CONCRETE FEASIBILITY FOR THE LIMESTONE OF THE KOHAT FORMATION, DISTRICT KOHAT
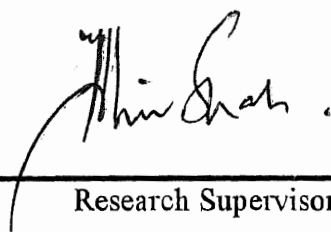
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"CONCRETE FEASIBILITY FOR THE LIMESTONE OF THE KOHAT FORMATION, DISTRICT KOHAT"

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIRMENT FOR THE DEGREE OF

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NATIONAL CENTER OF EXCELLENCE IN GEOLOGY, UNIVERSITY OF PESHAWAR, PESHAWAR, PAKISTAN.

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ABSTRACT

Limestone is a valuable raw material, which is widely used in the chemical and construction industries throughout the world. With huge deposits of limestone in Pakistan, it is immensely used as concrete aggregates. The Eocene limestone of the Kohat Formation is generally exposed in the Kohat, Hangu and Bannu districts. It is cream to gray in color, hard, compact, well-bedded and fossiliferous. The limestone of Kohat Formation has been evaluated mineralogically, chemically and physically, for its use as concrete aggregates during present study.

Mineralogically, the studied limestone is dominantly calcite with abundant fossil shells. Fine-grained quartz, chalcedony, clay, dolomite and opaque phases are present in minor amount. The limestone generally has fine to medium-grained granular mosaic with bioturbated microfossils. Deleterious minerals to concrete are generally found in the argillaceous variety of the studied limestone.

Chemically, the studied limestone (by weight) is classified as high-calcium limestone, with $CaCO_3$ between 81.23 and 98.93%. The SiO_2 varies from <0.50 to 13.90 wt %, Al_2O_3 from 0.47 to 0.74 wt %, Fe_2O_3 from 0.05 to 0.30 wt %, CaO from 46.07 to 57.03 wt %, Na_2O from 0.35 to 0.48 wt % and K_2O from 0.01 to 0.05 wt %. MnO and MgO are up to 0.25 and 2.69 wt %, respectively. The average chemical compositions of various cements manufactured in N.W.F.P. are within the ASTM limits. The alkali-silica reactivity graph for the limestone aggregates based upon ASTM C 289-90 also verify the petrographic observations. Physical properties (i.e., soundness, water absorption, Los Angeles abrasion and specific gravity) are generally in accordance with the ASTM standards for aggregates to be used in concrete.

The studied limestone of the Kohat Formation except its argillaceous variety found in the eastern part of the study area, is generally free of dolomitization and has no other deleterious substances as far as the durability of concrete is concerned. This Eocene limestone of the Kohat Formation is therefore, recommended for its use as concrete aggregates.

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CHAPTER 1

INTRODUCTION

1.1 GENERAL

Limestone is a sedimentary rock composed of calcium carbonate. It is polygenetic and generally derived from the calcareous remains of marine or fresh water organisms, embedded in calcareous mud. Limestone may be mechanically transported and deposited (hydrodynamic featured) or chemically or biochemically precipitates and formed in situ exhibiting current and growth bedding. They vary in type from the soft chalks to hard crystalline rocks. There have been number of uses for the limestone. It includes construction (asphalt filler, concrete, fill, railroad ballast, rip-rap, road stone, roofing granules, stone sand, terrazzo etc.), Portland and other masonry cements, agriculture limestone, flux-stone, glass, mineral food, fillers (caulking compounds, floor covering material, paints, paper, plastic, putties, rubber, and whiting, etc.), rock dust for coal mining, chemical industries (ceramic, ferro-silicates, filter stone, insulation, paper pulp, sulfur dioxide removal, etc.) (Pettijohn, 1976; Boynton, 1980). Generally, the limestone is most chemically stable substance (except infinitesimal dissolution) with minute expansion at temperature $300^{\circ}C$ (Lea, 1976).

Pakistan has tremendous resources of limestone, which can be utilized for construction purposes. There are extensive limestone beds exposed in the entire foreland and thrust belts including Kohat (Kohat Basin), Nowshera (Attock-Chharat Range), Hassanabdal (Lesser Himalayan Range), Wah (Margalla Hills), Beth Kas-Khairabad-

DaduKhel (Salt Range), Pezu (Marwat Range), Moghal Kot and Zinda Pir (Sulaiman Range), Rohri-Hyderabad-Thatta (Indus platform), Jangshahi-Murli Hill-Mango Pir (southern Kirthar Range) and many other localities in Baluchistan and northern Pakistan (Gilgit-Baltistan) (Shah et al., 1977).

The northern Kohat Basin of which study area is located (Fig. 1.1), comprises of four formations of Chharat Group namely Panoba Shale, Sheikhan Formation, Kuldana Formation and Kohat Formation (Meissner et al., 1968 & 1974; Shah et al., 1977). The Eocene limestone of the Kohat Formation comprising of the Habib Rahi Member (upper member) and the Kaladhand Member (lower member). The formation form's 30% of Eocene limestone in the area (Gauhar, 1966). It is creamy to light gray, hard, compact, thinly bedded with abundant fossils of Assilina and Nummulites (Meissner et al., 1968 & 1974; Shah et al., 1977). The Kohat Formation is widely exposed in the Kohat Province of the upper Indus Basin (Meissner et al., 1968 & 1974). It is exposed in the Kohat, northern Bannu and eastern Hangu districts and is a dominant rock unit in the study area of Kohat. Presently the limestone of Kohat Formation is used as a raw material for cement manufacturing by the Kohat Cement Factory.

According to Lea (1976) and Boynton (1980), the use of limestone as concrete aggregate has been sometimes suspected because its concrete is less resistant to the action of fire relative to the concrete made from other aggregates. But many recent researchers like Mehta, (1986), Hobb, (1988) etc., emphasis that the limestone has excellent thermal resistant. The surface concrete containing limestone aggregates provide a good shield against fire after calcining. This also has been

Fig. 1.1. LOCATION MAP OF THE KOHAT BASIN

STUDY AREA

■ Town

0   5   10   15   20   25 Kms

INDUS RIVER

SURGHAR RANGE

KOHAT

BANNU

Thal

Panoba

Gumbat

Shadi Khel

Nare Algad

Pattan Algad

Jatta

Banda Daud Shah

Lodi Khel

Hangu

Bagatu

Sirki Plaza

Anar China

Mardan Khel

Gurguri

Bahadur Khel

Latambar

Chasnmal

Doaba

Dallan
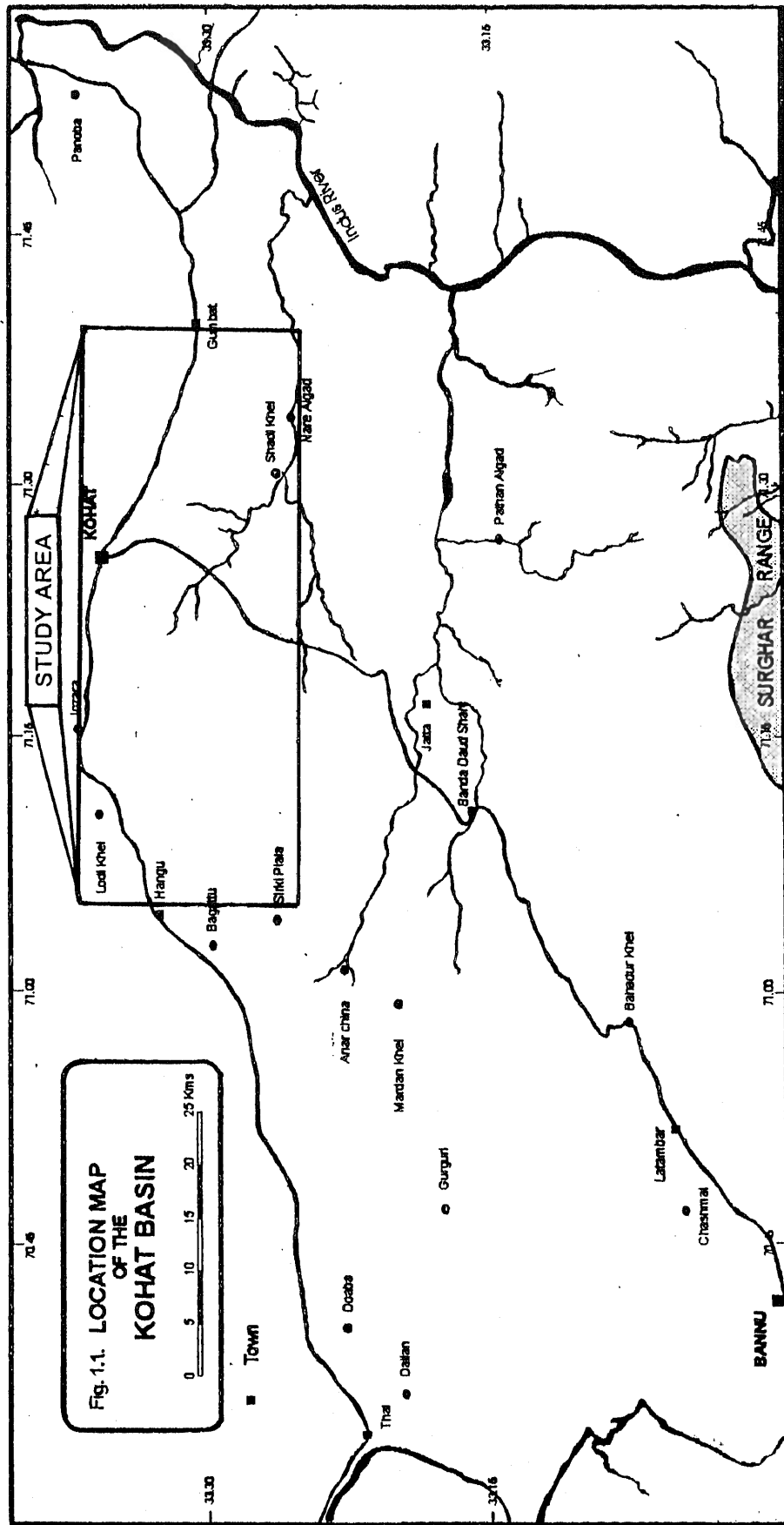
experienced after damages to one of the thermal power stations (Muzaffargarh thermal power plant) in Pakistan, which was constructed with the limestone aggregates. Thus, most of limestone aggregates used in the concrete have good performance records are innocuous. The limestone of the Kohat Formation with over 1.5 million tons surface exposure (Gauhar, 1966) can be used as a concrete aggregate. But before its use as concrete aggregates, it should be evaluated by using different international standards regarding e.g., American Society for Testing and Materials (ASTM). Although no proper scientific published data for this limestone has so far been reported regarding its evaluation as a concrete aggregates except some preliminary project feasibility reports on Gandially dam and Kohat tunnel.

1.2 AIMS AND OBJECTIVE

The present study deals with the evaluation of mineralogical, geochemical properties and inherent reactivity along with the physical properties (i.e., soundness, water absorption, Los Angeles abrasion and specific gravity) for the limestone coarse aggregates of the Kohat Formation, exposed in the Kohat district. These studies will be carried out in conjunction with the chemistry of local ordinary Portland cements, in order to figure out its use as a concrete aggregate.

1.3 AREA LOCATION

The study area (longitude: 71°05' to 71°40'N and latitude: 34°26' to 34°38'E) is situated in the Kohat district and covers approximately 1207 Km^2 area on Survey of Pakistan topographic sheet No. 38-O (scale 1:250,000). Metalled roads links major towns of the study area through Indus Highway with rest of the country whereas, there is a weekly train service for Rawalpindi. The main population of the area consists of

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Afridi, Bangash, Khattak and Paracha tribes, with estimated population of 557,000 (1998 census) and sex ratio 1:1.

1.4 PREVIOUS STUDY

The Eocene strata of the Kohat Plateau because of its salt and gypsum deposits received attention of geologists since long ago (Burnes, 1832; Oldham, 1864; Wynne, 1879; Davies, 1926; Eames, 1952). Gee (1945) in his detailed reports on the evaporate deposits of Kohat, differentiate them from the Eo-cambrian of the eastern Salt Range. A detailed stratigaphic and structural study for the Kohat area was conducted by Meissner et al., (1968 & 1974) which provides key for the correlation between Eocene facies of the basin. Wells (1984) introduced some modification in the Eocene succession of the basin and discussed the environment of deposition of these lithologies. Latif and Iqbal (1986) provided a tentative model for paleogeographic reconstruction of the early Eocene Kohat Basin. Abbasi and McElory (1991) and McDougal and Hussain (1991) discussed the Kohat Basin structural analyses.

CHAPTER 2

G E O L O G Y

2.1 REGIONAL TECTONIC SETTING

In this section, the regional geological setting and tectonic zones (Fig. 2.1) in context to the study area has been discussed as follows:

2.1.1 Kohistan magmatic arc and Karakoram block

The Himalayas-Karakoram-Hindukush ranges in the northern Pakistan are considered to be a broad collision zone between the Asian plate in the north and the Indian plate in the south. Several microcontinents mostly of Gondwana affinity (Searle, 1991) and more than one island arcs (Dietrich et al., 1983) are involved in this collision zone. The microcontinents such as the Afghan Block, Karakoram Plate and Kohistan Island Arc were developed to the north of the Indian continent during the Mesozoic era. The first block to collide with southern margin of the Asian Plate was Karakoram Plate followed by the Afghan Block and at the end Kohistan Island Arc came in contact with the system (Gannser, 1964; Le Fort, 1975; Windley, 1983). In the northwestern Himalaya, continent-continent collision followed the accretion of the Kohistan Island Arc, which had been formed by northward subduction in late Cretaceous to late Jurassic time (Windley, 1983). The Kohistan Island Arc is bounded to the north by Main Karakoram Thrust (MKT) and to the south by the Main Mantle Thrust (MMT).

The MKT is a major tectonic feature in northern Pakistan and is resultant of collision between the Karakoram Plate in the north and

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1. **INDUS PLATFORM & FOREDEEP**
   - Buried Ridges.
     a, Sargodha-Shahpur; b. Nagar Parkar.
   - Zones of upwarp.
     c. Mari-Khandkot; d. Jacobabad-Khairpur;
     e. Thatte-Hyderabad; f. Tharparkar.
   - Zones of downwarp & platform slope.
     g. N. Punjab monocline; h. S. Punjab mono-
     cline; i. Cholistan shelf; j. Panno Aqil graben;
     k. Nawabshah slope; l. Lower Indus trough;
     m. Nabisar slope; n. Sulaiman foredeep;
     o. Kirthar foredeep.

2. **BALOCHISTAN OPHIOLITE & THRUST BELT**
   - a. Bela ophiolite & thrust belt.
   - b. Zhob ophiolite & thrust belt.

3. **SULAIMAN–KIRTHAR FOLD BELT**
   - al. Sulaiman fold belt; all. Mari-Bugti fold zone;
     b. Sibi trough; c. Kirthar fold belt (i) Kalat
     anticlinorium, (ii) Kalat plateau, (iii) Khuzdar
     knot, (iv) Khude Range, (v) Nagau-Kirthar
     Range, (vi) Karachi embayment zone,
     (vii) Sanbakh-Lekhra uplift zone.

4. **NW HIMALAYAN FOLD & THRUST BELT**
   - al. Hazara-Kashmir Syntaxis; all. Outer Hima-
     layas; b. Salt Range-Kohat-Potwar plateau.
   - cl. Kalachitta-Margalla thrust belt;
     cll. Lesser Himalayas.
   - d. Swat-Hazara crystalline nappe & thrust
     belt.(i) Peshawar basin, (ii) Khyber-Hazara
     metasedimentary fold & thrust belt, (iii) zone
     of crystalline nappes, (iv) Kashmir basin.

STUDY AREA

5. **KOHISTAN MAGMATIC ARC**

6. **KARAKORAM FOLD & THRUST BELT**
   - a. Chitral Region; b. Yasin–Hunza Region;
     c. Upper Hunza–Baltoro Region.

7. **KAKAR KHORASAN FLYSCH BASIN & MAKRAN ACCRETIONARY ZONE**
   - a. Kakar Khorasan; b. Chaman fault zone;
     c. Makran.

8. **KHARAN BASIN**

9. **CHAGAI MAGMATIC ARC.**
   - a. N.Chagai; Volc. & magmatic zone;
     b. Mirjawa–Dalbandin trough; c. Ras Koh
     Range.

Fig. 2.1. Map showing tectonic zones of Pakistan.

(after Kazmi & Jan, 1997)

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Kohistan Island Arc in the south (Tahirkheli, 1979; 1982 & 1983). It was named as Northern Suture Zone by Pudsey et al. (1986). Coward et al. (1986) emphasis that, it was formed during late Cretaceous period. The MMT or Indus Suture Zone was formed as a result of collision and subduction of Indian Plate underneath the Kohistan Island Arc during Eocene time (Gannser, 1964; Tahirkheli, 1979; 1982 & 1983). In India and Tibet, the MMT and MKT join together as the Indus-Tsangpo Suture (ITS) of the central Himalaya.

The Karakoram Plate to the north of MKT is composed of high-grade metamorphic rocks with granitic intrusions (Searle, 1991). To the south of MKT, there lie the metamorphic basic and ultra-basic rocks of Kohistan Island Arc (Brad et al., 1980; Bard, 1983). The ocean between the Karakoram Plate and the Kohistan Island Arc (Tethys ocean) was closed in the late Cretaceous time at the site of MKT (Coward et al., 1986). Continuous subduction between the Kohistan Island Arc and the Indian Plate had produced an extensive intrusive body, known as Kohistan Batholith. The ocean between the Indian Plate and the Kohistan Island Arc was closed in Eocene at the site of MMT (Gannser, 1964; Tahirkheli, 1979; 1982 & 1983).

2.1.2 North-western Himalayan fold-and-thrust belt

The convergence in between Karakoram, Kohistan and India resulted the continent-arc-continent collision however, it remained continued with the formation of MMT. This convergence resulted in the deformation of the Indian crust, giving rise to the Himalayan foreland fold-and-thrust belt of the northern Pakistan. This belt is located to the south of the MMT and is about 250 Km wide and about 500 Km long.

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This gradual southward propagation of deformation resulted, development of south younging fault system. The major member of this fault system are the Main Boundary Thrust (MBT) and the Salt Range Thrust (SRT) (Zeitler, 1982; Zeitler, 1985; Yeats & Hussain, 1987). This region is comprised of mountain ranges of Nanga Parbat, southern Kohistan, Hazara, Swat, Margalla, Kalachitta, Kohat, Sufed-Koh, Salt Range and their western extension.

The Salt Range Thrust (SRT) in the southwestern part of the northwestern Himalaya is the lateral equivalent of the Main Frontal Thrust (MFT) of the central Himalaya. In the central Himalaya, the foreland fold-and-thrust belt is internally subdivided by two major north dipping thrust faults that is, early to late Miocene age Main Central Thrust (MCT) in the north and late Miocene Main Boundary Thrust (MBT) in the south. The MBT in the north western Pakistan runs east west along most of the foreland basins but turns northward west of the Jhelum River, in the form of a major bend known as the Hazara-Kashmir syntaxis.

The Kohat Province of upper Indus Basin constitutes the western part of the Himalayan fold-and-thrust belt, which is resultant of ongoing collision between the Indian and Asian, plates. The upper Indus Basin is divided in to two areas, the Potwar Plateau (Cis-Indus Range) to the east of the Indus River and the Kohat Plateau (Trans-Indus Range) lies west of the Indus River. The Kohat-Potwar fold-and-thrust belt is the deformed terrain of the Himalayan foreland basin and the Kohat Plateau has distinct passive roof duplex geometry between the MBT and the Surghar Range (Abbasi & McElory, 1991) (Fig. 1.1). The plateau is a narrow, highly deformed/shortened and structurally elevated as

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compared to the adjoining Potwar Plateau (Baker et al., 1988). The style of deformation varies in the basin, which is relatively great in the northern and central parts, where Eocene succession is well exposed with respect to that in southern part, where molasses sediments are exposed. The MBT brings the Mesozoic platform rocks over the Miocene molasses sediments whereas, Kalabagh Fault (dextral fault) in the south at Surghar Range, thrust the late Paleozoic/Mesozoic strata over the Miocene Siwaliks.

2.1.3 Sulaiman-Kirthar fold belt

The Sulaiman-Kirthar fold belt (Kazmi & Jan, 1997) is a structurally complex zone which is about 1300 Km long and less than 180 Km wide. It has faulted contact with the Himalayan fold-and-thrust belt in the north and west whereas, its southern and eastern contact with Indus platform and fore deep zone is weakly defined. On the basis of varying lithological, structural and tectonic features, this belt has been divided into Sulaiman Arc, Sibi Trough and Kirthar fold belt (Kazmi & Jan, 1997).

2.1.4 Indus platform and fore deep

The Indus platform and fore deep (Kazmi & Jan, 1997) comprised of Indus plain and Thar-Cholistan deserts, in the southeastern portion of Pakistan. This zone cover vast area (over 2500 Km^2) and having dense population, extensive mineral resources (especially, hydrocarbons and coal) and tremendous ground water reservoirs. This zone has various structural domains such as buried ridges, zones of upwarp, zones of downwrap and platform slopes and fore deeps (Kazmi & Rana, 1982). This zone has basement rocks such as the Kirana Group and Nagar Parker Igneous complex (Davies & Crawford, 1971) whereas;

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quaternary deposits occur as sedimentary cover.

2.2 LOCAL GEOLOGICAL SETTING

The study area (Fig. 2.2) lies in the Kohat Province of the upper Indus Basin. The basin generally consists of Eocene rocks, except in the northern hinterland and Surghar Range, where Mesozoic-Paleozoic succession is exposed (Meissner et al., 1968 & 1974). The northern Kohat Basin comprises of four formations namely Panoba Shale, Sheikhan Formation, Kuldana Formation and Kohat Formation (Meissner et al., 1968 & 1974; Shah et al., 1977). The previous studies of early workers suggested that the nonclastic facies of the Sheikhan Formation in the northern part laterally change to clastic facies of the Chashmai Formation in the west and to evaporate in the central and southern part of the basin. The Kohat Basin was a part of an epicontinental sea, which was developed during late Paleocene transgression marked by the underlying Patala Formation. High sea stand existed during deposition of the basal part of the Panoba Shale, after which marine regression started. The Sheikhan Formation, Chashmai Formation and evaporates (Bahadur Khel Salt and Jatta Gypsum) were deposited during late early Eocene period. The red beds of the Kuldana Formation mark the total retreat of the sea from the basin, during late early Eocene time. By early middle Eocene, the Kohat Basin was once again under sea water and the youngest marine strata of the Kohat Formation were deposited (for details see, Burnes, 1832; Oldham, 1864; Wynne, 1879; Davies, 1926; Gee 1945; Eames, 1952; Meissner et al., 1968 & 1974; Shah et al., 1977; Wells, 1984; Latif & Iqbal, 1986; Abbasi & McElory, 1991; McDougal & Hussain, 1991). The Eocene stratigraphy of the northern Kohat Basin is as follows:
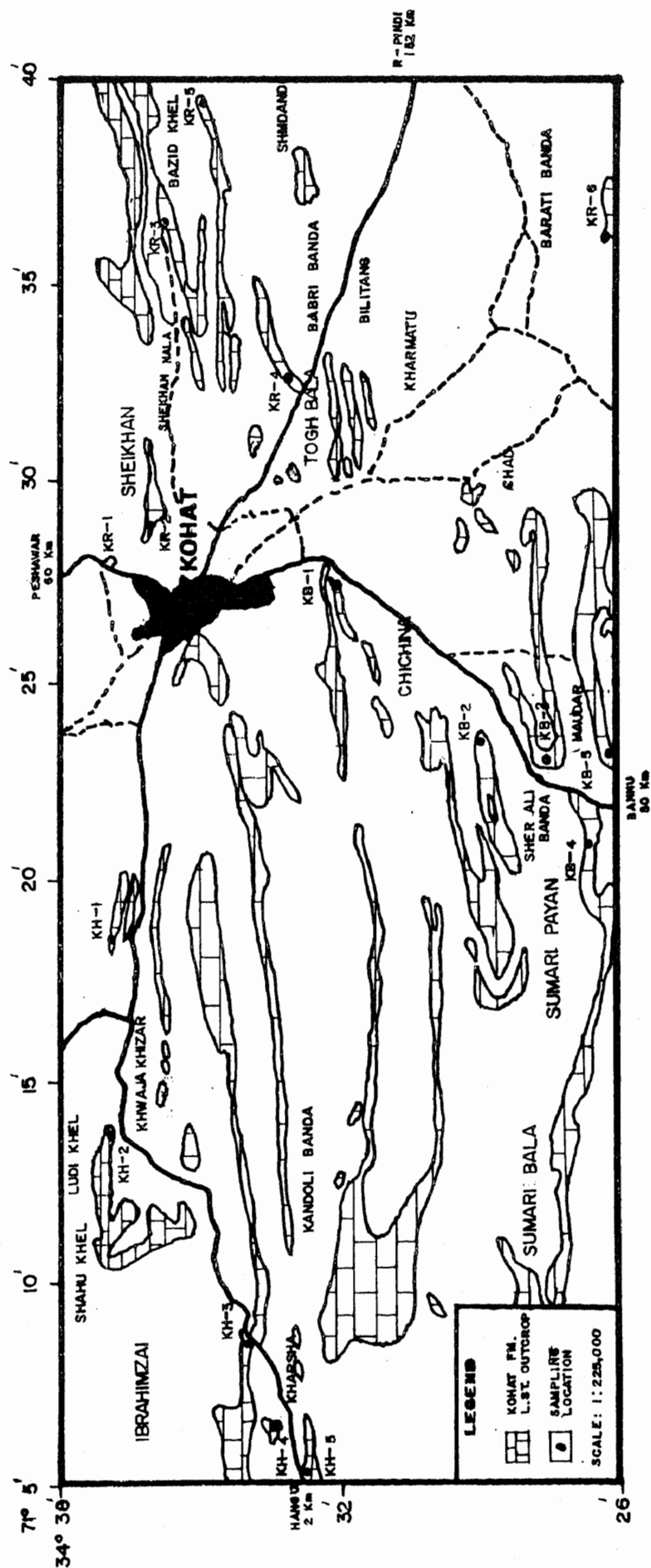
Fig. 2.2. Geological map of the Kohat and surroundings area. showing the out crops and samples locations for the limestone of the Kohat Formation. (after Meissner et al., 1974)

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2.2.1 Panoba Shale

Eames (1952) introduced the term Panoba Shale. The formation is confined to the Kohat area and the section exposed south of Panoba village (Fig. 1.1) have been designed as type locality (Shah et al., 1977). The formation consists of shale with occasional bands of sandstone. The shale is greenish-gray to light gray, slightly silty and is calcareous towards the base. Flaggy limestone bands and gypsum veins are also present. The formation lies conformably over the Patala Formation and underlain by the Sheikhan Formation. Base upon the foraminiferal evidence, the Panoba Shale is designated as early Eocene age.

2.2.2 Sheikhan Formation

The term "Sheikhan Limestone" of Davies (1926) and "Gypsiferous beds" and "Sheikhan Limestone" of Eames (1952) was formalized as Sheikhan Formation. The formation is restricted to Kohat area and the Sheikhan Nala (Fig. 2.2) has been nominated as a type section (Meissner et al., 1968 & 1974; Shah et al., 1977). The formation consists of limestone and shale. The limestone is yellowish-gray to gray, thinly to massive bedded and nodular whereas, shale is gypsiferous. Both the lower and upper contacts of the formation with the Panoba Shale and Kuldana Formation respectively, are conformable. Based upon fossil indication the formation is designated as Early Eocene.

2.2.3 Kuldana Formation

The "Kuldana Beds" of Wynne (1879), "Kuldana Series" of Middlesmiss (1896), "Variegated Shales" of Pinfold (1918), "Lower Chharat Series" of Eames (1952) and "Mami Khel clay" of Meissner et

al., (1968 & 1974) were renamed as Kuldana Formation after Latif (1970). The village Kuldana in the Murree Hills is the type locality of the formation. The formation is composed dominantly of shale and marl with occasional beds of sandstone, limestone, conglomerate and bleached dolomite (Shah et al., 1977). The formation has conformable lower and upper contacts with Sheikhan and Kohat Formations, respectively. The fossil indication gives early to early middle Eocene age of the formation.

2.2.4 Kohat Formation

The "Kohat Shale" of Eames (1952) with its three subdivision "Nummulitic Shale", "Kohat Limestone" and "Sirki Shale" and "Kohat Formation" of Meissner et al., (1968 & 1974) with its three subdivision "Kaladhand Limestone" ("Kohat Shale" of Eames, 1952), "Sadkal Shale, ("Nummulitic Shale" of Pinfold, 1918) and "Habib Rahi Limestone" ("Kohat Limestone" and "Sirki Shale" of Eames, 1952) were formally accepted as Kohat Formation by the Stratigraphic Committee of Pakistan which has also approved its two members following Meissner et al., (1968 & 1974). The members includes (in ascending order of age) "Kaladhand Limestone" and "Sadkal Shale". The Kohat Formation is the uppermost formation of the Chharat Group and the section exposed about 10 Km south of Gumbat (longitude 71°35'E, latitude 32°27'N) on the Kohat-Rawalpindi road (Fig. 2.2) is proposed as type locality.

The Kohat Formation is confined to Kohat quadrangle and it consists of interbedded limestone and shale. The limestone outcrops (Plates 2.1, 2.2 and 2.3) composed predominantly of limestone, which is creamy to gray in color, hard, compact and well-bedded with shale

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intercalation particularly in the lower part. The shale outcrops is composed of greenish-gray calcareous shale with subordinate light-gray limestone. The lower contact is sharp and conformable with the Kuldana Formation but the upper contact with the Murree Formation is unconformable, marked by MBT. The formation yields abundant fossils of foraminifers and mollusks including assilina, cancellate, dictyoconoides, vredenburgi, fasciolites, oblonga, orbitolites complanatus and various types of nummulites (Meissner et al., 1968 & 1974; Shah et al., 1977). Based upon faunal studies, the formation is assigned middle Eocene age.

Plate 2.1. A view of the outcrop of limestone of Kohat Formation, exposed at Bazid Khel, in district Kohat.
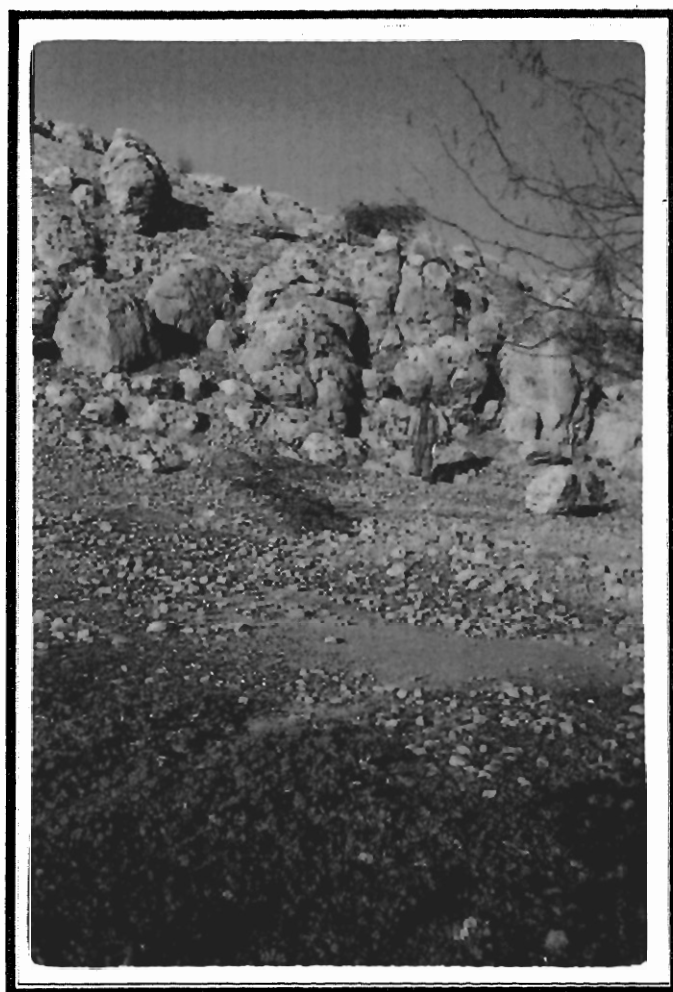
Plate 2.2. A view of the outcrop of limestone of Kohat Formation, exposed at Toag Bala, in district Kohat.

Plate 2.3. A view of the outcsrop of limestone of Kohat Formation, exposed at Baratai Banda, in district Kohat.

CHAPTER 3

CONCRETE

3.1 HISTORICAL BACKGROUND OF CONCRETE

Concrete is a material that forms the basis of our modern society. Scarcely any aspect of our daily life does not depend directly or indirectly on concrete. The word concrete comes form the Latin term *concretus*, which means to grow together (Mindess & Young, 1981). It is a composite hardened product created by mixing generally chemically inert, granular particles or fragments of aggregates with a matrix of cementitious binder (natural or artificial cement) and water, that fills the spaces between the aggregate particles and glue them together (Encyclopaedia Britannic, 1975; Mindess & Young, 1981; Hawkins, 1986; ASTM, 1994). In building construction, concrete means the Portland cement concrete, which is widely used throughout the world (Mindess & Young, 1981). Although there are other cements and concrete which have their limited use (Gilkey, 1962).

From very early times, builders have tried to find material that could be used to cement stones or bricks in order to acquire more flexibility in construction (Mindess & Young, 1981). Thus the use of concrete, an artificial conglomerate or gravel or broken stone with sand and lime or cement was of great antiquity, as most of the early civilizations flourished near natural cement deposits (Lea, 1976; Hawkins, 1986). Egyptians were considered as pioneer for use of mortar made up of calcareous materiel (gypsum or lime) used as cement mixed with water during construction of Cheops Pyramid (Mindess & Young,

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1981). Later, both the Greeks and the Romans also produced hydraulic lime mortars by calcining limestone containing argillaceous (clayey) impurities (Lea, 1976; Mindess & Young, 1981; Hawkins, 1986). Romans also introduced use of animal fats, blood and milk to improve the concrete strength (Mindess & Young, 1981). Roman buildings including the vaults of Thermæ, basilica of Constantine and Pantheon temple, were some early examples of concrete structures (Lea, 1976; Mindess & Young, 1981). The present condition of many buildings of these classes along the coast of Tyrrhenian sea is sufficient testimony to the durability and excellence of the material used in their construction despite the weathering effect of the sea (Lea, 1976). Concrete was employed in building walls throughout the middle ages but with inferior quality cementing material (Lea, 1976; Mindess & Young, 1981). By the end of fourteenth century, pozzolan based high quality mortar regain attention but the cementing material quality assumed importance with the construction of West Indian docks, in eighteenth century (Lea, 1976; Mindess & Young, 1981). In 1756, a British builder John Smeaton, while reconstructing Eddystone Lighthouse, performed extensive series of experiments with different limes and pozzolans (Lea, 1976; Mindess & Young, 1981). He found that the best quality limestone for use in mortar was that containing a high proportion of clayey material. This leads for the first time to the controlling factor for the formation of hydraulic lime. Later, number of other systematic studies followed quite rapid contributions by Parker, Vicat, Michaelies, Le-Chaterlier etc., regarding the cement formation (Lea, 1976; Mindess & Young, 1981). In 1824, Joseph Aspdin took out a patent on "Portland cement" (Lea, 1976; Mindess & Young, 1981). He prepared the cement by calcining some finely grind limestone with clay in a kiln until CO_2 was driven off. The mixture was then finely ground and used as cement. The name

"Portland" cement was coined by Aspdin because of the real or fancied similarity of the hardened cement to a popular, naturally occurring building stone quarried at Portland, England. (Mindess & Young, 1981; Hawkins, 1986). The use of hydraulic cement spread rapidly through Europe and North America (Mindess & Young, 1981).

Structural concrete was developed following the early 19th century invention of Portland cement. Since that time the rapid and continuos development of Portland cement concrete used in masonry of harbors, dams and other structures required massive construction thus, becoming most versatile constructional material (Gilkey, 1962; Encyclopaedia Britannica, 1975; Lea, 1976). The use of reinforced concrete was started in Britain and France in mid nineteenth century, permitting its use for structures containing beams and other members that are subjected to bending action and consequently to compressive and tensile forces (Gilkey; 1962; Encyclopaedia Britannica, 1975; Hawkins, 1986). Later in 1930, a French engineer Freyssinet, introduced the pre-stressed concrete (Encyclopaedia Britannica, 1975).

As the need for a prime quality material along with perfect code of practice for concrete structure increased, it became desirable that standards of quality should be set up, by which any consignment could be judged after the performance of certain agreed tests. The first association on cement was found in Germany, in 1877. In United States of America, the first joint committee on specification for concrete and reinforced concrete was set up in 1904, which established the pattern for concrete practice throughout USA and much of the present world (Gilkey, 1962). The American Concrete Institute (ACI) was organized in 1905 (as the National Association of Cement Users) and it functioned in

closed cooperation with other related organizations. The American Society for Testing and Material (ASTM) was established in 1904 and it continuously makes important contributions by its published researches and standardizing activities furnished by its committee C-9, on Concrete and Concrete Aggregates (Gilkey, 1962; ASTM, 1994).

3.2 CONCRETE RELATED PROBLEMS

From the standpoint of cost and suitability, concrete can vied steel, timber and other construction materials, for engineering structures. As a structural material, concrete own its importance due to economic utilization, highly resistant to natural and man-made hazards and tends itself readily to almost any type of decorative or architectural expression ranging from the conservative to the fantastic (Gilkey, 1962). Concrete properly designed, compacted and cured with adequate cover to reinforcement, will normally give good performance in service. The problems which sometimes arise are normally due to design and constructional faults (Hobb, 1988). The most common causes of deterioration in structural concrete is inadequate cover to reinforcing steel duly effected by chlorides (Hobb, 1988). The problem of possible deterioration between aggregates and cement in either mortars or concrete failure includes cycles of freezing and thawing, carbonation, sulfate attack and shrinking aggregates. But one kind of interaction rise up, where certain kind of reactive siliceous aggregates reacts with hydroxyl ions in the pore water of a concrete furnishing alkali-silicate gel (Jones, 1952; Lea, 1976; Derucher & Heins, 1981; Hobb, 1988; ASTM, 1994; Helmuth et al., 1994). The swelling of this gel set up an expansion stress, which may be sufficient to crack the mortar or concrete (Jones, 1952; Hobb, 1988). Such type of deterioration in the concrete is known as alkali-aggregate reactivity.

3.3 ALKALI-AGGREGATE REACTIVITY

Attention was first time drawn to the problem of alkali-aggregate reactivity in a paper published by Stanton in 1940 on the expansion and disruption of concrete (Jones, 1952; Hobb, 1988). The first structure noted in which failure was later traced due to alkali-aggregate reaction, was the King City Bridge in California, which was built in 1919-20 (Jones, 1952). By 1924, all the pier caps of the bridge were affected by extensive expansion and random cracking. Failure were noticed in other roads and structures including schools, bridges, pavements etc. in Los Angeles, Monterey, Obispo, San Luis, Santa Barbara and Ventura counties (Jones, 1952; Hobb, 1988). Stanton, an American engineer, after several experiments comes to a conclusion that the reaction between high alkalies of Portland cement with certain types of shale, chert and impure limestone are found as deleterious. Later, different European researchers made several experiments regarding alkali-aggregates reactivity.

In Pakistan, the alkali-aggregate reaction was noticed for the first time in the Warsak Dam, Peshawar. Warsak Dam built over river Kabul in 1952 is a concrete gravity dam and the concrete is composed of reactive aggregates with high alkali cement. Researchers from National Research Council of Canada conducted large-scale studies on this dam (Grattan-Bellew et al., 1997). They took numerous cores from the powerhouse and spillway and tested the reactivity of representative gravels that were used as coarse aggregate in concrete, in terms of alkali-silica reactivity. They concluded that, the alkali-silica reactivity expansion rate for these coarse aggregates was 0.05-0.10% (as per Canadian Standard Concrete Prism test) and was the major cause of cracking in the concrete (Grattan-Bellew et al., 1997).

There are three types of alkali-aggregate reactions that is, alkali-silicate reaction, alkali-carbonate reaction and alkali-silica reaction. Generally, limestone concrete aggregates are most affected by the alkali-carbonate reaction and alkali-silica reaction (Jones, 1952; Lea, 1976; Hobb, 1988).

The alkali-aggregate reactivity mechanism causes internal micro-cracking, associated with individual expansion of the particles, surface macro-cracking, overall dimensional change of the structure, induced tensile stresses in reinforcement and compressive stresses in concrete, induced bond stress between steel and concrete and differential movement between separate pours of concrete expanding at different rates (Tayler, 1977; Soroka, 1979; Mindness & Young, 1981; ACI committee, 1984; Neville & Brooks, 1987; Hobb, 1988; Grattan-Bellew et al., 1997)

The hydration of Portland cement generally results in the formation of pore solution containing calcium, sodium and potassium hydroxides (Hobb, 1988). The concentration of sodium and potassium hydroxides depend upon their representative ions in the anhydrous ordinary Portland cement represented as Na_2O equivalent (Lea, 1976). On the other hand, certain silica minerals present in either fine or coarse aggregates when immured in water, display a weak acid characteristic, which increases with increasing surface area or increasing disorder (Hobb, 1988; ASTM, 1994; Helmuth et al., 1994; Grattan-Bellew et al., 1997). In the alkaline environment within concrete, an acid/alkali reaction occurs at the accessible surface of the silica forming a hydrous silicate. The hydroxyl ions are imbibed in the silica particles damaging the silicon oxygen linkage and calcium, sodium and potassium cations

will diffuse to maintain electrical neutrality by forming gelatinous mixture. Water will be attracted to this mixture, forming calcium alkali-silicate hydrate gel and alkali-silicate hydrate gel, both are commonly known as Silica Gel (Hobb, 1988; Helmuth et al., 1994). As the silica gel absorb water, internal swelling pressure develops causing volume change and fracturing of the reacting aggregate particles, cracking of the surrounding cement paste (mortar) resulting deterioration of concrete. This phenomenon is known as alkali-silica reactivity. Although the pressure generated by the silica gel is balanced by tensile stress in the nearby concrete and by any external restraint but may relieve when cracking occur or as gel flow and creep (Helmuth et al., 1994). Chloride salts (added through mixing water, deicing agents or by penetrating mortar after its hardening and forming Friedel's salts or other complex salts) and calcium content of reactive particles (27-52% of CaO: anhydrous basis) may also aggravate the reaction (Helmuth et al., 1994). Therefore, alkali-aggregate reactivity will induct concrete deterioration depending on the availability of moisture, pH of the concrete pore solution and inherent reactivity of the aggregate minerals.

The alkali-carbonate is a reaction between certain dolomitic limestone and the metal hydroxides in the pore water of concrete (Hobb, 1988; ASTM, 1994). Typically, the reaction zones up to 2 mm are formed around the active aggregate and cracking develops within these rims and leads to a network of cracks and loss of bond between the aggregate and the cement paste (Hobb, 1988). In the alkali-carbonate reaction, the volume of the dedolomitization reaction products of are generally less than that of their reactants, it has been suggested that the dolomite crystal contained trace elements of clay, within which water

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was absent but which became exposed when dedolomitization occurred. The clay then expands by imbibing water, inducing pressures large enough to crack the concrete.

The studied limestone of the Kohat Formation is generally inert to any alkali-aggregate reaction. As no dolomitization is reported in this limestone therefore, chances of alkali-carbonate reactivity are negligible. But due to higher silica contents in its argillaceous variety, it is most suspicions to alkali-silica reactivity. Therefore, use of the studied limestone' argillaceous variety as concrete aggregate, may aggravate the alkali-silica reaction.

CHAPTER 4

METHODOLOGY

4.1 CRUSHING OF ROCK SAMPLES

The limestone samples were collected from the outcrops of the Kohat Formation in the study area and that of ordinary Portland cements, from the local market of Peshawar. Representative limestone samples were crushed in the jaw crusher. To determine the physical properties of the limestone, the crushed aggregates (passing ¾" size) were packed in the polythene bags and were transferred to the relevant laboratories. For the geochemical examination, selective crushed aggregates were pulverized in a tungsten-carbide ball mill to finer than No. 200 mesh size. A portion of individual sample was collected after proper quartering and coning. During this whole process greater care was taken to avoid contamination. The powdered samples of both aggregates and cement were stored in the airtight glass bottles after drying in oven at 110°C, over night.

4.2 GEOCHEMICAL EXAMIANATION

4.2.1 Preparation of stock solutions

The moisture free powders of the samples were converted into stock solutions of known volume by two different methods. These stock solutions were used for the determination of major and minor elements by instrumental methods. Stock solutions were prepared by the following methods:

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4.2.1.1 Stock Solutions A, using acid digestion method

0.500 gm of powdered rock sample was accurately weighed in a plastic crucible. It was then moist with few drops of deionized water and 10 ml of concentrated Hydrochloric acid (HCl) (for limestone specimens) or 10 ml Hydrofluoric acid (HF) and 4 ml Hyprochloric acid ($HClO_4$) (for cement and argillaceous limestone specimens only) were added. The sample was mildly heated on the hot plate, until a small portion is evaporated and a semi dry paste was obtained. The crucible was removed from the hot plate and the contents of the crucible were then transferred to 250 ml beaker by washing with deionized water in to the beaker until no particle is left in the crucible. Generally, the solution in the beaker is crystal clean but if there was some precipitation or turbidity observed in the solution, the solution was heated until clear solution obtained. But if there was any persistence of precipitation in the solution then about 2 ml of HCl was added and heated to boiling. The final solution was made to 250 ml in the volumetric flask with deionized water. All the samples were treated by the same procedure for the preparation of solution A.

4.2.1.2 Stock solution B, using Sodium hydroxide fusion method

Sodium Hydroxide (NaOH) solution was prepared by dissolving 30 gm of NaOH pellets in 100 ml deionized water and stored in a polythene bottle. 5 ml of NaOH solution was added to a series of already cleaned nickel crucibles. The crucibles were kept on sand bath for complete dryness. Accurately weighed 0.050 gm of limestone, cement and certified rocks were added to the crucibles. One crucible was used for the preparation of blank in which nothing was added except 5 ml NaOH solution. The crucibles were covered with lids and were heated to

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mildly redness, over a gas burner for a period of 5 minutes. The crucibles were swirled while hot. Deionized water (5-10 ml) was added to each crucible after they become mildly cool, in order to avoid splashing. The contents of each crucible were washed into 800 ml glass beakers, which already contained 400 ml of deionized water and 10 ml of concentrated HCl. In most cases crystal-clean solution was obtained but if it is not clear then warmed it until transparent solution was obtained. The resulting solution was transferred to a liter volumetric flask and was made to the volume with deionized water and was stored in polythene bottles for the determination of silica (SiO_2) and alumina (Al_2O_3).

4.2.2 Determination of major and minor oxides

SiO_2 and Al_2O_3 were determined by the spectrophotometeric method (using SP8-400 Pye Unicam UV/VIS spectrophotometer) whereas, ferric oxide (Fe_2O_3), manganese oxide (MnO), calcium oxide (CaO), magnesium oxide (MgO), sodium oxide (Na_2O) and potassium oxide (K_2O) were determined by atomic absorption spectrophotometeric method (using SP-191 Pye Unicam atomic absorption spectrophotometer).

4.2.2.1 SiO_2

Reagents used during examination were:

1. Ammonium molybdate solution: 7.500 gm of ammonium molybdate was dissolved in 70 ml deionized water having 20 ml of 9N H_2SO_4. A solution of 100 ml volume was made and was kept in a polythene bottle.

2. Tartaric acid solution: 25 gm of the tartaric acid was dissolved in 250 ml with deionized water.

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3. Reducing solution: 0.700 gm of sodium sulfate (Na_2SO_4), 0.150 gm of 1-amino-2-naphthol-4-suphonic acid and 9 gm of sodium metabisulfate ($Na_2S_2O_5$) was dissolved in 100 ml of deionized water and was refrigerated. This solution was prepared freshly, as it becomes deleterious to use, after storing few days.

Procedure

10 ml of stock solution B of each of the sample was taken in a series of 100 ml volumetric flasks. About 50 ml of deionized water was added to each flask. 2 ml of ammonium molybdate solution was added to each flask and was swirled to mix well. After exactly 10 minutes, 4 ml of tartaric acid solution was added to each flask and again swirled and mixed well. At the end 1.0 ml of reducing solution was added to these flasks and each flask was diluted to 100 ml with deionized water. All these solutions were set aside for at least 30 minutes and blue color solution was obtained at the end. The silica determination was then made on the spectrophotometer at a wavelength of 650 ηm relative to the reference rock standards.

4.2.2.2 Al_2O_3

Reagents used during examination were;

1. 8-hydroxyquinoline solution: 1.250 gm of the 8-hydroxyquinoline was dissolved in 250 ml of pure grade of chloroform and was stored in a refrigerator.

2. Complexing reagent: 1.000 gm of hydroxylamine-hydrochloride ($HONH_2HCl$), 3.600 gm of sodium acetate trihydrate and 0.400 gm of beryllium sulfate tetrahydrate were dissolved in 50 ml of deionized water. 0.040 gm of 2.2 dipyridyl was also dissolved in 20 ml of 0.2N HCl. Both the solutions were then mixed and diluted up to 100 ml

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with deionized water.

Procedure

5-10 ml of each stock solution B was taken into a series of 100 ml separatory funnels. 5 ml of deionized water and 10 ml of complexing reagent solution were added to these funnels and mixed well. After few minutes, 20 ml of 8-hydroxyquinoline solution was added to each funnel. These solutions were then shake for about 8 minutes by an automated flask shaker. The organic layers obtained at the bottom of these solutions in the separatory funnels, were then separated into 25 ml volumetric flasks by washing the funnels with chloroform for several times. The final volume of 25 ml for each sample was made with chloroform. The yellow color extracts obtained through this process were suitable for spectrophotometric determination. The Al_2O_3 was determined at wavelength of 381 ηm relative to the reference rock standards.

4.2.2.3 Fe$_2$O$_3$

1. Stock solution of 1000 ppm was prepared from 1.000 gm of pure iron metal, which was dissolved in minimum amount of HCl and was made to the volume with deionized water in one liter volumetric flask.

2. Stock solution of 100 ppm was prepared from 10 ml from 1000 ppm stock solution and was taken in 100 ml volumetric flask and made to the mark with deionized water.

3. Working standard solutions of 1, 2, 4 and 8 ppm were prepared by taking 1, 2, 4 and 8 ml from the 100 ppm standard solution in a 100 ml volumetric flask and made to the volume with deionized water.

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Procedure

The atomic absorption spectrophotometer cathode lamp was set at the wavelength 248.3 ηm and was calibrated with the iron working standard solutions of 4 and 8 ppm. The working standards 1, 2, 4 and 8 ppm was then run as unknown. After verification of accuracy, the stock solution A was run on the machine. The results were compared with the certified values and were found within the confidence limit. After verifying the instrument calibration, the rest of the sample solutions were run on the atomic absorption and the results of iron as Fe_2O_3 were determined. When ever the solution were out of range, those solutions were diluted accordingly.

4.2.2.4 MnO

1. Stock solution of 1000 ppm for manganese (Mn) was made by using 4.058 gm of hydrous manganese sulfate ($MnSO_4$ $4H_2O$) dissolved in 20 ml of 1N H_2SO_4. It was then transferred to 1000 ml volumetric flask and was made up to the mark with deionized water.
2. Stock solution of 100 ppm was made by taking 10 ml of 1000 ppm stock solution taken in 100 ml volumetric flask and was made up to the volume with deionized water.
3. Working standards of 1, 2, 4 and 8 for Mn were prepared by taking 1, 2, 4 and 8 ml of 100 ppm standard solution in 100 ml volumetric flasks and were made to volume with deionized water.

Procedure

Atomic absorption spectrophotometer was calibrated for Mn at wavelength of 279.5 ηm cathode lamp. It was then calibrated and standardized with the working standards and the certified rock standards,

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which were run to check the accuracy of the machine. After verification, samples concentration was noted.

4.2.2.5 CaO and MgO

1. Stock solution of 1000 ppm for calcium (Ca) and magnesium (Mg) was prepared by using 2.497 gm calcium carbonate ($CaCO_3$) and 3.057 gm magnesium carbonate ($MgCO_3$) and were dissolved in 1N HCl and diluted to one liter with deionized water in a 1000 ml volumetric flask.

2. Stock solution of 100 ppm for Ca and Mg was prepared from 10 ml of 1000 ppm stock solution and was taken in 100 ml volumetric flask the marked with deionized water.

3. Lanthanum solution (5%) was prepared from 58.64 gm of lanthanum oxide (La_2O_3) dissolved in 200 ml deionized water to which 150 ml 60% $HClO_4$ was added. It was heated till it was completely dissolved. The solution was then filtered through ordinary filter paper into 1000 ml volumetric flask and the volume was made up to the mark with deionized water.

4. Working standards of 1, 2, 4 and 8 ppm for Ca and Mg were prepared by taking 1, 2, 4 and 8 ml of 100 ppm standard solution in a series of 100 ml volumetric flasks. To these flasks 10 ml lanthanum solution was added and the volume was made up to the mark with deionized water.

5. Dilution of samples was made by taking 5 ml (depending upon the expected concentration of Ca and Mg) of the stock solution A of both certified rock standards and the studied rock samples and were taken in a series of 50 ml volumetric flasks. 5 ml of lanthanum solution was added to each flask and the volume was made to the mark.

Procedure

Using Ca and Mg cathode lamps, the atomic absorption spectrophotometer was calibrated for Ca and Mg separately at wavelength of 422 ηm and 285.2 ηm, receptively. The instrument was then calibrated and standardized with the working standards of 1, 2, 4 and 8 ppm. All the working standards and the certified rock standards were checked and their actual concentration was verified. Then studied rock sample solutions (in diluted form) were run on the atomic absorption and the concentrations of Ca and Mg were noted for each sample. The CaO and MgO concentration in each sample was then calculated. The concentrated solutions were accordingly, to bring the concentration within the range.

4.2.2.6 Na_2O and K_2O

1. Stock solution of 1000 ppm for sodium (Na) and potassium (K) was prepared from moisture-free 3.087 gm sodium sulfate (Na_2SO_4) and 2.228 gm potassium sulfate (K_2SO_4), respectively, dissolved in deionized water and the volume was made to 1000 ml in a volumetric flask. The solution was stored in a polythene bottle.

2. Stock solution of 100-ppm for Na and K was made using 10 ml of 1000 ppm standard solution taken in a 100 ml flask and made to mark with deionized water.

3. Working standards of 1, 2, 4 and 8 ppm were prepared by taking 1, 2, 4, and 8 ml from 100 ppm standard solution in 100 ml volumetric flasks and were made up to the mark with deionized water.

4. Dilution of the samples all the samples as well as certified rock standards were diluted to 20 times.

Procedure

Atomic absorption spectrophotometer was calibrated for Na and K separately at wavelength of 589 ηm and 766 ηm, receptively. The instrument was set on emission mode and a conical burner head was used. The instrument was calibrated and standardized by working standards for Na and K, separately. The diluted solutions for the samples were sprayed one by one through the flame and the concentration of Na and K was noted in different runs.

4.2.2.7 Loss on ignition

The determination of loss on ignition was practiced through gravimetric method, on over-night oven dried specimens. Samples of known weight were taken in already weighed porcelain crucibles. The crucibles were kept in the furnace at 950°C for 2 hours. After completion of ignition period, they were cooled in a desecrator and weighed again. The difference in the weight was noted and the amount of ignition loss (in percent) was calculated for each sample.

4.3 PREPARATION OF THIN SECTIONS

For the petrographic study of Kohat Formation's limestone, thin sections of the rock specimens were prepared by using ASTM method No. C 295-90 (Guide for petrographic examination of aggregate for concrete). Using diamond cutter "Discoplan-TS", approximately one square inch representative portion (chip) of a rock specimen was cut. The chip was mounted on a glass slide by using an adhesive and was grind on the "Cut Rock" machine. Using corundum powder of mesh No. 400 and No. 1000, further grinding of the thin section was made. A glass cover was mounted over the prepared thin section.

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4.4 PHYSICAL EXAMINATION

Based upon the whole rock geochemistry, the limestone aggregates have been grouped for their physical examination according to the standard specifications of ASTM C 33-93. Following four tests have been performed on the studied limestone, for the determination of their physical properties:

1. Soundness, (ASTM method No. C 88-90),
2. Water absorption (ASTM method No. C 127-88),
3. Los Angeles abrasion examination (ASTM method No. C 131-89),
4. Specific gravity.

4.4.1 Soundness

Na_2SO_4 solution was prepared using 350 gm of anhydrous salt mixed in one liter of deionized water and keeping solution's specific gravity not more than 1.174.

Procedure

Generally limestone is virtually insoluble in pure distilled water in CO_2 free environment but certain saline solutions may affect the solubility of calcium carbonates in different ways e.g., the solubility of limestone increases in Na_2SO_4 solution (Boynton, 1980). Therefore, for soundness of the limestone aggregates, ASTM method No. C 88-90 was practiced. In this method, aggregate of known gradation was repeatedly immersed in a saturated solution of Na_2SO_4 followed by oven drying which partially or completely dehydrate the salt precipitated in permeable pore spaces. This would simulate the expansion/deformation process of the aggregate.

The test sample was prepared according to following gradation;

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S. No.	Size (Square-opening sieves)	Weight (gms)
1.	9.5 mm (3/8") to 4.75 mm (No. 4)	300 ± 5
2.	19.0 mm (¾") to 9.5 mm (3/8")	1000 ± 10
	12.5 mm (1/2") to 9.5 mm (3/8")	330 ± 5
	19.0 mm (¾") to 12.5 mm (1/2")	670 ± 10
3.	37.5 mm (1½") to 19.0 mm (¾")	1500 ± 50
	25.0 mm (1") to 19.0 (¾")	500 ± 30
	37.5 mm (1½") to 25.0 mm (1")	1000 ± 50
4.	63 mm (2½") to 37.5 mm (1½")	5000 ± 300
	50 mm (2") to 37.5 mm (1½")	2000 ± 200
	63 mm (2½") to 50 mm (2")	3000 ± 300
5.	Each fraction larger by 25 mm (1") in sieve	7000 ± 1000

The sample thus prepared by the said gradation was immersed in the Na_2SO_4 solution for 16-18 hours at 21 ± 1°C. Then it was placed in an oven at 110°C and dried to constant weight. The procedure was repeated for five cycles. After the fifth cycle, the sample was washed free from the Na_2SO_4 by the reaction of barium chloride ($BaCl_2$) with water. After that, it was washed and dried to constant weight and the percentage of weight loss was recorded by using following sieves;

S. No.	Size of Aggregate	Loss determination sieve
1.	63 mm (2½") to 37.5 mm (1½")	31.5 mm (1¼")
2.	37.5 mm (1½") to 19.0 mm (¾")	16.0 mm (5/8")
3.	9.5 mm (3/8") to 4.75 mm (No. 4)	8.0 mm (5/16")
4.	19.0 mm (¾") to 9.5 mm (3/8")	4.0 mm (No. 5)

Therefore, soundness can be calculated as;

$$Soundness\ (\%) = \frac{100\ (Weight\ retained\ on\ sieve\ to\ determine\ loss)}{(Initial\ weight\ of\ the\ specimen)}$$

4.4.2 Water absorption

Procedure

For determination of water absorption of the aggregates, 2000 gms of oven dried ½" sieve passing material was immersed in the deionized water, for 24 ± 4 hours. After the completion of immersion period, sample was removed from water and the thin film of water present on the aggregate was roll off by an absorbent cloth. The percentage in the weight gain is calculated as water absorption as follows;

$$\text{Water absorption (\%)} = \frac{100 \text{ (Final weight} - \text{Initial weight)}}{\text{(Initial weight)}}$$

4.4.3 Los Angeles abrasion test

Procedure

The Los Angeles abrasion test (ASTM method No. C 131-89) is a measure of degradation of mineral aggregates of smaller than 37.5 mm (1½") size resulting from a combination of actions including abrasion or attrition, impact and grinding in a rotating steel drum containing a specified number of steel spheres, the number depending upon the grading of the test sample. This test has been widely used as a tool of relative quality or competence of various sources of aggregate having similar mineral composition. The test sample was initially washed and oven dried and was graded according to the following gradation;

Sieve size (square opening)		Grading (Weight of indicated size in gm)			
Passing	Retained on	A	B	C	D
37.5 mm (1½")	25.0 mm (1")	1250 ± 25			
25.0 mm (1")	19.0 mm (3/4")	1250 ± 25			

19.0 mm (¾")	12.5 mm (1/2")	1250 ± 10	2500 ± 10		
12.5 mm (½")	9.5 mm (3/8")	1250 ± 10	2500 ± 10		
9.5 mm (3/8")	6.3 mm (¼")			2500 ± 10	
6.3 mm (¼")	4.75 mm (No. 4)			2500 ± 10	
4.75 mm (No. 4)	2.36 mm (No. 8)				5000 ± 10
Total		5000 ± 10	5000 ± 10	5000 ± 10	5000 ± 10
No. of sphere		12	11	8	6

The graded aggregates along with steel sphere charges were placed in the Los Angeles abrasion machine and were revolved for 500 revolutions at the rate of 30-33 rpm. After completion of test, sample was sieved with No.12 ($\approx$ 1.7 mm), washed and oven dried. The percentage loss in the initial weight is calculated as the Los Angeles Abrasion value as follows;

$$L.A.A.V. = 100(\text{Weight retained on \#12})(\text{Total weight of test sample})^{-1}$$

4.4.4 Specific gravity

Procedure

The specific gravity for the coarse aggregate was calculated by taking ratio between weigh of the aggregate in the air and the water. The test sample was oven dried over night in order to get moist free sample. Then the test sample was weighed in air by using electronic balance. Afterward, the sample is weighted in the deionized water. Thus the ratio of sample weight in air and water will give us its specific gravity by using the following formula;

Specific gravity (σ) = (Weight in air) / (Weight in air – Weight in water)

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CHAPTER 5

PETROGRAPHY

In hand specimens the limestone of the Kohat Formation varies in color from creamy to gray. It is fine to medium-grained, well-bedded, compact and hard rock. Majority of the samples is having microfossils, which can be visible with the help of hand-lens.

In thin sections, the limestone is dominantly composed of calcite and fossil shells, with lesser amount of dolomite, quartz, clay and opaque phases (Table 5.1). The rock has fine to medium grained, granular mosaic with bioturbated microfossils.

Calcite (40 to 90%) is generally fine-grained (Plate 5.1) but patches of medium to coarse-grained anhedral calcite (Plate 5.2 a & b) are also common. This calcite seems to be authigenic (primary) in origin and has been precipitated in situ. The medium to coarse-grained calcite grains is interlocked and shows well-developed cleavages. Micro-fractures filled with fine to medium grained calcite micro-veins (Plate 5.3 a & b) are also common in these rocks which are considered as diagenetic (secondary).

Various types of microfossils belonging to calcareous foraminifers recognized as Assilina and Nummulites are very common in these rocks (Plate 5.4 a, b, c & d) and some time reaches more than 60% of the whole rock (Table 5.1). These fossils are set in a fine-grained calcite mass, which also act as a cementing material. The tests or shells of the fossils are dominantly calcitic. The interior of these tests is filled

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Table 5.1. Petrographic analysis for Eocene limestone of Kohat Formation.*

Sample No.	Locality	Mineralogical Composition (%)							
		Calcite	Fossil	Dolomite	Clay	Quartz	Chalcedony	Opaque mineral
KR-1	Kohat Township	80	20	0	Trace	0	Trace	Trace
KR-2	Sheikhan village	80	20	0	Trace	0	Trace	Trace
KR-3	Sheikhan Nala	75	25	0	0	0	Trace	Trace
KR-4	Toag Bala	60	40	0	0	0	0	0
KR-5	Bazid Khel	85	5	0	0	10	0	0
KR-6	Baratai Banda	65	35	Trace	Trace	0	0	Trace
KB-1	Chichina	60	40	0	Trace	0	0	Trace
KB-2	Sher Ali Banda	40	60	0	Trace	0	0	Trace
KB-3	Jurma	50	50	0	Trace	0	0	Trace
KB-4	Sumari Payan	50	50	Trace	Trace	0	0	Trace
KH-1	Mitha Khan	90	10	0	0	0	0	0
KH-2	Khawaja Khizar	50	50	0	Trace	0	0	Trace
KH-3/a	Ibrahimzai post	65	30	0	Trace	0	0	Trace
KH-3/b	Ibrahimzai post	70	35	0	Trace	0	0	Trace
KH-4	Ibrahimzai village	40	60	0	0	0	0	0
KH-5	Bahadur Banda	60	40	0	0	0	0	0

* Analyzed by AQEEL GOHER.

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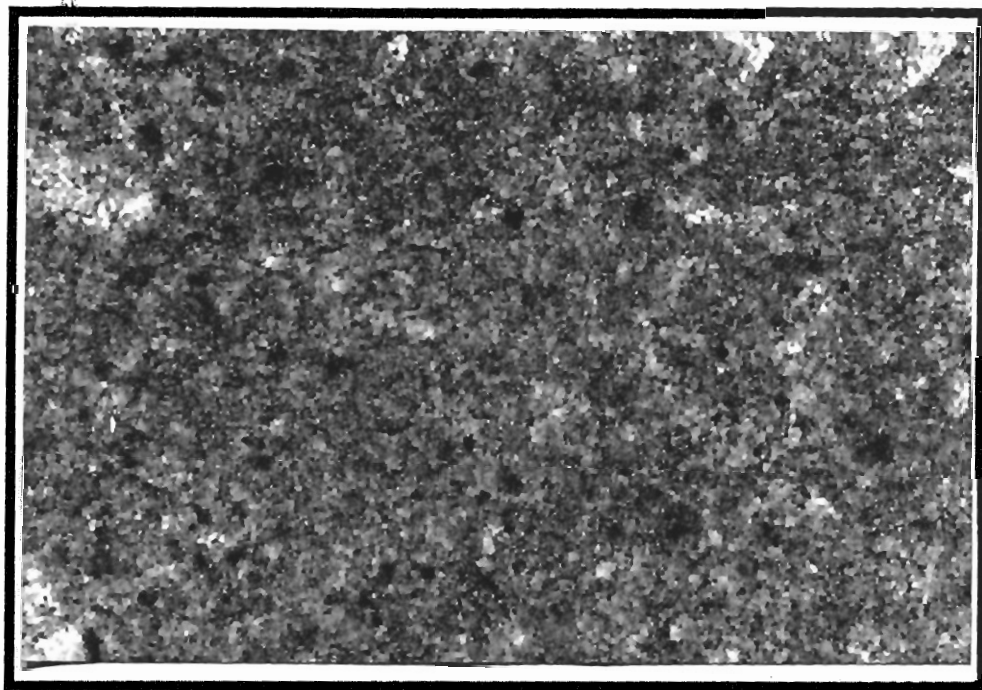
Plate 5.1. Photomicrograph showing the fine-grained calcite matrix of the limestone of the Kohat Formation. The iron-bearing phase (siderite) is also disseminated. (cross light, X4)

Plate 5.2 (a). Photomicrograph showing medium to coarse-grained calcite occurs in the form of patches within the fine-grained calcite matrix. (plane light, X2.5)
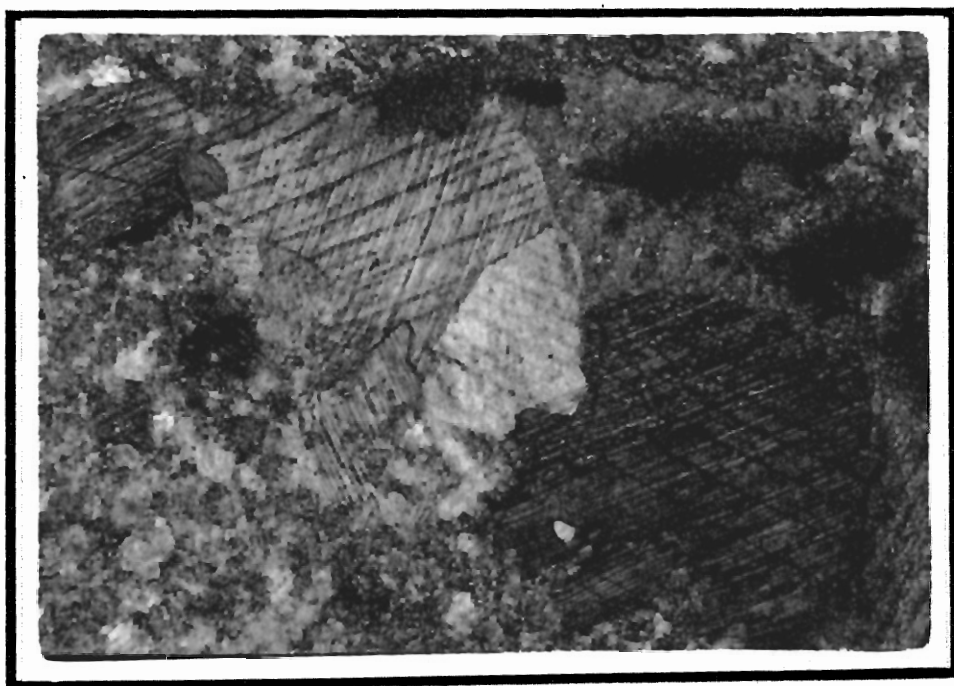
Plate 5.2 (b). Photomicrograph showing medium to coarse-grained calcite occurs in the form of patches within the fine-grained calcite matrix. (cross light, X2.5)

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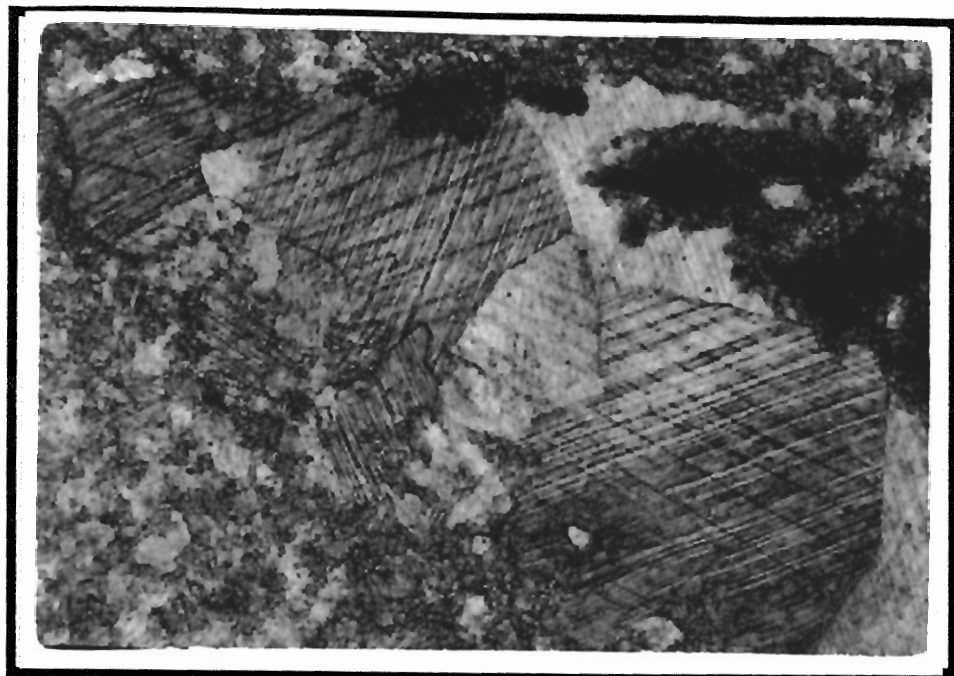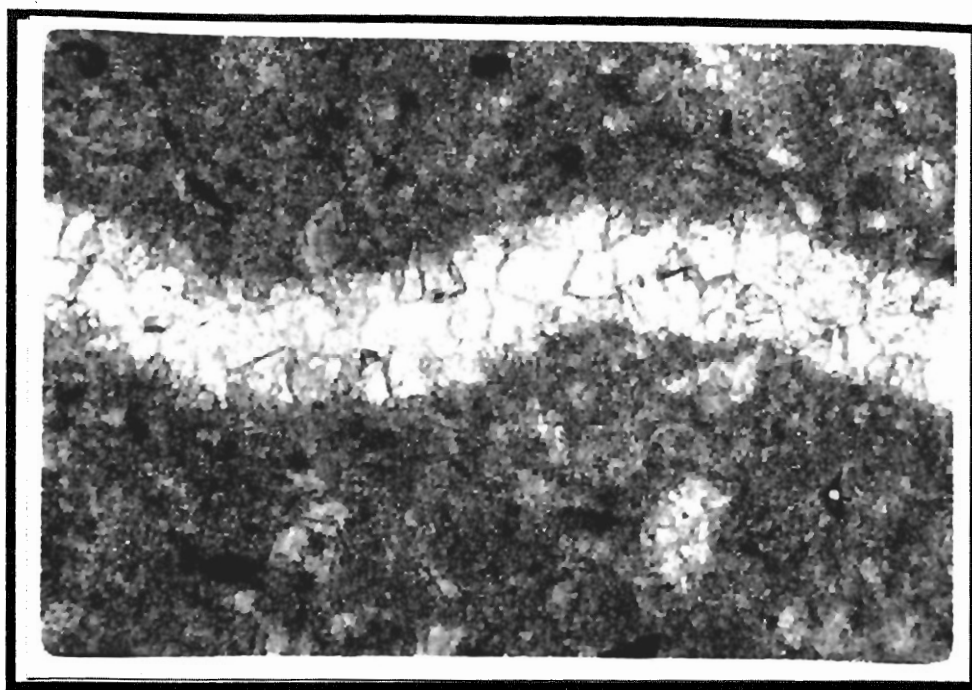**Plate 5.3 (a).** Photomicrograph showing fractured filled or bioturbate filled vein of calcite (secondary) which appear to be little coarser than the fine-grained calcite (primary) matrix. (plane light, X4)
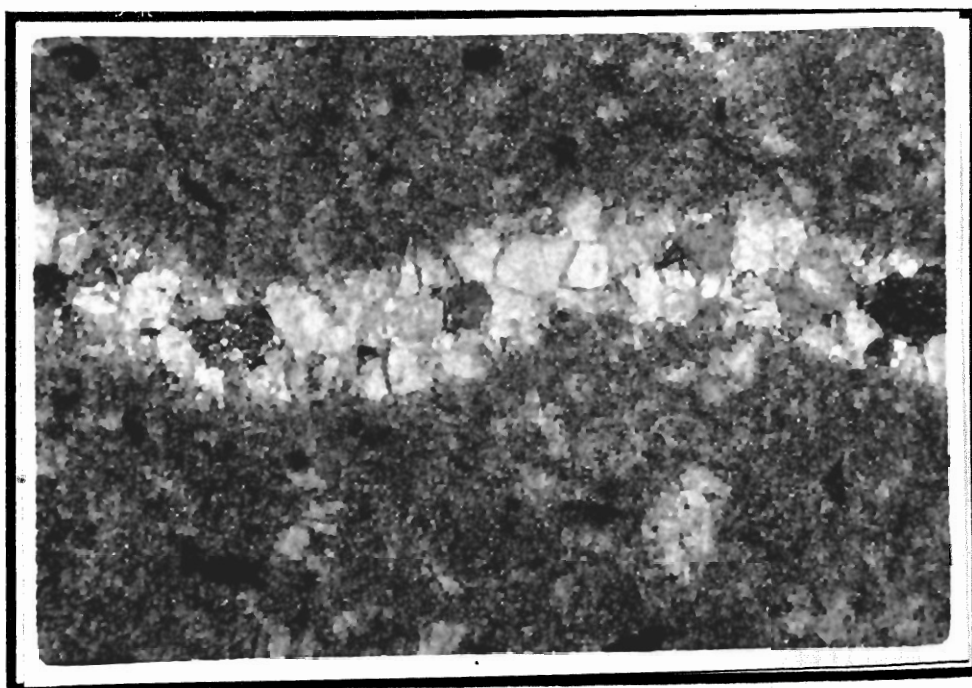
Plate 5.3 (b). Photomicrograph showing fractured filled or bioturbate filled vein of calcite (secondary) which appear to be little coarser than the fine-grained calcite (primary) matrix. (cross light, X4)

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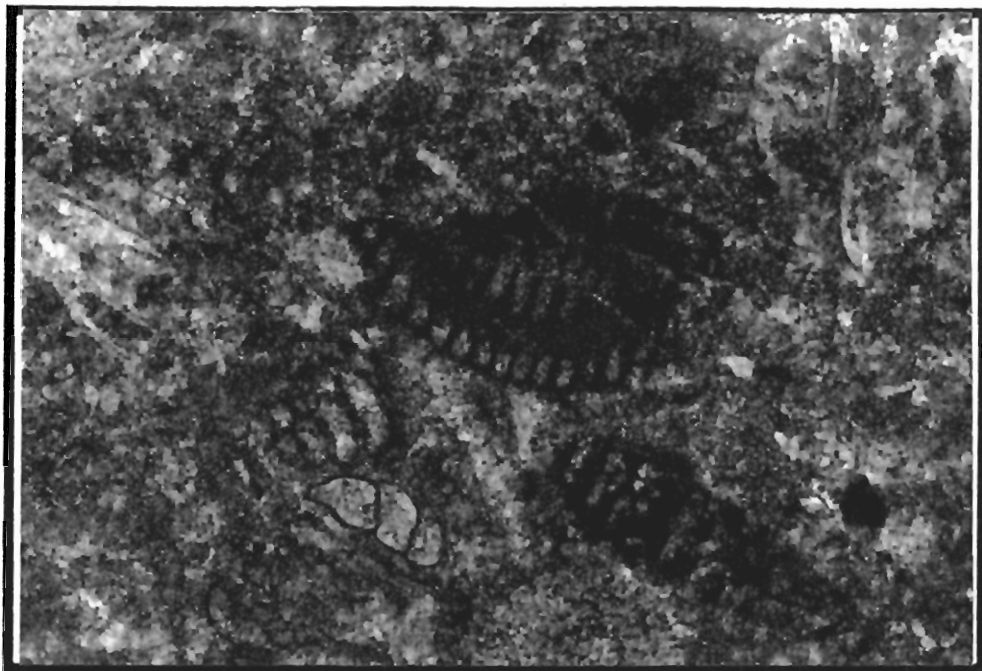
Plate 5.4 (a). Photomicrograph showing various types of microfossil tests embedded in a fine-grained calcite matrix. (plane light, X2.5)
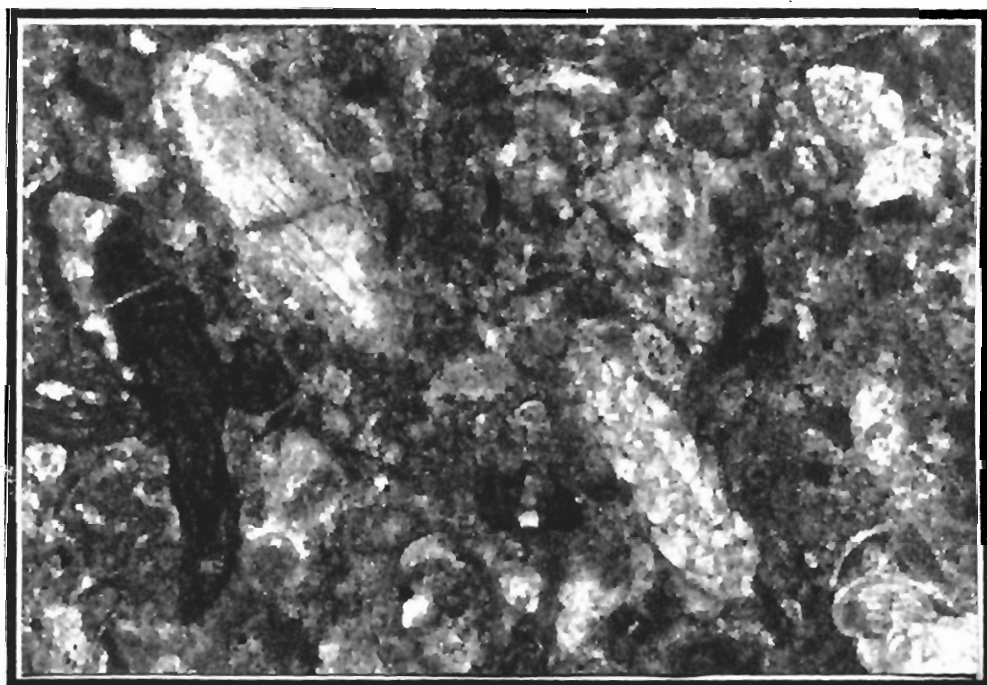
Plate 5.4 (b). Photomicrograph showing microfossil tests embedded in a fine-grained calcite matrix. (plane light, X2.5)
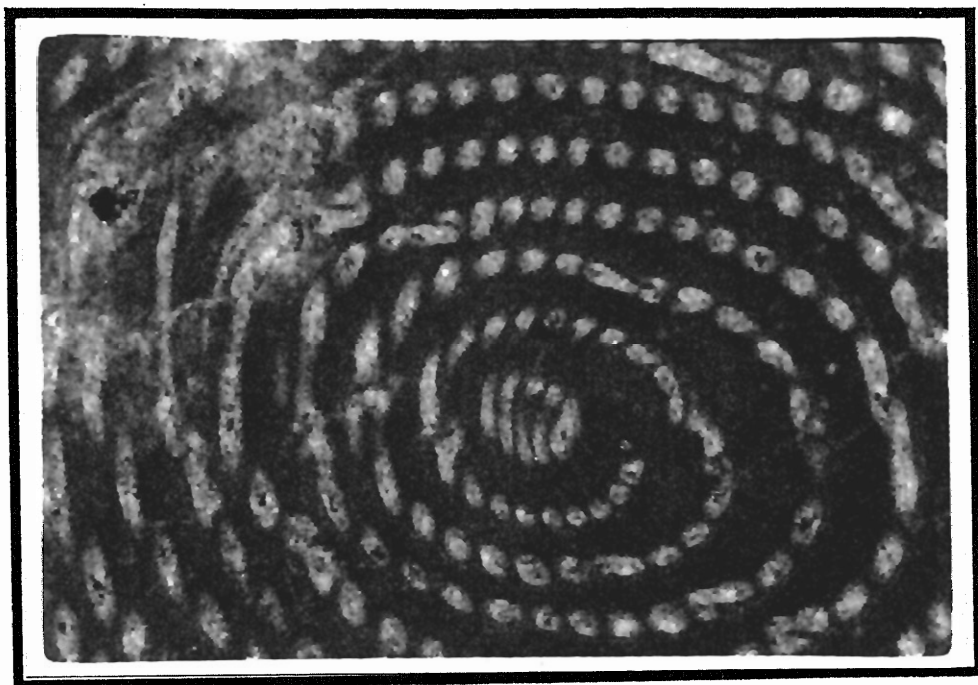
Plate 5.4 (c). Photomicrograph showing beautiful concentric rims of fossil's test, filled in by the fine-grained matrix. (cross light, X2.5)

Plate 5.4 (d). Photomicrograph showing beautiful concentric rims of fossil's test, filled in by the fine-grained matrix. (cross light, X2.5)

in by the crystalline calcite (Plate 5.5 & 5.6). In most cases, the original foraminiferal tests are replaced by calcite and the filling is left in the form of interior mold or cast (Plate 5.7 a & b). These are, therefore, appear as pseudofossils. These fossils are generally bioturbated and are generally filled in by the secondary calcite.
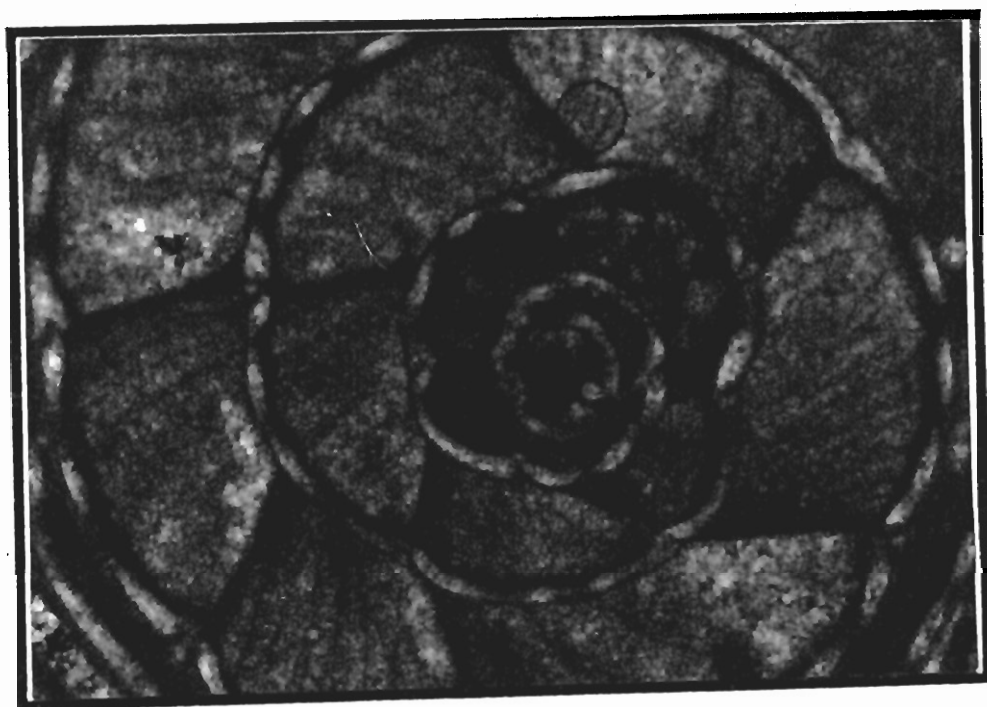
Dolomite is intimately associated with calcite in the micro-veins and is therefore, considered as secondary phase (Plate 5.8). It is generally found in traces (Table 5.1). Dolomite grains are very difficult to distinguish in the thin sections however, it can very easily be recognized after staining. It is medium grained having rhombohedral habit.

Quartz (trace to 10%) is either absent or present in traces in almost all the thin sections (Table 5.1). However, one sample collected from Bazid Khel (KR-5) has about 10% quartz (Table 5.1). In this thin section, quartz in the form of subhedral medium-grained, detrital material is disseminated through out the rock (Plate 5.9). The chalcedony in certain cases has been noticed in the form of spherulite in the fossil's test, where the irregular out-lines of spherulite, lack of concentric structures and radial arrangement of fibers of chalcedony are prominent (Plate 5.10).

Clay in trace amount is present in few thin sections (Table 5.1). It is fine-grained and disseminated. The opaque phase also occurs in traces and is generally iron carbonates (siderite). It is fine-grained and disseminated (Plate 5.1). In most cases the leaching of iron is very common and this is clearly evident in the form of staining along micro-fractures.
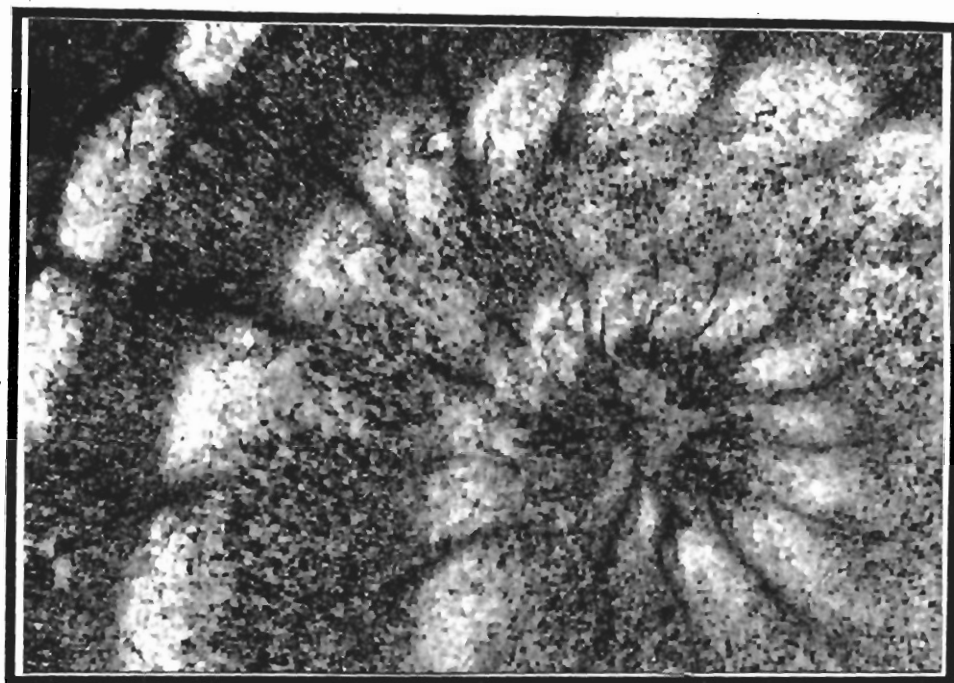
Plate 5.5. Photomicrograph showing fossil's test filled in by fine-grained calcite. (plane light, X4)

Plate 5.6. Photomicrograph showing fossil's test filled in by fine-grained calcite and also the radially arranged chalcedony in the form of spherulite is visible. (cross light, X2.5)
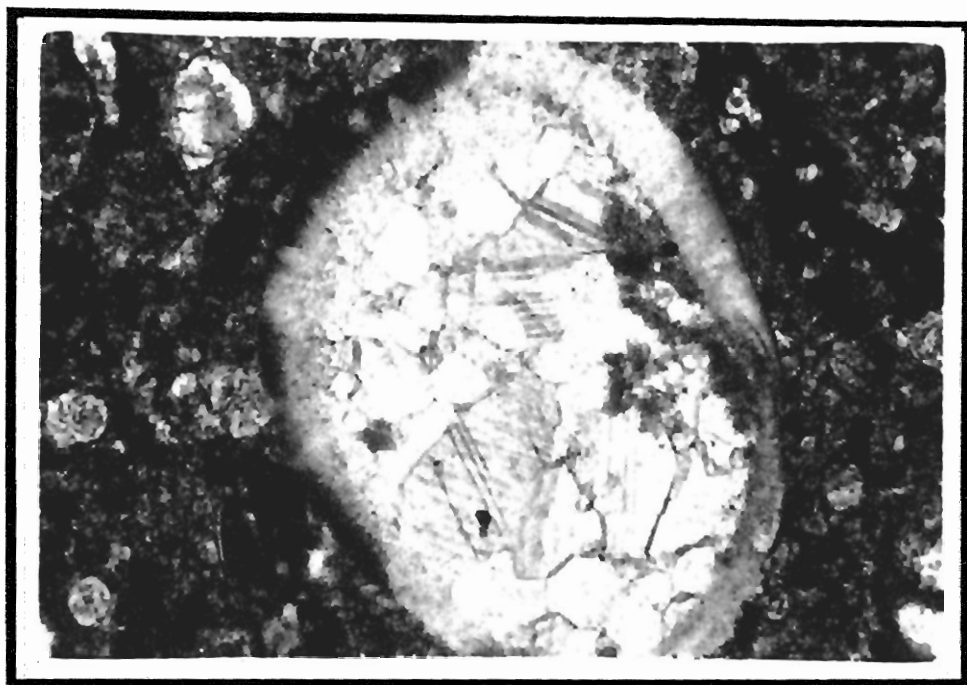
Plate 5.7 (a). Photomicrograph showing test of a fossil filled in by the medium-grained calcite. (plane light, X2.5)
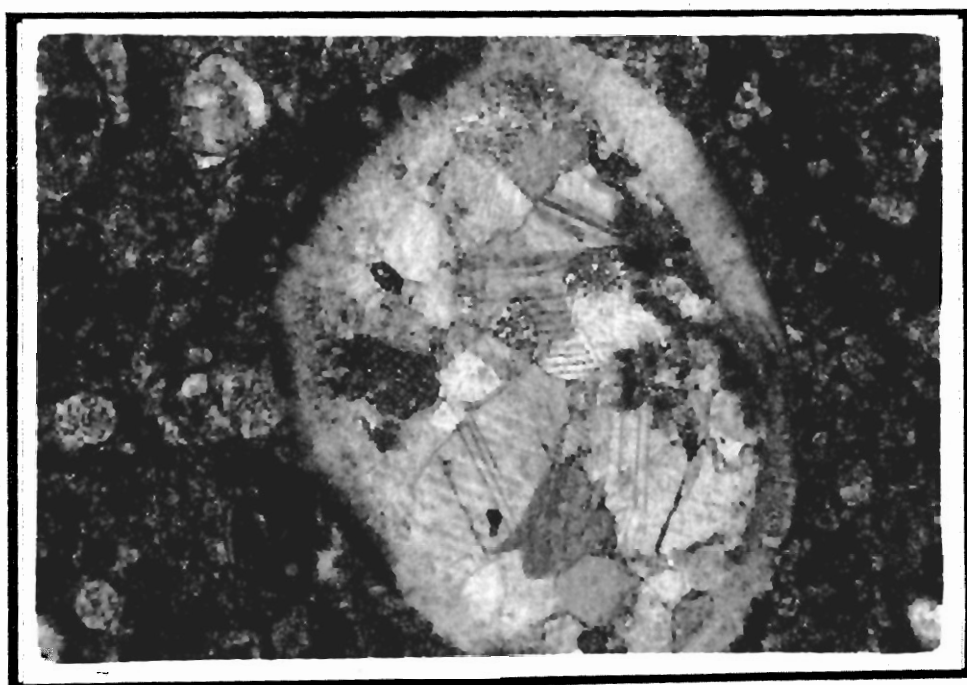
Plate 5.7 (b). Photomicrograph showing test of a fossil filled in by the medium-grained calcite. (cross light, X2.5)
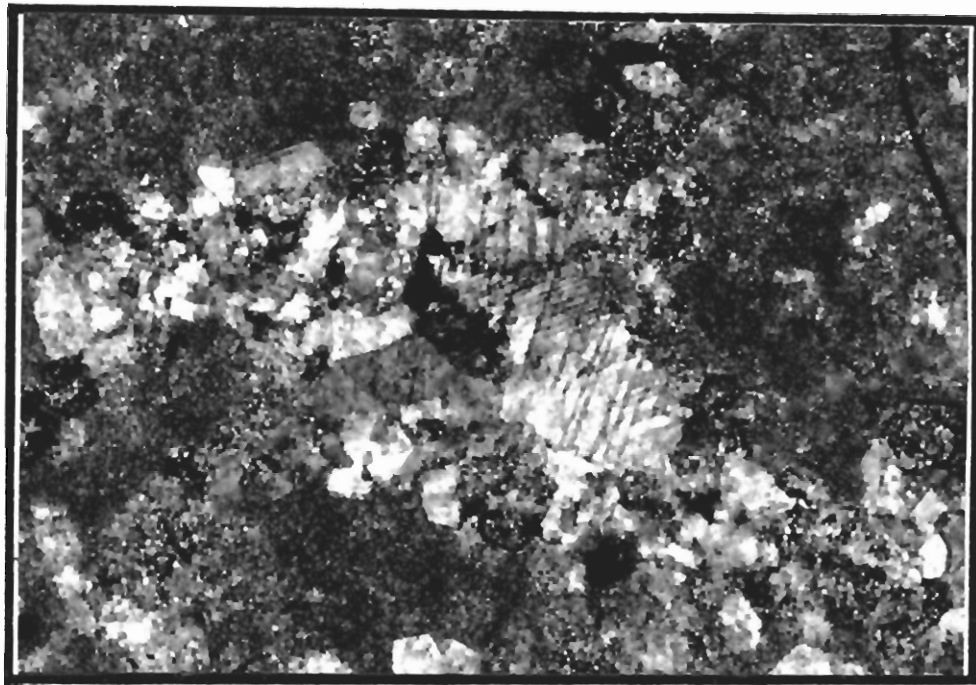
Plate 5.8. Photomicrograph showing anhedral grains of dolomite showing the perfect rhombohedral cleavages. It is present within the fine-grained calcite matrix. (cross light, X4)
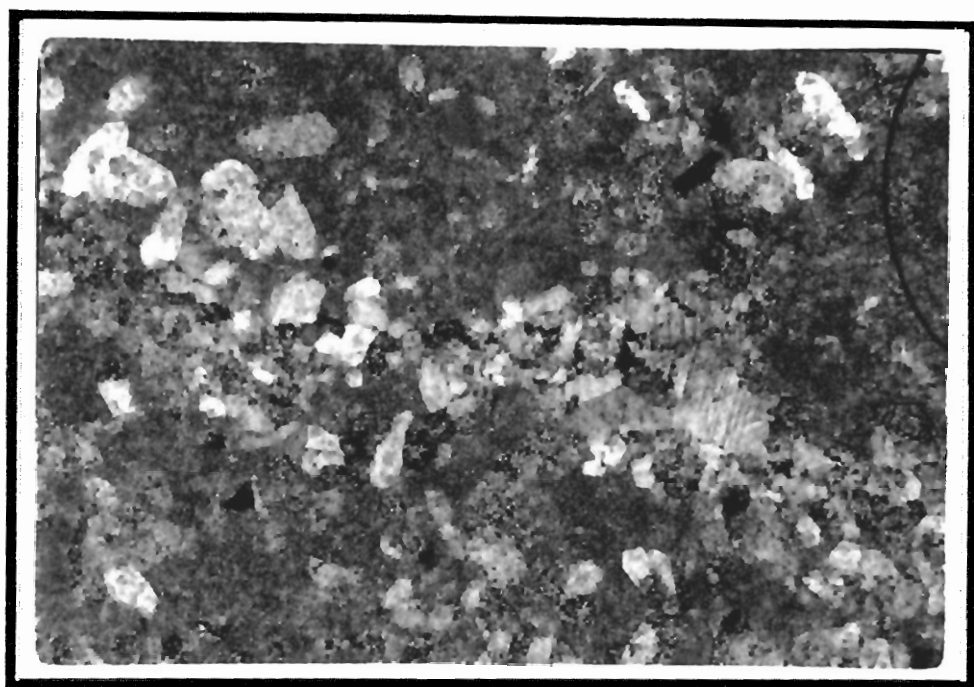
Plate 5.9. Photomicrograph showing rounded to sub-rounded grains of quartz disseminated with the fine-grained calcite matrix. (cross light, X2.5)
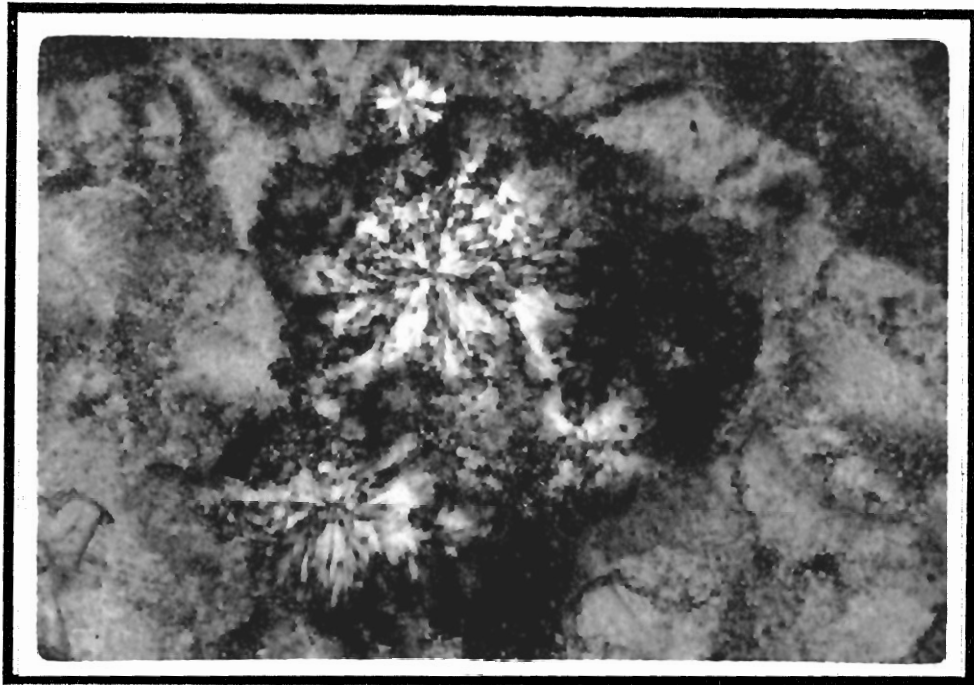
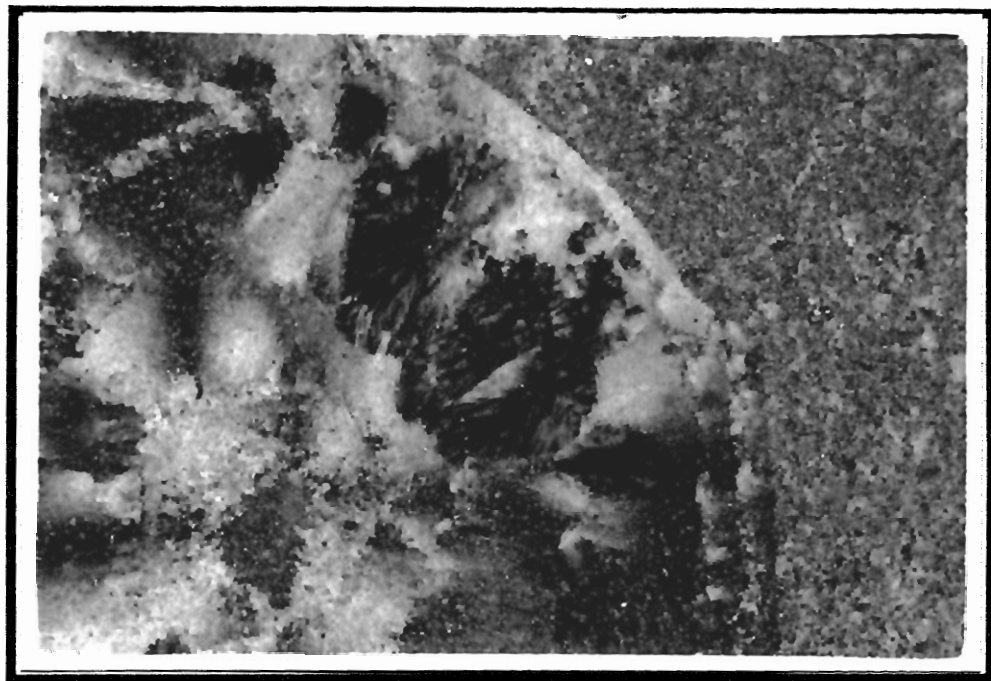**Plate 5.10.** Photomicrograph showing fossil's test filled in by fine-grained calcite and also the radially arranged chalcedony in the form of spherulite is visible. (cross light, X2.5)

The ASTM method No. C 294-86 and C 295-90 provide outlines for the petrographic examination of an aggregate proposed to be used in the hydraulic concrete. It includes identification for the types and varieties of minerals present in the potential aggregates, which may be deleterious to concrete (alkali-aggregate reaction etc.). Beside, weathered or altered particles which tend more susceptible of freezing and thawing action, unstable sulfides that may form sulfuric acid or create distress in concrete exposed to high temperature and volumetrically unstable materials such as smectite causes post-casting expansion in the concrete, are also identified by the petrographic examination. Petrography also calculates the proportions of cubic, spherical, ellipsoidal, pyramidal, tabular, flat and elongated particles in the aggregate samples.

In the petrographic analyses for the Kohat Formation's limestone, no deleterious minerals to concrete was observed as specified by ASTM with exception minute chalcedony, dolomite and quartz in the argillaceous variety of this limestone. The limestone was further examined by ASTM C 289-94 (chemical method) to ensure its feasibility for concrete.

CHAPTER 6

GEOCHEMISTRY

6.1 CHEMISTRY OF LIMESTONE

The major element chemistry for the limestone of the Kohat Formation is given in Table 6.1. It is evident from this table that, the limestone samples have SiO_2 in the range of < 0.50 to 13.90 wt %, Al_2O_3 is less than 0.74 wt %, Fe_2O_3 is less than 0.30 wt %, MnO is negligible; MgO is up to 2.69 wt % and CaO is ranging from 46.07 to 57.03 wt %. Among alkalies, Na_2O is less than 0.50 wt % while the K_2O is negligible. The loss on ignition is more or less constant about 43 wt % with the exception of one sample (KR-5) which has 35 wt % of loss on ignition. The chemical composition for the limestone samples collected from different localities of the study area are compared diagrammatically (Fig. 6.1 to 6.8).

SiO_2 in various forms is present as impurities in the limestone e.g., argillaceous limestone, cement stone, cherty limestone (Pettijohn, 1976; Boynton, 1980). Generally, it has very low concentration (< 0.50 wt %) in the studied specimens (Fig. 6.1). Three samples KR-1, KR-3/a and KH-2, collected from Kohat Township, Sheikhan Nala and Khawaja Khizar area respectively, are having up to 3.50 wt % SiO_2 (Fig. 6.1). One sample (KR-5) collected from Bazid Khel has the highest silica (13.50 wt %) (Fig. 6.1). This can be classified as argillaceous limestone.

Alumina (Al_2O_3) is the second largest impurity in the limestone. Both the alumina and silica concentration in the limestone originate

Table 6.1. Chemical composition of the limestone of Kohat Formation at different localities.*

	KR-1	KR-2/a	KR-2/b	KR-3/a	KR-3/b	KR-4	KR-5	KR-6	KB-1	KB-2	KB-3	KB-4	KB-5	KH-1	KH-2	KH-3/a	KH-3/b	KH-4	KH-5
SiO_2	1.30	0.60	<0.50	3.50	<0.50	<0.50	13.90	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	1.50	<0.50	<0.50	<0.50	<0.50
Al_2O_3	0.67	0.52	0.53	0.52	0.53	0.47	0.74	0.57	0.51	0.62	0.47	0.53	0.58	0.49	0.47	0.46	0.51	0.58	0.51
Fe_2O_3	0.27	0.19	0.24	0.30	0.16	0.13	0.25	0.25	0.19	0.10	0.10	0.15	0.12	0.05	0.15	0.08	0.22	0.15	0.06
MnO	0.00	0.00	0.00	0.01	0.01	0.02	0.25	0.01	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.02	0.01
MgO	0.93	1.24	0.62	0.73	1.04	0.93	0.62	0.62	0.21	0.31	0.83	0.00	0.00	0.00	1.24	0.62	1.14	1.97	2.69
CaO	52.61	55.54	56.80	52.79	54.91	53.69	46.07	52.43	57.03	54.76	55.12	53.74	53.60	55.52	52.20	53.51	53.74	54.59	56.11
Na_2O	0.37	0.47	0.46	0.43	0.48	0.43	0.45	0.35	0.40	0.44	0.41	0.46	0.42	0.43	0.36	0.39	0.43	0.36	0.39
K_2O	0.04	0.04	0.03	0.04	0.03	0.01	0.02	0.05	0.03	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.02	0.03	0.02
L.O.I.	41.88	42.33	42.78	42.36	42.97	42.81	35.74	42.36	43.15	43.21	43.12	43.21	43.17	42.88	43.21	43.53	43.35	43.41	42.67
Total	98.07	100.93	101.96	100.68	100.63	98.99	98.04	97.14	102.03	99.97	100.57	98.61	98.41	99.90	99.17	99.12	99.93	101.61	102.9
$CaCO_3$	95.18	96.20	97.23	96.27	97.66	97.30	81.23	96.27	98.07	98.20	98.00	98.20	98.11	97.45	98.20	98.93	98.52	98.66	96.98
S_c	21.66	9.99	7.50	58.31	7.50	7.50	231.57	7.50	7.50	7.50	7.50	7.50	7.50	7.50	24.99	7.50	7.50	7.50	7.50
R_c	60.00	36.50	22.50	47.50	16.50	9.00	10.00	22.50	32.50	38.75	17.50	50.00	27.50	21.50	62.50	25.00	27.50	40.00	8.50
$35+\frac{1}{2}R_c$	65.00	53.25	46.25	58.75	43.25	39.50	40.00	46.25	51.25	38.75	43.75	60.00	48.75	45.75	66.25	47.50	48.75	40.00	39.25

*Analyzed by AQEEL GOHER.

KR-1:Kohat Township, KR-2/a:Sheikhan village, KR-2/b:Sheikhan village, KR-3/a:Sheikhan Nala, KR-3/b:Sheikhan Nala, KR-4:Toag Bala, KR-5:BazidKhel, KR-6:Baratai Banda, KB-1:Chichina, KB-2:Sher Ali Banda, KB-3:Jurma, KB-4:Sumari Payan, KB-5:Mandur, KH-1:Mitha Khan, KH-2:Khawaja Khizar, KH-3/a:Ibrahimzai post, KH-3/b:Ibrahimzai post, KH-4:Ibrahimzai village, KH-5:Bahadur Banda.

Fig. 6.1. Comparison of silica (SiO₂) concentration in the various samples of limestone of the Kohat Formation.

Fig. 6.2. Comparison of alumina (Al₂O₃) concentration in the various samples of limestone of the Kohat Formation.

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Fig. 6.3. Comparison of ferric oxide (Fe₂O₃) concentration in the various samples of limestone of the Kohat Formation.
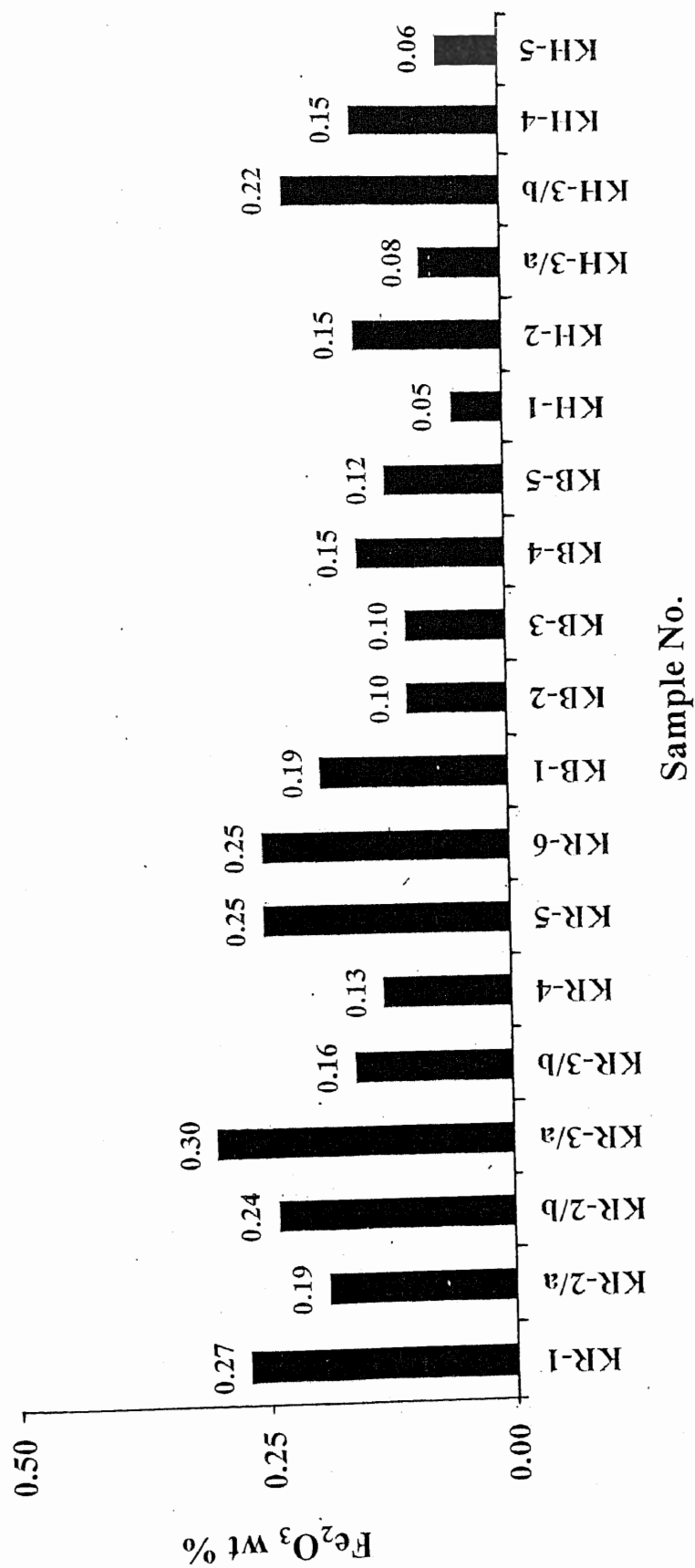
Fig. 6.4. Comparison of manganese oxide (MnO) concentration in the various samples of limestone of the Kohat Formation.

Fig. 6.5. Comparison of magnesium oxide (MgO) concentration in the various samples of limestone of the Kohat Formation.

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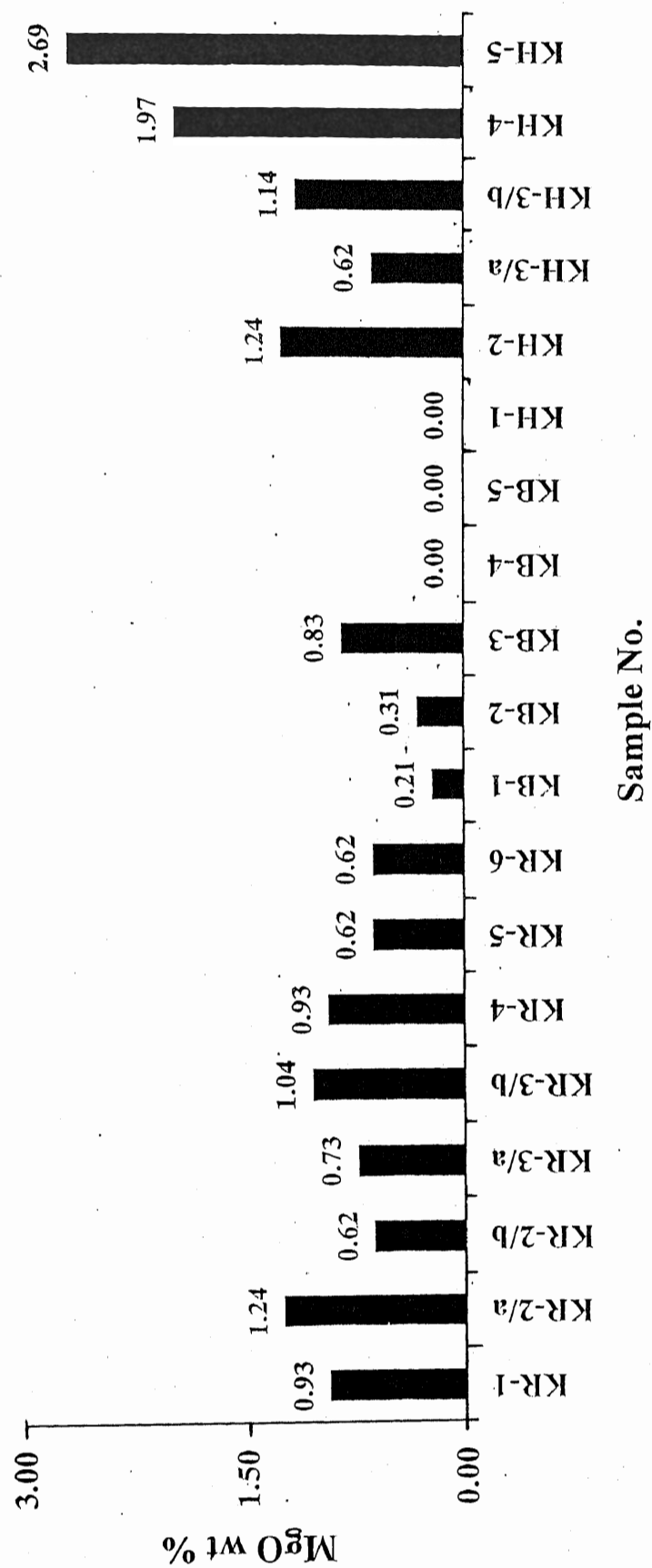
Fig. 6.6. Comparison of calcium oxide (CaO) concentration in the various samples of limestone of the Kohat Formation.

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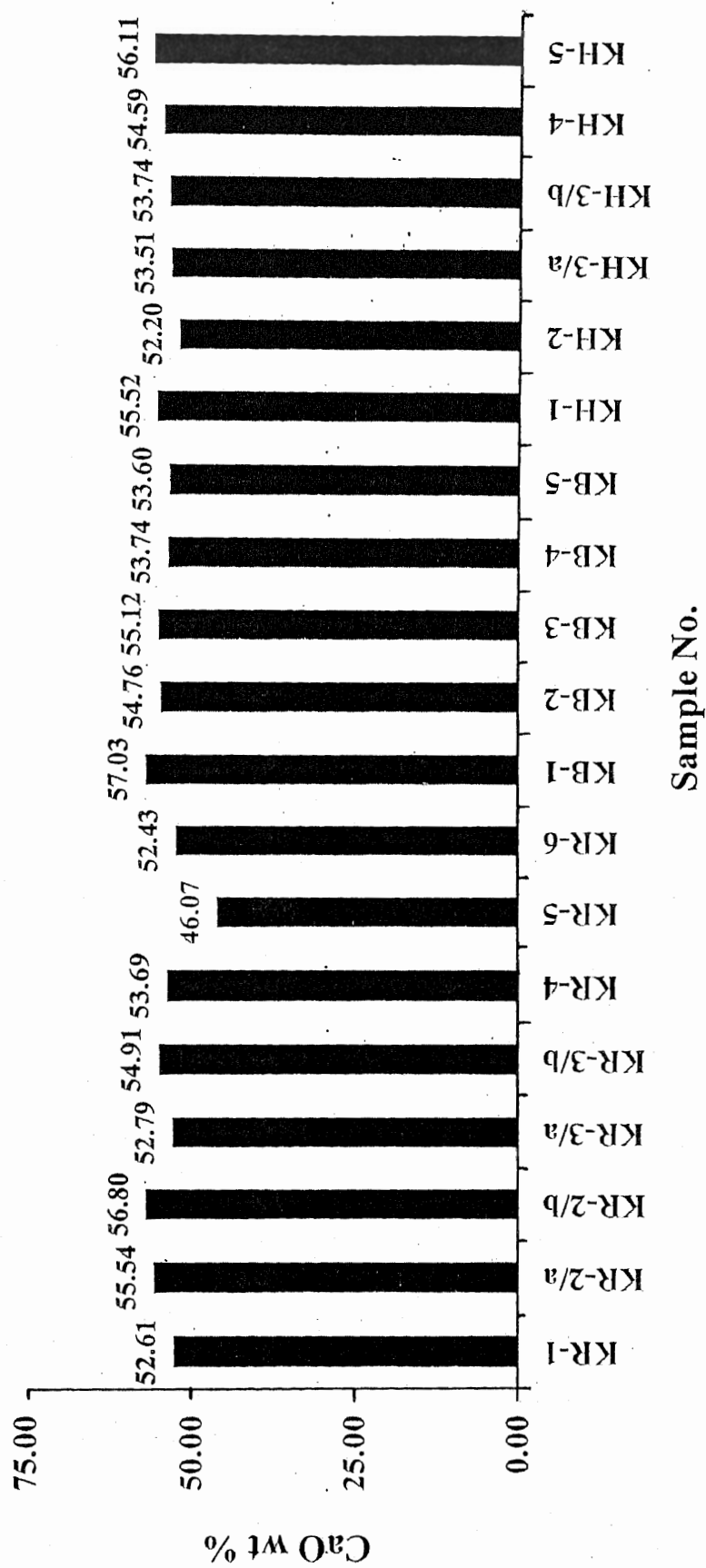
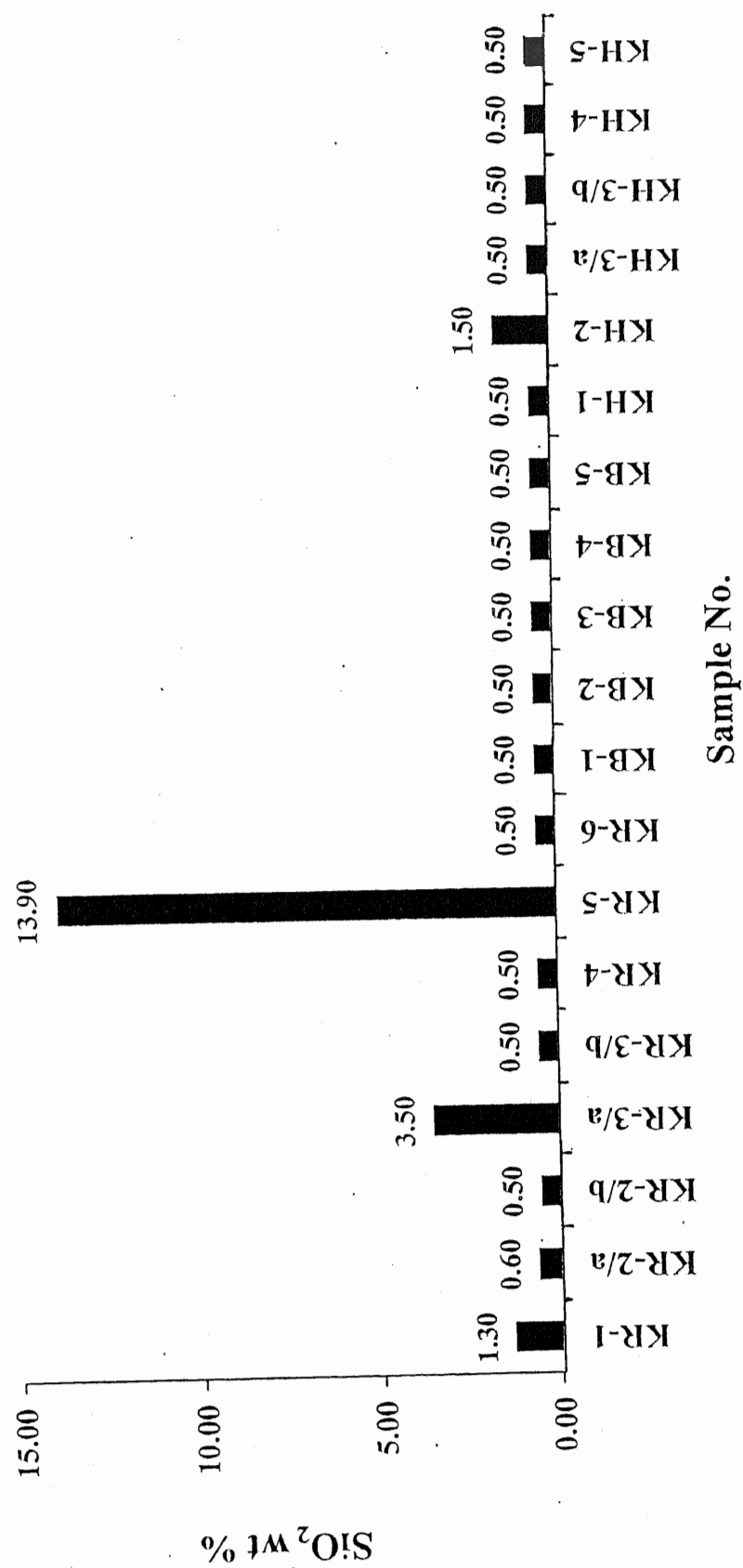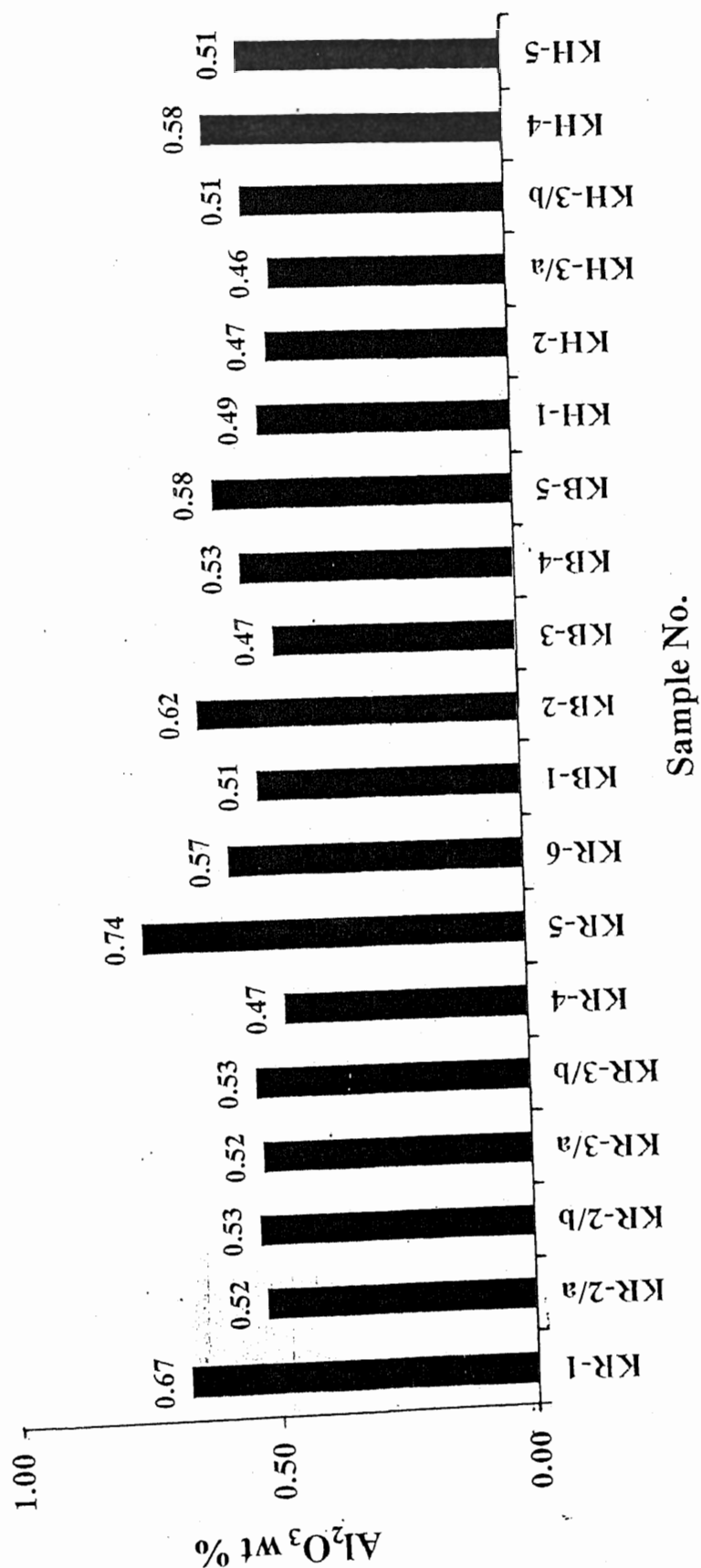Fig. 6.7. Comparison of sodium oxide (Na$_2$O) concentration in the various samples of limestone of the Kohat Formation.
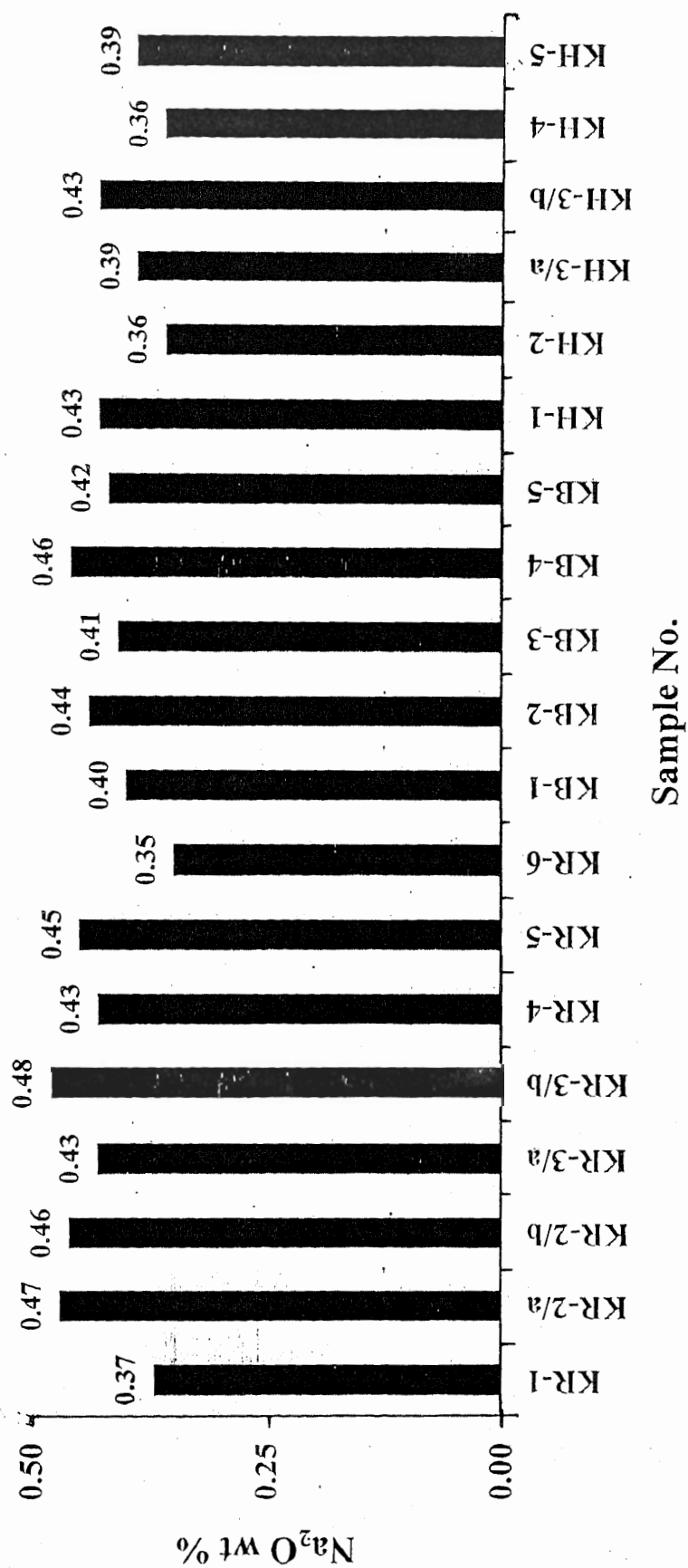
Fig. 6.8. Comparison of potassium oxide (K_2O) concentration in the various samples of limestone of the Kohat Formation.
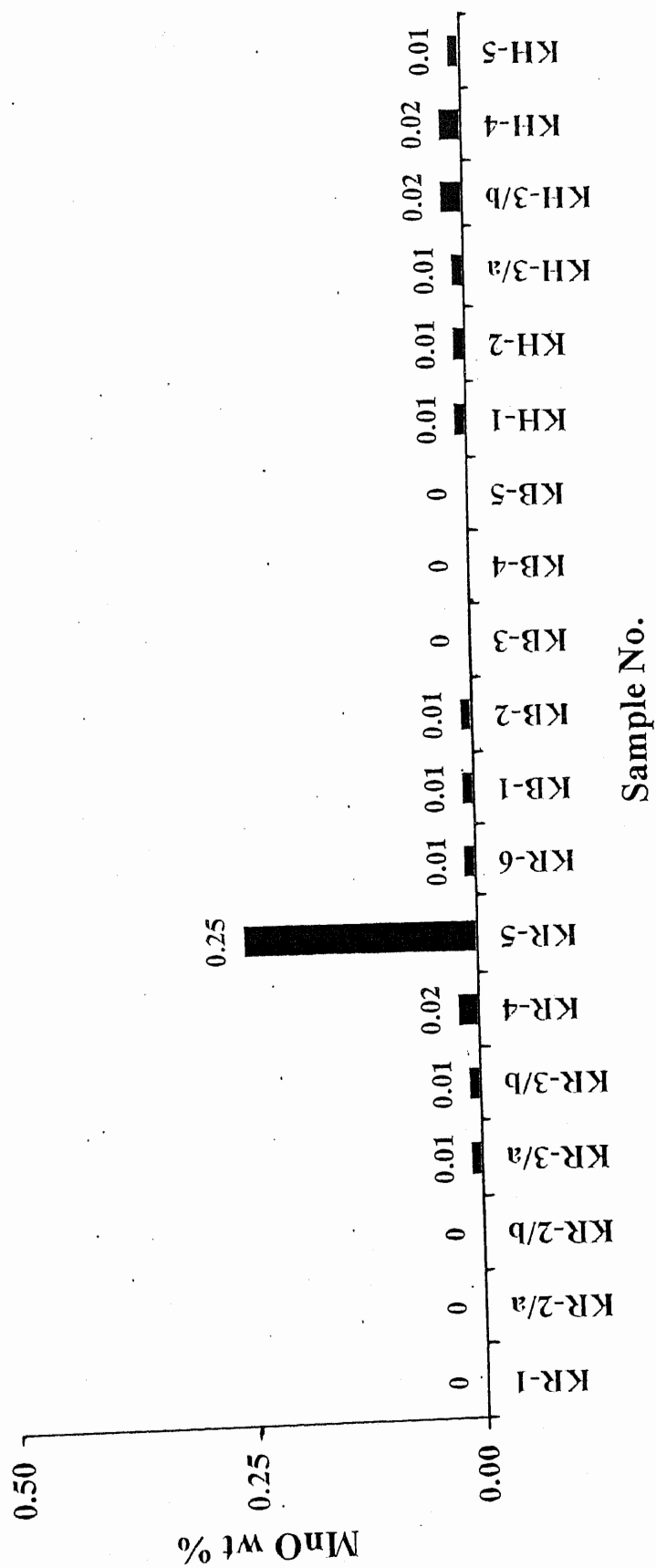
64
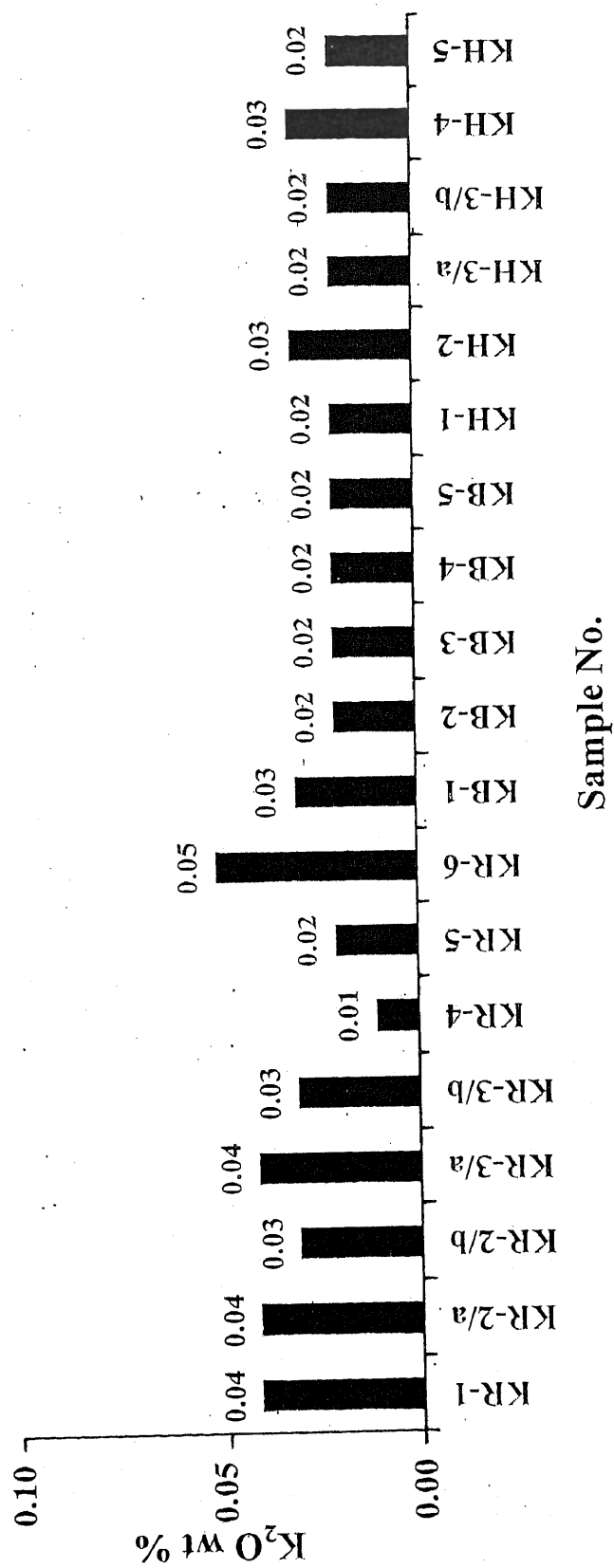
from the shelly matters (Pettijohn, 1976). The Al_2O_3 content of the studied samples is more or less constant. However, two samples KR-1 and KR-5 collected from Kohat Township and Bazid Khel are having little higher Al_2O_3 (Fig. 6.2).

Iron in the form of oxides and sulfides occurs as another impurity in the limestone which if present in higher amount can cause deterioration in the building construction (Boynton, 1980). Iron can be homogeneously disseminated during chemical displacement of the calcium bearing iron carbonate or can heterogeneously distribute through iron bearing strata. Fe_2O_3 contents of the studied limestone are negligible at Mitha Khan, Ibrahimzai post and Bahadur Banda (Fig. 6.3). Few other localities such as Kohat Township, Sheikhan village, Sheikhan Nala, Bazid Khel, and Baratai Banda have relatively high Fe_2O_3 contents (Fig. 6.3). The rest of the samples have less than 0.20 wt % Fe_2O_3 (Fig. 6.3).

Manganese oxide (MnO) in the limestone is generally found in traces (Boynton, 1980). There is no or negligible amount of MnO in almost all the samples except one sample (KR-5) at Bazid Khel which has high (0.25 Wt %) MnO content (Fig. 6.4).

Magnesium oxide (MgO) in the limestone is a function of both the magnesium content of skeletal debris and also the other dolomitization process due to post-depositional events (Pettijohn, 1976). The increase of MgO in limestone therefore, increases the dolomitic component of limestone and may aggravate the alkali-carbonate reaction. The studied limestone specimens are having very low amount

of MgO (< 2.69 wt %) and are therefore, considered as pure limestone. Majority of the aggregate samples have low (< 1.0 wt %) MgO (Fig. 6.5). The sample (KH-5) taken at Badadur Banda however, is having relatively high (2.69 wt %) MgO (Fig. 6.5).

Calcium oxide (CaO) and CO_2 are the highest constituent of limestone. The replacement of CaO by MgO in limestone is the indication of dolomitization of limestone (Pettijohn, 1976). The limestone of the studied area is have high (above 52 wt %) and more or less constant amount of CaO in almost all the samples, except one sample (KR-5) taken at Bazid Khel which has the lowest (46.07 wt %) CaO content (Fig. 6.6).

Sodium oxide (Na_2O) and potassium oxide (K_2O) are considered as trace with respect to the pure stone chemistry (Boynton, 1980). Both these oxides are very low (< 0.50 wt %) in total and more or less constant in almost all the samples (Fig. 6.7 and 6.8).

During the determination of loss on Ignition (L. O. I.), the bond between $CaCO_3$ molecule is broken to form lime (CaO) and CO_2. This CO_2 is the measure of ignition loss. In the limestone of the studied area, due to high concentration of calcite ($CaCO_3$), the loss on ignition is high (> 42 wt %) and more or less similar in almost all the samples. One sample (KR-5) taken from Bazid Khel have relatively low content of L. O. I. and is consistent with the low concentration of $CaCO_3$ in this sample (Table 6.1). The calculated $CaCO_3$ content (Table 6.1) agrees with the petrographic observation (Chapter 5) that almost all the studied aggregates of the Kohat Formation are pure high-calcium limestone, having calculated calcium carbonate more than 95% except one sample (KR-5) which has about 81% $CaCO_3$ (Table 6.1).

6.2 CHEMISTRY OF N.W.F.P. CEMENTS

The chemistry of Ordinary Portland Cement (OPC) largely depends upon the geochemistry of its raw materials that is, limestone, argillaceous rocks (e.g.. clay, shale and slate etc.), gypsum and silica sand (Lea, 1976). Therefore, lime content in any OPC is very high. In the recent years, the lime content in the cement were rising steadily and that of silica falling somewhat (Lea, 1976). This was rendered possible by improving methods of manufacturing resulting, soundness and rapid strength development in the cement.

The Kohat Province is rich in cement raw materials (Gauhar, 1966; Shah et al., 1977). Therefore, three cement factories that is Cherat Cement Company, Kohat Cement Company and Lucky Cement Company is functioning in the area whereas, another (Askari Cement Company) is under-construction. These cement factories not only fulfil the cement demand in the area but also have wide network of consumers in the country. Cement samples collected from different markets of Peshawar of these companies were chemically studied for their use in concrete. A brief chemistry of these samples is as follows:

It is clear from Table 6.2 that, chemically the Lucky Cement has SiO_2 19.10-21.70 wt %, Al_2O_3 4.21-5.89 wt %, Fe_2O_3 2.73-2.79 wt %, MnO up to 0.05 wt %, MgO 1.92-2.38 wt %, CaO 65.66-66.45 wt %, Na_2O 0.52-0.56 wt %, K_2O 0.68-0.80 wt %, L. O. I. 0.77-1.22 wt %. tricalcium aluminate (C_3A) 6.54-10.99 wt % and equivalent alkalies 0.97-1.05 wt %. The Kohat Cement is having SiO_2 in the range of 16.60 to 19.50 wt %, Al_2O_3 6.75 to 7.89 wt %, Fe_2O_3 2.32 to 2.66 wt %, MnO about 0.05 wt %, MgO 1.47 to 1.66 wt %, CaO 64.92 to 65.75 wt %, Na_2O up to 0.29 wt %, K_2O 0.44 to 0.75 wt %, L. O. I. 0.22 to 0.90 wt%

Table 6.2. Chemistry of N. W. F. P. Cements.*

	ASTM max. limit C 150-94	Lucky Cement Co.				Kohat Cement Co.				Cherat Cement Co.			
		I	II	III	Avr.	I	II	III	Avr.	I	II	III	Avr.
SiO_2	20.00%	21.00	21.70	19.10	20.6	19.50	17.80	16.60	18.0	19.50	18.20	18.50	18.7
Al_2O_3	6.00%	4.36	4.21	5.89	4.82	6.75	7.48	7.89	7.37	7.73	7.81	7.58	7.71
Fe_2O_3	6.50%	2.79	2.73	2.73	2.75	2.41	2.32	2.66	2.46	2.75	2.75	2.66	2.72
MnO		0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.06	0.05	0.05	0.05
MgO	6.00%	2.38	1.92	2.01	2.10	1.65	1.66	1.47	1.59	1.77	1.05	0.99	1.27
CaO		65.87	66.45	65.66	65.99	65.75	64.92	65.04	65.24	64.53	65.67	65.84	65.35
Na_2Os		0.52	0.56	0.52	0.53	0.29	0.28	0.29	0.29	0.44	0.47	0.47	0.46
K_2O		0.80	0.71	0.68	0.73	0.75	0.69	0.44	0.63	0.66	0.71	0.71	0.69
Loss on ignition	3.00%	0.97	1.22	0.77	0.99	0.69	0.22	0.90	0.60	0.80	0.91	0.97	0.89
Total		98.74	99.55	97.41		97.84	95.42	95.34		98.24	97.62	97.77	
C_3A	15.00%	6.83	6.54	10.99	8.12	13.81	15.90	16.41	15.37	15.83	16.04	15.59	15.82
Equivalent alkalies	0.60%	1.05	1.03	0.97	1.02	0.78	0.73	0.58	0.70	0.87	0.94	0.94	0.92

* Analyzed by *AQEEL GOHER*.

C_3A 13.81 to 16.41 wt % and equivalent alkalies 0.58 to 0.78 wt %. In Cherat Cement, SiO_2 varies from 18.20 to 19.50 wt %, Al_2O_3 from 7.58 to 7.81 wt %, Fe_2O_3 from 2.66 to 2.75 wt %, MnO about 0.05 wt %, MgO from 0.99 to 1.77 wt %, CaO from 64.53 to 65.84 wt %, Na_2O from 0.44 to 0.47 wt %, K_2O from 0.66 to 0.71 wt %, L. O. I. from 0.80 to 0.97 wt %, C_3A from 15.59 to 16.04 wt % and equivalent alkalies from 0.87 to 0.94wt %.

The averages of the major oxides, tricalcium aluminate and equivalent alkalies for the ordinary Portland cement of these three companies are diagrammatically compared with the maximum limits specified by ASTM C 150-94, in figures 6.9 to 6.14.

Silica (SiO_2) in cement may comprises up to 25% of total constituents (Lea, 1976). The average SiO_2 contents in the studied cement are within the limits of ASTM C 150-94. The Lucky Cement however, has relatively high SiO_2 (Fig. 6.9).

Although the alumina (Al_2O_3) and ferric oxide (Fe_2O_3) by no mean equivalent to each other but their effects are closely interconnected (Lea, 1976). Their excess may form rings in the kiln and abnormal variation in their proportion hastens the cement's setting time. Thus the main role of alumina and ferric oxide in the OPC .is to reduce the clinking temperature and production of high early strength. The Al_2O_3 content in the studied cement specimens of Kohat and Cherat brands are slightly higher where as in Lucky it meets with the ASTM standards (Fig. 6.10). The Fe_2O_3 concentration in·all the three varieties are similar and is within the specified limits of ASTM C 150-94 (Fig. 6.11).

The concentration of manganese oxide (MnO) is usually less that

Fig. 6.9. Comparison of average silica (SiO$_2$) concentration in the various cements of N.W.F.P. with ASTM C 150-94.

Fig. 6.10. Comparison of average alumina (Al₂O₃) concentration in the various cements of N.W.F.P. with ASTM C 150-94.

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Fig. 6.11. Comparison of average ferric oxide (Fe_2O_3) concentration in the various cements of N.W.F.P. with ASTM C 150-94.
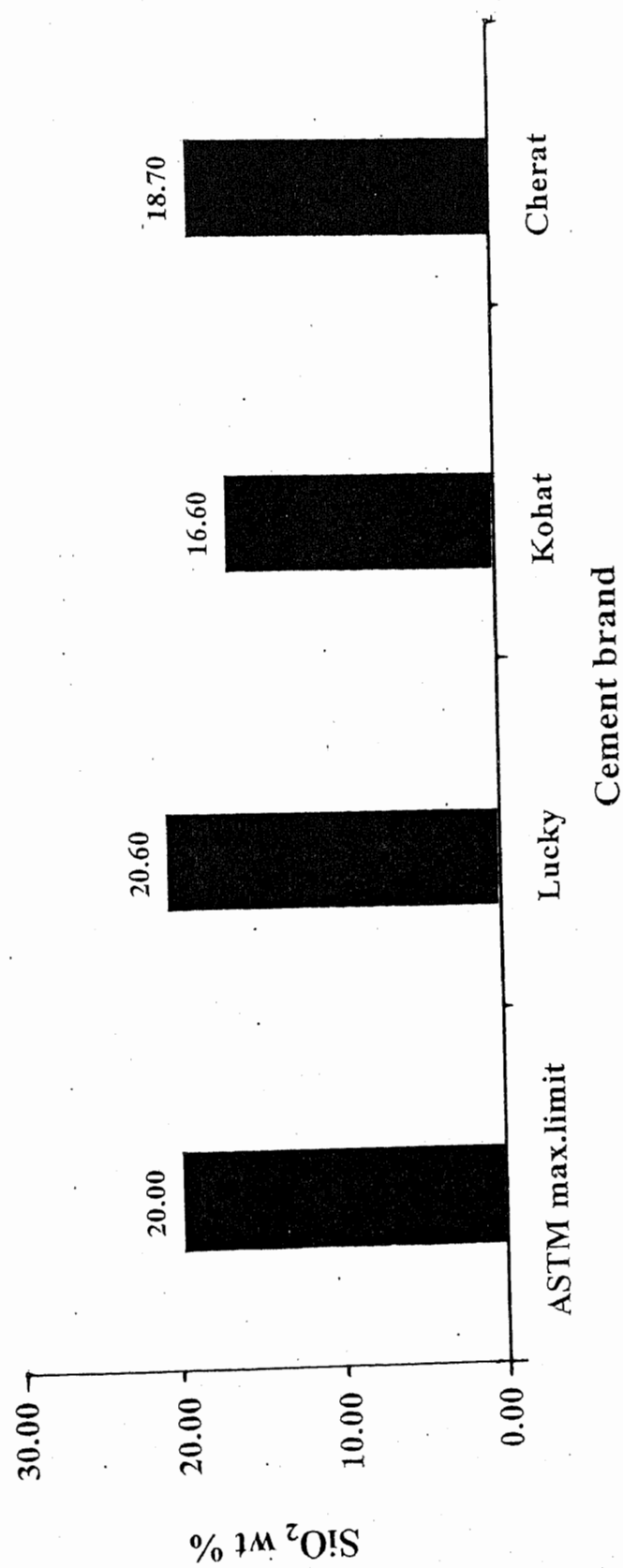
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Fig. 6.12. Comparison of average magnesium oxide (MgO) concentration in the various cements of N.W.F.P. with ASTM C 150-94.

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Fig. 6.13. Comparison of average Tricalcium aluminate (C_3A) concentration in the various cements of N.W.F.P. with ASTM C 150-94.
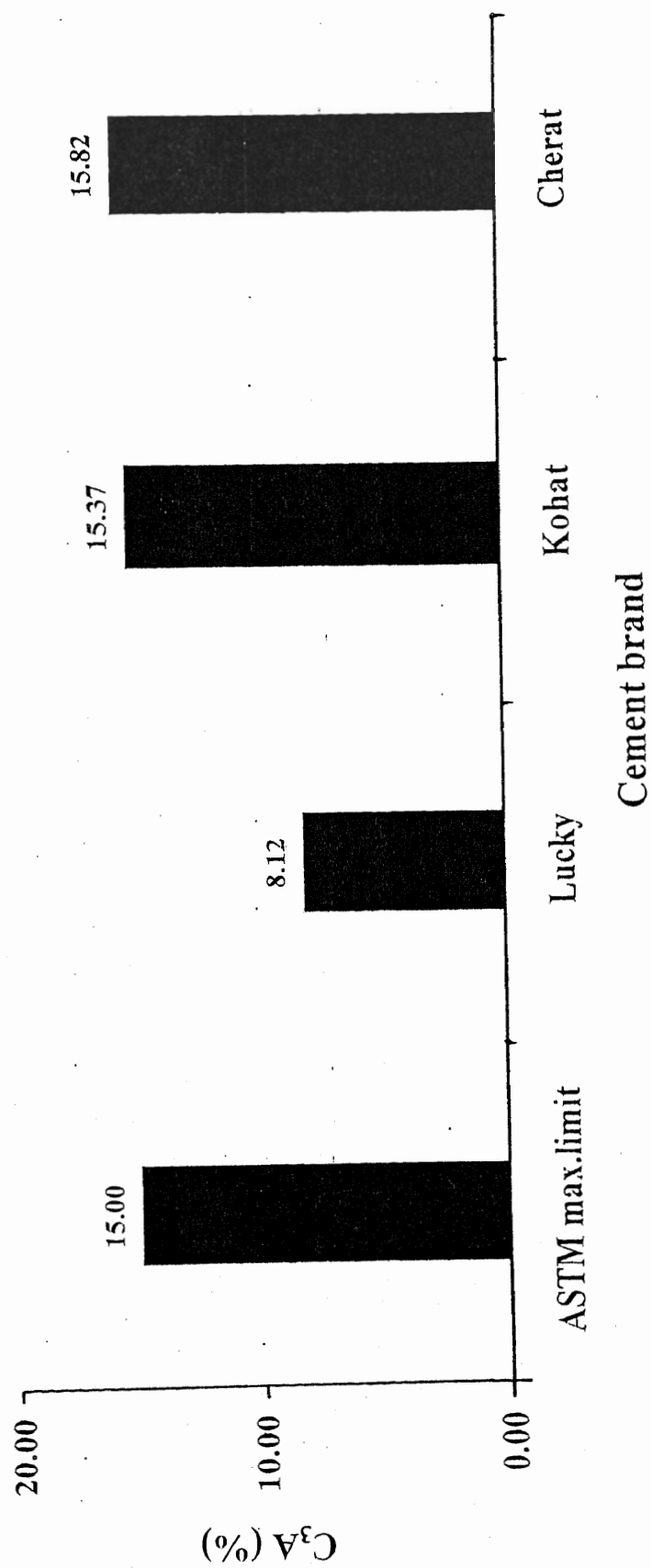
Fig. 6.14. Comparison of average equivalent alkalies concentration in the various cements of N.W.F.P. with ASTM C 150-94.
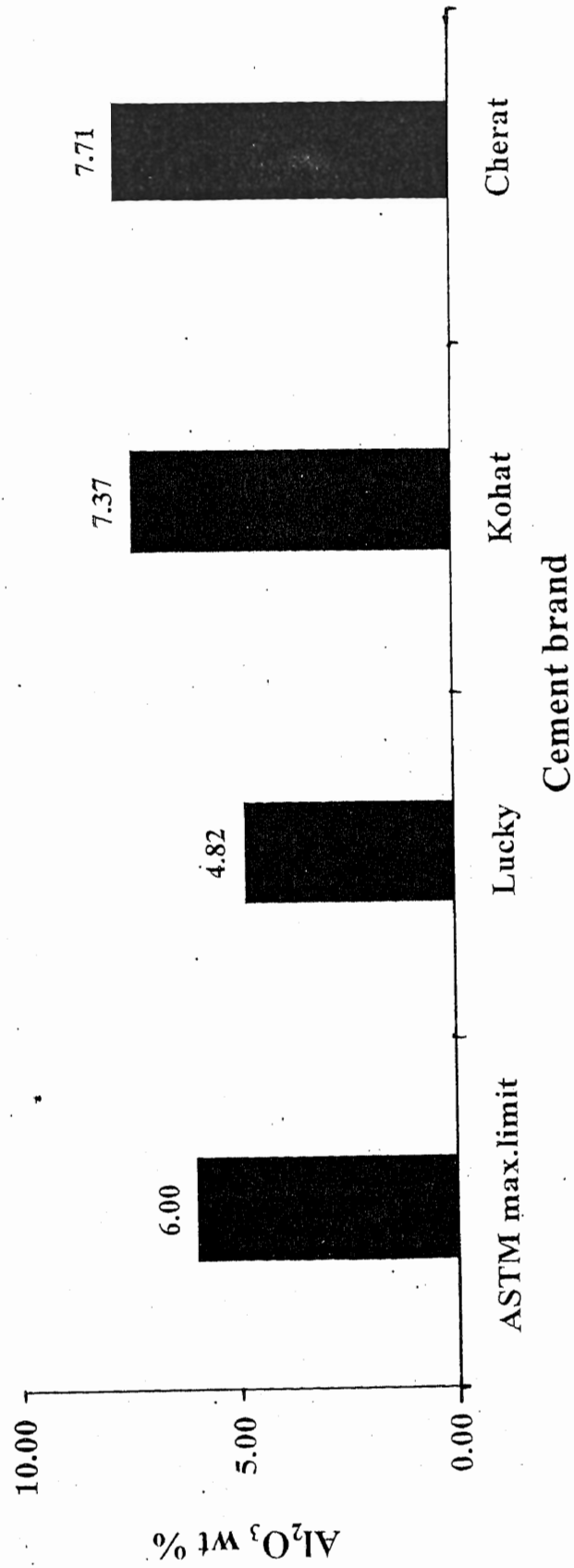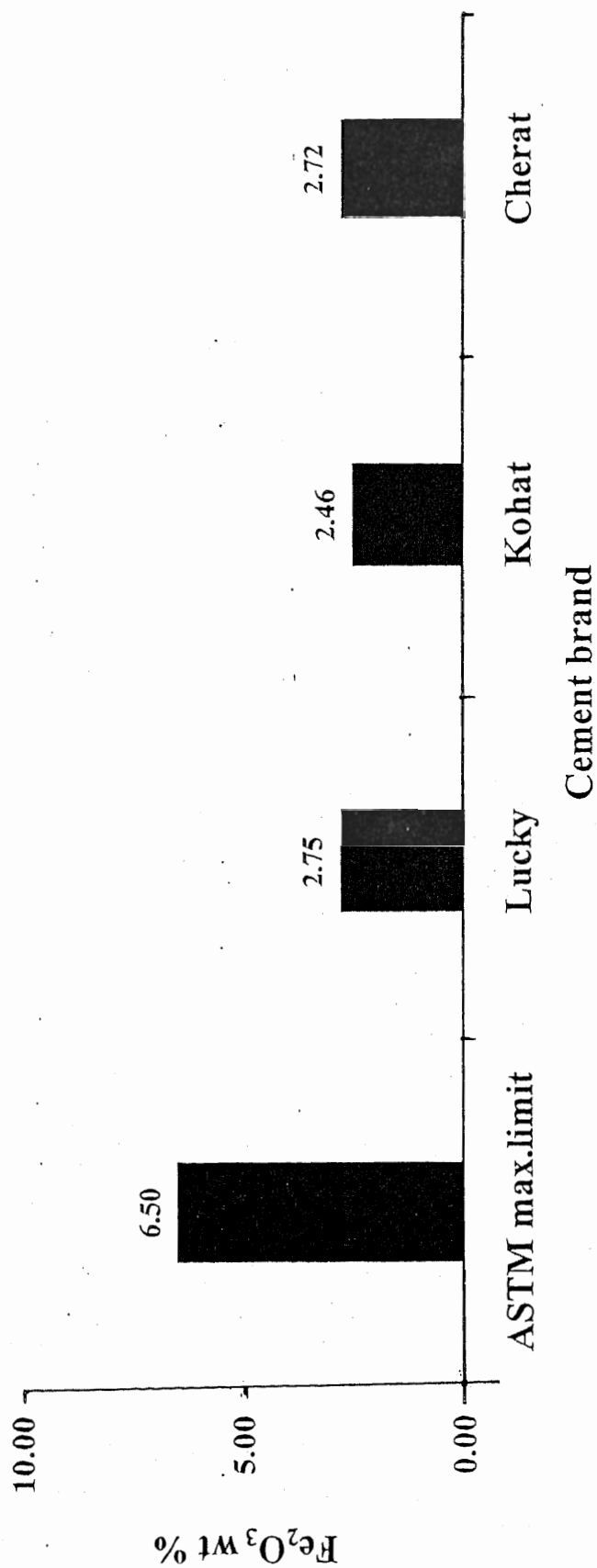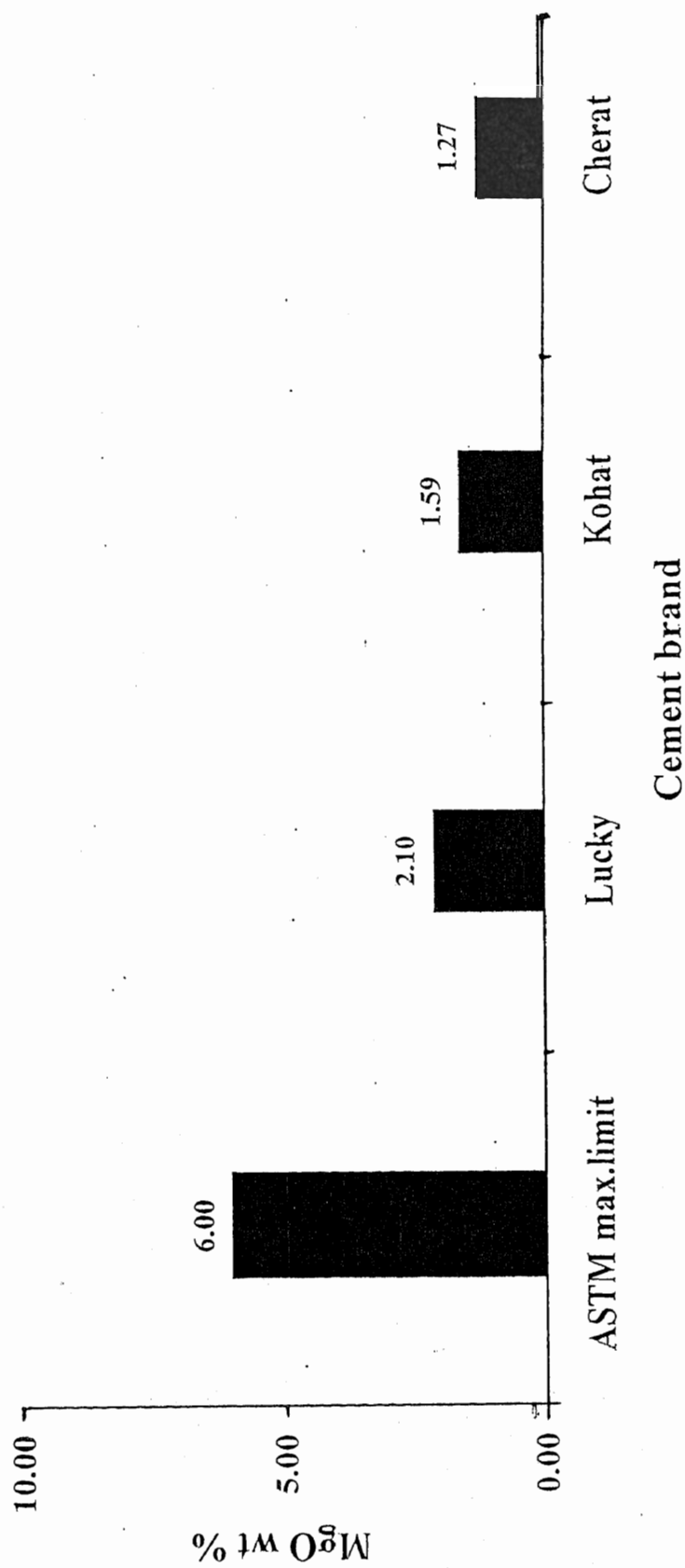
75
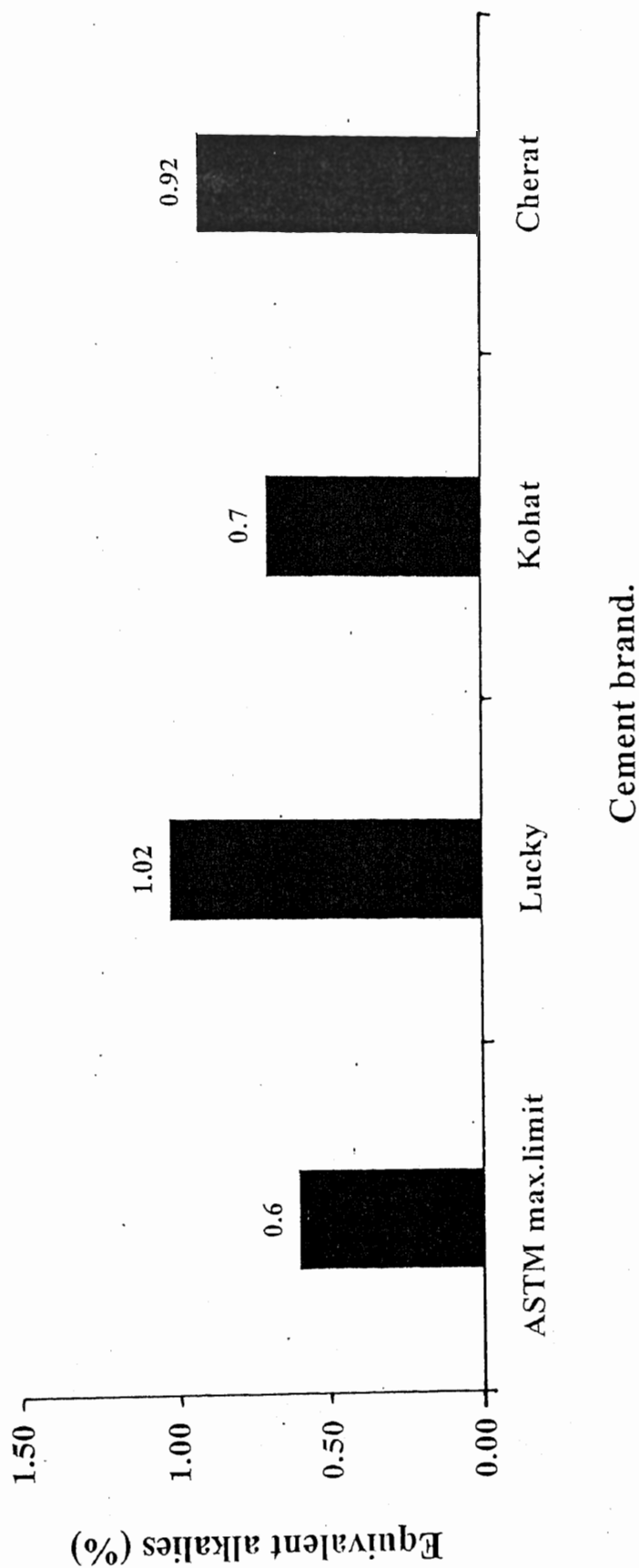
0.1% for cement made from normal raw material (Lea, 1976). The MnO content of all the three varieties of cement is almost negligible and similar (Table 6.2).

Magnesia (MgO) usually act as flux during cement manufacturing thus, facilitating combustion and rendering of clinker (Lea, 1976). But its abnormal concentration led to long term unsoundness. The average MgO contents of Lucky cement are relatively high but are with in the maximum limits specified by ASTM C 150-94 (Fig. 6.12).

Approximately 75% of Portland cement raw material consist of lime (CaO) bearing material. Due to better cementization property of hydraulic lime, it is widely used in cement manufacturing. The concentrating of many cement compounds (tricalcium silicate, dicalcium silicate etc.) largely depends upon the lime contents (Lea, 1976). The average CaO content in all the three varieties of cements are more or less similar (Table 6.2).

Sodium oxide (Na_2O) and potassium oxide (K_2O) are generally found as minor constituents in the OPC (Lea, 1976). They form water-soluble alkalies. The average Na_2O and K_2O contents of the Kohat cement are relatively low (Table 6.2).

The tricalcium aluminate (C_3A) control's the setting time of the OPC (Gilkey, 1962; Lea, 1976). Its concentration in the cement largely depends upon alumina and ferric oxide contents. The average C_3A contents in the studied cements are within specified limits (Fig. 6.13).

The potash and soda contents are usually present in minute quantity in ordinary Portland cement clinker which are readily soluble in water resulting increase in the pH for the concrete pore solution (Lea, 1976; Hobb, 1988). This increase in pH of pore solution may aggravate the alkali-aggregate reaction thus damaging the concrete structures. The equivalent alkalies in the studied cements are relatively higher to its permissible limits of ASTM C 150-94 (Fig. 6.14). Therefore, expansion tests (ASTM C 227-90, C 342-90 and 1260-94) should be conducted to ensure possible reactivity caused by cement's alkalies in the mortar.

6.3 ALKALI-SILICA REACTIVITY OF KOHAT FORMATION LIMESTONE, BASED UPON CHEMICAL REACTIVITY METHOD (ASTM C 289-94)

Generally common concrete aggregates except, those reacts with alkalies, are considered to be inert in the water-cement system (Soroka, 1979). It has been observed that sodium-potassium content of reactive siliceous material in the aggregates when react with the hydrated cement alkalies results in the expansion and cracking of concrete. If these alkalies content are of silica minerals in the aggregate, then the phenomena is known as alkali-silica reactivity (Gilkey, 1962; Lea, 1976; Boynton, 1980; Hobb, 1988; Halmuth 1994).

There are numbers of tests currently being used to establish whether an aggregate or cement-aggregate combination is deleteriously reactive or not. It included, the service performance record of the concrete aggregates, petrographic studies of the aggregates (ASTM

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C 294-86 and C 295-90), chemical test expansion tests and for the aggregates. The most widely used tests by ASTM are, quick chemical test on aggregate (C 289-94) and the mortar-bar expansion tests (C 227-90, C 342-90 and C 1260-94) (Hobb, 1988; ASTM, 1994). If the aggregate passes in the quick chemical test, it is regarded as innocuous but if it fails, a mortar-bar expansion test is carried out to check percentage expansion of the aggregate (Lea, 1976; Hobb, 1988).

The quick chemical test C 289-94 is a rapid, economical and accurate method to determine alkali-silica reactivity of a concrete aggregate (ASTM, 1994). Although recent experiences of various investigators and project studies indicate that this test is not always necessarily accurate therefore, it cannot be used to reject the specimen especially that of carbonate rocks with high ferrous and magnesium concentration due to reduction in their ions (Derucher & Heins, 1981; ASTM, 1994). The basic theme of this test is that the reactive material will release more molar equivalent of silica into solution for a given reduction in alkalinity and that this greater proportion of silica will form swelling gel in the concrete. Therefore, reaction between sodium hydroxide solution and siliceous aggregate is correlated with the performance of aggregate in concrete structure (Lea, 1976). Thus the quantity of dissolved silica (S_c) and reduction in alkalinity (R_c) determined in millimoles per liter is plotted against each other as per ASTM C 289-94. This graphical representation between dissolved silica and reduction in alkalinity for Kohat Formation limestone illustrate that only argillaceous limestone stands potentially deleterious where as, generally the studied limestone is found innocuous for concrete (Fig. 6.15). This can further be justify by ASTM C 33-93 (specification for

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concrete aggregates) that aggregate will be consider potentially deleterious if,

$$S_c > (35 + \frac{1}{2}R_c), \forall R_c < 70$$

It is evident from table 6.1, that the sample No. KR-3/a and KR-5 have relatively higher or equal S_c to the relation $35 + \frac{1}{2}R_c$ thus stands reactive and vices versa. Further, almost all the studied limestone samples are plotted in the field of innocuous for concrete and only two samples KR-3/a and KR-5 collected for Sheikhan Nala and Bazid Khel respectively, are plotted in the field of deleterious aggregates (Fig. 6.15) Therefore, argillaceous limestone at Sheikhan Nala and Bazid Khel is found to be potentially deleterious for concrete and its use without satisfactory mortar-bar expansion testing is prohibited. Rest of the limestone of the Kohat Formation is suitable for its use as concrete aggregates.

Fig. 6.15. Division between innocuous and deleterious aggregates of limestone of Kohat Formation, on the basis of reduction in alkalinity.

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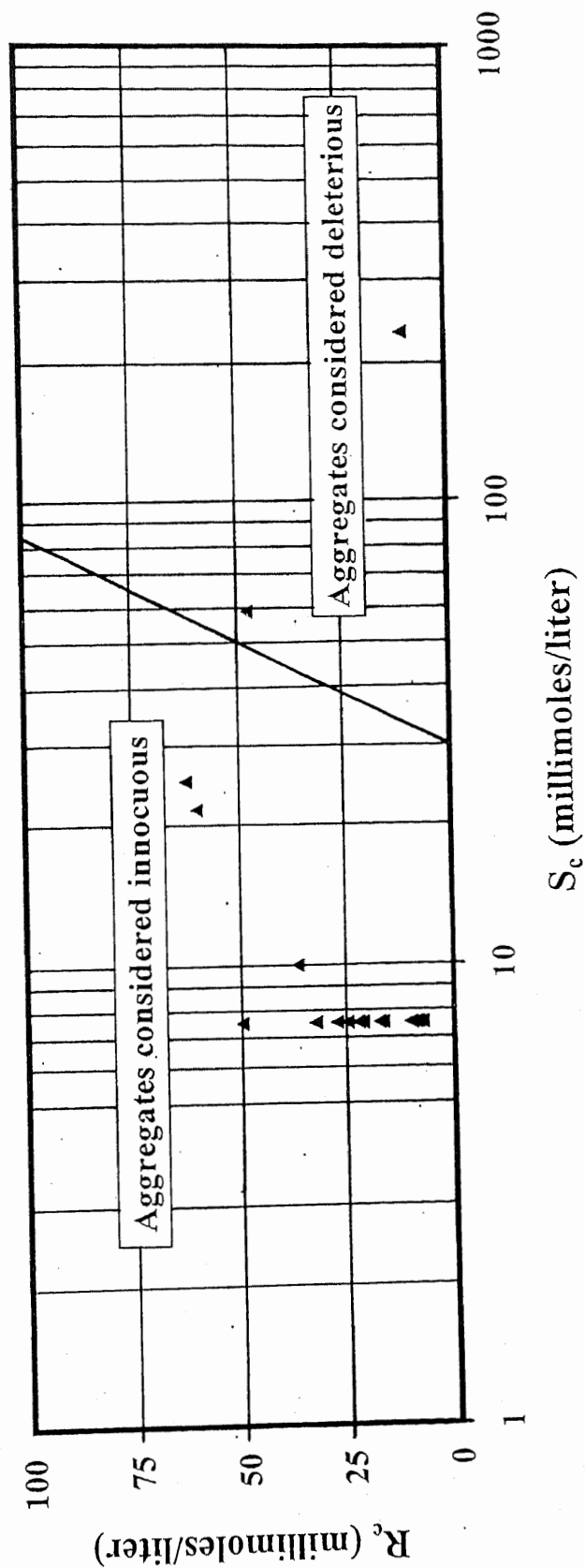
CHAPTER 7

PHYSICAL PROPERTIES

7.1 GENERAL

Aggregates constitute about 60-80% of the concrete by volume. Therefore, their characteristic influences the workability, strength and durability of the concrete (Smith, 1979; Boynton, 1980; Derucher & Heins, 1981). Generally, the properties of the concrete depend primarily on the quality and amount of interstitial mortar but secondarily on the coarse aggregate (Lea, 1976). The soundness, impermeability and resistance to abrasion become vital to concrete aggregates in order to withstand the pressure to which concrete is stressed and about shrinkage caused by dehydration. Limestone is a sedimentary rock composed of calcium carbonate. It vary in types from the soft chalks to hard crystalline rocks (Pettijohn, 1976). The limestone generally yield's good quality concrete aggregates under normal conditions (Lea, 1976; Tayler, 1977 Metha, 1986; Hobb, 1988). The Eocene limestone of Kohat Formation has been grouped based upon their geochemical composition and these groups have been evaluated for their physical properties (Table 7.1). Some of important physical properties of the Kohat Formation limestone aggregates are as follows;

7.2 SOUNDNESS

The soundness of the aggregate furnishes useful information for predicting its resistance against the weathering effects. It is, therefore, becoming essential to test soundness of aggregates with insufficient service record. The repeated immersions in the solution followed by

Table 7.1. Physical properties for the limestone coarse aggregates of Kohat Formation.*

Physical Properties

Group No. Test title	Soundness (%)	Water absorption (%)	Los Angeles Abrasion value (%)	Specific gravity**
ASTM method No.	C 88-90	C 127-88	C 131-89	
ASTM max. limit (C 33-93)	12		50.0	
A.	3	0.6	21.2	2.68
B.	1	0.3	20.4	2.70
C.	1	0.4	20.7	2.60
D.	0	0.7	20.8	2.69
E.	0	1.2	21.3	2.72
F.	1	0.7	18.2	2.67

* Analyzed by *AQEEL GOHER.*

** *Based upon average specific gravity for the geochemical samples, in a group.*

Group A comprises of geochemical sample no. KH-2, KR-1, KR-3/a, KR-3/b & KR-6.
Group B comprises of geochemical sample no. KR-2/a, KR-2/b & KR-4.
Group C comprises of geochemical sample no. KB-1, KB-3, & KH-1.
Group D comprises of geochemical sample no: KB-2, KB-4/a & KB-4/b.
Group E comprises of geochemical sample no. KH-3/a, KH-3/b, KH-4 & KH-5.
Group F comprises of geochemical sample no. KR-5.

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drying, dehydrate the salt which precipitate into the aggregate's pore. For this purpose, aggregates are usually immersed in the Na_2SO_4 or $MgSO_4$ solution as per ASTM method No. C 88-90. The re-hydration of the aggregates simulates internal expansion of water on freezing. This freezing and thawing of aggregate may effect the resistance of concrete. Therefore, unsound aggregates may bring pitting, pop out, D-line or map cracking in the concrete structures (Derucher & Heins, 1981).

Aggregates for the studied limestone of the Kohat Formation were tested in accordance to ASTM C 88-90 (for the aggregates size, 3/8" pass and No. 4 retain). The test results exhibit that, these aggregates have sufficient resistance to freezing and thawing effects, justifying ASTM C 33-93 specifications (Table 7.1; Fig. 7.1).

7.3 WATER ABSORPTION

Water absorption test helps to calculate the change in the aggregate weight due to water absorption within its pore spaces in the moist environment such as in concrete. Greater the water absorption, more the aggregate tends to expand in the concrete and vice versa, causing D-line and progressive cracking, defection and steel corrosion. Although the deterioration of the aggregate can be judged within the wet concrete but it increases severely with the degree of concrete drying.

The studied limestone of the Kohat Formation was tested as per ASTM method No. C 127-88 and the porosity/absorption for the studied limestone varies from 0.3 to 1.2% (Table 7.1). Majority of the studied aggregates (except one) has low water absorption (Table 7.1).

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Fig. 7.1. Soundness characteristics for limestone aggregates of Kohat Formation.

% age loss

15 · 10 · 5 · 0

| 12 | .3 | 1 | 1 | 0 | 0 | 1 |
| ASTM max. limit | A. | B. | C. | D. | E. | F. |

Group No.

84
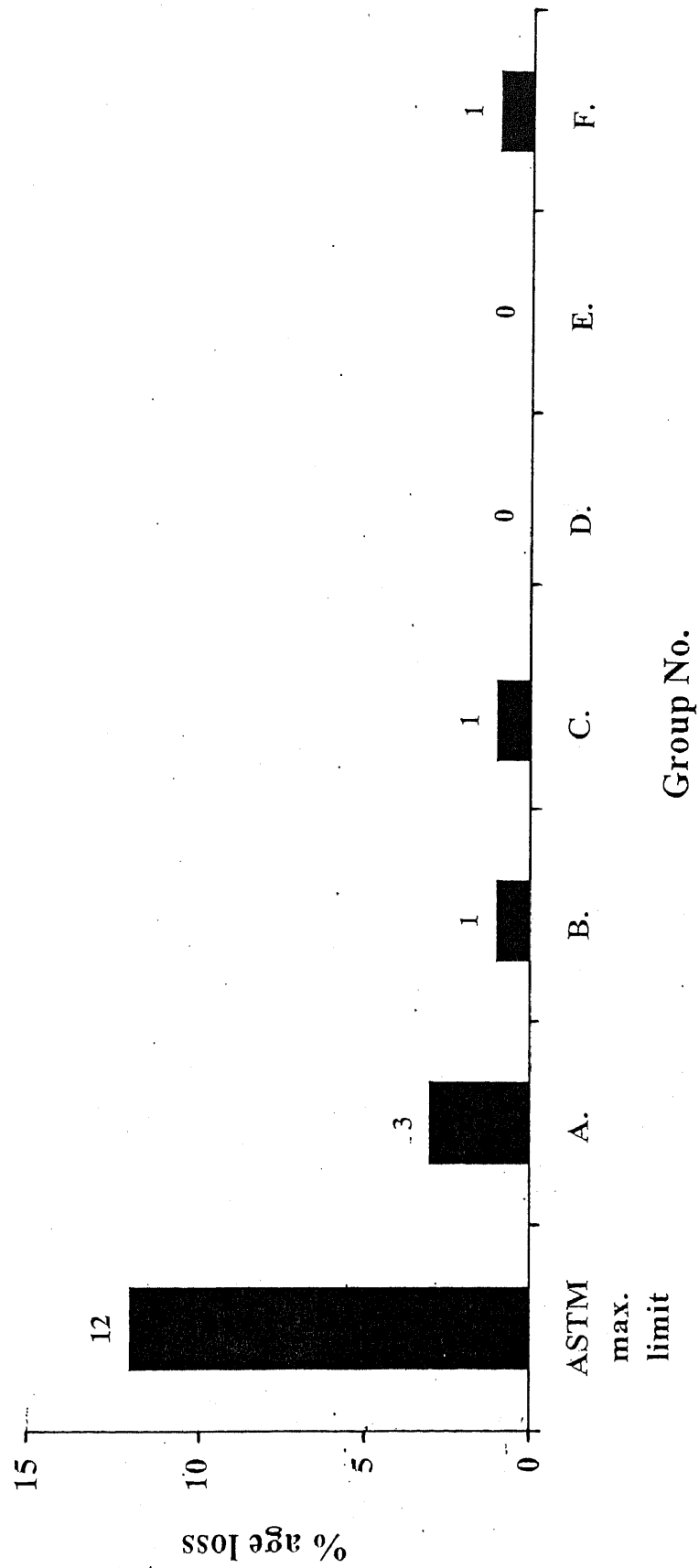
7.4 LOS ANGELES ABRASION CHARACTERISTIC

The principle of Los Angeles abrasion test (ASTM C 131-89) is to find the percentage wear due to the relative rubbing action between the aggregate and steel balls used as an abrasion charge to evaluate its strength for concrete (Lea, 1976; Khanna & Justo, 1992). Powdering action of these balls existed during the test and the resistance to wear and impact is evaluated. The Los Angeles test has been widely used as an indicator for the quality or competence of the concrete aggregates. Woolf (1937) compared the Los Angeles abrasion results with the service record of coarse aggregates and concluded that it gives accurate indication for material quality (also see Derucher & Heins, 1981). For the determination of the Los Angeles abrasion, aggregates of grading B and C as per ASTM C 131-89 method were used and the values of these studied aggregates for the limestone of Kohat Formation were compared with that of ASTM specified limit. All these samples very well meet the specified limit (Table 7.1; Fig. 7.2).

7.5 SPECIFIC GRAVITY

Specific gravity of an aggregate effects the concrete weight-age in the structure. In practice, sometimes it is essential to use aggregates with lesser specific gravity as to ensure lightness in the structure e.g.; lightweight aggregates are used in the non-structural concrete. As the most of the world high-calcium limestone, the studied limestone of the Kohat Formation have the specific gravity varies from 2.60-2.72 (Table 7.1) evaluating its calcite nature (Boynton, 1980).

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Fig. 7.2. Los Angles Abrasion characteristics for limestone aggregates of Kohat Formation.

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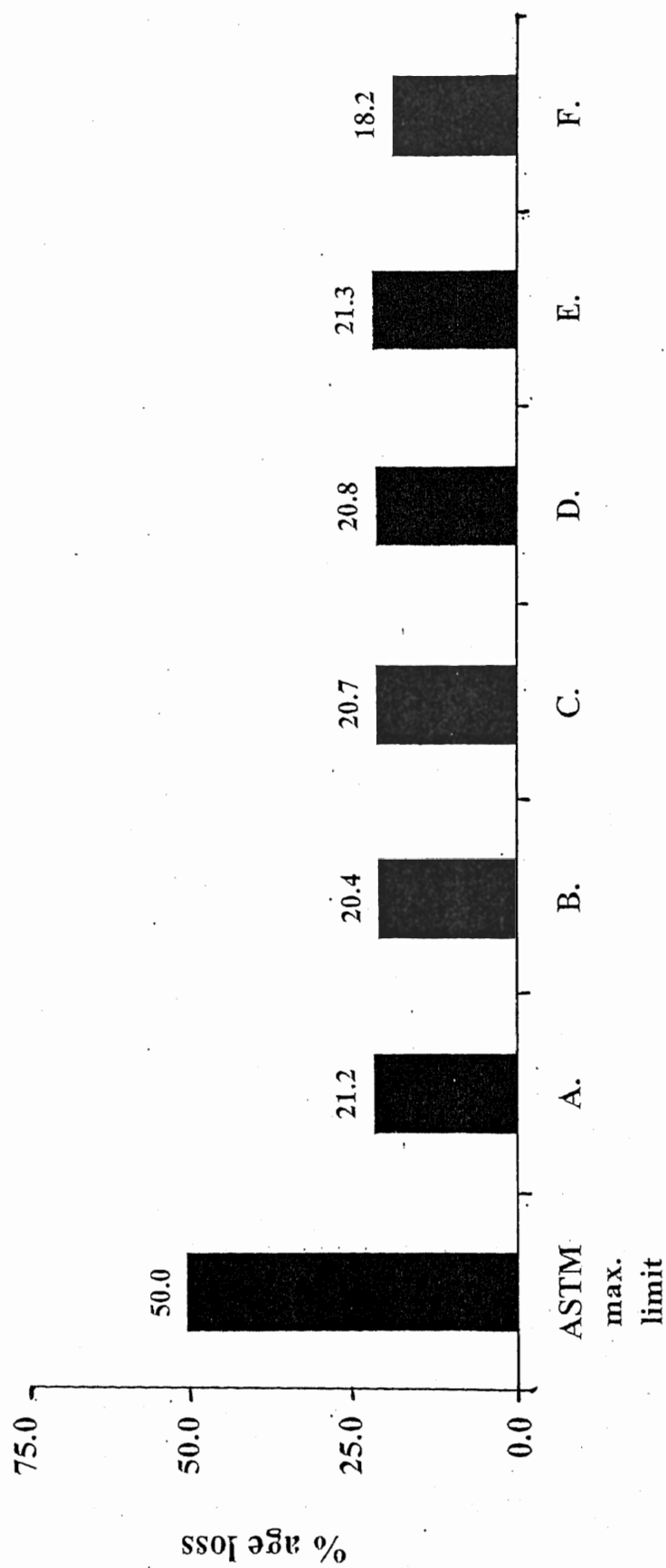
CHAPTER 8

DISCUSSION

Limestone is a general term used for those rocks in which carbonate fraction is composed primarily of calcite or aragonite (Pettijohn, 1976; Boyntone, 1980). It is a common sedimentary rock and forms one fifth to one fourth of sedimentary record. It is polygenetic. Some are fragmental or deterital and are mechanically transported and deposited exhibiting hydrodynamic texture. Other is chemically or biochemical precipitates and formed in situ exhibiting current and growth bedding. Limestone mainly consists of carbonate minerals of calcite, aragonite and dolomite with minor ankerite and siderite. The calcite of limestone is both primary and diagenetic mineral. Rock-building organism use both calcite and aragonite in their skeletal structures thus some skeletal minerals are calcitic, some are aragonitic and others are homogenic composite of both. The calcite limestone with few exception are quite pure $CaCO_3$, where as hard parts of some invertebrate skeletal structures contain a significant proportion of $MgCO_3$ in solid solution the so called high magnesium calcite or dolomite (Pettijohn, 1976). Therefore, there are two fundamental types of limestone, high calcium and dolomite. Pure high calcium limestone (i.e., calcite and aragonite) is 100% calcium carbonate where as pure dolomite is 54.3% $CaCO_3$ and 45.7% $MgCO_3$ (Boynton, 1980). But no limestone of these purity occurs naturally, therefore, for practical purpose high quality high calcium limestone contain 97-99% $CaCO_3$. Dolomite is having 40-43% $MgCO_3$ with slightly higher $CaCO_3$ component than theoretical value.

The chemical composition of limestone reflects its mineral composition. As high-calcium limestone is primarily calcite therefore, the content of both CaO and CO_2 are extremely high (Pettijohn, 1976). Among other constituents that commonly become important is MgO that is derived either by the magnesium content of skeletal debris or due to post-depositional additions. The important minor constituents (impurities) in limestone are silica and alumina, which forms 85-95% of total impurities (Boynton, 1980). These are followed by iron, phosphorus and sulfur but other impurities are so minute that they may be considered as trace elements relatively to pure stone chemistry. These included manganese, copper, titanium, sodium, potassium (as oxides), fluorine, arsenic, strontium and others. The source of these impurities are non-carbonate detritus minerals incorporate during the formation of limestone (Pettijohn, 1976). Chemically, the studied limestone of Kohat Formation is considered as high-calcium limestone with the exception of few species found in eastern region of the study area where argillaceous matter (especially silica content) increases.

The chemical properties of aggregates are of greater importance because the aggregates contain those constituents, which can undergo chemical change or react with the cement in such a way as to cause deterioration or is interface with its setting and hardening. Ferric/iron compounds in aggregates are not considered as deleterious because they react with lime in aggregates without any deleterious effect. However, the oxidation of iron such as oxidation of pyrite, marcasite and pyrrhotite are reported to cause popping out or expansion and deterioration of the concrete. Very low Fe_2O_3 content (< 0.30 wt. %) and invisible pyrite or any other iron-bearing sulfide in the studied aggregates favor no any kind of deleterious effect due to oxidation in these aggregates.

The reaction of the active silica with lime improves the strength however, its reaction with alkalies causing intensive deterioration (ACI Committee, 1984; Building research Establishment, 1982). These reactions occur when there is high content of alkali in the cement and the presence of higher amount of free silica or other reactive constituents in the aggregates. This reaction however, doesn't occur when the aggregates of sufficiently low silica or reactive constituents are used with the cement having high (> 1.0 wt. %) alkali contents. Considering the very low silica content (<1.5 wt. %), except two samples (KR-3/a and KR-5) and the absence or negligible amount of other reactive constituents in the studied aggregates, it is suggested that although, the various types of cement (Table 6.2) have more than 0.60 % of total alkalies but still the use of these aggregates may not cause any alkali-aggregate reaction in the concrete. The plotting of majority of these aggregates in the field of innocuous aggregates in dissolved silica (S_c) verses reduction in alkalinity (R_c). (Fig. 6.15), is in consistence with above discussion. The chemical composition of the aggregates (Table 6.1) further suggest that there are greater chances of formation of insoluble calcium-silicate or calcium-alkali-silicate gel instead of soluble alkali-silica gel, which favor the use of these aggregates in concrete.

Alkali-carbonate reaction is another expansion type of reaction in limestone aggregate's concrete under moist condition. This reaction generally occurs between the alkalies of the cement and the aggregates of dolomitic limestone and dolomite. This reaction cause extensive expansion and swelling in the rock which has deterioration effect in the building construction. It is clear from the petrography (Chapter 5) and the geochemistry (Chapter 6) of the studied aggregates that the

aggregates are of pure limestone and no dolomitization has been noticed in these aggregates. This is suggestive of no possibility of alkali-carbonate reaction in the concrete of these aggregates.

Petrographic analysis plays an important role in identification of deleterious substances in the aggregates. The petrography of coarse aggregates also identifies the extent of the weathering and alteration of the aggregates. This kind of study on aggregates in building construction is used to determine quantitatively the abundance of potentially alkali-aggregate reactive constituents. According to ASTM (C 295-90), the aggregate constituents capable of alkali-silica reaction in the concrete are; opal, chalcedony, cristobalite, tridymite, siliceous volcanic glass, chert, glassy to crystalline acid volcanic rocks, some argillites, phyllite, metamorphic graywacke, schist, gneiss, granite gneiss, quartz veins, quartzite and sandstone. Among the most important potentially alkali-carbonate reactive rocks are the calcareous dolomite or dolomitic limestone with clayey insoluble residues.

There are certain chemically unstable minerals such as soluble sulfates, unstable sulfides which may form sulfuric acid or create distress in concrete whenever are exposed to high temperature and also volumetric unstable minerals such as smectite, montmorillonite and other clay minerals which cause swelling, cracking and expansion in the concrete (Hobb, 1988).

It is clear from the petrography of the studied limestone aggregates in chapter 5 that there are no deleterious constituents, which can cause alkali-silica, alkali-carbonate or any physical distortion in the concrete structure. The occurrence of high amount of medium-grained

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quartz in the aggregates collected at Bazid Khel may cause alkali-silica reaction (see section 6.3).

The physical properties of the aggregates are relevant to the behavior of aggregate in concrete and to the properties of concrete made with the given aggregates (Neville & Brooks, 1987). The various physical properties such as, soundness, water absorption, Los Angeles abrasion and specific gravity have been determined for the limestone of Kohat Formation (chapter 7). The composite aggregates of the Kohat Formation are having physical properties within the specified limits of ASTM C 33-93.

It is, therefore, concluded from this whole discussion that the limestone of the Kohat Formation has no mineralogical, chemical or physical reasons that could render the use of this limestone in the concrete construction. Argillaceous limestone variety present in the eastern part of the study area, especially at Sheikhan Nala and Bazid Khel however, not been recommended for use in concrete at this stage with out further detail investigation.

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