Chemical and Structural Characterization of Bangladesh Zircon and its Application

A thesis submitted to the Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology, Dhaka, in partial fulfillment of the requirement for the degree of Master of Science in Engineering (Metallurgical)

by

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DECLARATION

This is to certify that this thesis which is presented for an MSc Engineering Degree by the candidate includes the results of investigations carried out by her under the direct supervision and guidance of Dr. A. S. M. A. Haseeb, Associate Professor, Materials and Metallurgical Engineering Department, BUET, Dhaka. The work of this thesis has not been presented for any other degree or diploma in any other University and no other person's work has been used without due acknowledgement.

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DEDICATED TO MY BROTHER
ZAHIRUL HOQUE BHUIYAN
WHO IS ONE OF THE GREATEST MEN IN THE WORLD

Abstract

Zircon is one of the most important among the heavy minerals occurring in the beach sand along the coastal belt of Bangladesh. The present work attempts to make chemical and mineralogical characterization of zircon beneficiated at the Cox's Bazar Pilot Plant of Bangladesh Atomic Energy Commission (BAEC). The mineral is investigated by means of chemical analysis, optical microscopy and X-ray diffraction (XRD). Potentiality of Bangladesh zircon as a raw material for zirconia, opacifier and refractory brick production is also examined. From the chemical analysis it is found that Bangladesh zircon has 95.88% purity. The main impurity in Bangladesh zircon is titanium oxide (3.01%). This is followed by iron oxide (0.42%). Trace amounts of other oxides are also found. From the mineralogical study it is found that Bangladesh zircon have an elongated, prismatic shape with pyramidal termination in half of the grains and the rest are more or less rounded. Some fractured and irregular grains are also found. Bulk sample of Bangladesh zircon in the as-received condition shows golden yellowish brown color. However, individual grains were found to be almost colorless an d transperent under polarized light. XRD study confirmed good crystallinity in the sample. Under the microscope, it is found that in Bangladesh zircon, zircon grains constitute 94% and total impurities amount to 6%. This result agrees fairly well with the chemical analysis results. The main impurities in the present sample of Bangladesh zircon are found to be oxides of titanium (both rutile and ilmenite). This is also consistent with the findings of chemical analysis. Further, monazite was identified as an important impurity under the microscope. Most of the impurities found in Bangladesh zircon exist as discrete minerals. As a result, it should be possible to remove these impurities fairly easily by physical mineral processing methods and thereby improve the grade of Bangladesh zircon. The iron bearing coating found on some zircon grains can be removed by acid washing. In the disintegration experiments, it has been found that the heating period of 30 minutes is not sufficient to result in complete disintegration of Bangladesh zircon into zirconia even at the highest temperature (1500°C) and the largest sodium oxide concentration (30%) used in the present study. Practical experiments have demonstrated that Bangladesh zircon is quite satisfactory for preparation of zircon flour in ceramic industries. Zircon flour made from Bangladesh zircon can effectively replace imported zircon flour, if adequate size reduction and purification is carried out. Bangladesh zircon can also be used successfully for preparation of refractory bricks for high temperature use.

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Chapter One

1. INTRODUCTION

Zircon is one of the most important among the minerals occurring along the coastal belt of Bangladesh. The reserve of Zircon in the Bangladesh coast is roughly estimated to be one million ton [1]. Zircon is a valuable mineral used as a raw material in various industries including foundry, ceramics, refractories etc [2-3]. In Bangladesh approximately three hundred tons of Zircon flour is consumed every year in ceramic industries; the entire amount being currently imported. However, zircon occurring in the Bangladesh coast has so far not been utilized.

Little work has been done on beach sand zircon of Bangladesh. Naher and Haseeb [4-5] attempted a preliminary characterization of Bangladesh zircon and investigated its use as molding material in steel foundries. Zircon sand as extracted at the Beach Sand Exploitation Center, Cox's bazar is found to be very suitable for steel casting. Use of Bangladesh zircon is found to eliminate various surface defects in cast steel spares. In order to explore the full potentiality of Bangladesh zircon in foundry, ceramics, refractories and other industries it is necessary to make an in-depth characterization of this mineral and study its various physico-chemical properties. So, the objectives of the present work is to characterize Bangladesh zircon, particularly to find out its impurity content and state of impurity and ways to remove the impurities from Bangladesh zircon. Attempts have also been made to investigate the suitability of Bangladesh zircon in the manufacture of opacifier for glaze and in the production of refractory bricks. The out come of this study is expected to provide a scientific basis for the use of Bangladesh zircon in ceramics and refractory industries.

Chapter Two

2. LITERATURE SURVEY

2.1 CHEMICAL CHARACTERIZATION OF BANGLADESH ZIRCON

2.1.1 Introduction

Elemental analysis [6] is the first and routine work for the characterization of chemical compound. From the analytical data the empirical formula of the compounds can be easily deduced. To determine different elements present in an unknown zircon sample, highly sophisticated instruments were used. Absorption spectroscopy is one of the most useful instrument available to the laboratory for quantitative analysis. Here for this purpose a Spectrophotometer of model UV-2201, Shimadzu, Japan and Flame photometer were used.

2.1.2 Theoretical Aspects of Molecular Spectroscopy (UV-Visible)

Beer's Law:

The amount of monochromatic radiation absorbed by sample is described by the Beer-Bouguer-Lambert Law, commonly called Beer's Law. Consider the absorption of monochromatic radiation of radiant power P_0 which Passes through a solution of an absorbing species at concentration C and path length b, and the emergent (transmitted) radiation has radiant power, P. This radiant power is the quantity measured by spectrometric detectors. Bouguer and Lambert recognized that when electromagnetic radiation is absorbed, the power of the transmitted energy decreases in exponential manner as transmitted.

$$P = P_0\ 10^{kb}$$

$$\Rightarrow \frac{P}{P_0} = 10^{-kb} = T \text{-----------} (i)$$

Where 'K' is a constant and 'T' is called the transmittance, the fraction of radiant energy

Logarithmic form of the equation is:

$$Log\, T = Log \frac{P}{Po} = -Kb \text{ ------------ } (ii)$$

In 1852, Beer and Bernard, each stated that a similar law holds for the dependence of 'T' on the concentration, C

$$T = \frac{P}{P_o} = 10^{-K'c} \text{ ------------------------ } (iii)$$

$$=> \quad Log\, T = Log \frac{P}{Po} = K'c \text{ -------- } (iv)$$

Where K' is a new constant. Combining these two laws Beer's Law is obtained. It describes the dependence of T on the path length and the concentration of the absorbing species as,

$$T = \frac{P}{Po} = 10^{-abc} \text{ --------------- } (v)$$

where 'a' is a combined constant of K and K^1. The logarithmic form of equation *(v)* is

$$Log\, T = Log \frac{P}{P_o} = -abc \text{ ---------------------- } (vi)$$

It is more convenient to omit the negative sign on the right hand side of the equation and to define a new term, absorbance:

$$A = -Log\, T = Log \frac{1}{T} = Log \frac{P_o}{P} = abc \text{ ------- } (vii)$$

Where, A is the absorbance. This is the common form of Beer's law. It is the absorbance that is directly proportional to the concentration. The path length 'b' in equation *(vii)* is expressed in centimeters, the concentration C is in gram per litre. The constant 'a' is then called the absorptivity or extinction coefficient. 'C' is expressed in moles/litre; 'b' in cm, the constant 'a' is replaced by $\in$ and the Beer's Law is written as

$$A = \in bc \text{ --------------------- (viii)}$$

This new quantity, $\in$ is known as molar absorptivity. Since A is unitless, $\in$ has the unit of litre mol^{-1} cm^{-1}. Molar absorptivity and absorptivity are dependent on the nature of the absorbing material and the wave length of measurement. Beer's Law holds strictly for monochromatic radiation, since the absorptivity varies with long wavelength.

Application of Beer's Law:

Beer's Law is the basis of all quantitative application of UV-Visible spectroscopy. Generally a method of calibration or standardization is used for determining the concentration of the analyte.

Beer's Law will generally hold over a wide range of concentration if the structure of the coloured ion or the coloured non electrolyte in the dissolved state does not change with concentration. Small amounts of electrolytes, which are chemically unreactive with the coloured components, do not usually affect the light absorption; large amounts of electrolytes may result in a shift of the maximum absorption, and may also change the value of the absorptivity. Discrepancies are usually found when the coloured solute ionizes, dissociates, or associates in solution, since the nature of the species in solution will vary with the concentration. The Law does not hold when the coloured solute forms complexes, the composition of which depends upon the concentration.

The procedural detail includes the following steps for analysis [6]

a) Selection of wavelength:

Spectrophotometric absorbance measurements are ordinarily made at a wavelength corresponding to a highest absorption peak because the change in absorbance per unit of concentration is greatest at this point. Under these circumstances, good adherence to Beer's Law can be expected.

b) Variables that influence Absorbance:

Common variables that influence the absorption spectrum of a substance include the nature of the solvent, the pH of the solution, the temperature, high electrolyte concentrations and the presence of interfering substances. The effects of these variables must be known conditions for the analysis must be chosen such that the absorbance will not be materially influenced by small, uncontrolled variations in their magnitudes.

Determination of the Relationship between absorbance and concentration:

After deciding upon the conditions for the analysis, it is necessary to prepare a calibration curve from a series of standard solutions. These standards should approximate the overall composition of the actual samples and should cover a reasonable concentration range of the analyte. For this purpose suitable quantities of the constituents within the linear range were taken and treated in the same way as the sample solution for the measurement of absorbance at the optimum wave length. The absorbance was plotted against the concentration, a straight line was obtained which obeyed the Beer's Law. The curve then used for quantitative determination of the constituents under the same experimental conditions.

2.1.3 Theoretical Aspects of Flame photometry:

The facts that sodium and several other common elements impart characteristic colors to the Bunsen flame and that the brightness of the flame varies with the amount of sodium or other element introduced have been known for a long time [7]. Flame photometry is concerned with the emission of characteristic radiation in flames by individual elements and the correlation of the emission intensity with the concentration of these elements.

The method of excitation in the flame is as follows. A small volume of the solution of the sample is placed in a cup of an atomizer: air or oxygen and a combustible gas are fed to the atomizer at controlled rates of flow, and the solution is vaporized in a special burner. The following events occur in rapid succession when the solution is sprayed into the flame:

(1) the water, or other solvent, evaporates, leaving minute particles of the salt or mixture of salts.

(2) At the high temperature of the flame the salts or their decomposition products vaporize, and they may also dissociate into the constituent atoms or radicals.

(3) The vapors of the metal atoms or of the molecules containing the metal atom are then excited by the thermal energy of the flame. The resulting emission spectra may be of several types: these include those consisting of lines originating from excited atoms or ions, and banded spectra are of main interest; spectra arising from ions may be produced at high temperatures and at high concentrations of the atoms in the flame.

2.2 PROPERTIES OF MINERALS

2.2.1 Introduction

A mineral is a naturally occurring homogeneous solid, inorganically formed, with a definite chemical composition and an ordered atomic arrangement [8].

2.2.2 Physical Properties of Minerals

Minerals possess certain physical properties [9] that are considered in the following order:

1. Certain characters depending upon light, such as color, lustre, transparency, phosphorescence and fluorescence.
2. Characters depending upon certain senses such a those of taste, odor and feel.
3. Characters depending upon the state of aggregation such as form, pseudomorphism, polymorphism, hardness, tenacity, fracture, cleavage, and surface tension effects. Crystallography,- the study of crystals.
4. The specific gravity of minerals
5. Characters depending upon heat, magnetism, electricity and radioactivity.

2.2.2.1 Color, Lustre, Transparency etc.

Color – Color depends upon the absorption of some and the reflection of others of the colored rays or vibrations which compose ordinary white light. The color of a mineral is often its most striking property. Unfortunately for purposes of identification, however, the colors of minerals vary very greatly. Even in the same species specimens are found having very different colors. The streak of a mineral is the color of its powder and may be quite different form that of the mineral in mass. For instance, black hematite gives a red powder. Change of color is a somewhat similar phenomenon extending over broader surfaces, the succession of colors being produced as the mineral is turned. Some crystals (anisotropic minerals) display different colors when viewed in different directions by transmitted light. This property called pleochroism.

Lustre- The lustre of minerals differs both in intensity and kind, depending upon the amount and type of reflection of light that takes place at their surfaces.

There are six kinds of lustre:-

1. Metallic- The ordinary lustre of metals.
2. Vitreous-The lustre of broken glass.
3. Resinous-The lustre of resin.
4. Pearly-The lustre of a pearl.
5. Silky-The lustre of silk.
6. Adamantine-The lustre of a diamond.

When the surface of a mineral is sufficiently brilliant to reflect objects distinctly, as a mirror would do it is said to be splendent. When the surface is less brilliant and objects are reflected indistinctly it is described as shining. When the surface is still less brilliant and it is termed glistening and minerals with no lustre are described as dull.

Transparency and Translucency-A mineral is transparent when the outlines of objects seen through it appear sharp and distinct. A mineral which, though capable of transmitting light, cannot be seen through is translucent. When no light is transmitted the mineral is opaque.

Phosphorescence and Fluorescence-Phosphorescence is the property possessed by some substance of emitting light after having been subjected to certain conditions such as heating, rubbing or exposure to electric radiation or to ultra violet light. Some minerals emit light whilst exposed to certain electrical radiations. This phenomenon is best exhibited by fluor-spar and for this reason is called fluorescence.

2.2.2.2 Taste, Odor and Feel

Taste- The characters of minerals dependent upon taste are only perceptible when the minerals are soluble in water .

Odor- Some minerals have characteristic odors when struck, rubbed, breathed upon or heated.

Feel- Smooth greasy or unctuous, harsh or meagre or rough are kinds of feel of minerals that may aid in their identification. Certain minerals adhere to the tongue.

2.2.2.3 State and Aggregation

State- Minerals can be any state e.g. solid, liquid or gas.

Form- Under favorable circumstances minerals assume certain definite geometrical forms called crystals, the recognition of which is a valuable aid in the identification of minerals. Minerals assume various indeterminate forms that are not necessarily dependent on crystal character.

Pseudomorphism- Pseudomorphism is the assumption by a mineral of a form other than that which really belongs to it.

Polymorphism- It has already been mentioned that two minerals of markedly different physical properties, such as color, hardness, crystal form, specific gravity, etc., may have identical chemical compositions. Such substances are said to be dimorphous and illustrate the general property of polymorphism.

Hardness- Hardness varies very greatly in minerals. Its determination is one of the most important tests used in the identification of minerals and may be made in several ways. The scale in general use, and known by the name of *Mohs' Scale* of Hardness is given below.

MOHS' SCALE OF HARDNESS

Hardness	Standard Mineral
1	Talc
2	Rock-salt, or gypsum
3	Calcite
4	Fluor-spar
5	Apatite
6	Orthoclase felspar
7	Quartz
8	Topaz
9	Corundum
10	Diamond

Tenacity- Minerals possess certain properties dependent upon their tenacity, of which the following are the most important:

(a) *Sectility-* A mineral is said to be sectile when it can be cut with a knife and the resulting slice breaks up under a hammer. Examples: graphite, steatite, gypsum.

(b) *Malleability-* A mineral is malleable if a slice cut from it flattens out under a hammer. Examples: native gold, silver and copper.

(c) *Flexibility-* Flexibility is the property of bending.

(d) *Elasticity-* Elasticity is the portion bent springs back to its former position. Mica yields flexible elastic plates, whilst the somewhat similar mineral, chlorite, gives plates that are flexible but not elastic.

(e) *Brittleness-*Brittleness is the character common to many minerals and is shown by their crumbling or flying to powder instead of yielding a slice. Examples-iron pyrites, apatite and fluor-spar.

Fracture- It is very important to note the characters of the fractures displayed on the broken or chipped surfaces of minerals. Fracture is said to be:

(1) *Conchoidal-*The mineral breaks with a curved concave or convex fracture.

(2) *Even-* The fracture surface is flattish or nearly flat, as in chert.

(3) *Uneven-*The fracture-surface is rough by reason of minute elevations and depressions. Most minerals have an uneven fracture.

(4) *Hackly*- The surface is studded with sharp and jagged elevations, as in cast-iron when broken.

(5) *Earthy*- As in the fracture of chalk, meerschaum, etc.

Cleavage- The tendency to split along certain definite planes-the cleavage planes-possessed by many minerals is closely related to crystalline form and the internal structure of the crystal [10]. So, cleavage may be defined as the ever-present ability of a mineral to separate into smaller and smaller particles bonded by smooth surfaces parallel to the directions of faces of possible crystal forms. Cleavage is frequently acts an instance distinguishing properties of minerals. Unfortunately, many minerals show little or no cleavage. If cleavage is well developed, however, a mineral may be identified at times by this property alone. Some minerals separate only occasionally or break along planes of twinning. This may be called parting. Cleavage is a crystallographic feature and may be discussed in terms of direction. Cleavages in one, two or three directions are frequent; fluorite and diamond cleave in four directions, while sphalerite cleaves in six directions.

<u>Cleavage in one direction:</u> A number of minerals have a single plane of cleavage, muscovite and topaz being examples. In thin section, crystals showing one direction of cleavage usually exhibit systems of parallel lines. Occasionally, a cleavage plane may be almost parallel to the section, in which instance practically no cleavage line will appear.

<u>Cleavage in two directions:</u> Several common minerals develop prominent cleavage in two directions, The pyroxenes, amphiboles, and feldspars are outstanding illustrations.

<u>Cleavage in three directions:</u> The types produced due to cleavage in three directions vary considerably. One of the simplest type is that produced by cleavage parallel to the faces of the cube.

<u>Cleavage in four direction:</u> One common mineral, fluorite has cleavage in four direction parallel to the faces of an octahedron.

<u>Cleavage in six directions:</u> Sphalerite is one of the few minerals with cleavage parallel to the six different directions of a dodecahedron.

Surface Tension Effect: The difference in adhesive power of various liquids to different minerals has formed the basis for numerous processes of ore separation and concentration. The various Flotation Processes depend on surface tension property.

2.2.2.4 Density and Specific Gravity

The two terms density and specific gravity are often used interchangeably, although strictly speaking there is a distinction between them. According to the convention in English-speaking countries, the density of a substance is the mass per unit volume, and it is therefore necessary to specify the units used-generally grams per cubic centimeter or pounds per cubic foot. Specific gravity, however, is a number-the number of times heavier a body of any volume is than an equal volume of water; in other words, it is the ratio of the density of the substance to the density of water. The density of a substance is primarily determined by its crystal structure and its chemical composition. Density will vary somewhat with varying temperature and pressure, since changes in these factors cause expansion or contraction. Thus the density of a pure substance with a fixed chemical composition and crystallizing in a specific structure should be constant at a stated temperature and pressure. The density of a substance therefore reflects the nature of the atoms in the structure and the manner in which they are packed together. The density of a crystalline substance is a fundamental property and is characteristic for that substance. Thus, it is a valuable diagnostic property.

2.2.2.5 Characters Dependent upon Heat, Magnetism, Electricity and Radioactivity

Fusibility- The relative fusibility of certain minerals is a useful character as an aid in their determination by the blowpipe.

Magnetic Properties- Only a few minerals are ferromagnetic, that is, strongly attracted by a simple bar or horseshoe magnet. Of these the commonest are magnetite, Fe_3O_4, pyrrhotite, $Fe_{1-n}S$, and a polymorph of Fe_2O_3, maghemite. Minerals which are slightly repelled by a magnet are said to be diamagnetic, those which are slightly attracted are said to be paramagnetic. Minerals containing iron are generally magnetic, but not necessarily so, and the degree of magnetism displayed does not, in all cases, depend on the iron content. Minerals containing no iron may also be sufficiently magnetic to permit of their separation from non-magnetic materials, for example, monazite and some other cerium-bearing minerals. The electromagnetic separation of minerals is an important ore-dressing process. By varying the strength of the electromagnet, minerals of varying magnetism can be separated from one another. Examples of such separations are the purification of magnetite from apatite, etc. The separation of pyrites from blende, siderite from blende, wolfram from tinstone, and monazite from magnetite and garnet. It is sometimes necessary to roast the ore is order to convert feebly magnetic materials, such as pyrites and siderite, into strongly magnetic materials. A small electromagnet is used in the laboratory to separate the heavy residues obtained by the use of heavy liquids into magnetic and non-magnetic portions.

Highly magnetic -Magnetite, pyrrhotite

Moderately magnetic-Siderite, iron-garnet, chromite, ilmenite, hematite, wolfram.

Weakly magnetic- Tourmaline, spinels, monazite.

Non-magnetic-Quartz, calcite, felspar, topaz, corundum, cassiterite, zircon.

Electricity- Electricity may be developed in minerals either by friction or heat, and in the latter case the mineral is said to be pyroelectric. Tourmaline is an example of a pyroelectric mineral. The degree of electrification varies widely among minerals, and this variation is applied in the Electrostatic Separation Process. In one type of this process the finely crushed and dried ore is dropped on to a rotating iron cylinder which is electrically charged. Good conductors become charged and are repelled from the cylinder, bad conductors are repelled to a less degree, and hence the shower of ore is separated out into several minor showers which can be separately collected. For example, blende a bad conductor, is separated from pyrites, a good conductor, in this way.

Good conductors- Native metals, graphite, sulphides(except blende)

Bad Conductors- Blende, quartz, calcite, barytes, fluor-spar.

Insulators-Zircon.

Radioactivity- Many minerals containing elements of high atomic weight are radioactive, and emit an emanation which affects a photographic plate and may be rendered visible by means of a sensitive phosphorescent screen. The chief radioactive elements are radium itself, uranium and thorium. Pitchblende is the most important radioactive mineral, others being autunite, monazite, thorite and carnotite.

2.2.3 Optical Characteristics of Minerals

Now some optical properties of minerals can be considered. When a mineral is illuminated with light there are several processes that can occur as a result of the interaction between the light and the material. Some light may be lost and the energy transformed into heat in which case it is absorbed. Some, however, may pass through without loss, i.e., transmitted, or scattered back from the surface of the material, i.e., reflacted.

By using all of these optical behavior, optical characteristic of the minerals can be determined under a microscope. The examination under the microscope consists of a group of operations, namely, those carried out by using (1) ordinary light (2) polarised light, (3) crossed nicols.

(1) Ordinary light- In this case both polariser and analyser are removed. Ordinary light can be used to determine color, transparency, inclusions, cleavage, crystalline form and refractive index.

(2) Polarized light- In this case the lower nicol or polarizer is put into place between the mirror and the stage. The following may be observed:

(a) Pleochroism- Pleochoric minerals show a change in the quantity or quality of their color, this change depending upon the direction followed by the polarised light as it traverses the mineral. Pleochroism is observed by rotating the polariser.

(b) Pleochroic Halos-The presence of Pleochroic halos–small spots more strongly Pleochroic than the main part of the mineral-may be observed by rotating the lower nicol. They are characteristic of certain minerals.

(c) Twinkling- The phenomenon of twinkling is well seen in calcite. In calcite the refractive index for the ordinary ray is 1.66, for the extraordinary ray 1.49. The refractive index of balsam is 1.54. If a granular mosaic of calcite is examined in polarised light, it is obvious that some grains will transmit the ordinary ray and some the extraordinary ray. Those grains transmitting the ordinary ray have a refractive index much greater then that of balsam, and therefore their borders will be well marked; those grains transmitting the extraordinary ray have a refractive index a little lower than that of balsam, and their borders will not be so strongly marked. Hence, when the polariser is rotated beneath the slice of calcite, certain grains have alternately strongly marked and slightly marked borders, and a twinkling effect is noticed.

(1) Crossed Nicols-For the examination of mineral between crossed nicols both polariser and analyser are inserted, and the nicols are so arranged that their vibration planes are at right angles to one another, or are crossed.

(a) Isotropism and Anisotropism:-all sections of isotropic transparent minerals are black between crossed nicols. Such minerals belong to cubic system. Minerals of the other crystal systems are anisotropic, but it must be noted that basal sections of uniaxial minerals are black between crossed nicol.

Many important optical materials however, such as single crystals are anisotropic. Atomic and hence dipole density vary with crystal direction and as a result the polarization is electric field direction dependent. Then the refractive index will be dependent upon the plane of polarization of the light. This is an important phenomenon and one which is utilized in many optical devices. It is termed birefringence and occurs naturally in some materials. Birefringence may be enhanced by the application of external forces such as electric and magnetic fields and even induced by the same means in otherwise non-birefringent materials.

(b) Extinction: Extinction may occur when the particular crystallographic direction makes an angle with the cross-wires. This is oblique extinction, and the angle made between the crystallographic direction and the cross-wires-the angle of extinction is of diagnostic value. Again it may be noted that a doubly refracting crystal, mineral plate, or grain, when dark between crossed nicols, is in the position of extinction. Extinction angle is usually determined in terms of the slower of the two rays or the one having the greater index of refraction.

Parallel Extinction: If the mineral becomes dark between crossed nicols, with the cleavage parallel to the vibration directions of the two nicols, the extinction is said to be parallel.

Inclined Extinction: Many minerals extinguish between crossed nicols when cleavages or crystal houndries lie at oblique angles to the planes of vibration of the two nicols. These are said to have inclined extinction.

Symmetrical Extinction: Many minerals become dark between crossed nicols when the planes of vibration of the nicols are parallel to the diagonals of the rhombic patterns. Extinction of this type is described as symmetrical. Several minerals forming crystals with square outlines may also yield symmetrical extinction.

(c) Twinning: Twinning can be best seen between crossed nicols. Plagioclase felspar is usually twinned, and between crossed nicols an apparently homogeneous crystal shows two sets of twin lamella, each set extinguishing in a different position from that of the other.

Alteration – alteration can be observed in ordinary light, but its nature is best seen between crossed nicols. An altered, mineral is usually turbid or cloudy, and alteration products may be developed along cleavages, cracks or otherwise. Between crossed nicols, altered minerals usually show aggregate polarisation, because the originally homogeneous crystal has been converted by alteration into a multitude of irregularly arranged crystals of the alteration product.

(d) Elongation- some minerals occur as elongated crystals. The sign of elongation can be determined by producing compensation with a quartz-wedge with the mineral in the 45° position between crossed nicols. If the vibrations along the elongation-direction are slow, the mineral is said to have positive elongation, if fast, negative elongation.

2.2.4 Mineralogical Properties of Zircon:

2.2.4.1 Important mineralogical properties of zircon as collected from literature are given below:

Chemical Composition: $ZrO_2\,SiO_2$ [11]

System: Tetragonal

Habit: Euhedral; prysmatic; bipyramidal; Prisms usually square or elongated in the direction of the principal axis, then terminated by pyramid faces (111)

Twinning: Rare

Structure: Crystalline

Cleavage: Absent

Fracture: Conchoidal

Hardness: 7.5 in Mohs' scale of hardness

Specific Gravity: 4.5-4.7g/c.c.

Lustre: Adamanite, vitreous

Color: Colorless, yellow, brown, pink, mauve, purple, and rarely green.

Streak: White [12]

Magnetic Property: Non-magnetic

Electric Property: Non-conductor

2.2.4.2 Optical Characteristics of Zircon:

Relief: Very high, n>balsam.

Refractive Index: Very high, $\varepsilon=1.991$, $\omega=1.936$.

Birefringence: Strong, $\varepsilon-\omega=0.055$; the maximum interferance colors are usually pale tints of the fourth order, but minute crystal shows lower interference colors.

Extinction: Parallel

Pleochorism: Pleochoric in thick crystals and strongly colored varities.

Interference Figure: The interference figure is uniaxial but may be difficult to obtain on account of the small size of the crystals.

Distinguishing Feature: Zircon is distinguished from apatite by stronger birefringence and higher relief. It may be separated from crushed rocks with bromoform or other heavy liquids.

Related Minerals: Malacon is the metamict alteration product of zircon. It is an amorphous mineraloid.

2.2.4.3 Occurrence:

Zircon is a widely distributed mineral in granite and other granite igneous rocks. In some syenites it is prominent enough to furnish the name zircon syenite. Zircon also occurs in certain metamorphic rocks. It is one of the most widespread and abundant detrital minerals being unusually resistant to destruction during erosion and deposition. The forms of zircon crystals observed in sandstones have been summarized by poldervaart (1955).

Zircon ($ZrSiO_4$) and thorite ($ThSiO_4$) appear to form a structural series. Zircon also alters chemically with the addition of U, Th, Pb and H_2O accompanied by a loss in silica. Altered zircon may consist of microcrystalline aggregates which become isotropic and opaque. Minute zircon crystals included in biotite are often surrounded by pleochroic halos.

Zircon is the most common zirconium mineral found in the nature. It occurs mostly as a constituent of acid to intermediate type of igneous rocks whereform it may be derived by weathering and such natural processes, to form placer or littoral deposits. Practically all the economic resources of zircon, formed in this way, are found in the beach deposits.

2.2.4.4 Crystal Structure of Zircon:

Zircon crystallises in tetragonal system and the crystals take the form of a combination of square prisms terminated at either ends by a square pyramid or pyramids of different inclinations [13]. The prism is usually elongated and the habit of the crystal is prismatic. In certain cases when the prism is small, the crystal assumes a pseudo-octahedral habit. The atomic arrangements of zircon correspond to the formula ZrO_2SiO_2 [14]. The value of 'a' being 6.60A° and that of 'c' 5.88A° [15]. The usual silica tetrahedra (SiO_4) are linked together by Zr^{4+} ions in 8 coordination pattern. But the coordination number of 8 is too high with respect to the size of Zr^{4+}ions (radius 0.87KX) and actually the tetrapositive zirconium should be close to the border line on the 6 coordination side, rather than the 8 coordination [16]. This unnatural coordination number leads to the fact that the crystal structure of zircon is unstable. Zircon is isotypic with zenotime (YPO_4) [17a] and thorite ($ThSiO_4$) is isomorphic with zircon [17b]. Hafnium resembles zirconium very closelyin the chemical properties and ionic size [17c]; that is the reason why it always accompanies zirconium in nature.

2.2.4.5 Geochemistry and Metamictization of Zircon:

Zircon occurs most frequently as accessory silicate minerals in igneous rocks, accounting for most of the zirconium present in the upper lithosphere. The crystal structure of zircon, as has been mentioned previously, appears less stable than is often assumed. This circumstance, which is due to the fact that Zr^{4+} ions relatively small in size (radius 0.87KX), affects the manner of occurrence of zircon and also influences the crystallisation of the zirconium minerals in late magmatic stages. Due to the unstable nature of the lattice structure, zircon grains frequently show break down of lattice leading to the dissociation of zircon into ZrO_2 and SiO_2 either partly or completely. As a result, there is some volume expansion of the mineral. The process of such structural breakdown is known as metamictization [18]. Several physical and chemical forces of nature and sometimes a feeble but prolonged radiation dose from associated or neighbouring radioactive sources, (ZrO_2 may have U & Th compounds in solid solution) have been reported to cause such dissociation and decay leading ultimately to an amorphous product called zirconoid.

The notable physical changes brought about by metamictization is a volume expansion as a result of which the density and hardness of the mineral is found to decrease [19]. Cracks and cleavages are often developed through which iron bearing solutions sometimes penetrate to limonitize the grains. The refractive indices are also found to decrease and the development of pleochoric halos are observed within the grains [20]. In the extreme case of metamictization, the grains of zircon develops deeper colors (metamicted zircon grains from Ceylon exhibit deep green color) and become completely isotopic under microscope.

Detailed petrographic study of zircon grains from Kerala Beach, under microscope revealed that there were primarily two major groups of zircons, distinguishable on the basis of physical appearance, all most all grains are fresh transparent grains without any marked color or ferruginous stains and only a few of the colored grains included olive green (occasionally deep green) semi-opaque grains and limonitised brown grains (with ferruginous stains) usually semi-opaque to opaque in nature. The grains belonging to this group were apparently more weathered and rounded and appeared to be comparatively less hard than the other grains which were mostly euhedral in shape [21].

Even though changes in several physical properties of calcined grains like color, specific gravity, etc. were observed, no mineralogical change could be detected under microscope. At higher temperature some of the grains developed cracks and cross fractures, nevertheless they maintained their original mineralogical identity as zircon [21].

2.2.4.6 Specific Gravity:

The specific gravity of zircon was measured at the stated [13] value of 4.68-4.70, but after calcination it gradually went up. This increase in specific gravity indicated a lattice compaction and consequent increase in density of the material. Thus it appears that due to its inherent tendency to decompose, the natural zircon of beach was slightly affected, probably by the radio-activity of monazite etc., and a less dense form resulted which attained its normal denser state only after calcination. The specific gravity of greenish grains were found to be significantly higher than that of zircon. This high specific gravity of the material may be due to the presence of a moderate proportion of huttonite ($ThSiO_4$) later which was identified by X-ray analysis [21].

2.2.4.7 Radioactivity:

A comparative study of the intensity of radiation from the different types of grains by a G. M. Counter and a Gamma-ray diffractometer showed that the radiation from greenish zircon is fairly strong than the as it zircon. The calcined zircon also showed feeble radiation. Hence in the greenish grains, concentration of the radioactive elements appeared more than in the zircon as such and calcination did not appear to have much effect on the radioactive nature of the sample.The nature of the radiation detectable with the available set up was only γ-type [21].

The light zircon varieties contain free amorpous silica and also free amorpous zirconia [22]. Zircons sometimes contain uranium and thorium [23]. In such cases, zirconium silicate is decomposed to a significant degree to silica and zirconia, obviously products of irradiation by the alpha-rays. Possibly, the low density zircon also are products of a radioactive influence.

Particle-counting instruments are frequently used by health physicists [24] to determine the radio activity of the sample taken from the environment, such as an air sample, or to measure the activity of the activity of a biological fluid from someone suspected of being internally contaminated. Particle-counting instruments may be very sensitive-they literally respond to a single ionizing particle. They are widely used for searching for unknown radiation source. The detector in particle-counting instrument may be either a gas or a solid. In either case, passes of an ionization particle through the detector results in energy dissipation through a burst of ionization. This burst of ionization is converted into an electrical pulse that actuates a readout device, such as a scaler or a ratemeter, or register a count.

2.3 PREPARATION OF ZIRCONIA FROM ZIRCON

2.3.1 Introduction

As a high refractory material, zirconium oxide for a long time was the subject of particular interest Soon after the discovery of rich zirconia ores of relatively high purity in Brazil toward the end of the 19th century, many efforts were made to utilize the "nonfusible" material for the industry of refractories and of white enamel. The first dependable studies concerning this material were made just before World War I. Gradually various favorable properties of zirconia came to light. With the progress of time, a growing number of scientists and technologists lent their attention to zirconia. Not all attempts at its application were successful, but all studies contributed to its knowledge and its final good use. Zirconium oxide is not a rare substance by far. In the form of zirconium silicate, or zircon, $ZrSiO_4$ it is widespread in many igneous rocks and crystalline schists, although in only small concentration.

According to American geologists and mineralogists, the content of zirconium oxide in the earth's crust is approximately 0.02%. W. Vernadsky estimates is to be 0.03% [25].

Chemically, zirconium belongs to the fourth group of the periodic table, situated between the lighter titanium and the heavier hafnium. There is only one stable oxide of zirconium: $Zr(IV)O_2$, and its tetravalent derivatives. Careful investigations [26] have proven conclusively that the system Zr-O does not show the presence of an oxide with less oxygen than corresponds to the ratio 1Zr: 2O. Therefore, zirconium monoxide does not exist within the temperature range from room temperature to the melting point of zirconia. However, in the spectra of some stars, the existence of the bivalent zirconium ion has been reported. In the old crystallographic literature many and various modifications and forms of zirconia with sometimes fantastic data are mentioned. For example, H. Collins enumerates ten modifications of zirconia [27]. Zirconium oxide, ZrO_2 exists in three polymorphic forms, i.e. monoclinic (m-), tetragonal (t-) and cubic (c-); only the m-ZrO_2 exists as the themodynamecally stable phase at room temperature [28]. The temperatures of phase transformation in pure ZrO_2 are [29]:

$$\text{Monoclinic} \underset{950^{\circ}\text{C}}{\overset{1150^{\circ}\text{C}}{\rightleftarrows}} \text{Tetragonal} \xrightarrow{2370^{\circ}\text{C}} \text{Cubic} \xrightarrow{2680^{\circ}\text{C}} \text{Melt}$$

The monoclinic structure is the stable form of zirconia below about 1100°C; above this temperature the tetragonal form is stable [30]. The high temperature tetragonal form can be prepared at low temperatures and may be heated to temperatures as high as 600°C before transforming. A number of explanations, e.g. Refs. 31 and 32, have been advanced to account for the retention of the metastable tetragonal phase with heating to 600°C, but general agreement is lacking [33].

The processing of zirconia ore is more difficult because it contains a great amount of silica. A commercial process consists in melting zircon with coke, in a sufficient amount to reduce silica, and iron in an electric furnace, with a simultaneous addition of calcia in order to obtain stabilized zirconia as the final product of the operation. A by-product is ferro-silicon, formed from reduced silica and added iron metal [34].

2.3.2 Some Commercially Available Methods for the Production of Zirconia

For the preparation of ZrO_2 powder, the production routes of commercially viable processes normally use the economically available natural sources, namely, baddeleyite (ZrO_2) and zircon ($ZrSiO_4$). Of the two, zircon is more important because of its wide availability as beach sand deposits [28]. There are various processes for the extraction of zirconia form zircon. They are classified into several groups, as described below.

2.3.2.1 Precipitation and Calcination Technique:

Pure zirconia can be prepared from a favas ore in the following way: finely ground ore is treated with concentrated sulfuric acid in the proportion 1:2. Most of the practically uncombined zirconium oxide is dissolved as zirconium sulfate, silica, and zircon remaining unattacked. The strongly acidic mixture is diluted with water, and the solution is filtered. The filtrate is concentrated again, and the solution is neutralized, whereby a precipitate of the basic zirconiaum sulfate is formed. The precipitate is filtered off, and washed. It can be decomposed to free zirconia by calcination, or it can be dissolved, precipitated as zirconium hydrate, and calcined [35].

2.3.2.2 Chlorination and Thermal Decomposition Technique.

A higher purity grade of zirconia can be prepared in another way: The ore mixed with coke, in an amount sufficient to bind the total oxygen of the ore, and the mixture is heated in a shaft kiln with a silica lining to a red heat. Chlorine gas is introduced into the hot mixture, whereby a complete chlorination of the ore takes place. Zirconium tetrachloride, iron trichloride, titanium tetrachloride, and so on, are formed. Silica is not substantially attacked in this operation. All the chlorides formed are volatile, and sublime out of the shaft. The sublimate is conducted into water, where soluble chlorides and oxychlorides are formed. The solution is boiled down, and zirconium oxychloride is precipitated. By recystallization in strong hydrochloric acid the oxychloride is obtained in a pure state and in a good yield. It can be calcined immediately to zirconium oxide, or dissolved in water and precipitated with ammonia as zirconium oxide hydrate. After calcination, a heavy pure white zirconia powder is produced.

An intimate mixture of zircon and carbon is obtained after milling and pelletizing. When this is directly chlorinated at 800-1200°C in a shaft furnace or fluidized bed, the following reaction occurs [36, 37]:

$$ZrSiO_4+4C+4Cl_2 \longrightarrow ZrCl_4+SiCl_4+4CO$$

Zirconia tetrachloride, after being distilled, is selectively condensed at 150-180°C when the major impurities, i. e. chlorides of silicon, iron, titaniumand aluminium are separated. After hydrolysis with water, a solution of zirconium oxychloride or zirconyl chloride ($ZrOCl_2$) is obtained. The $ZrOCl_2$ solution is used for the preparation of ZrO_2 powers.

2.3.2.3 Alkali Oxide Decomposition Technique:

It is well known that zircon is decomposed at high temperature in reducing media [38]. The decomposition temperature, however, is lowered when the silicate is mixed with fluxing agent such as NaOH [39]. Na_2CO_3 [40, 41] $CaCO_3$ or $MgCO_3$ [42, 43].

One method [44] consists in the fusion of zircon ore with sodium hydroxide at approximately 600°C, to form a mixture of sodium zirconate with sodium silicate. The mixtur is leached out with water, dissolving the silicate and leaving the hydrolyzed zirconnate as an insoluble oxide hydrate. The filtered zirconia hydrate is treated with hydrochloric acid to produce zirconium oxychloride.

Zircon may be decomposed either with NaOH [45] or Na_2CO_3 [46] which act as the fluxing agents. In presence of NaOH, zircon decomposes at 600-700°C, forming sodium zirconate, sodium zirconate silicate and sodium silicate. The degree of decomposition depends on parameters like particle size of zircon alkali/zircon molar ratio, temperature and time of decomposition etc. By careful control of the process parameters, the following reaction products are obtained:

$$ZrO_2.SiO_2 + 4NaOH \longrightarrow Na_2ZrO_3 + Na_2SiO_3 + 2H_2O$$

In presence of Na_2CO_3, the conversion occurs at a much higher temperature, e. g. 1000-1100°C as follows:

$$ZrO_2.SiO_2 + Na_2CO_3 \longrightarrow Na_2ZrSiO_5 + CO_2$$

$$ZrO_2.SiO_2 + 2Na_2CO_3 \longrightarrow Na_2ZrO_3 + Na_2SiO_3 + CO_2$$

Leaching with water of the decomposed mass removes the soluble sodium silicate and simultaneously hydrolizes sodium zirconate to hydrated zirconia. The impure hydrated zirconia is dissolved in concentrated HCl, HNO_3 or H_2SO_4 at 80°C for obtaining a zirconyl chloride, nitrate or sulphate solution respectively.

These solutions are then purified either by precipitation as basic zirconium sulphate [47-49] or by crystallization as the corresponding zerconium salt [45, 49]. Further chemical treatment of the precipitates or crystals, as described in the subsequent sections generates ZrO_2 powders. The $NaZrSiO_5$ phase is decomposed by the action of mineral acids. Silica precipitates out and is separated; the rest forms an impure zirconyl salt which is purified [49].

2.3.2.4 Lime Fusion Technique.

When a mixture of $ZrSiO_4$, and calcia (in differents proportions) is heated at various temperatures. Calcium zircoium silcate, calcium zirconate and calcium silicate are formed [36]:

$$ZrO_2.SiO_2 + CaO \longrightarrow CaZrSiO_5$$

$$ZrO_2.SiO_2 + 2CaO \longrightarrow ZrO_2 + CaSiO_3$$

The second reaction is more suitable because $CaSiO_3$ can be removed by a treatment with HCl. When doloma (calcined dolomite) is mixed with zircon, followed by heating, various mixtures of zirconia and calcium magnesium silicate are produced. In presence of an equimolar mixture of $ZrSiO_4$ and limestone, heated at 1100-1500°C\3-9h, decomposition of zircon occurs as follows [50]:

$$ZrSiO_4 + CaCO_3 \longrightarrow ZrO_2 + CaSiO_3 + CO_2$$

From the mixture of ZrO_2 and $CaSiO_3$ thus obtained, $CaSiO_3$ is removed first by leaching with HCl at 90°C followed by treatment with NaOH at 15°C.

2.3.2.5 Plasma Decomposition Technique:

When zircon particles are introduced into a stable argon plasma reactor at a temperature range of 6000-1500°C and quenched rapidly, dissociation of zircon occurs with the formation of the constituent oxides, i. e. ZrO_2 and SiO_2 [51]. The degree of dissociation depends on a number of process parameters, e.g. the particle size of zircon, flow rate of Argon gas, arc current, feed rate etc. The decomposed mass is treated with NaOH or H_2SO_4.

2.3.2.6 Thermal Dissociation Technique:

Zircon can be thermally dissociated in an arc furnace or an electric reactor [37] when heated above 1750°C (followed by rapid cooling); into its constituent oxides and the chemical reaction that takes place is essentially as follows:

$$ZrSiO_4 \longrightarrow ZrO_2 + SiO_2 \text{ (fumes)}$$

ZrO_2 and SiO_2 are recovered separately as discussed above.

2.4 OPACIFIERS

2.4.1 Introduction

Normal glazes are transparent, they offer a homogeneous medium to light rays which may be reflected at the surface, or refracted on entering and leaving it. In opaque glazes the medium is not homogeneous, particles are suspended in the glassy matrix each of which reflects, refracts and diffracts light. The refractive index of the suspended particle must differ from that of the glass phase, and irregularly shaped particles are the most effective [52]. The particles may be:

(1) A finely divided raw material that has not reacted and dissolved.
(2) A compound formed in the reactions that is immiscible with the rest of the glass.
(3) Crystallites formed on cooling.
(4) Minute gas bubbles (this makes the glaze mechanically weak and is inapplicable).

The opacity of a surface coating is its ability to obscure the color or color differencees of the substrate. The choice of the opacifier therefore depends on the nature of the glaze.

More clearly, Opaque glazes are those sufficiently low in light transparancy as to effectively hide the body from the view. They usually are white, but this is not a requrement. The more opaque the glaze, the greater the hiding power per unit of glaze thickness [53].

2.4.2 Types of Glazes

According to the mechanism of the opacification, opacifiers can generally be classified [54] into two groups: (1) Those which remain in the glaze essentially in the same form in which they are added and (2) Those which go into solution and then crystallize form the glaze during cooling.

According to the maturing temperature of the glazes, zirconium glazes can be classified into three groups (a) glazes maturing at high temperature (b) glazes maturing at moderate temperature (c) glazes maturing at lower temperature.

2.4.3 Mechanism of Glazing:

Zircon is classified in that type of inert opacifiers which remain in the glaze essentially in the same form in which they are added. The performance of an opacifier of this type depends on the amount present, its particle size and on the difference between the index of refraction of the opacifier and that of the glassy matrix in which it is present.

It was also observed that opacification by zircon is not purely a recrystallization effect, i.e., all the zircon does not dissolve in the glaze and precipitate again on cooling, some zircon does dissolve in the glaze and more opacifier remains dissolved in the glaze matrix when zircon is used [54].

2.4.4 Zircon as an Opacifier

Zirconium compounds have found increasing use in the development of opaque glazes. Formerly they were used in glazes mainly in the form of ZrO_2 but at present zircon i. e. zirconium silicate is being used for this purpose, primarily, for its low cost and wide availability [55]. At present zirconium opacifiers are available commercially in the form of pure zirconium oxide, milled zircon, zirconium spinel and double silicates of zirconium. One of the opacifiers gained wide popularity and usage which was made by fusing zircon with alkali and removing a part of the alkali by leaching with water or a weak acid. It is reported that 5 percent ZrO_2 gave a thorough white opaque glaze but necessitated increase in the maturing temperature.

The main disadvantage of using ZrO_2 as an opacifier is the high cost of its production by process of removing silica from zircon in electric furnaces. Hence experiments were undertaken to use in opacifiers the naturally occurring mineral zircon itself instead of ZrO_2. C. J. Kinzie and C. H. Commons [56] while discussing the effect of zirconium oxide in glasses, glazes and enamels, observed that good opaque glaze could be produced by adding 15 per cent ZrO_2 in the form of inexpensive pure zircon, but the form in which this zircon was to be added required adjustment. The higher the percentage of opacifier the better is the opacity but the maximum limit is determined by the ability of the glaze to take in increased quantity of opacifier without impairing the gloss and texture or introducing any other defect like crawling, pinholing, etc [57].

2.4.4.1 Preparation and Purification of Zircon Flour from Raw Zircon Sand

Purification of raw zircon sand ore is based on the chemical resistance of zirconium silicate to strong mineral acids. The process of purification consists of two steps. First, the raw material is subjected to a magnetic treatment in order to remove iron compounds. In the second step, the sand is treated with concentrated sulfuric acid [35]. It is preferable to grind the material before the benefication process. Most contaminants of zirconium silicate are soluble in hot concentrated sulfuric acid. After the treatment the initially gray-brown material becomes bright and white. After filtering, washing, and drying, the product may be of 98-99% purity.

Another method of purification uses smelting of the ore with an equal amount of alkali-hydrogen sulfate (bisulfate) [58]. This method, thus, basically represents the same treatment as mentioned above. After eliminating coarse-grained gang, mostly quartz, a product assaying approximately 97% of zirconium silicate is obtained. For a further refining, the ground product is mixed with a fine carbon powder, just as much as is needed for reduction of foreign oxides: TiO_2, Fe_2O_3, etc., and then treated with chlorine gas at red heat. Most of the impurities volatilize in the from of chlorides, leaving white zircon of 99+%purity as the final product. The French glass company St. Gobain, Chauny et Cirey has suggested the preparation of pure zirconium silicate synthetically from silica and zirconium dioxide in equimolecular ratio. The method is capable of giving a very pure product indeed, but it appears to be too expensive for commercial ceramic purposes.

Chemically, zircon is a very stable substance, especially at lower temperatures. With respect to acids, zircon is one of the most resistant substances and materials. Only concentrated hydrofluoric acid violently attacks zircon, forming zirconium-oxyfluoride, $ZrOF_2.2HF$.aquous, and silicon tetrafloride. Phosphoric, sulfuric, hydrochloric, and nitric acids do not decomposes zircon, naturally, not to mention organic acids. On the contrary, basic substances easily attack and decompose zircon, particularly at elevated temperatures. The relative stability of zircon, molecules can be seen from the reported fact that lithium-ortho-silicate, Li_4SiO_4 dissolves zirconium silicate, $ZrSiO_4$ as a monomolecular substance, without association or dissociation [59].

The visual color of the zircon is improved in two steps of processing. The first step of acid washing probably removed some lighter dusts mixed up with the sand and some amount of ferruginous matter by solution, which would occur as stains. In the second step of calcination, the grains become more buff and less greyish in appearance at 1300°C. The color improved further with the subduing of the buff shade at higher temperatures of calcination above1350°C. This could have been due to the fact that on calcination there was an improvement in the degree of crystallinity of the zircon grains, resulting in the improvement of color and transperency [21].

2.4.4.2 Preparation of Zircon Glazes:

To make a design for a glaze, it is difficult to generalize on the formulation of zircon glazes since the influence of any one component of the base glaze depends on the properties and proportions of the other constituents. There are signposts rather than specific directions for zircon glaze, because the correct formulation of any zircon glaze is a compromise between desiderata that sometimes conflict.

During glaze preparation most zircon glazes benefit by fine milling. As zircon glazes tends to be more viscous in the kiln than tin oxide glazes, the fine milling by increasing the surface area and therefore the reactivity of the glaze constituents reduces the viscosity. The difference between the texture of an undermilled and a properly milled zircon glaze is remarkable.

Opacifiers which have been made by over-grinding zircon sand are revealed by the poor shade which they give in white glazes. Whites of inferior, dirty appearance can also be due to the use of a grade of zircon which is too coarse. More coarse zircon has to be used in attempting to achieve the opacity which a smaller amount of fine zircon will readily give, and the appearance and texture of the glaze suffer accordingly.

During glaze formulation, the amount of zircon which remains in solution and does not contribute to the opacity is unknown and will in any case vary form glaze to glaze, so the base glaze formulations really provide the best means of comparing one glaze with another.

2.4.4.3 Advantages of Using Zircon Glazes

1. A zircon opacifier considerably reduces the cost of the final glaze as compared to the one opacified by tin oxide.
2. In addition to their cheapness zircon opacifiers have their own intrinsic value of imparting desirable properties to the glaze, such as increased chemical durability, resistance to abrasion and to crazing. When used in suitable proportions the zircon opacifiers also improve the texture of glazes making them finer grained.
3. The firing condition and the kiln atmosphere do not affect their

performance.

4. All types of finish can be obtained form them
5. Opacity can be obtained without the use of zinc oxide, an ingredient often giving rise to difficulties with some colors.
6. More stable colors can be obtained with them.
7. Although antimony oxide and titania have the highest values for refractive index their uses are restricted to low temperature glazes and enamels only, because antimony oxide has a tendency to volatilize at glaze maturing temperature and titania imparts an yellowish tint in presence of traces of iron or chromium. Naturally the field was thus left to zirconium compounds on which considerable volume of work has been carried out in different countries.

2.5 ZIRCON REFRACTORIES

Zircon containing materials which are used in refractories may divided into pure zircon silicate materials, which in part still contained free zirconia (ZrO_2) and sintered or fused alumina-zirconia-silica (AZS) materials, which are mixture of zircon, mulite, and corundum [60].

Zircon containing bricks are pressed isostatically, slip cast, shaped by hand, pressed unixally, or compacted by vibration. Brick containing zircon are distinguished by high corrosion resistance against several types of aggressive media, and are commonly used in the glass and steel industries [60].

Zircon refractory products may be split between:

- Dense and sintered materials with usually 15% by volume apparent porosity, variant reinforced with zirconia have apparent porosity of 5-9% of volume, and
- Ceramically bonded (porous) materials with an apparent porosity of 15-24% by volume.

Dense zircon sillicate bricks are installed in glass melting furnaces as soldier bricks in the melting and refining areas of borosilicate glass tanks. In electrical tanks, they are installed in the bottom and as rear lining. Owing to the low electrical conductivity at high temperatures, so called electrode bricks for electric heating are also manufactured out of dense zircon silicate minerals. Casting nozzles may also be made of zirconium silicate, and in Japan, such bricks are used in steel ladles. AZS materials contains sintered and fused synthetic raw materials (corundum, mullite, and corundum-zirconia) as admixture.

There are three main families of refractory products based on zircon commonly used in the glass industry:

1. sintered zircon

2. sintered zircon-mullite
3. fused cast aluminium-zirconia-silica (AZS)

Sintered Zircon Refractories:

The compositions are based on grog (ground zircon, fired and crushed), raw sand, ground zircon and sintering additives (TiO_2, silica, clays). The raw materials are shaped by pressing or casting and fired. Machining after firing may be requested on the joint faces.

Many grades are manufactured and they differ by grain size, residual porosity and purity.

The top quality is the dense, fine grained, zircon obtained by isostatic pressing or slip casting, firing at high temperature (up to 1,600°C) and extensively machined. Their apparent porosity is below 1%. Blocks weighing up to 450kg, 200x500x1,000 mm size are available.

A complete range of larger grain size materials, with an intermediate level of porosity, is obtained by isostatic or unidirectional pressing and slip-casting, firing around 1,550°C followed by machining. Their porosity varies between 10-15%. Blocks as well as complex shapes are available.

The lowest quality grades are made with sand grains as the larger size fraction and clay binders. They are pressed and fired around 1500°C and the porosity is 15-20%. Standard bricks, up to 30kg, are available, and they are usually not machined.

Specific Properties of Zircon Glass Refractories [60]

1) The solubility of zirconium in molten silica or silicates is low. For this reason, materials containing zircon and zirconia are resistant to

the attack by most glasses. The corrosion resistance of zircon leads to their nain use in the most exposed areas of the furnaces. A fused cast refactory will have a corrosing resistance around twice as high as sintered material.

2) When comparing the resistance to the atmosphere, zircon is also generally favorable. Here, dense materials, like fused-cast refractories, display only surface reactions. They are more resistant then porous sintered products, which show penetration and structural transformation.

3) To the contrary of another highly resistant compound, Cr_2O_3 zircon or zirconia dos not color the glass when dissolving. This is important for flat and some container glasses.

4) Regarding defects, the use of zircon or zirconia refratories depends widely on the type of glass, its temperature, and on the type of refactory. It is a complex phenomenon.

5) As for the resistance to cracking, dense sintered zircon are less resistant than porous sintered refractories.

Characteristics: Acid refractory. No crystalline inversions, uniform thermal expansion curve (4.5×10^{-6} per ^{0}C from 20-500^{0}C) [52]. Good resistance to molten metals except under strongly oxidizing conditions. Exceptional resistance to molten aluminium which does not wet it, also little alummina dross forms and this is not strongly adhesive. Resistant to borosilicate glasses, metaphosphates, sodium chloride, sodium chloride-zinc chloride flux, potassium pyrosulphate, phosphorus pentoxide. Attacked by sodium carbonate and sodium fluoride, fluorspar, cryolite, molten barium sulphate, and tetrasodium pyrophosphate [61]. Good thermal shock resistance.

Uses. Aluminium remelting furnaces. Calcium phosphate fertiliser furnaces. Glass tanks:for superstructures, feeder parts, feeder forehearths and in the 'balanced' glass furnace. Crucibles for platinum.

Body Type. Single-component refractory.

Raw Materials. Natural zircon sand. Micronised zircon. Garvie [62] published some evidence for improvement in the mechanical properties of the $ZrSiO_4$ with the addition of ZrO_2. The two phases are mutually compatible in all proportions at temperatures up to the zircon dissociation temperature, 1670°C. Zircon materials often find applications as refractories because of their relative stability to most steels at temperatures below the dissociation temperature [63]. However generally sintering of $ZrSiO_4$ is difficult, and up to 10%clay is added to bond these materials [64].

Prepration: Natural fine zircon sand → Partial sintering → grog →.crushing → grinding → blending: 2 parts zircon sand: 1 part micronised zircon. or equal parts grog-14+72 mesh, sand and micronised.

Shaping: Dry pressing. Slip casting. Ethyl silicate casting [65]. Pneumatic tamping [66]. Hand molding. Extrusion.

Firing: 1300°C to over 1500°C according to purity of zircon sand. If impure, resistance to load at high temperatures is increased by firing to 1650-1700°C for at least one hour.

Chapter Three

3. EXPERIMENTAL

3.1 CHEMICAL ANALYSIS

Chemical analysis of zircon was carried out and the detail procedures for those chemical analysis are given in Appendix-A to E.

3.2 MINERALOGICAL CHARACTERIZATION

3.2.1 X-ray Diffraction Study

X-ray diffraction pattern of as received zircon, was carried out. In this case small amount of sample was taken on the agate mortar and grinding of zircon was done manually. This ground sample was ready for X-ray diffraction. X-ray diffraction pattern was recorded in a JEOL, X-ray powder diffractometer using Mok_{α} radition. The pattern was recorded between two-theta range of 5-55° at 30 kV and 20 mA. A scanning speed of 1°/ minute and a chart speed of 5mm/minute were used with a full scale of 4×10^4 cps.

3.2.2 Grain Slide Petrography

Slides of as received zircon, different meshed zircon after sieving, 50%sulphuric acid treated zircon for 10 hour at a temperature of 110°C, 20%sodium hydroxide treated zircon at a temperature of 800°C for 2 hours, zircon calcined at 1400°C and 1600°C were prepared separately. For the preparation of slides, enough grains of each type were placed on a glass slide containing Canada Balsam which acts as a binder. The slides were then heated to about 120°C and a thin glass cover was placed over the grains. After that, the slides were cooled down and washed with acetone. The minerals were identified under the polarizing microscope.

Microscope slides used in this purposes were wheel brand, Cat No. 7101, made in China, 72 pieces, clear glass ground edges 25.4×76.2 mm (1×3 inches), 1-1.2 mm thick.

Microscope slides cover slips used in this purposes were manufactured by CHANCE PROPER LTD. SMETHWICK, Warily, England, No 1.5, 22×44mm, BSS 3836-17, Average contents 100pieces.

3.2.3 Thin Section Slide Petrography

The first step in the manufacturing of a thin section [48] involves production of a smooth flat surface impregnated with sand grains suitable for mounting on a glass slide. For this purposes, equal amount of araldite binder and araldite resin were properly mixed with sand grains and then was placed over a glass slide just forming roughly a rectangular block making a flat surface by covering with a cover slide. Then the block was placed on a flat surface of a glass slide and retained for two days for adhering purposes. After two days, the block became hard. Then the block was placed on Precision Thin Section Equipment and gradually cut from the cover slide side with slow feed. During each cut special care was taken for moving the side away handle. When the chip was brought to 1mm thickness the cutting in this machine was stopped. The flat and smooth surface of the slab was mounted on a clean microscope slide applying araldite glue (resin and hardener=1:1) on the polished surface. Care was taken so as to remove any excess glue and any air bubbles from the glue. Then it was placed at a room temperature for 72 hours as the slab become fixed on the glass slide. The free face of the sample was ground on a coarse grinding lap until light could pass through it. Then it was further ground on a glass plate using 400 grade and after rinsing 600 grade carboruodum powder. The thickness of the sand sample was checked regularly using a polarizing microscope. The thin slice was kept uniform in thickness during grinding and it was continued until a thickness of about 0.03mm was attained. The thickness of the slide was controlled through the final stage by the microscope observation of the interference color given by some known mineral (zircon in our case) in the section when covered with a film of water. As zircon is frequently present in our sample the resulting interference color were almost entirely yellowish-gray.

When the section was ground to the proper thickness, it was washed free from grinding powder and dried. Fresh balsam was then smeared over the surface of the slice. It was heated and faced with a cover glass slide. The slide was then cooled and excess balsam around the edge of the cover glass was dissolved with acetone followed by a wash with kerosene. The thin section was then covered and ready for petrography.

3.2.4 Examining the Grain Slides and Thins Sections

A detail qualitative and quantitative analysis was carried out by using Research Petrography Microscope (MEIJI) model ML-POL-T. The mode of the occurrence of each individual detritus and authigenic components and their relative abundance were carefully examined from standard thin section. Proportion of various sand components in each slide were estimated by using point counter with 500 counts being made per slide. "SWIFT' Automatic Point counter model F415C was used for this purpose.

Textural parameter of the sand especially grain size, grain shape, sorting and gain contacts were studied with visual competitors.

The step by step examination of zircon sample in slide:

1st step: To view the specimen in plane polarized light at low magnification; the magnification may be increased as necessary.

Next step: To view the specimen between crossed poplars, that is with the analysis most of the particles show up light or colored against the dark background and as the specimen is rotated all charges alternately between bright and dark. When they are dark every 90° they are said to be extinguishes, they are at maximum brightness at 45° from the extinction position. The bright appearance of the particles means that light is travelling through them perpendicular to a non-circular section of the indicatrix, this confirms that all are anisotropy and therefore, as we suspected, crystalline and non cubic.

Determination of extinction angle of mineral requires fixing a mineral longitudinally. Under crossed Nicole, the inclination angle was measured, by rotating the stage of the microscope. The angle was again measured when the mineral became totally dark. Subtracting the value of these two angles from the stage, the angle of the extinction was measured.

Opaque grains were counted separately. The opaque grains consist mainly of illuminate, magnetite and hematite. Unidentified grains consist of minerals that have been altered to such an extent that their optical properties are impossible to recognize

Determination of Radioactivity

The radioactivity of the raw zircon and variously treated zircon were measured by a particle-counting instrument named Geiger Mueller Counter of model Philips ZP1481, Scalar Griffin Cat. No. XKS-350-OTOF, Britain.

3.3 DECOMPOSITION OF BANGLADESH ZIRCON

Decomposition of Bangladesh zircon ($ZrSiO_4$) to produce zirconia (ZrO_2) was attempted by using caustic soda (NaOH) as the decomposition agent. For this purpose, finely ground zircon of average particle size 5-10μm was mixed with NaOH whose amount was varied between 5-30wt. %. The mixture then pressed into pellet's of size 10mm diameter and 2-3mm thickness in a compression press under

500Kg cm^{-2}. Before the preparation of the pellet an optimum amount of water, found out by trial and error, was added to each mixture as binder.

The pelted samples were then heated in a muffle furnace at temperature ranging from 1300-1500°C. Heating time was kept constant at 30 minutes. The pellets were then furnace cooled and then grounded in to powder. The powdered samples were subsequently investigated by X-ray diffraction method using MoK$_\alpha$ radiation in order to find out the extent of decomposition of Bangladesh zircon into zirconia.

3.4 BANGLADESH ZIRCON AS AN OPACIFIER

3.4.1 Preparation and Purification of Zircon Flour from Bangladesh Zircon:

Zircon flour was prepared from Bangladesh zircon by ball milling and purified by acid leaching. Ball milling was carried out in alumna lined ball milled using alumna balls as the grinding media. The wet and dry grinding results after 24hr are given below in Table 1.

Table 1: Comparison of wet and dry grinding result.

U.S.A. Sieve No.	Dry Grinding	Wet Grinding
100	24.51g	500mg
200	99.26g	500mg
325	93.68g	63g
400	60.22g	61g
Pan	22.30g	164g

From the above table it is clear that wet grinding is suitable for zircon sand. After 2hr leaching treatment the zircon powder had no effect; it remained as the same as before after grinding. 10hr leaching was more effective. When the concentration of sulfuric acid increases up to 80% it gives good result than lower concentration of the acid and again the time for purification should be a limit otherwise the final product of the glaze will be mat.

Preliminary study showed that wet milling is more efficient than dry milling. That is why wet milling was used in all subsequent experiments. The volume of the pot was 1100cc and that of the grinding ball was 270cc. Each charge to the mill consisted of 300g of zircon sand and 400cc of water. The grain size distribution of Bangladesh zircon was determined earlier [67] and is reproduced in Table2.

Table 2: Grain size distribution of Bangladesh zircon

U.S.Sieveno.	Weight in grams	Percent retained	Multiplier	Product
70	0	0	60	0
100	11.34	11.34	70	793.8
140	76.76	76.764	100	7676.4
200	11.58	11.58	140	1621.2
270	0.082	0.082	200	16.4
PAN	0.234	0.234	270	63.18
	100			10170.98

Milling was carried out at 78rpm for 240hr. After milling, the mill was discharged and zircon flour separated which was subsequently dried in a water bath and stored in sample bottles.

Part of the zircon flour produced was purified by leaching in a custom made leaching apparatus. Fig. 1 shows the leaching set up which essentially consists of a conical leaching flask (1000cc) with two condensers in series and a magnetic stirrer hot plate. The flask was also fitted with a thermometer to monitor the temperature which was controlled by the thermostatic controller of the hot plate. During leaching 100gm of zircon flour and 500cc of sulfuric acid was used in each batch. Leaching temperature was maintained at 180°C (approx.), leaching time varied from 2-20 hours and sulfuric acid concentration varied from 10-80ml/l. Constant stirring was used during the entire period. At the end of the treatment, the flask was taken out and allowed to cool, and the zircon flour allowed to settle. It was then washed thoroughly in distilled water and dried first in a water bath and finally in an oven at 110°C.

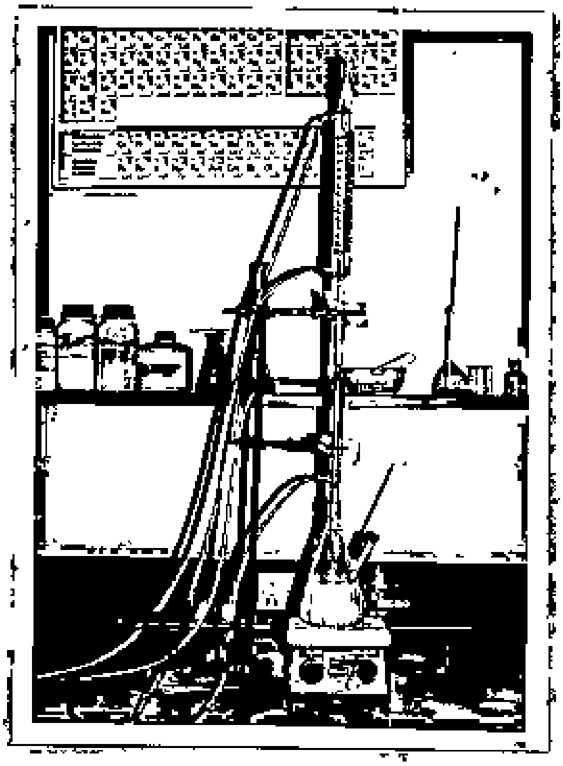


Fig. 1:Experimental setup for the purification of zircon.

3.4.2 Test of Bangladesh Zircon as an Opacifier:

The suitability of Bangladesh zircon as an opacifier is investigated in some local ceramic industries which includes table ware and sanitary ware manufraturers. For this purpose, both as-received and purified zircon flour as discussed above were used. Proprietary transparent glaze of each factory was used as the base. Zircon flour was added to the base glaze in an amount ranging from 8-12%. For every sample, 400g of glaze was prepared by milling for 15hours. The prepared glaze was passed through 200 mesh sieve and its properties recorded. Glaze was then applied onto ceramic bodies of proprietary compositions, which were then fired at 150°C temperature. The appearance, color and relevant properties of the glaze were then studied.

The particle size and distribution were determined by Micrometrix Sedigraph 5100.

3.5 PREPARATION AND TESTING OF ZIRCON BRICKS

Refractory bricks were made from Bangladesh zircon in a local brick factory using different types and amount of binder. The size of the bricks made were 63.5×63.5×25.4 cubic mm which were shaped in a compression mould under a pressure of one ton.

The percentage which were varied during brick making include firing temperature (1360°C and 1430°C), grain size of zircon, type and amount of binder. CMC (Carboxi Methyal Celollose) and iron oxide were used as binder. The prepared zircon bricks were then tested for cold crushing strength and bulk density.

Chapter Four

4. RESULTS AND DISCUSSION

4.1 CHEMICAL ANALYSIS

The result of chemical analysis of Bangladesh zircon in the as received condition is shown in Table 3. The percentage of different constituents as shown in the table is an average value obtained in at least three tests. It is seen from Table 3 that the present sample of Bangladesh zircon contains a slightly lower percentage of zirconium dioxide (63.29%) as compared to the theoretical percentage (66%) of the same in pure zircon. Based on the stoichiometric formula of zircon ($ZrSiO_4$), the silica content of the present sample (32.59%) agrees well with its zirconium dioxide content. This means that there should be little, if any, free silica in the present sample. The main impurity in Bangladesh zircon is found to be titanium oxide (3.01%). This is followed by iron oxide (0.42%). Among the alkali oxides, the content of CaO is found to be higher than the others.

Table 3: Chemical analysis of Bangladesh zircon.

Constituent	Percentage
Zirconium dioxide (ZrO_2)	63.29
Silica (SiO_2)	32.59
Titanium oxide (TiO_2)	3.01
Iron oxide (Fe_2O_3)	0.42
Calcium oxide (CaO)	.367
Sodium oxide (Na_2O)	0.026
Aluminium oxide (Al_2O_3)	0.021
Magnesium oxide (MgO)	0.019
Sulphur (S)	Nil
Potassium oxide (K_2O)	0.01567
Phosphorous penta oxide(P_2O_5)	0.0067

The chemical analysis of Bangladesh zircon is now compared in Table-4 with that of some available zircon deposits of the world. Analysis of typical commercial grade zircon is also presented in the same table (last column). It is seen that the zirconium dioxide content of Bangladesh zircon is lower than that of all other deposits shown in the table. It is actually slightly lower than the minimum zirconium content of

Table 4: Comparison of Bangladesh zircon with some available zircon deposit in the world

Constituent	Bangladesh	Kerala, India [21]	South India [68]	Austr-alia [69]	Egypt [70]	Spain [71]	China [72]	Korea [73]	Specific commercial grade [1]
Zirconium dioxide (ZrO_2)	63.29	65.12	65.5-66.5	66	66	64.3	63.54	64.3	64-67
Silica (SiO_2)	32.59	32.5	31-32	33.3	32.13	32.84	31.17	33.5	32-34
Titanium oxide (TiO_2)	3.01	0.71	0.3-2.5	0.1	0.17	0.04	0.44	0.77	0.5
Iron oxide (Fe_2O_3)	0.42	0.19	0.1	0.05	0.29	0.14	0.14	0.29	0.5
Calcium oxide (CaO)	0.367	---	---	---	---	0.02	0.27	---	---
Sodium oxide (Na_2O)	0.026	0.16	---	---	---	0.03	---	---	---
Aluminium oxide (Al_2O_3)	0.021	0.26	0.7	0.15	0.23	0	3.17	0.33	---
Magnesium oxide (MgO)	0.019	0.73	---	---	---	---	0.081	---	---
Sulphur (S)	Nil	---	---	---	---	---	---	---	0.035
Potassium oxide (K_2O)	0.01567	0.03	---	---	---	0.07	---	---	---
Phosphorous penta oxide (P_2O_5)	0.0067	---	0.5	---	---	---	---	---	0.035

commercial grade of zircon. The main reason for this is the high percentage of titanium oxide in the present sample. The content of iron oxide, although higher than that of other deposits, is well within the specified range of the commercial grade. The removal of titanium oxide and iron oxide should improve the grade of Bangladesh zircon. The ease of removal of these oxides of course depends upon the state in which they exist. This will be further discussed in the section dealing with the mineralogy of Bangladesh zircon (See 4.3).

4.2 CRYSTALLINITY

The result of the X-ray diffraction pattern of the as received Bangladesh zircon is shown in Fig. 2. A large number of sharp peaks are observed in the pattern. The positions of these observed peaks are compared with that of the standard powder pattern of zircon in Table 5. It is observed that almost all the peaks in the XRD pattern of Bangladesh zircon correspond to those of the standard pattern of zircon. From this pattern it is clear that Bangladesh zircon possesses good crystallinity.

Table 5: Comparison of the observed and standard peak position of zircon.

Plane(hkl)	observed peak position	standard peak position [74]
(101)	9	9.20
(200)	12	12.36
(112)	16	16.22
(220)	17.2	17.49
(202)	18	18.44
(301)	19.5	19.80
(103)	21.2	21.6
(321)	23.15	23.41
(312)	23.6	23.96
(400)	24.6	24.85
(411)	26.2	26.55
(004)	27.5	27.50
(332)	29.5	29.82
(204)	31.6	30.25
(413)	32.4	33.08
(440)	37.3	35.45
(611)	39	38.86
(532)	39.4	39.21
(325)	41.4	41.56
(115)	42.4	42.77

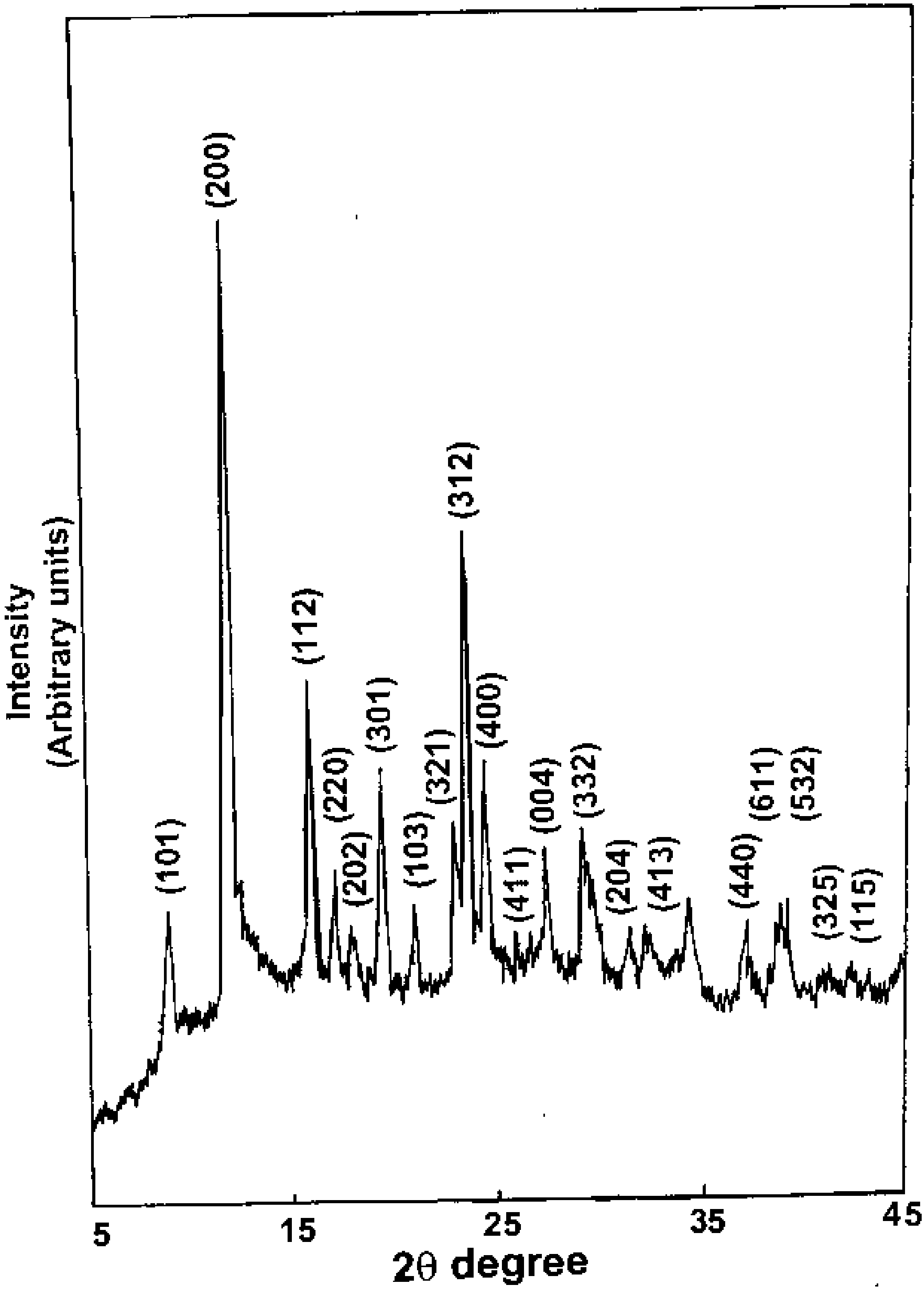


Fig. 2: X-ray diffraction pattern for Bangladesh zircon.

4.3 MINERALOGICAL INVESTIGATION

Fig. 3 shows the general appearance of Bangladesh zircon in a microscope under transmitted light. Elongated prismatic crystal with pyramidal termination as well as rounded grains are observed. A typical prismatic and rounded grains are shown at a higher magnification in Fig. 4a and 4b respectively. Occasionally one or two pseudo-octahedral crystals were also found (Fig. 5). Haloes were also found (Fig. 6) in Bangladesh Zircon. Under cross nicol crystal of Bangladesh zircon show parallel extinction (Fig-7a and 7b) which is typical of zircon mineral. A number of mineralogical features were observed in the sample of Bangladesh zircon. Fig. 8 shows a crystal having concoidal fracture. This type of concoidal fracture is a characteristic of zircon [11]. Cleavage which is rare in zircon was also observed in one grain (Fig. 9). Although not so common, a twinned crystal was also identified (Fig. 10). The crystals of Bangladesh zircon show pleochoric character under cross nicol (Fig. 7), as expected. Bangladesh zircon posseses strong birefringence (Appendix-F). Zoning was also observed in the sample (Fig. 11). A number of grains were found to contain inclusions (Fig. 12). In fact, presence of inclusions is a common occurance. Inclusions are sometimes arranged parallel to the length of the crystal, at other times these are irregularly arranged (Fig. 13). Inclusions within inclusions were also found. Different types of inclusions have been found in zircon crystals by different workers. These includes fluid, glassy, gaseous, solid (Fig. 14) minerals such as iron bearing minerals apatite and hematite, monazite etc [11]. Some crystals show a dusky appearance (Fig. 15). This is thought to be due to the presence of highly dispersed crowds of inclusion, not decomposition product. Fig 16 shows the high relief in zircon grain. A few crystals show a yellow-brownish tint (Fig. 12), presumbly due to the presence of an iron-bearing coating on the surface.

The present sample of Bangladesh zircon contains a number of impurities in the form of discrete particles. These could be identified by their characteristic appearance. Fig. 17, 18, 19, 20, and 21 show the presence of rutile, ilmenite, magnetite, monazite, silica respectively in the present zircon sample.

Fig. 3: The general appearance of Bangladesh zircon.

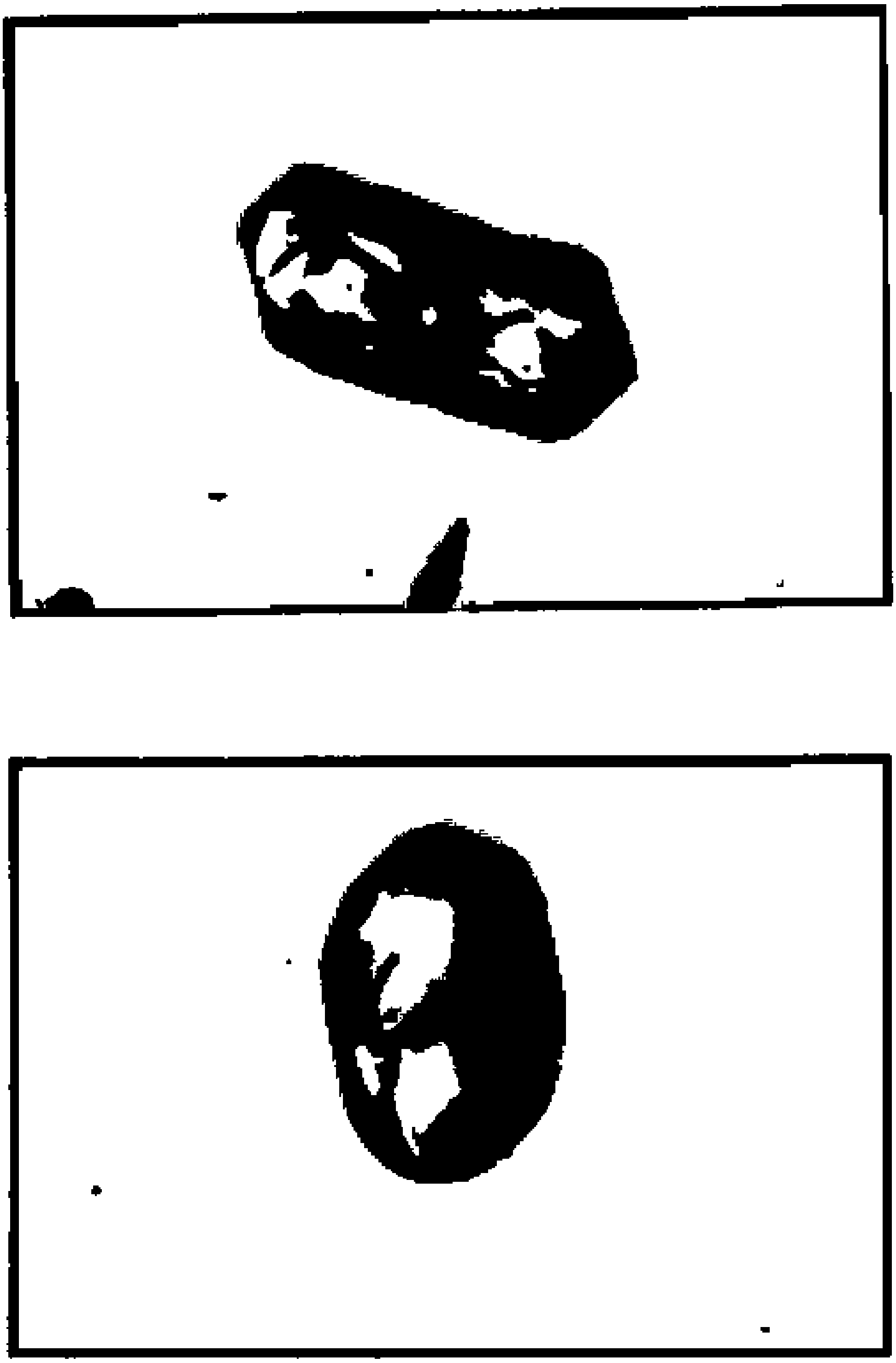


Fig. 4: A typical prismatic (a) and a rounded (b) grain of zircon. Plain light (×400)

Fig. 5: Photomicrograph showing the presence of psuedo octahedral crystal in zircon. Plain light (×400)

Fig. 6: Photomicrograph showing the presence haloes in zircon. Cross light (×400).

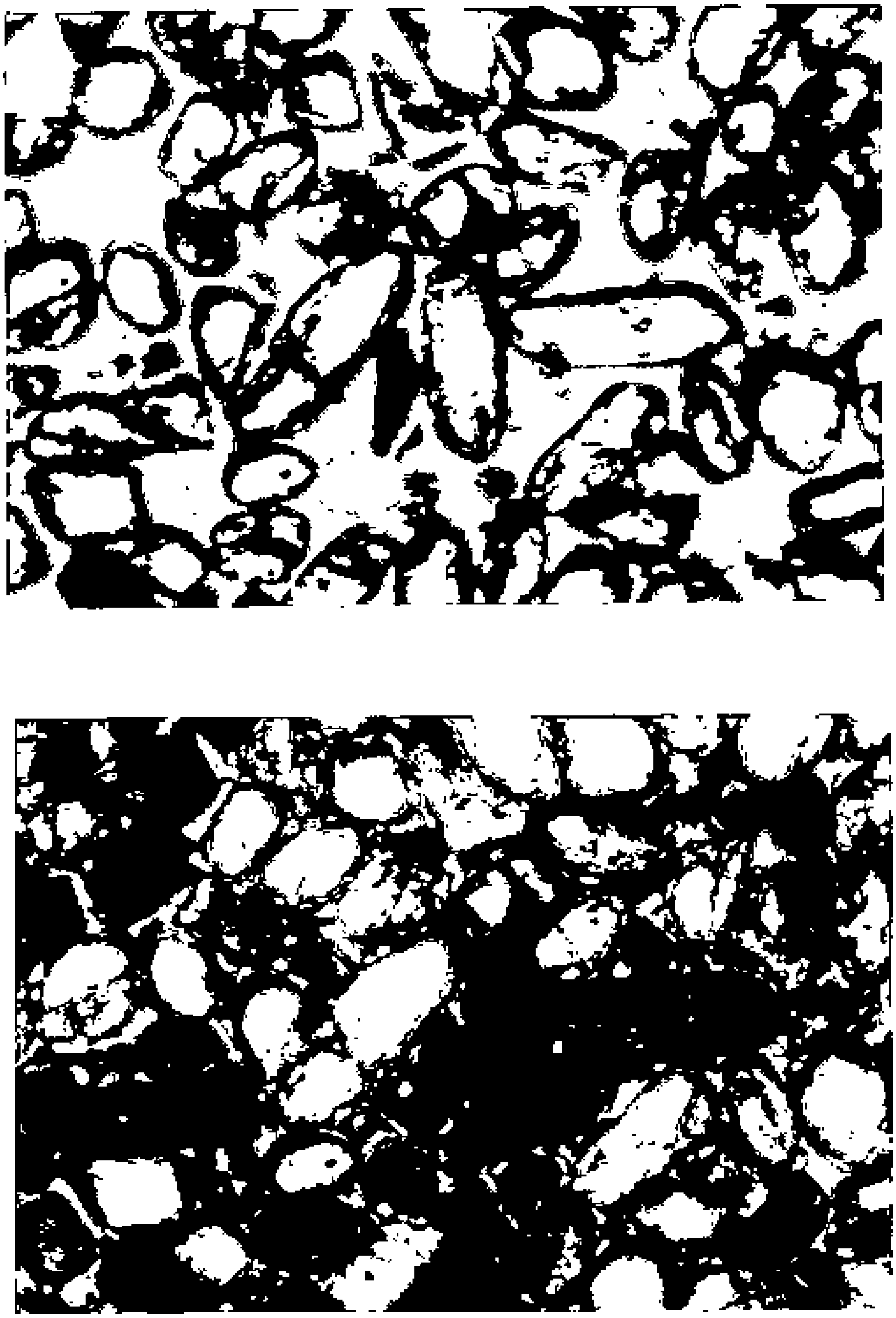


Fig. 7: Photomicrograph showing the presence extinction in zircon. (a) No extinction under plain light (×125) and (b) Parallel extinction under cross light (×125).

Fig. 8: Photomicrograph showing the presence of conchoidal fracture in zircon grain. Plain light (×400).

Fig. 9: Photomicrograph showing the presence of cleavage in zircon grain. Cross light (×400).

Fig. 10: Photomicrograph showing a rare twined zircon crystal.
Plain light (×400).

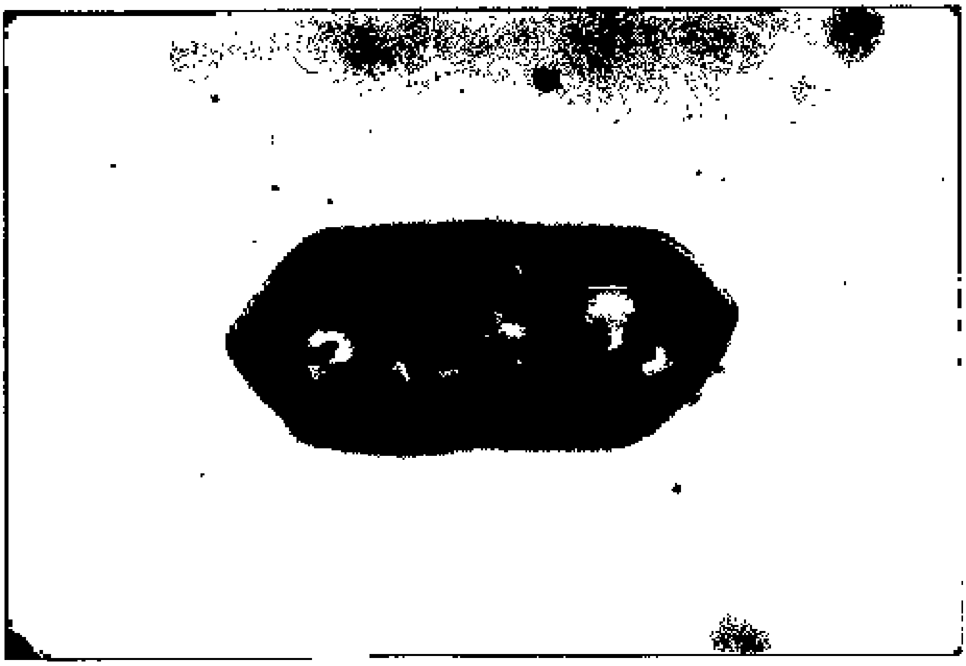


Fig. 11: Photomicrograph showing the presence of zoning in zircon grain.
Plain light (×400).

Fig. 12: Photomicrograph showing the presence of inclusion arranged parallel to the length of one crystal and brownish tint in another zircon crystal. Plain light (×400).

Fig.13: Photomicrograph showing the presence of irregular inclusion in zircon grain. Plain light (×400).

Fig. 14: Photomicrograph showing the presence of solid inclusion in zircon grain in thin section. Plain light (×400).

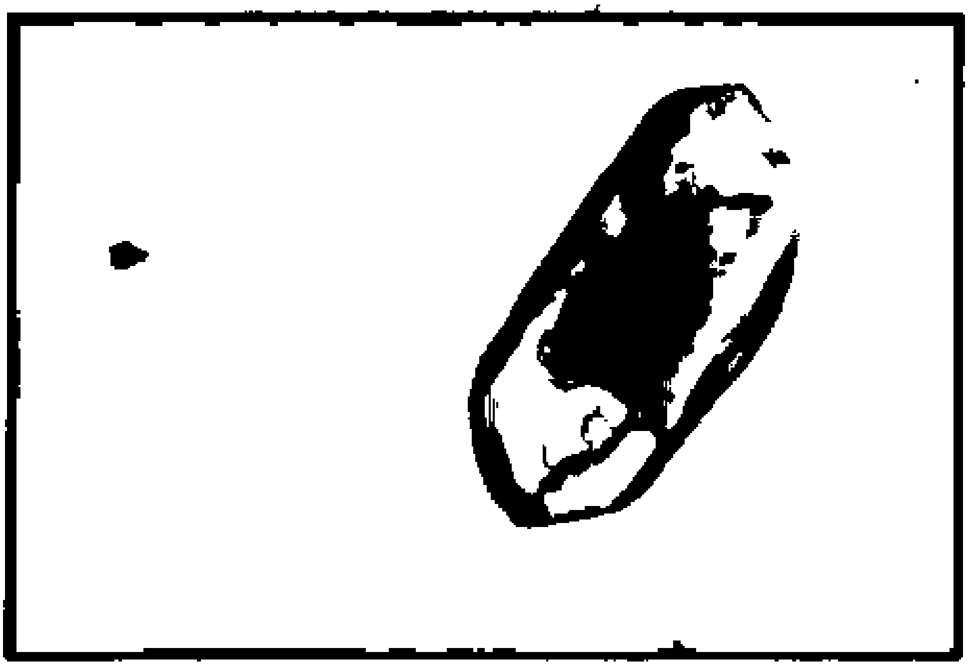


Fig. 15: Photomicrograph showing the presence of dusky appearance in zircon grain. Plain light (×400).

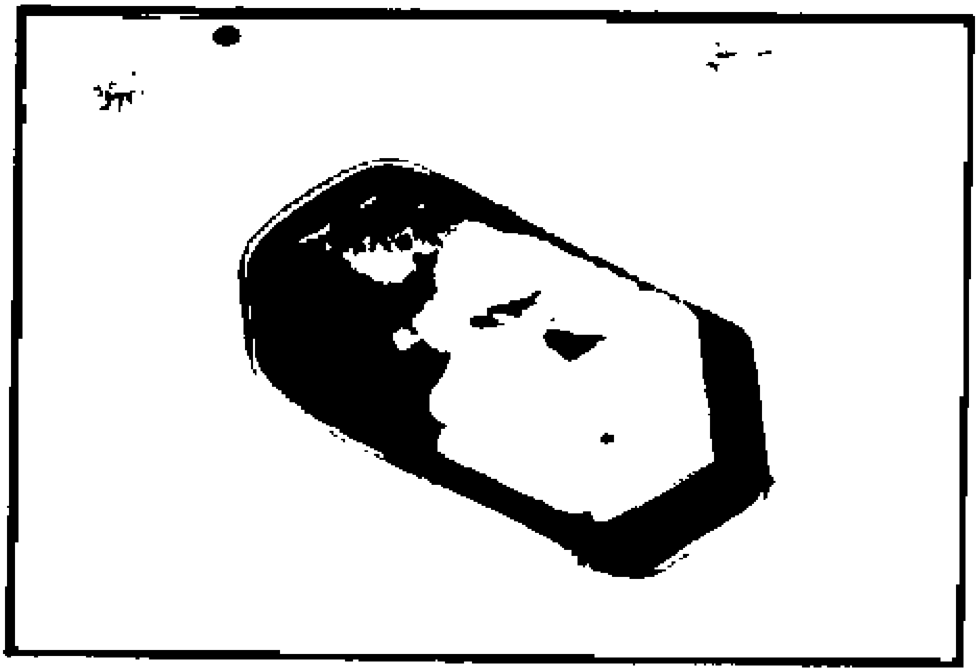


Fig. 16: Photomicrograph showing high relief for zircon grain.
Plain light (×400).

Fig. 17: Photomicrograph showing the presence of rutile in zircon grain in thin section. Plain light (×400).

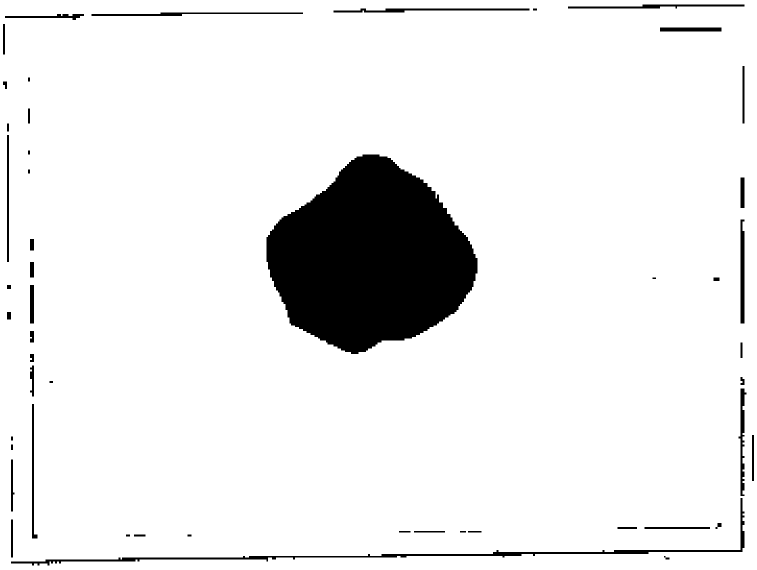


Fig. 18: Photomicrograph showing the presence of ilmenite in zircon grain. Transmitted light (×100).

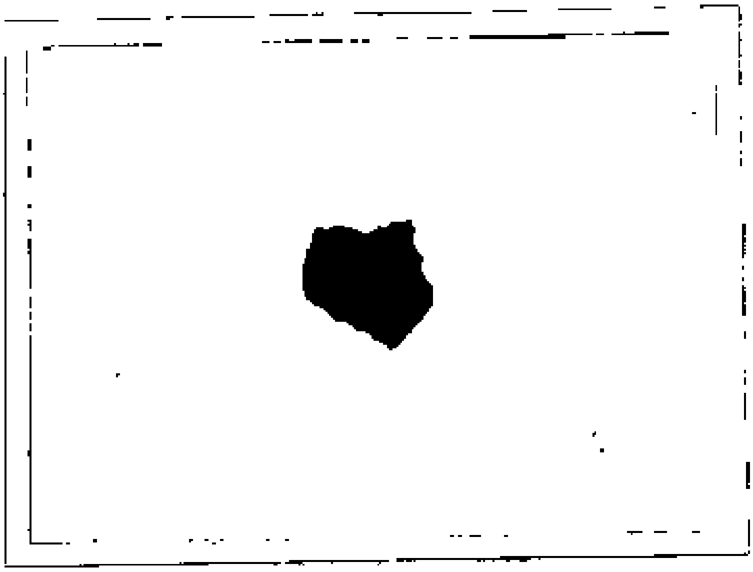


Fig. 19: Photomicrograph showing the presence of magnetite in zircon grain. Transmitted light (×100).

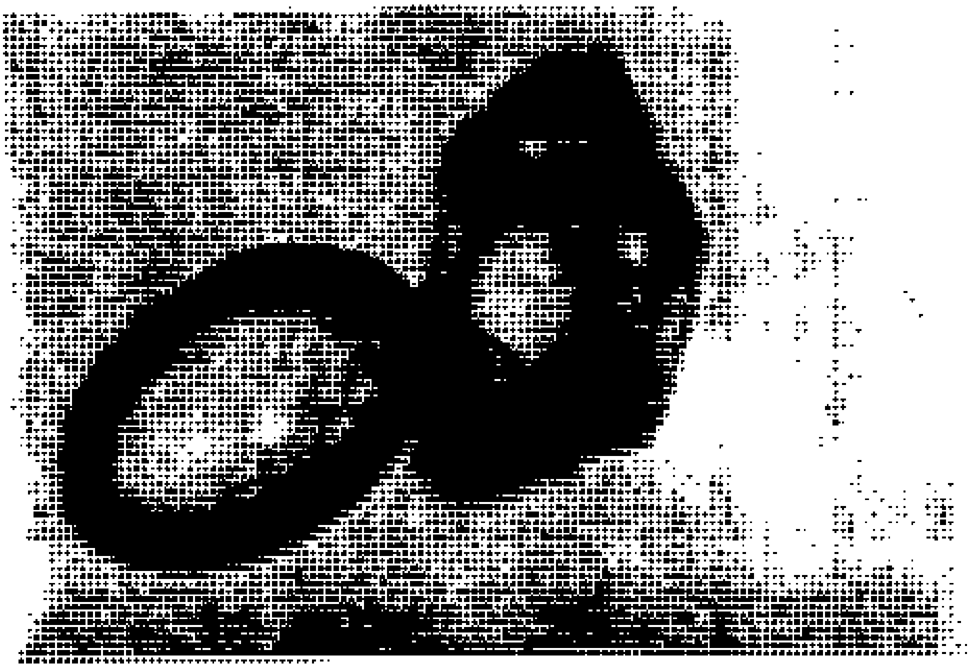


Fig. 20: Photomicrograph showing the presence of monazite in zircon grain.
Plain light (×400).

Fig. 21: Photomicrograph showing the presence of silica in zircon grain.
Cross light (×400).

Bulk sample of Bangladesh zircon in the as-received condition shows golden yellowish brown color. However individual grains were found to be almost colorless and transparent under polarized light. The color of the zircon improves when it is calcined. Calcination of as received zircon at 1400°C gives nearly white color to the bulk sample.

The analysis of Bangladesh zircon was attempted by the grain counting method under the microscope the result of which is given in Table 6. It is seen from the table that zircon grain constitute 94% and total impurities amount to 6%. This result agrees fairly well with the chemical analysis results given in Table 3. The main impurities in the present sample of Bangladesh zircon are found to be oxides of titanium (both rutile and ilmenite). This is also consistent with the findings of chemical analysis (Table 3). Further, monazite was identified as an important impurity under the microscope.

Table 6: The percentage of minerals in as received zircon by grain counting method.

Type of Minerals	% of Minerals
Zircon ($ZrSiO_4$)	94
Rutile (TiO_2)	2
Monazite (Ce, Y, La, Th)PO_4	1.4
Ilmenite ($FeO.TiO_2$)	1
Garnet	0.6
Magnetite (Fe_3O_4)	0.2
Silica, Hematite (Fe_2O_3) and others	Rest

It should be noted here that most of the impurities found in Bangladesh zircon exist as discrete minerals. As a result, it should be possible to remove these impurities fairly easily by physical mineral processing methods and thereby improve the grade of Bangladesh zircon. The coating of iron bearing mineral on some zircon grains can be removed by acid washing [21].

It was found in radioactivity measurement that the as-received Bangladesh zircon exhibits a count rate of 42 counts/minute. The background radioactivity of normal environment is 40-45 counts/min. Thus Bangladesh zircon does not particularly show any enhanced radioactivity.

The present mineralogical study of Bangladesh zircon shows that about half of the grains are prismatic and euhedral while the rest is more or less rounded. Weathering causes the rounding of the grains. Extent of weathering is different in different part of the world. Zircon deposit found in eastern Australia is characterized by sub-angular to rounded shapes while zircon from Trail Ridge, Florida is mostly rounded [75]. Kerala beach zircon (India) is also mostly rounded [21]. Under the action of physical and chemical agents in nature as well as prolonged exposure to radiation, zircon can undergo structural changes. This can lead to dissociation of zircon into ZrO_2 and silica SiO_2, which is called metamictization. Metamictization results in amorphous product and changes the color of zircon into green. Metamicted "green zircon" have been found in Sri Lankan deposit [76]. Indian zircon from Kerala Beach was reported to contain 2-3% metamicted grain. In the case of Bangladesh zircon, the grains were mostly colorless. Green grains of zircon were not found in this sample. A very faint green tint was found in one sample only. Larger proportion of prismatic crystals, higher degree of crystalinity (as evidenced by XRD), and absence of any significant amount of metamicted grains suggest that Bangladesh zircon is a relatively fresh mineral. Radioactivity test also gives support to this opinion.

4.4 DECOMPOSITION OF ZIRCON:

In this study, the effect of sodium hydroxide percentage and temperature on the decompositon of Bangladesh zircon is described. For this purpose, zircon flour of average particle size of 8μm was used. The X-ray diffraction patterns of the decomposed samples using 5%, 20% and 30% sodium hydroxide are shown in Fig. 22. In sample decomposed with 5% NaOH, almost all the peaks correspond to that of the standard x-ray diffraction peaks of zircon, except one peak. This peak is corresponds to standard peak for monoclinic zirconia from the plane (020). The intensity of this peak is very weak. The X-ray diffraction pattern of sample decomposed with 20% sodium hydroxide shows a number of peaks which correspond to standard peaks of zircon but there are also some prominant peaks which correspond to the standard peaks of the monoclinic zirconia. These peaks are from (100), (111), (112), (022) and (113) plane of monoclinic zirconia. All these peaks for plane (100), (111), (112), (022) and (113) were absent in the sample decomposed by 5% NaOH. It indicates that the use of 20% sodium hydroxide increasres the extent of decomposition of zircon as compared with 5% sodium hydroxide at 1500°C. The X-ray diffraction pattern for 30% sodium hydroxide decomposed sample is also shown in Fig. 22. In addition with the peaks which correspond to standard peaks of zircon, there are also a number of prominant peaks which correspond to the standard peaks of the monoclinic zirconia. These peaks are from (100), (111), (102), (220), (300, 202) and (130) plane of monoclinic zirconia. All these peaks for plane (100), (111), (102), (220), (300, 202) and (130) were totally absent in the pattern for the sample decomposed by 5% NaOH. From these figures it is clear that the peak of zirconia for plane (111) becomes stronger relative to zircon peaks as higher amount of sodium hydroxide is used for decomposition.

Now the effect of increase in temperature on the decomposition of zircon can be seen in Fig. 23. The XRD pattern for the sample decomposed at 1300°C shows lots of peaks. Most of the peaks correspond to the standard peak of zircon and some of the remaining peaks correspond to the peaks of monoclinic zirconia. Zirconia peaks are observed from (100), (111), (021), (022) and (113) plane. The XRD pattern for the sample decomposed at 1400°C also gives lots of peaks. In this pattern most of the peaks belong to the standard peak of zircon and some of the rest peaks correspond with that of the peaks of monoclinic zirconia. These peaks come from (100), (111), (022), (220) and (130) planes. For the sample decomposed at 1500°C, most of the peaks corresponds to the standard peaks of zircon and some of the peaks correspond to that of the standard peaks of monoclinic zirconia. The peaks for monoclinic zirconia come from (100), (111), (002), (210), (211), (112) and (022) plane respectively. This is the most decomposed one among these three samples; zirconia peaks comes from seven planes and these peaks are comparatively stronger than the same peaks in the other pattern. In both cases, there are some peaks which could not be identified. Some symbols are given in Table 7 to identify the peaks that come from different planes of zirconia and z is using for zircon peak for Fig. 22 and

23. Comparison of the observed and standard peak position of zircon and zirconia sample using, 5%, 20% and 30% sodium hydroxide at 1500°C are given in Table 8, 9 and 10. Comparison of the observed and standard peak position of zircon and zirconia of decomposed zircon sample using 10% sodium hydroxide at 1300°C, 1400°C and 1500°C are given in Table 11, 12 and 13.

Table 7: Symbols of the peaks come from different plane of zirconia

Plane of zirconia	Symbol
(100)	a_1
(111)	a_2
(002)	a_3
(020)	a_4
(021)	a_5
(210)	a_6
(112)	a_7
(211)	a_8
(102)	a_9
(112)	a_{10}
(022)	a_{11}
(220)	a_{12}
(300, 202)	a_{13}
(130)	a_{14}
(113)	a_{15}

From the results described above, it is clear that the heating period of 30 minutes is not sufficient to result in complete disintegration of Bangladesh zircon even at the highest temperature (1500°C) and the largest sodium oxide concentration (30%) used in the present study.

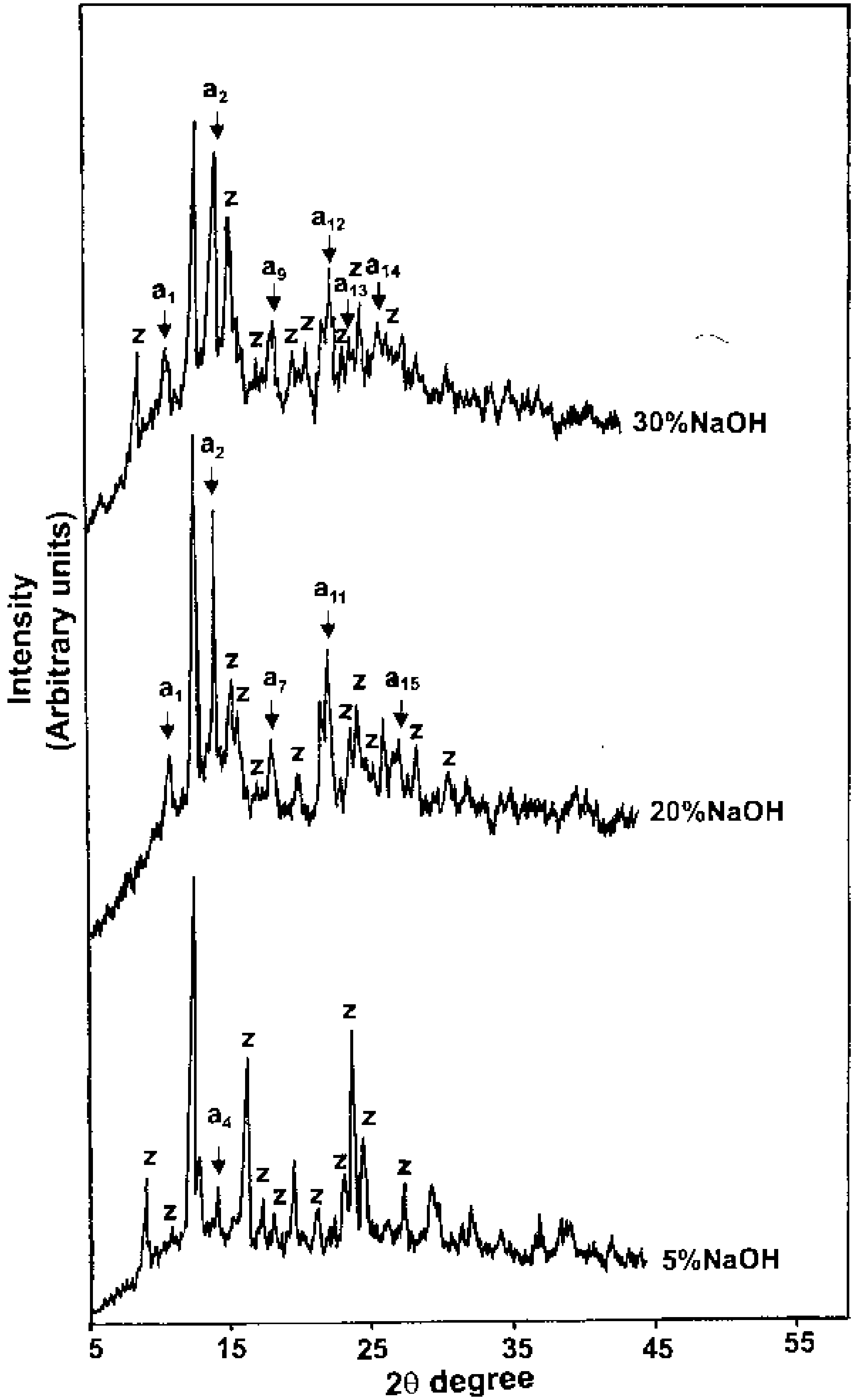


Fig. 22: X-ray diffraction patterns of decomposed zircon samples using 5%, 20% and 30% sodium hydroxide at 1500°C.

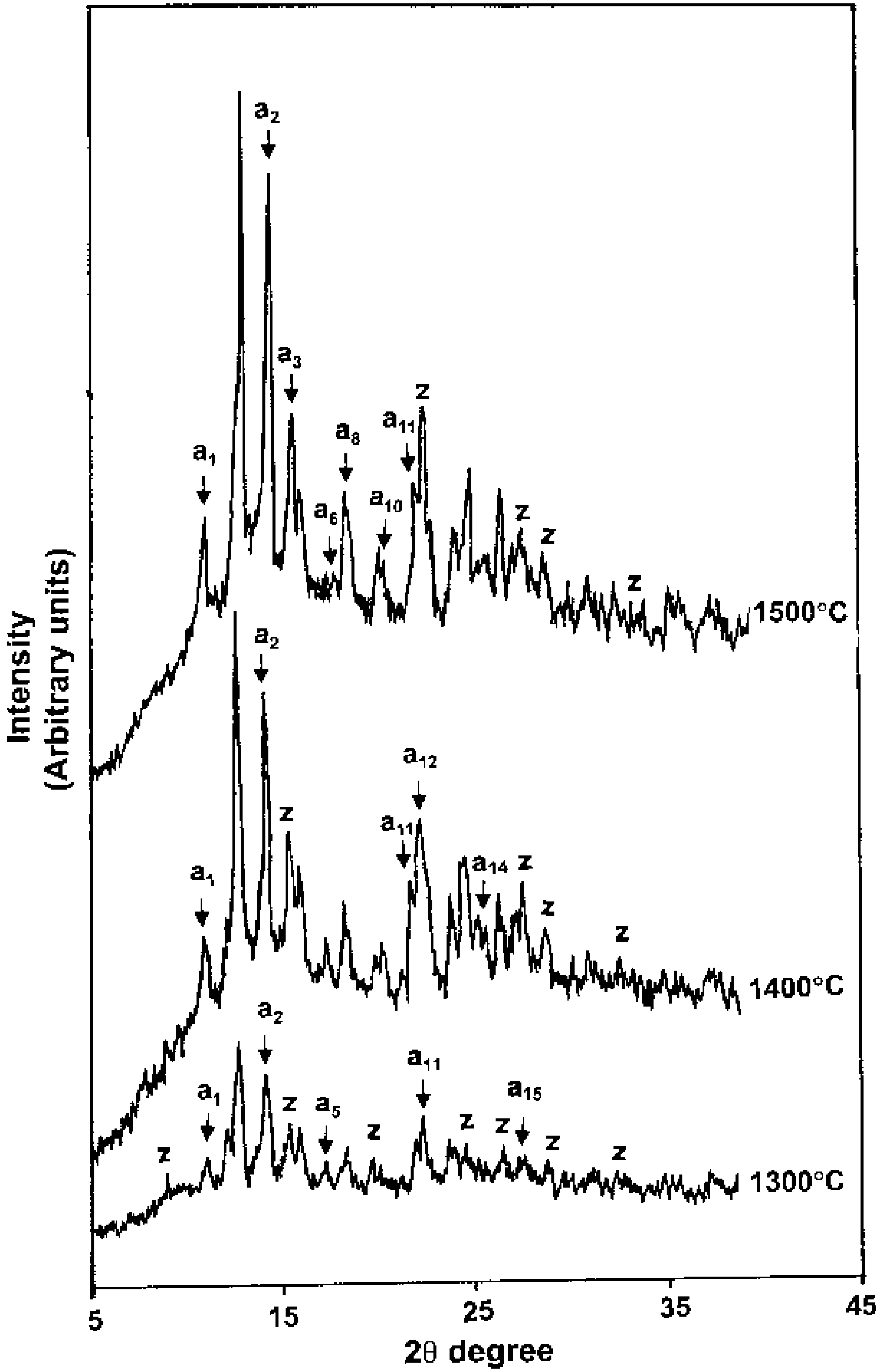


Fig. 23: X-ray diffraction patterns of decomposed zircon samples using 10% sodium hydroxide at 1300°C , 1400°C and 1500°C

Table 8: Comparison of the observed and standard peak position of zircon and zirconia of decomposed zircon sample using 5% sodium hydroxide at 1500°C.

Observed peak position	Standard peak positions for Zircon [74]	Standard peak positions for Zirconia [77]	Plane for Zircon (hkl)	Plane for Zirconia (hkl)
8.8	9.2	------	(101)	------
12	12.36	------	(200)	------
12 6	------	------	------	------
14	------	------	------	------
15.9	16.23	15.72	(112)	(020)
17.2	17.49	------	(220)	------
18	18.45	------	(202)	------
19.4	------	------	------	------
20 09	19.81	------	(301)	------
20.2	------	------	------	------
21.1	21.47	------	(103)	------
22	------	------	------	------
22.4	------	------	------	------
23.1	23.42	------	(321)	------
23.6	23.96	------	(312)	------
24.5	24.86	------	(400)	------

Table 9: Comparison of the observed and standard peak position of zircon and zirconia of decomposed zircon sample using 20% sodium hydroxide at 1500°C.

Observed peak position	Standard peak position for Zircon [74]	Standard peak position for Zirconia [77]	Plane for Zircon (hkl)	Plane for Zirconia (hkl)
10.9	------	11.05	------	(100)
12.6	------	------	------	------
14.2	------	14.4	------	(111)
15.4	15.41	------	(211)	------
15.9	16.23	------	(112)	------
17.2	17.49	------	(220)	------
18.2	------	18.16	------	(112)
20	19.81	------	(301)	------
21.8	------	------	------	------
22.2	------	22.2	------	(022)
24	23.96	------	(312)	------
24.4	24.86	------	(400)	------
26.3	26.56	------	(411)	------
27.4	------	27.26	------	(113)
28.6	27.5	------	(004)	------
30.8	30.25	------	(204)	------

Table 10: Comparison of the observed and standard peak position of zircon and zirconia of decomposed zircon sample using 30% sodium hydroxide at 1500°C.

Observed peak position	Standard peak position for Zircon [74]	Standard peak position for Zirconia [77]	Plane for Zircon (hkl)	Plane for Zirconia (hkl)
8.8	9.21	------	(110)	------
10.9	------	11.05	------	(100)
12.8	------	------	------	------
14.2	------	14.4	------	(111)
15.3	15.41	------	(211)	------
17.3	17.49	------	(220)	------
18.6	------	18.75	------	(102)
20	19.81	------	(301)	------
21	21.47	------	(103)	------
22.6	------	22.54	------	(220)
23.6	23.42	------	(321)	
24.2	------	24.26	------	(300,202)
24.6	24.86	------	(400)	------
25.1	------	------	------	------
25.4	------	25.02	------	(130)
26 6	26.56	------	(411)	------

Table 11: Comparison of the observed and standard peak position of zircon and zirconia of decomposed zircon sample using 10% sodium hydroxide at 1300°C.

Observed peak position	Standard peak position for Zircon [74]	Standard peak position for Zirconia [77]	Plane for Zircon (hkl)	Plane for Zirconia (hkl)
8.9	9.20	------	(101)	------
11	------	11.05	------	(100)
12.2	12.36	------	(200)	------
12.7	------	------	------	------
14.1	------	14.40	------	(111)
15.4	15.41	------	(211)	------
15.9	16.23	------	(112)	------
17.2	------	17.56	------	(021)
18.3	18.45	------	(202)	------
19.7	19.80	------	(301)	------
21.9	21.47	------	(103)	------
22.3	------	22.21	------	(022)
23.6	23.42	------	(321)	------
24.6	24 86	------	(400)	------
26.4	26.56	------	(411)	------
27.2	------	27.26	------	(113)

Table 12: Comparison of the observed and standard peak position of zircon and zirconia of decomposed zircon sample using 10% sodium hydroxide at 1400°C.

Observed peak position	Standard peak position for Zircon [74]	Standard peak position for Zirconia [77]	Plane for Zircon (hkl)	Plane for Zirconia (hkl)
11	------	11.05	------	(100)
12.8	------	------	------	------
14.2	------	14.41	------	(111)
15.4	15.41	------	(211)	------
16	16.23	------	(112)	------
17.3	17.49	------	(220)	------
18.2	18.47	------	(202)	------
20.2	19.81	------	(301)	------
21.3	21.47	------	(103)	------
21.9	------	22.21	------	(022)
22.4	------	22.54	------	(220)
23.8	23.42	------	(321)	------
24.6	24.86	------	(400)	------
25.2	------	25.02	------	(130)
26.3	26.56	------	(411)	------
27.6	27.50	------	(004)	------

Table 13: Comparison of the observed and standard peak position of zircon and zirconia of decomposed zircon sample using 10% sodium hydroxide at 1500°C.

Observed peak position	Standard peak position for Zircon [74]	Standard peak position for Zirconia [77]	Plane for Zircon (hkl)	Plane for Zirconia (hkl)
11	------	11.05	------	(100)
12.7	------	------	------	------
14.2	------	14.4	------	(111)
15.5	------	15.61	------	(002)
15.8	16.28	------	(112)	------
17.4	17.49	------	(220)	------
17.8	------	17.89	------	(210)
18.3	------	18.48	------	(211)
20	19.8	------	(301)	------
20.4	------	20.31	------	(112)
22	------	22.21	------	(022)
22.4	------	------	------	------
24	23.96	------	(312)	------
24.7	24.86	------	(400)	------
25.8	------	------	------	------
26.4	26.56	------	(411)	------

Disintegration of zircon has been reported by a number of worker [78] using Na_2CO_3 [78] CaO [70], and CaO+MgO [79] as the decomposition agents. It has been found that the extent of decomposition brought about by various agents varies. Ayala et al [71] found that at 20% sodium oxide concentration decomposition of zircon was complete just in 5 minutes at 1350°C. Whereas when calcium oxide was used at a molar ratio of $CaO/ZrSiO_4=1.2$, complete decomposition of zircon required two hours at 1400°C [71]. Use of (CaO+MgO) mixture, instead of CaO improved the extent of decomposition [79]. It seems that NaOH which was used in the present study is not as effective as Na_2O_3. Further test are necessary to compare the effectiveness of NaOH with that of CaO and (CaO+MgO).

4.5. BANGLADESH ZIRCON AS OPACIFIER

As has been mentioned, the opacifier tests were carried out in local ceramic factories. For proprietary reasons, these factories did not disclose the composition of the base glaze and bodies used.

Fig. 24 shows three glazed samples prepared in an insulator factory. The base glaze and the body composition are the same as those used in their production line. The usual glaze of the factory with the addition of imported zircon flour is shown in Fig. 24a. Fig. 24b shows the transparent glaze without the addition of any opacifier. In Fig. 24c is shown the glaze prepared by replacing the imported zircon flour with that produced from Bangladesh zircon. The zircon flour was produced from as-received Bangladesh zircon without any purification. It was found that the glaze prepared using as-received Bangladesh zircon posses white color with a grayish tint. Its color was slightly darker than that of the glaze with imported zircon (although not very evident in Fig. 24). It was found however that the glossyness of the glaze containing Bangladesh zircon was similar to that of the sample containing imported zircon. The former sample did not show any tendency to craze. The irregular line in Fig. 24c was the result of incomplete spreading of the glaze caused by inadequate viscosity. The grayish tint of the glaze containing Bangladesh zircon is believed to be due to presence of impurities.

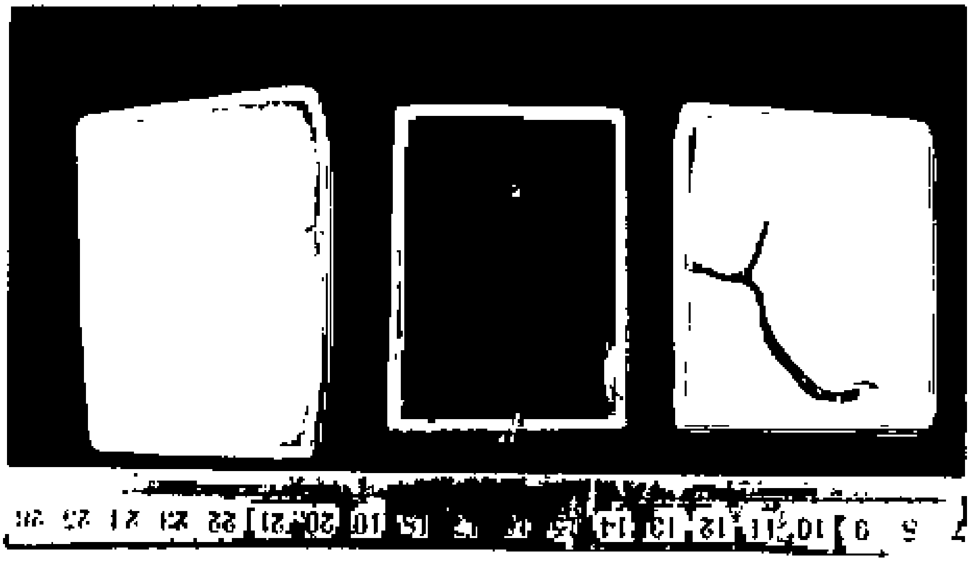


Fig. 24: Three glazed samples prepared in an insulator factory. (a) the usual glaze of the factory (b) transparent glaze without addition of opacifier, and (c)glaze prepared with Bangladesh zircon. [In each case 10 percentage of zircon were used]

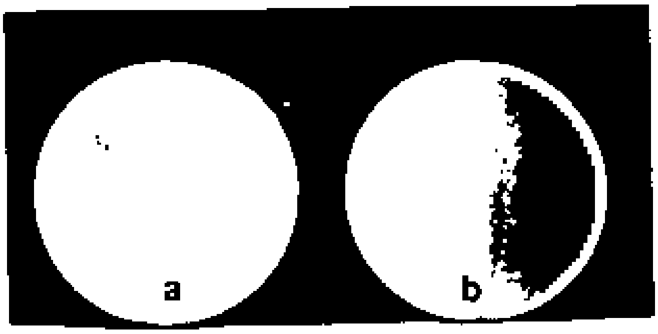


Fig. 25: Samples prepared in an tableware factory. (a) Glaze prepared by purified Bangladesh zircon (b) the usual glaze of the factory. [In both case 10 percentage of zircon were used]

In order to remove the impurities. flour made from Bangladesh zircon was given an acid treatment in H_2SO_4 for 20 hours at 180°C. Zircon flour so purified was then tested as opacifier in a local ceramic factory producing high quality tableware. This glaze with the purified Bangladesh zircon is shown in Fig. 25a. Fig. 25b shows the usual glaze of the factory contains imported zircon. In these glazes the zircon content in 8wt.%. It was seen that although the color of the glaze containing purified Bangladesh zircon flour (Fig. 25a) was comparable with that of the usual glaze of the refactory containing imported zircon fig. 25b, the later was more whitish. Glaze containing purified Bangladesh zircon was found to have the same gloss as the usual glaze used by the tableware factory. Further, when examined closely the former did not show any crazing tendency in an oven test. However, the glaze containing Bangladesh zircon was found to be slightly rougher. It may me due to the coarser distribution of grain size.

From the limited number of test discussed above, it appears that the as-receievd zircon flour produced from Bangladesh zircon does not provide a completely white color. With presumely removes impurities, improved the whiteness of the glaze. Although Bangladesh zircon flour produced adequate glossiness, it was found to yield a slightly rough surface. This is thought to be linked to the particle size of zircon flour. In the present study, flour produced from Bangladesh zircon has peak particle size at 8μm. Particle size could not be reduced due to experimental limitations. It is well established that finer zircon particles, with peak size at around 2μm, are for optimum for glaze applications [80]. The slightly rougher surface of the glaze containing Bangladesh zircon is thought to be larger particle size of the flour. It is concluded that zircon flour made from Bangladesh zircon can effectively replace imported zircon flour, if adequate size reduction and purification is carried out.

4.6. ZIRCON BRICKS FROM BANGLADESH ZIRCON

The surface appearance of the fired as received zircon bricks fired at 1360°C are described now. For 1% CMC (carboxi methyal celollose) binder one crack was observed from one end to another end along the Weight near about middle of the brick. Rougher surfaces of the bricks are observed. The color of these bricks were whitish brown. Bricks made of 1% CMC and 4% Fe_2O_3, gives good appearance, good surface finish and a blackish color. Bricks made of same composition but fired at 1430°C gives better fired properties for out look. Bricks made of ground zircon gives smooth surface finish and uniform color shade.

The effect of binder on the properties of zircon bricks prepared from as received Bangladesh zircon is given in Table 14. These bricks were fired at 1430°C. For the bricks prepared with 1% CMC binder and this firing temperature, crushing strength and density is found to be 433 psi and 3.1 g/cc respectively. Bricks prepared with 1% CMC and 4% Fe_2O_3 gives a crushing strength of 2333 psi and density of 3.06 g/cc respectively. From these results it is clear that with increasing firing temperature the properties of zircon bricks increases. It is thus found that addition of 4% Fe_2O_3 increases the crushing strength and density of zircon bricks.

Table 14: Properties of Zircon bricks made from as received zircon fired at 1430°C:

Binder	Properties
1% CMC	Crushing Strength: 433 psi Density: 3.1 g/cc
1% CMC 4% Fe_2O_3	Crushing Strength: 2333 psi Density: 3.06 g/cc

Initially, bricks containing 1%CMC fired at 1360°C were tested for crushing strength. This firing temperature yields a crushing strength of 370psi. Thus comparing this result with the crushing strength of 1%CMC brick fired at 1430°C, it can be said that increasing firing temperature yield higher strength.

A number of bricks were made using 25% as-received zircon and 75% ground zircon. The size distribution of the ground zircon is given in Table16.

Particle size distribution of as received zircon and grounded zircon making for refractory bricks are shown in Table 15.

Table 15:Partical size distribution of as-received zircon and ground zircon making for refractory bricks

U.S. Sieve No.	Weight percentage retained in each sieve in gram	
	As received zircon	Grounded zircon
80	0.5	0
100	11.34	1.7
140	76.764	41.05
200	11.58	20.7
Pan	1.0234	26.5

The properties of zircon bricks made from the mixture of as-received and ground zircon fired at temperature 1430°C are shown in Table 16. For 1% CMC bricks gives 7739 psi and 3.04 g/cc crushing strength and density respectively. Use of 1% CMC and 1% Fe_2O_3 gives 6029 psi crushing strength and 2.98 g/cc density.

Table 16: Properties of Zircon bricks made of ground zircon fired at a temperature 1430°C.

Zircon	Binder	Properties
25% as received 75% Ground	1% CMC	Crushing Strength: 7739 psi Density: 3.04 g/cc
25% as received 75% Ground	1% CMC and 1% Fe_3O_4	Crushing Strength: 6029 psi Density: 2.98 g/cc

Comparing Table 16 with Table 15, it is seen that mixture of as-received and ground zircon improve the crushing strength to a higher values as compared with bricks made from as-received zircon only. The crushing strength of zircon bricks reported in the literature is 1200 psi and density is 3 g/c.c. [52] The density for zircon bricks is not difficult to achieve because of its high specific gravity. Only 1% CMC bricks made of as received zircon gives the crushing strength below 1200 psi. So, to produce zircon bricks achieving crushing strength will not be a problem. Refractoriness under load is one of the most important tests for refractory materials. This test should have done for the prepared zircon bricks. But it was not possible for lack of test facilities.

Chapter Five

5. CONCLUSION:

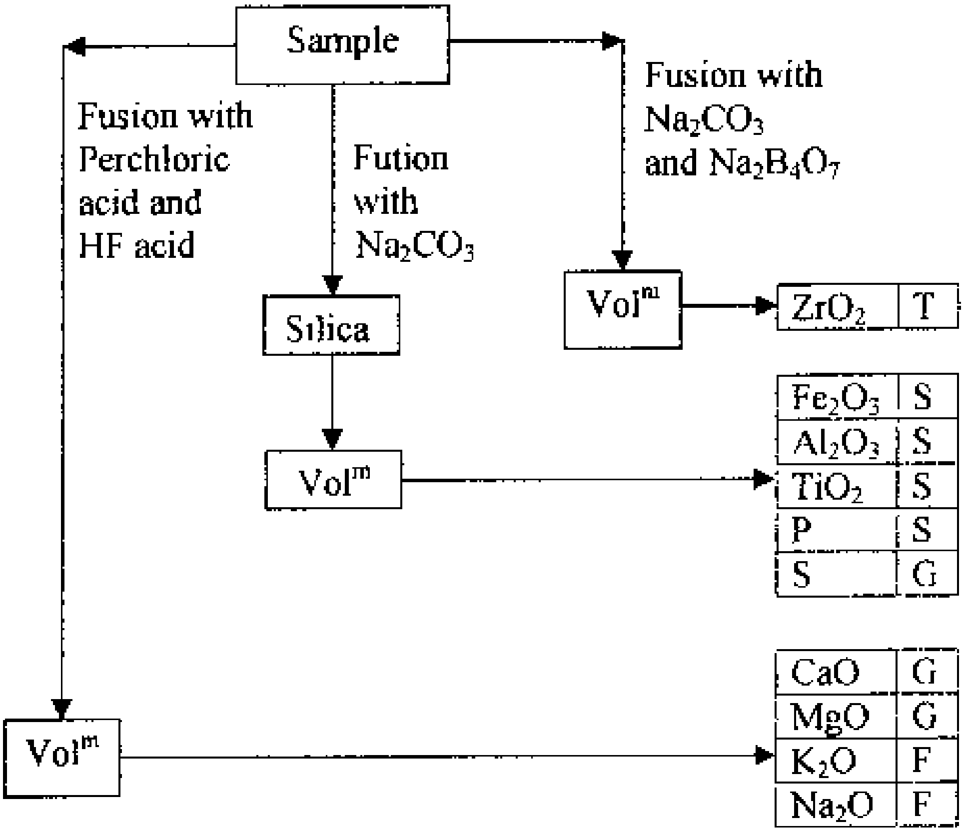
In this thesis, the characterization of Bangladesh zircon was made satisfactorily. From the chemical analysis it is found that Bangladesh zircon has 95.88% purity. The main impurity in Bangladesh zircon is titanium oxide (3.01%). This is followed by iron oxide (0.42) and traces amounts of other oxides are also found. From the mineralogical study it is found that Bangladesh zircon have an elongated, prismatic shape with pyramidal termination in half of the grains and the rest are more or less rounded along with some fractured and irregular grains and posses transparent, brownish yellow color. XRD study confirmed good crystallinity in the sample. Under microscope it is found that Bangladesh zircon grain constitute 94% and total impurities amount to 6%. This result agrees fairly well with the chemical analysis results. The main impurities in the present sample of Bangladesh zircon are found to be oxides of titanium (both rutile and ilmenite). This is also consistent with the findings of chemical analysis . Further, monazite was identified as an important impurity under the microscope. It should be noted here that most of the impurities found in Bangladesh zircon exist as discrete minerals. As a result, it should be possible to remove these impurities fairly easily by physical mineral processing methods and thereby improve the grade of Bangladesh zircon. The heating period of 30 minutes is not sufficient to result in complete disintegration of Bangladesh zircon even at the higher temperature (1500°C) and the largest sodium oxide concentration (30%) in the present study. Further tests are necessary to study the effectiveness of NaOH for the decomposition of the zircon. The coating of iron bearing mineral on some zircon grains can be removed by acid washing. Practical ceramic experiments have demonstrated that Bangladesh zircon is quite satisfactory for preparing zircon flour in ceramic industries. Zircon flour made from Bangladesh zircon can effectively replace imported zircon flour, if adequate size reduction and purification is carried out. Bangladesh zircon can also be used successfully for preparation of refractory bricks for high temperature use. It has been demonstrated that Bangladesh zircon can be used in ceramic industries as opacifier after grinding and subsequent purification. By grinding zircon in ball mill its size can be reduced 6-8μm so as to make it suitable for ceramic industries as opacifier. But ball milling for grinding zircon is not economical. Study should be under taken to employ zircon flour in ceramic industries based on Bangladesh zircon. Literature study has shown that grinding of zircon in a vibrating mill can produce zircon flour of less than 2 micron size for use in ceramic industries. In Bangladesh different ceramic industries consume about 200-300tons of zircon flour per year all of which is imported. If Bangladesh zircon can be processed for using different industries then a lot of money will be saved. So, for grinding Bangladesh zircon for using in ceramic industries immediate steps should be taken to grind Bangladesh zircon to size ≤ 2 micron. There are no refractory brick which is made in our country. Bangladesh zircon gives quite satisfactory result for the making refractory bricks which will be suitable for the manufacturing of glass melting furnaces.

Chapter Six

6. APPENDIX

Appendix-A: Scheme of Analysis

The major constituents present in zircon and zircon sand are zirconium dioxide (ZrO_2) and Silicon dioxide (SiO_2); however iron oxide (Fe_2O_3), aluminum oxide (Al_2O_3), titanium oxide (TiO_2), sulfur, phosphorous, sodium and potassium oxides are often present as minor constituents. The scheme of the present analysis is given in Fig. 26



Here, T = Titrametric method.

S = Spectrophotometric method.

G = Gravemetric method.

F = Flame photometric method.

Fig. 26: Schematic Diagram Showing the Chemical Analysis Procedures Carried Out for the Determination of Each Component in Bangladesh Zircon.

Appendix-B: Preparation of Sample for Analysis

Few grams of the representative sample in a clean agate mortar were taken and thoroughly grind it to pass thoroughly -200mesh. The sample were dried in a weighing tube in an electrically heated air oven at 105-110°C for 2hrs and were weighed. The process of drying were repeated for another 1 hr to get a constant weight. The stupider weighing tube were kept in a desecrator and cool to the room temperature. Thus the sample were prepared for analysis.

Appendix-C: Determination of Loss on Ignition

Accurately one gram of the ground sample was weighed into a platinum crucible in a muffle furnace and slowly raises the temperature to 1025+25. After ignition, it was cooled in a desiccator and it was weighted to a constant weight [81]. Thirty minutes ignition is usually sufficient.

Calculation: $\%L.O.I.=(W_1.W_2)/(W_1-W)\times100$

Where, W = Weight of platinum crucible

W_1= Weight of platinum crucible + sample

W_2= Weight of platinum crucible +sample after ignition

Appendix-D: Decomposition of Sample for the Determination of Zirconium Dioxide

Reagents:

Sodium carbonate

Borax

Nitric acid

Hydrochloric

Potassium chloride

Citric acid

Sodium fluoride

Bromothymol blue indicator, 0.5% (m/v) in alcohol

Sodium hydroxide solution (N/15)-5.5 gram NaOH were dissolved in two litters of water in a plastic beaker and it was standardized against a standard potassium hydrogenphthalate.

Wash solution: 120gram KCl and NaF were dissolved in 500ml water and then diluted to one liter. A few drops of bromothymol blue indicator and a few drops of HCl (1:3) were added to make the solution just yellow.

Accurately about 0.5 gram of well agated and dried (105°-110°) sample in a platinum crucible and the mass was heated with 6g of fusion mixture (3g Na_2CO_3+3g $Na_2B_4O_7$). The crucible was first heated over a low flame to dull redness for 10 minutes to get a transparent mixture. The crucible was cooled and placed it in a beaker containing 100 ml nitric acid (1:1). The beaker was covered with a watch glass. It was put on a hot plate till the fused mass goes completely into the solution. The beaker was remove from the hot plate. The crucible was take out from the beaker and wash thoroughly. The solution was boiled for 5 minutes and transfer it to a 250 ml calibrated flask and dilute to the mark (stock solution).

Reagents:

EDTA solution (0.025 M)- EDTA solution was prepared by dissolving 9.31g of the disodium salt of EDTA in distilled water and diluting to 1 liters. It was Standardized by titrating the solution with a standard zinc solution in acetate buffer (pH 5.3) with xylenol orange as indicator.

Standard alumina solution - A portion of polished aluminum foil was washed in absolute alcohol and dried in a desecrator. Accurately 0.6745 g of it was weighted and placed it in a 400ml beaker containing 150ml water and 25ml HCl acid. The solution was boiled to dissolve the metal. The solution was cooled and diluted to 500 ml in a calibrated flask. A working ammonium solution (0.02 M) was prepared by pipefitting out 100 ml of 0.05M aluminum solution, transferring it to a 250 ml calibrated flask and diluting with water to the mark (1ml of this solution ≡ 0.0010194 g Al_2O_3).

Zinc acetate (0.025 M) :- 5.5 g of zinc acetate $(CH_3CO)_2Zn.2H_2O$ was dissolved in water containing 0.05 ml acetic acid and 20 ml acetate buffer (pH 5.3) and diluted to 1 liter. The zinc acetate solution was standanised by standard aluminum solution.

Standard titania solution - Accurately 0.5 g titanium dioxide (TiO_2) was weighed in a platinum crucible. It was fused with 5 g of potassium bisulfate. The cool melt was dissolved in 200ml water containing 25 ml of H_2SO_4 by heating over a steam bath. The solution was cooled and diluted to 500 ml in a calibrated flask. One ml of the solution ≡ 1.0 mg TiO_2 (solution A). 10 ml of solution A was pipetted into a 100 ml calibrated flask containing 50 ml H_2SO_4 (1:1) and diluted to mark (solution B). 1 ml of solution B ≡ 0.01mg TiO_2.

Standard iron solution - 0.4911 g of ferrous ammonium sulfate, $FeSO_4 (NH_4)_2 SO_4 . 6H_2O$, was dissolve in water and 10 ml of H_2SO_4 (1.1) was added. The solution was heated and diluted to 1 litter in a calibrated flask. One ml of this solution ≡1.0 mg Fe_2O_3. The solution was standardizing by the volumetric potassium dichromate method.

Buffer solution (p^H5.3) :-21.5g of sodium acetate with 2ml of acetic acid in 300ml water and diluted to one liter.

Hydrochloric acid, 3%(v/v)

Hydrogen peroxide, 6%(v/v)

Tylenol orange, 0.1% in water. slightly acidified

Determination of Zirconia:

25 ml stock solution was pipetted out in a 500 ml conical flask and the calculated amount of 8 N HNO_3 was added and also some water was added to make the volume up to 40-60 ml to make its acid strength 3N. The solution was boiled for five minutes to deploymerize any zirconyl ions. The solution was diluted to 180ml with water to bring the acid strength 1N. The solution was boiled for two minutes and was titrated in hot condition (above 90°C) with drop wise addition of 0.025 M EDTA using xylenol orange (0.1%) as indicator. The end point is indicated by a sharp change of color from violet to yellow. The percentage of zirconium dioxide was calculated from the EDTA consumed.

Appendix-E: Determinatiopn of all other constituents in as received zircon sample.

Determination of Silica (Gravimetric method):

Principal: The gravimetric method for the determination of Silica is based on the insolubilization of silicic acid from an acid solution of a decomposed silicate sample through dehydration and backing.

Chemicals: All the chemicals used for the determination of silica were of reagent grade.

a) Sodium carbonate (Anhydrous)

b) Hydrochloric acid Sp. gr. 1.18

Preparations of reagent:

a) Hydrochloric acid (1:1): 40 ml of concentrated hydrochloric acid was diluted to 80 ml by double distilled water into a 100ml volumetric flask.

b) Hydrochloric acid (1:20): 5 ml of concentrated hydrochloric acid was diluted to 100 ml by double distilled water into a 100 ml volumetric flask.

Determination of the Silica from the sample: 1 gram of finely grounded sample was dried at 110°C in a platinum crucible. The sample was mixed with 6-8 grams of sodium carbonate. The platinum crucible was covered by the lid and then placed in a muffle furnace. Then the sample was fused in the muffle furnace at 1000°C. The sample was cooled and then placed into a porcelain basin. When the reaction ceases, the crucible was washed out with water. The porcelain basin was then placed on steam bath and the solution was evaporated to dryness until the smell of hydrochloric acid was no longer detected. Finally the dish was heated in an air oven and backed it at 110°C.

The disk was cooled and 10 ml of hydrochloric acid and 40 ml of hot water was added to the dish. The dish was covered with watch glass and the mixture was digested on a steam bath for 10 minutes. The digested mixture was then filtered though No.41 what man filter paper or its equivalent. The silica was transferred to the filter paper with hot water and the basin was scrubbed with a rubber-tipped glass rod. The precipitated was washed three times with hot 1.20 hydrochloric acid and then with hot water till free from chloride. The filtrate was then preserved.

The paper along with in the precipitate was transferred to an ignited and tared platinum crucible. The crucible containing precipitate was heated at a low temperature to remove carbonaceous matter and then heated in the muffle furnace at 1175°-1200°C to constant weight.

Calculation:

$\% \ SiO_2 = (W_1 - W_2) \times 100 / W$

Where, W_1 = Weight of platinum crucible precipitated sample.

W_2= Weight of crucible

W = Weight of sample taken.

Determination of Titanium oxide [82]

Preparation of standard titanium solution: One gram of the pure titanium dioxide was fused with 10g of potassium bisulfate and dissolved, at a low temperature to avoid hydrolysis, in 200ml of water containing 20ml of sulfuric acid. It was cooled and diluted to 1000ml in a calibrated flask (1ml=1.0mg TiO_2).

Determination of Titanium: Two 10ml of the stock solution was transferred to a 50 ml calibrated flasks A and B. 5ml of hydrogen peroxide to flask A and dilute both the solutions with water to the mark. The optical density was measured at 410 nm of the solution in A against in B.

A calibration curve with 0, 1, 2, 3, 4, and 5 ml of standard titania solution in 100 ml flasks after developing the color in the same way as in test solution in A. The titania content of the solution with reference to the calibration graph was determined.

Determination of Iron oxide by Ammonia Method [82]

Principle:

Ammonia reacts with trivalent iron in presence of thioglycolic acid produces pink color. Depending upon the intensity of pink color, iron content could be determined spectrophotometrically. The maximum molar absorptivity of the above developed color was found at 540 nm.

Apparatus:

A spectrophotometer of model UV-2201 Shimadzu, Japan was used for the above determination.

Chemicals:

All the chemicals used for the determination of iron were of reagent grade.

a) Tartaric acid

b) Thioglycolic acid

c) Ammonia

d) Nitric acid

Preparation of standard stock solution:

0.864 g predrilled AR ferric ammonium sulfate was dissolved with double distilled water containing 1 ml conc. HCl into a 100 ml volumetric flask and diluted unto the mark. It produced a solution of iron concentration of 1 mg/ml.

Preparation of Reagent:

a) Thioglycolic acid: 10 ml thioglycolic acid was diluted to 100 ml by double distilled water into a 100 ml volumetric flask.

b) Tartaric acid: 10 g tartaric acid was dissolved with water and diluted to 100 ml into a 100 ml volumetric flask.

c) Ammonia: 1 : 1 ammonia was used for the purpose.

d) Preparation of standard sample: 1 ml stock solution of concentration 1 mg/ml iron was taken in a 100 ml volumetric flask and diluted upto the mark by water to give a solution of 0.01 mg/ml iron content.

Preparation of a calibration curve:

1.0 ml, 2.0 ml, 3.0 ml, 4.0 ml and 5.0 ml standard 0.01 mg/ml iron content solutions were taken into 5 different 10 ml volumetric flasks. 1 ml tartaric acid solution was introduced into each of the volumetric flask followed by 1 ml thioglycolic acid solution. Then 3 ml 1:1 NH_3 was added into it and make it unto the mark with water if necessary. The solution was mixed thoroughly and the color was developed instantly. The absorption's were measured at 535 nm in a 1 cm cell against a regent blank and the absorption reading were plotted against concentration. A linear straight line was obtained intercepting zero which was used for future sample determination.

Determination of Iron from the sample:

5 ml of the sample stock solution was transferred in a 250ml beaker and diluted to 100 ml. Into this, 5 ml conc. nitric acid was added and heated for fifteen minutes on hot plate. It was then transferred qualitatively into a 50 ml volumetric flask and make up to the mark. Then the amount of iron was determined spectrophotometrically according to the procedure already mentioned.

Determination of Calcium and Magnesium oxide: During determination of calcium and Magnesium oxide, British standard methods for analysis were followed [83]

Determination of Aluminum oxide:

Eriochrome Cyanide R Method [82]

The color of Eriochrome Cyanide R (ER. Solochrome Cyanide R) (formula, p.51) in aqueous solution depends on the p^H.

ER^+	ER	ER^-	ER^{2-}	ER^{3-}	
	p^H~0	p^H~1	p^H~3	p^H~7	p^H~12
	pink	orange	pink-red	yellow	violet

In weakly acidic medium, Eriochrome Cyanide R reacts with aluminum to form a violet red, water soluble complex which is used for the spectrophotometric determination of aluminum. Hill proved that the ratio Al:ER in the complex is 1:3 in the presence of an excess of Eriochrome Cyanide R. At lowest Eriochrome Cyanide R concentrations, 1:1 and 1:2 complexes are formed.

The absorption spectra of Eriochrome Cyanide R and its aluminum complex at p^H 6.2 are shown in Fig. 5.1. The molar absorptivity of the complex at λ_{max}=535 nm is ~ 6.5×10^4 (a=2.4). The Eriochrome Cyanide R method is , therefore, the most sensitive spectrophotometric method for determining aluminum. The optimum p^H for the color reaction lies between the rather narrow limits 6.1-6.2. The absorptivity of the complex drops rapidly at higher or lower p^Hvalues.

Eriochromic Cyanide R should be added to an acidic solution of aluminum (p^{H} 1-2) before an acetate buffer is introduced. The aluminum complex is unstable at elevated temperatures; heating the solution (even to 40°C) probably accelerates hydrolysis of the complex.

Determination of Sulfur [7]

The method consists in slowly adding a dilute solution of barium chloride to a hot solution of the sulfate slightly acidified with hydrochloric acid:

$$Ba^{++} + SO_4^{--} \longrightarrow BaSO_4$$

The precipitate is filtrated off, washed with water, carefully ignited at a red heat, and weighted as barium sulfate. The percentage of Sulfur was calculated from the weight of barium sulfate. Calculating the percentage of SO_4 in the sample, the factor for converting $BaSO_4$ to S is 0.13737 was used.

Determination of Phosphorous:

Molybdovanadophosphoric Acid Method:

Principle:

Addition of molybdate to an acidic solution containing orthophosphate and vanadate results in the formation of yellow-orange molybdovanadophosphoric acid having the P:V: Mo ratio of 1:1:11.

The absorption maximum of the compound is in the ultraviolet at 315nm ($\varepsilon=2{\cdot}0\times10^4$). At 4nm,$\varepsilon=2{\cdot}5\times10^3$ (specific absorptivity 0·08). In the molybdovanadophosphoric acid method, the absorbency is measured either at 315 nm (sensitivity as high as that in the phosphomolybdenum blue method), or between 400 and 470 nm (much lower sensitivity).

Apparatus: A spectrophotometer of model UV-2201 Shimadzu, Japan was used for the above determination.

Reagents:

Ammonium metavanadate: 0.25% solution. Dissolve 1.25 g of NH_4VO_3 in 250 ml of hot water. Cool the solution and add 10ml of conc. HNO_3. Allow the solution to stand overnight, filter (if necessary), and dilute with water to 500 ml. Store the solution in a polyethylene container.

Ammonium molybdate: 5% solution. Dissolve 25 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ in 250 ml of water (at ~ 50°C). Allow the solution to stand overnight, filter (if necessary). dilute with water to 500 ml, and store in a polyethylene container. Standard phosphorus (V) solution: 1 mg/ml [37].

Procedure:

To the slightly acidic sample solution containing not more than 0.70 mg of P, add successively 5 ml of nitric acid (1+1), 5 ml of the vanadate solution, and 5ml of the molybdate solution, mixing the solution after the addition of each reagent. The solution was diluted to a volume with water in a 50-ml volumetric flask. After 30 minutes, the absorbance at 400 nm against a reagent blank solution was measured.

Determination of Na_2O and K_2O (flame photometry) [82]

Reagents:

Sodium chloride
Potassium chloride
Perchloric acid, 60%
Hydrofluoric acid, 40%

Standard Na solution (200 ppm)-Dissolving 0.2542g of dry NaCl in water and diluted to 500 ml in a calibrated flask. 1, 2, 3, 4 and 5 ppm solutions by proper dilutions were prepared.

Standard K solution (200 ppm)- Dissolving 0.1907g of dry KCl in water and diluted to 500 ml in a calibrated flask. 1, to 15ppm standard solutions by proper dilutions were prepared.

Preparation of sample solution:

0.1 g of abated (-200 mesh) and dried (105°-110°C) sample were weighed in a platinum basin, moistening with water and adding to it 1 ml of Perchloric acid ($HClO_4$) and 5 ml of Hydrofluoric acid (HF). The basin was placed on a heated sand bath and were evaporated until strong fumes of perchloric acid come out. The basins were collide and another 5 ml of HF were added to it and were evaporated in the same way as before. The inner sides of the basin were cooled and washed with water and again evaporated to dryness on the sand bath. To the dry mass in the basin 5 drops of HCl (1:1) and water were added. The basin was placed on a steam bath. After 5-10 minutes the contents were transferred to a 250ml calibrated flask quantitatively. If the solution is turbid, it could be filtered or centrifuged.

Determination of Na_2O:

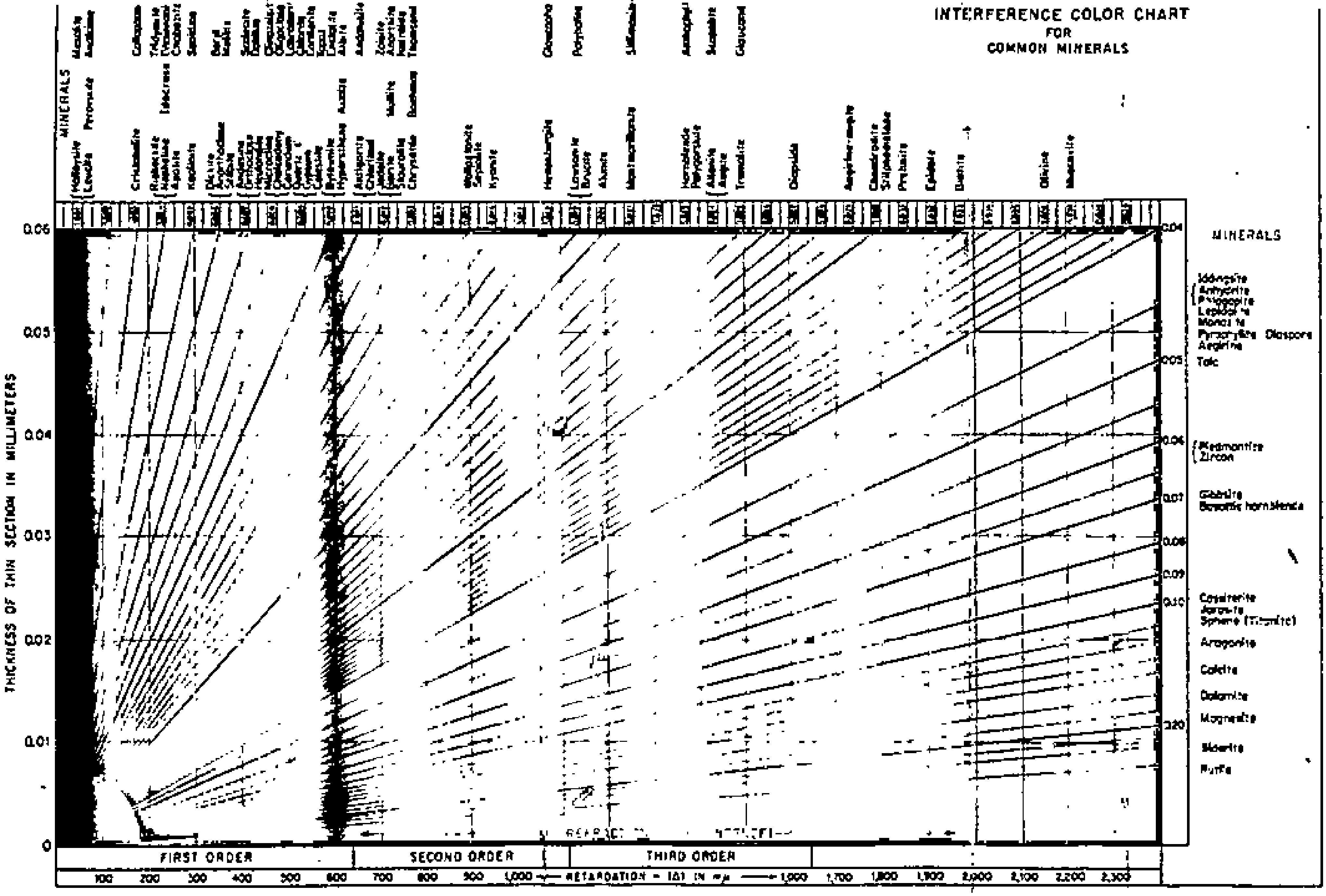
A few ml of the sample solution were placed in the cup of a flame photometer provided with monochromatic arrangement or sodium filter. The emission at 589 nm or through the filter against water was measured. Drawing a calibration graph with 1to5 ppm of standard sodium solutions, the sodium content of the sample by referring to this graph could be calculated.

Determination of K_2O:

A few ml of the sample solution were placed in the small cup of a flame photometer provided with monochromatic arrangement or potassium filter. The emission at 767 nm or through a potassium filter against water was measured. Drawing a calibration graph with 1to15 ppm of standard potassium solutions, the potassium content of the sample by referring to this graph could be calculated.

Appendix-F: TheInterference Color Chart for Common Minerals is given in the next page

INTERFERENCE COLOR CHART
FOR
COMMON MINERALS



Chapter Seven

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