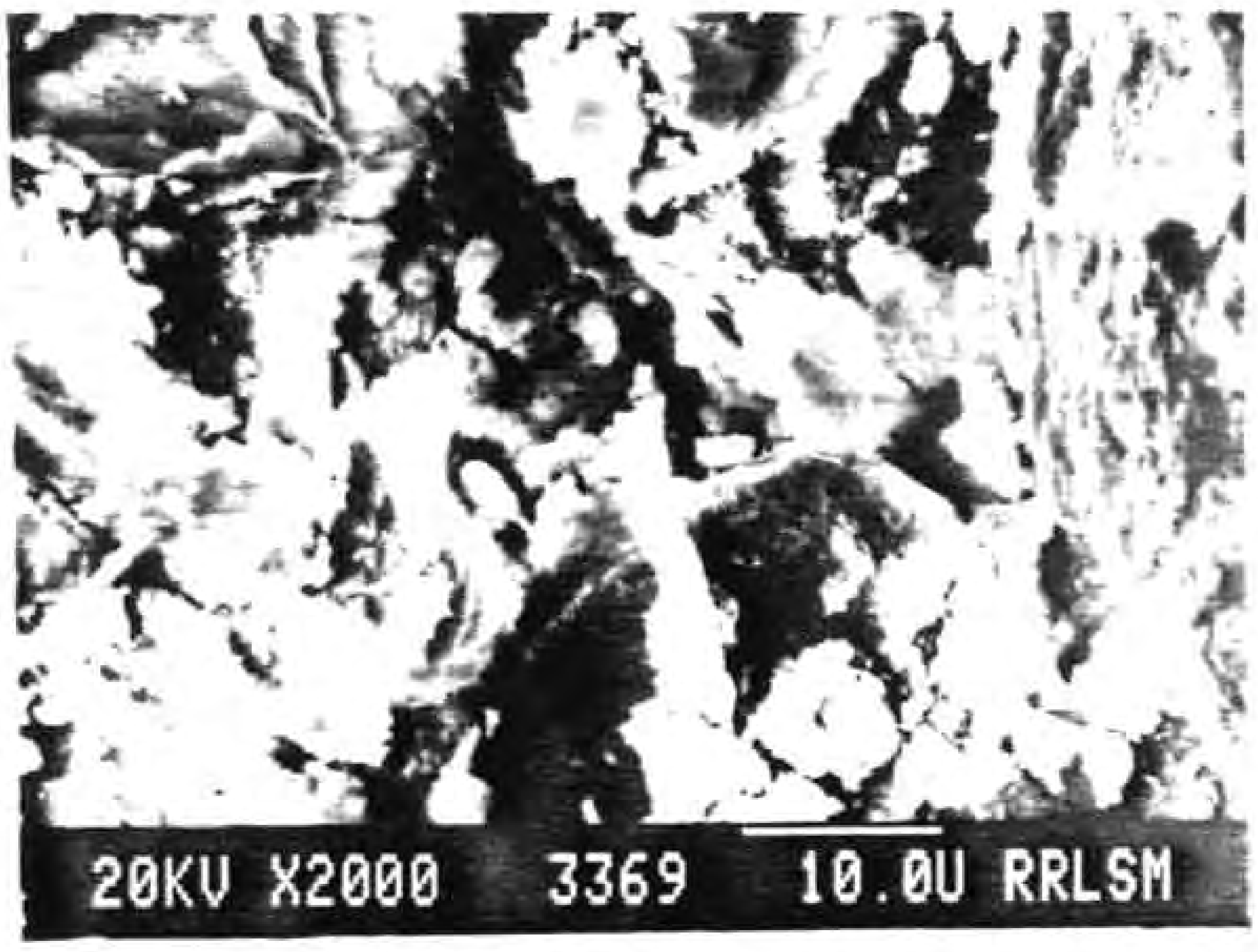
Fig. 8: Different stages in the alteration of minerals during diagenesis.

a. Formation of kaolinite



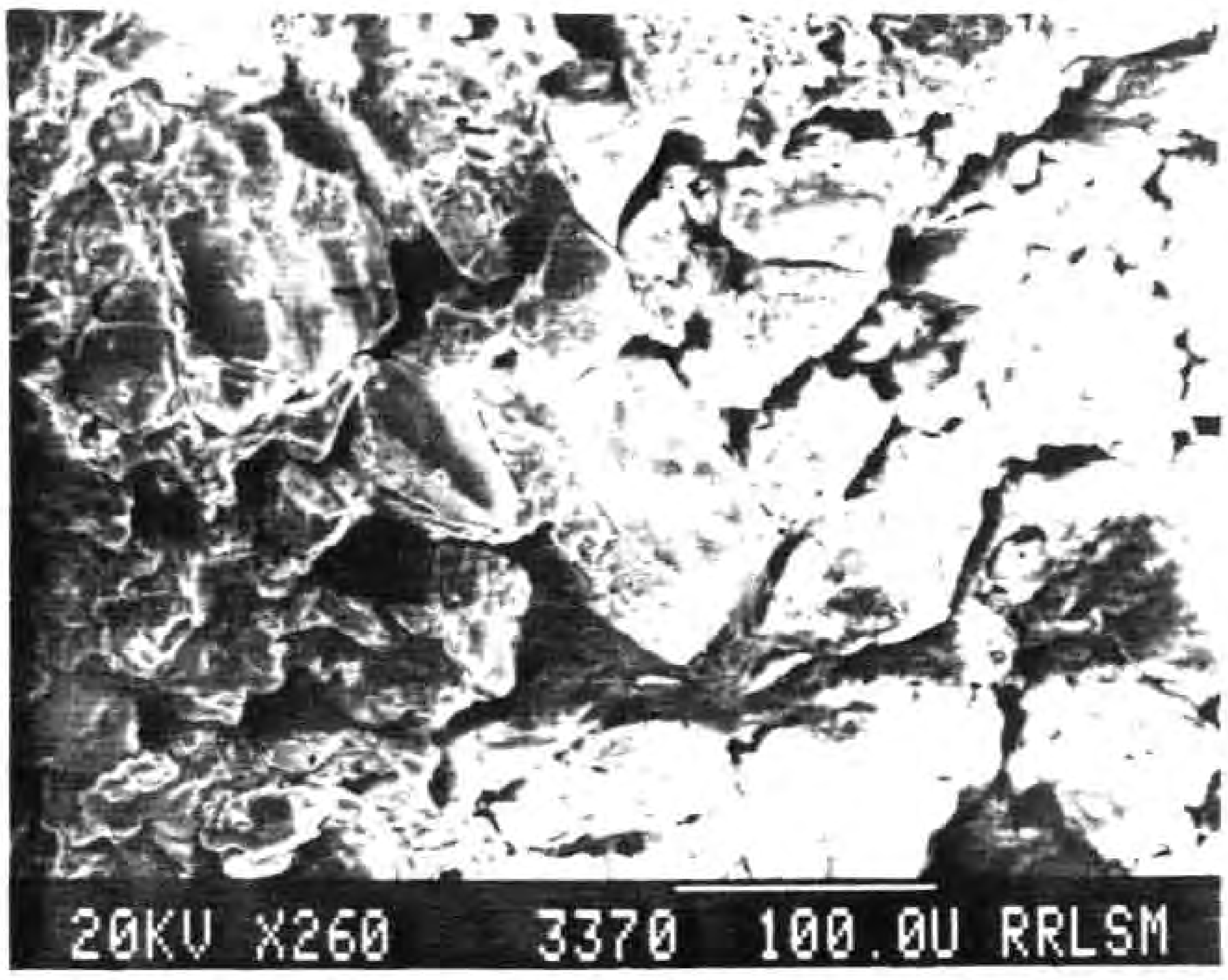
(a)$_1$. Subcubic particles of feldspar indicating alteration

(a)$_2$. One of the grains of feldspar magnified showing pits on the surface

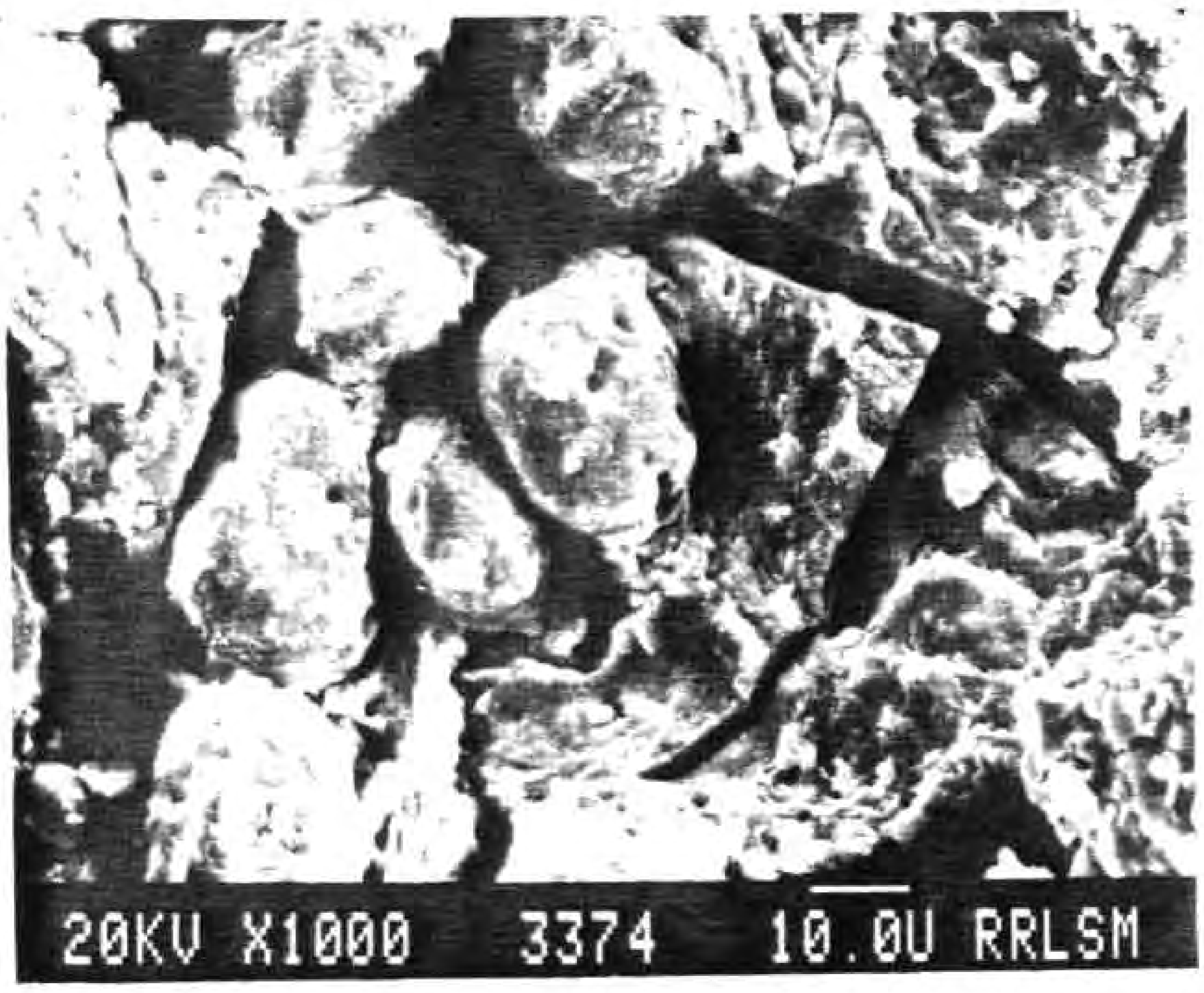


(a)$_3$. A porefilling indicating the precipitated clay
An effect of increasing diagenesis

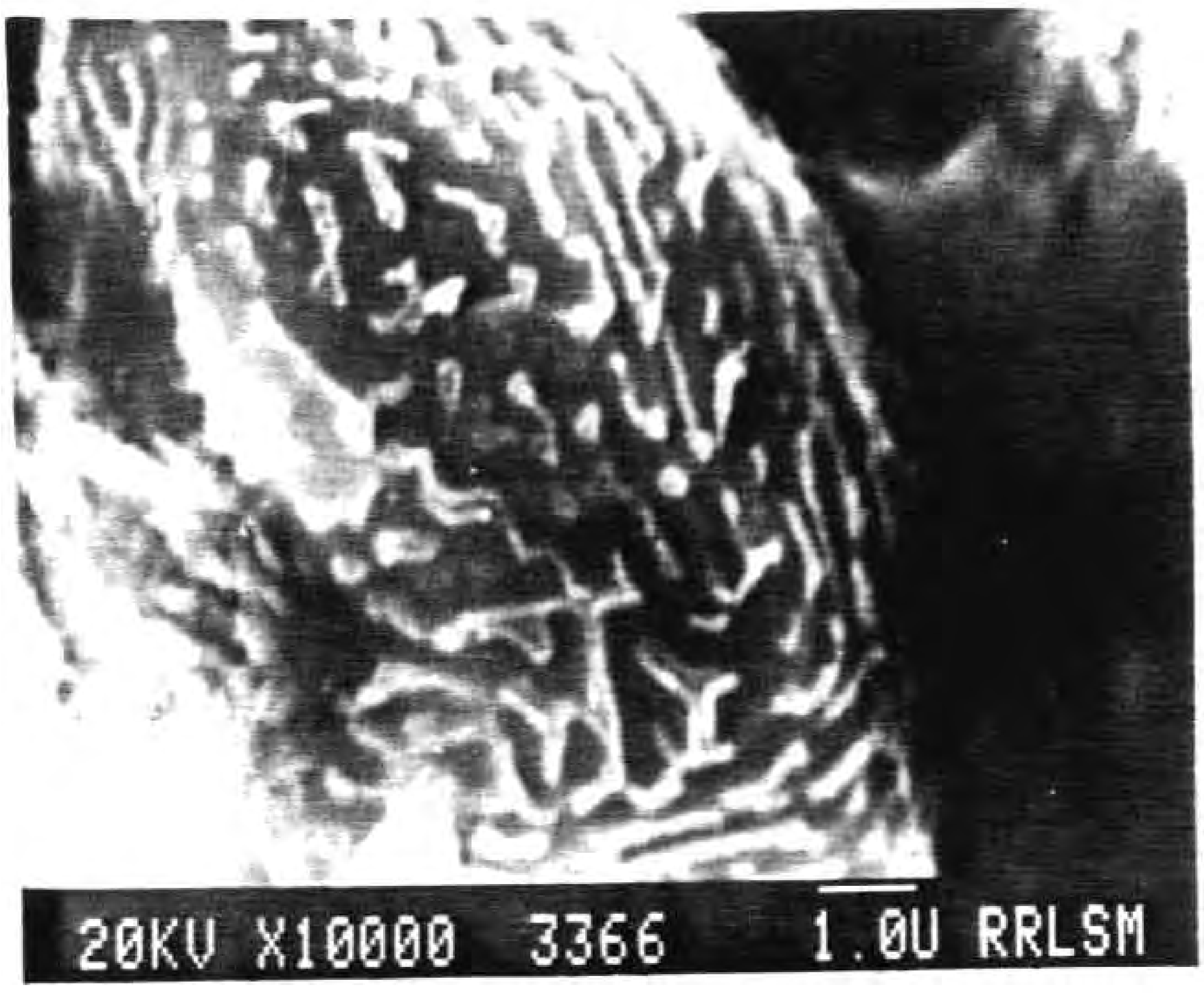
Fig. 8(b): Formation of silica (quartz)



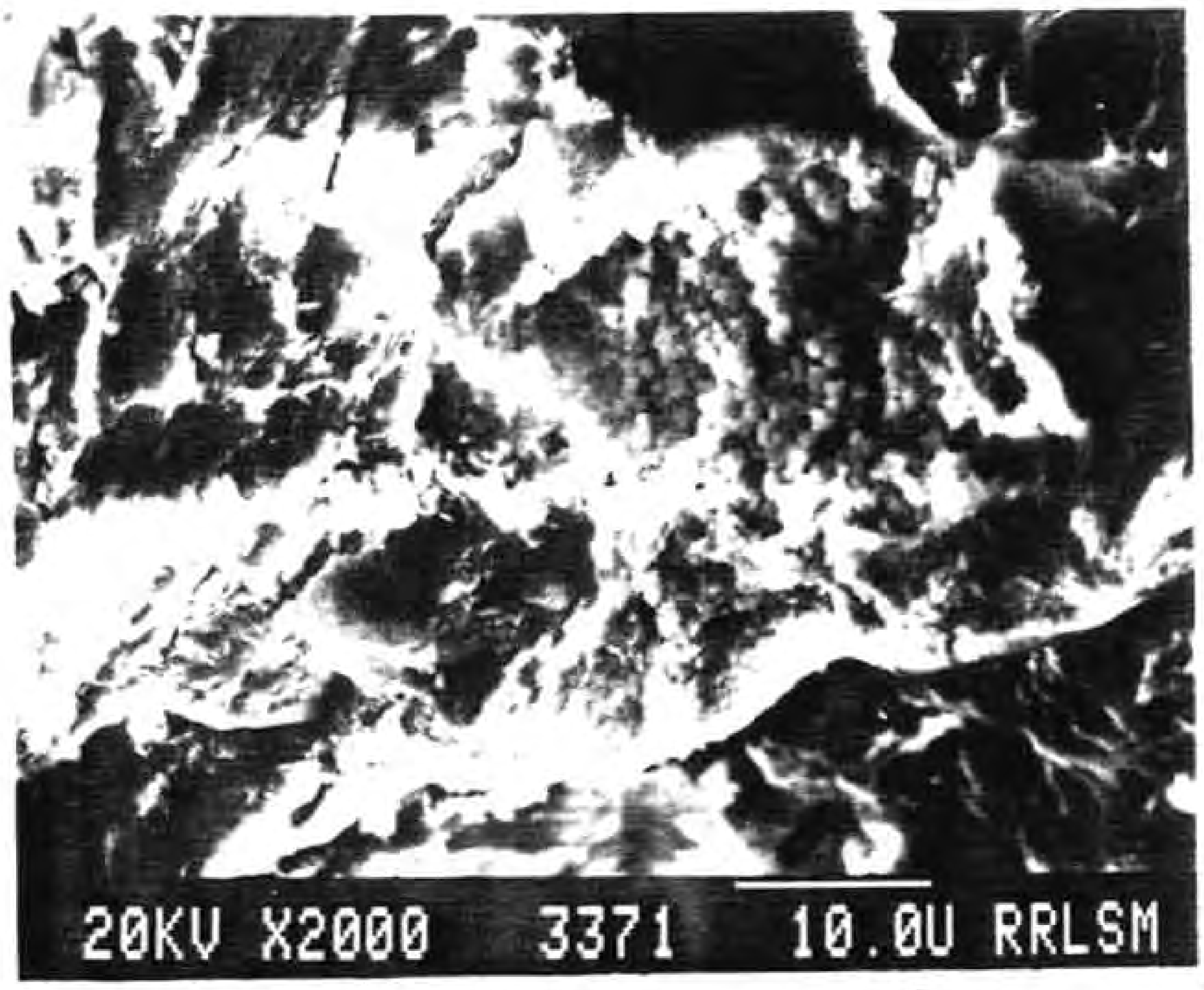
$(b)_1$. Detrital subangular quartz grains



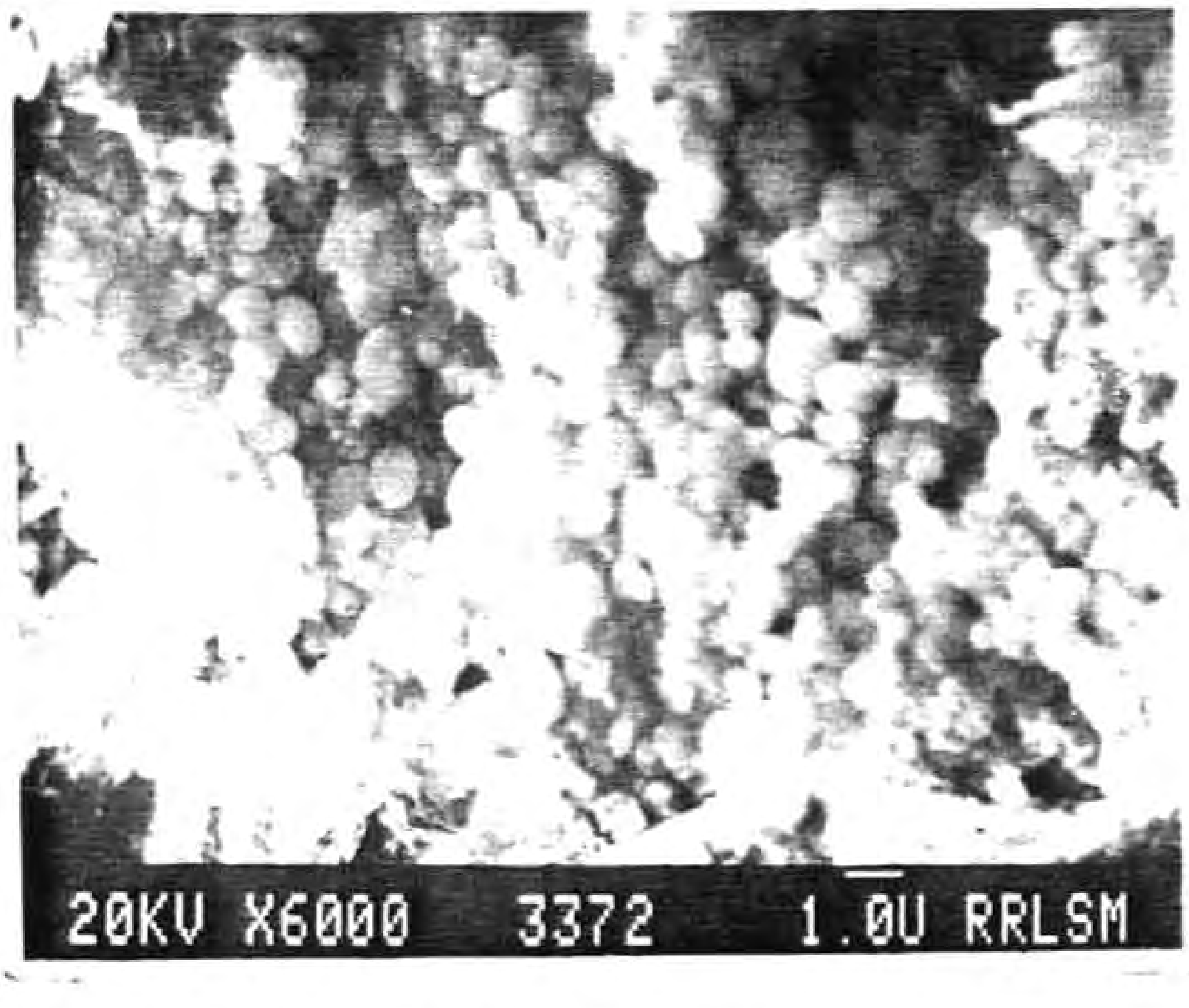
$(b)_2$. Rounded crystals of quartz indicating transported nature



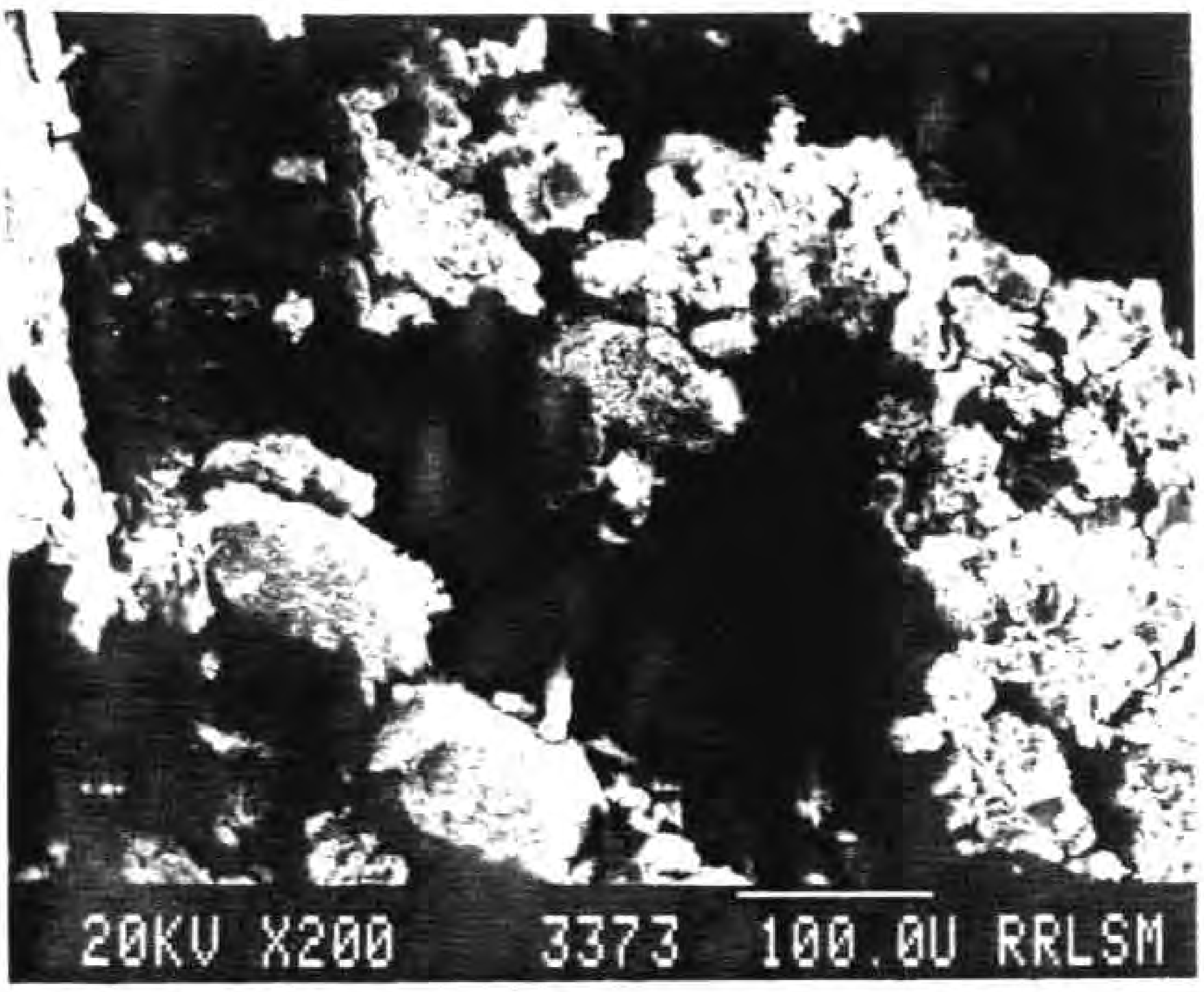
$(b)_3$. Surface of quartz grain magnified
(Note the pits on the surface)



(b)$_4$. One of the cavities of a quartz grain seen with spherical particles
(Leached out silica is seen as minute particles)



(b)$_5$. Enlarged view of the spherical particles is shown

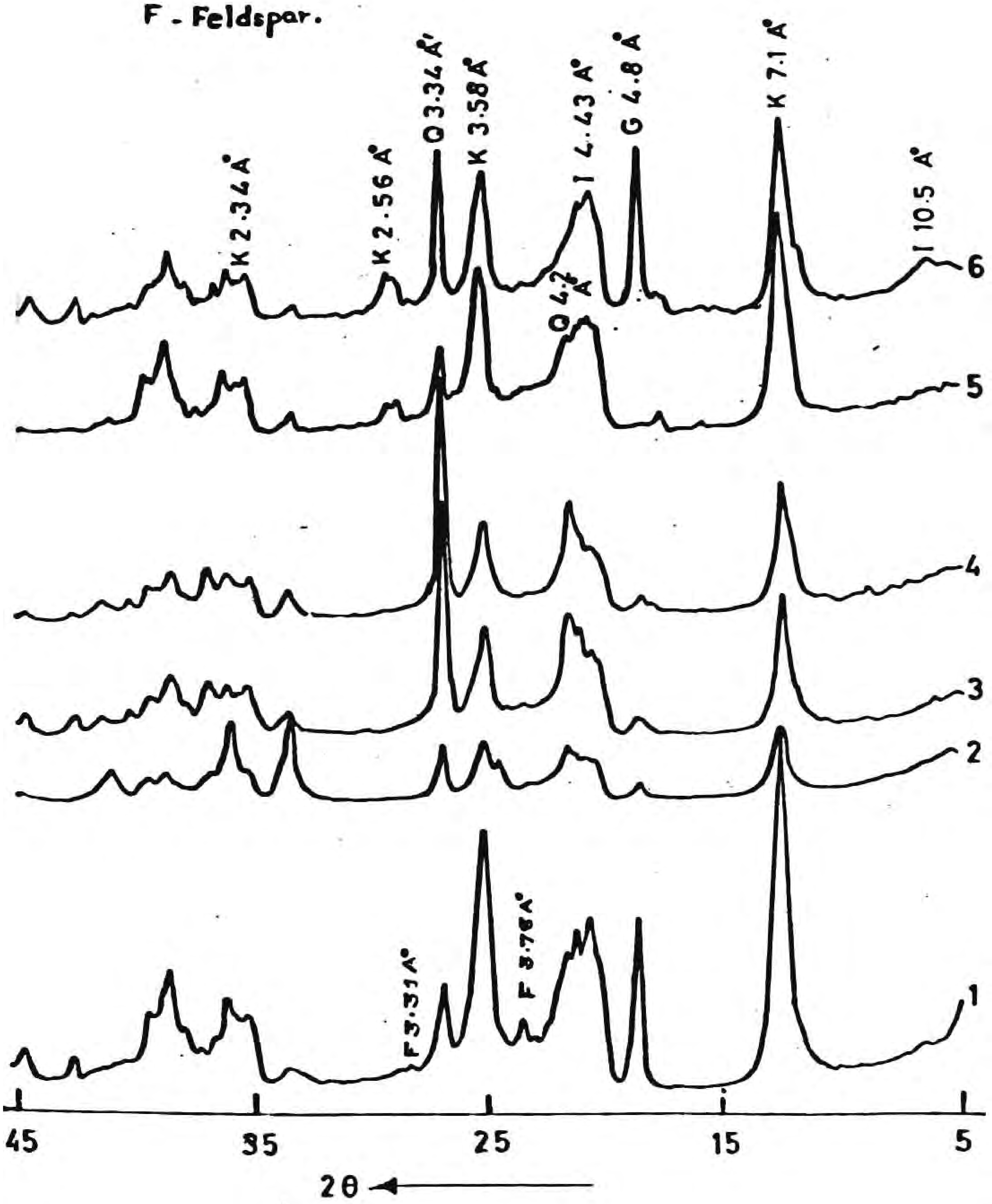


(b)$_6$. Diagenetically formed quartz crystals with clay coating

Fig. 9 X-ray diffraction patterns of samples from top to bottom

1 - PS1, 2 - RS2, 3-YS3, 4- BC,
5- G, 6 - B

K - Kaolinite Q - Quartz I - Illite G - Gibbsite
F - Feldspar.



The nodular inclusions in the clay are marked with arrows in Figure 10.

Shelf regions, deltas or other sedimentary environments, such as abyssal planes in particular richly fed by turbidity currents, have their benthonic populations constantly smothered by seasonal or larger cyclic inversions of sediment that seal off the organic debris and provide a large reservoir of bacterial nutrients which makes an ideal site for authigenic formation of FeS_2 by reduction (Charmley, 1989). The principal minerals formed in these environments are the ferrous sulphides, viz. marcasiite and pyrite, (FeS_2). These can be produced by the reduction of iron oxides and the various hydrates to FeS and later to FeS_2. Another possible environment for the formation of ferrous sulphides (White, 1991) is the alteration of iron containing mica (Fig. 11). The origin of diagenetically formed pyrite in the underlying Quilon limestone has already been reported (Menon, 1963). However, both the reactions are occurred due to the action of hydrogen sulphide liberated by sulphur-reducing bacteria. Berner (1964) and Kalliokoski (1966) attributed the origin to the reaction of hydrogen sulphide formed by sulphate reduction, with iron-bearing minerals in sediments. The reactions involved in this mechanism are given below:

(a) Sulphate reduction

$$2\ Fe_2(SO_4)_3 + 2\ H_2O \longrightarrow 4\ FeSO_4 + 3\ O_2 + 2\ H_2S$$

(b) Pyritisation

$$\underset{\text{iron containing mica}}{K(Mg, Fe)_3\ (Al, Si_3)\ O_{10}\ (OH)_2} \xrightarrow{+\ H_2S} \underset{\text{pyrite}}{FeS_2}$$

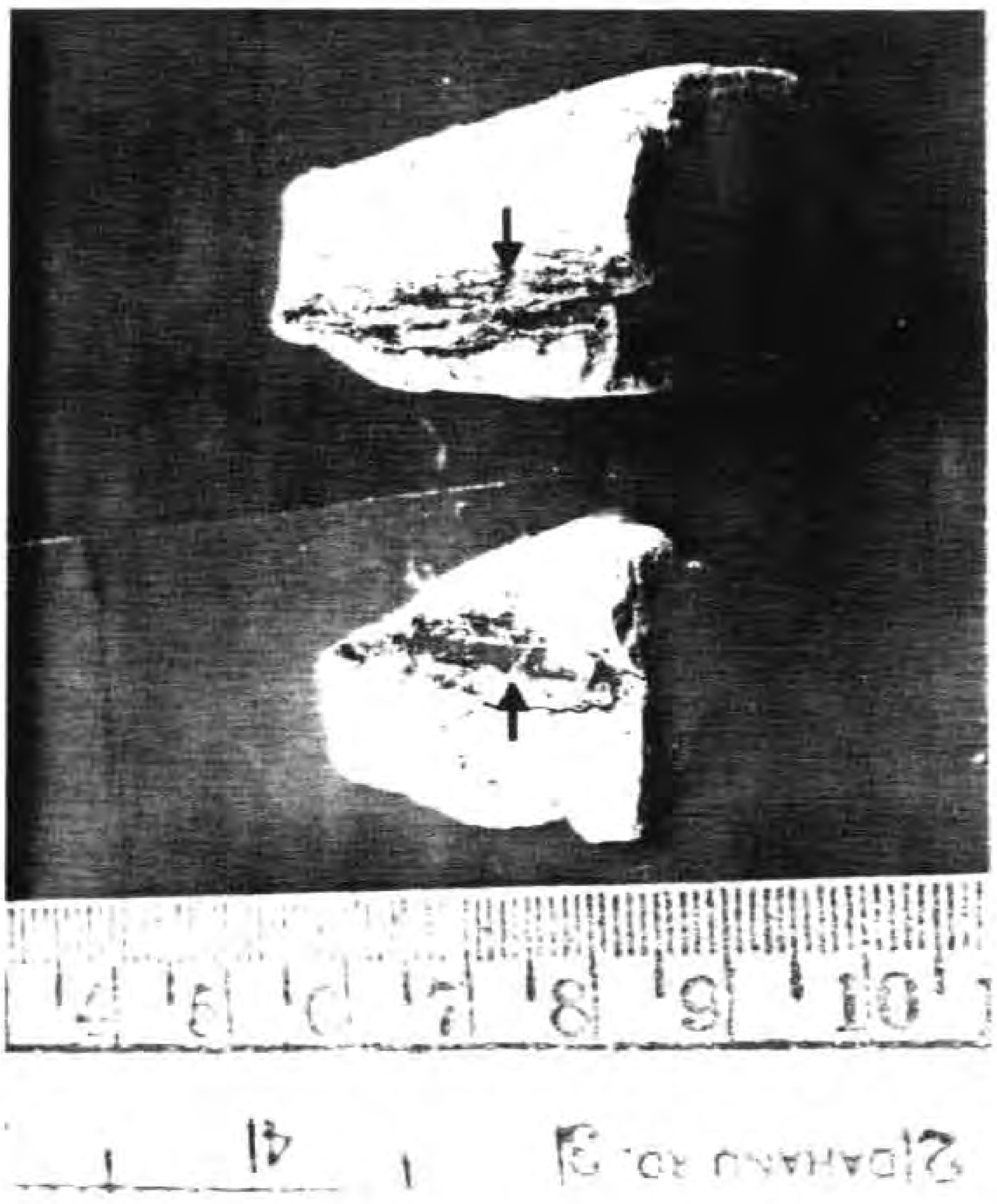


Fig. 10: Photograph of nodular inclusions in the clay bed

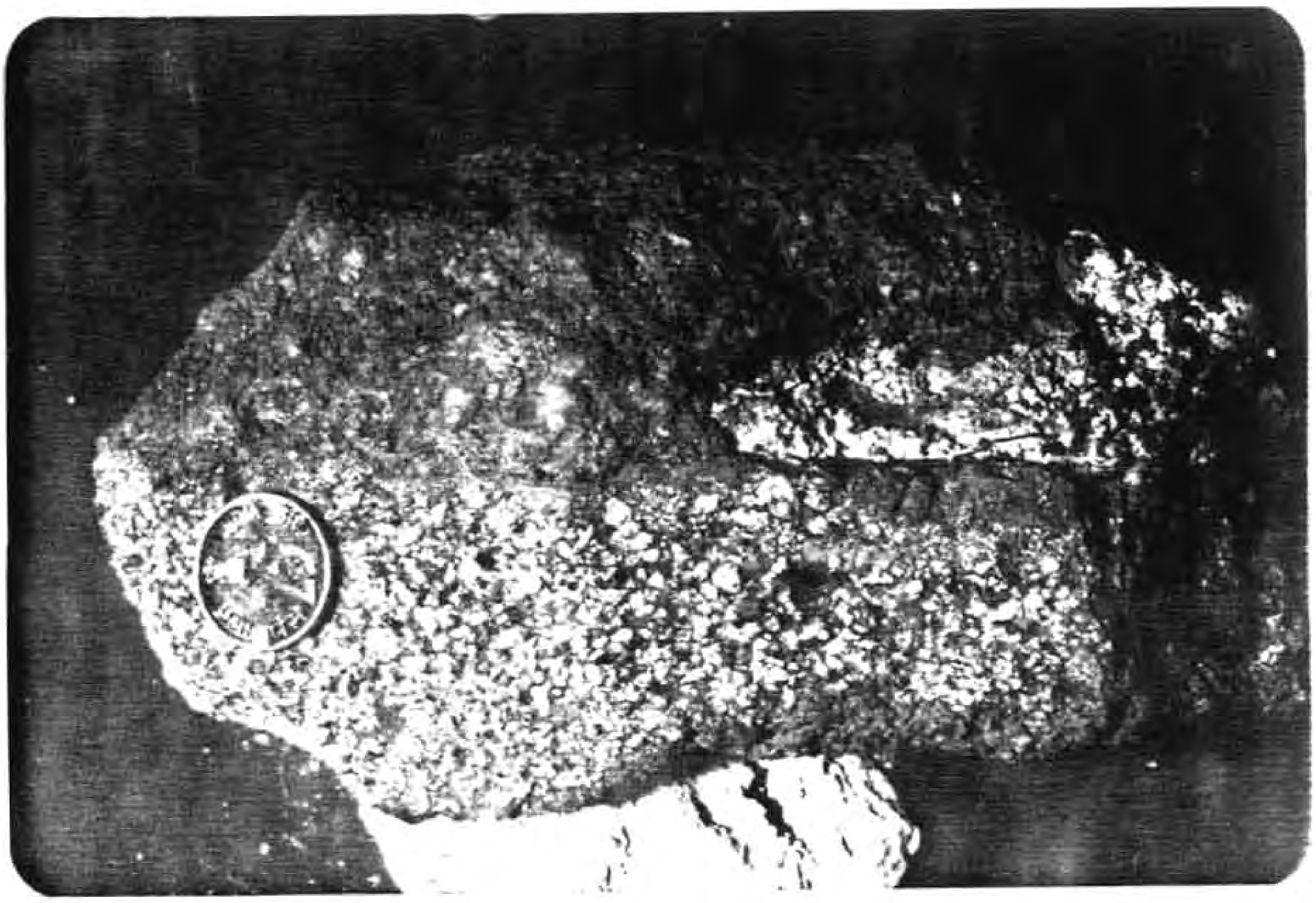


Fig. 11: Sample with iron-containing mica (black spots) obtained from the red sandstone

It seems that marcasite (orthorhombic form) is produced under neutral to acidic conditions whereas pyrite is favoured by slightly alkaline conditions. The X-ray diffraction pattern (Fig. 12) and scanning electron micrograph (Fig. 13) of nodules indicated that the crystals are of psuedomorphic pyrite. The crystal shape as seen from SEM shows that there are some crystals with cubic structure (Fig. 13(2)) but majority of the crystals show only a pyramidal prism indicating crystal shape typical of marcasite. However, the X-ray pattern clearly shows the pyrite peaks (JCPDS powder diffraction file) which suggests psuedomorphic replacement of initial marcasite by pyrite . Hence it is inferred that the iron sulphide could exhibit psuedomorphism, a phenomenon which is very much prevalent in the mineral kingdom (Sikankar, 1984). Octahedral pyrite forms with less prominent cubic faces have recently been reported by Norman et al., (1991). This mineral identification was further substantiated by differential thermal analysis which gave a large exothermic peak of FeS_2 at $450^{o}C$. The photographs (Fig. 14) of the FeS_2 show that the nodule has a central cavity. This could possibly be due to the microfaunal infillings or by the segregation of minerals by ground water percolation occurred during diagenesis.

Another interesting observation in the field is the yellow coloured deposit of elemental sulphur. It is known that at acidic pHs the FeS_2 can be leached out as sulphur by bacterial action. Agate (1982) has suggested that under suitable weathering conditions, in the presence of a microbe called thiobacillus ferroxidane, the ferrous sulphide is reduced to sulphur as:

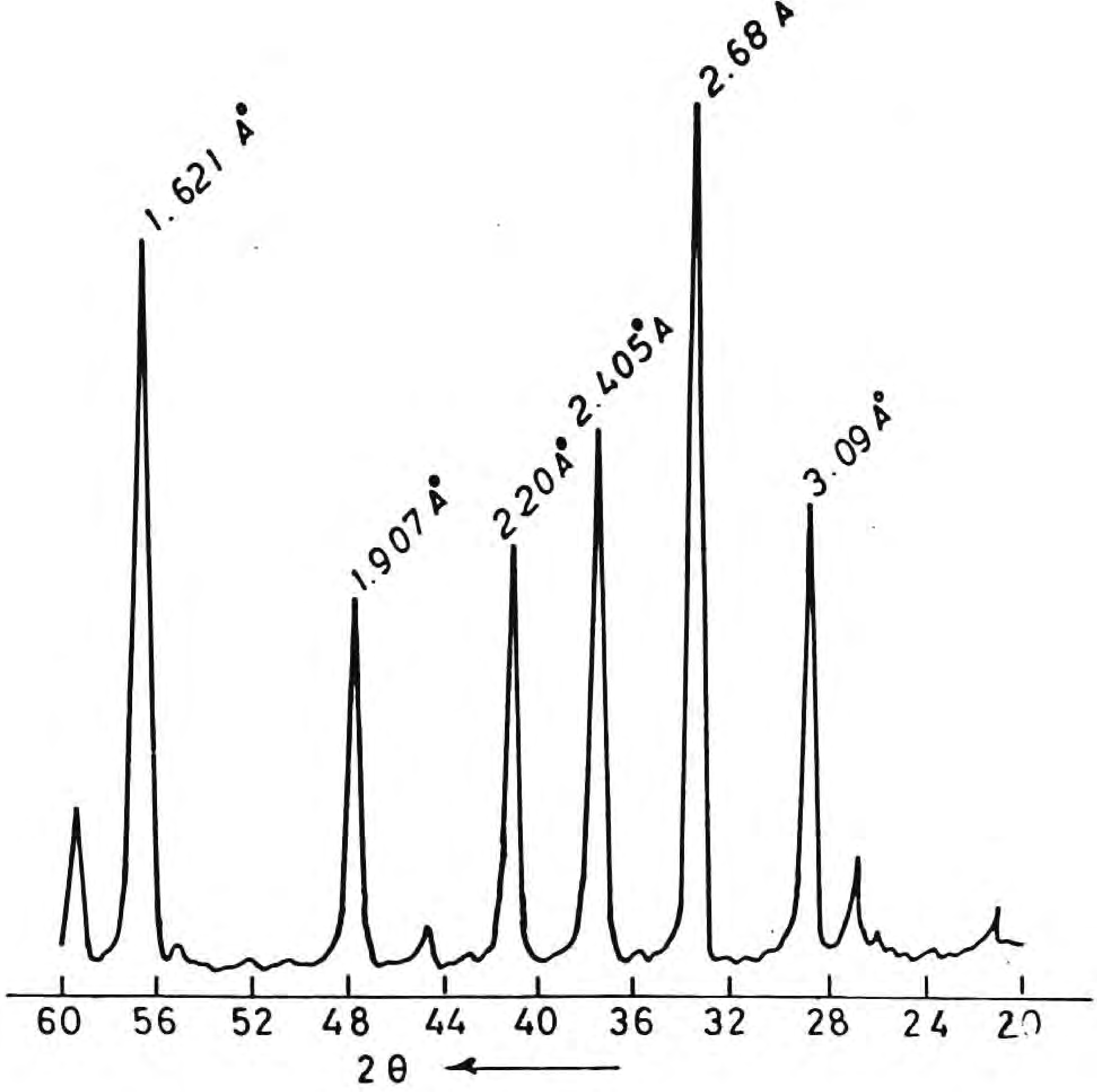


Fig. 12. X - ray diffraction pattern of the nodular formation
Cu Kα - radiation

Fig. 13: Formation of pyrite

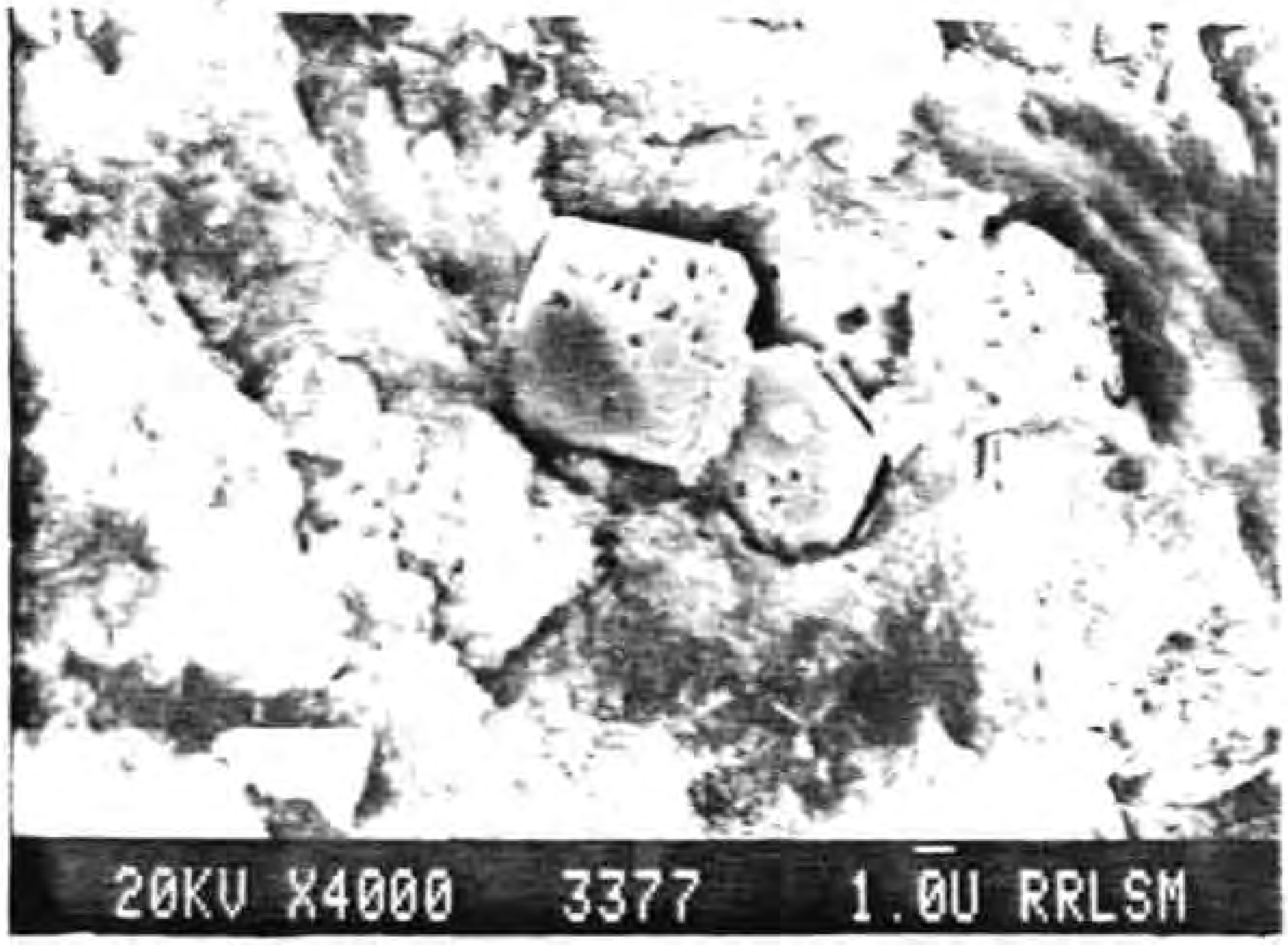


Fig. 13(1): Octahedron of marcasite/pyrite (precipitated) in the clay matrix

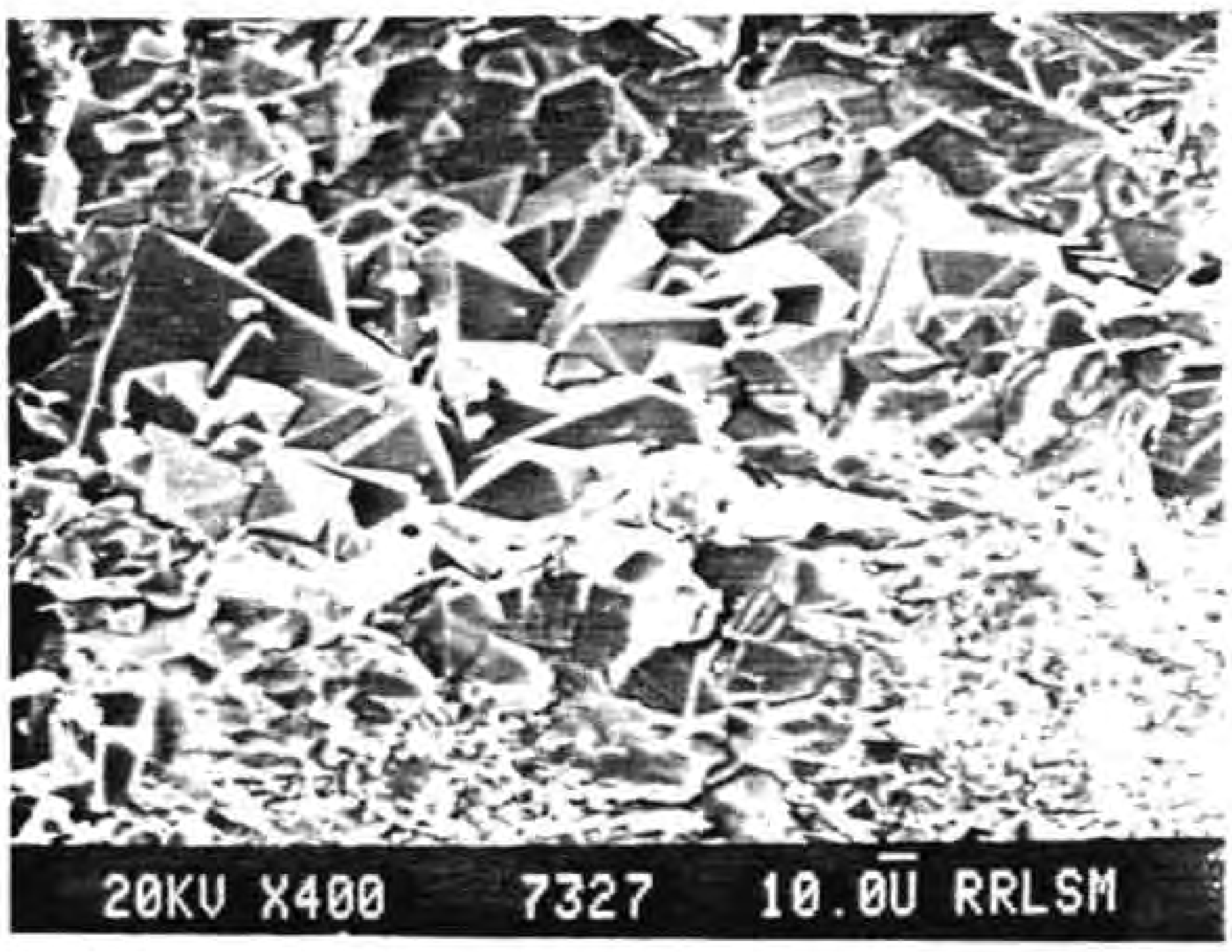
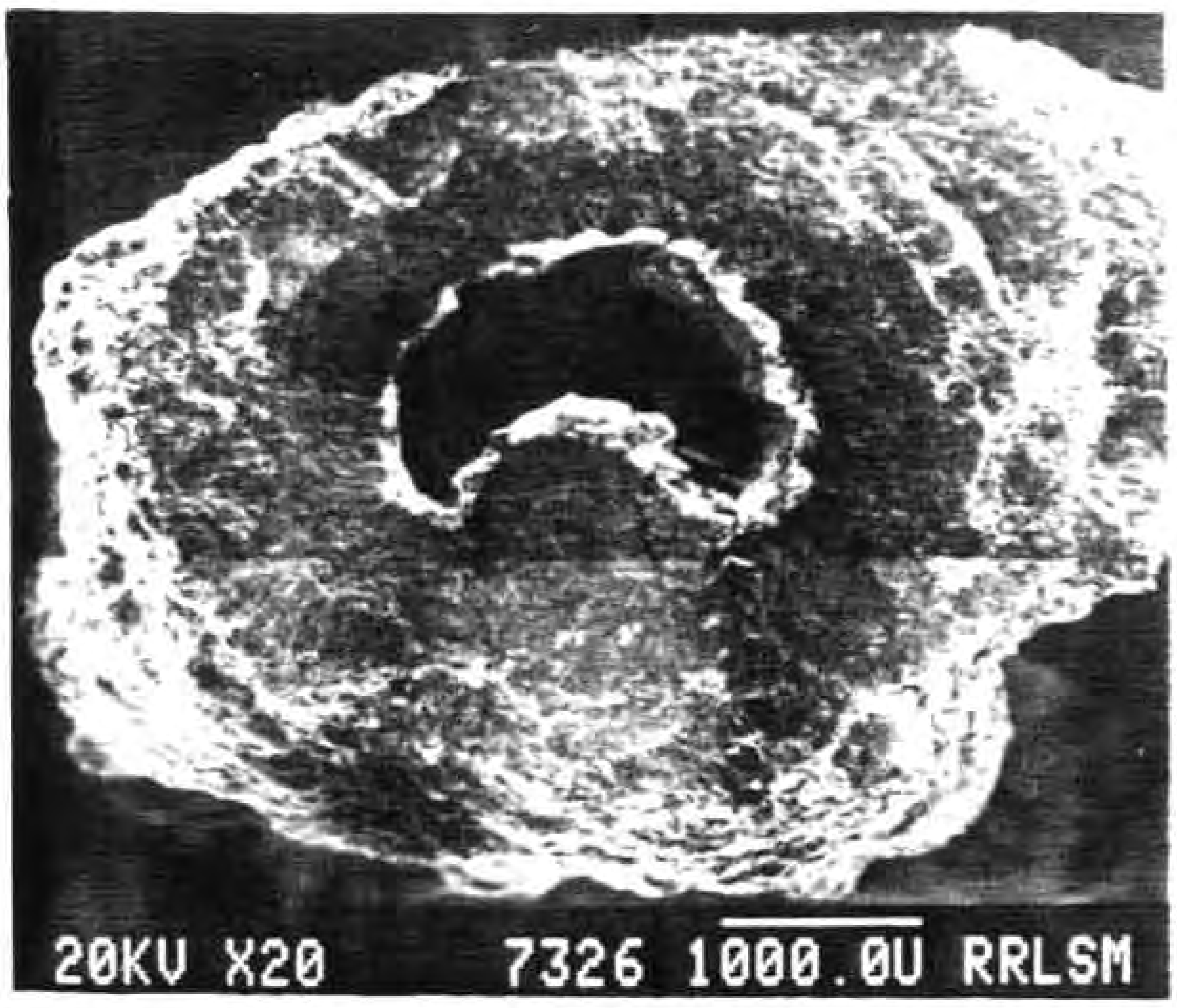


Fig. 13(2): Cluster of well-developed pyrite crystals



(a)

(b)

Fig. 14: Electron micrographs of the cross sectional view of the nodular formation
(a) Nodule in gray clay bed
(b) Nodule in black clay bed

$$FeS_2 + Fe_2(SO_4)_3 \xrightarrow{\text{low pH 3}} 3\,FeSO_4 + 2\,S$$

A deposit of white crystals is found to form on the surface of the washed black clay on storage. XRD studies indicate that these are the crystals of melanterite ($FeSO_4 \cdot 7\,H_2O$). The conversion of FeS_2 to $FeSO_4 \cdot 7\,H_2O$ is reported to be due to microbial action.

The detailed X-ray diffraction studies show that besides quartz and pyrite, the clay samples from Padappakkara contain illite (Fig. 15), gibbsite (Das et al., 1991) traces of halloysite and rutile as impurities.

2.5 PROPERTIES RELATED TO INDUSTRIAL APPLICATION OF THE PROMINENT BALL CLAY SEAMS

The gray and black ball clays occur in large quantities and can be processed into economically viable products. Hence, an investigation on these two varieties was carried out.

The -350 mesh fraction of each sample is taken for the detailed study. Particle size distribution analysis by sedigraphic method (Fig. 16) shows that the gray ball clay contained 89% of the fine fractions ($< 2\,\mu m$). A comparative study of the chemical composition (Table 2) indicates that the silica content in the gray clay (G) is higher than that in the black variety, whereas the loss on ignition is greater for the black variety (B). Since these samples are from adjacent layers, it can be presumed that 5% greater LOI in the black clay cannot be

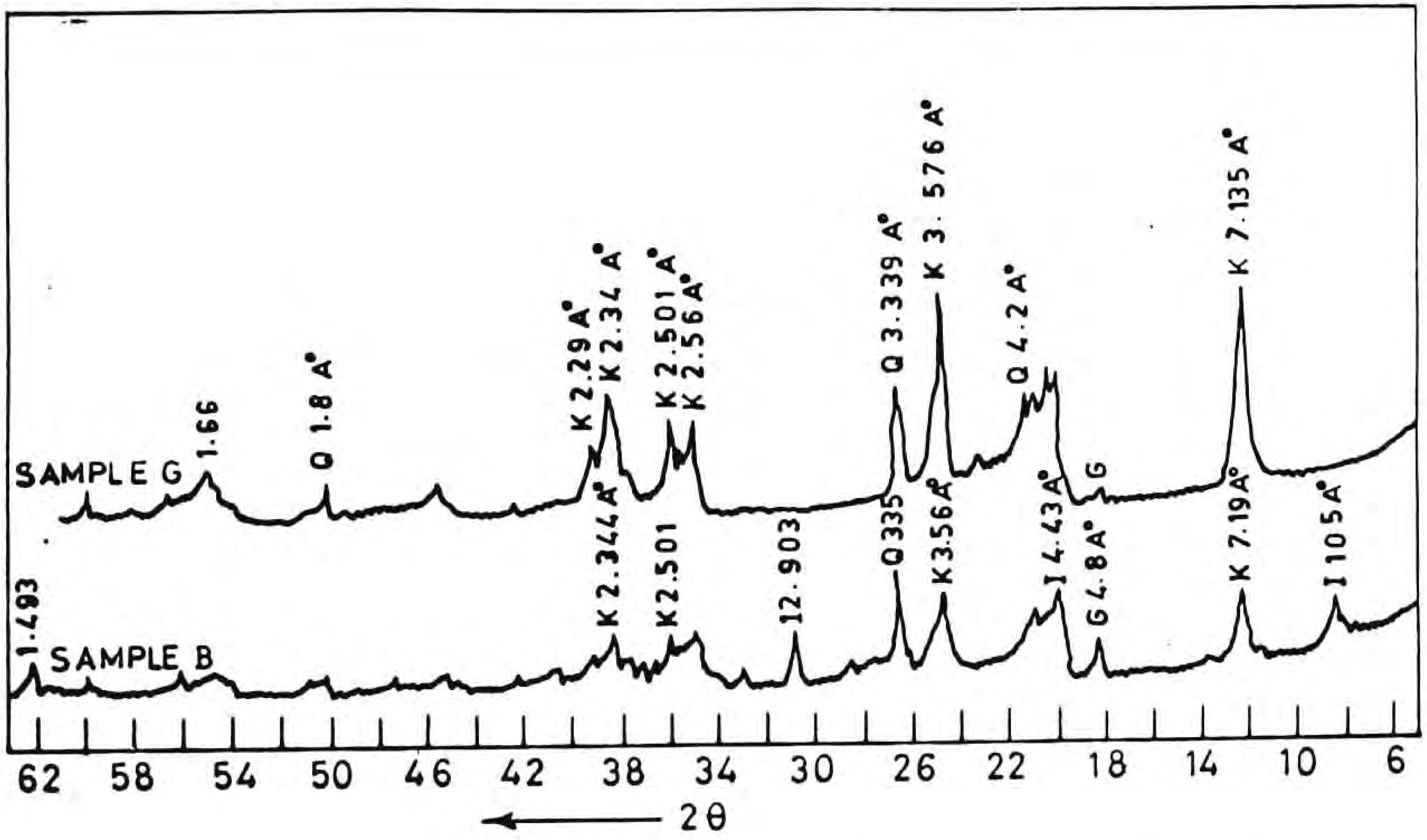


Fig.15. X-ray diffraction patterns of samples G and B Cu Kα - radiation

K - Kaolinite Q-Quartz I - Illite G- Gibbsite

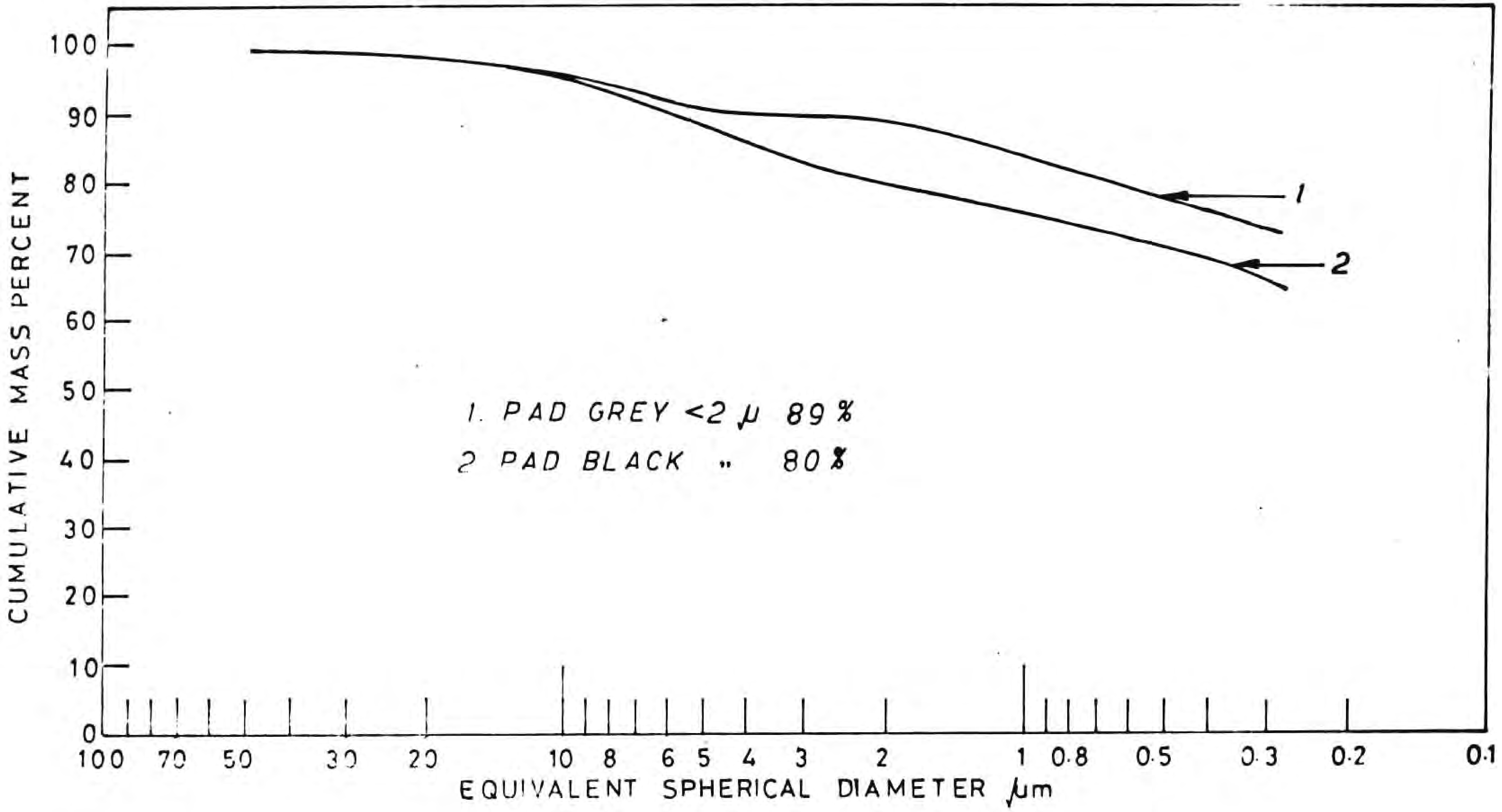


Fig.16 Particle size distribution

due to organic matter alone. This is further confirmed by finding out the loss at 420°C which indicates that sample B shows a loss of $\sim$13%, the weight loss experienced by sample G is only around one fifth of the black variety. Since both the samples have inclusions of ferrous sulphide, it is evident that the latter sample is contaminated with more of ferrous sulphide impurities which is responsible for $\sim$ 13% loss at 420°C.

Fig. 15 shows the X-ray diffraction patterns of the sample G and B. From the diffractogram, sample G shows kaolinitic peaks in addition to peaks of quartz and gibbsite. In the XRD pattern of sample B, one could notice additional peaks of d values at 10.5, 4.6, 4.4, 3.32 and 2.47 A° which are due to gibbsite and illite.

2.6 SUMMARY

Evidences revealed by the field studies indicate that the diagenetic alteration of feldspar has resulted in the formation of ball clays in the coastal region of Quilon District in Kerala. Study of the distribution of iron in layers of the ball clays showed that it is a sedimentary deposit. Detailed investigation of gray and black ball clays which occur in significant quantities indicates that the gray variety is mainly kaolinitic and contains moderate iron content. The black ball clays contain more organic matter, gibbsite and small amounts of illite. These constituents gave higher plasticity. Black ball clay also has a higher iron content due to more abundant pyrite nodules.

The occurrence of pyrite in these ball clays suggests that early formed marcasite is transformed by diagenesis to psuedomorphs of pyrite. Furthermore, pyrite is abundant enough in the ball clays to affect ceramic properties such as softening point (PCE) and colour. The formation of nodular pyrite with a central cavity indicates the bacterial activity as an agent in its formation. However, because of the high plastic nature of these clay, both materials find use in ceramic industry as a binding material after beneficiation for removal of pyrite.

CHAPTER III

CRYSTALLINITY OF KAOLINITES IN BALL CLAYS AND CALCULATION OF CELL PARAMETERS

3.1 GENERAL

The crystallinity of kaolinite is of considerable importance since it is responsible for many of the properties of the material related to structural, genetical and industrial characteristics. In the case of clay minerals the use of crystallinity numerical indices provided by XRD and IR experimental data has been well known for more than forty years (Ruiz and Galan, 1991).

Several methods of measuring the crystallinity of kaolinite have been described in the literature, most of which involve X-ray diffractometry. Murray and Lyon (1956) were able to arrange some kaolinites in order of their crystallinity by a visual inspection of the X-ray diffractometer traces but no attempt was made to express the different degrees of crystallinity in terms of a numerical value. Johns and Murray (1959) suggested that the ratio of the relative intensities of two kaolinite X-ray reflections ($02\bar{1}$ and 060) could be used as a crystallinity index. Hinckley (1963 and 1965) determined the crystallinity of well-crystallised kaolinite by measuring the ratio of the intensities of the ($1\bar{1}0$ and $11\bar{1}$) reflections. Parker used infrared spectroscopy to distinguish between various types of kaolinite (eg. well-crystallised and disordered) and he found that when the ratio of the absorption band at 3700 cm^{-1} to that at 3620 cm^{-1} for oriented samples was plotted against that for unoriented samples, concentration of points occured in certain areas, a single type of kolinite being dominant in each area. He concluded that changes in the ratio of the absorption bands for a randomly oriented sample were related to the form of kaolinite present, i.e. whether it is triclinic (well crystallised) or monoclinic (disordered) where comes the significance of cell parameter calculation.

Kaolinite (well crystallised) and dickite (disordered or poorly crystallised) are dioctahedral 1:1 layer silicates. The structure of kaolinite has been studied by Brindley Robinson (1946), Brindley and Nakahira (1958), Zvyagin (1960), Giese (1982), Adams (1983) and Suitch and Young (1983). The structure of dickite has been examined by Newnham and Brindley (1956 and 1957), Newnham (1961), Giese and Datta (1973) and Adams and Hewat (1981). Bailey (1963) demonstrated that both kaolinite and dickite are based on a 1 M stacking sequence of layers, and that the minerals would be identical if they were trioctahedral. The two minerals have various degrees of structural disorder or crystallinity produced either by geological conditions of formation, transport or deposition or by mechanical treatment such as grinding. According to Brindley et al. (1986), crystallinity has generally been used in the past to refer either to the fraction of crystalline material in a mixture of crystalline and non-crystalline materials or crystallite size.

3.2 INTRODUCTION

Several methods for the measurement of crystallinity of kaolinite have been described in the literature among which X-ray diffractometry (XRD) and Infra-red absorption spectroscopy (IRAS) are the most important. Schultz has investigated the X-ray diffraction traces of oriented aggregates of artificial binary mixtures containing approximately equal weight of samples of illite, montmorillonite, mixed layer combinations of illite and montmorillonite, and kaolinite samples having different degrees of crystallinity. He found that "fire clay-type" kaolinites gave 7 A^o peak areas about equal to the area of the 10 A^o peak of an equal amount of illite, montmorillonite or mixed layer clay, whereas well crystallised kaolinite gave 7 A^o peak areas generally about twice that of the 10 A^o peak of an equal weight of the illite-montmorillonite minerals. The elucidation of the crystallinity of kaolinite is not an easy task, since more than one crystal type is present; usually several clay and non-clay minerals other than kaolinite are present in appreciable quantity, often interfering with the X-ray and IR absorption of kaolinite. Hence concentration of the mineral content by size fractionation ($<$ 1 μm esd) combined with purification by chemical treatment becomes necessary to characterise the mineral completely.

In this study seven different ball clay samples from certain potential sources in and outside the country were taken, namely, Padappakkara (Quilon District, Kerala) A, Payyangadi (Cannanore District, Kerala) B, Bikaner (Rajasthan) C, Bimadole (Andhra Pradesh) D, Than

(Gujarat) E, Westerwald (W. Germany) F and Inagaki-kibushi (Japan) G. All the seven samples were treated in the same way for purification and concentration of kaolinite material.

3.2.1 Preparation of fine fractions

The separation of the fine fractions ($< 1\ \mu m$ esd) was carried out according to the process based on Stoke's law which consists briefly of a gravity sedimentation (ISI-4589) (ASTM Part 19, 1971) using tetra sodium pyrophosphate as deflocculent (Detailed Procedure given in Appendix). This enables particles of diameter less than 1 μm to be siphoned off and concentrated by evaporation. The size distribution can be calculated from Stoke's law, which may be expressed as follows (Grimshaw, 1960).

$$r = \sqrt{\frac{9\ h\eta}{2\ (D_1 - D_2)\ gt}}$$

r - radius of spherical particle in cm

h - distance in cm between liquid surface and pipette tip when suspension is drawn

η - viscosity of suspending medium (g/cm sec)

D_1 - true specific gravity of the particle (g/cm^3)

D_2 - true specific gravity of suspending medium (g/cm^3)

g - gravitation constant (981 cm/sec^2) and

t - time in second from start of the test

3.2.2 Removal of carbonate

Carbonates were removed by digesting the sample in a boiling water bath for 30 min with acetic acid buffered to pH 5 with intermittent stirring. The suspension was centrifuged until the supernatant liquid was clear. Two additional washings were given with the same reagent, and the 30 minute water-bath treatment was repeated for samples that were known to be calcarious (Al-Khalissi and Worrall, 1982).

3.2.3 Removal of organic matter

The previous treatment to remove carbonate facilitated the removal of organic matter. The amount of water used in the transfer from the centrifuge tube to the beaker was kept at a minimum to avoid dilution of H_2O_2. Each 1 gm sample of clay was treated with 10 ml of 30% H_2O_2 and the mixture heated on a boiling water bath (Al-Khalissi and worrall, 1982).

3.2.4 Removal of iron oxides

Coatings of amorphous or crystalline iron oxides have been found associated with clay particles. The removal of iron oxides assists dispersion and separation of the fine fraction and moreover facilitates X-ray diffraction, DTA, TGA, infra-red and electron microscopic examination. The extractable iron oxide from each sample was collected by buffered citrate - bicarbonate - dithionate (CBD) method (Jackson, 1973, Worrall, 1982); sodium dithionate ($Na_2S_2O_4$) acts as a reducing agent, sodium bicarbonate (pH 7.3) as a buffer, and sodium citrate as a chelating or complexing agent for ferrous and ferric iron.

3.3 INFRA-RED ABSORPTION CRYSTALLINITY INDICES IN KAOLINITES

The most relevant characteristics of kaolinite IRAS crystallinity indices found are given in the Table (1) (Gomes, 1989). Among these, the indices of common use are: (i) IA 3696 cm^{-1} /IA 3624 cm^{-1} - Lyan and Tuddenham (1960); (ii) IA 3696 cm^{-1} /IA 3625 cm^{-1} (in oriented specimen inclined at 45^{o}) - Parker (1969); (iii) IA 3700 cm^{-1} /IA 910 cm^{-1} Neal (1974). Another index IA 795 cm^{-1} /IA 755 cm^{-1} was developed by CSF Gomes in 1987.

The purified and dried sample fractions were mixed with finely ground potassium bromide in the ratio 1:50 by weight and mixed thoroughly in a pestle and mortar. Each sample was then pelletised and the infrared spectrum was recorded using a Perkin Elmer Infrared spectrometer (normal slit width and medium scanning speed). Low temperature IR spectrum was taken since it was found to be more sensitive for estimating degree of disorder (Prost et al., 1989).

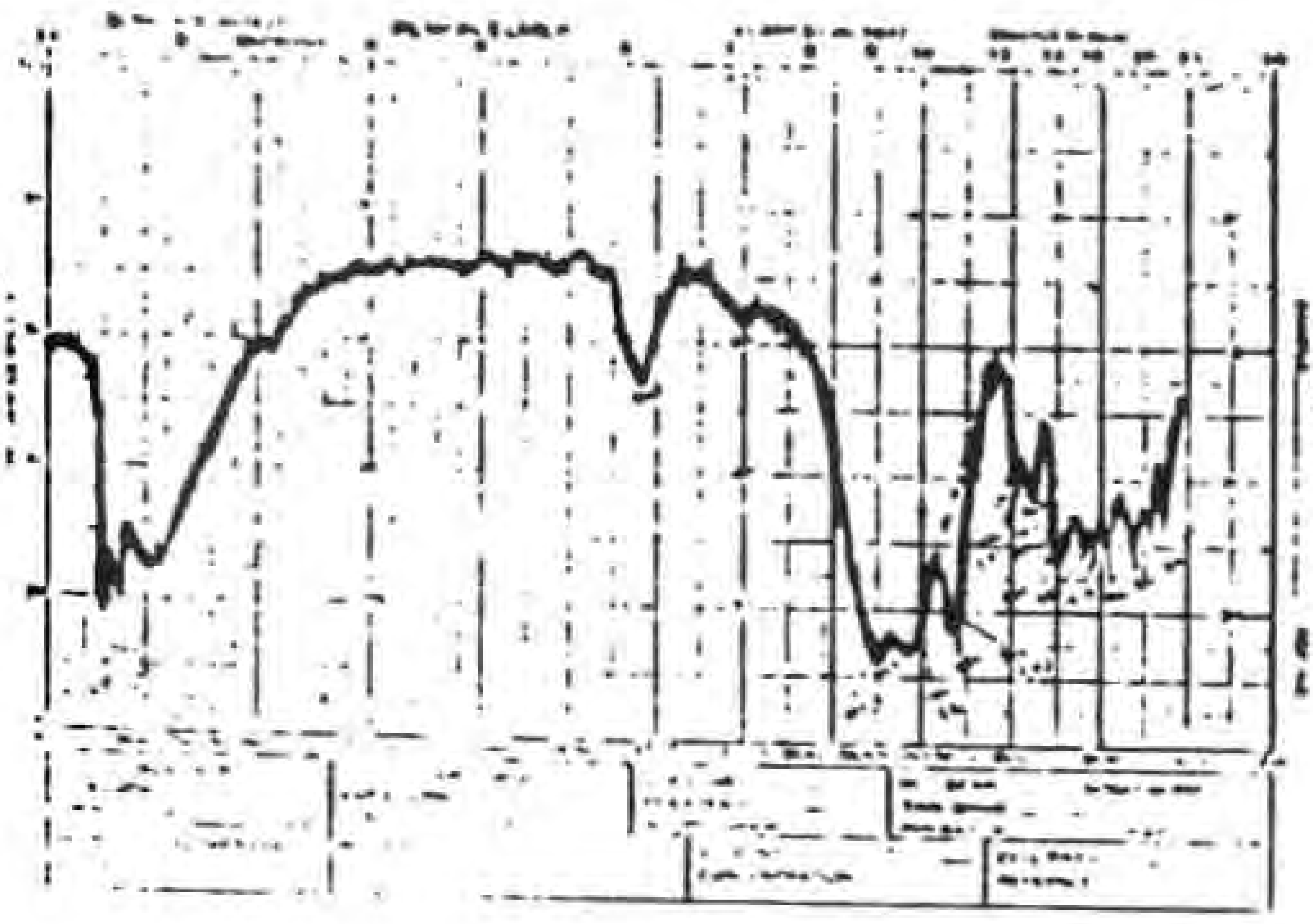
For ball clays, infrared spectra bands are of large intensity at 3700, 3621, 1100, 1032, 1008, 910, 694, 539, 471, 431 cm^{-1} (Fig. 1) (Vander and Beutelsphacher, 1976). The absorption bands at 3700 cm^{-1} and 910 cm^{-1} have been attributed to O-H vibration modes and Al-OH modes respectively. The crystallinity of kaolinite in ball clays was determined by the method of Neal and Worral (1977) by measuring the ratio of the intensities of the absorption band at 3700 cm^{-1} to that at 910 cm^{-1} by constructing the tangent base lines.

Table 1: IRAS crystallinity indices

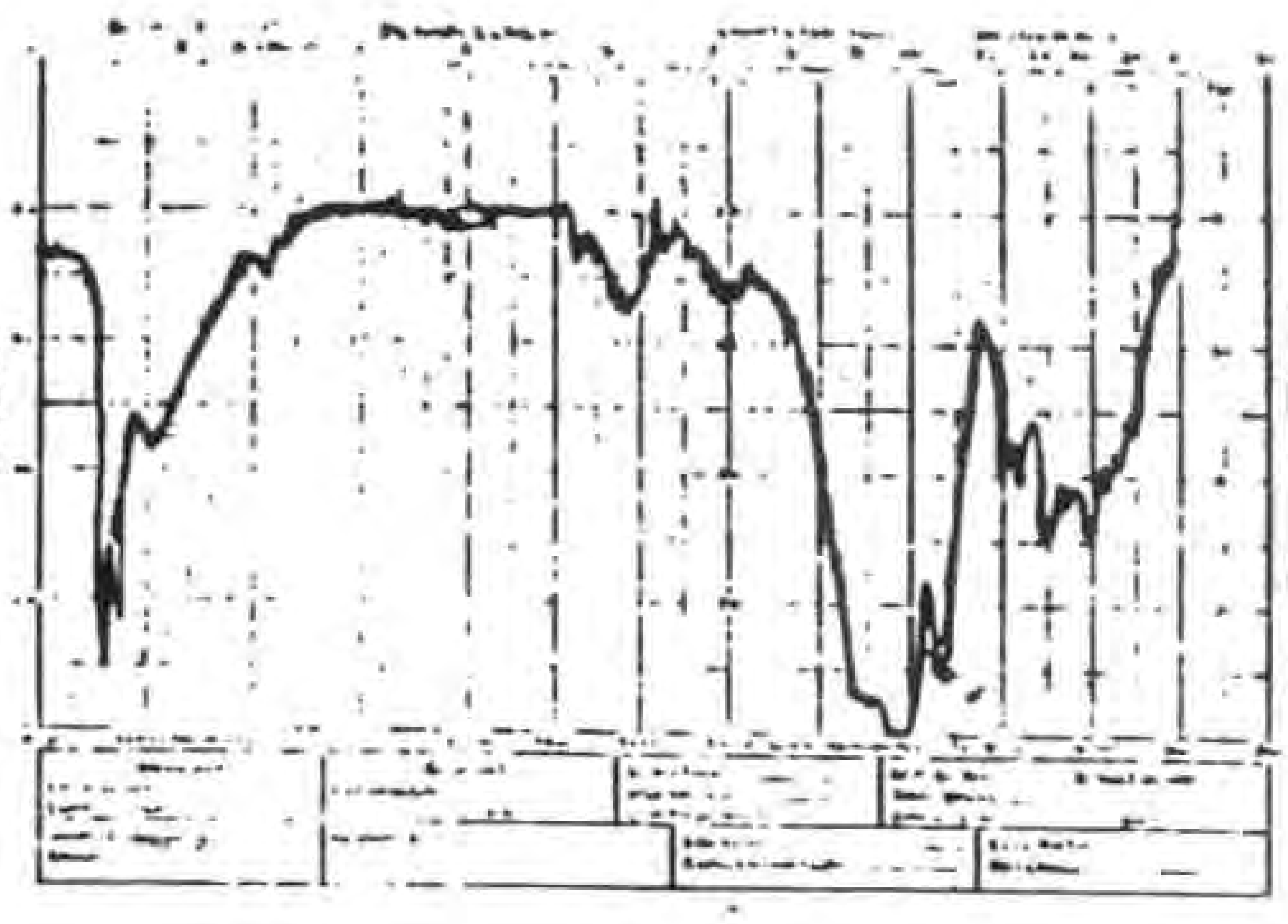
Crystallinity indices/ general requirements	IA 3969 cm^{-1}/IA 3624 cm^{-1} Lyon and Tuddenham(1960)	IA 3695 cm^{-1}/IA 3625 cm^{-1} (orient. specimen inclin. at 45^o) vs. IA 3695 cm^{-1}/ IA 3625 cm^{-1} (randomly oriented specimen). Parker (1969)	IA 3700 cm^{-1}/IA 910 cm^{-1} Neal (1974)	IA 795 cm^{-1}/ IA 755 cm^{-1} Gomes (1979)
1	2	3	4	5
Significance	Provides good information about the kaolinite structure organization and in some cases facilitates the differentiation of the kaolin mineral species	Provides a classification of kaolinites according to their general O-D but cannot provide information on the quality or type of disorder. Both ratios decrease with increasing kaolinite disorder. Satisfactory correlation between Parker's IRAS crystallinity index and Hinckley's XRD crystallinity index has been found.	Measures the disorder in the structure produced mainly by atomic isomorphous substitution.	Provides information about the symmetry of the unit-cell. The index reflects the variability in crystal symmetry due to distortions of the silicon-oxygen anion. Distinguishes the pseudo-monoclinic kaolinites of the triclinic ones.
Reproducibility	Good in low-impurity and non-textured kaolinite bearing specimens.	Good in low-impurity kaolinite bearing specimens.	Good whenever the impurity quantities able to cause disturbing absorption coincidences are not influential.	Good in low-impurity and non-textured kaolinite bearing specimens.
Limitations	Applicable to kaolinites with any type and degree of crystal defectiveness	Applicable to kaolinites of all types and degrees of crystallinity.	Applicable to kaolinites of all genetic types and degrees of crystallinity	Applicable to kaolinites of all genetic types and degrees of crystallinity

1	2	3	4	5
Disturbances	Impurities of 2:1 clay minerals (micas, illites and smectites) diminish the index values. Other kaolin mineral species such as dickite and halloysite can interfere with index assessments. Dickite and halloysite diminish the index values.	Very sensitive to impurities such as: 2:1 clay minerals and dickite. These impurities produce an enhancement of the absorption band at 3625 cm^{-1} unbalanced in both oriented and non-oriented specimens.	Dickite associated to kaolinite affects the intensity of the 3700 cm^{-1} absorption band of kaolinite. 2:1 clay minerals associated to kaolinite affect the intensity of the 910 cm^{-1} absorption band.	Quartz is an impurity which can interfere with the triclinicity index measurements.
Range of variability	Appreciable. 1.2-1.5-kaolinites 0.8-0.9-halloysites 0.6-0.8-dickites	Wide range of variability.	Wide range of variability, 0.5-1.2, with values increasing towards the low defective kaolinites.	Appreciable. 0.9-well crystallized. 0.9-1.1-medium crystallized. 1.1-poorly crystallized.
Sensitivity to specimen preparation procedure and analytical equipment performance conditions	The intensity of the 3696 cm^{-1} absorption band is orientation depentent. The intensity of the 3624 cm^{-1} absorption band is little affected by the texture of the specimens.	Texture effects are not important if the preparation of oriented and non-oriented specimens is carried out properly.	Applicable only to non-oriented mounts.	Applicable only to non-oriented mounts.

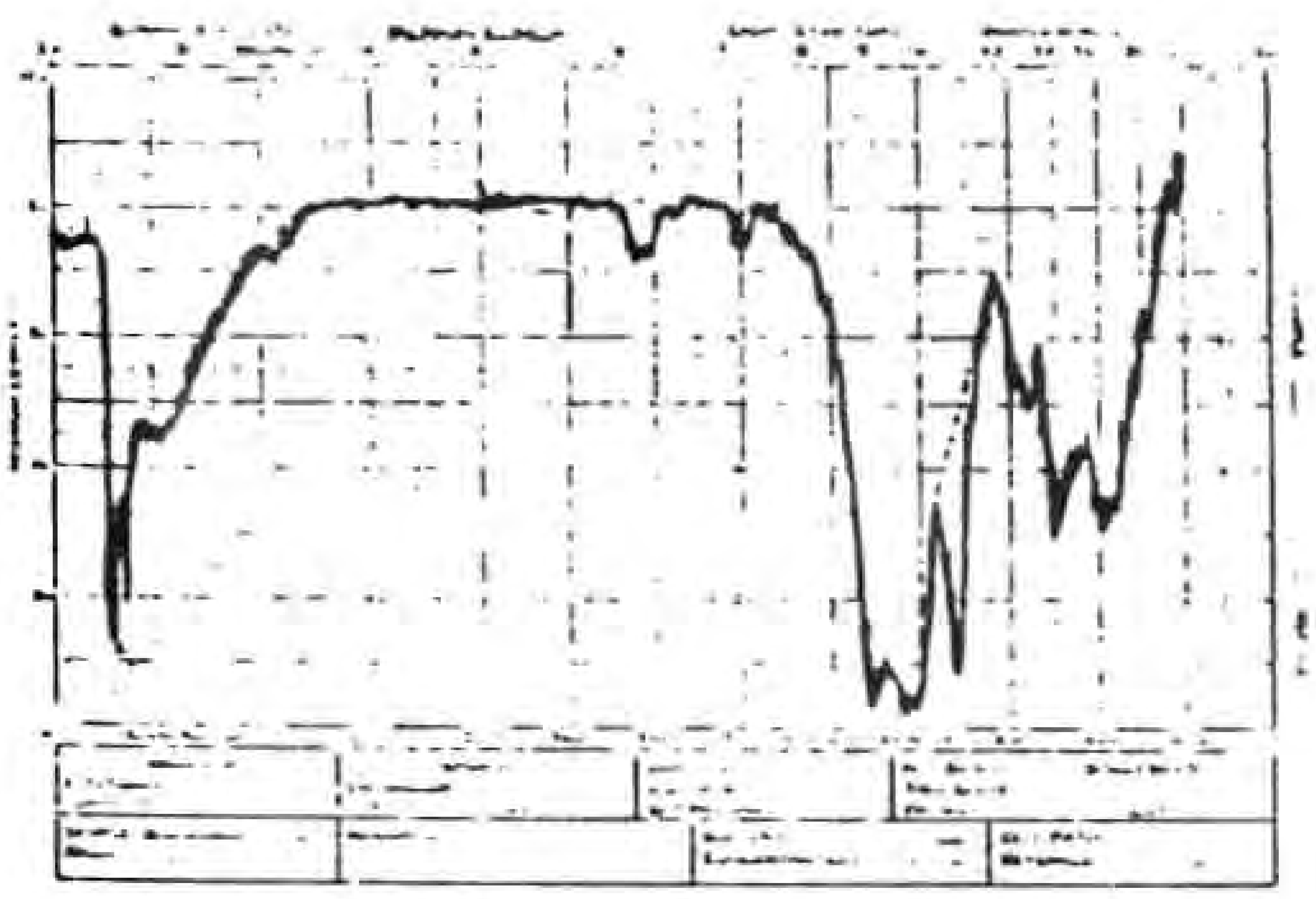
Fig. 1: IR spectra of ball clays



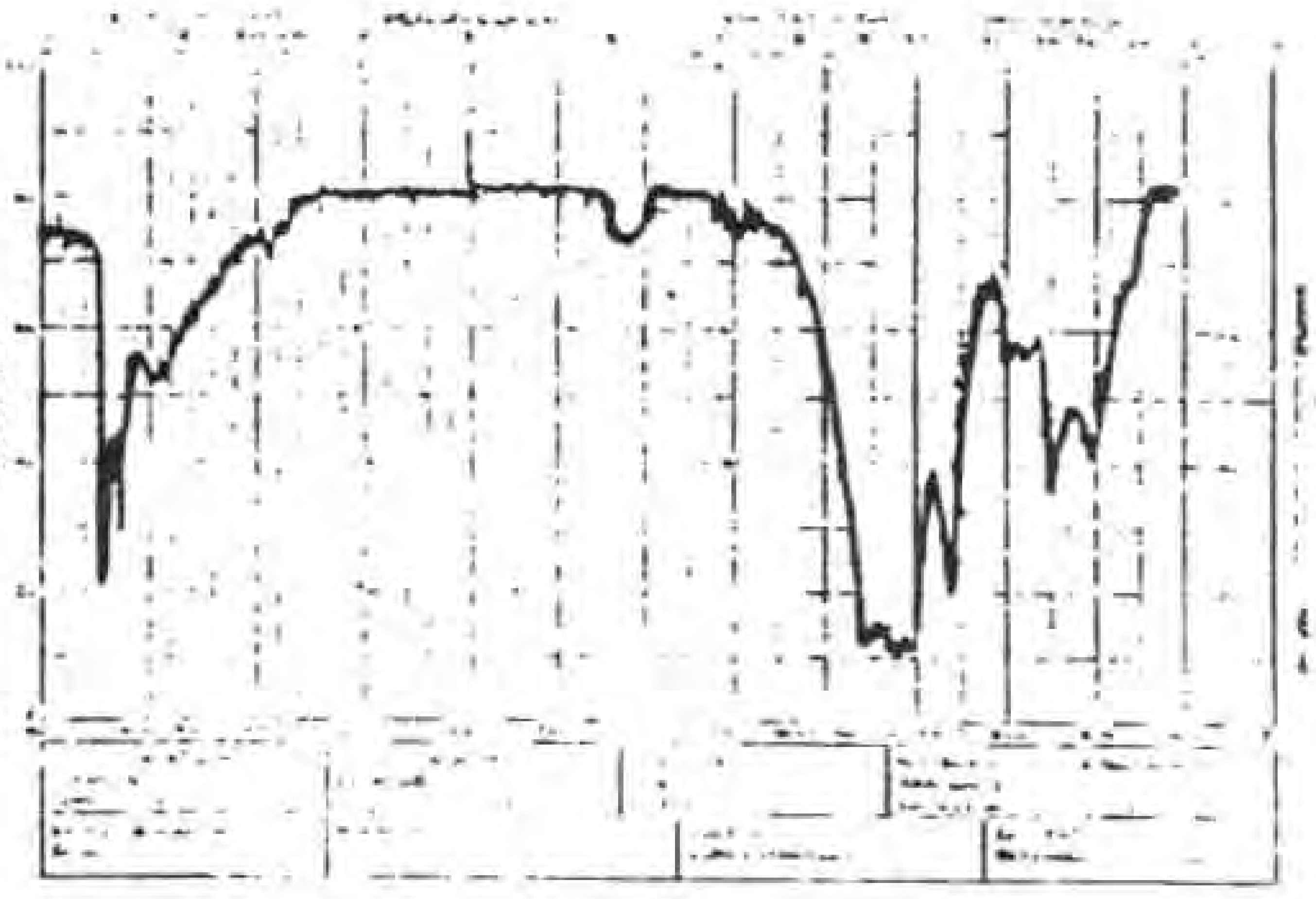
Padappakkara, A



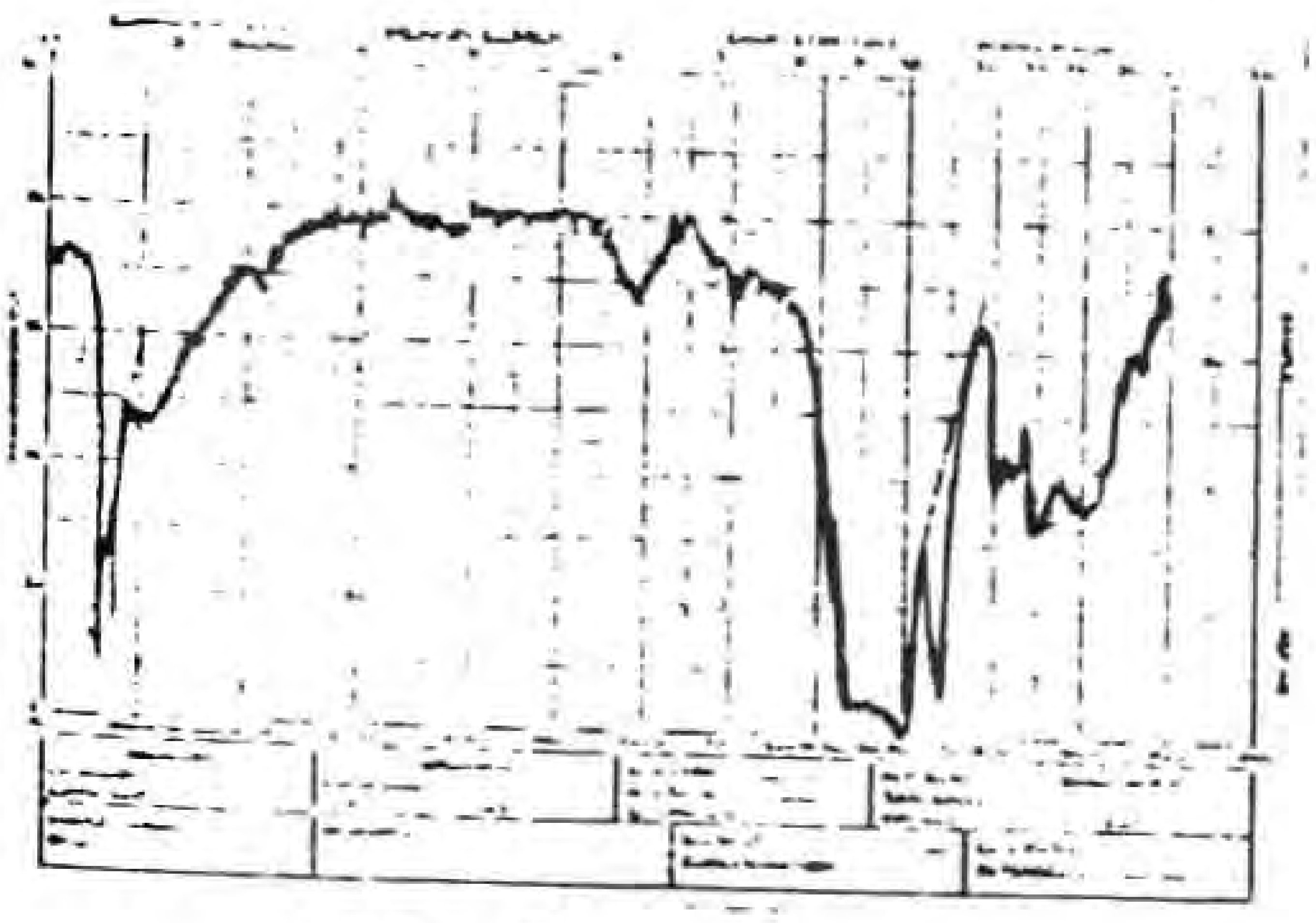
Payyangadi, B



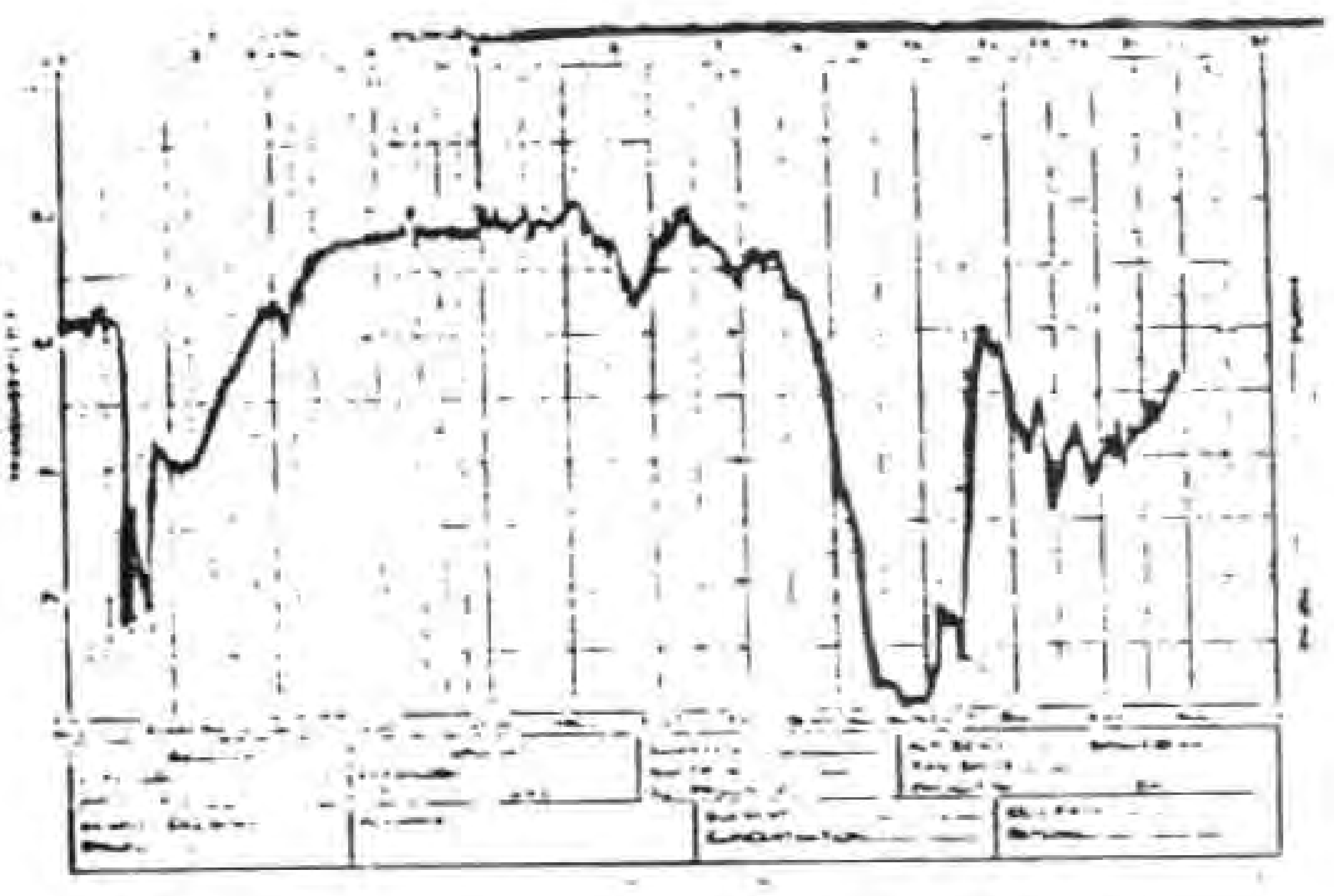
Bikaneer, C



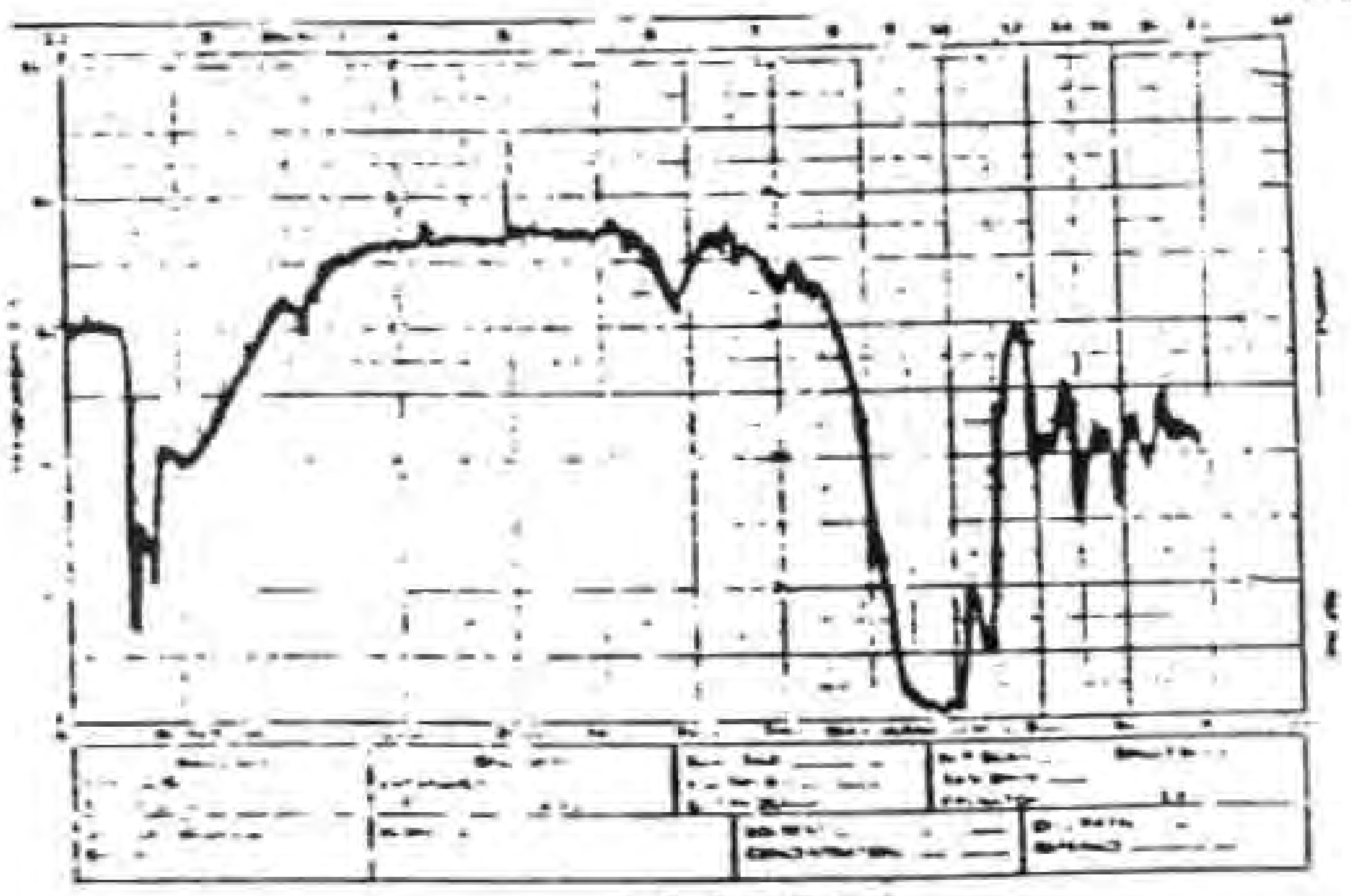
Bimadole, D



Than, E



Westerwald, F



Inagaki-kibushi, G

The IR crystallinity indices obtained along with the other expemental results are given in Table 4 from which it can be seen that Bimadole D, has the highest value of 0.97 and Padappakkara A, has the lowest, 0.5. According to Neal and Worral (1977) disorder in the structure of kaolinite is caused by isomorphous substitution of Mg and/or Fe for Al in the octahedral layer of kaolinite. Worrall (1959, 1982) suggested that since the radius of the substituent Mg is greater than that of Al, the inner and the basal hydroxyl group coordinates with the latter ion, which can affect the absorption band at 3700 cm^{-1}. Therefore as the amount of substitution increases - which can be almost measured from cation exchange capacity (CEC) values, Table 4 - the amount of disorder also increases, and this is reflected in the ratio of the absorption band at 3700 cm^{-1} to that at 910 cm^{-1}. Thus the crystallinity index determined here by the infrared absorption spectroscopy is a measure of the disorder in the kaolinite lattice produced mainly by isomorphous octahedral substitution.

3.4 X-RAY DIFFRACTION CRYSTALLINITY INDICES IN KAOLINITES AND THEIR CELL PARAMETERS

3.4.1 Determination of XRD crystallinity indices

The XRD crystallinity indices found in the literature are given in Table 2. They were (i) $I(1\bar{1}0)/I(020)$ - Murray and Lyons (1956); (ii) (001) - Brindley and Kurtossy (1961); (iii) $I_C = \frac{A+B}{At}$ Hinckley (1963); (iv) $Q = \frac{FII}{FI + FII}$ - Range et al. (1969); (v) Δ (02, 11) - Gomes (1979); (vi) $(1\bar{3}1)\leftrightarrow(131)$ - Gomes (1979); (vii) SK (001) - Gomes

Table 2: XRD crystallinity indices

Crystallinity indices/ general requirements	$I(1\bar{1}0)/020$ Murray and Lyons (1956)	(001) Brindley and Kurtossy (1961)	$I_c = \frac{A+B}{A_t}$ Hinckley (1963)	$Q_F = \frac{F_{II}}{F_I + F_{II}}$ Range et al. (1969)
1	2	3	4	5
Significance	Provides good information about the O-D related with the layer stacking arrangement. Increasing disorder due to planar stacking faults localized at the layer planes as the result of layer random displacements, will be clearly shown up.	Random shifts between the structural layers can lead to a weakning of the interlayer bonding energies and consequently to an increase in the diffusiveness of the (001) reflections.	Give general representation or a general 3-dimensional picture of the O-D since in its evaluation structure atomic sequences of types (OkO), (hkO) and (hkl) participate in the index.	Random interlayer displacements, both in direction and amplitude will be shown up.
Reproducibility	Reasonable	Good in specimens with equivalent grain size and texture.	Reasonable	Good
Limitations	Applicable only to kaolinites with medium to good crystallinity where $(1\bar{1}0)$ reflection is clearly observed.	Almost nonexisting limitations.	Applicable to completely texture-free specimens. Not applicable to many poorly crystallized kaolinites where reflections $(1\bar{1}0)$ and (111) are weak or absent	Not applicable to highly disordered kaolinites.

Table 2 Contd.

1	2	3	4	5
Disturbances	Sensitive to the presence of other clay minerals, particularly illite and mica which would enhance the intensity of the (020) reflection.	Little disturbance by impurities. Chloride is the only known disturbing impurity.	Enhanced by impurities such as quartz, cristobalite, gibsite, goethite and dickite. Reduced by impurities such as micas, chlorites and smectites.	Impurities such as quartz, cristobalite, and goethite can interfere.
Range of variability	Appreciable 1-well crystallized. 0.7 - 1-medium crystallized. 0.7-poorly crystallized.	Appreciable	Large range variability, from 0 up to values just over 1. 0.9-1.2-well crystallized. 0.5-0.9-medium crystallized. 0.5-poorly crystallized.	Appreciable
Sensitivity to specimen preparation procedure and analytical equipment performance conditions	Texture effect is not important since planes $(\bar{1}10)$ and (020) that are nearly to (001) planes are equally influenced.	Affected by crystal size, particularly when 0.1 um.	Very sensitive to specimen texture. Applicable only to completely texture free specimens.	Applicable only to texture-free specimens.

Table 2 Contd.

(02.11) Gomes (1979)	$(1\bar{1}1)$ (111) Gomes (1979)	SK (001) Gomes (1979)	$\mathrm{HYD} = \frac{I_K}{I_K + (I_{K+H})^{/8}}$ Ichoubar et al. (1982)
6	7	8	9
Measures the extent of the layer stacking disorder parallel to the layer plane. It can provide crystallinity differentiations among highly disordered kaolinites.	Denotes the general organization of the structure. Gives an indication of the symmetry of the unit-cell. The magnitude of the resolution $(1\bar{1}1)$ (111) can be considered as a triclinicity index.	Denotes irregularities in the layer stacking arrangement to the layer plane due to random interstratifications of kaolinite layers with layer sequences typical of other clay minerals and to layer distortions.	Provides good information about defects that impede the intercalation to the hydrazine hydrate. Interlayer cations, interstratified layers, atomic isomorphous substitution and distortions of the layers are examples of those defects.
Good	Good	Good reproducibility in specimens with equivalent texture.	Good in specimens where intercalation attains its maximum ability.
Applicable only to highly disordered kaolinites	Applicable to kaolinites with various types and degrees of disorders.	As for index (001)	Intercalation is complete or almost complete in highly ordered kaolinites. Intercalation becomes more difficult and incomplete with increasing defectiveness.

Table 2 Contd.

6	7	8	9
Cristobalite and goethite impurities may interfere.	In specimens with mica and/or illite impurities the line (131) may make resolution estimations difficult.	As for index (001).	Impurities such as mica, illite and chlorite can interfere.
Limited but appreciable range of variability. Values ranging from 0.20° (2θ)up to 0.45° (2θ)	Appreciable. Values ranging from 0.45° (2θ) up to 0.94° (2θ) 0.8-0.95-well crystallized. 0.6-0.8-medium crystallized. 0.6-poorly crystallized.	Appreciable. Values close to 1 for low defective kaolinite s. Values increasingly different from 1 for more defective kaolinites.	Appreciable. Decreases with increasing defectiveness.
Applicable only to texture-free specimens.	Applicable only to texture-free specimens.	Sensitive to specimen grain size and texture.	Sensitive to specimen grain size and dryness.

(1979); (viii) HYD = $\frac{IK}{IK + (IK+h)/8}$ - Tchoubar ét al. (1982).

A method based itself on the comparison of experimental diffraction patterns with calculated X-ray diffraction profiles using a model of the defect structure (including types of defects and abundance) was performed by Plancon and Tchoubar (1977). Moreover for the easy calculation, Plancon and Zacharia (1990) have recently proposed an approach using an expert system which runs on a PC or compatible, and accurately describe the defect structure of kaolinite based on a few measurements taken from a normal powder diffraction profile. However, these last methods work well with high kaolinite content samples but cannot be used as routinely in systematic studies. So, even taking into account the fact that crystallinity parameters are, until now, lacking in precision and highly limited (sample impurities, particle size, sample preparation for analysis, non-reproducible data) (Gomes, 1987), these methods can inform us about relative crystallinity variations within a group of samples, which could have a genetic interest for basic analysis and could also be related to the kaolin's industrial properties.

X-ray diffraction patterns of the -350 fraction of samples were obtained using unoriented mounts. They were made with a Philips X-ray diffractometer, using Ni-filtered CuKα radiation, from 5^{o} to 60^{o} at a scan rate of 1^{o} θ/min. Fig. 2 shows the X-ray diffraction patterns of plastic clays and their mineralogical contents.

The crystallinity indices were determined by taking into consideration the intensities of $11\bar{1}$, $1\bar{1}0$ and 020 reflections (Fig. 3) (Hinckley,

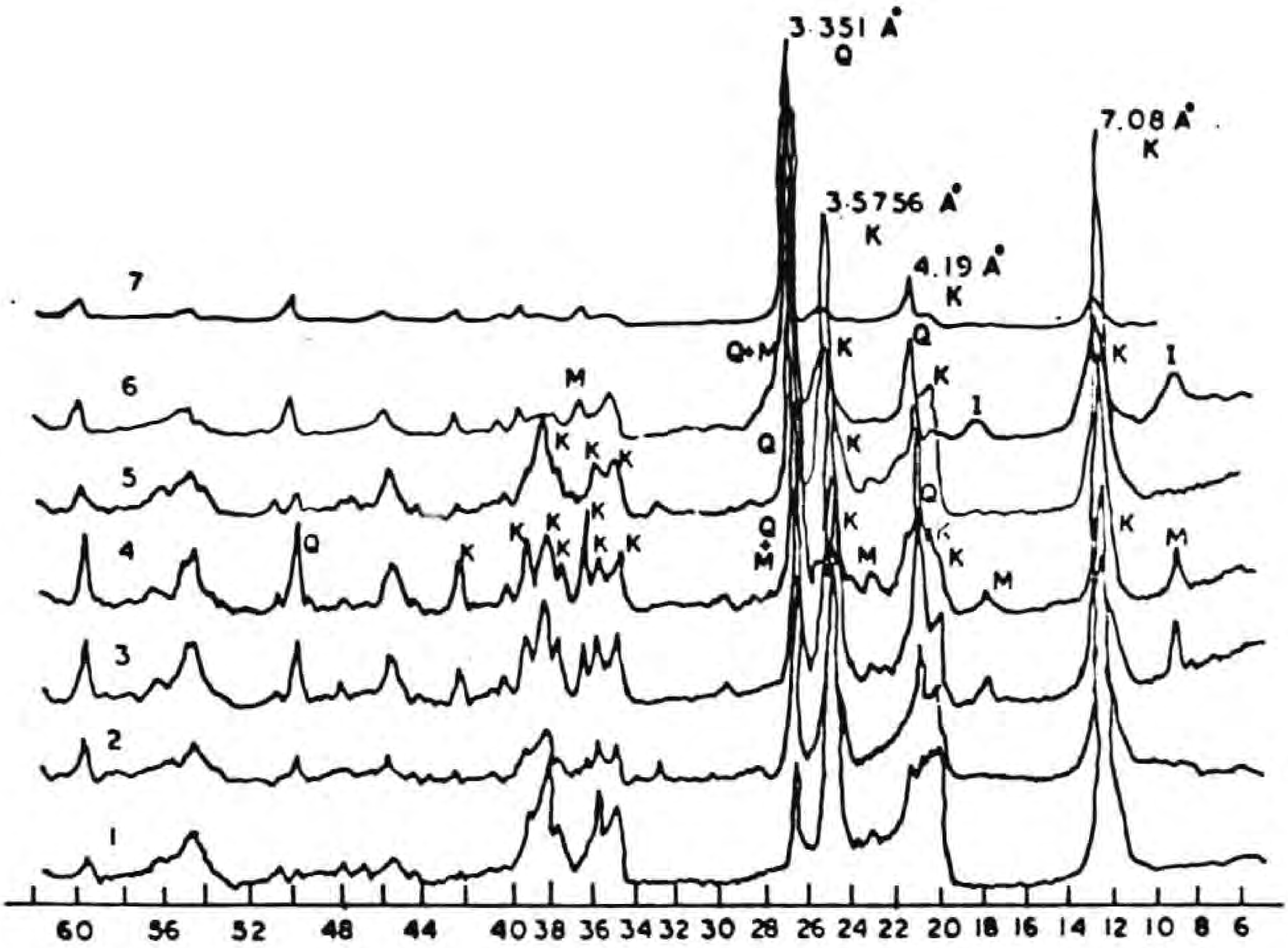


Fig. 2. X-ray diffraction patterns of plastic clays

1. PADAPPAKARA 2 PAYYANGADI, 3 BIKANEER, 4 BIMADOLE, 5 THAN, 6 WESTERWALD 7 INAGAKI - KIBUSHI

K - Kaolinite, M- Mica, I-Illite, Q - Quartz

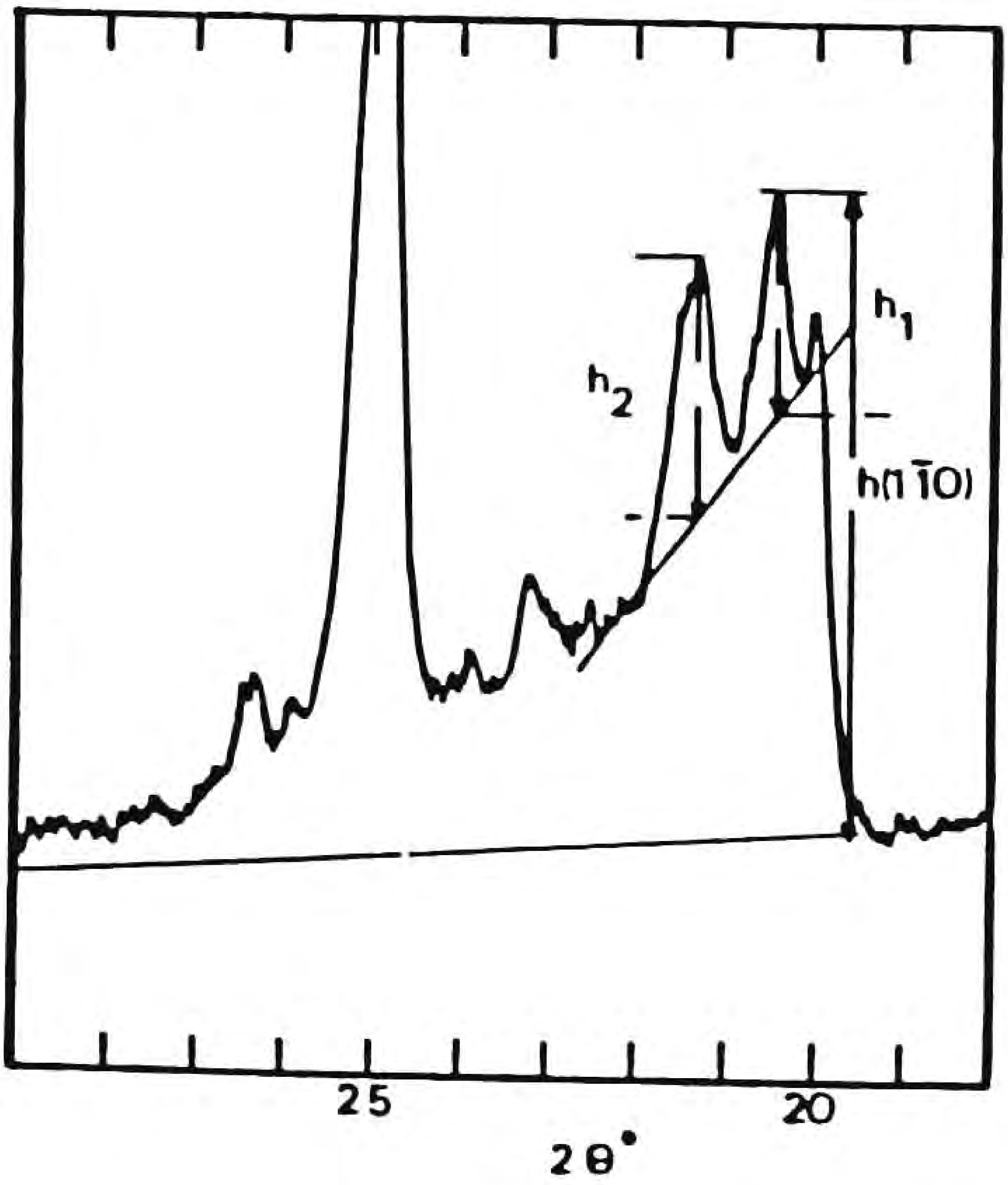


Fig. 3: Hinckley index determination

1963). The results are given in Table 3. In 1988, Plancon et al. found that combined interlayer translations and admixed dickite layers failed to model the observed (01, 11) XRD band pattern, i.e. the Hinckley index accurately. However, X-ray diffraction crystallinity indices in kaolinites essentially measure the clarity of the closely spaced 020, $11\bar{1}$ (021, $11\bar{1}$) diffractions. According to Hinckley, the heights of $1\bar{1}0$, $11\bar{1}$ diffraction peaks are measured above the local background drawn through the minima between these peaks which are not true peak intensities (h1 and h2). The true height of $1\bar{1}0$ peak (h) is measured above the true background i.e. the base line. Then the crystallinity index is taken as $(h1 + h2)/h(1\bar{1}0)$.

Table 3: Lattice parameters of the kaolinites in ball clays - In the order of decreasing crystallinity

Sample	a A^{o}	b A^{o}	c A^{o}	α	β	γ
D	5.15	8.997	7.426	91.93	104.49	90.21
B	5.19	8.892	7.408	92.0	104.09	90.26
G	5.188	8.883	7.379	92.11	104.22	90.21
C	5.24	8.857	7.361	91.54	104.76	90.86
F	5.147	8.84	7.429	91.96	104.22	89.38
E	5.21	8.97	7.40	92.91	104.42	90.25
A	5.18	8.90	7.38	90.0	104.70	89.88

3.4.2 Computation of cell parameters

The development of X-ray diffraction and other techniques in comparatively recent times has revealed that the majority of solids are crystalline, the principal exceptions being glasses and gels.

The solid crystals are composed of a regular array of atoms called a lattice which contains a definite pattern repeated throughout in a systematic manner. This repeat pattern is turned out to be a unit cell and its three dimensional parameters as cell parameters.

The cell or lattice parameters were computed from the XRD data using the least square refinement technique. PC version of the computer programme LCLSQ was used for this. The test/cell parameters were taken from the data on kaolinite (Brindley, 1980).

3.5 PARTICLE SIZE, CATION EXCHANGE CAPACITY AND MORPHOLOGY - OTHER RELATED PROPERTIES

3.5.1 Particle size distribution

Particle size analysis curves generally plot the weight percentage of a sample finer than given values in terms of equivalent spherical diameters of particles. The analysis was carried out by sedigraphic method using the Micromeritics particle size analyser model D-5000. To obtain a single number that represents the distribution of sizes, the total percentage of fine fractions $< 2\ \mu$ was taken for each sample. Fig. 4 indicates the particle size distribution. Sample A was found to have the maximum percentage of fine particles. The particle size $< 2\ \mu$ of A, B, C, D, E, F and G are 89, 64, 76, 61,

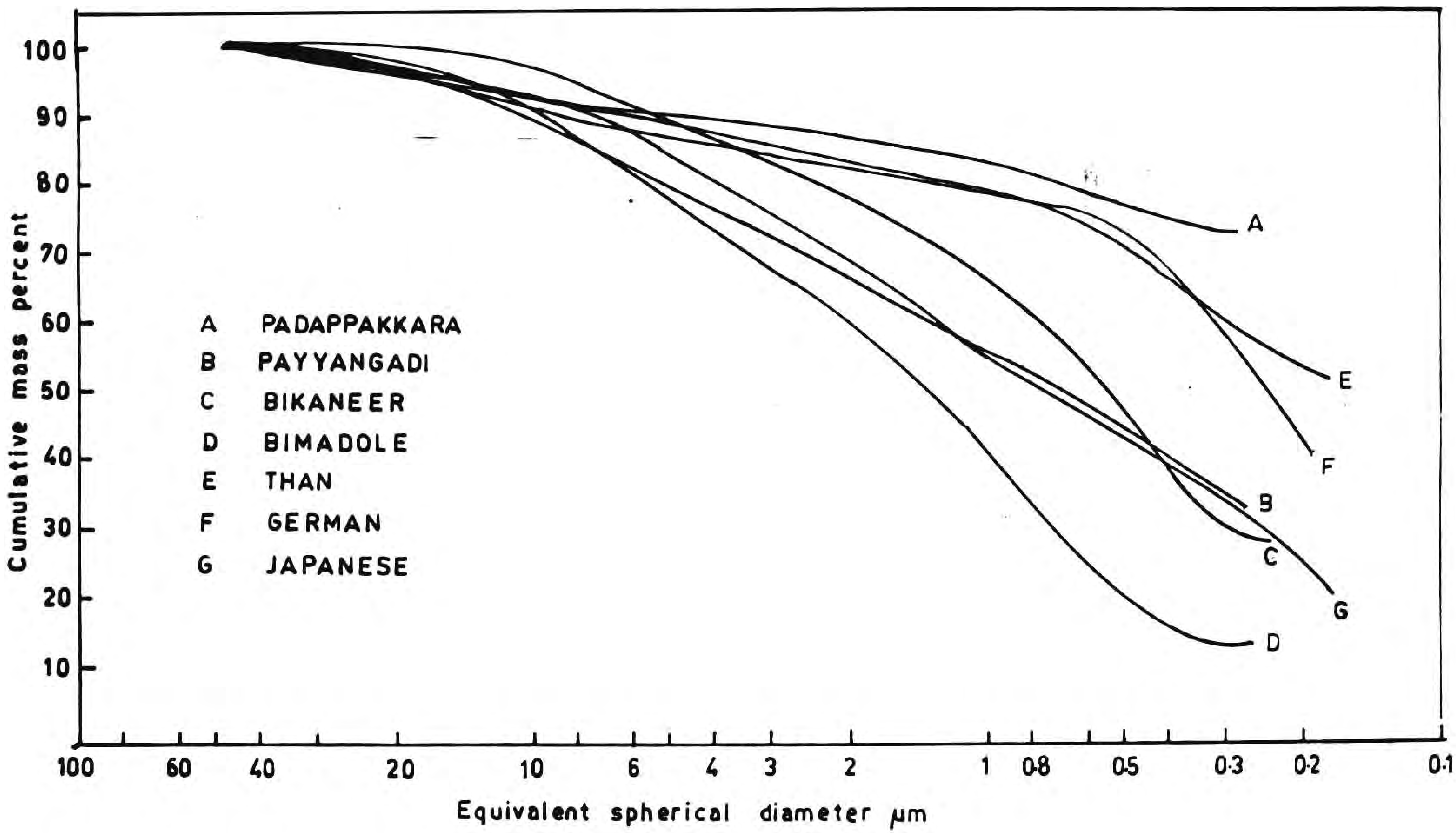


Fig.4 Particle size distribution

Table 4: Crystallinity indices (CI) and other related properties - (In the order of decreasing CI)

Sample	XRD CI	IR CI	Particle size ($< 2\mu$)	CEC (meq/100 gm)
D	0.97	0.833	61	8
B	0.75	0.67	64	8
G	0.75	0.65	68	9
C	0.69	0.58	76	8
F	0.66	0.56	82	9
E	0.59	0.55	82	12
A	0.5	0.343	89	10

82, 82 and 68 respectively. The Bimadole clay was found to have the lowest percentage of fines.

3.5.2 Cation exchange capacity (CEC)

Cation exchange capacities of all the kaolinite samples were determined using NH_4^+ as the exchangeable cation. With the exception of sample E, the cation exchange capacities of the kaolinites are in the range 8-10 meq/100 g. There can be noted a more or less increase in the value of CEC if samples G and E are avoided with the decrease in Hinckley indices.

3.5.3 Morphology by SEM

Morphology of the samples were studied by scanning electron microscopy (SEM). $< 1\ \mu$ fraction of the samples were dispersed in water and SEMs were taken at different magnifications in order to get the maximum possible clarity. Since Georgia kaolins are well known for its large range variation in crystallinity and morphology (Lambardi et al, 1987 and Brindley et al. 1986), they were taken as a standard for the comparison in morphology, namely the well crystallised kaolinite sample from Washington county (KGaI) and the poorly crystallised kaolinite sample from Warren county (KGa2). From the micrographs it can be seen that the grain size and shape of the samples from Bimadole (D) and Payyangadi (B) resemble the most with those of the well crystallised kaolinite whereas the sample from Padappakkara (A) is the least which has the lowest crystallinity index value.

3.6 SUMMARY

The estimation of crystallinity indices determined by room-temperature IR spectroscopy indicated that the degree of disorder varies with the changes in the amount of isomorphous substitutions in octahedral layer. However from the Table 4 it can be seen that there is a linear relationship existing between the IR and XRD crystallinity indices. Eventhough Hinckley index cannot work for combined interlayer translations and admixed dickite layers, the present study with comparatively well crystallised kaolinites shows that this index may have some practical value in comparing kaolinites. From the lattice parameter computations it can be seen that the Padappakkara (A) has got more or less a monoclinic (α = 90, $\gamma \approx 90$) crystal structure whereas all others can be included in the triclinic system. Hence as far as the mineral contents of ball clay from Padappakkara is concerned, it is more appropriate to say that the major mineral in this sample is dickite rather than it is called as a kaolinitic one. The relation between the crystallinity and industrial application of the kaolinite are discussed in detail in the last chapter.

Another observation is the decrease of crystallinity index with the increase in the percentage of fine particles. This indicates that crystal size and texture can affect crystallinity index so that any comparative studies should be carried out in specimens with equivalent purity, crystal size and crystal orientation. As the cation exchange capacity increases the amount of substitutions also increase which will cause variations in the crystallinity index.

Fig. 5: Scanning electron micrographs of the fine fractions ($<1\,\mu m$)

Fig. 5.1: Padappakkara, A

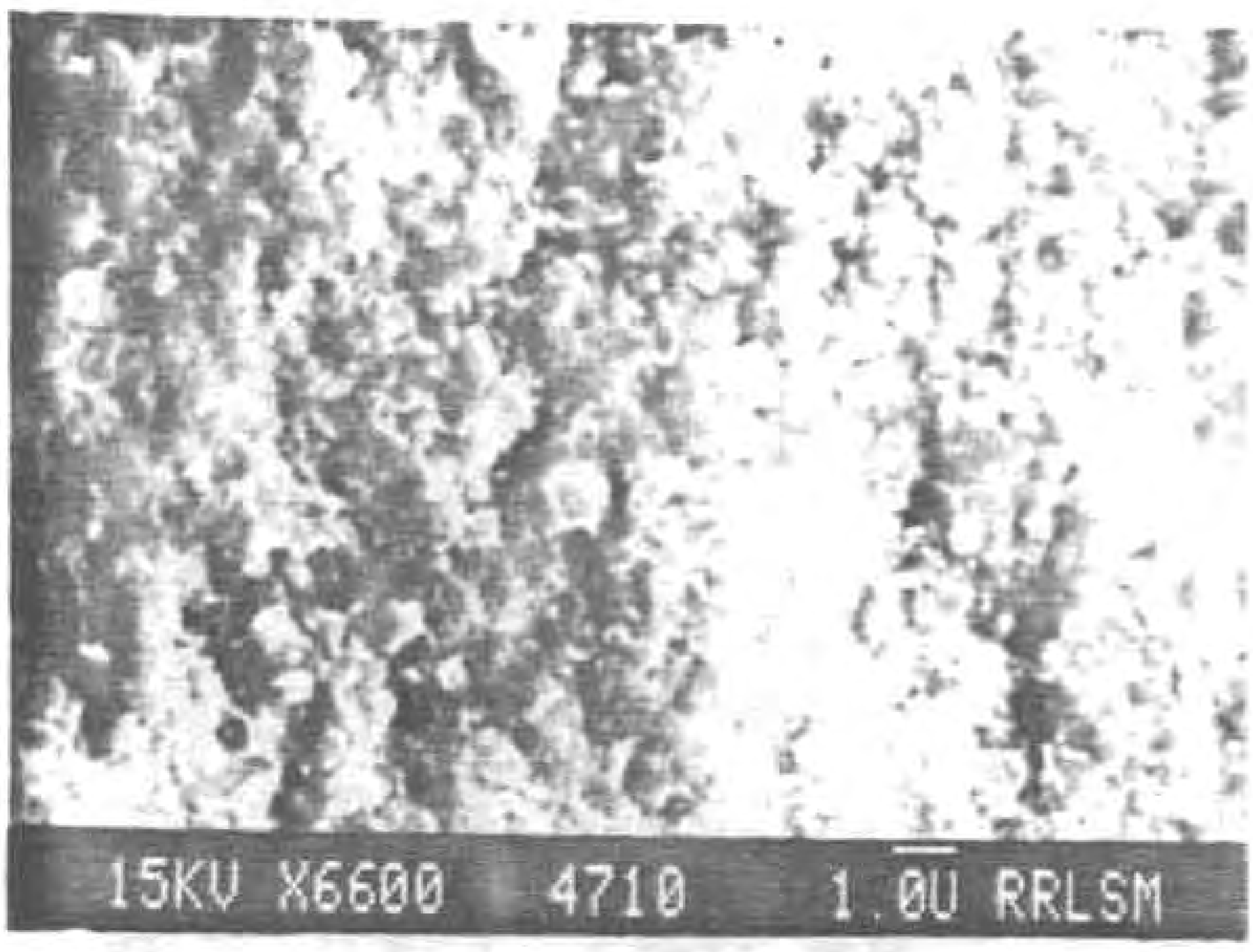


Fig. 5.2: Payyangadi, B

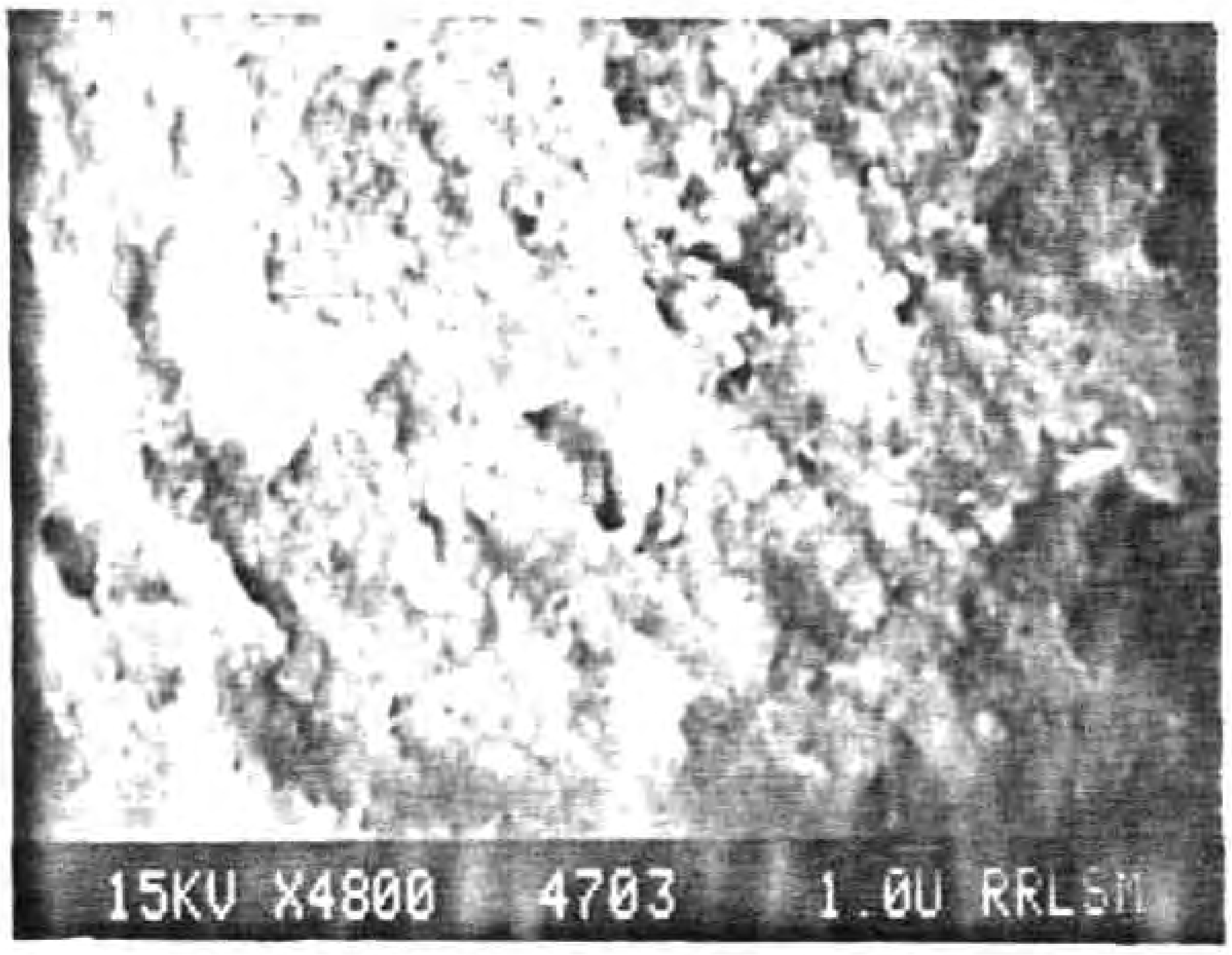


Fig. 5.3: Bikaneer, C

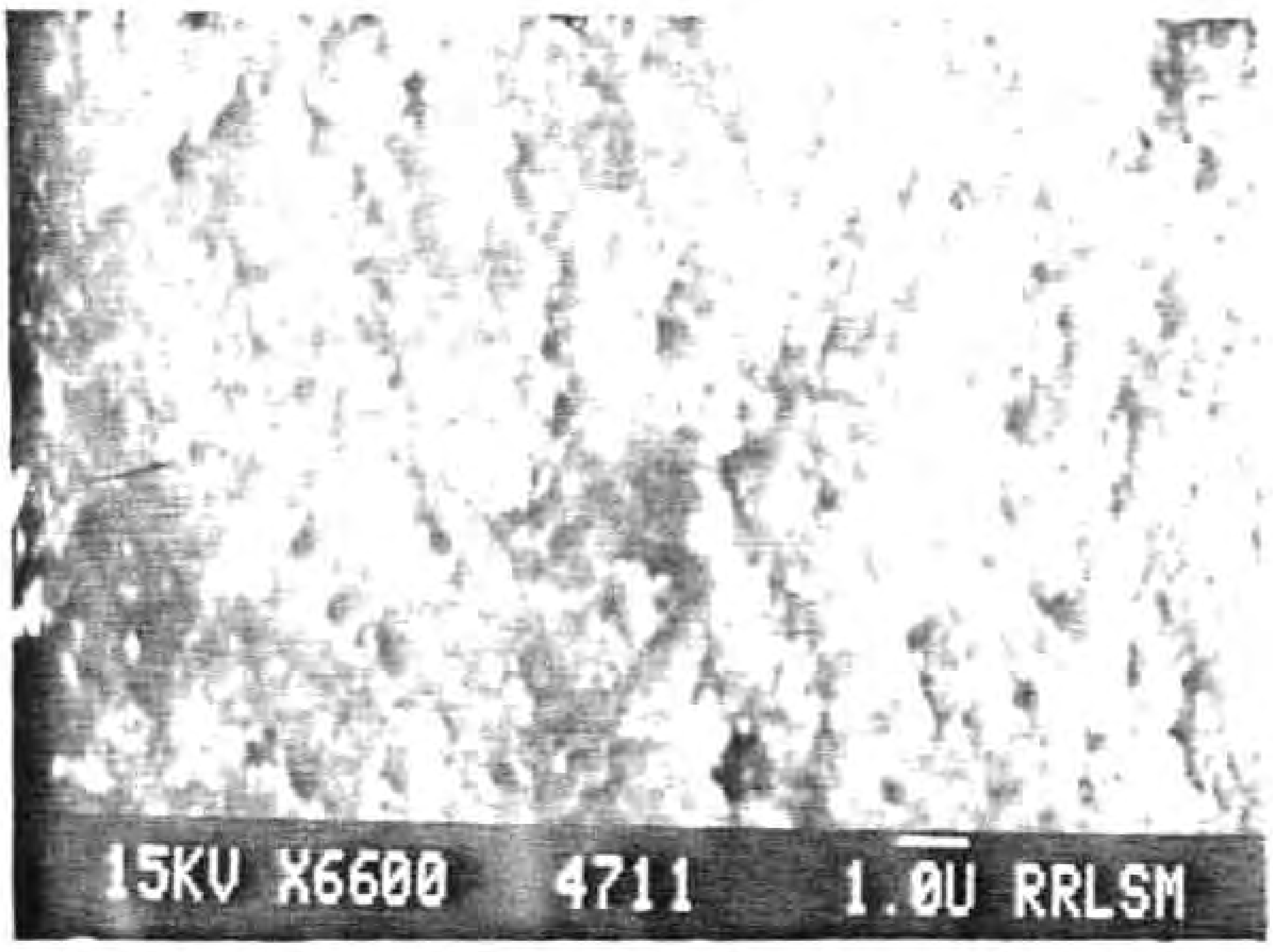


Fig. 5.4: Bimadole, D

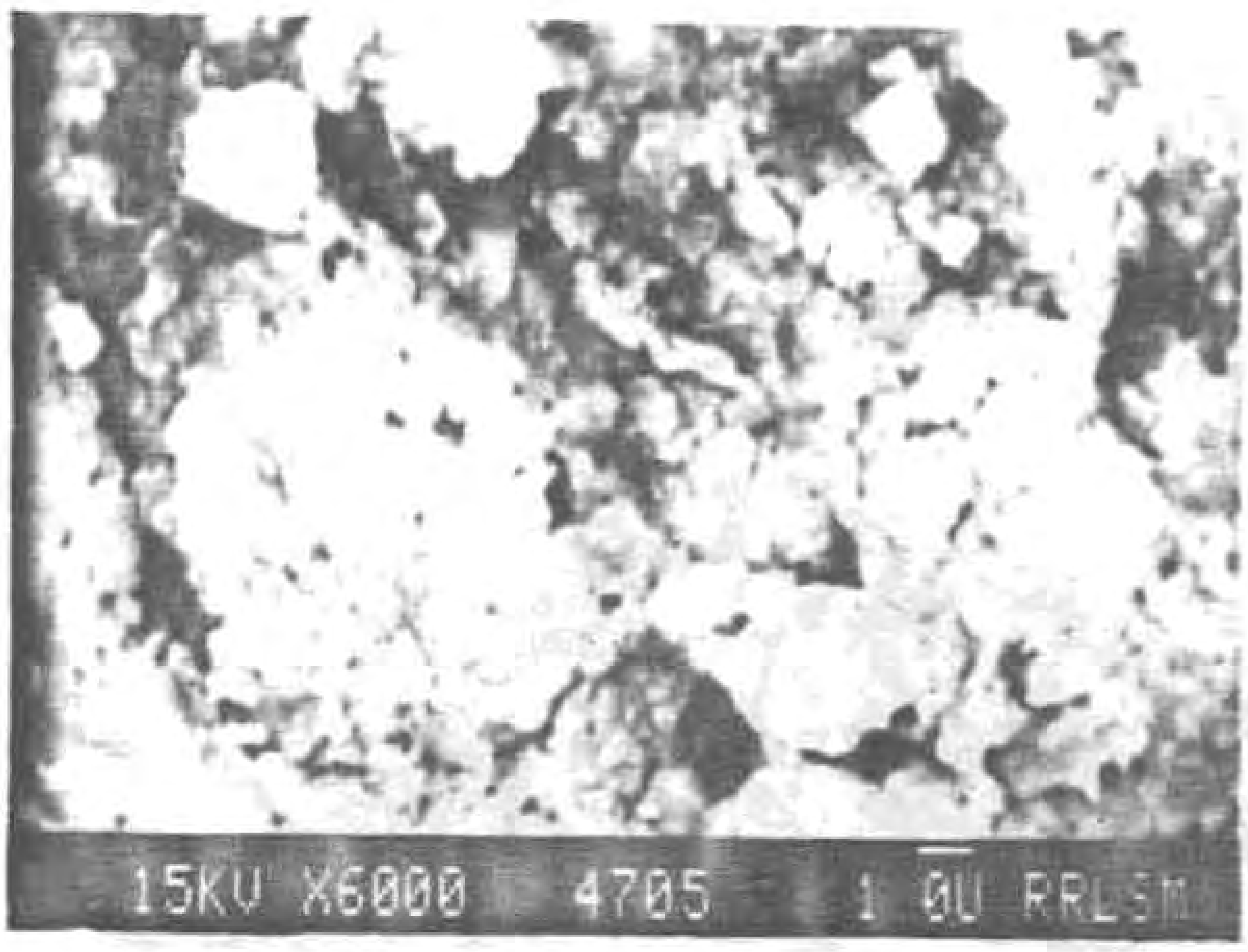


Fig. 5.5: Than, E

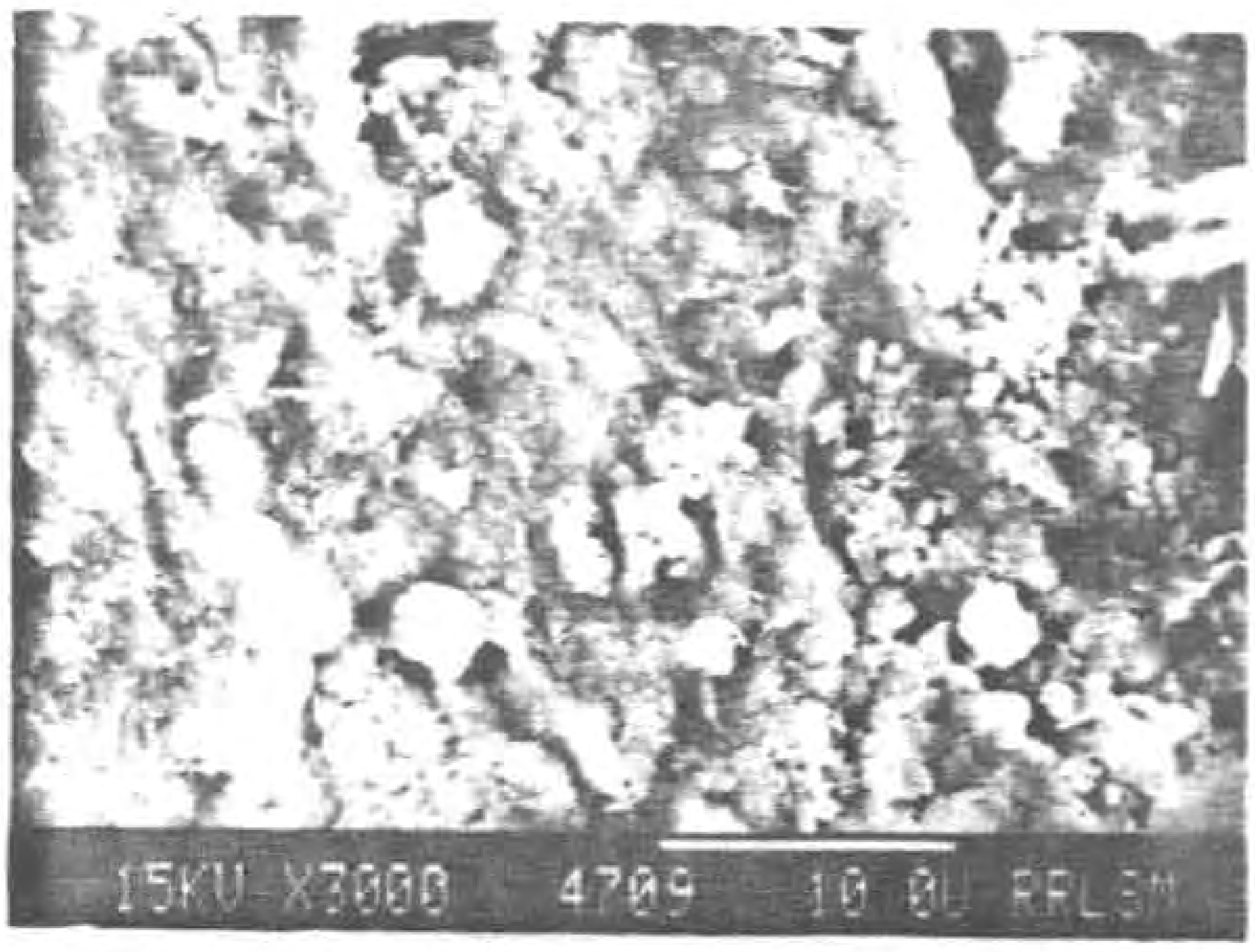


Fig. 5.6: Westerwald, F

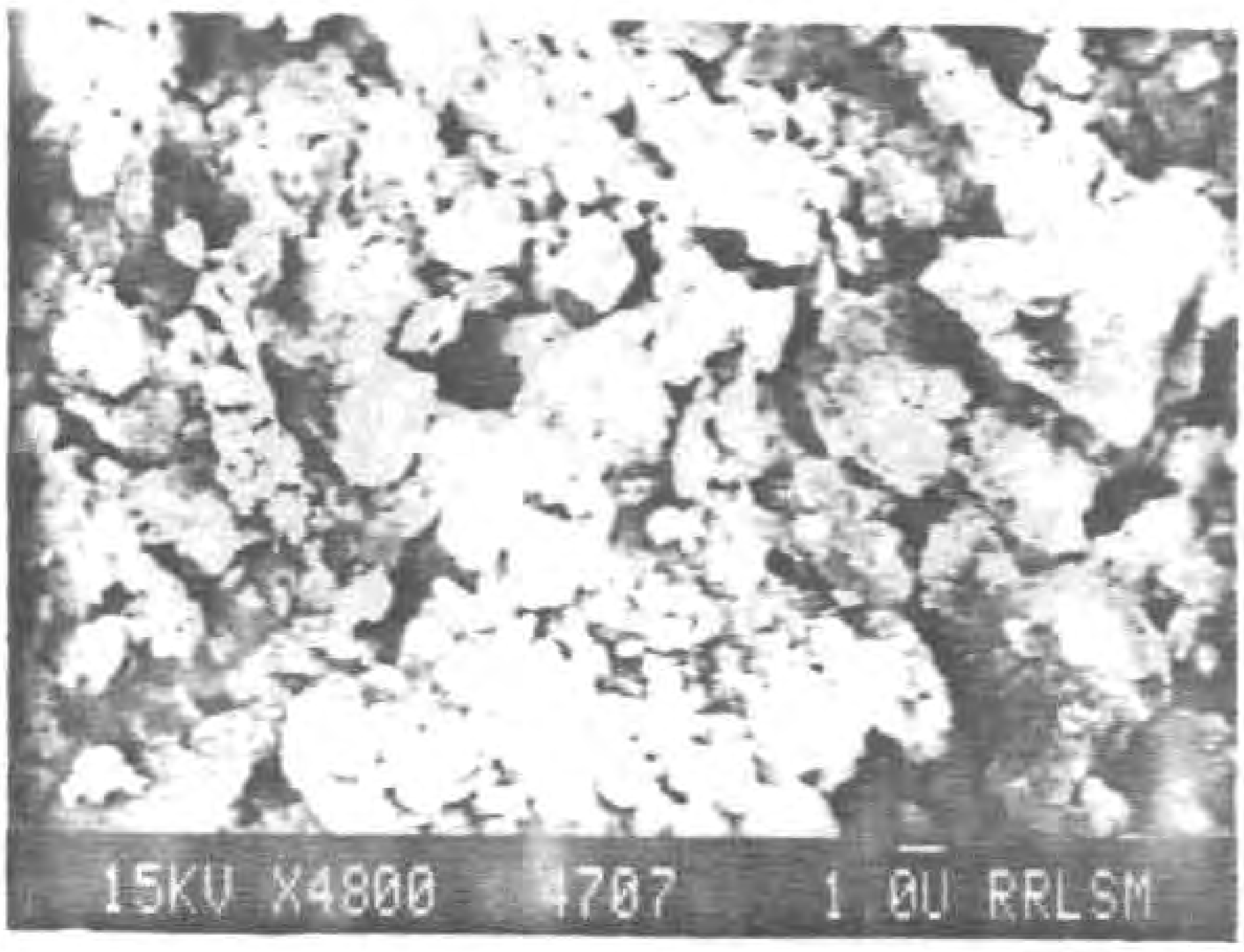


Fig. 5.7: Inagaki-kibushi, G

Fig. 6: Scanning electron micrographs of the standard samples

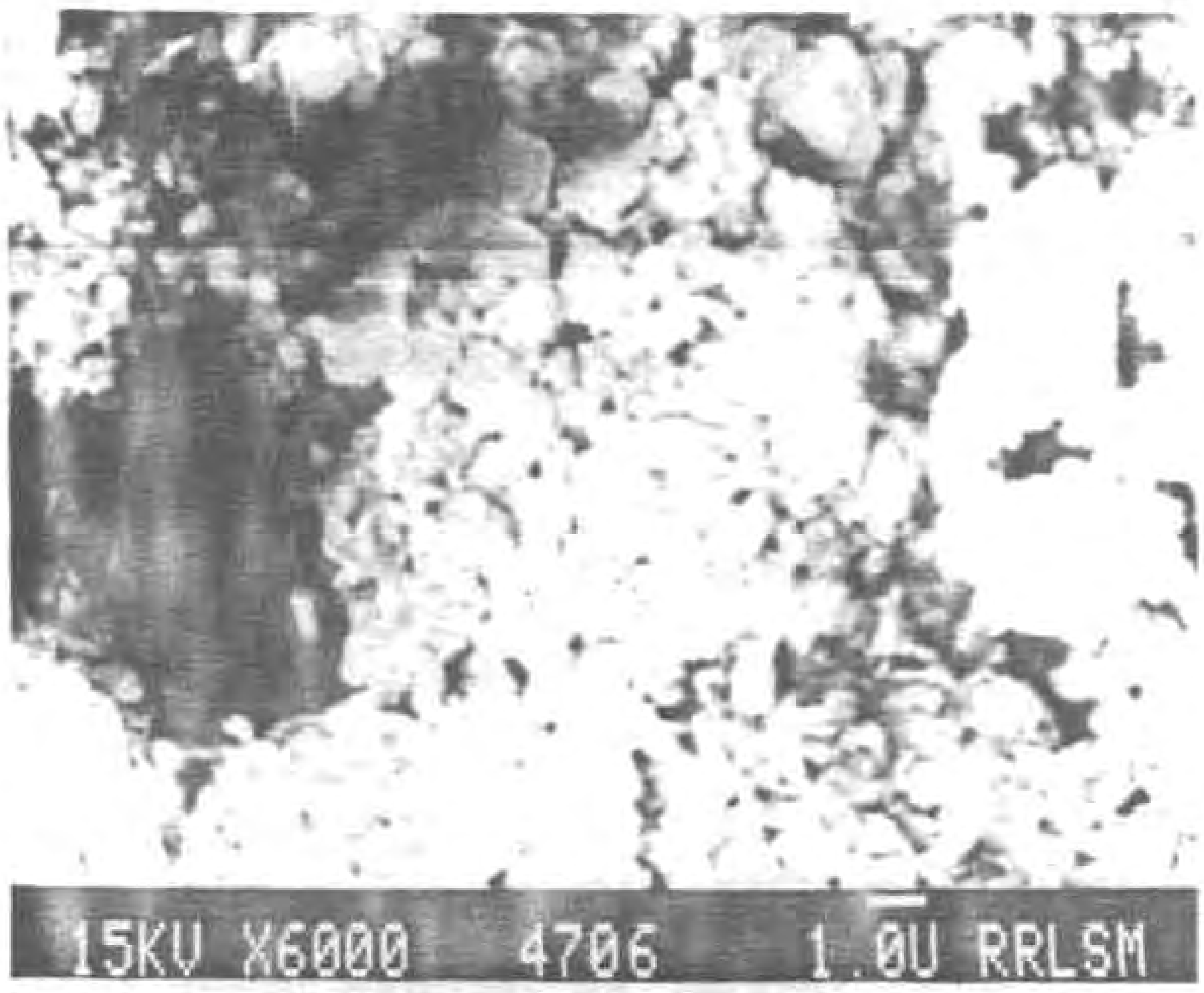


Fig. 6.1: Well crystallised KGa-1
Washington County, Georgia

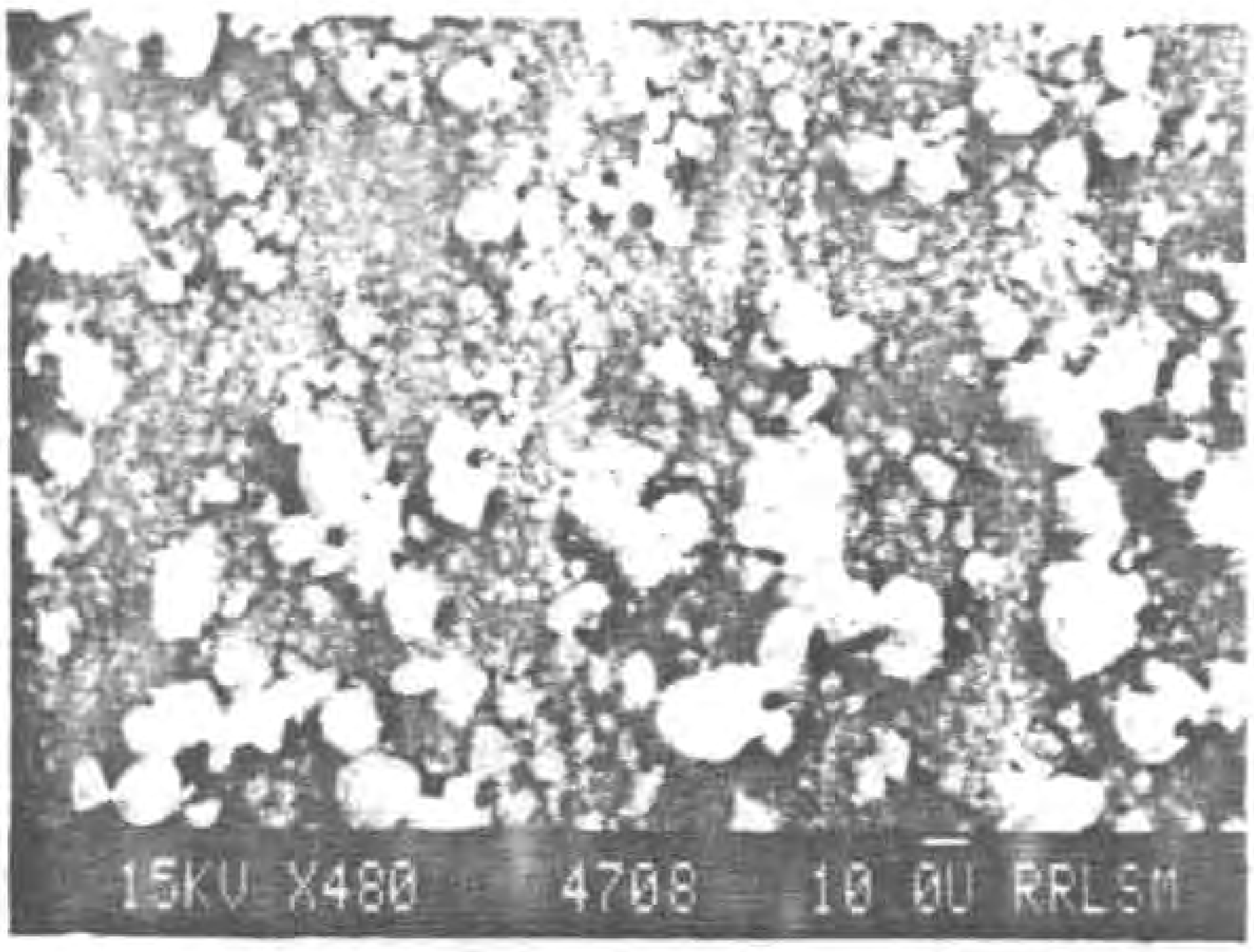


Fig. 6.2: Poorly crystallised KGa-2
Warren County, Georgia

CHAPTER IV

PLASTICITY OF BALL CLAYS

4.1 GENERAL

As far as the properties of clays are concerned, plasticity deserves an important position since it is very much relevant in the stage of shape retention of clay articles. It is a characteristic of clay that when mixed homogeneously with water in suitable propertions, it becomes capable of being moulded in any desired shape and retains that shape when the moulding stress is removed. The properties of mouldability and possibility to take part in high temperature reactions have made clay a basic material for ceramic industry.

Many materials are plastic but clays are unique in the fact that their plasticity is destroyed, though their new shape is retained, by removing the water content. Hence water is found essential for the property of plasticity. It is generally accepted that plasticity is associated mainly with particles of colloidal size, therefore it is to be expected that it will be related to the fundamental concepts of colloidal micelle. When clay particles are suspended in water, each particle is surrounded by a hydrosphere within which are contained ions of different charges. Around the ultimate particle, there is a layer of negatively charged ions. These are balanced by a swarm of cations which are diffused through the hydrosphere. Thus the charge in the particle is counterbalanced by the cations and so causing a rigidity in linkage which is turned out to be plasticity. If the hydrosphere present is large, the particles are at maximum separation and free viscous flow is possible. If it is reduced, water film becomes less and more cohesive (Searle and Grimshaw, 1960).

4.2 THEORY OF PLASTICITY

The most widely accepted theory of ceramic clay plasticity is the so called "stretched membrane theory" (Macey, 1940 and Norton, 1948). Acoding to Janny (1982), an isotropic stress from capillarity was necessary to impart plasticity to clay. Alternate sources of isotropic stress include externally applied stress and van der Walls bonding.

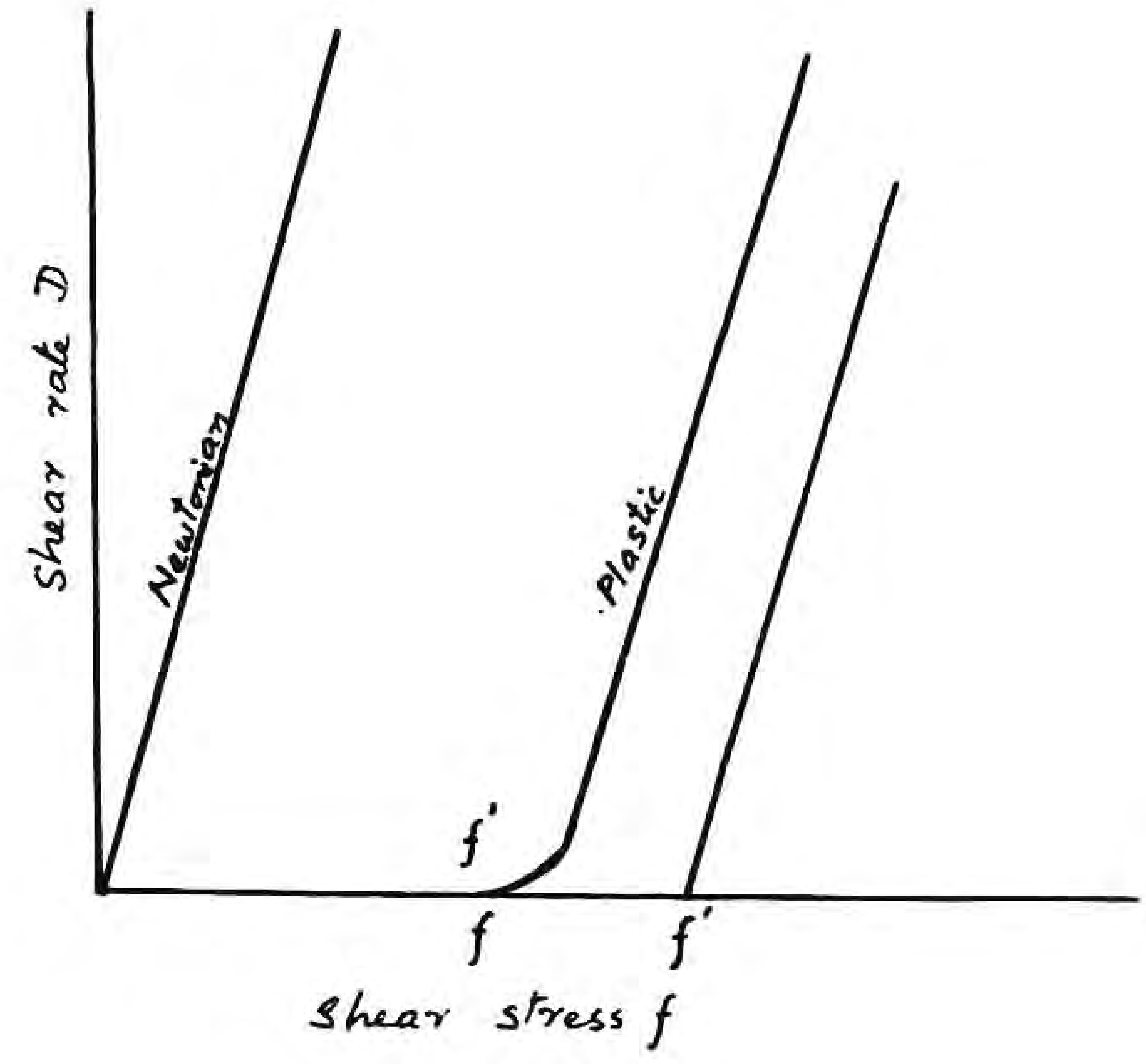
Pure liquids such as water, alcohols, glycerine etc. at constant temperature obey Newton's law of viscous flow. In abbreviated form it may be written as

$$f = \eta D \qquad \text{--------(1)}$$

where f - shear stress, η - coefficient of viscosity and D - shear rate.

If a graph is plotted with shear stress against shear rate, a straight line with gradient $1/\eta$ is obtained. But in the case of suspension the graph will be a curve either concave or convex. Their flow can be considered as non-Newtonian flow.

A plastic type of flow curve is given by the majority of clay-water suspensions and pastes in the flocculated states.



An important characteristic of curve is that it does not pass through the origin but intersects the stress at a point f. This means that a definite minimum stress called the yield stress or yield value, f has to be applied before the system begins to flow.

Occasionally a system gives a stress-shear graph that is linear but still shows a yield value. In this case the relationship between f and D may be explained by Bingham's law

$$f - f' = \eta_o D \qquad (2)$$

where f' is the yield value and η_o is a constant, absolute viscosity. Though not exactly, many clay suspensions obey Bingham's law approximate closely to it, only deviating at low shear rates. The above equation can be written in an alternative form

$$f = \eta_0 D + f'$$

$$f/D = \eta_0 + f'/D$$

$$\eta = \eta_0 + f'/D$$

Plastic flow has also been described by equations of type

$$f^n = k \cdot D$$

where n and k are constants.

If the pressure-flow curves of different clays are compared there can be seen certain striking differences. Since the relative plasticities are usually considered to be in order:

Montmorillonite clay $>$ ball clay $>$ fire clay $>$ china clay

It appears that high plasticity is characterised by a high yield value and a small degree of bottom curvature. Worrall has found that the flow curves of plastic clays generally obey the same empirical equation as suspensions

$$f - f' = \eta_0 D + g\, b \,.\, D/(a\, D + b)$$

a and b are coefficients of break down and build-up and g is another constant related to the degree of flocculation. Since the magnitude of the bottom curvature is given by $g\, b/a$ and the yield value is f', the ratio f'/(g b/a) is an indication of the degree of plasticity.

Table 1: Typical values of the ratio f'/(g b/a) for various clays

Clay	f'/(g b/a)
Ball clay (natural)	2.8
Na-ball clay	5.6
H-ball clay	3.33
Ca-ball clay	2.33
China clay	0.54
Fire clay	1.23
Montmorillonite	4.7

For attaining the proper plasticity of clay materials the water film between the particles should have a specific thickness. It is different for different clay samples (Table 2).

Table 2: Film thickness for clays to get maximum plasticity

Materials	film thickness (A^o)
China clay	2100
Ball clay	2400
Brick clay	3100
Bentonite	3400

(Measurement at pressure of 8 kg/cm^2 . Since if water separates two parallel plates at a distance of 2000 A^o apart, the force acting between them will be 8 kg/cm^2).

The more plastic a clay, the more water it can tolerate. This is the basis of the Atterberg plasticity index which is defined as the difference between liquid limit and plastic limit values.

There are several factors governing the Atterberg limits for clay. At the plastic limit, there is just sufficient water to form stable films and so the magnitude of plastic limit will depend on the specific surface area of the clay and to some extent the nature and amount of the exchangable cations. At the liquid limit, the water films have built up to their maximum thickness and therefore much of the water present is free water. This free water mechanically entrapped in this way depends on the ability of the clay particles to form links with one another. Hence Ca-kaolinites have higher liquid limits than Na-kaolinites. In addition, the entrapment of water will also depend on the particle size. The smaller the clay particles, the greater the efficiency of the entrapping network.

4.3 FACTORS AFFECTING PLASTICITY

a. Effect of water on the solid particles and colloidal phenomena connected with it.

b. Size of solid particles.

c. The composition of the solid particles.

d. The shape of the solid particle and the internal structure.

e. The aggregation of solid particles.

f. The surface area of the solid particles.

g. Presence of other materials which may have an influence on the properties of the particles.

h. The orientation of the particles in the mass.

i. The previous history of the material.

All these factors are briefly explained below under three major heads.

4.3.1 Effect of water content on plasticity

The maximum plasticity of clay is developed at a specific water content.

Table 3: Water required to develop maximum plasticity for various clays

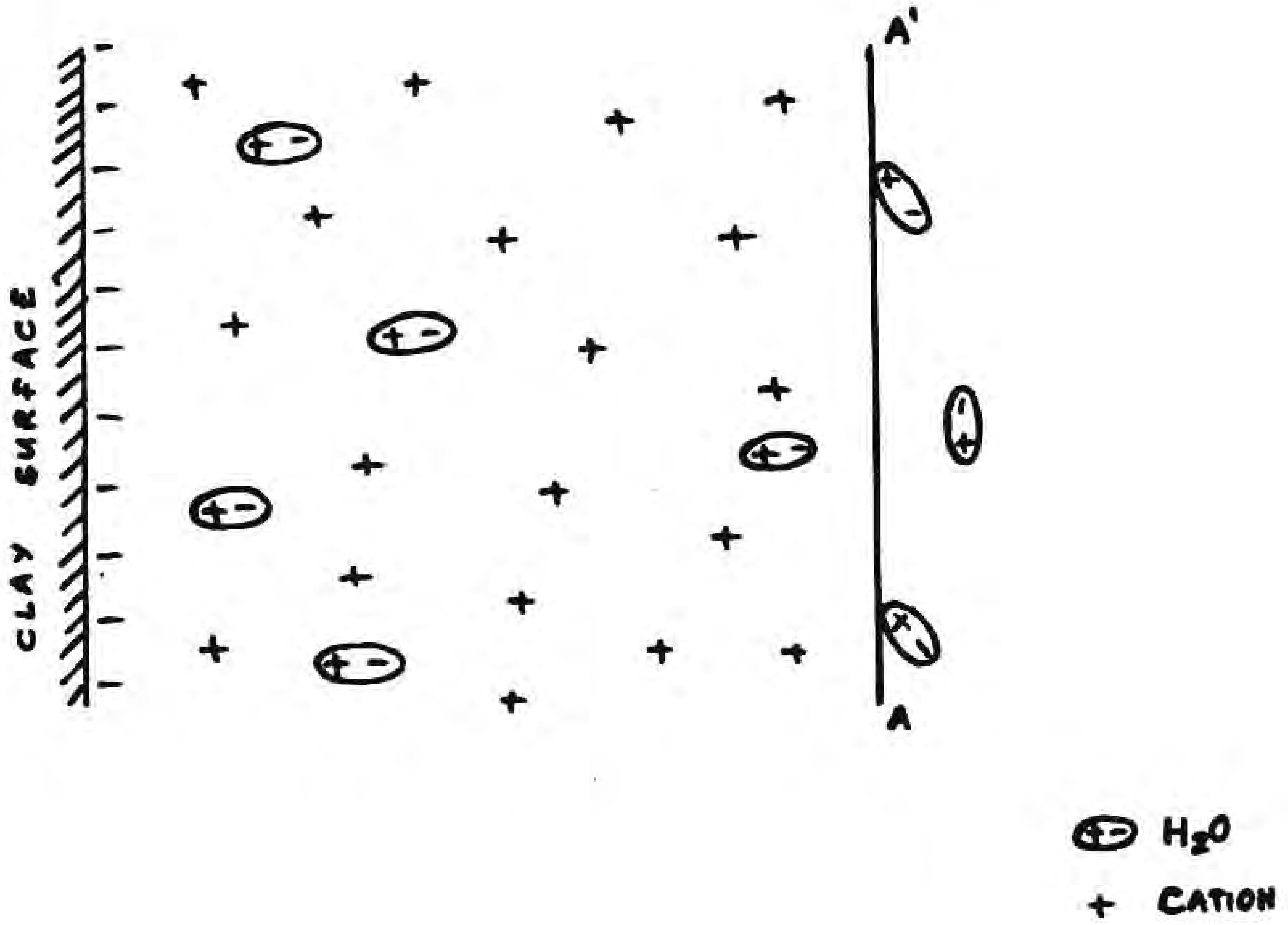
Material	Water content (%)
Brick clay	15-25
Fire clay	15-35
Shales	15-25
Pottery clay	15-50
Flint clays	15-24
China clays (kaolins)	18-50
Ball clays	25-50

The amount of water required to make a suitable paste is dependent to a large extent on the nature of the particles. The coarse particles will need less water than fine grained clays.

4.3.2 Colloidal phenomena associated with plasticity

Apart from adsorbing exchangable cations clay surfaces adsorb water molecules also. Because at the clay surface, the concentration of electrical charge is high and the water molecule itself is polar. The water molecules are uniformly oriented and rigidly held close to the surface of the clay. As the distance from the surface is increased, the degree of orientation and the rigidity with which water molecules are held decrease. The exchangable cations are also high in concentration near to the clay surface, the concentration falling off with increasing distance from the surface (Ryan, 1978 and Ryan and Radford, 1987) .

Fig. A: Adsorbed water molecules and exchangable cations in a clay-water system

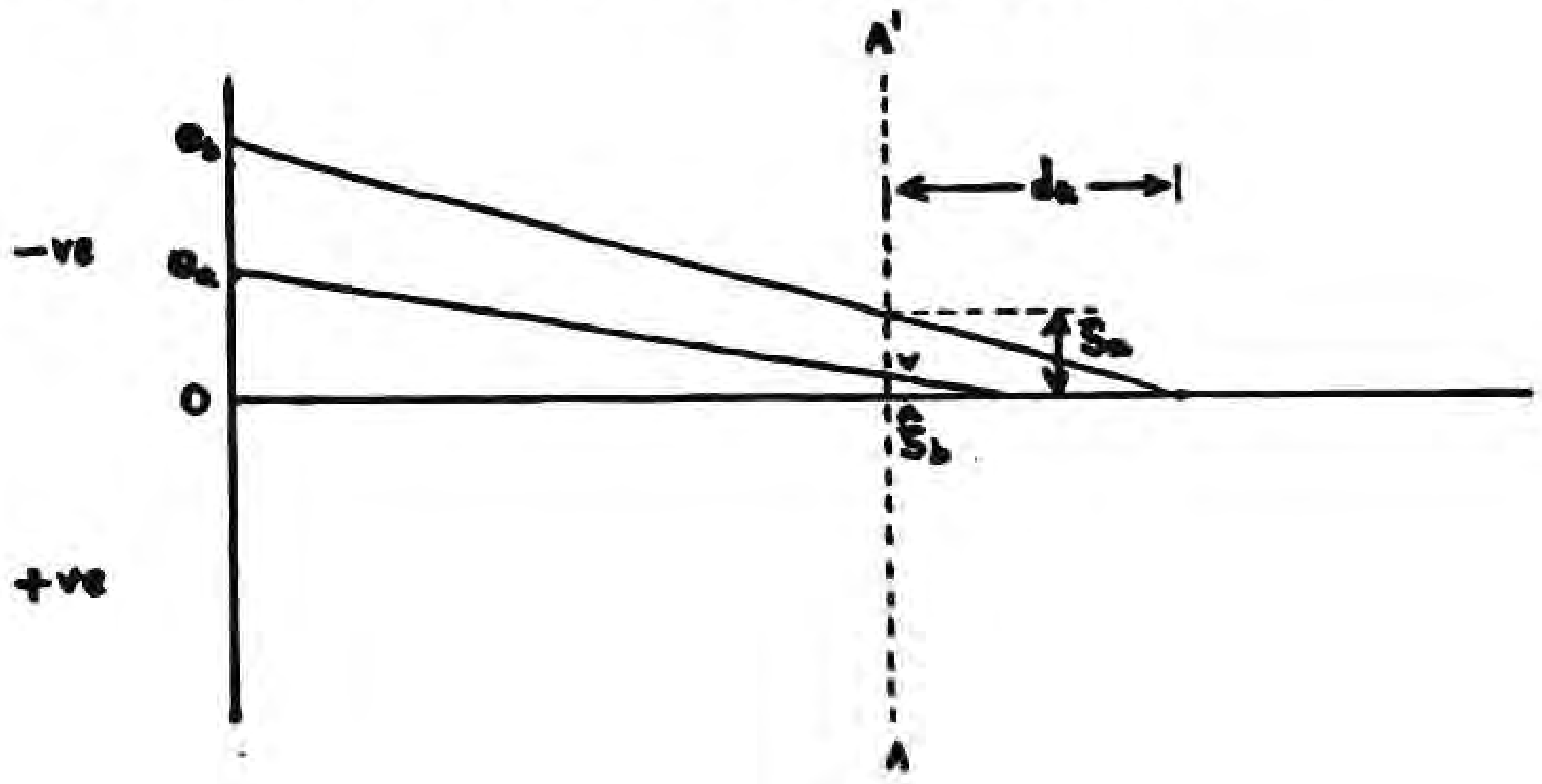


A-A' is the limit of the zone of rigidly held water molecules. At the clay surface the charge will be negative and at a small distance from the surface, the negative charge will be partly neutralised by the cations and as the distance increases the charge will become more and more reduced, and finally ceases to zero. For some materials the concentration of the cations in the zone of rigidly held water is sufficient to neutralise and reverse the surface charge. However, there also the charge will fall to zero in the free water zone.

The magnitude of the charge at the limit of the rigidly held water layer, i.e. A-A', is known as the electrokinetic or zeta potential (ζ) and it is the value of electrokinetic potential which largely determines whether particles will repel one another or floc together to form agglomerates i.e. it determines whether the suspension will be flocculated or deflocculated.

When the exchangable cation is highly electropositive, it ionises well and the zeta potential is high. When the exchangable cation is not so electropositive, ionisation is limited and the potential at the particle surface is comparatively small, and the charge is reduced to zero at a lesser distance from the surface.

Fig. B: Mathematical form of Zeta-potential



A mathematical form of zeta potential was expressed in 1934, as

$$\zeta = \frac{4\pi ed}{D}$$

ζ - zeta potential

e - is the surface density of charge on the particles

d - is the double layer thickness

D - is the dielectric constant of the liquid medium

4.3.3 Size and shape of solid particles

Size of grains has some effect as the plasticity of clay often be increased by finer grinding. At the same time, plasticity is not wholly due to the small size of particles because when a clay is decomposed by heat into silica and alumina, the resulting particles are smaller than the original grains and consequently should be more plastic when wetted, yet this is not the case.

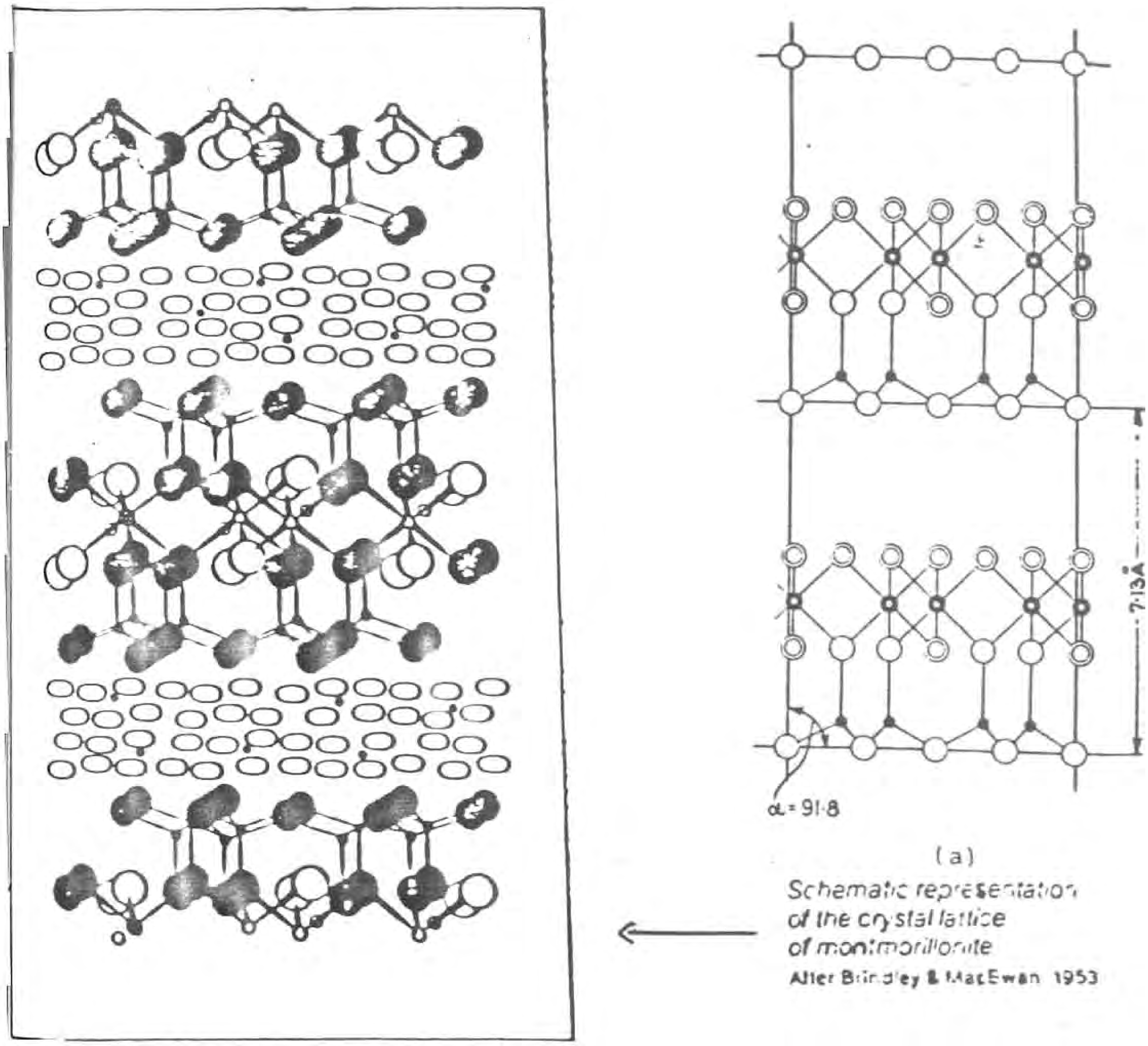
As well as size, the shape of the particles is also important. Clay particles are thin plates, hexagonal in shape. Because the clay particles are so small, the surface area is very great, and many of the atoms making up the clay structure are at the surface, i.e. they are joined to other atoms only on one side unlike atoms in the interior which are joined to other atoms on all sides. To satisfy their unbalanced charge the surface atoms attract water molecules to the surface of the clay, with the result that the clay acquires a layer of adsorbed water at the surface of its particles. This adsorbed water can lubricate the movement of one clay plate over another, and thus aid the deformation of a clay mass and promote plasticity.

The shape of the ultimate solid particle and their internal structure are also important. The two major clay mineral groups are kaolinites and montmorillonites.

The structure of the kaolin minerals is based on the condensation of two layer structures, viz. silica layer, composed of silicon and oxygen atoms and the gibbsite layer, made up of aluminium atoms and hydroxyl groups. Each silicon atom is surrounded by four oxygen atoms, the oxygens being at the corners of a regular tetrahedron. Three of these four oxygen in every tetrahedran are now valency satisfied receiving one valency electron from each of two silicons to which they are linked. The fourth oxygen in each tetrahedron is joined to only one silicon, and so has one valency unsatisfied. It is through this valency unsatisfied oxygens that the silica layer can join via cations to similar structures. Thus the basic formula for the sheet structure therefore $(Al_2(OH)_4^{2+} \quad Si_2O_5\}^{2-}$. Each unit in the gibbsite layer consists of a central aluminium atom surrounded by six hydroxyl groups in a regular octahedral structure. Since every OH group receives half a valency share from two trivalent aluminiums, the hydroxyl groups are all valency satisfied in the layer. The dimensions of the hexagonal rings in the silica and gibbsite sheets are very similar and it is possible for the two sheets to condense together.

In montmorillonites, the central layer is gibbsite and the condensation of silica layers on each side of it leads to the formula

$$Al_2(Si_2O_5)_2 \cdot (OH)_2$$



(a)

Schematic representation of the crystal lattice of montmorillonite

After Brindley & MacEwan 1953

(b)

● silicium (Si)

○ aluminium (Al)

• calcium (Ca)

● oxygen (O)

◯ hydroxy groups (OH)

⬭ water molecules (H_2O)

Structure of clay minerals
(a) Kaulinite, (b) montmorillonite

4.3.4 Cation exchange reactions

When a clay sample is placed in a solution of a given electrolyte, an exchange occurs between the ions of the clay and those of the electrolytes (Ryan, 1978).

$$\text{X-clay} + Y^{+} \rightleftharpoons \text{Y-clay} + X^{+}$$

This cation exchange capacity (CEC) varies from one ion to another and is given by the lyotropic or Hofmeister series.

$$H > Al > Ba > Sr > Ca > Mg > NH_4 > K > Na > Li$$

In the kaolinite minerals, the oxygen and hydroxyl valencies at the planar surface of the structure are completely satisfied. But at the edges, cations such as Al, O, Si and hydroxyl groups are not satisfied. These valencies are satisfied by external ions preserving electrical neutrality. These additional cations are capable of being exchanged and probably account for the greater part of the CE occurs in disordered kaolinites. Another possible cause is the ionisation of basal hydroxyl group to produce a -ve charge. Thus CEC can be dependent on pH also. The pH of most clay suspensions lies between 4.2 and 7.0 indicating that they behave as weak acids.

4.3.5 Presence of other materials and previous history of the material

Many clays owe their acidity not only to the exchangeable hydrogen which they have absorbed but to associated organic matter. Humic acid and other soil acids are frequently associated with clays and these even in small amounts may produce marked acidity in clay suspensions.

Deposits of organic matter has also formed in clay deposits from time to time. The forests in pasts were decayed and through a series of complex physical and chemical changes were converted into sedimentary deposits of lignite, bituminous coal or anthracite (Worrall, 1982). These organic deposits are mostly found associated as clay-lignin with ball clays and bituminous coal and anthracite with fire clays. Lignite has the empirical formula $C_{20} H_{28} O_7$ which is derived from wood fibres, more or less unaltered in the lignite. It is insoluble in water or common organic solvents. In some way part of the organic matter became adsorbed on to the clay and cannot be separated readily; this organic matter is very finely divided and has a marked influence on the physical properties of certain clays.

Humic acid extracted from lignite by strong alkalies is related to lignin, but the exact relationship is not known. However, it is believed that in the transformation of wood to coal, the lignin side chains became oxidised to carboxyl groups, forming the so-called 'humic acids'. Humic acids represent usually a group of closely related substances being primarily in non-nitrogenous form although in many cases nitrogen is present in their molcules, coming from proteins combining with quinones in the main molecules (Burges, 1960). The free radical content of humic acids is quicte high (above 10 molar percent) (Steelink, 1964) and as such they form easily additive complex with many of the nitrogenous compounds such as urea, $HCONH_2$ and $ACNH_2$

(Dragunova, 1981). Again, many of the soil properties, such as its aggregate structure, water-holding and sorption capacities, etc. are largely determined by the nature and character of the humic acids. Attempts have been made to characterize humic acids from different origins by such physical methods as differential thermal analysis, electron microscopy (Seharpenseel et al., 1964 and Virser, 1963) an infrared spectroscopy (Kshama et al., 1990). DTA diagrams of humic acid samples collected from various sources have been found to be similar to each other, which indicates that their chemical structures are essentially of the same type. Electron microscopic study of humic acids reveals that they are amorphous in nature and consist of spherical aggregates of colloidal dimensions. Their equivalents as well as molecular weights vary over a wide range. These variations were reported to be within the ranges of 111-345 and 1000-59,000 respectively (Idem, 1964). Again the extent of aromatisation as well as the arrangement of different groups in their structures varies with the soil type (Kasatochkin, 1958). An attempt was made by Roy et al. (1968) to study the humic acids extracted from three Indian soils and a ceramic clay with particular reference to the structural and other characteristics of the humic acids. He found that the DTA thermograms of humic acids show two distinct peaks - one sharp endothermic peak at $90\text{-}110^{o}$ C due to the removal of adsorbed water and the other exotherm in the region $290\text{-}400^{o}$C due to the decomposition of humic acid molecules. Lignin and humic acids are highly colloidal materials, possessing cation exchange properties due to their functional groups -OH and -COOH. Humic acids can act as a protective colloid on the surface of the clay particles and then can increase the binding power of clay and thus increasing its plasticity. A sample formula of humic acid can be written as

$$C_{68}H_{53}O_4OCH_3(OH)_4(COOH)_4$$

4.4 INTRODUCTION

There is an estimated reserve of 1.3 million tons of ball clay at Padappakkara in Quilon District of Kerala. This is a potential plastic clay deposit of south India. The various parameters affecting plasticity namely pH, base exchange capacity, humic acid content and mineralogical composition on this clay have been investigated in the present work. The properties of this clay were also compared with the plastic clays from Payyangadi (Kerala) B, Bikaneer (Rajasthan) C, Bimadole (Andhra Pradesh) D, Than (Gujarat) E, Westerwald (West Germany) F and Inagaki-kibushi (Japan) G. A regression analysis was also done to correlate the properties of clays with plasticity.

A number of mine faces are found at an interval of 50-60 metres along the steep bank of Ashtamudi lake (8^{o}59' N: 76^{o} 39' E). Clays from Padappakkara and Payyangadi regions were collected by groove technique and sampling done by coning and quartering. These two raw samples were found to be contaminated with nodules of ferrous sulphide impurities. Hence -350 mesh fractions were taken for the studies. Other clays used for comparison were the commercially available ones.

Chemical characterisation was done by classical methods as well as instrumental methods like flame photometry, molecular and atomic adsorption spectrophotometry. Physical properties were determined by ISI and ASTM methods (ISI-4589, 1968, ASTM, 1959 and Bennet and Reed, 1971). Estimation of humic acid was carried out by extraction with alkali (Black, 1965). This extract was acidified with Con. HCl to pH 1 and the precipitated humic acid was filtered and dried in vacuum. Particle size distribution analysis was carried out using micromeritics sedigraph model D-5000 and mineral identification by XRD and SEM studies.

4.5 CHEMICAL, PHYSICAL AND MINERALOGICAL CHARACTERIZATION OF THE CLAYS

Chemical analysis given in Table 4 showed that silica content is the least in Padappakkara clay and maximum in the German clay. The Westerwald clay contains illite and is mainly used for stoneware products. As far as Al_2O_3 content is concerned, it can be noted that all the Indian clays have higher values (26-36%) whereas the German and Japanese clays contained only 23-24%. The lower alumina content results in a lower fusion point facilitating early maturing of ceramic products. The iron content is more or less same in sample 3, 4 and 7 whereas it is fairly high in 1, 2 and 5. TiO_2 content was more or less same in all ball clays. But sample 4 contained only a smaller amount of 0.38%. The values of K_2O and Na_2O indicate that this flux content is fairly uniform in all the samples, being $<$ 2.5%. It can be noted that other ball clays from USA, UK and USSR also possess more or less similar chemical composition (Ghosh and Guha, 1981).

Table 4: Chemical assay of the plastic clays

Constituent %	Padappakkara A	Payyangadi B	Bikaneer C	Bimadole D	Than E	Westerwald F	Inagakikibushi G
SiO_2	43.98	48.55	52.16	55.98	45.69	65.25	66.01
Al_2O_3	36.15	29.07	29.65	26.81	30.01	23.52	23.2
Fe_2O_3	2.09	2.99	1.08	1.17	2.96	1.95	1.2
TiO_2	2.51	1.48	1.07	0.38	1.29	1.61	1.3
Na_2O	0.62	0.82	1.41	0.72	0.82	0.71	1.03
K_2O	0.39	1.16	2.78	2.45	0.41	0.91	1.93
CaO	0.06	0.07	0.03	0.01	0.07	Nil	0.06
MgO	0.09	0.09	0.04	0.07	0.02	0.67	Nil
LOI	14.94	18.8	12.04	10.05	15.12	8.84	9.5

Table 5 indicates the comparative data of plastic properties like water of plasticity, Atterberg number, particle size distribution and mineralogical composition. It is associated with the phenomenon of water film formation of a certain order of thickness around each grain. More water permits free flow and less water makes the particles touch each other. Both the cases result in the reduction of plastic properties. Thus plasticity is a function of optimum water content which in turn depends on the above factors. It is interesting to note that the water of plasticity of Padappakkara ball clay is the maximum i.e. 43-44%. The next in plasticity is sample 5 having 38-40%, whereas all others fall in the range of 28-35%. Atterberg number also bears direct relationship as that of water of plasticity, the maximum being for sample 1, i.e. 65-67%.

4.5.1 Effect of humic acid

The plasticity of ball clays has been attributed in part, at least to relatively small amount of organic materials which they contain. It was noticed that sample 1, 2 and 5 have a high amount of humic acid content whereas in sample 3 it is only a very nominal quantity. Hence the increased plasticity of sample 1 can be due to the presence of high amount of HA. It is reported that addition of humic acid by 0.1% can increase the order of plasticity by 100% (Worrall, 1975).

In order to find out the effect of humic acid, the organic content of the clay was removed (a) by the oxidative decomposition of organic matter by 30% H_2O_2 and (b) by extraction with NaOH. By the first method it was found that the water of plasticity has been

Table 5: A comparative data of the plastic properties of clays

Property	Padappakkara	Payyangadi	Bikaneer	Bimadole	Than	Westerwald	Inagakikibushi
Water of plasticity (%)	43-44	28-30	28-30	33-35	38-40	32-34	31-34
Atterberg Number	65-67	30-34	21-24	21-25	48-50	33-35	17-19
BEC (me/100 g)	10	8	8	8	12	9	9
pH	4.4	4.6	7.8	7.5	7.3	6.4	6.2
Humic acid content (%)	0.15	0.15	0.001	0.042	0.20	0.13	0.26
Particles (%) ($< 2\mu$)	89	64	76	61	82	82	68
Zeta potential (ζ)	+7.94	-56.6	+21.36	-85.8	+80.8	-93.45	-65.7

reduced from 46 to 41% and similarly Atterberg number from 67 to 51. After the extraction of HA with 5 N NaOH, the pH of the clay was adjusted to be its original value of the raw clay by acetic acid. Then it was found that water of plasticity, against the expectation, was found to increase and this may be due to the Na^+ ion exchange which the clay has undergone during the extraction of humic acid. In this process the free hydroxyl ions in the clay might have exchanged Na^+ ions which resulted in a strong dipolar interaction with the water and in turn an increase of zeta potential and hence plasticity. Fig. 1 shows the IR spectra of humic acids extracted from different clays under investigation and are found to be identical and comparable to standard humic acid procured from Fluka, West Germany.

As the IR spectra of different humic acids are similar, it is likely that their chemical structure is essentially of the same type (Ruggiero et al., 1980). But a closer examination reveals that the peak 1080 cm^{-1} differs in different humic acids, which may arise from some variation in the arrangement of different structural units of humic acids which in effect may affect plasticity also. Distriubution of peaks in the IR spectra of humic acids is described in Table 6.

4.1.2 Effect of pH, BEC, particle size distribution and zeta potential

Water of plasticity of H or Ca clay will be more than a sodium or potassium clay as the water sheath is more strongly held in the former case. In the case of Padappakkara clay the natural pH is 3-4 and the acidic nature of the clay also contributes to the higher water of plasticity.

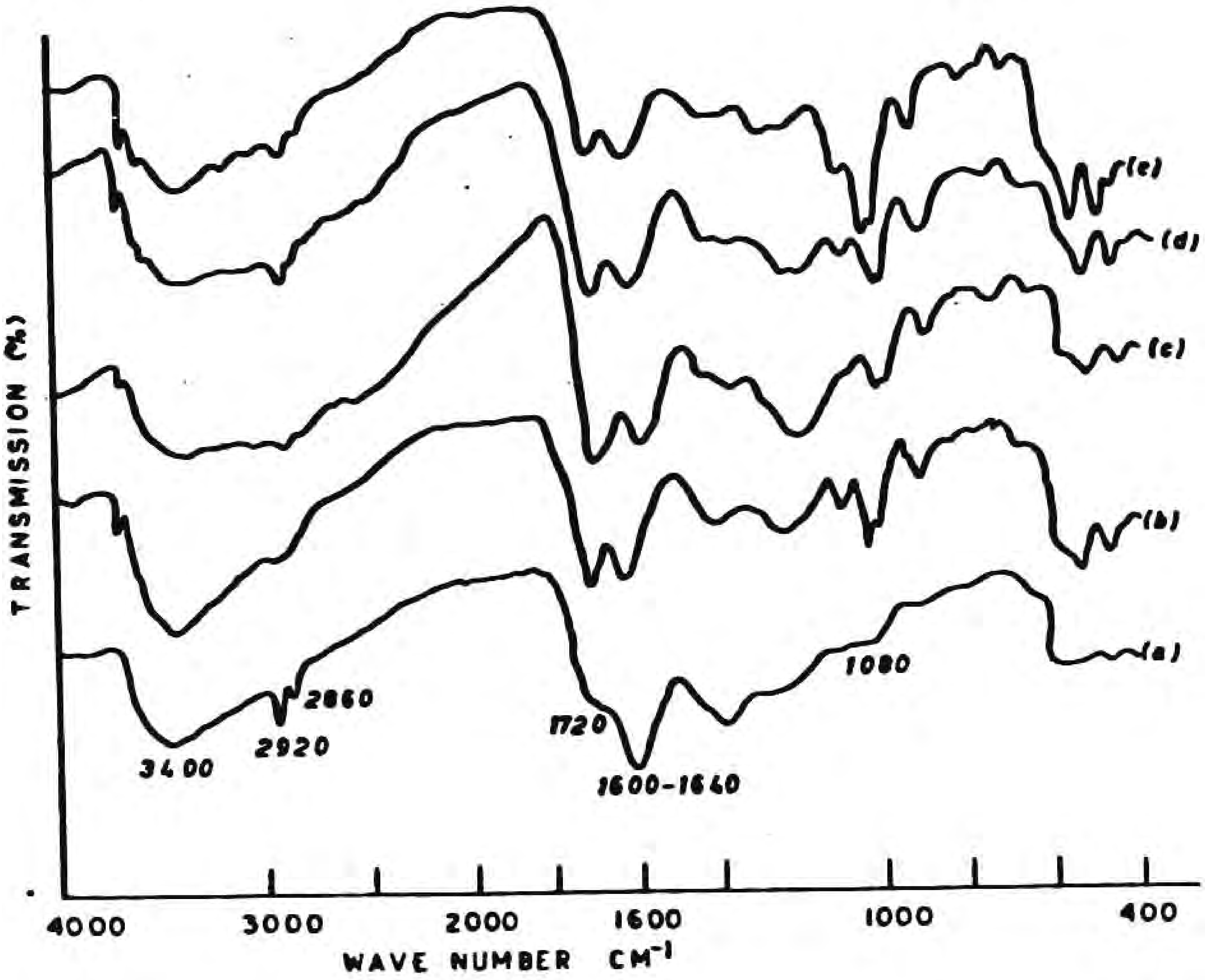


Fig. 1. I R Spectra of humic acids

a - STANDARD. b - FROM PADAPPAKKARA CLAY

c - FROM PAYYANGADI CLAY d - FROM JAPANESE CLAY

e - FROM THAN CLAY

Table 6: Distribution of peaks in the IR spectra of humic acids

Sample	Peak range (cm^{-1})	Peak range (u)	Intensity	Group
Standard	3415	2.96	Broad	O-H stretching polymeric association
Extracted	3430	2.9	Broad	O-H stretching or may be amine secondary, free N-H stretching
Standard	1597	6.25	Strong	Carboxylic acid Carboxylate anion stretching
Extracted	1630	6.1	Strong	Carboxyl stretching diketones or C = N stretching
Standard	1375	7.5	Strong	Carboxylic acid Carboxylate anion stretching
Extracted	1410	7.15	Variable	Carboxylic acid or may be O-H stretching, i.e. tertiary alcohol
Standard	1020	9.6	Variable	C-X stretching, it can be C-F
Extracted	970	10	Variable	C-X stretching

BEC is also related to plasticity and directly proportional to particle size and hence directly related to plasticity too. For example in samples 1, 5 and 6 the percentage of clay content $< 2\ \mu$ is 89, 82 and 82% respectively and from the table it can be seen that their BEC values are also higher.

From the particle size distribution of the clays it is evident that samples 1, 5 and 6 are having the maximum percentage of particles less than 2 μ. The particle size distribution is found to be directly in relation with plasticity, meaning higher the percentage of finer particles, the higher the plasticity.

As far as the zeta-potential of clay is concerned, it is expected that if the cationic charge is greater, the resultant charge will be positive. On the other hand, if the surface charge is higher, the zeta-potential will be negative. However, from the table 5, there is no direct relationship was found between zeta potential and any of the other single property. .

4.5.3 Effect of mineralogy

a. XRD analysis

Fig. 2 shows the XRD patterns of the clays. All the clays exhibited the characteristic 001, 002 and 003 reflections of kaolinite corresponding to d values at 7.13, 3.53 and 2.3 A^o. The Kerala clays are found to contain pyrite and gibbsite as impurities which cannot be detected from Fig. 2, besides quartz as the major accessory mineral and Padappakkara clay contains small peaks of halloysite also.

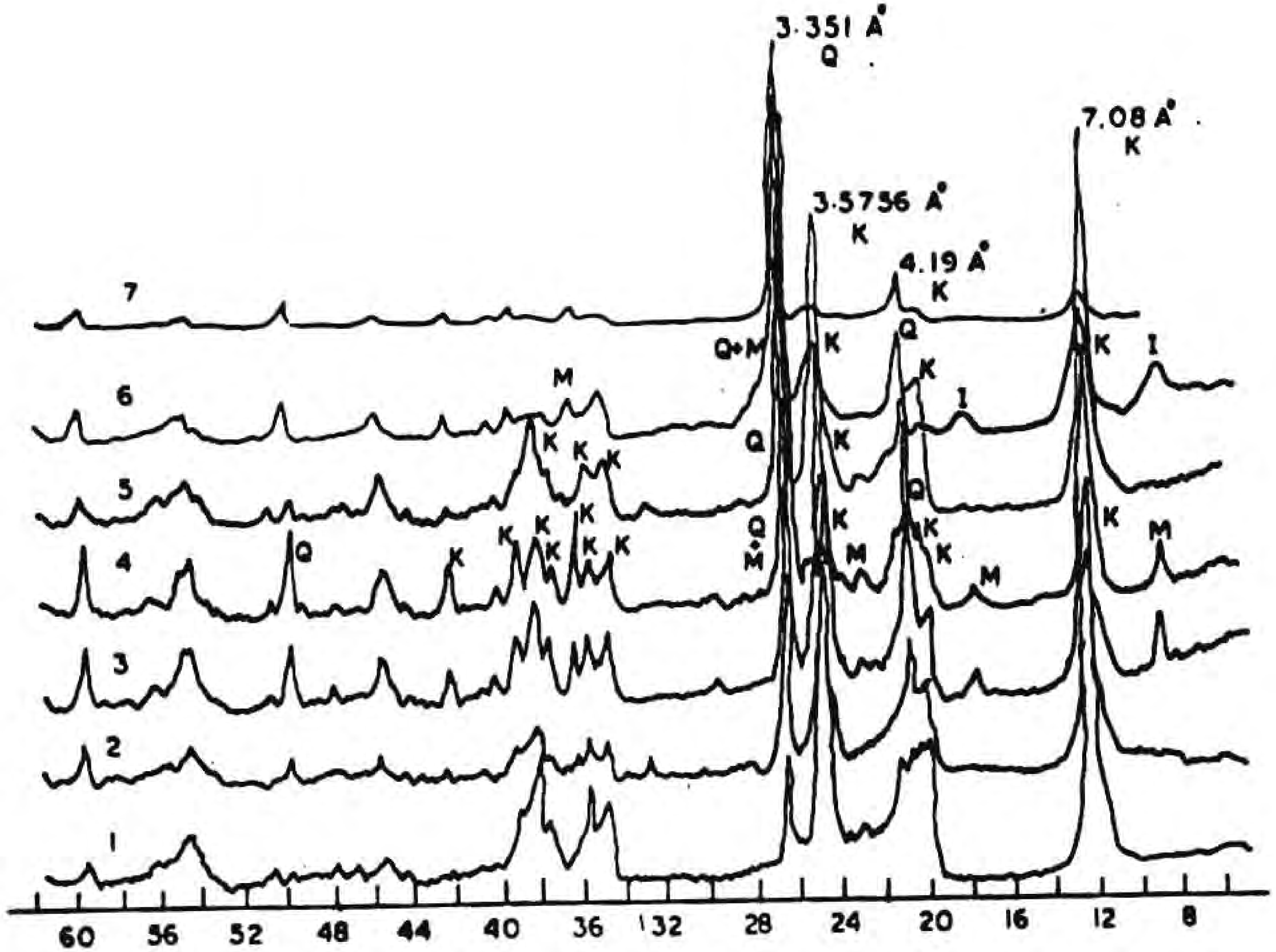


Fig. 2. X - ray diffraction patterns of plastic clays

1. PADAPPAKARA 2 PAYYANGADI, 3 BIKANEER, 4 BIMADOLE, 5 THAN, 6 WESTERWALD
7 INAGAKI - KIBUSHI

K - Kaolinite, M- Mica, I-Illite, Q - Quartz

Sample 3 and 4 indicate the presence of micaceous impurities. Westerwald clay contains illite (the DTA of this clay showed a large endothermic peak at 550^{o}C and a small exothermic peak at 950^{o}C) and XRD patterns indicate the peaks with d values 9.98, 4.47 and 2.56 A^{o}. In spite of the absence of montmorillonite, the clay from Padappakkara is showing a higher water of plasticity. Partly this may be due to the presence of traces of halloysite present in it and mainly it could be due to the organic matter and the fine-grained nature of the clay. It is worthwhile to note here that kaolinite formation in this region is preceded by the formation of halloysite in the weathering crust (Lalithambika et al., 1987).

b. Rational analysis

The chemical analysis result, given in terms of percentage composition is often referred to as the ultimate analysis. Since the clay does not occur naturally in the form of oxides, it is having some importance to know its mineralogical composition. The ultimate analysis can be converted into approximate amounts of mineralogical constituents by simple calculations. The result is known as a rational analysis, proximate analysis or calculated mineralogy which is only an approximation.

The calculated mineralogy from the chemical assay based on certain conventions (Ryan and Redford, 1987) is presented in Table 7.

c. SEM analysis

Structure of ultimate particles and their aggregation to larger ones has an important influence on plasticity. Very fine grained and

Table 7: Calculated mineralogy by rational analysis

	A (%)	B (%)	C (%)	D (%)	E (%)	F (%)	G (%)
Feldspar	7.1159	13.98	29.51	22.33	8.69	20.99	20.88
Kaolinite	89.936	68.5	62.79	63.96	73.38	59.44	45.00
Quartz	-2.5014	7.1098	3.816	11.74	8.91	18.9	29.55
Haematite	2.0821	2.98	0.05353	1.17	2.95	0.63	1.195
Rutile	2.500	1.47	0.0837	0.38	1.28	1.41	1.295
Calcite	0.1071	0.13	1.0759	0.018	0.042	0.55	0.11
Magnesite	2.0821	0.19	1.0659	0.15	0.125	0.71	*

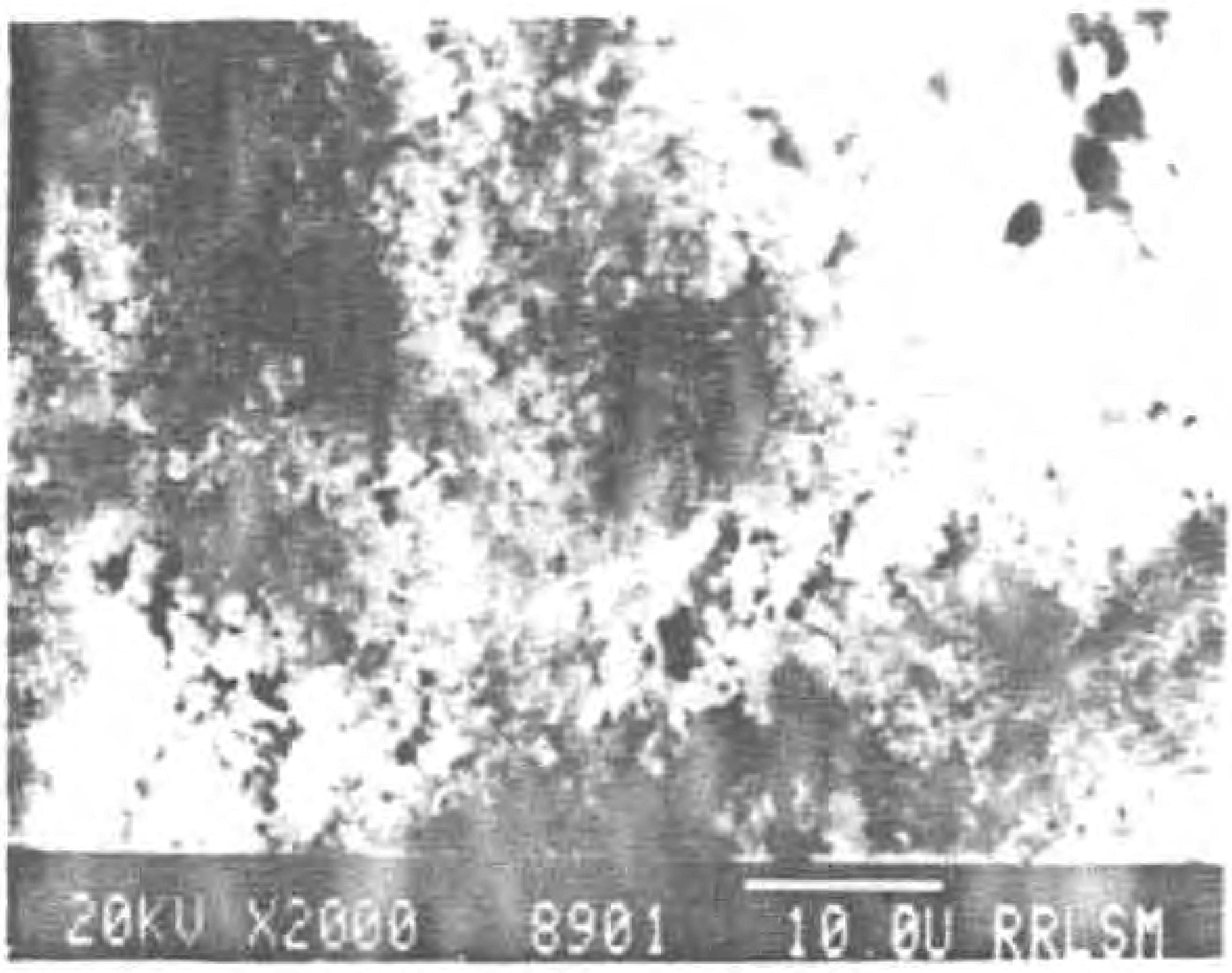
very coarse grained particles are less plastic than those containing both large and small grains. Hence a comparison of microstructure was carried out. Fig. 3 (1-7) shows the SEM pictures of the clays under investigation. SEM picture of sample 1 shows that the particle size is fine and are densely packed and aggregates of different size and shape can be seen in the picture whereas the other clay from Kerala has a loose compaction and hence a higher natural porosity. Sample 3, 4, 5 and 7 were found to be more or less crystalline and the clays indicated tthe presence of aggregates. Often plastic clays are found to show aggregation and quite often the clays which contain aggregates are found to be more plastic than very fine grained or very coarse grained particles. The Westerwald clay was the most fine grained.

4.5.4 Effect of heat changes

The important property of kaolinite which gives value in the ceramic industry is its plasticity. The application of thermogravimetry to the characterisation of kaolinitic clays was carried out using a manual thermogravimmetric analyser.

The analysis of kaolinite specimens by thermogravimetry is based on the loss of water in two regions of the TG thermal curve. First the desorption of water will be observed for all kaolinite specimens in the ambient to 110°C temperature range. The magnitude of this event is largely dependant upon the particle size (surface area) of the kaolinites under study (Earnest, 1988). The well ordered specimen is expected to show only a 0.2% weight loss from ambient to 200°C. In this study, comparatively highlycrystalline kaolin specimens

Fig. 3: Scanning electron micrographs of balls clays from:
(1) Padappakkara A, (2) Payyangadi B, (3) Bikaneer C,
(4) Bimadole D, (5) Than E, (6) Westerwald F,
(7) Inagaki kibushi G.



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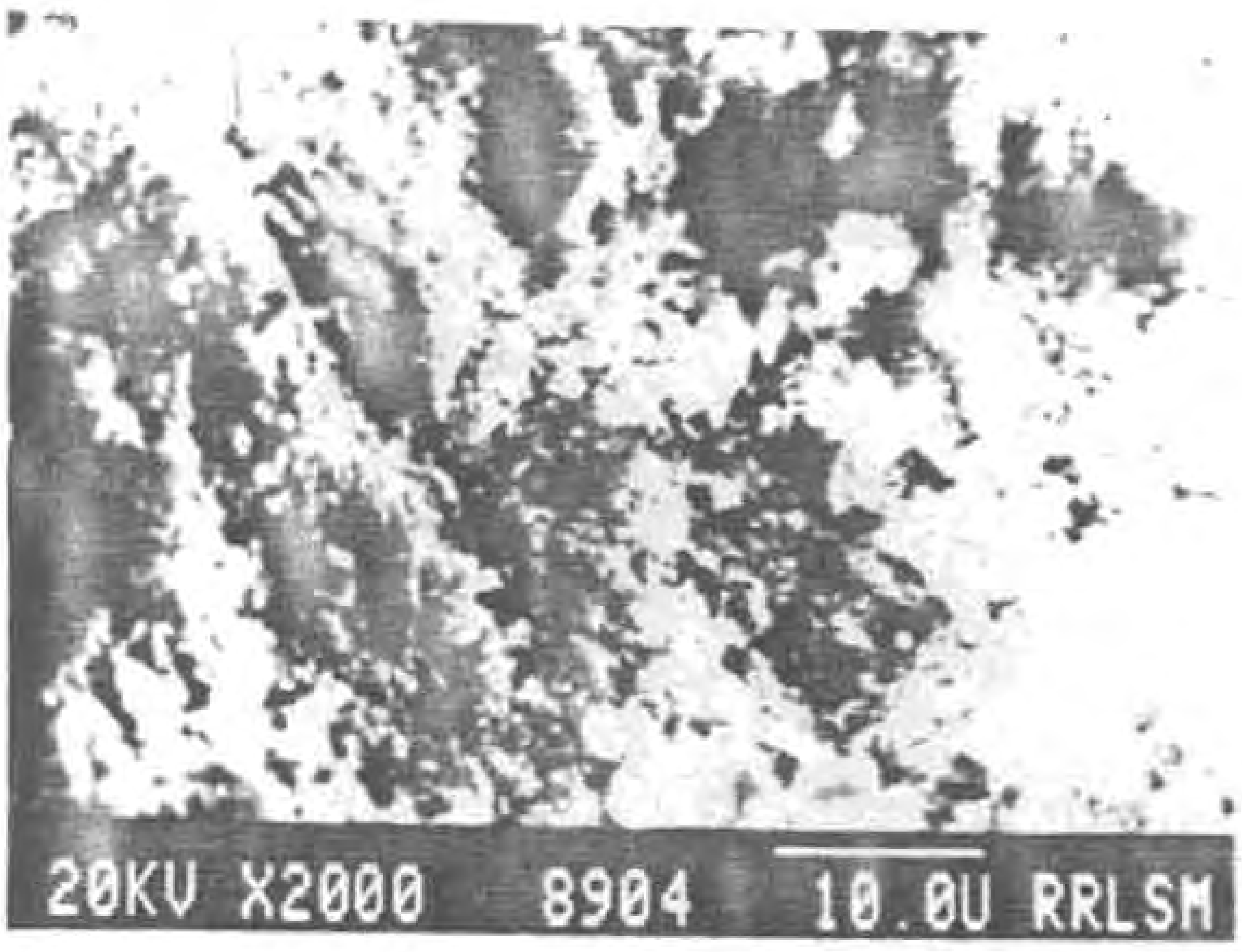

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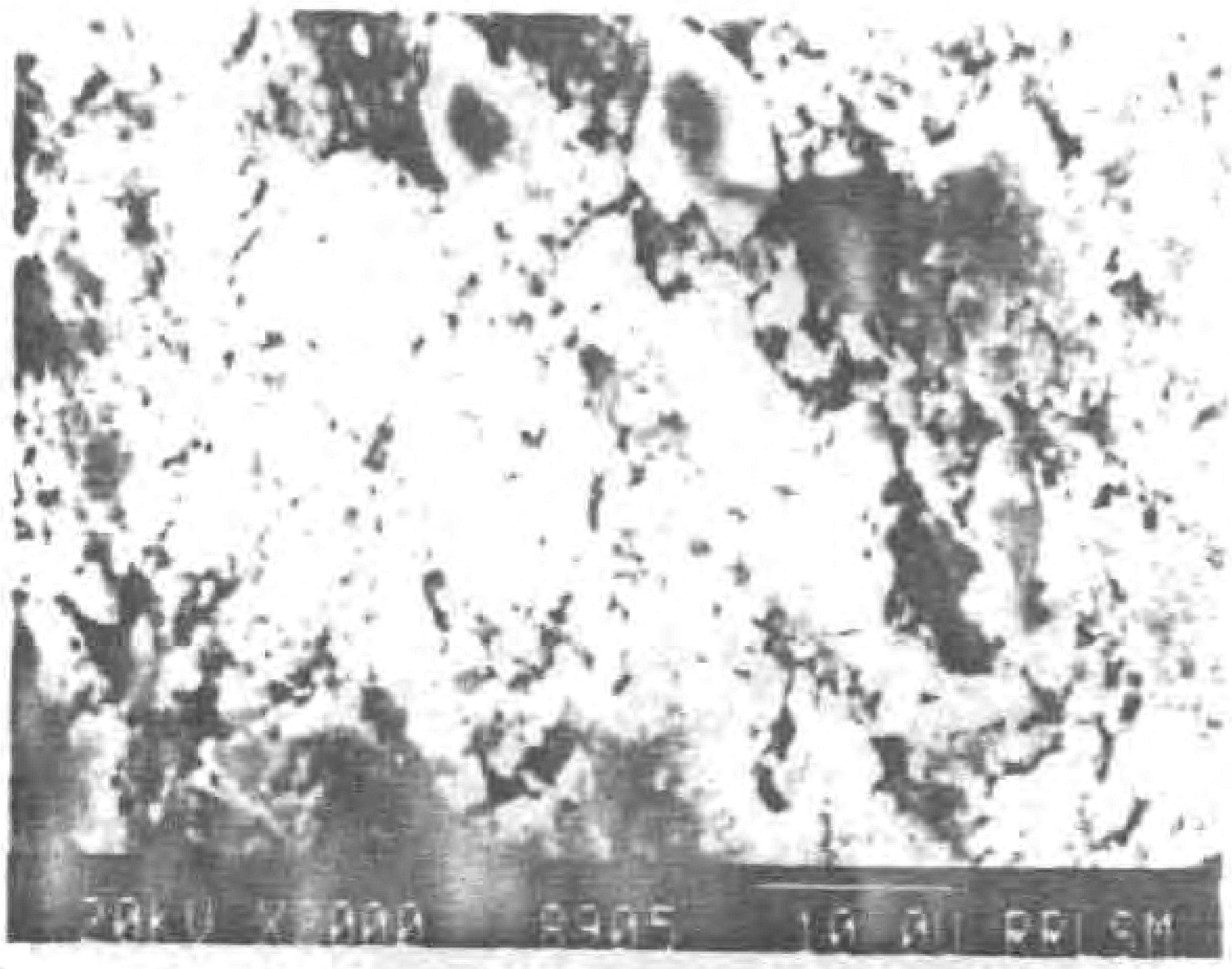

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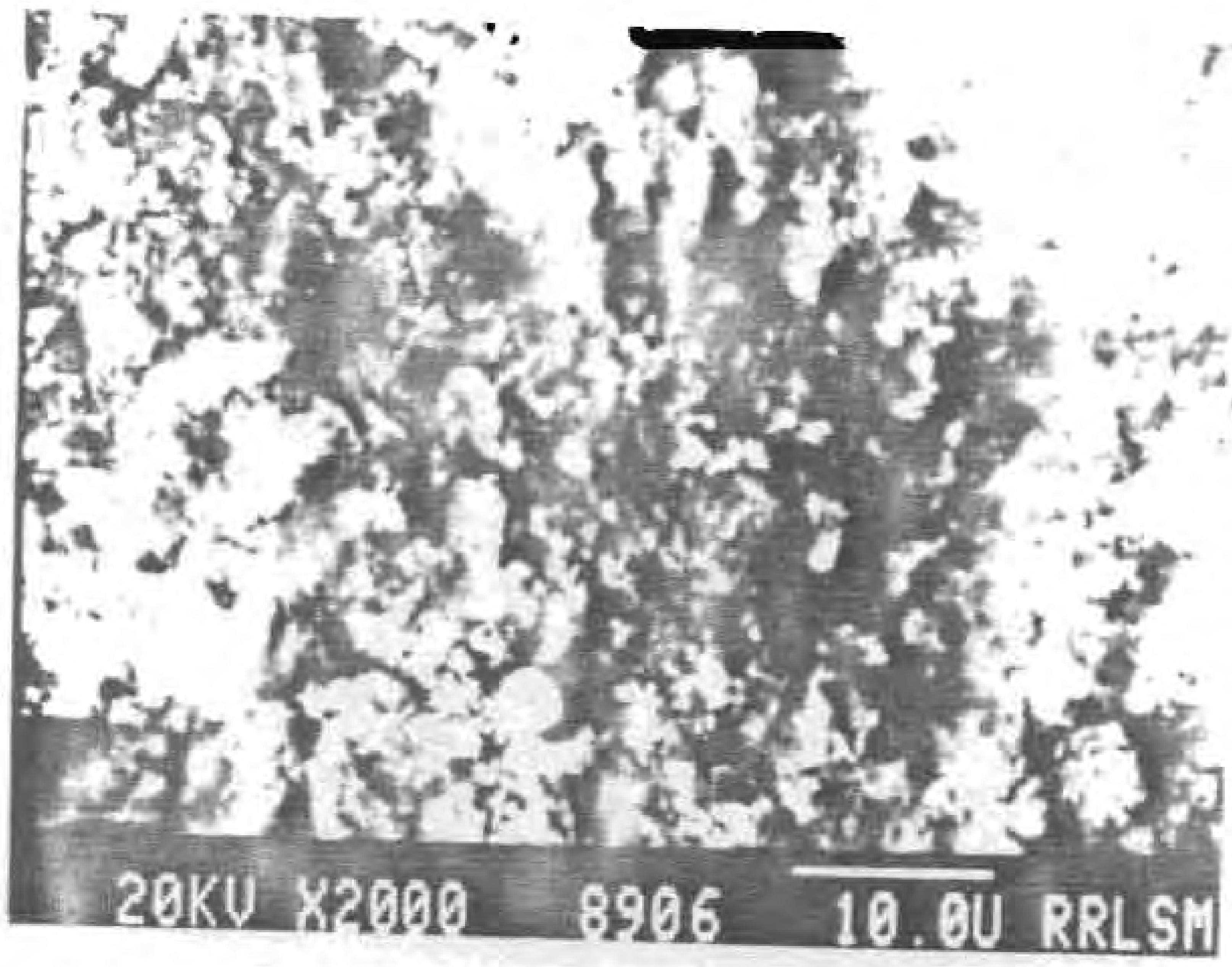

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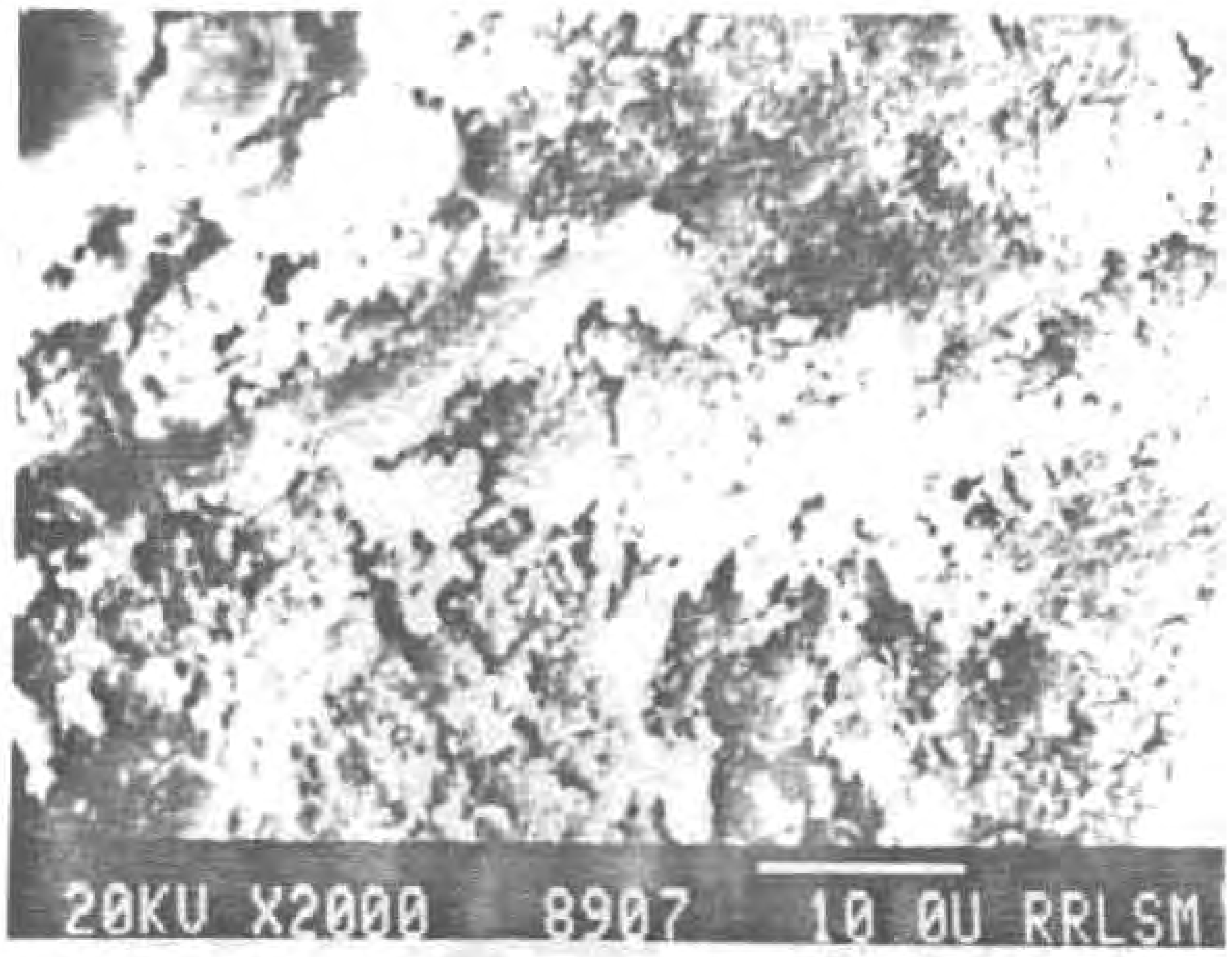

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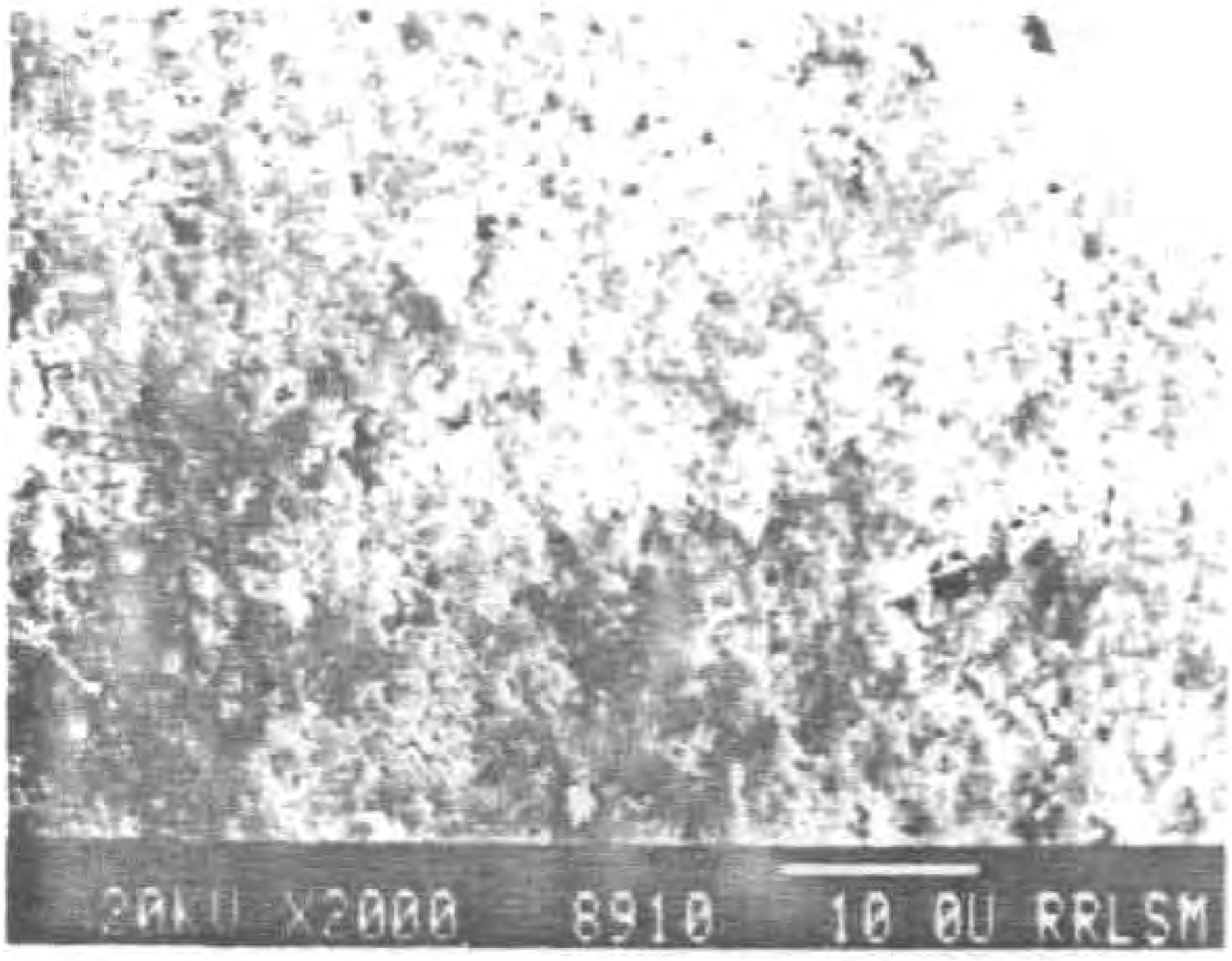

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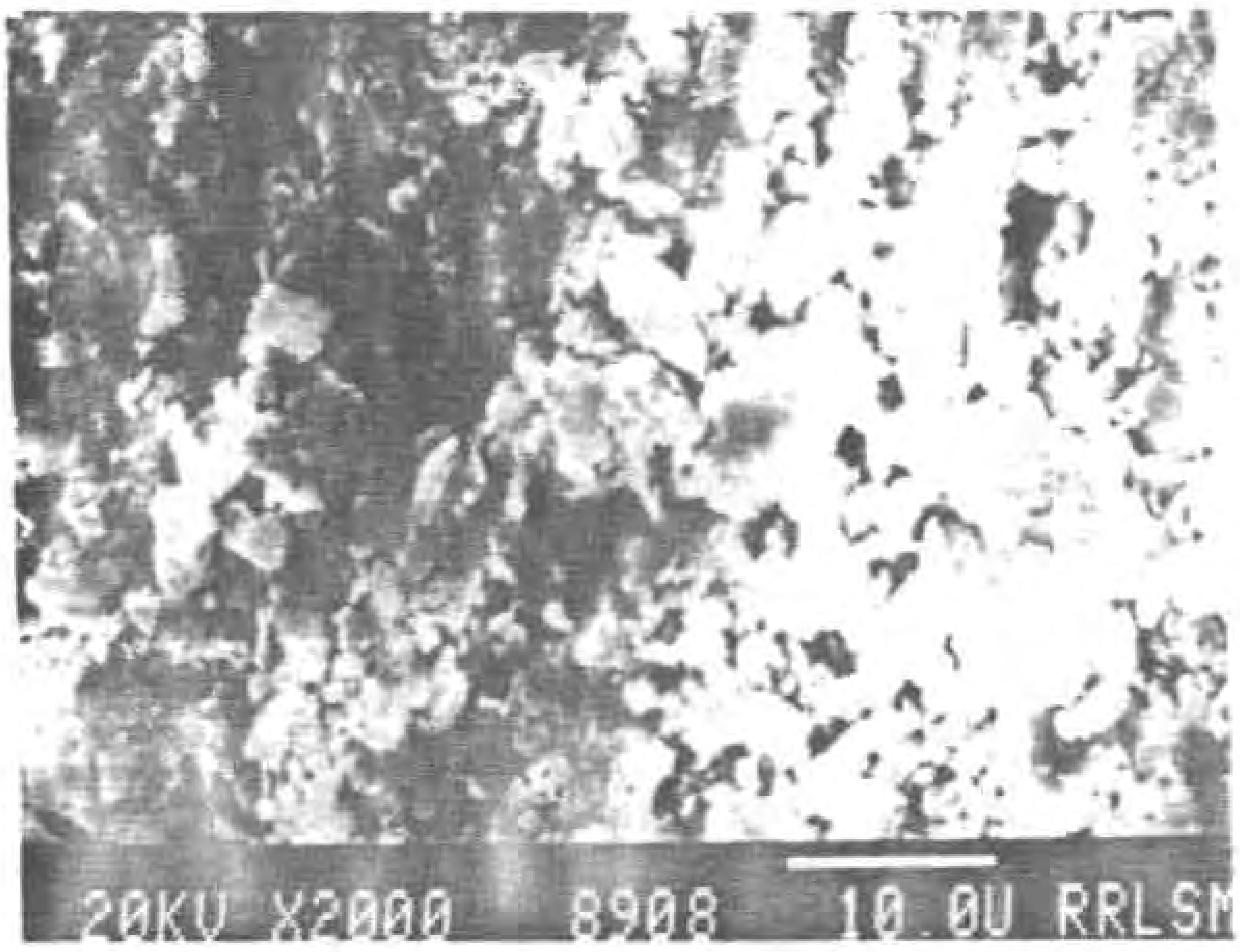


(7)

such as Bimadole D, showed the presence of very little adsorbed water. The second weight loss event is observed in the 400 to 600°C temperature range corresponds to the dehydroxylation of the silicate lattice. The meta-kaolinite thus formed is in an amorphous state and on further heating to temperatures of 950 to 1000°C undergoes an exothermic phase change.

4.5.5 Effect of grinding on plasticity

The sample 1 was wet ground in a corundum planetary ball mill for different periods (2 hrs, 5 hrs and 10 hrs) and the plasticity was measured. It was found that the plasticity decreased with the increasing grinding time indicating that prolonged grinding will not help in improving plasticity. Table 5 gives the water of plasticity and Atterberg number for different durations of grinding of Padappakkara ball clay. In order to find out whether any mineralogical change has been taken place during grinding XRD analysis was carried out. A detailed study of grinding on plastic clays has been dealt in the coming chapter.

4.6 REGRESSION ANALYSIS TO FIND OUT PLASTICITY PARAMETER

Regression analysis was carried out using HCL Horizon III system. The programmes were written in Fortran 77. The analysis was done to fit Atterberg number in terms of BEC, SiO_2 content and particle size where BEC and particle size are generally found to be directly proportional to plasticity and SiO_2 in the reverse order. A linear equation of the form $y = a_0 + a_1x_1 + a_2x_2 + a_3x_3$ was fittted and the related equations were solved by Gauss Jordan method (Bajpai et al.1976)

The idea of Gauss Jordan reduction is to transform a linear system into a system of the special upper triangular form

$$\begin{aligned} a'_{11}x_1 + a'_{12}x_2 + \text{-------} + a'_{1n}x_n &= b'_1 \\ a'_{22}\ x_2 + \text{--------------} + a'_{22}x_n &= b'_2 \quad\text{———}(1) \\ a'_{nn}x_n &= b'_n \end{aligned}$$

where a'_{ij} and b'_i are modified coefficients. The solution is then found directly by backsolving. That is the last equation and is solved for x_n

$$x_n = b_n/a'_{nn}$$

This value is used in the next to last equation to determine x_{n-1},

$$x_{n-1} = (b'_{n-1} - a'_{n-1,\ n}\ x_n)/a'_{n-1}$$

which in turn is used in the $(n-2)^{nd}$ equation to determine x_{n-2} etc.

The transformation can be done in such a way that, if arithmatic is used, the solution of the triangular system will be the same as the solution to the original system. However, computations and the transformation will involve rounding errors. Transformations of Eq. 1 is carried out in several steps. These are illustrated below.

Suppose $a_{11} \neq 0$. We substract the multiple a_{i1}/a_{11} of the first equation from the i^{th} equation, $i = 2, \ldots\ldots\ldots, n$ to get the first transformed system,

$$
\left.
\begin{array}{llll}
a_{11}x_1 + a_{12}x_2 & + \cdots\cdots\cdots + & a_{1n}x_n & = b_1 \\
 & & & \\
\quad a_{22}^{(1)}x_2 & + \cdots\cdots\cdots + & a_{2n}^{(1)}x_n & = b_2^{(1)} \\
\quad \vdots & & & \\
\quad a_{n2}^{(1)}x_2 & + \qquad\qquad\quad + & a_{nn}^{(1)}x_n & = b_n^{(1)}
\end{array}
\right\} \quad (2)
$$

The new coefficients a_{ij} and b_j are given by

$$a_{ij}^{(1)} = a_{ij} - m_{i1}\,a_{1j} \qquad i = 2, \ldots\ldots\ldots, n$$

$$b_j^{(1)} = b_j - m_{j1}\,b_1 \qquad j = 2, \ldots\ldots\ldots, n$$

where $m_{j1} = a_{i1}/a_{11}$, $i = 2, \ldots\ldots\ldots, n$. If $a_{11} = 0$, then because the coefficient matrix is nonsingular, by interchanging the two rows of Eq.1 we can get a nonzero element in the upper left hand corner.

Now, if $a_{22}^{(1)}$ in Eq. 2 is nonzero we subtract $m_{i2} = a_{i2}^{(1)}/a_{22}^{(1)}$ times the second equation from the i^{th} equation in Eq. 2, $i = 3, \ldots\ldots\ldots, n$, and get third transformed system

$$\begin{array}{l}
a_{11}\,x_1 + a_{13}^{(2)}\,x_3 + \text{--------} + a_{1n}^{(2)}\,x_n = b_1^{(2)} \\
a_{22}^{(1)}\,x_2 + a_{23}^{(1)}\,x_3 + \text{--------} + a_{2n}^{(1)}\,x_n = b_2^{(2)} \\
a_{33}^{(2)}\,x_3 + \text{------------} + a_{3n}\,x_n = b_3^{(2)} \\
a_{n3}^{(2)}\,x_3 + \text{------------} + a_{nn}\,x_n = b_n^{(2)}
\end{array} \qquad \text{—— (3)}$$

in which the element in the first row and second column has also been reduced to zero. Continuing in this way so that at each step all the elements in a column except the diagonal element are reduced to zero we finally get

$$\begin{array}{l}
a_{11}\,x_1 = b_1^{n-1} \\
a_{22}^{(1)}\,x_2 = b_2^{n-1} \\
a_{nn}^{(n-1)} = b_n^{(n-1)}
\end{array} \qquad \text{—— (4)}$$

with $a_{ii}^{(i-1)}$ and with

$$b_i^{(k)} = \begin{cases} b_i^{(k-1)} - m_{ik}\,b_k^{(k-1)} & i = 1, \ldots\ldots\ldots, k-1,\ k+1, \quad, n \\ b_k^{(k-1)} & k = 1, \quad, n-1 \end{cases}$$

Solution of the set of equations is given by

$$x_i = \frac{b_i^{(k-1)}}{a_{ii}^{(1-1)}} \qquad i = 1, \ldots\ldots\ldots, n$$

Table 8 represents the data taken for regression analysis, in this context. The analysis indicated that the Atterberg number can be expressed by the equation

$$y = -10.96 + 4.62\, x_1 - 0.90\, x_2 + 0.69\, x_3$$

where

y - Atterberg number

x_1 - BEC

x_2 - SiO_2

x_3 - particle size

This equation gives an average deviation of ± 9.149%. Hence refinement on the above equation introducing additional parameters like humic acid content, green strength and water of plasticity can be done further.

Table 8: **Fitting the linear equation viz. expressing Atterberg number in terms of BEC, SiO_2 content and particle size**

x_1	x_2	x_3	y	x_1x_2	x_2x_2	x_3x_3	x_1y
8.00	55.98	86.00	23.00	64.00	3133.76	7396.00	184.00
8.00	52.16	64.00	23.00	64.00	2720.67	4096.00	184.00
12.00	45.69	76.50	49.00	144.00	2087.58	5852.25	588.00
8.00	45.55	61.00	32.00	64.00	2357.10	3721.00	256.00
10.00	47.63	82.00	66.00	100.00	2268.62	6724.00	660.00
9.00	67.33	82.00	34.00	81.00	4533.33	6724.00	306.00
9.00	52.86	69.00	18.00	81.00	2794.18	4761.00	162.00
64.00	370.20	520.30	245.00	598.00	19893.23	39274.25	2340.00

x_2y	x_3y	x_1x_2	x_2x_3	x_1x_3	Cal y=y	y-y
1287.54	1978.00	447.84	4814.28	688.00	34.96	11.96
1199.68	1472.00	417.28	3338.24	512.00	23.22	0.22
2238.81	3748.50	548.28	3495.28	918.00	56.14	7.14
1553.60	1952.00	388.40	2961.55	488.00	24.39	-7.61
3143.58	5412.00	476.30	3905.66	820.00	48.95	-17.05
2289.22	2788.00	605.97	5521.06	730.00	29.66	-7.40
951.48	1242.00	475.74	3674.34	621.00	30.68	12.66
12663.91	18592.50	3359.81	27683.42	4785.00		-0.08

4.7 SUMMARY

The comparison of plastic clay from Quilon District in Kerala with the ball clays from certain potential sources in and outside the country indicates that the clay sample from Padappakkara is the best in plastic properties. Mineralogy indicates that all the clays are kaolinitic with quartz as the major accessory mineral though some visible impurities are found in Kerala clays. Its fine particle size and fairly high humic acid content are responsible for its increased plasticity. Study of the effect of grinding on plasticity of this clay indicated that grinding destroys its crystal structure resulting in lowering of plasticity. The regression analysis shows that an overall idea regarding the plasticity of clays can be obtained from the derived equation.

CHAPTER V

GRINDING STUDIES ON KAOLINITES

5.1 GENERAL

It is well known that grinding of clay minerals can produce various effects on their different properties. The effect of grinding on the structural characteristics of clay minerals is interesting as the process of grinding can cause polymorphic transformations, phase changes and chemical reactions (Grim, 1968). Since the platelets of kaolinite and montmorillonite are broken up during grinding the structure and properties of these minerals depend very much on the grinding behaviour. In the case of kaolinitic clays, the rate of decomposition on dry grinding depended on the minerals present in it. Grinding is an essential operation during the processing of ceramic raw materials and hence the investigations on the changes brought about by grinding is of extreme significance.

The literature survey on the subject indicates that grinding studies on minerals like kaolinite, montmorillonite, halloysite (Grim, 1968), gibbsite, alumina, quartz (Cases et al., 1986) and pyrophyllite (Sanchez-Soto and Perez-Rodriguez, 1989) have been carried out by many scientists. Kodama et al. (1989) carried out grinding studies on kaolinite, and the crystalline contents in the ground samples were estimated by X-ray powder diffraction, infrared and solid state nuclear magnetic resonance spectra and chemical dissolution techniques. Prolonged grinding of montmorillonite was found to destroy the structure of the mineral and to release part of the alumina and magnesia as well as the crystalline OH-groups. The experiments carried out on montmorillonite and kaolinite by Mdivnishvili et al. (1963) indicated that the interplanar spacings in kaolinite do not change during grinding, while in montmorillonite the interplanar spacing d_{001} decreases from 15.3 to 12.14 A^{o} due to the rapid decrease in interplanar water during particle size reduction. Comminution of gibbsite in a centrifugal planetary ball mill is found to be accompanied by mechanical activation and amorphisation. The reactivity of these 3-dimensional layered aggregates was dependent on the microcrystalline components and the specific surface area of these aggregates (Isupov, 1986). Tanaka Kenji et al. (1988) have investigated the grinding of alumina powder and found that submicron grinding of alumina powder is possible using balls of 2 mm diameter, when the grindiing time is short. Interestingly, it was observed during the above experiment that part of the alumina was converted to gibbsite. The grinding of quartz by attrition modified its structure into amorphous silica. This phase change was utilized for the recovery of quartz from rocks and ores by flotation techniques.

According to Herman and Marcus (1961), the fineness of kaolin increases upto 12 hrs grinding and thereafter the finest particles cake together again to form loose aggregates. After 600 hrs comminution is complete, the loose aggregates gradually became firmer (Gregg, 1953). The ion exchange is found to be raised as a result, surface area will be increased and thus the severing in chemical bonds (Jackson and Truog, 1939, Kelley and Jenny, 1936). Heats of solution and wetting increase to higher values, and the X-ray structure changes. Huttig (1952) stated that the extent to which a substance can be broken down by dry grinding is limited by the size of the elementary blocks of the crystal mosaic. These then tend to reunite so that, on prolonged grinding, an equilibrium establishes itself between the subdivision of coarse grains and their reconstitution from elementary crystal blocks. An increase in grain size occurs when very fine-grained clay suspensions are dried (Corneus and Schott, 1933).

The comminution of hard ceramic raw materials involves considerable expenditure of energy. Only 0.5% of the energy expended is required for the actual cleavage of the crystal lattice (Budnikov and Neikritsh, 1929). For the same type of grinding (i.e. material and equipment) the increase in surface is proportional to the energy expended. This law is for homogeneous bodies whereas many hard materials are heterogeneous. Coarse particles are broken down in grinding mills but very fine powders are compacted, so that after prolonged grinding the same state of fineness in the materials is reached (Huttig, 1952). Podmore (1952) expressed the efficiency of grinding by the formula $[(S_2-S_1)C]/KWh$, where S_1 is the initial & S_2 the final specific surface (cm^2/g), C the weight of the charge in tons & Kwh the kilowatt hours consumed. In coarsely ground quartz, for particles < 1.2 mm some seggregation is unavoidable, this is least when the grain size distribution corresponds to that of closest packing.

5.2 INTRODUCTION

Ball milling is a process of comminution where strains in the nature of dislocations, formation of crystallites and subgrain boundary formation were shown to occur in addition to normal particle fragmentation with increase in surface area (Sarkar, 1975). It has been observed that apart from particle fracture, ball milling may induce lattice strain in ceramic oxides. In the context of present studies the nature of new phase formed during grinding is outlined and the contribution made by particle fracture during ball milling is discussed.

The effect of grinding on different physico-chemical parameters of clays such as plasticity, particle size and shape, cation exchange capacity and mineralogy was studied in three kaolinitic raw materials. Two ball clays (P from Padappakkara, Kerala and B from Bikaneer, Rajasthan) and one china clay (T from Thonnakkal, Kerala) were chosen for the study. Consequently, a high temperature phase α -alumina or corundum was found to form during grinding of ball clay P and was attributed to the presence of gibbsite as an impurity. Mineralogically, no change was observed in the case of other clays.

5.2.1 Preparation and characterisation of the starting materials

The preliminary original sample from the Padappakkara region was collected by groove technique and sampling done by coning and quartering. By quartering, it is effected that the material should be thoroughly mixed and placed in a symmetrical and rather flat pile and divided into four equal parts. Two opposite parts are removed, the material in them is again mixed and then quartered, this being continued until a sample weighing about 10 kg is obtained. This is coarsely crushed and again quartered so that by still further crushing and quartering a representative sample of suitable quantity is obtained. The other two samples namely, the ball clay B and the china clay T were the commercially available ones. All the samples were passed through 350 mesh (45 μm) BS sieve before subjecting them to the detailed studies.

The characterisation of the starting material was carried out chemically by classical methods and mineralogically by rational analysis. Besides classical methods, the chemical analysis includes atomic absorption spectrophotometric and flame photometric studies.

5.2.2 Studies on grinding

Wet grinding of kaolinite was conducted in a planetary ball mill (FRITSCH). The grinding vessel contained eleven balls of 2 cm diameter and was made up of corundum.

Grinding studies were carried out on the -350 mesh fractions of the clay from Padappakkara, Bikaneer and Thonnakkal with an average particle size of 0.27, 2 and 1.75 μm respectively. These were wet-milled upto 10 hrs in a planetary ball mill. 300 gm of each sample finely ground was mixed with 200 ml distilled water. The ground samples were taken out after 2, 5 and 10 hrs in order to determine the effect of grinding on various parameters.

The mineralogical composition of the clays were studied by X-ray diffraction analysis (Philips PW 1710). Micromeritics particle size analyser model D-5000 was used for the particle size distribution analysis. Cation exchange capacity was estimated as per standard

Table 1

Mineralogical composition of the clays

Sample	Mineralogical composition	
	From XRD	From calculated mineralogy (%)
1. Ball clay-P	Kaolinite Gibbsite Quartz	Kaolinite 89.9 Feldspar 7.1 Quartz -2.5
2. Ball clay-B	Kaolinite Illite Quartz	Kaolinite 62.8 Feldspar 29.5 Quartz 3.8
3. China clay-T	Kaolinite Quartz	Kaolinite 97 Feldspar 1.4 Quartz 1.3

Table 2

Chemical analysis

Constituent	Ball clay (P)	Ball clay (B)	China clay (T)
SiO_2, %	43.98	52.16	46.44
Al_2O_3, %	36.15	29.65	37.85
Fe_2O_3, %	2.09	1.08	0.90
TiO_2, %	2.51	1.07	0.69
Na_2O, %	0.62	1.41	0.12
K_2O , %	0.39	2.78	0.08
CaO, %	0.06	0.03	Traces
MgO, %	0.09	0.04	Traces
LOI, %	14.94	12.04	13.18

procedure (Singer and Singer, 1963) by treating the samples with ammonium acetate and estimating the amount of ammonia absorbed. Electron microscopic and differential thermal analytical studies were carried out by Jeol Scanning Electron Microscope and Linseis Differential Thermal Analyser respectively.

5.3 FORMATION OF NEW PHASES DURING GRINDING

Samples were wet ground for 2, 5 and 10 hrs. Fig. 1(1) shows the X-ray pattern of randomly oriented aggregates of the washed ball clay-P ($< 45\ \mu m$). The reflections at 7 A^{o} and 3.56 A^{o} are characteristic of kaolinite. This sample also shows the presence of gibbsite as indicated by a strong reflection of 4.79 A^{o} (Fig. 2). The reflections at 4.23 A^{o} and 3.32 A^{o} indicate the presence of quartz. The X-ray diffraction pattern of the ball clay B (Fig. 3(1)) shows reflections at 9.82 A^{o} and 4.67 A^{o}, which are the 001 and 002 reflections of illite and the kaolinite is indicated by its characteristic basal reflections at 7.02 A^{o} with its second order at 3.56 A^{o}. Along with illite and kaolinite, this sample also contains quartz as the accessory mineral. XRD pattern of china clay T (Fig. 4(1)) exhibits the characteristic basal reflection of kaolinite at 7 A^{o} with its second order at 3.56 A^{o}. The reflections at 4.23 A^{o} and 3.33 A^{o} correspond to those of quartz. The mineralogical and chemical compositions of the starting materials are summarised in Tables 1 and 2.

Figs. 1, 3 and 4 show the XRD patterns of ball clay P, ball clay B and china clay respectively, which were ground for different lengths of time. In Fig. 1, the XRD of the ground sample of ball clay

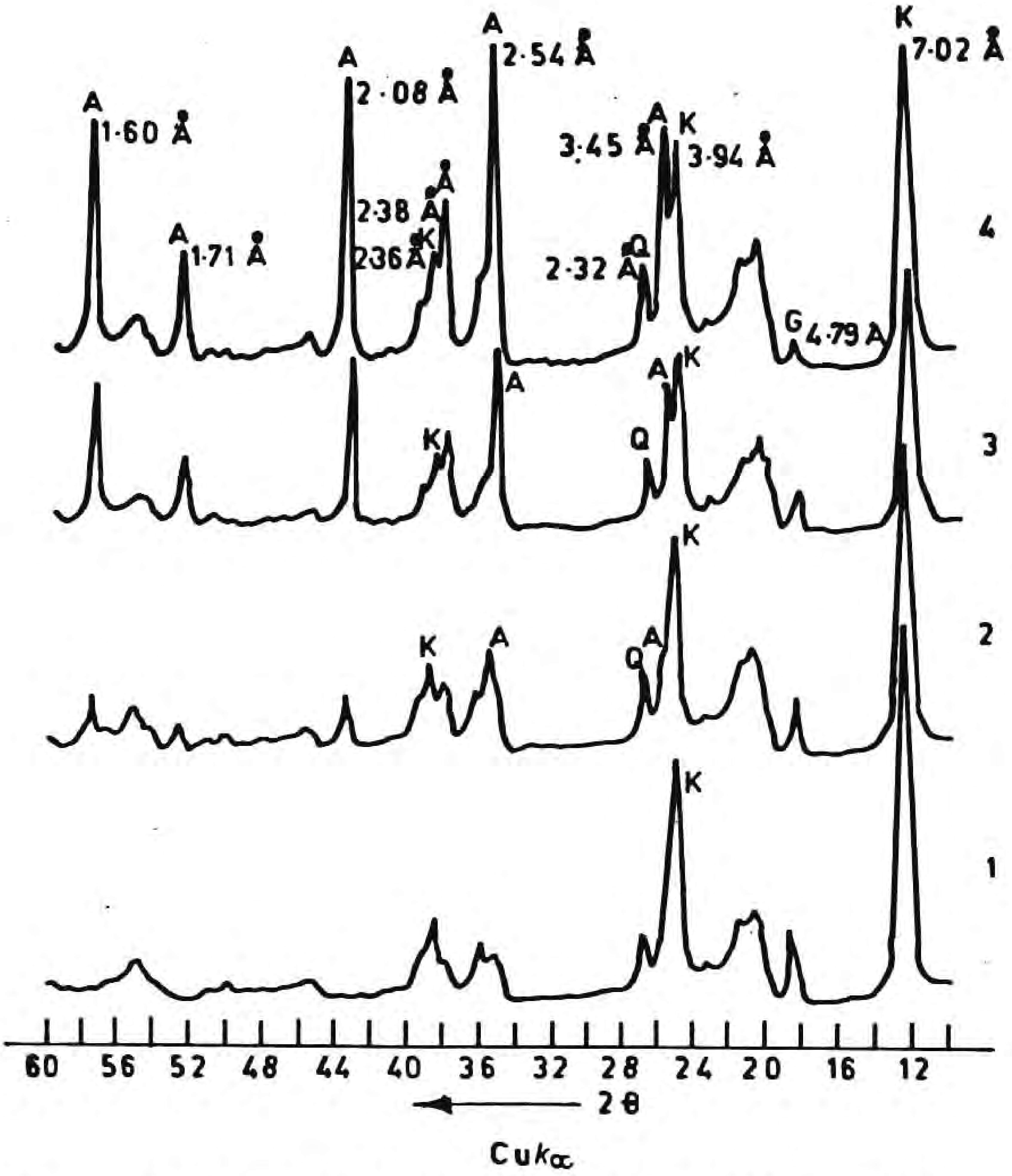


Fig. 1. XRD patterns of ground ball clay (P)

1- 0 hrs , 2 - 2 hrs , 3 - 5 hrs 4 - 10hrs

G. GIBBSITE, K. KAOLINITE, Q. QUARTZ, A. ALUMINA

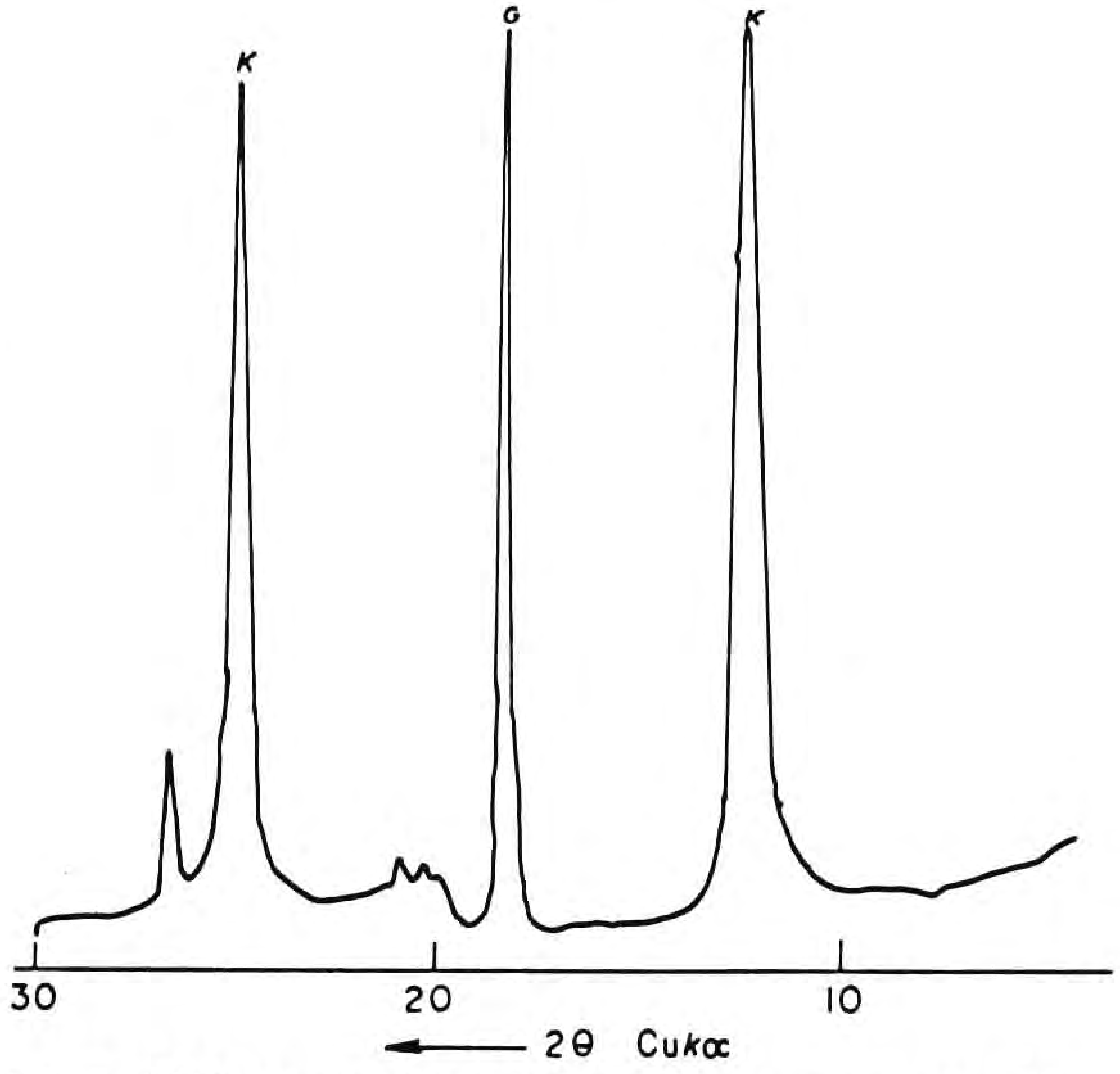


Fig. 2. XRD pattern of oriented aggregate of ball clay(P)

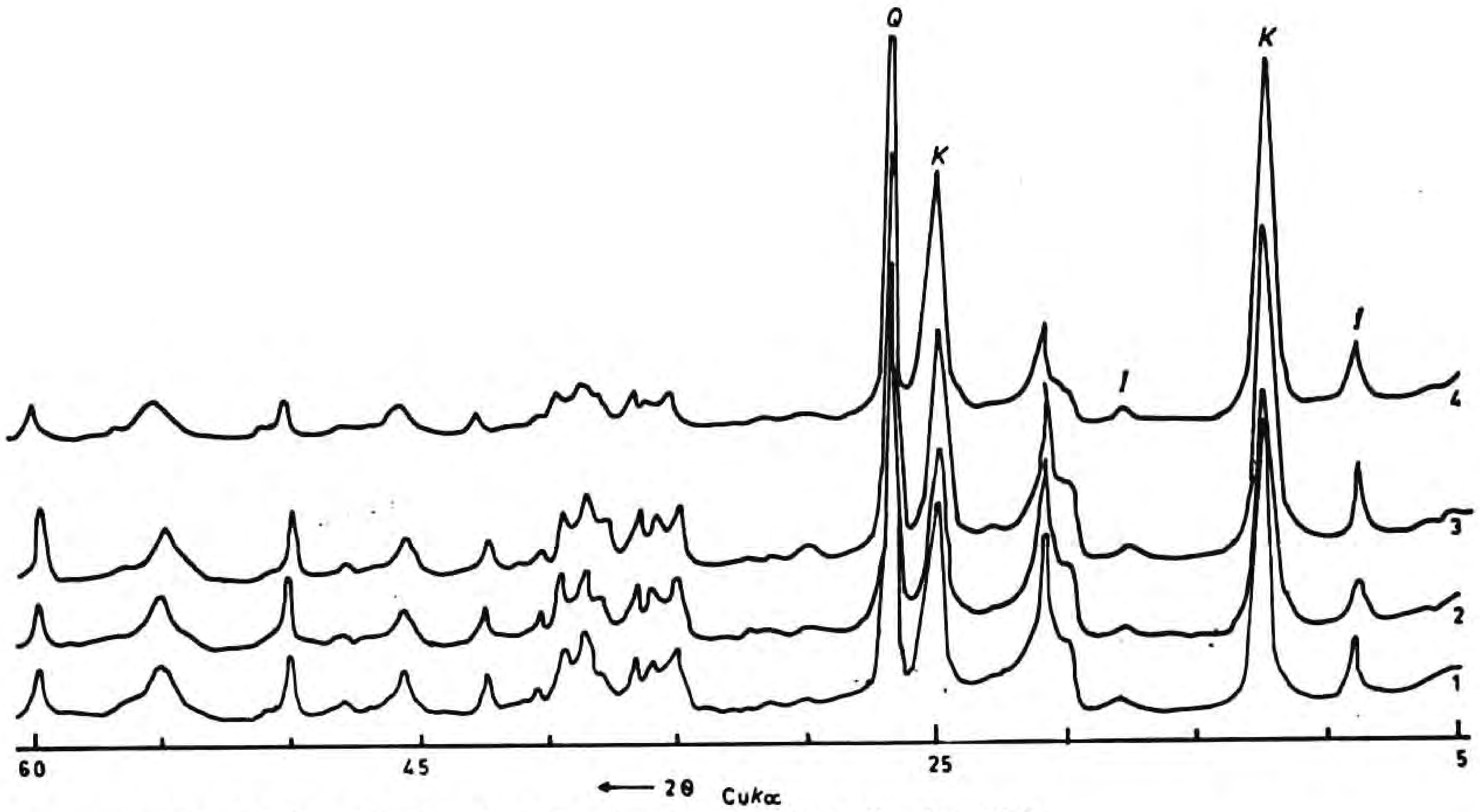


Fig. 3. XRD patterns of ground samples of ball clay (B)

1-0 hrs, 2-2 hrs, 3-5 hrs, 4-10 hrs.

I - ILLITE, K - KAOLINITE, Q - QUARTZ

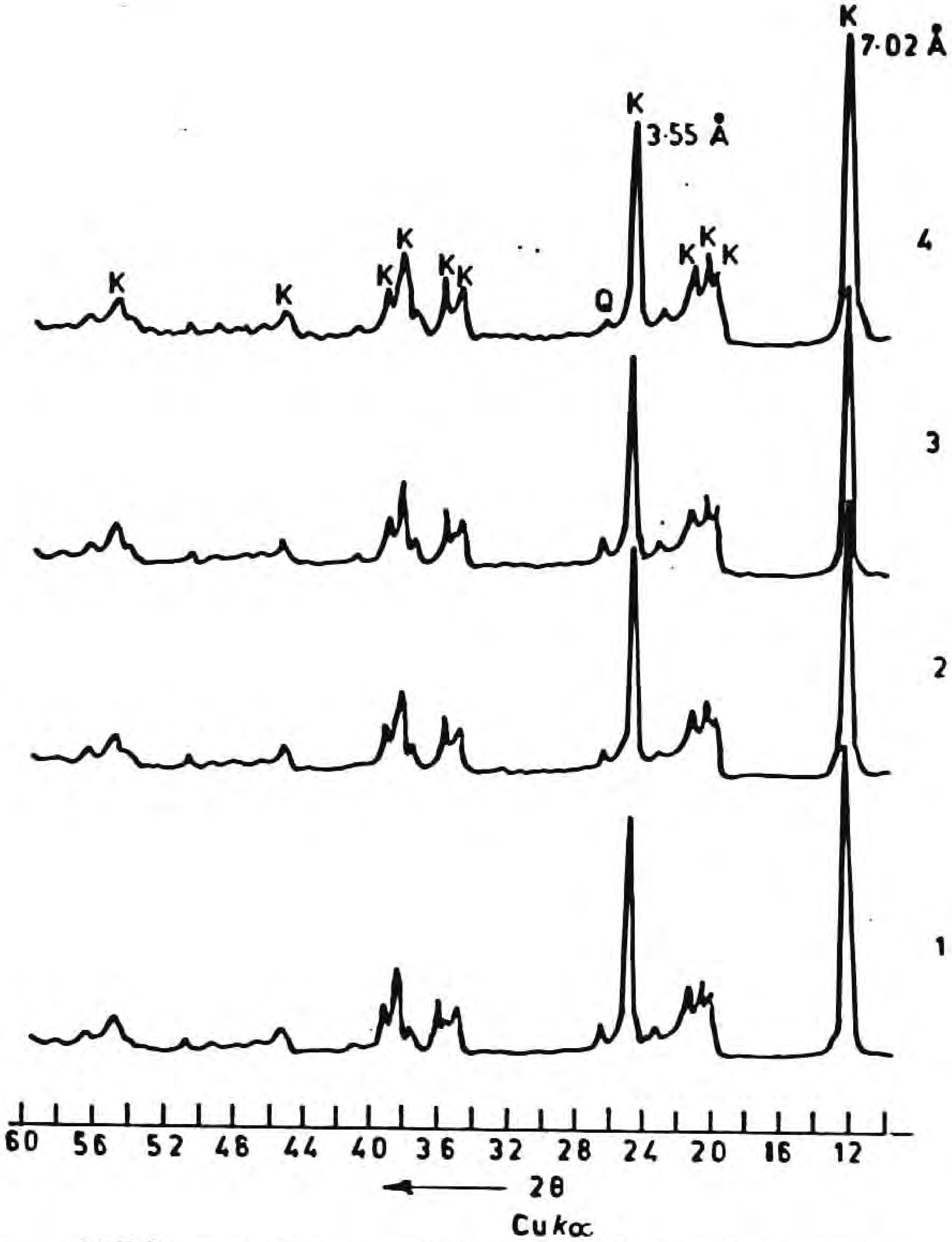


Fig.4. XRD patterns of ground china clay (T)

1-0hrs , 2-2 hrs , 3-5hrs , 4-10 hrs

K - KAOLINITE, Q- QUARTZ

P (1) shows the presence of kaolinite, gibbsite and quartz. Curves 2-4 correspond to the XRD patterns of the samples ground for 2, 5 and 10 hrs respectively. With grinding it is noticed that new reflections appear at d-values 3.46 A^o, 2.54 A^o, 2.08 A^o and 1.66 A^o indicating the formation of a new phase. These reflections increase in intensity with increase in grinding time. Simultaneously, a gradual reduction in the intensity of reflection corresponding to gibbsite at 4.79 A^o has also been noticed. Based on the X-ray characteristics, the new phase has been identified to be α -alumina (corundum) (Powder Diffraction File No. 10-173). It is known that heat treatment of gibbsite gives rise to α -alumina (Brindley and Brown, 1980). For crystals finer than 1 μm, the following reaction is envisaged.

$$\text{Gibbsite} \xrightarrow{270\text{-}800^{o}C} \chi\text{-}Al_2O_3 \xrightarrow{800\text{-}1200^{o}C} k\text{-}Al_2O_3 \xrightarrow{1200^{o}C} \alpha\text{-}Al_2O_3$$

Since wet grinding also has resulted in a similar finding it is possible that the inside of the gibbsite crystals might have experienced a similar hydrothermal condition during this process. It is possible that the alumina formed may have been derived from the grinding medium since alumina balls were used for grinding. In order to verify this, 300 g of quartz was ground for 5 hrs under identical conditions and the product was studied by X-ray diffraction. The XRD pattern (Fig. 5) of ground quartz shows the reflections of quartz only and does not show any reflections of alumina. Hence it can be concluded that it is the presence of gibbsite which is responsible for

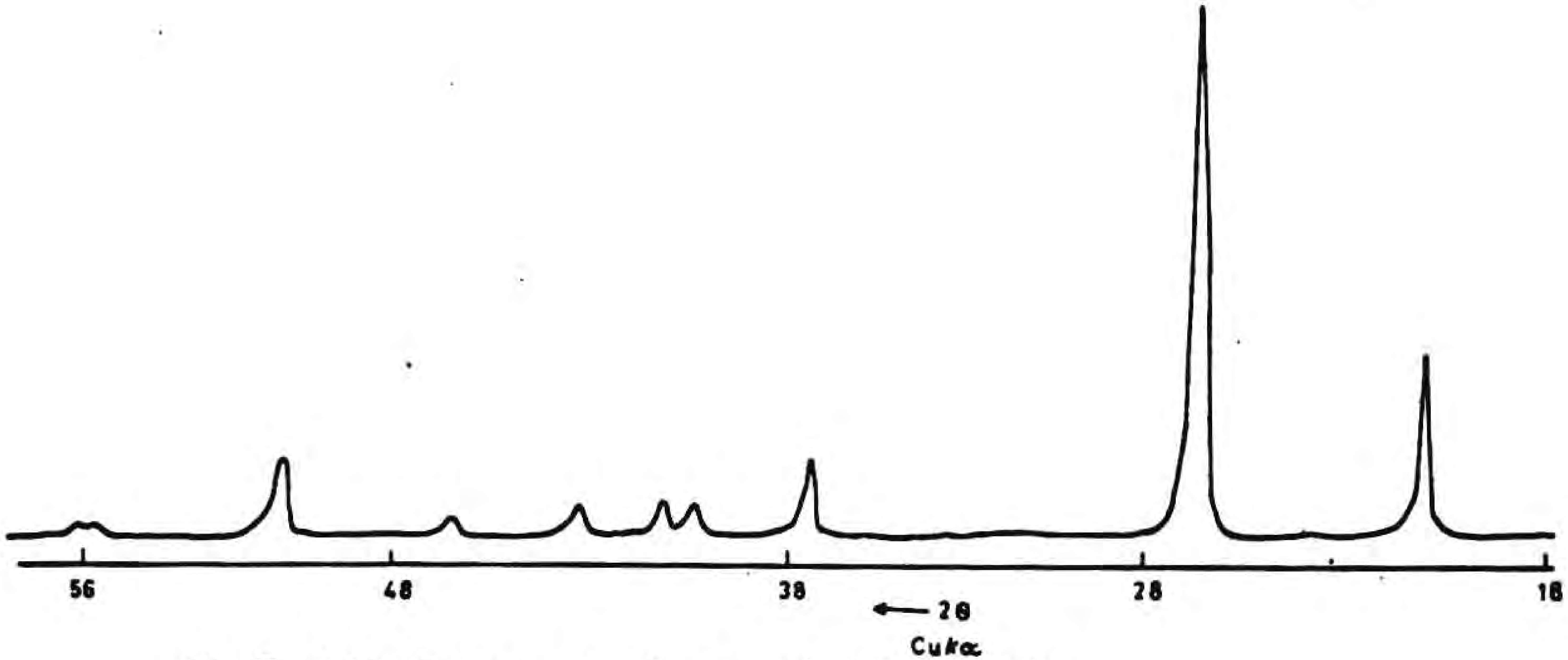


Fig 5. XRD Pattern of Quartz ground for 5 hrs.

the formation of α -alumina during the grinding of ball clay from Padappakkara.

Bikaneer clay contains mica and quartz as impurities along with kaolinite which is the major constituent. The XRD patterns (Fig. 3) show that the intensity of quartz reflections decreases during grinding. This may be due to the partial loss of crystallinity of silica. However, the kaolinite reflections are not affected during grinding. It is observed that, apart from the loss in crystallinity of quartz, no significant change has taken place during this wet grinding. It is worth indicating that there is no new phase formation during grinding of the Bikaneer clay. Also, in the case of china clay, wet grinding for 10 hrs did not show any loss of crystallinity or phase changes.

5.4 EFFECT OF OTHER PROPERTIES ON GRINDING

5.4.1 Particle size

Many of the properties of ceramic materials are dependant upon the particle size and size distribution of the minerals which are present. Table 3 shows the particle size distribution analysis of the ground samples at different intervals. It is worth noting that the average particle size decreases from 0.27 to 0.17 µm in the case of Padappakkara clay, from 2 to 1.3 µm in the case of China clay T.

5.4.2 Plasticity

Plasticity was measured in terms of Atterberg Number and water of plasticity. Table 4 indicates the variation of plasticity with

Table 3: Particle size distribution analysis

Particle size	Ball clay-P				Ball clay-B				China clay-T			
	0 hr	2 hrs	5 hrs	10 hrs	0 hr	2 hrs	5 hrs	10 hrs	0 hr	2 hrs	5 hrs	10 hrs
Coarser than 25 μ	0	1	0	0	2	0	0	0	0	0	0	0
25-15 μ	3	4.5	2	1	6	2	3	1.5	0	0	0	0
15-10 μ	2	6.5	1.5	2.5	7	4	5	3.5	1	1	0	0
10-5 μ	75	8	2.5	3	15	11.5	15	11	5	3	2	1
5-3 μ	4	4	1	3.5	10	10.5	8	10	10	10	1	2
3-2 μ	45	3.5	3	2	10	12	10	12	21	9	4	2
2-1 μ	6	4.5	3	4	25	28	27.5	27	58	81	85	86
Finer than 1 μ	73	69	88.5	85	25	32	31.5	35	5	6	8	9
Average particle size μ	0.27	0.25	0.175	0.16	2	1.45	1.5	1.3	1.75	1.45	1.15	0.89

Table 4

Effect of grinding on plasticity

Property	Time of grinding (hrs)	Ball clay (P)	Ball clay (B)	China clay (T)
Atterberg number	0	65-67	24	33
	2	44	18	34
	5	38	16	38-39
	10	16	19	39
Water of Plasticity (%)	0	46	30	35
	2	45	35	47
	5	35	34	42
	10	18	36	45

grinding of the clay samples. It is evident from the table that the Atterberg number as well as plasticity increase with grinding time in the case of gibbsitic ball clay P.

In the case of Bikaneer ball clay, the Atterberg Number was found to decrease only to a small extent. Water of plasticity showed a 5-6% increase. In the case of china clay, there is a gradual increase in Atterberg number as well as water of plasticity, as usually expected in the case of pure kaolinite (Herman and Marcus, 1961).

The decrease in the Atterberg number as well as water of plasticity in the case of ball clay P indirectly suggests the formation of new phases during grinding. The non-plastic nature of the new phase formed may be responsible for the low Atterberg number and plasticity of Padappakkara clay during grinding.

5.4.3 Cation exchange capacity

Clay particles dispersed in water carry a negative charge due to isomorphous substitution in the structural lattice of the clay (Ryan and Radford, 1987). The broken bonds around the edges of silica-alumina units formed during grinding give rise to unsatisfied charges which could be balanced by adsorbed cations (Lalithambika et al. 1991). Table 5 indicates the variation of CEC with grinding time.

With grinding, the cation exchange capacity varies with the type of changes taken place in matrix. Kaolinite particles are split into thinner platelets causing an increase in the amount of fraction finer than 1 μm and thereby increasing the surface area. This is indicated by the increase in

Table 5

Variation of Cation Exchange Capacity with grinding time

	Grinding time (hrs)	CEC me/100 gm
Ball clay-P	0	12
	10	2
Ball clay-B	0	9
	10	12
China clay-T	0	5
	10	13

CEC in the case of ball clay B and china clay T. In the case of ball clay P, the formation of α-alumina may be responsible for the considerable decrease in cation exchange capacity.

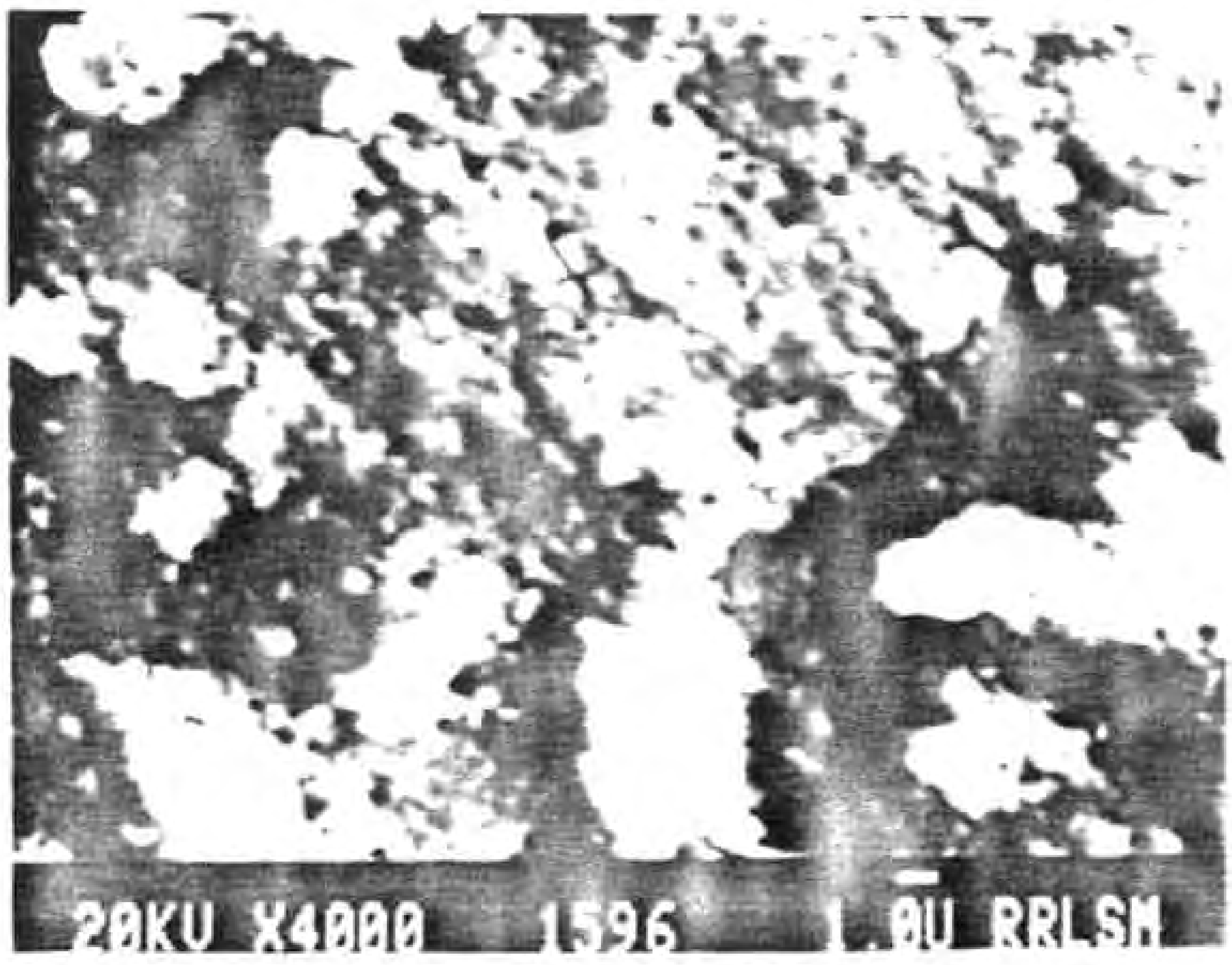
5.4.4 Morphology

The evidence for the morphological variation with grinding was obtained by scanning electrion microscopy (SEM). The SEM pictures of ball clay P and china clay T ground for 2, 5 and 10 hrs are shown in Figs. 6 and 7. The samples were prepared after dispersing in acetone. The shape of the crystals indicates that these samples are disordered kaolinites since the characteristic psuedohexagonal geometry of the individual platelets are not seen. The decrease in particle size due to grinding can be clearly seen from the micrographs. However, the alumina crystals cannot be distinguished from the kaolinite in Figs. 6b and 6c. Similar size reduction was observed in the case of ball clay B, and for this reason, the micrographs are not given.

5.5 SUMMARY

Grinding of kaolinitic clays results in the variation of properties such as particle size, plasticity, Atterberg number and cation exchange capacity. The presence of gibbsite as an impurity in ball clay from Padappakkara is conclusively found to be responsible for the formation of the new phase α-alumina. The finding is interestin g as this indicates the formation of a high temperature phase by wet grinding.

Fig. VI: Scanning electron micrographs of ball clay-P
1-0 hrs ground, 2.5 hrs ground, 3-10 hrs ground



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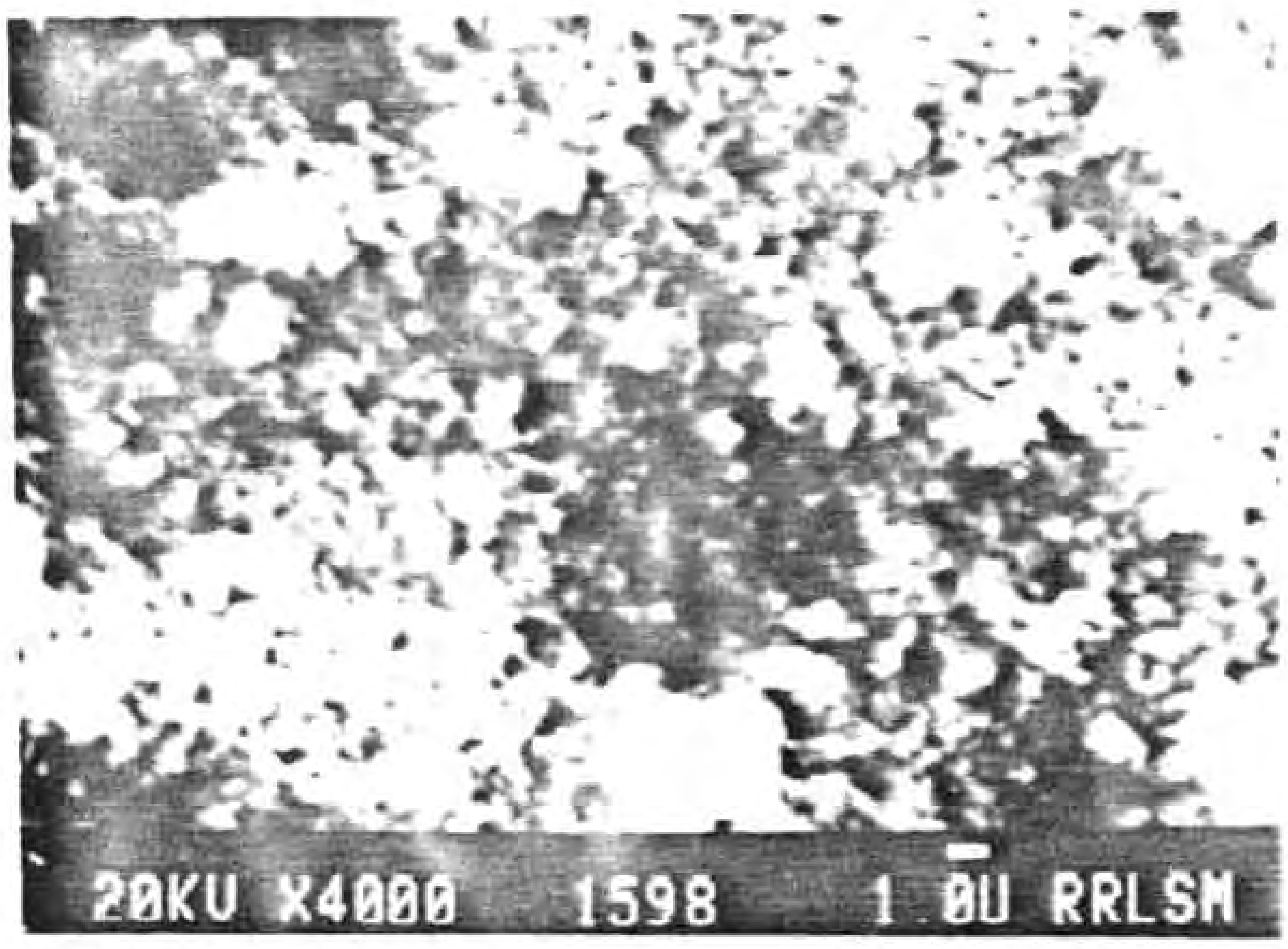

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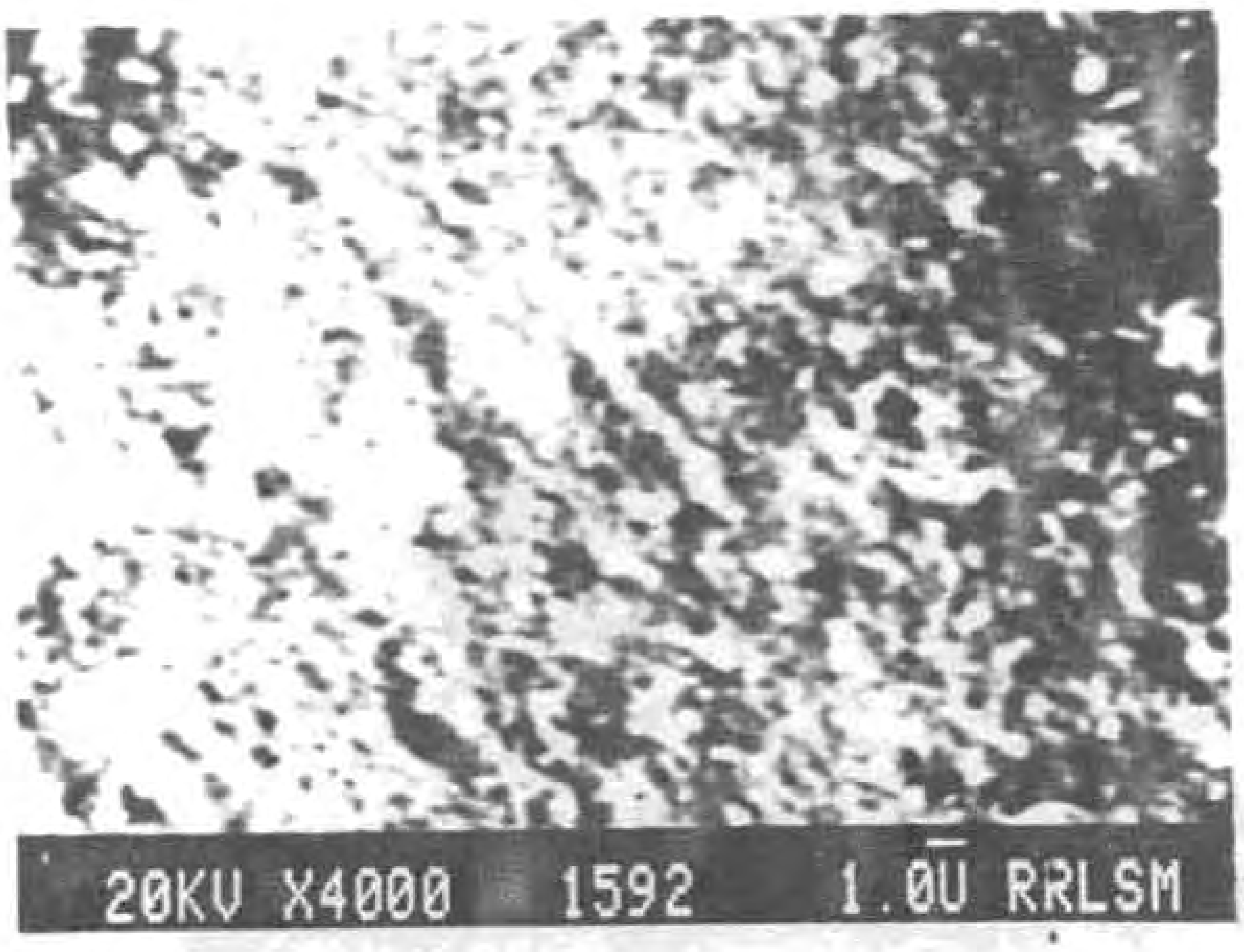

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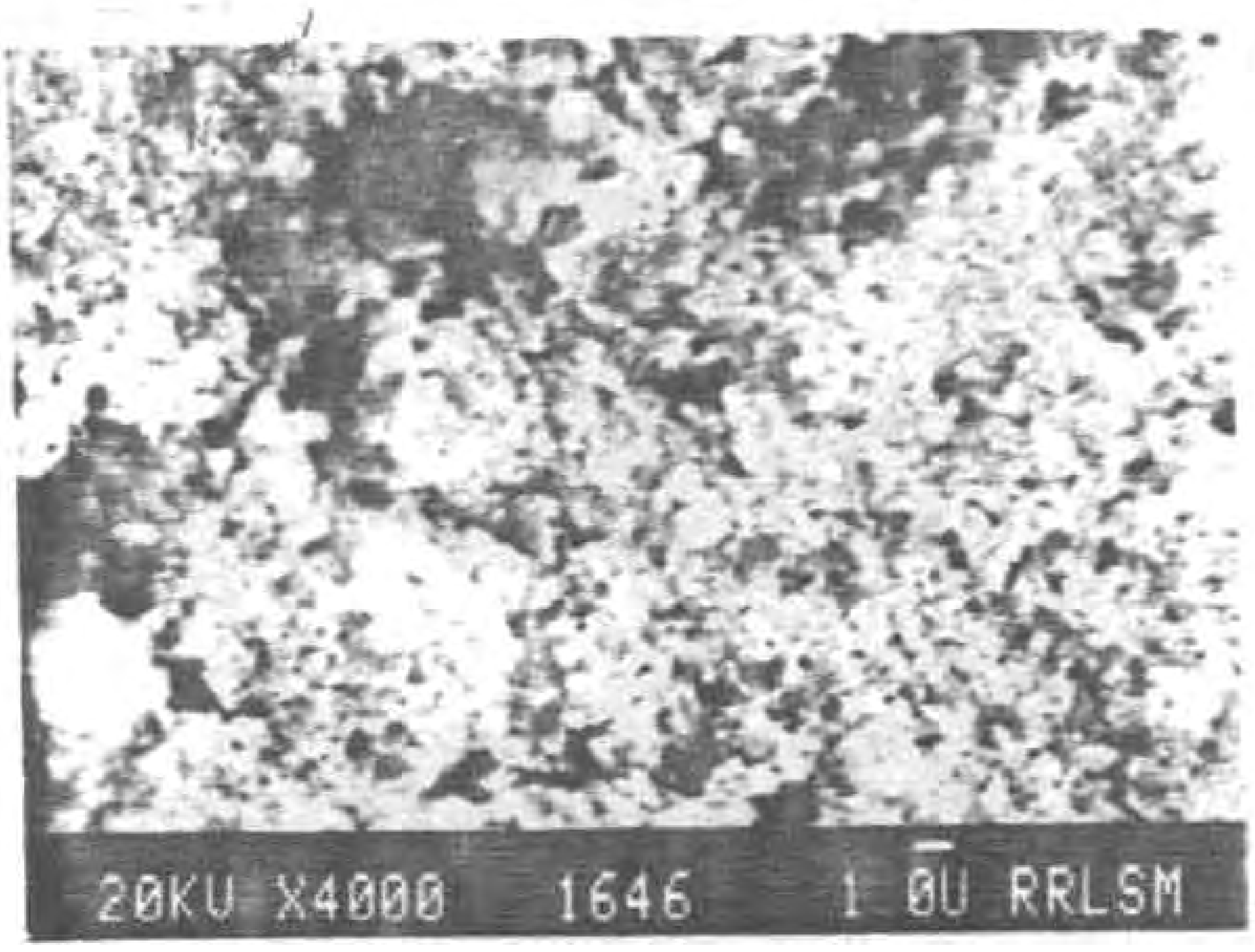
Fig. VII: Scanning electron micrographs of china clay-T
1-0 hrs ground, 2-5 hrs ground, 3-10 hrs ground



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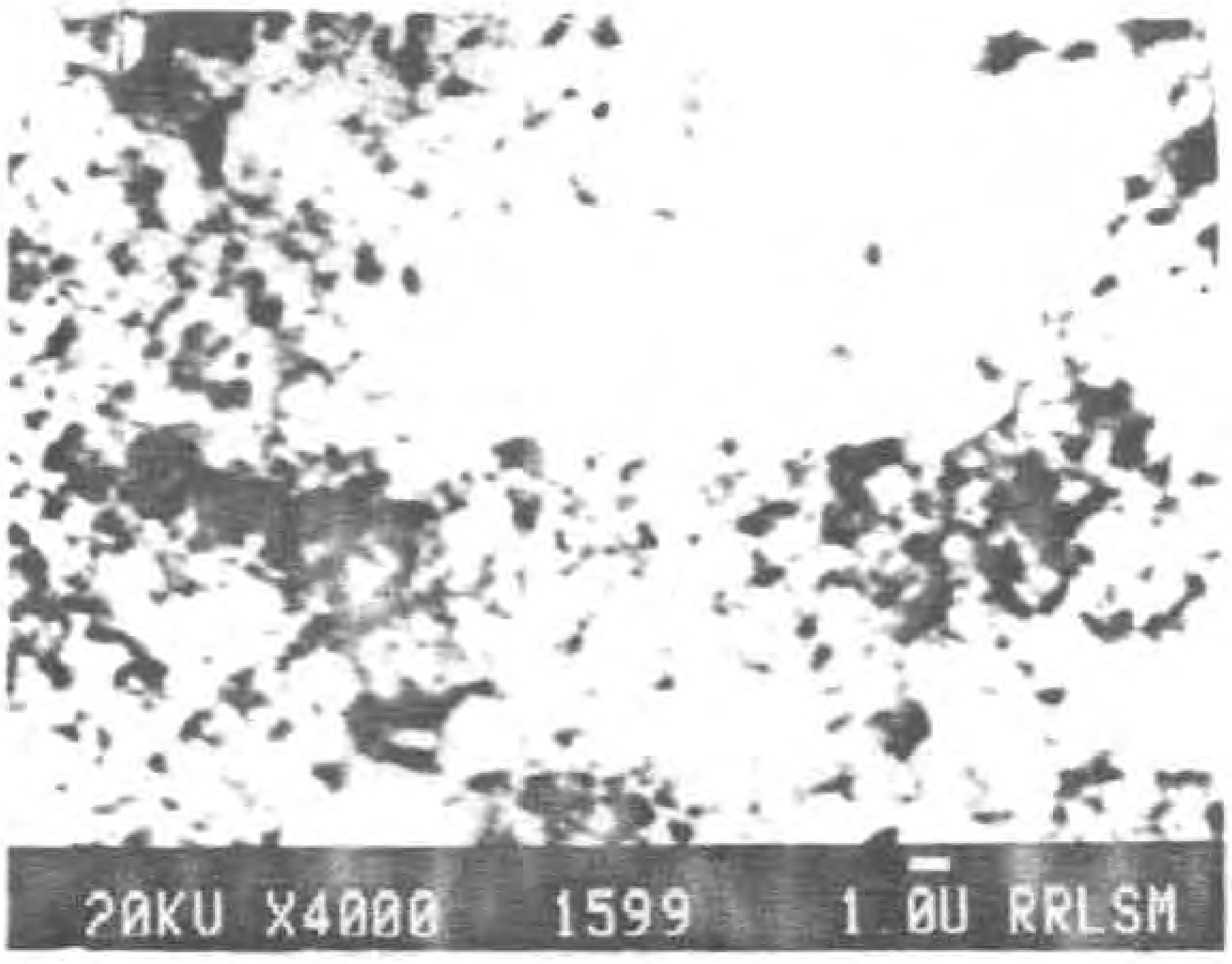

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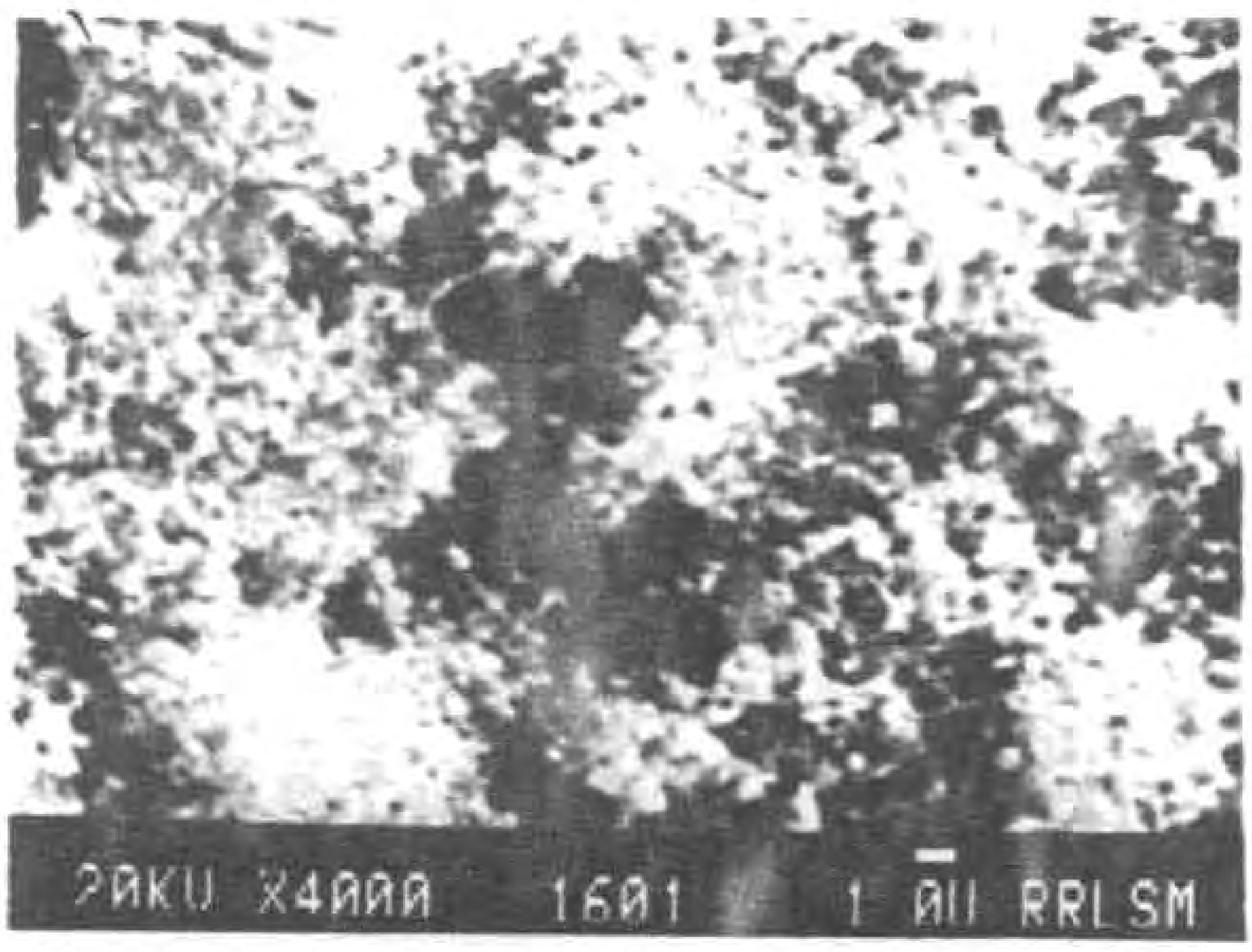

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CHAPTER VI

SINTERING STUDIES ON PLASTIC CLAYS

6.1 GENERAL

Plastic clays are essential ingredients for ceramic body manufacture as binding agents for imparting plasticity, workability and green strength to raw materials. They are dominantly kaolinitic with low mica and quartz contents and they frequently contain appreciable quantities of carbonaceous matter which acts as a protective colloid in the production of clay water slips. Ball clays adjusted for lower carbon content and coarser particles size are used where faster firing and casting are required.

There are two entirely distinct phenomena occurring in clays heated at high temperatures. These are crystal formations due to the recombination and recrystallisation reactions and liquid formation. The latter may crystallise on cooling, but siliceous melts are prone to super cooling and often freeze to a homogeneous glass or a partially crystallised system (Searle and Grimshaw, 1960). It has been shown that mullite-corundum refractories can be made from kaolins (Davydov et al., 1979) by briquetting and heating at 1750°C for 10 hrs. These refractories were used for air-heater walls and hot air blowing pipes. In 1979, Jovani studied the scanning electron microscopic features of the refractory ceramic pastes and of the mullite formed in them. He reported that at ordinary pressures, mullite is the only compound of Al and Si.

6.1.1 Changes in composition of heating clays

One of the most important steps in the manufacture of clay based products, especially refractories is the firing process, in which the raw clay is altered into a vitreous mass (Norton, 1949). The steps occurring in the process are also important since the proper heat treatment of a clay will give the greatest efficiency in firing and the most satisfactory finished product. These reactions can be summarised as follows:

1. Loss of hygroscopic and hydrate water
2. Decomposition reactions
3. Reforming reactions
4. Liquid formation

The loss of hygroscopic water is usually complete at a temperature of about 100° C (Searle and Grimshaw, 1960). The amount liberated depends largely on the fineness of grain-size of the minerals in the clay, because the moisture is associated with the surface area. Decomposition of clays mainly include oxidation and reduction processes. For example, kaolinite clay minerals decomposes at 415-560°C. Both recrystallisation and recombination reactions take place in the matrix. In recrystallisation reactions, the individual oxides undergo atomic transformations to form crystalline compounds whereas the recombinations occur between two or more of the amorphous or crystallised components of heated clays. Kaolinite dissociates at 550°C to an intimate association of amorphous alumina and silica. At 980°C, it goes to recrystallisation. The best known reaction in clay systems is the combination of alumina with silica to form mullite as

$$\underset{\text{alumina}}{3\ Al_2O_3} + \underset{\text{silica}}{2\ SiO_2} \xrightarrow{\text{starts at } 920^{\circ}C} \underset{\text{mullite}}{3\ Al_2O_3 \cdot 2\ SiO_2}$$

It has been proved that in pure kaolinite, crystals of mullite develops at 980° C onwards. The excess silica recrystallises from an amorphous form to either cristobalite or tridymite (Comefero et al., 1948). Navias (1925) reported that the theoretical amounts of mullite were formed in all cases when a range of ball clays were fired to cone 10 and it is always the principal crystalline component of fired alumino silicates . Liquid formation in clays commences at the temperature of the lowest eutectic point of the components in the mixture. Alkali-bearing minerals or clays with a high flux content begin to fuse at low temperatures. These minerals are of frequent occurrence in clays and the particle size of this component largely determines the vitrification rate at a particular temperature. The rate at which the temperature rises affects the amount of liquid formation and the time at which the maximum temperature of heating is maintained determines the uniformity of the product (Grimshaw and Searle, 1960).

6.2 INTRODUCTION

The effect of sintering of a body mainly depends on the rate of heating and the soaking period. Vitrification of the body will cause shrinkage and distortion which would occur in firing and hence it is seldom desirable to produce a product directly from a raw plastic clay. The amount of pore space in a ceramic material whether green or fired has a far reaching effect on its properties. Hence the vitrification characteristics of a ceramic material or body may be determined by measuring the apparent porosity or water absorption on samples fired at different temperatures (Ryan and Redford, 1987). Shrinkage of the shaped ceramic article occurs during the drying and firing stages of manufacture. The extent of these contractions is important since if they are allowed to occur too rapidly, cracking or distortion will take place besides the fact that the size of the finished product depend on their values. The modulus of rupture (MOR) of the fired body is measured on rods made by extrusion, dust pressing or slip casting. The body is always fired according to the production schedules. Any variation in raw materials, material treatment such as grinding, slip control etc. and variation in firing schedule and temperature can bring in changes in properties of the finished products. The aim of the study on sintering is to determine the relationships between raw material characteristics and the phase composition on the physical properties of the fired samples.

The properties of the fired samples such as water absorption, linear shrinkage and MOR are determined and correlation of the strength of the sintered material with the microstructure is attempted. The observed variation in the properties is explained as a function of mineralogy, crystallinity and the amount and nature of the impurities present in the clays. The investigation of the raw material was carried out by classical wet chemical methods. The XRD patterns were obtained by means of a Philips 1710 diffractometer using Ni filtered CuK α radiation with a scanning range (2θ) of 5-60°. Water absorption, shrinkage and MOR were determined according to the standard procedure (Indian Standards 1528, 1974). Test rods for the above studies were prepared by mixing a 100 mesh fraction of the sample with 50% quartz (150 μm) and made into a soft mass by adding water. This was kept for ageing for 24 hrs. The test rods of about 7 cm length and 1 cm diameter were prepared with an extruder fabricated in the laboratory (no vacuum applied) and were fired in an electric muffle furnace at 1300°C at a heating rate of 200°C/hr with a soaking period of 1 hr. The samples were subjected to natural cooling inside the furnace. Measurements of MOR were made using an Instron 1195 Universal Testing Machine. Samples fired at 1300°C were polished and etched in 1% HF for 1 minute and were used for SEM studies using a JEOL scanning electron microscope.

The samples taken for the studies are ball clays from Padappakkara (A), Payyangadi (B), Bikaneer (C), Bimadole (D), Than (E), Westerwald (F) and Inagaki-kibushi (G). The mineralogical details of these clays are published elsewhere (Kshama et al., 1990).

6.3 PROPERTIES OF THE SINTERED BODIES

6.3.1 Correlation of the raw materials with their fired properties

It is known that the effect of weathering (Fischer, 1983) as well as the mineralogical composition of the raw clay samples (Chernyak and Gontmakher, 1980) influence the physical properties of the sintered samples. Hence a preliminary investigation on the raw materials was carried out to get a better picture of the properties of the sintered bodies.

The general characteristics and the chemical analysis of the raw materials are presented in Tables 1 and 2 respectively. Compositionally these plastic clays differ significantly. They can be divided into two groups (a) silica rich and (b) alumina rich. The Clays, C, D, F and G have high silica contents varying from 52% to 64% and lower percentages of alumina, 21.2 - 29.65%. Clays A, B and E are rich in alumina with Al_2O_3 and SiO_2 contents varying from 36.15 to 29.07% and 48.69 to 43.98% respectively. Mineralogically all the clays are mainly kaolinitic with minor amounts of quartz, gibbsite, pyrite, mica and illite. In all the clays quartz is the major accessory mineral. Clay A contains gibbsite and pyrite in addition to kaolinite and quartz. It is also seen that clays A and B contain a high humus content. Clays C and F are also kaolinitic with illite and quartz as accessory minerals. The results of the mineralogical analysis of the clays are given in Table 3.

Westerwald clay (F) contains illite without any appreciable content of organic matter (LOI only 7.5%). Kibushi clay is a detrital clay containing lignite fragments. It is an industrially important material which comprises a large quantity of very fine kaolinite particles having colloidal properties. A base material made from this clay has good workability (Geol. Survey of Japan, 1960). This clay often contains humus ($\sim$ 0.25%) which has an advantageous effect on its green strength.

Table 1: General characteristics of the clay samples

Sample	Raw colour, general observation
A (Padappakkara, India)	Greyish lump with visible impurities
B (Payyangadi, India)	Dark grey coloured with large fraction of impurities
C (Bikaneer, India)	Light cream coloured with no visible impurities
D (Bimadole, India)	Cream coloured with no visible impurities
E (Than, India)	Dark greyish with visible impurities
F (Westerwald, W. germany)	Cream coloured powder with no visible impurities
G (Inagaki-kibushi, Japan)	Greyish coloured with visible impurities

Table 2: Chemical composition of plastic clays

Constituent	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	TiO_2 %	Na_2O %	K_2O %	CaO %	MgO %	LOI %	Flux content %
A	43.98	36.15	2.09	2.51	0.62	0.39	0.06	0.09	14.94	5.76
B	48.05	26.07	2.99	1.48	0.82	1.16	0.07	0.09	18.1	6.61
C	52.16	29.65	1.08	1.07	1.41	2.78	0.03	0.04	12.04	6.41
D	55.98	28.81	1..17	0.38	0.72	2.45	0.01	0.07	10.05	4.8
E	48.69	30.01	2.96	1.29	0.82	0.41	0.07	0.02	15.12	5.07
F	60.17	26.82	0.63	1.42	0.68	2.3	0.3	0.34	7.5	5.67
G	64.01	21.2	1.2	1.3	1.03	1.93	0.06	trace	9.5	2.96

Table 3: The mineral constituents in the plastic clay

Sample	Principal clay mineral	Accessory mineral	
		Major	Minor
A	Kaolinite	Quartz	Gibbsite, Pyrite
B	Kaolinite	Quartz	Pyrite
C	Kaolinite	Quartz	Illite
D	Kaolinite	Quartz	-
E	Kaolinite	Quartz	-
F	Kaolinite	Quartz	Illite
G	Kaolinite	Quartz	-

Its content of coarse grained materials is relatively low and hence it is used without refining in many cases. The mineralogical composition arrived at by rational analysis also indicated that the major mineral constituent of all clays is kaolinite. Fig. 1 indicates the particle size distribution. Sample A was found to have the maximum percentage of fine particles. The particle size < 2 μm of A, B, C, D, E, F and G are 89, 64, 76, 61, 82, 82 and 68% respectively. The Bimadole clay (D) was found to have the lowest percentage of fines. Since the crystallinity of a given clay mineral has an important bearing in the sintering characteristics of the clay a correlation of the sintered properties with crystallinity was also attempted (Wilson, 1987).

The dimensional changes taking place during firing process depend on mineralogical composition, drying and firing condition. The overall structure of fired products is mostly an amorphous-glassy matrix throughout which primary minerals, neoformation crystals and pores are dispersed (Nosbusch and Mitchell, 1988). Table 4 indicates the properties after firing. Samples A, B and F have higher values ranging from 5.4% to 6.36%. The higher values of A, B and F may be due to the higher amounts of organic and inorganic impurities in A and B and the presence of illite in sample F. The values of shrinkage of all clays, however, are within the range of industrial clays (Spinks Clay Data Book). It is also evident from Table 4 that sample A has maximum porosity. A comparison of porosity and particle size distribution indicated that samples with higher porosity,

i.e. A and E,

have higher percentages of finer particles (Fig. 1). This indicated

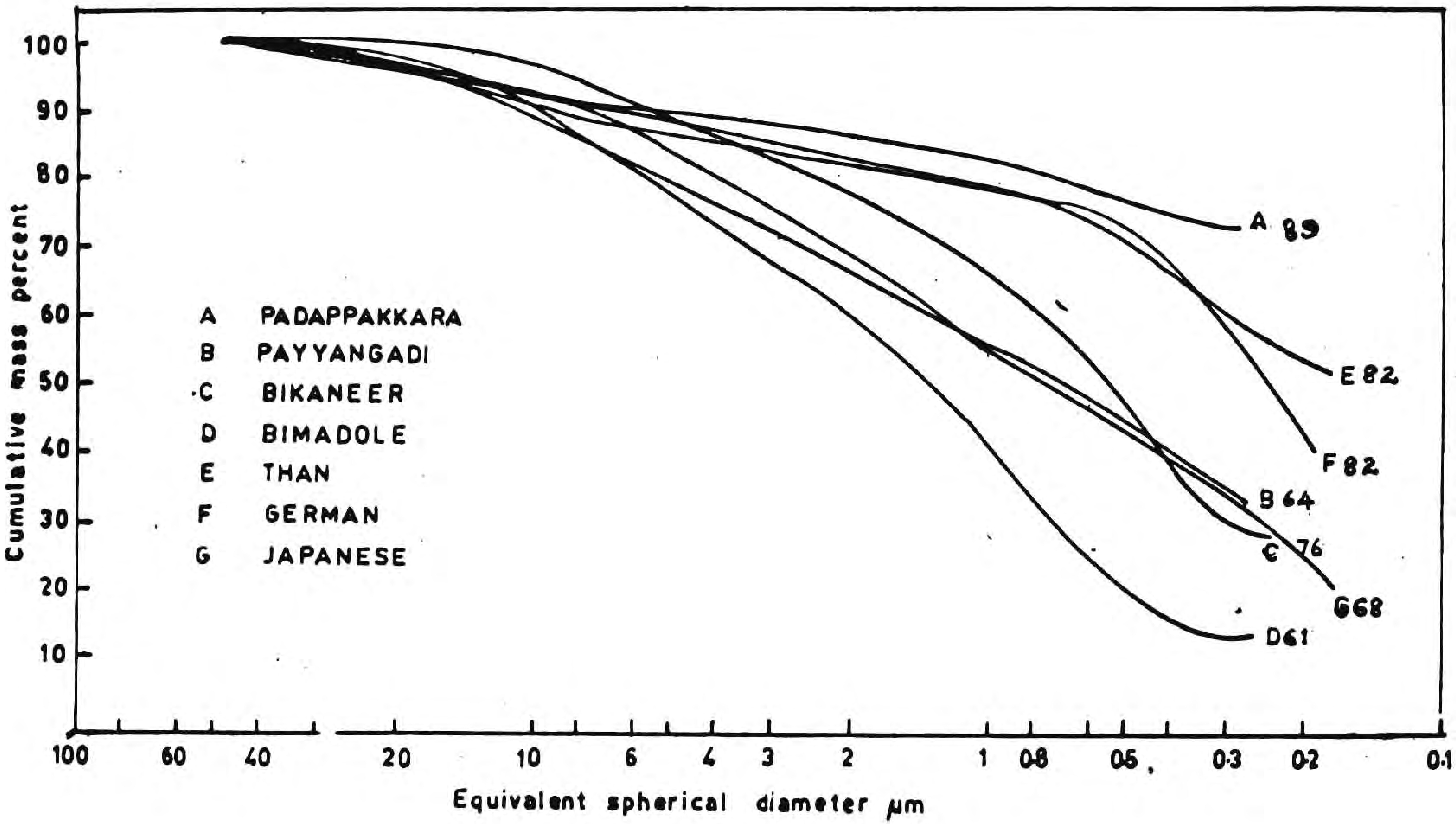


Fig.1. Particle size distribution

Table 4: Properties of fired ball clays* ($1300^{\circ}C$)
(in the decreasing order of crystallinity of the raw material)

Sample	Linear shrinkage (%)	Water absorption (%)	MOR Kg/cm^2
D	5.54	12.71	287
B	7.27	14.95	272
G	5.4	10.1	434
C	5.88	10.83	377
F	7.28	12.1	310
E	6.36	6.36	214
A	9·0	16.9	210

*50% sample + 50% quartz

that a material with a wider particle size distribution is compacted better compared to samples of very fine or coarse particles. The porosity is also a function of fluxes contained in clays. The flux content in the ball clays under investigation was found to vary in the range 2.96-6.6%. The lowest flux content was found with Japanese clay (G) and the highest with Payyangadi (B). It is seen that sample A has the maximum water absorption and sample G has the least. This could be explained by the percentages of alumina content in the original raw materials. The former contains 36% alumina and the latter 21%. It is thus evident that the alumina content plays an appreciable role in the process of sintering although total flux content is also responsible for the densification.

Fig. 2 shows the X-ray patterns of the clays sintered at 1300^{o}C at a rate of 200^{o}C/hr with a soaking period of 1 hr. In clay A, maximimum mullite and cristobalite formation is seen. The cristobalite formation is least, in Westerwald clay (F). Sample G shows prominent peaks of cristobalite but the lowest mullite content is found in this sample. The distribution of phases in the sintered matrix is given in Table 5.

6.3.2 Effect of crystallinity and microstructure

The crystallinity indices calculated by Hinckley's method are 0.5, 0.75, 0.85, 0.97, 0.59, 0.66 and 0.75 for samples A, B, C, D, E, F and G respectively (Brindley and Brown, 1980). On correlating this parameter with MOR it is observed that there is no linear relationship with MOR which is a measure of the strength of the

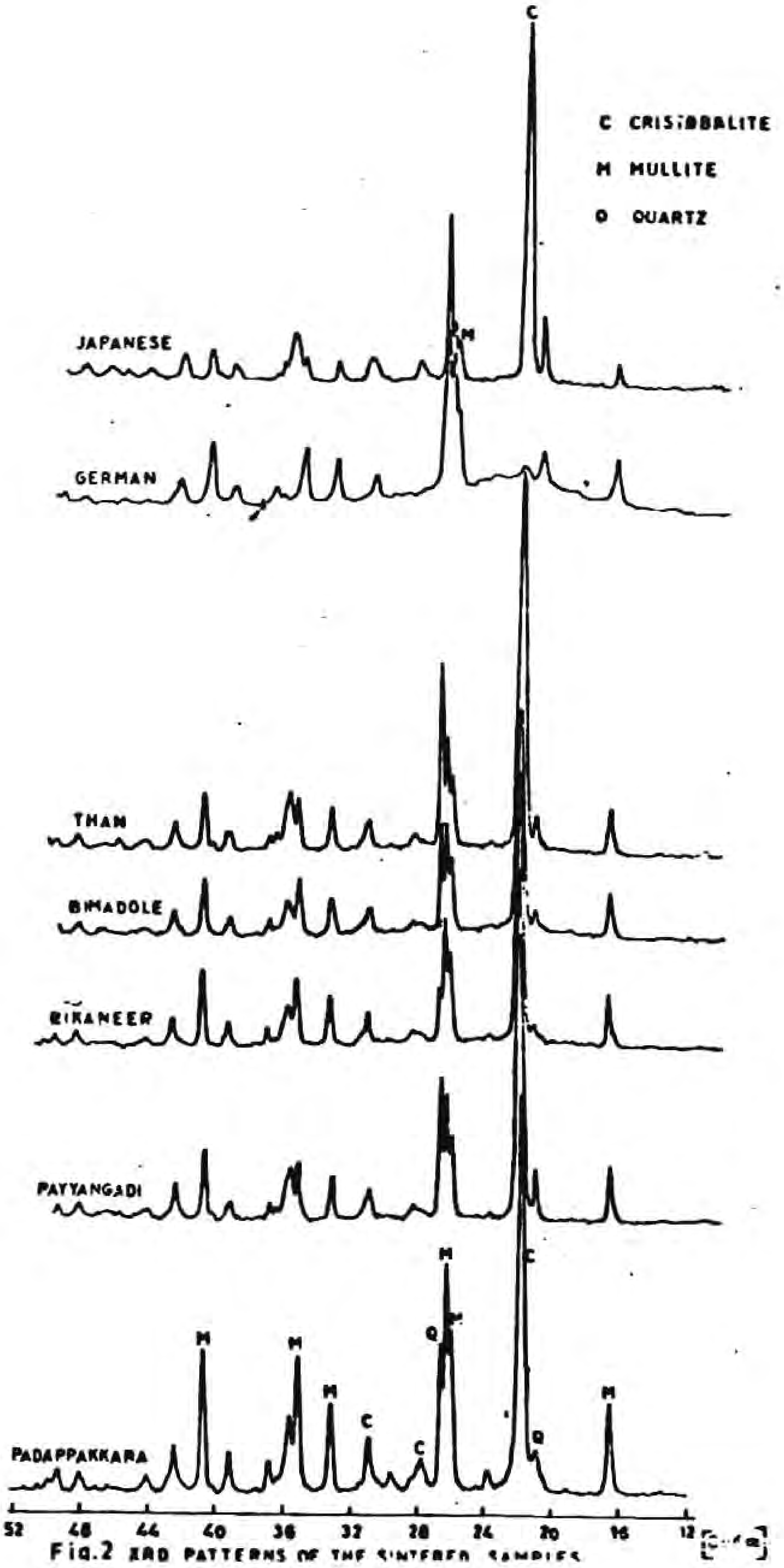


Fig.2 XRD PATTERNS OF THE SINTERED SAMPLES

Table 5: Distribution of phases in the sintered matrix

Sample	Mullite	Cristobalite	Quartz
A	m	M	m
B	m	M	m
C	m	M	m
D	m	M	m
E	m	M	m
F	M	m	M
G	m	M	m

M - Major m - minor

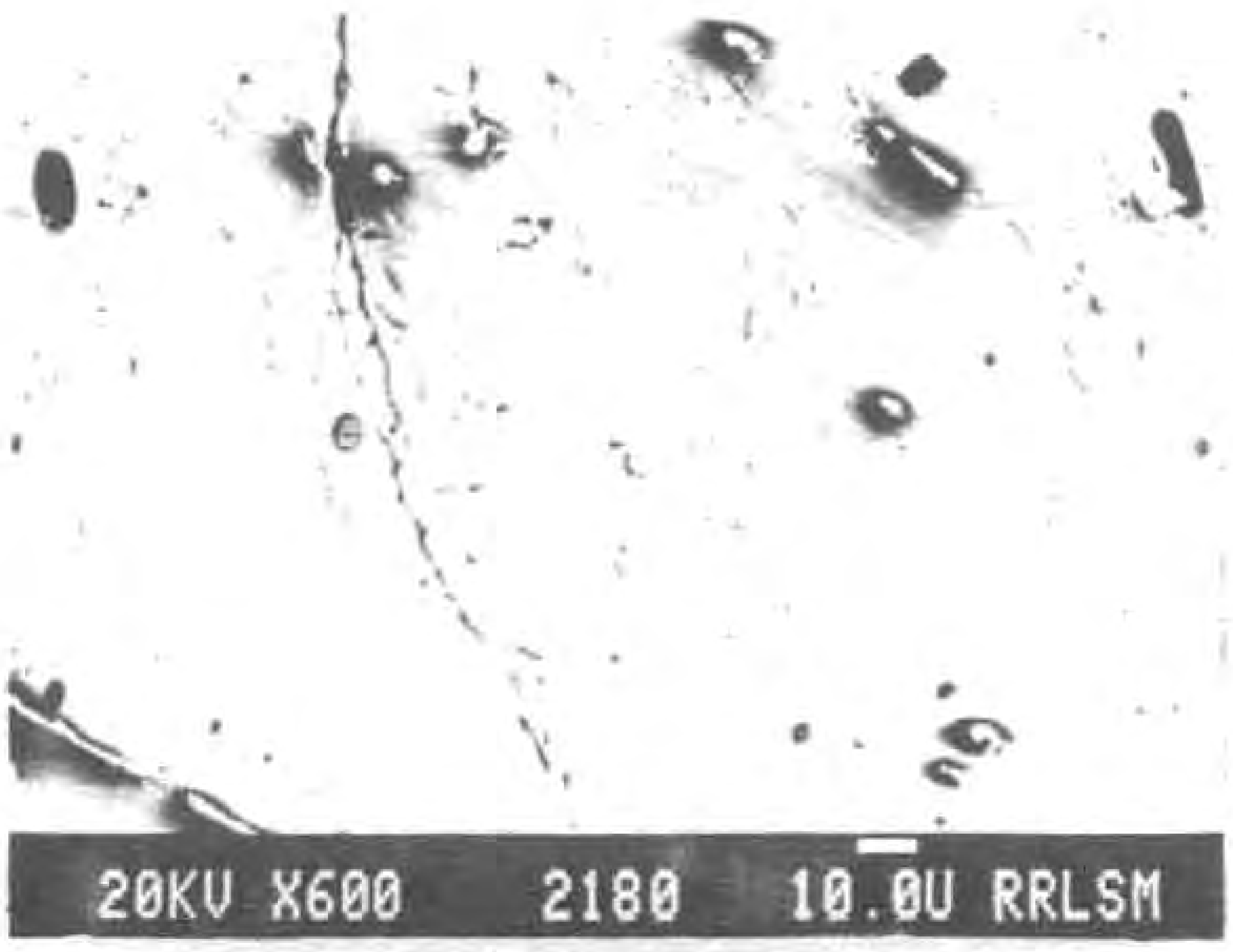
material. However, it is interesting to note that there exists a linear relationship between the crystallinity index and particle size although this observation could not be generalised (Brindley et al., 1986).

SEM micrographs (Fig. 3) of the sintered samples indicate that the formation of mullite occurs only upto the primary mullite stage. The quartz grains of various sizes with glassy solution rims and primary mullite crystals embedded in the glass matrix are seen in the case of samples A and F. Samples D, E and G showed a very uniform distribution of finer sand grains. The glassy phase formation was more or less uniform in the case of sample G.

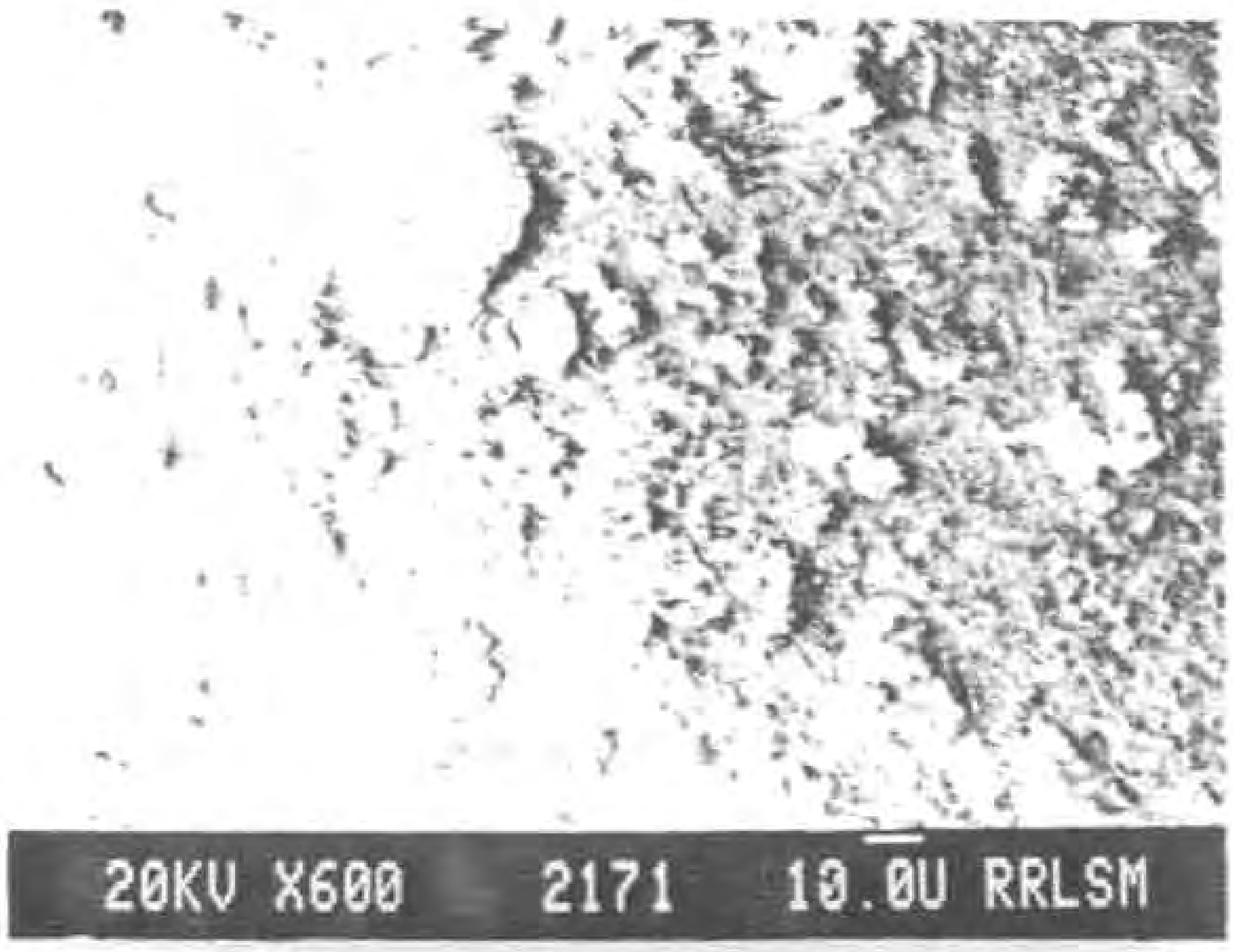
6.4 SUMMARY

The crystallinity of kaolinite is found to have a direct relationship with the grain size of the clay and thus can affect the properties of the sintered bodies. However, it does not predominate over the effects due to the quantity of the consctituents as no linear relationship was found between the Hinckley's crystallinity index and modulus of rupture. The higher percentage of alumina content in sample A, necessitates a higher fusion temperature for its full vitrification. This fact was proven by the higher shrinkage, low MOR and higher water absorption values. Crystallinity studies indicate that the samples with a medium value of crystallinity index (0.65-0.85) and grain size (75-85% of < 2 μm) give higher values of MOR after sintering.

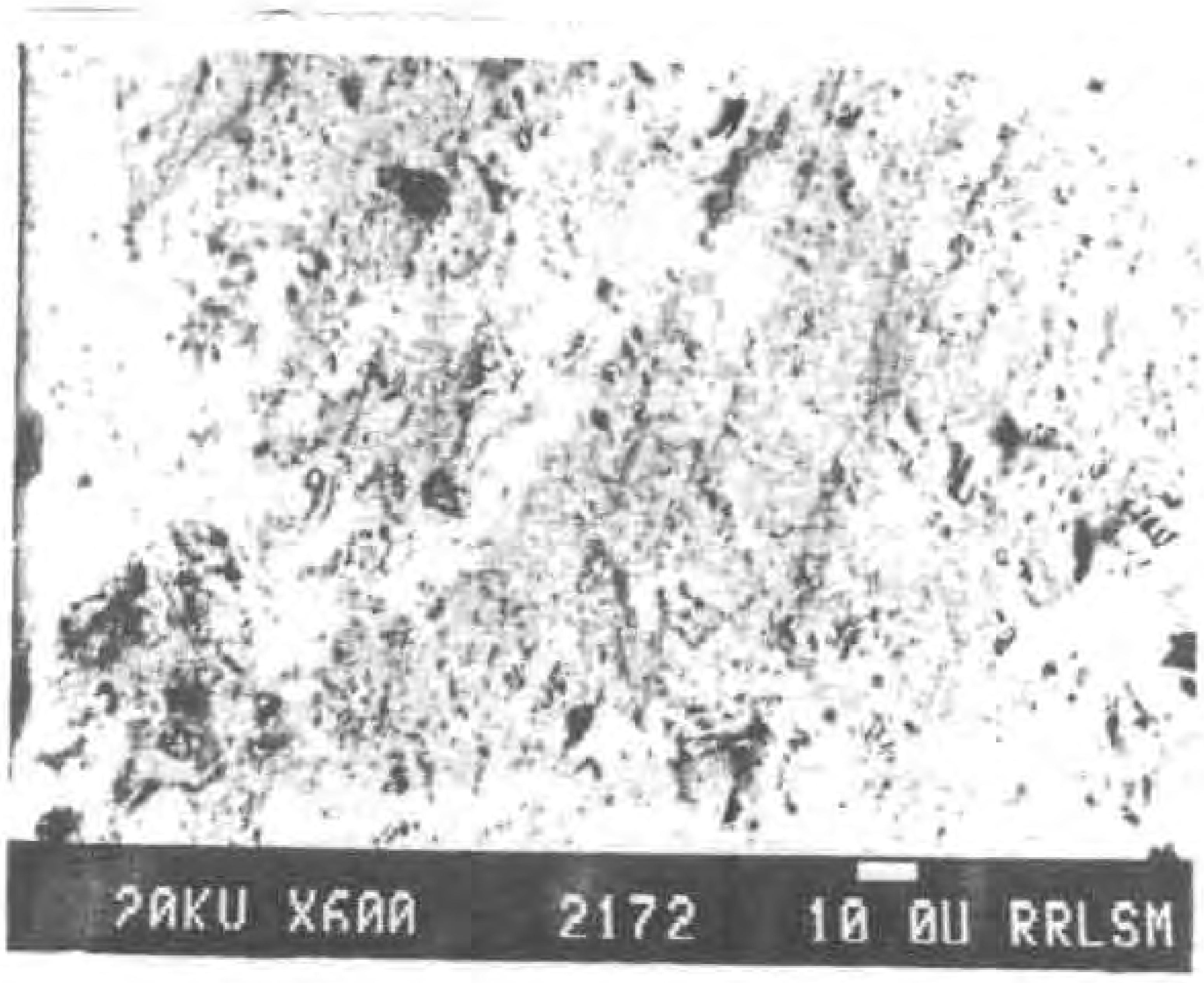
Fig. 3: SEM of sintered samples



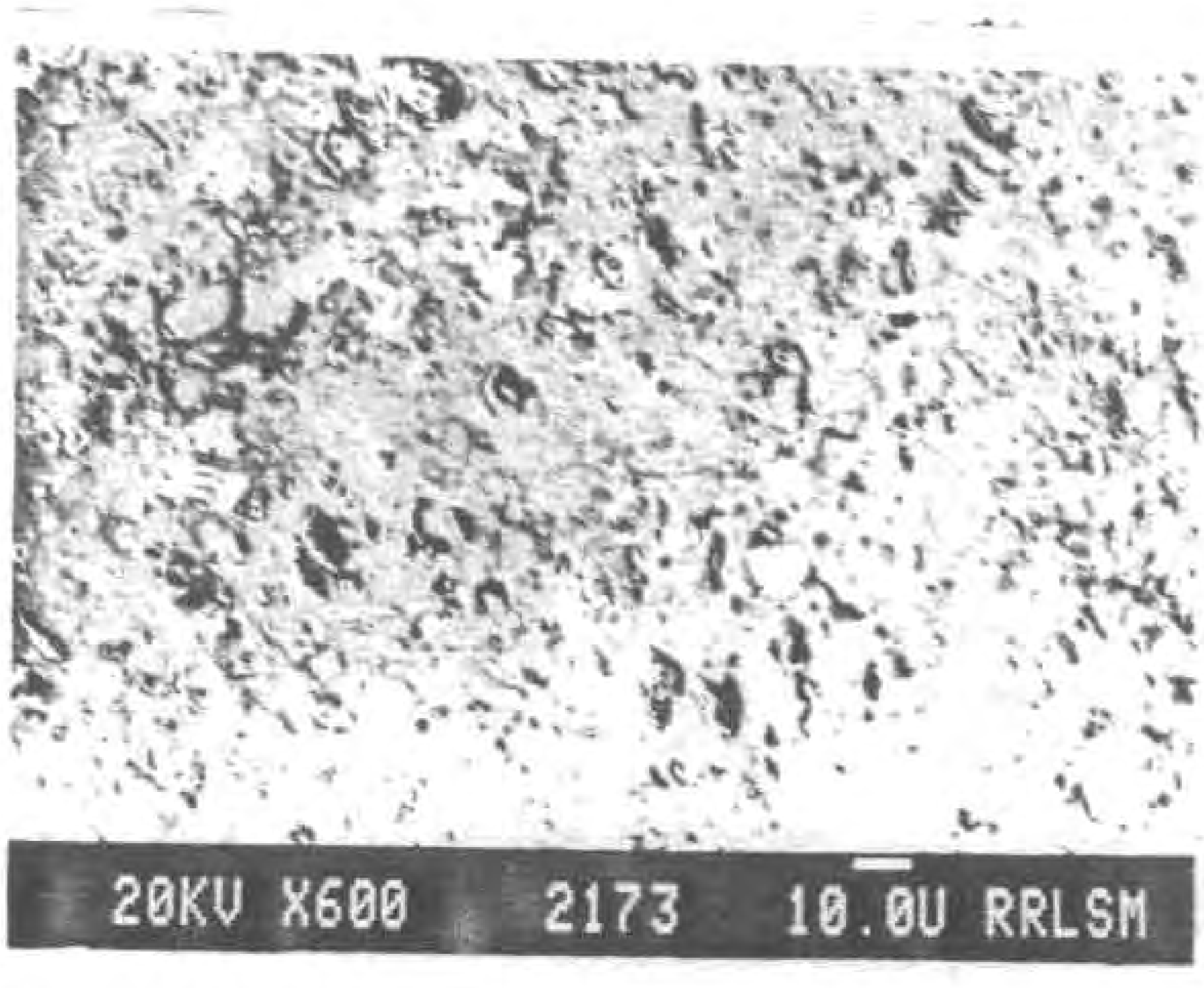
Padappakkara, A



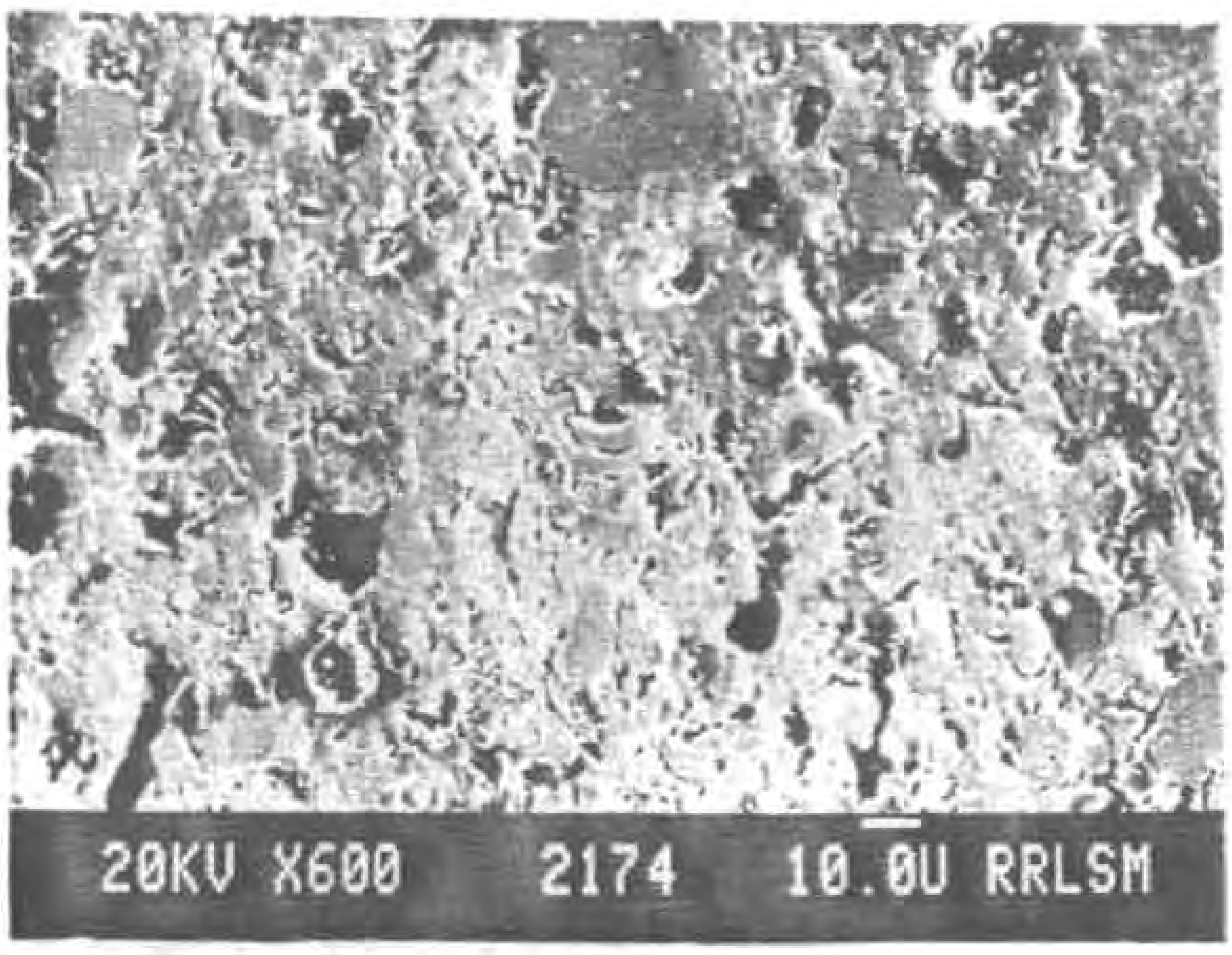
Payyangadi, B



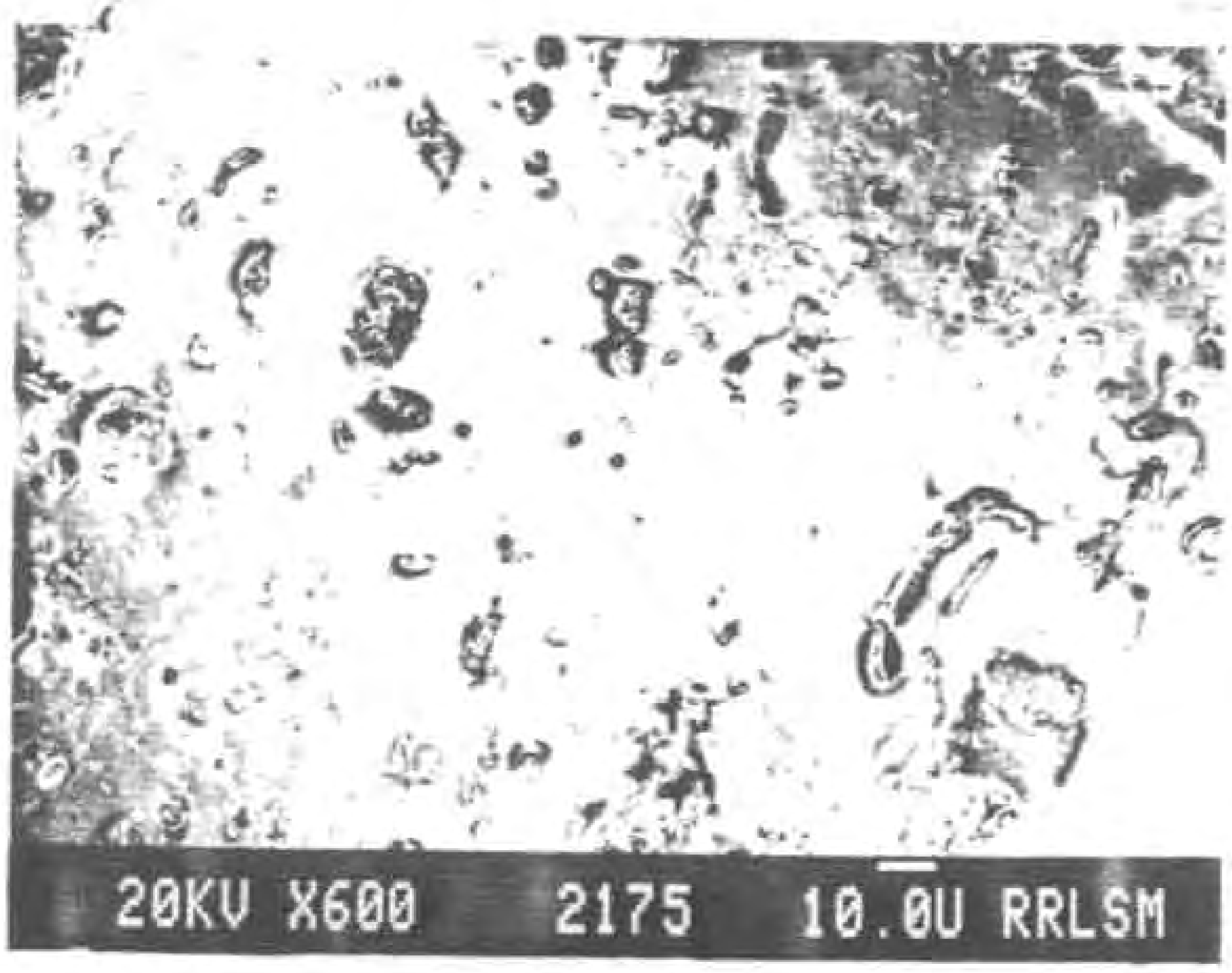
Bikaneer, C



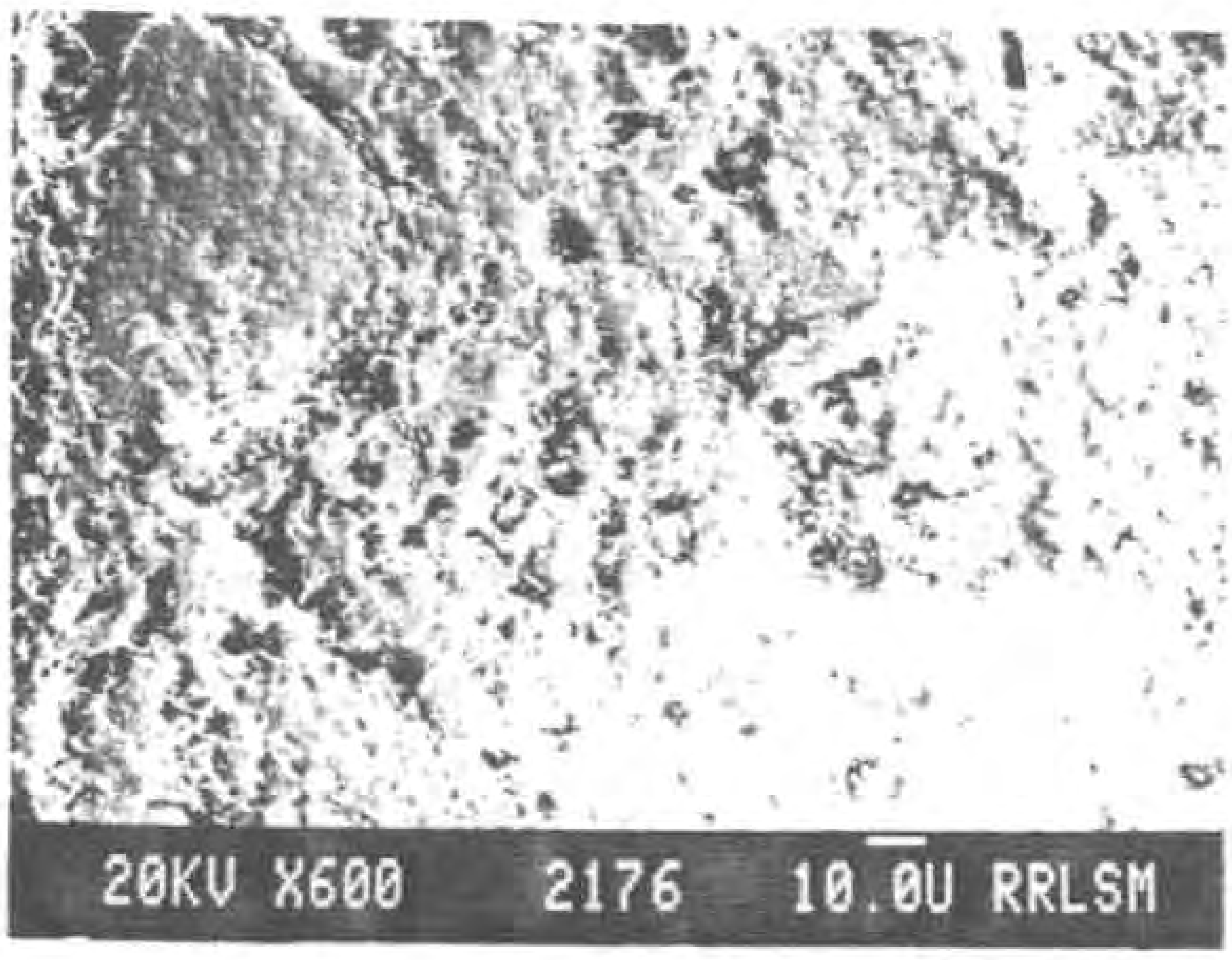
Bimadole, D



Than, E



Westerwald, F



Inagaki-kibushi, G

CHAPTER VII

BLENDING OF CLAYS

7.1 GENERAL

It is rare that any clay can be found which satisfies all the manufacturing requirements of any one product. For this reason blended clays are produced which consist of many components from several individual seams each contributing to the physical properties of the final blend. Ball clay components with small amounts of montmorillonite ($<5\%$) are sufficient to have a marked effect on many of the physical properties of the blends. The purpose of blending of the raw materials is to transform the solid components which have different grain size composition and the liquid additions into a homogeneous mixture that can be subsequently moulded or shaped by one of the numerous processing methods employed by modern refractory manufacture (Shaw, 1972).

Plastic clays can be adjusted to the required carbon content and particle size and then can be used in ceramic industries where faster firing and casting are required. Gresan C, Sandblend 75, Sandblend 90, SPPWS, Caroso and ball clay TA are some of the blended ball clays commercially produced for different applications by M/s. Watts Blake Bearne & Co., UK which is the world's first to develop them for specific purposes (Watts, Blake, Bearne & Co. P.L.C., 1973). ECC International the world's largest producer of kaolin is a major supplier of ceramic ball clay from its extensive deposits in the South of England, operating from three locations, South Devon, North Devon and Dorset

(Glasson, 1989). Dorset-ECCI markets have a pallet of over 30 standardised ball clay blends namely, Hycast VC, Hycast Classic, Hycast Rapide etc. with a wide range of properties for many ceramic applications. These products are claimed to provide a range of properties from which a selection will satisfy the variety of needs of the sanitaryware producer from bench and battery casting to pressure casting.

7.2 INTRODUCTION

Blending of the particles of raw materials is only one of the processes in the continuous chain of process, starting with the mining or winning of the raw material and finishing up with the reconstituted fired mixture of these materials. The final result of blending is largely determined by particle shape and size, the overall grain size, composition of each component, the total number of materials being blended, their ratios, the frictional properties of the particles with respect to each other, the sticking capacity of the materials in the pan and the mills, the presence and amount of water, adhesive components and the degree of 'grinding' of the materials taking place in mixing (Kenneth, 1972). Thus blending has a critical effect on the properties of refractory materials.

On the basis of the entire observations of the physical, chemical and mineralogical characteristics of all the seven clay samples which have been examined (details given in previous chapters), some additives are incorporated in two of them namely, Padappakkara A and Bikaneer C. The effect of blending of an aluminosilicate gel and other mineral constituents with clays on their properties after sintering are studied in this context.

7.2.1 Preparation of blends

Usually plastic clays are prepared by blending techniques for tailormade properties. Clay-gel blends were prepared by mixing the clay with different percentages of aluminosilicate gel prepared from Zeolite 4A. Another set of blended clays was also prepared by mixing quartz, feldspar, bentonite etc., in different proportions with the refractory plastic clay, Padappakkara A.

The zeolites are based on frame work structures of $(SiAl)O_2$ units, but the lattice is more open than that of feldspars, and cavities and wide channels are also present (Searle and Grimshaw, 1960). The framework has a net charge deficiency which is electrically balanced by large-sized cations contained in the voids in the lattice. Unlike those in the fledspar structure, these cations are not held firmly, but can move freely within the more open cavities and channels. Consequently they can be readily exchanged and in addition large quantities of water may be contained which can be driven off by heat without destroying structure. The zeolite-4A of Faujasite group (Barrer, 1978) prepared from kaolinite was converted to zeolite 3A by exchanging the Na^+ ions with K^+ ions by treating with 0.1 N KCl. 100 gm of this K-exchanged material was slurried in 300 ml water and was sieved through 350 mesh. This slurry was treated with approximately 200 ml of 1:1 HCl. The solid dissolves, and this clear liquid was heated on a water bath to get the gel which was washed several times with water till it was free from chloride. The morphology of gel was studied by taking the scanning electron micrographs of the spray dried gel.

The second set of blends was prepared with the clay sample from Padappakkara, A which contains nodular iron impurities. The sample was beneficiated before preparing the blends. The principal effect of nodular iron contaminents within clays is on the fired colour, where it results in specking, the specks produced being red through brown to black (Watts, Blake, Bearne & Co. P.L.C., 1979). The sample slurry was dispersed with 1:1 ammonia solution so that the denser iron sulfide particles were settled down. The iron removed fraction of the sample was used for making blends.

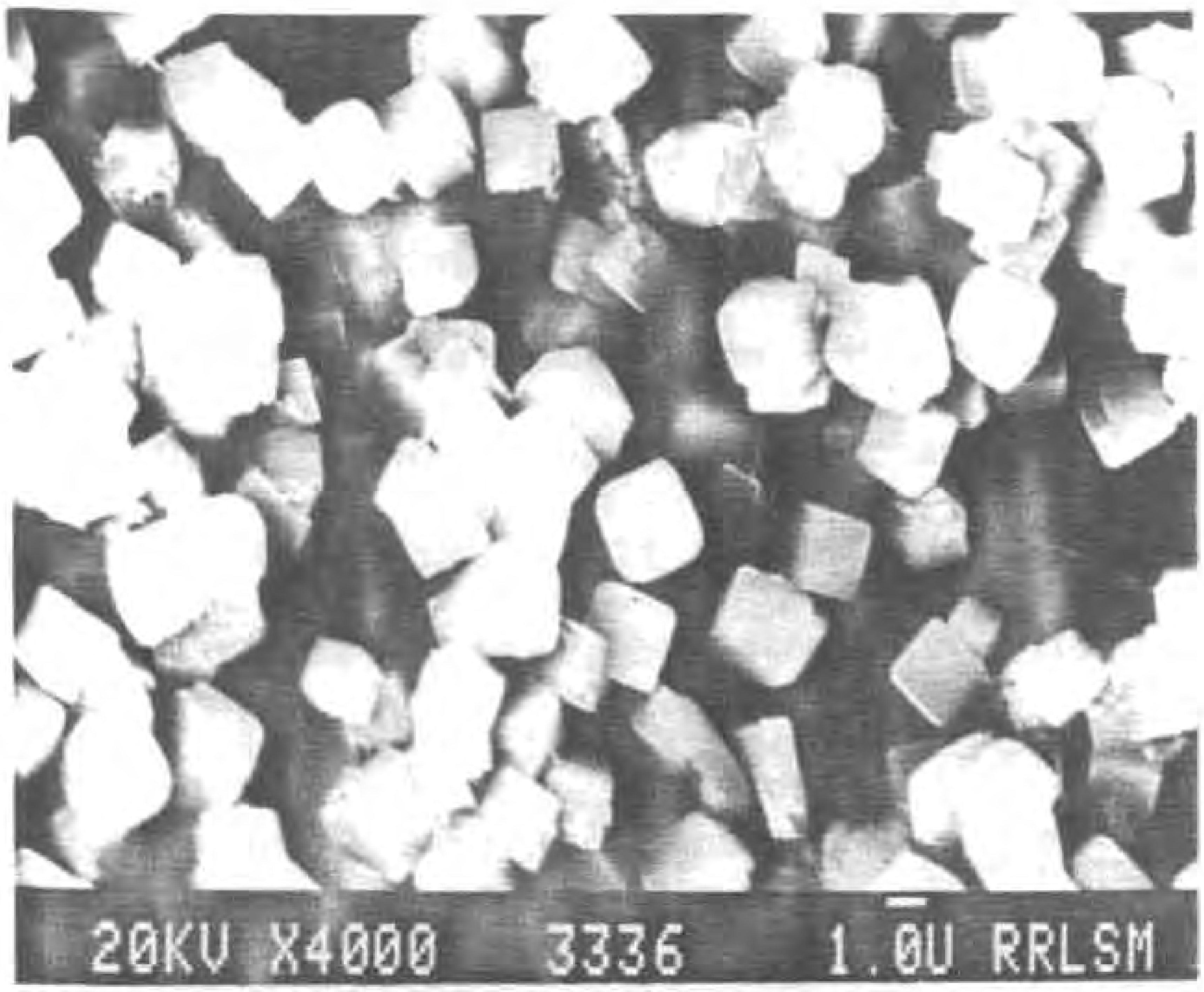
7.3 EFFECT OF ADDITIVES ON THE PROPERTIES OF PLASTIC CLAYS

7.3.1 Aluminosilicate gel

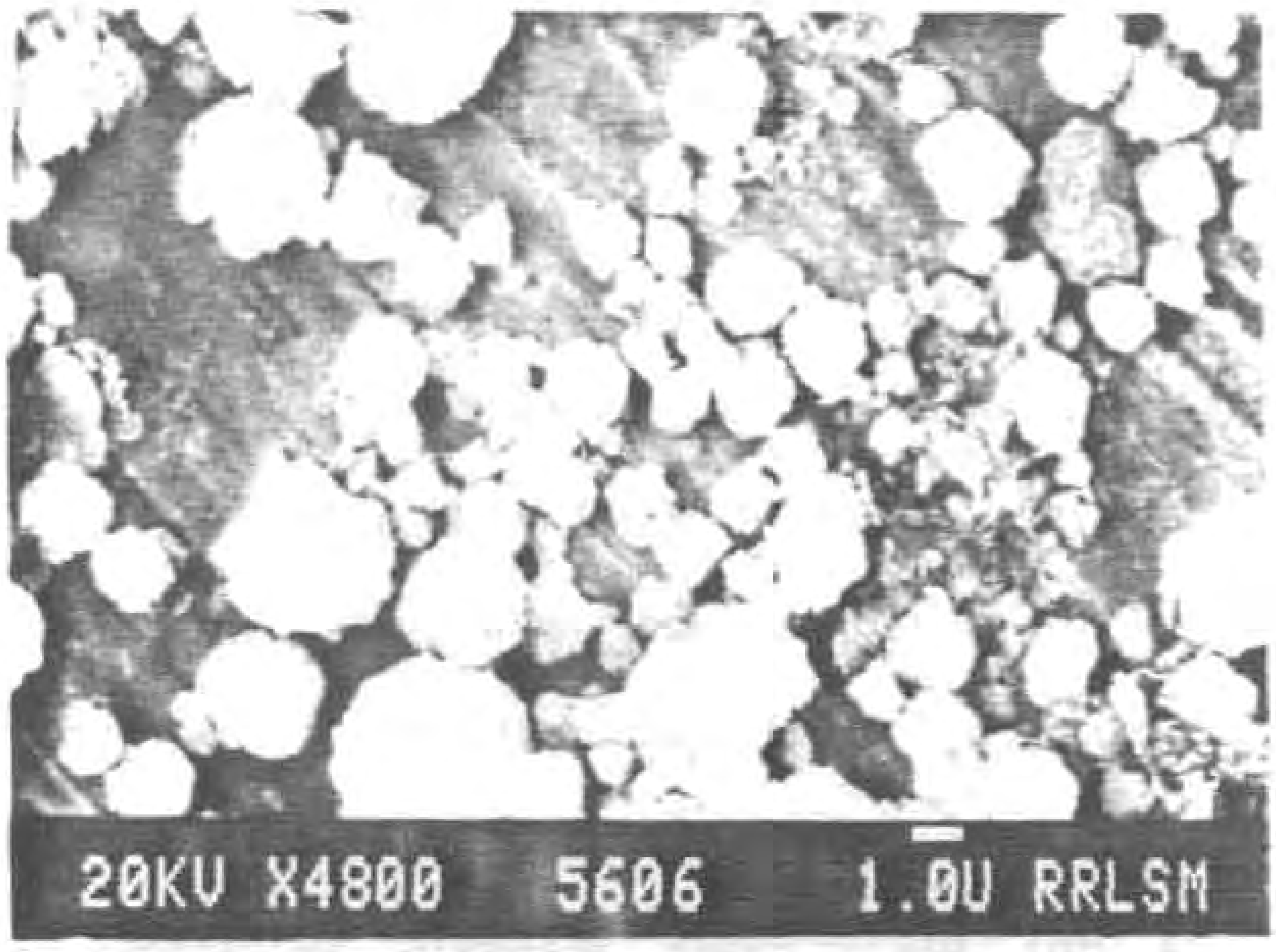
Inorganic colloidal gels such as silica and alumina can be added for improving the green and fired properties of ceramic materials. In the present investigation an aluminosilicate gel prepared from a sodium aluminosilicate, $Na_{12}(AlO_2)_{12}(SiO_2)_{12} \cdot 27\ H_2O$ (Zeolite 4A) was used for preparing the gel. The extent of gelling from the cubic Zeolite particles to amorphous gel can be seen from the micrographs [Fig. 1(a and b)]. The changes occurring in the green and sintering properties of ball clays are studied with the addition of different percentages of gel. To assure good mixing of gel and clay the latter was mixed with gel in the wet condition.

It is noticed that in the case of Bikaneer clay the dry linear shrinkage shows a very slight increase upto 10% addition. But with 15% addition the linear drying shrinkage is found to increase by 3 units

Fig. 1: SEM picture of the zeolite and the spray-dried gel prepared



(a) Zeolite



(b) Gel

and the firing shrinkage by 1 unit (Table 1). The green MOR which is very important as far as shaping of ceramic articles is concerned is found to decrease when the gel addition increased above 10%. Water absorption of the fired samples showed a decrease upto 10% gel addition and the value is found to increase when the addition is raised to 15%. The gel addition is found to reduce the dry MOR but on the other hand, the fired MOR is found to increase by addition upto 10%. The experiment indicates that though this aluminosilicate gel does not have good cementing properties in the green stage, the fired properties are improved upto an addition of 10%. Since Padappakkara clay, blended with the gel does not ensure the consistency in sintered properties, these values cannot be taken into account. However, the obtained values are recorded in Fig. 2.

7.3.2 Mineral constituents

Bikaneer clay has been widely used as a ball clay for high tension insulators. Attempts were made to improve the properties of Padappakkara clay A so that the properties match with that of Bikaneer clay. Blended samples were prepared with a view to attain the specific properties. The composition and the properties of the blends are given in Table 2. Since Bikaneer clay had a higher silica content and the plasticity was less compared to sample A, addition of quartz (20%) and a plastic clay (15%) (supplied by M/s. Kerala Ceramics Ltd.) was tried so that the mix would have almost similar chemical composition as Bikaneer clay. But the green strength was found to be slightly higher than that of Bikaneer clay, i.e. 75 ± 20 kg/cm^2 and 10 ± 1%.

Table 1: Effect of gel addition

Sample property	0	5	10	15
Dry linear shrinkage, %	4.6	5.44	5.48	8.4
Fired linear shrinkage, %	11.8	12.04	12.08	13.12
Green MOR, kg/cm^2	10.03	7.99	6.24	4.49
Fired MOR, kg/cm^2	350.76	382.3	423.36	*
Water absorption	12.174	11.567	9.526	*

* Measurements were not made since the sample showed cracks on the surface

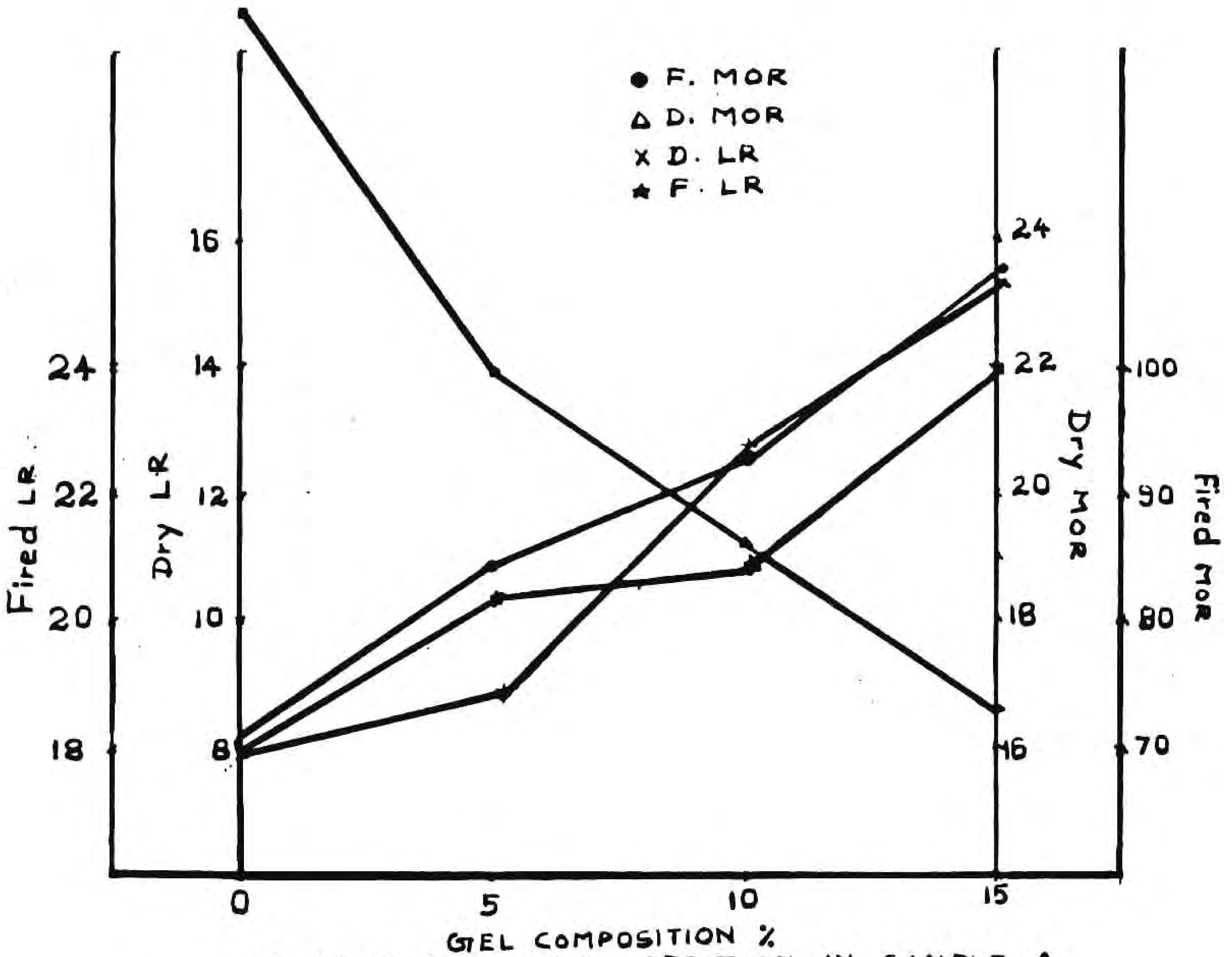


FIG.2 EFFECT OF GEL ADDITION IN SAMPLE A

Table 2: Properties of the blended clays

Sample	Residue over 45 μ (%)	Dry shrinkage (%)	Fired shrinkage (%)	Water absorption (%)	Green strength (%)
Bikaneer clay	1.5	5 ± 1	10 ± 1	0.5	75 ± 20
B_I	1.5	6.38	12.55	11.82	36.7
B_{II}	1.5	2.128	9.14	5.77	58
B_{III}	1.5	4.255	11.00	0.32	73

On comparing the mineralogical composition obtained on the basis of the rational analysis of Bikaneer clay, it was found that it contains significant amounts of feldspar. Hence a new mix was prepared with 25% quartz, 25% feldspar and 50% of the clay sample from Padappakkara A. The green strength was found to be only 58 kg/cm^2. In order to improve the green strength this blend was further modified by addition of 2% bentonite and 0.2% PVA, the compos ition of the final mix being 2% bentonite (Wyoming, USA) + 0.2% PVA + 23.9% feldspar + 23.9% quartz + 50% sample A. This mix was wet ground for 10 hrs to attain the right particle size distribution. It was found that the green strength was improved with other properties being acceptable for ball clays to be used in high tension insulators. This blended mix was tested by M/s. Bharat Heavy Electricals Ltd., Bangalore, and the results were found satisfactory. Thus the Padappakkara clay which otherwise could not have been used as a binding clay, inspite of its good plasticity, is modified by a blending procedure to obtain a tailormade product.

7.4 SUMMARY

Addition of aluminosilicate gel in clay is found to increase the fired MOR although it increases the linear shrinkage after drying. But gel addition upto 10% can be used as a technique for improving the fired strength. Blends prepared based on rational analysis are found to give improved properties and a clay with the properties required for high tension insulator application can be prepared from Padappakkara clay which is a refractory plastic clay.

APPENDIX

The various methods used in the characterisation of clays are described here. The raw samples were beneficiated by washing and sieving through 350 mesh.

1. METHODS OF CHEMICAL ANALYSIS

Methods are described for the determination of loss on ignition, oxides of silicon, iron, titanium, calcium, magnesium and the alkali metals in alumino-silicate minerals.

The loss of ignition is determined at 1025^{o}C, on a moisture free sample. The silica is determined by treating it with hydrochloric and sulphuric acid and is evaporated to dryness. The residue is fused with potassium bisulphate and the melt is dissolved in dil. sulphuric acid solution. Aliquots of the solution are used for determination of aluminium, calcium and magnesium by complexometry. Iron and titanium are determined by colourimetry. A further sample from which the silica is removed by hydrofluoric and perchloric acid is used for the determination of the alkali metals.

1.A. ESTIMATION OF SILICA

Weigh accurately 0.5 gm of the finely agated and dried sample (at 105^{o}-110^{o}C) in a platinum crucible. Add 3 gm of potassium/sodium carbonate mixture (1:1) and mix thoroughly. Cover the basin with its lid. Fuse the contents of the basin by placing it on a gas burner and gradually increasing the flame of the burner to its maximum.

Keep the melt at this stage for (10-15) minutes for complete decomposition. Remove the basin and allow to cool it. Add 30 ml of HCl acid (1:1) and 1 ml of H_2SO_4 (1:1). Quickly cover the basin so that there is no loss due to effervescence. Place the covered basin on a steam bath until disintegration of the melt is complete. Wash the inner surface of the lid and the inner walls of the basin. Evaporate the solution to dryness on the steam bath till there is no smell of hydrochloric acid. Bake the evaporated mass by heating the basin in an air oven at 110°C for 1 hour. Cool the basin, then add 10 ml of conc. HCl and 40 ml of hot water and digest on a steam bath for 10 minutes. Filter through Whatman No.40 or its equivalent filter paper and transfer the silica precipitate to the filter. Wash 3-5 times first with hot dil. hydrochloric acid and then with hot water till free from chlorides. Reserve the filtrate. Transfer the paper and the precipitate to an ignited, cooled and weighed platinum crucible. Burn off the filter paper by placing the crucible on the low flame of a gas burner and then heat it in an electric burner. Cool in a desiccator and weigh to constant weight. Moisten the contents of the crucible with water, add 4-5 drops of H_2SO_4 (1:1), 10 ml of HF (40%) and evaporate to dryness on a sand bath taking care to avoid spurting. Remove the crucible, cool and weigh to constant weight. Calculation of total silica content is as follows:

$$\text{Percent silica } (SiO_2) = \frac{(W_1 - W_2)}{W} \times 100$$

where

W — wt. of the sample
W_1 — wt. of the crucible and the impure silica before HF treatment
W_2 — wt. of the crucible and the residue after HF treatment

1.B. ESTIMATION OF ALUMINA, IRON OXIDE, TITANIA, LIME&MAGNESIA

1.B. i) Decomposition and preparation of sample solution

Weigh accurately 0.5 gm of well agated and dried sample (105-110°C) in a platinum basin, moisten with water, add 10 ml of H_2SO_4 (1:1) and 10 ml HF (40%); evaporate the contents of the basin on a heated sand bath to fumes of sulphuric acid. Cool the basin, again add 10 ml HF, evaporate to copious fumes and ultimately to near dryness. Fuse the residue with 10 fold quantity of potassium bisulphate (potassium pyrosulphate). Cool, take the melt in 3% H_2SO_4 acid solution in a 250 ml flask, cool and dilute to the mark. This solution is the stock solution for the determination of alumina, iron oxide, titania, lime and magnesia.

1.B. ii) Estimation of alumina

Transfer 20 ml of standard solution (0.02 M) to a 250 ml flask, add 25 ml of EDTA and a drop of methyl orange solution and then ammonia (1:3) dropwise until the colour of the indicator changes from red to yellow. Add 10 ml of buffer (pH 5.3) and heat to boiling for 5 minutes. Cool, add 5 ml of buffer (pH 5.3) and titrate with zinc acetate (0.02 M) using a few drops xylenol orange indicator. The end point is indicated by a clear change of colour from yellow to orange. Add about 1 gm NaF or NH_4F and boil for 5 minutes. Cool, add 10 ml of buffer (pH 5.3) and titrate with zinc acetate (0.02 M). Let the last titre value be 'a' ml. Find out the equivalent Al_2O_3 for 1 ml of zinc acetate (0.02 M) by dividing the amount of alumina present in 10 ml by the titre value 'a' , i.e. (10 x 0.0010194/'a' gm of Al_2O_3). following the same procedure determine the Al content in the unknown sample solution taking 25 ml of the stock solution.

$$\text{Percent alumina } (Al_2O_3) = \frac{V \times 100}{W} - 0.6378\ T$$

where

V - the titre value in ml of zinc acetate solution

X - equivalent Al_2O_3 in gm per ml of zinc acetate solution

W - weight in gm of the sample present in 25 ml of the stock solution

T - percent of titania in the sample

1.B. iii) Estimation of iron oxide

Transfer a 5 ml aliquot of the stock solution to a 100 ml calibrated flask. Add 1 or 2 drops of para-nitrophenol indicator and 10 ml of tartaric acid solution. Neutralise with conc. ammonia to the yellow colour of the indicator. Acidify with a few drops of HCl (1:1). Add 2 ml of hydroxylammonium chloride ($NH_2OH.HCl$) and 10 ml of 1:10 phenanthroline. Cool the solution in the flask and dilute to the mark. measure the optical density at 510 nm in a convenient cell against a reference test blank prepared in the same way without the sample. Draw a calibration graph with 0, 0.5, 1.0, 1 .5 and 2.0 ml of standard Fe_2O_3 solution in 100 ml flasks after developing the colour in the same way as in the test solution. Determine the unknown iron concentration by referring to this graph.

1.B. iv) Estimation of titania

Transfer two equal aliquots of 25 ml of the stock solution in 50 ml calibrated flasks A and B. Add 5 ml of hydrogen peroxide to flask A and dilute both the solutions with water to the mark. Measure the optical density at 410 nm of the solution in A against that in B without hydrogen peroxide. Draw a calibration graph with 0.0, 0.2, 0.4, 0.6, 0.8, 1, 1.2 ml of standard titania solution in 100 ml flasks after developing the colour in the same way as in the test solution in A. Determine the unknown titania concentration by referring to this calibration graph.

1.B. v) Estimation of lime and magnesia

Transfer two 25 ml aliquots of the stock solution separately to two 250 ml conical flasks. Neutralise the solutions in both the flasks with NaOH (2 N) in presence of a very small universal indicator paper. Acidify to pH 3-4 by dropwise addition of 30% HCl. Add 1 ml in excess. Mix the solution with 10 ml (or 20 ml when the alumina content is more than 40%) of 30% triethanol amine solution thoroughly. At this stage the solution must be clear and alkaline indicated by the pH paper already present in the solution. Add 5 ml of hydroxylammonium chloride and boil till the solution is colourless. Upto this stage the procedure for (CaO + MgO) and CaO is common. Then Ca and Mg can be estimated separately by addinng buffer and NaOH respectively and titrating with EDTA solution.

1.C. ESTIMATION OF Na_2O AND K_2O BY FLAME PHOTOMETRY

1.C. i) Preparation of sample solution

Weigh 0.1 gm of well agated and dried (105^o-110^o C) sample in a platinum basin, moisten with water and add to it 1 ml of perchloric acid ($HClO_4$) and 5 ml of HF. Place the basin and its contents on the sand bath and evaporate until strong fumes of perchloric acid comes out. Cool the platinum basin and add to it another 5 ml of HF and evaporate in the same way as before. Cool, wash the internal sides of the basin with water and again evaporate on the sand bath to dryness. To the dry mass in the basin add 5 drops of (1:1) HCl and water. Place the basin on a steam bath. After (5-10) minutes transfer quantitatively the contents to a 100 ml flask and dilute to the mark. If the solution is turbid centrifuge it.

1. C. ii) Estimation of soda

Place a few ml of solution in a cup of a flame photometer provided with monochromatic arrangement of sodium filter. Measure the emission at 589 nm or through the filter against the water. Draw a calibration graph with (1-5) ppm. Concentrations of standard sodium solutions. Calculate the unknown soda concentration. If it is more than 5 ppm, determine from a preliminary run, dilute the solution so that the concentration is close to 5 ppm, preferably on the lower side.

1.C. iii) Estimation of potash

Like soda determinaton, place a few ml of the stock solution in the small cup of a flame photometer. Measure the emission at 767 nm or through a potassium filter against water. Draw a calibration graph (1-15) ppm concentrations of standard potassium solutions. Calculate the unknown potash concentration by referring to this calibration graph.

The same sample solution and principle of method can be used for the determination of trace elements by atomic absorption spectroscopy.

II. X-RAY DIFFRACTION

The methods which are relevant to the study of clay minerals, especially kaolinites have been considered here.

II. A. RANDOMLY ORIENTED SPECIMENS

Different types of techniques have been suggested to obtain random orientation of powder particles. The most common method is to fill a sample holder from the back against a smooth glass surface and to press the powder gently without a shearing motion. Tamping the powder onto a mat surface, such as an emery paper surface, has been suggested but a roughening of surface is of questionable value. Side-packing of the sample holder has been suggested by some workers.

II.B. ETHYLENE GLYCOL SOLVATION

A diffractometer pattern from a strongly oriented clay specimen shows only the $00\bar{1}$ series of basal reflections. Patterns of this kind are useful for clay mineral identification because each basal spacing is related to the type of layer structure involved. It has been suggested that simply allowing a dispersion to dry slowly on a glass slide give the best orientation and will suffice for identification of the clay minerals and this method has been used to prepare the oriented specimens.

A suspension of the clay is obtained by adding a little 95% ethanol to make the supernatant liquid volume equal to the cake volume. The tube is tapped to suspend the clay as a slurry and immediately a subsample is taken in a pippette and transferred to a glass slide resting on a level surface so that the sample distributes itself evenly on the slide. The sample is allowed to dry and kept for 24 hours in a glass bowl of ethylene glycol maintained at 150° C. The specimen is examined to see if enough glycol has been applied. The surface should appear moist. The samples are scanned between 5^{o} and 60^{o} 2θ, with the following instrumental conditions:

Radiation:	$CuK\alpha$, Ni-filtered
Scanning speed:	1^{o} 2θ /min
Chart speed:	1 cm/min.

III. SCANNING ELECTRON MICROSCOPY

The basic reason for the utilization of the electron microscope is its superior resolution resulting from the very small wavelengths of electron compared to other forms of radiation for which an optical system can be constructed. The electron beam excites electromagnetic waves and electron signals from a thin surface layer of a target in a wide energy range from fractions of 1 eV upto the kinematic energy but also the location of their excitation. The scanning beam method consists in the coupling of the functions of two cathode ray tubes (CRT) of different dimensions. One of the CRT produces images in which the local brightness corresponds to the strength of the electron or photon signal which is excited by the fine-focussed scanning beam of the other CRT (i.e. microscope tube) in a thin-surface layer of the investigated specimen.

Clay mineral specimens for electron microscopy are usually prepared by air-drying of a small drop of its suspension (in water, acetone, alcohol etc.) on a microgrid. This method is however, not always preferable for the observation of lattice images of clay minerals because of their preferred orientation in the air drying process. The embedding method is more suitable in the preservation of the non-oriented part of the crystal than that of suspension method. The interstratified kolinite can be dehydrated progressively replacing water by C_2H_6O, C_3H_6O and Epon mixture.

IV. INFRARED SPECTROPHOTOMETRY

The infrared spectrum of a compound is essentially the superposition of absorption bands of specific functional groups, yet subtle interactions with the surrounding atoms of the molecule impose the stamp of individuality on the spectrum of each compound. For qualitative analysis, one of the best features of an infrared spectrum is that the absorption or the lack of absorption in specific frequency regimes can be correlated with specific stetching and bending motions and, in some cases, with the relationship of these groups to the remainder of the molecule. Thus by interpretation of the spectrum, it is possible to state that certain functional groups are present in the material and that certain others are absent.

The most frequently method used in IR spectroscopy of solid materials is the pellet method. The clay sample is mixed in an agate mortar with an excess of KBr (1:50) of analytical quality for IR spectroscopy. After drying the mixture at 120° C it is pressed in a die for 1/2 to 1 min. at ca. 10 ton/cm^2 under simultaneous suction of ca.0.1 mm Hg (to remove entrapped air) into a transparent pellet of 13 or 20 mm dia and ca. 1 mm thickness and again dried for 1 h at 120°C to remove the last traces of absorbed water.

V. PHYSICAL PROPERTIES OF CLAYS

V.A. PLASTIC PROPERTIES

V.A. i) Plasticity of clays

V.A. i(a) Determination of water of plasticity

The water content of the clay at the point of maximum workability is determined. This when expressed as a percentage of oven dried clay gives the value forwater of plasticity.

About 500 gms of the clay sample is crushed and the clay is worked up with distilled water by adding a small quantity at a time from a burette to a soft plastic consistency and is thoroughly wedged and kneaded by hand. It is covered with a wet cloth and is allowed to age for 20 hrs. Again the plastic mass is kneaded and pugged by adding small quantities of water as necessary, until the mass attains working consistency for either extrusion or moulding into bars. The mass is divided into three equal portions rounding the edges and corners to prevent loss of material in handling, and weigh immediately to the nearest 0.01 g. The clay masses are covered with wet cloth and are allowed to dry for 4 hours at 70 ± 2°C and is weighed to the nearest 0.01 g.

$$\text{Water of plasticity, percent by mass} = \frac{\underline{M} - \underline{M}_1}{\underline{M}_1} \times 100$$

where $\underline{M}$ - Mass in gm of the plastic clay mass, and

$\underline{M}_1$ - Mass in gm of the dried clay mass

V.A. i(b) Determination of Atterberg Number

The difference in water contents between the lower limit of fluidity (liquid limit) and the rolling limit (plastic limit) of the clay is determined. The value thus obtained is the Atterberg Number of the clay.

About 100 gm of the clay sample is crushed and is dried at $110^{\circ} \pm 5^{\circ}$C for 5 hrs. Then it is mixed with 10-15 ml of distilled water by kneading and chopping with a spatula. Add water further in increments of 1 to 3 ml and thoroughly mix each increment of water before adding the next increment. When sufficient water has been added to produce a proper consistency, place the clay mass in the cup above the resting spot. Squeeze it down, spread it evenly with the spatula and at the same time, care being taken to prevent entrapment of air bubbles. The clay mass is made level with the spatula and at the same time trim it to a depth of 1 cm at the point of maximum thickness. Return the trimmings to the basin. The clay mass in the cup is divided by firm strokes of the grooving tool along the diameter through the centre line so that a clean sharp groove of proper dimension is formed. To avoid tearing of the sides of the groove or slipping of the clay mass on the cup, upto six strokes, from front to back or from back to front shall be permitted. Each stroke will penetrate a little deeper until the last stroke from back to front scrapes the bottom of the cup clean. Make the groove with as few stroke as possible. Lift and drop the cup by turning and crank at the rate of two revolutions per second, until the two halves of the clay mass came in contact at any point along a distance of 1.25 cm on the line of the groove. Record the number of drops required to close the groove along a distance of 1.25 cm on the line of the groove.

Remove a portion of the clay mass approximately of the width of the spatula that just flowed and placed in a tared vessel. It is then weighed and dried at 110° ± 5°C in an air oven and is cooled in a desiccator. Weigh after cooling. The loss in mass due to drying is recorded as the mass of water necessary to attain proper consistency. Repeat the operation at least twice, adding more water each time to bring the clay to a more fluid condition. Thus values above and below 25 are obtained for the number drops required to close the groove. The number of drops required shall be between 15 and 35. The calculation is as follows:

$$\text{Water content, percent} = \frac{M_1}{M} \times 100$$

where M_1 - Mass in gm of water, and

M - Mass in gm of the oven dried clay

Plot a flow curve on a semi-logarithmic graph with the water contents as absissae on the arithmatical scale, and the corresponding number of stroke as ordinate on the logarithmic scale. The curve shall be a straight line drawn as nearly as possible through the three points. Taking the water content corresponding to the interaction of flow curve with the 25-drop ordinate as the liquid limit of clay. The liquid limit value can be reported to the nearest whole number.

The plastic limit can be determined as follows. About 8 gm of the clay sample is crushed and is thoroughly mixed with sufficient quantity of water to give a plastic mass which can be easily shaped into a ball. Roll it between the fingers and the ground glass plate into a thread of uniform diameter throughout its length. The rate of rolling shall be between 80 to 90 strokes per minute counting or stroke as one complete motion of the hand forward and back to the starting position again. When the diameter of the thread becomes 0.32 cm, break the thread into six or eight pieces. Squeeze the pieces together between the thumbs, knead and roll again. Continue this process of alternate rolling, gathering together, kneading and re-rolling, until the thread crumbles under the pressure required for rolling and cannot be rolled into a thread having diameter of 0.32 cm. Weigh the crumbled pieces of the thread together. Dry them in an air-oven at a temperature of $110^{o} \pm 5^{o}C$ and cool in a desiccator and weigh. The plastic limit is expressed by the water content as percentage of oven dried clay.

Calculate the difference in water content of clay between its liquid limit at 25 drops and its plastic limit. The value obtained is the Atterberg Number.

V.A. ii) Cation exchange capacity (CEC)

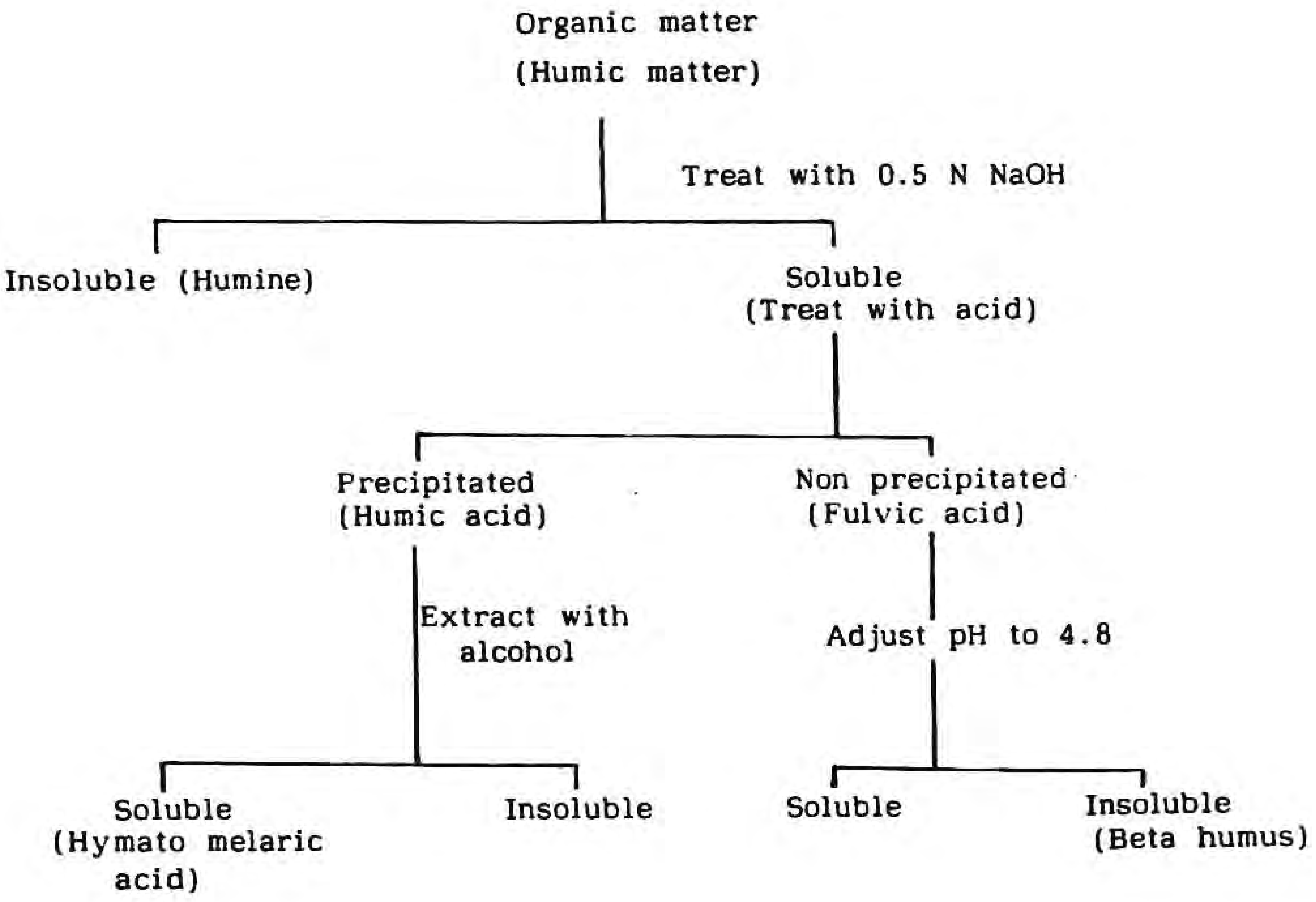
0.5 gm of the test sample is weighed and dried at 110^{o}C and is cooled in a desiccator. Transfer it to a dried 50 ml capacity centrifuge tube very carefully and cover it with a cork. Moisten the sample with N-NH_4^- OAC solution very slowly and then add about 30 ml of ammonium acetate solution and shake the tube thoroughly. After shaking wash the inner wall of the tube with a little quantity of ammonium acetate solution and allow it to remain as such for overnight. Next day again shake tube and centrifuge it till clear suspension is obtained. Remove the clear leachate by a syphon arrangement without disturbing the material settled at the bottom. Repeat the process for 5 times. Then add to it one drop of very dilute NH_4Cl solution. Now wash the sample with 90% alcohol in the centrifuge by the same procedure, till the leachate is free from chloride. Transfer the washed sample to the distilling flask very carefully and distill it with 100 cc of water and 0.5 gm AR MgO powder for half an hour. The distillate set up should be completely air tight. The tip of the condenser should be immersed in the conical flask containing 10 cc of saturated boric acid solution with mixed indicator so that all the evolved gas will be collected and absorbed in it. Colour of the distillate will be changed from pink to green. Collect about 40-50 cc of the distillate and titrate it directly against the standard sulphuric acid till the green colour of the solution changes to pink. One blank experiment should be done separately at the beginning and the cation exchange capacity is calculated as follows:

Let X be the volume of acid consumed due to the test solution, Y be the volume of acid for the blank. Duplicate reading will be within the range of 0.05 ml.

$$\text{CEC} = \frac{(X-Y) \times \text{strength or normality of acid}}{\text{wt. of sample taken}} \times 100$$

V.A. iii) Humic acid content

Fractionation of soil organic matter was carried out as indicated in the flow chart given below:



The clay sample was washed with 0.1 N HCl and 40 g of the washed soil was taken in a polythene centrifuge bottle. To this 200 ml of 0.5 N NaOH solution was added. The mixture was shaken for 12 hours on a mechanical shaker, and the sides of the bottle were washed with distilled water. The mixture was centrifuged. Dark coloured supernatant liquid was filtered and the pH of the solution was adjusted to 1.0 with conc. HCl. Additional 200 ml of 0.5 N NaOH was added to the clay, the content was shaken, centrifuged and filtered. The collected humic acid fraction is vacuum dried and weighed.

V.A. iv) Particle size

Particle size distribution is determined by sedigraphic analysis. The sedigraph determines, by means of a finely collimated beam of X-rays, the concentration of particles remaining in supension at various depths as a function of time. The logarithm of the transmitted X-ray intensity is electronically generated, scaled, and presented linearly as "Cumulative Mass Percent Finer" on the Y-axis of an X-Y recorder. To minimise the time required for analysis, the position of the sedimentation cell is continuously changed so that the effective sedimentation depth is inversely related to elapsed time. The cell movement is synchronised with the X-axis of the X-Y recorder to indicate directly the "equivalent spherical diameter" corresponding to the elapsed time and instantaneous sedimentation depth.

The slurry for the determination of particle size distribution contains 3% by weight of the suspended phase with tetrasodium pyrophosphate as deflocculant.

V.A. v) pH

Since hydrogen ions are preferentially absorbed by clay particles, most natural clays contain hydrogen, in past at least as their exchangeable cation. Consequently when such clays are suspended in water, dissociation occurs and the hydrogen ion concentration in the suspension is increased. The procedure for the determination of pH is described as follows. 20 gms sample in 80 ml distilled water (1:4) is taken. filter through Whatman No.40 and discard the first 20 ml. The filtrate is taken and pH is found out.

V.A. vi) Zeta-potential

The Zeta-potential analyser determines the electrophoretic mobilities of particles in suspensions containing upto 50 percent by volume of dispersed phase. The zeta potential, which expresses the net effective charge on the surface of particles is computed from electrophoretic mobility.

To measure electrophoretic mobility of suspended particles with the device the cell and chamber reservoir are filled with the colloid or suspension containing upto 50% by volume of dispersed phase to be studied. When a potential difference is applied be:tween the two electrodes, particles having an electric charge (±) will migrate either into or out of the cell, depending on the polarity of the cell electrode. After a certain time period, there will be a change in the particle concentration of the cell contents because of their migration from reservoir toward the electrodes. This change may be determined by analysis (usually gravimetrically), and from it, the mobility and the zeta potential are calculated. Typically, the time of the voltage gradient application is a few minutes.

V.B. FIRED PROPERTIES

V.B. i) Shrinkage

The wet to fired value of shrinkage will determine the size of the fired article, since the wet size of the product will be fixed and governed by the size of the mould used in production. Any variations in the value will therefore indicate a variation in size of the finished product. The test specimens made for measurement of shrinkage may be either slabs or rods of circular cross section. Rods are generally extruded and immediately after exrusion, they are placed in the grooves of a wooden pallet. Marks 10 cm apart are made on five rods and they are allowed to air dry for 24 hours, after which drying is completed in a drier at 110^{o} C. The rods should then be fired through the production kiln in such a position as to receive an average firing treatment. Again the distance between marks is measured on the rods, and the average fired length is calculated. It is suggested that the wet-to-fired shrinkage is reported on the wet basis. i.e. % linear firing shrinkage (wet basis) is given by

$$\frac{\text{wet length - fired length}}{\text{wet length}} \text{ (average) x 100\%}$$

V.B. ii) Water absorption

Water absorption test is determined by using the boiling technique. Test specimens - each of approximately 25 gm in weight -

are dried in an oven at 110^{0}C for 4 hours. The samples are cooled in a desiccator and weighed to an accuracy of 0.01 gm to give the dried weight (D). They are then placed in a beaker of water and boiled gently for 1 hour. Cold water is run into the container until room temperature is reached and the test pieces are left to soak for a further period of 1 hour. The specimens are then removed, excess moisture is wiped off the surface with a moist cloth and the samples weighed to give (S) the soaked weight. The values of (D) and (S) are used in the formula :

$$\text{Water absorption } \% = \frac{S-D}{D} \times 100$$

V.B. iii) Modulus of rupture

Test rods of about 1/2 inch diameter extruded using a small extruder are cut into lengths of about 6 inch are placed in the grooves of a wooden pallet and are allowed to air dry for at least 24 hours. Dyring is subsequently completedd over a period of at least 4 hours in a drier at a temperature of 110^{0}C. After this period the rods are cooled in a desiccator, and immediately broken on the bending strength apparatus noting the breaking loads, and measuring the diameters of the rods at the points of breakage. Modulus of rupture of each rod is then calculated using the formula:

$$\text{MOR} = \frac{8\ LD}{\pi\ d^3}$$

where

L is the breaking load

D is the distance between supports

d is the diameter of the rod

The test result is obtained by averaging values for at least 10 rods.. For the determination of fired MOR, the rods are carefully dried and then fired to the production schedule.

VI. MISCELLANEOUS

VI.A FRACTIONATION OF FINE PARTICLES

Place 5.5 gm of clay sample in a 250 ml wide-mouth bottle and add 200 ml of distilled water. Allow to stand for 24 hours. Add 10 ml of the sodium pyrophosphate solution. Agitate the bottle with its contents by rotating end-over-end. Transfer the dispersed sample to the Anderson pipette and add distilled water to bring the level of the suspension to the upper mark on the scale making the total volume 550 ml. This produces a 1% suspension, and the concentration of the electrolyte is 0.002 gram-molecule per litre.

Place the Andreason pipette in a constant temperature water bath of 30^{0}C for 15 to 30 minutes to permit it to attain the temperature of the bath. Remove it, shake by hand and replace immediately in the bath. Withdraw 10 ml of suspension at increasing intervals of time, at a uniform rate of about 20 secs. The samples are drawn at the intervals of 3 minutes and 30 minutes and then 1, 2, 3, 5, 8, 24, 49 and 96 hours. The grain size can be calculated from Stoke's law which has already been given in the text.

VI. B. REMOVAL OF Fe_2O_3 FROM THE SAMPLE AND ITS ESTIMATION

A suitable amount of sample containing 0.5 gm of extractable Fe_2O_3 or less, is placed in a 100 ml centrifuge tube and 40 ml of .0.3 M sodium citrate solution and 5 ml of 1 M $NaHCO_3$ solution are added. The temperature is brought to 75 to 80°C (not more) in a water bath and then 1 gm of solid $Na_2S_2O_4$ is added by means of a spoon, and the mixture is stirred constantly for 1 minute and occasionally for 5 minutes. A second 1 gm portion of $Na_2S_2O_4$ is added with stirring at the end of the second five minute period. Heating above 80°C is avoided because FeS forms at higher temperatures. At the end of 15 minute digestion period, 10 ml of saturated NaCl solution and 10 ml of acetone are added to the tube to promote flocculation. The suspension is then mixed, warmed and centrifuged for 5 minutes at 1600-2200 rpm. The clear supernatant is decanted into a 500 ml volumetric flask and the solution is kept for iron determination.

At pH 2-3 while other metal ions are unstable, the ferric iron forms a stable complex with EDTA. Salicylic acid is used as the indicator and gives a deep violet colour with ferric iron. The colour disappears when a quantitative amount of EDTA is added. Thus total iron can be directly estimated. A known volume of sample solution containing less than 10 mg of Fe^{3+} in 50 ml is taken and its pH is adjusted to around 2.5 by using dilute 1:1 ammonia and sodium acetate. At this pH metals like Al, Mn, Ca and Mg do not interfere. Crystals of salicylic acid are added to give a deep violet colour. The solution was titrated against 0.01 M EDTA, till the solution becomes colourless.

$$\text{One ml of EDTA (0.01 M)} \equiv 0.5585 \text{ mg of Fe}$$

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