FEASIBILITY STUDY OF LIMESTONE OF GANDGHAR RANGE AND ASSOCIATED DEPOSITS FOR CEMENT MANUFACTURING

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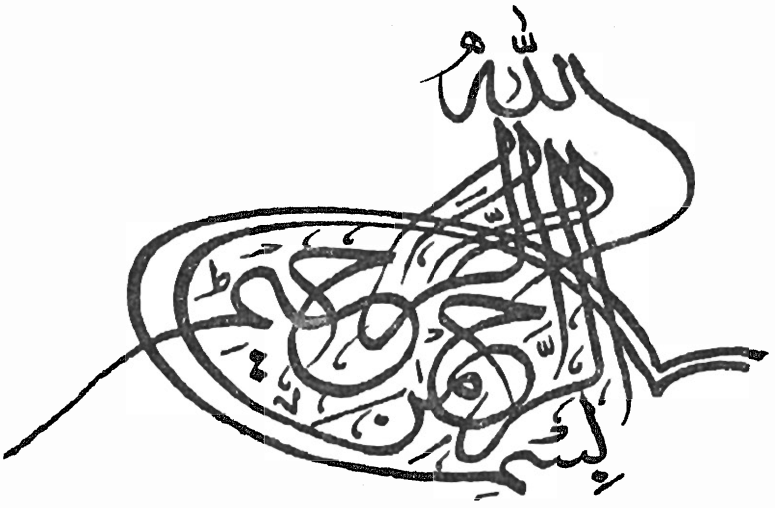

In the Name of the Allah,
the most Beneficent the most Merciful

Grace to Allah, whose help we seek, whose forgiveness we beseech, whose guidance we implore and on whom we rely. We pray and bid peace upon the Messenger of Allah, his family, his companions, his followers and those who spread his message and follow his tradition; they will last as long as there exist Heaven and Earth.

Dedicated

TO MY PARENTS

&

To All Those Whose
Love, Encouragement & Help Is Always
With Me, At Every Step In My Life

ACKNOWLEDGEMENT

All acclamations and appreciations are for Almighty Allah Who bestowed me the potential to complete this work.

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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 cement manufacturing. The extensive deposits of pre-cambrian limestone are exposed in Gandghar, Cherat and Khyber ranges around the southern Peshawar basin. It is light grey in colour, medium to thick bedded and masive. The limestone of Gandghar range has been evaluated mineralogically and chemically for its use for cement manufacturing during present study. Mineralogically, the studied limestone is dominantly calcite very fine grained. Quartz as an hedral small clastic sand grains, chert and chalcedony, some carbonaceous matter is also present in the form of layers or bands. Iron leaching and some of clay minerals by mixing of various raw material in different proportions then the portland cement of desired composition can be obtained. Chemically, the studied limestone of Gandghar range are compared with that of the normal and argillaceous limestone elsewhere in the world. All the three varieties of the studied limestone (Shekhai, Utch Khattak greenish grey) have more silica than normal limestone but less than that of the argilliceous limestone. Al_2O_3 *and* Fe_2O_3 *are relatively high in the studied limestone as compared to that of normal limestone, MgO in the studied limestone is less as compared to that of the normal limestone and more as compared to that of argilliceous limestone,* Al_2O_3 *and* Fe_2O_3 *are relatively high in the studied limestone as compared to that of normal limestone, MgO in the studied limestone is less as compared to that of normal limestone and more as compared to that of argilliceous limestone. The CaO is high in the studied limestone as compared to that of both normal and argilliceous limestone. Total alkalies in the studied limestones are relatively as compared to that of normal limestone. The average chemical compositions of various cements manufactured in N.W.F.P. are within the ASTM limits. The studied limestone of Gandghar range is generally free of dolomitization and has no other deleterious substances. This pre-cambrian limestone of the Gandghar range is therefore, recommended.*

CHAPTER-I

INTRODUCTION

Limestone is a sedimentary rock composed of calcium carbonate. The two most important constituents are calcite and dolomite, but also has small amount of iron bearing carbonates. Limestones can be classified into three major groups; organic, chemical and detrital or clastic.

Many of the commonly occurring limestones contain organic, detrital, and chemically precipitated material in varying proportions. Limestone is one of the raw materials used for cement manufacturing. In addition to other raw material such as chalk, clay, marl and shale, limestone is also used in other metallurgical and chemical industries such as in lime burning, metallic calcium and its alloys, calcium hydride, alkali manufacturing, sugar refining and paper manufacturing etc.

Pakistan has a great resources of limestone, which can be utilized for cement manufacturing. There are extensive limestone beds, exposed in all over Pakistan e.g., Nizampur area district Nowshera, Kohat district, Haripur district, Dera Ismail Khan division, Hyderabad division, Lockhart and Margalla hills.

The Gandghar Range, in which study area is located in the Haripur district, is about 40 km north-west of Islamabad. The limestone deposits of Gandghar range are of two types, Shekhai and Utch Khattak Formations, (Riaz et al., 1991). The Shekhai Formation is exposed in the south eastern part of the north Gandghar range in Hazara division. This formation is mainly composed of limestone, marble with subordinate argillite, shale and quartzite. The limestone is fine-grained and thin to medium-bedded. The exposures of Utch Khattak Formation are restricted to the south eastern Gandghar range and are mainly composed of limestone, argillite and shale. It is bluesh grey to dark-grey in colour and is generally fine-to medium-grained, thin-bedded.

There are huge reserves of Shekhai limestone in the Gandghar Range in addition to slates, shales and clays. Among these raw material limestone of the area is used as crushed aggregates for road and building construction. However, no scientific studies have been carried out in the project on this limestone and associated lacustrine, phyllites and shales in regard to cement manufacturing. This study, therefore, deals with the identification and characterization of limestone of Gandghar range and associated lacustrine, clay as well as shale and phyllites for cement manufacturing.

AIMS AND OBJECTIVES

1. To study the physical properties (i.e. colour, grain size, specific gravity, water absorption etc.) of limestone and other raw material (i.e., clay, phyllites and shales).

2. To determine the mineralogical and geochemical characteristics of the raw matrial.

3. To compare the chemical composition of portland cement of different industries.

4. To identify the mixing behaviour of various component of raw material of the study area (i.e, limestone, clay, phyllites and shales) for their use in cement manufacturing.

PREVIOUS WORK

The earliest published work available on the geology of the Gandghar Range is that of Waagen and Wynne (1872), who described the general geology of the Hazara area. Latter, Wynne (1879) prepared a geological map of the Hazara area at a scale of 1 inch = 8 miles, which contained three cross-sections through Hazara including the Gandghar Range. Middlemiss (1896) also prepared a geological map of Hazara, from Black mountain on the west bank of Indus River eastward to the Kunhar River, at a scale of 1/2 inch = 1 mile. Both Wynne and Middlemiss referred to various limestone units in the Gandghar Range but could not ascertain their age and relative stratigraphic positions.

Cotter (1933) while working in the Kalachitta Range also visited the southern tip of the Gandghar Range and specially mentioned the Slate Series, which he correlated with the pelitic rocks of Attock. He assigned Cambrian or Precambrian age to these slates.

Khan *et al.* (1949) described three lithological units in the Gandghar Range (a) the Hazara Slate Series (b) the Infra-Triassic limestones and (c) the Tanawal Quartzite.

Ali (1962) while working in the southern Tanawal area, also mapped the extreme northern end of the Gandhar Range.

Bakr and Jackson (1964) showed the Gandghar Range to have Precambrian rocks on its eastern side whereas the western half is consisting of Silurian - Devonian rocks.

The first considerably detailed map of the entire Gandghar Range was published by Tahirkheli (1971). He considered all the rocks exposed in the Gandghar Range to be of Paleozoic age and correlated them with lithologically similar units in the Attock-Cherat Range and southern Hazara.

Calkins *et al.* (1975) published a geological map of the northern Gandghar Range and described three rock units from northern Gandghar Range (i) the Precambrian (?) to Ordovician (?) Hazara Formation, (ii) the Ordovician (?) to Devonain (?) Tanawal Formation and (iii) the Triassic Kingriali Formation. They have shown the Panjal Fault passing through the eastern front of the range and separating the Hazara Formation to the west from the Kingriali Formation to the east.

Riaz (1990) and Riaz *et al.* (1991) carried out the systematic geological mapping of Gandghar Range and established the stratigraphic set up of exposed rocks. They correlated these rock sequences laterally with the same type of stratigraphic horizon within the Attock-Cherat Range. Their work also included the detail analysis of the Gandghar Range and worked out the deformation of these rocks associated with the Panjal Fault which lies south of Gandghar Range with Haripur and Hasanabadal plan. No published work is available in regard to the use of limestone and other associated rocks of the Gandghar Range in manufacturing of cement and many other industrial purposes.

CHAPTER II

REGIONAL GEOLOGICAL SET-UP

The sequence of tectonic events during Himalaya orogeny in the NW Himalayas and the subsequent development of a structural foreland and thrust belts towards south can be explained in the framework of tectonics.

The Himalayan orogeny dates back to the late Cretaceous and since then tectonism is taking place in the region till present. Though there are evidence of the presence of pre-Himalayan orogenic episodes (Baig *et al.,* 1987; Kumar *et al.,* 1978 and Saxena, 1980) but the development of major structures are generally related to the Himalayan orogeny. The foreland fold and thrust belt, where the study area is located, however, considered to be comprised of deformed rocks of Gondawana of Pre-Cambrian age with only thin younger units (Gansser, 1964; Le Fort, 1975; Singh, 1978; Ahmed & Alam, 1978 and Valdiya, 1980, 1984).

The geology of Himalayas has been sub-divided into following four tectonic zones (Fig. 2.1). Indus plateform and fore deep,2) Northwest Himalayan fold-and-thrust belt, 3) Kohistan-Ladakh magnatic arc, 4) Karakoram block (Kazmi and Jan, 1997).

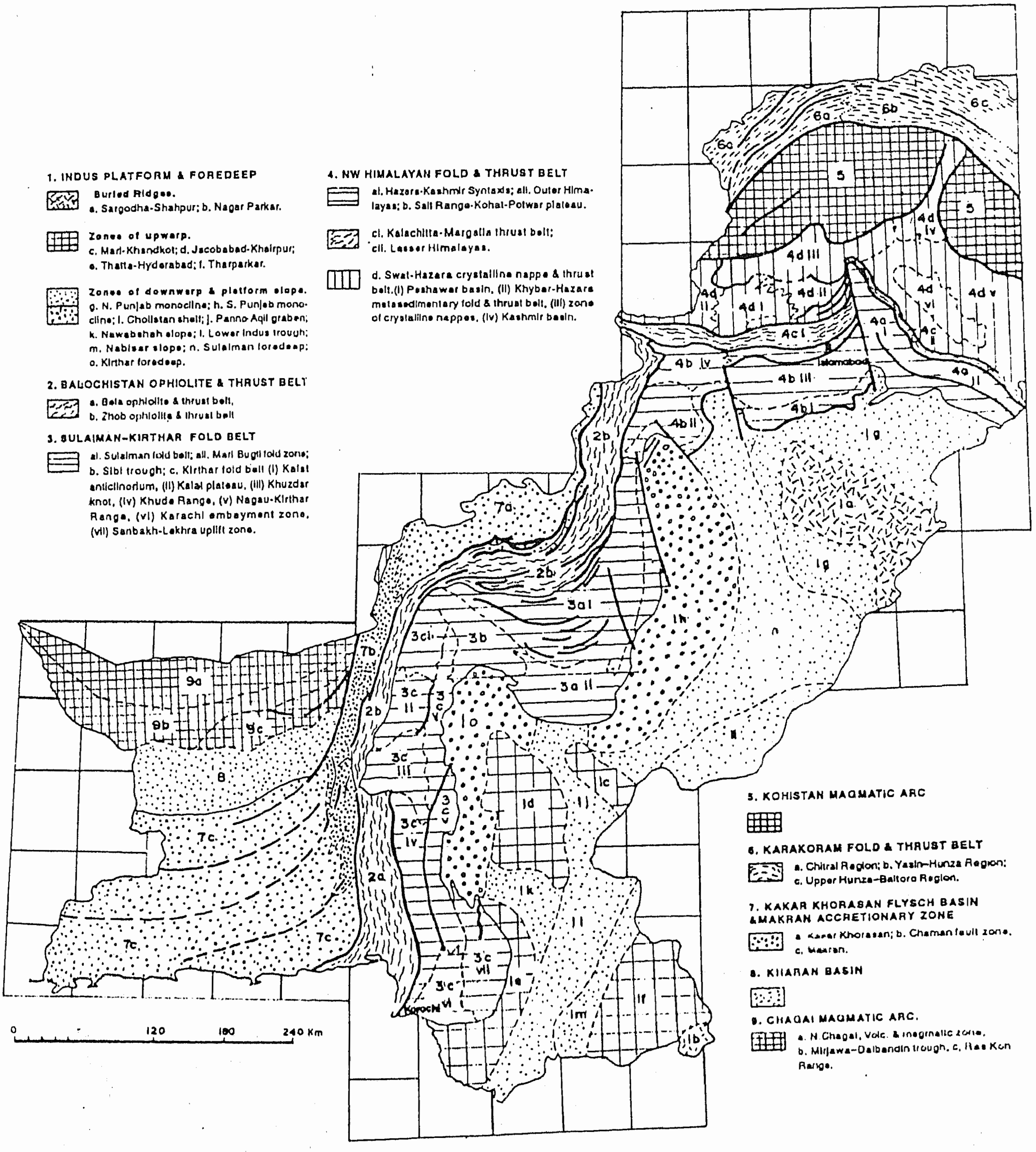

Fig. 2.1. Map showing tectonic zones of Pakistan after Kazmi and Jan, 1997.

These are briefly described here in order to understand the regional tectonics of the area.

1). Indus Plateform and fore deep

This zone extends over an area exceeding 250,000 km^2 in southeastern Pakistan and includes the Indus Plain and Thar-Cholistan Deserts. It hosts more than 80% of Pakistan's' population, extensive coal deposits, huge deposits of iron, valuable oil and gas fields, potential for geothermal energy and vast groundwater reservoirs.

Gravity and seismic surveys, supported by limited bore hole data, indicate that in the eastern part Precambrian rocks form a gentle westward dipping monocline covered by a veneer of Mesozoic to Cenozoic marine to deltaic sediments. The sedimentary cover is relatively thin in the upwarp zones. The downwarps contain a thick sedimentary pile, particularly the foredeeps at the western edge of the plateform slope where the sedimentary cover is upto 10,000 m thick.

STRUCTURAL ZONES

The Indus plateform and foredeep comprise the following main structural zones (Kazmi and Rana 1982, Balakrishnan 1977):

Buried ridges Sargodha-Shahpur ridge Nagar Parkar ridge.

Zones of upwarp	Mari-Khandkot high Jacobabad-Khairpur high Thatta-Hyderabad high Tharparkar high.
Zones of downwarp and plateform slope	Northern Punjab monocline Southern Punjab monocline Cholistan shelf Panno Aqil graben Nawabshah slope Lower Indus trough Nabisar slope.
Foredeeps	Sulaiman foredeep Kirthar foredeep.

These structural zones are shown in Figure 2.1.

BASEMENT ROCKS AND STRUCTURES

Precambrian basement rocks (Kirana Group), crop out in the form of small monadnocks in the Sargodha-Shahkot region. These are the exposed summits of the buried Sargodha-Shahkot ridge. Precambrian igneous rocks (Nagar Parkar Igneous Complex) crop out in the form of small scattered hillocks in Nagar Parkar area of Thar Desert. In the eastern part these rocks lie at shallow depths and gently slope westward.

Geophysical surveys (Balakrishnan 1977, Farah et al. 1977, Seeber et al. 1980,Malik et al. 1988) and remote sensing studies (Kazmi 1979a, Kazmi and Rana 1982) indicate that the basement is extensively traversed by NNE to NE, NNW and E-W trending faults. In Sindh they are largely concealed beneath the Deccan Trap basalts and younger sedimentary rocks. Subsurface seismic profiles indicate that in the foredeep zone and in Jacobabad-Khandkot zone some of the faults are likely to be post Eocene (Ligocene) and post Miocene (Raza et al. 1990a, Ahmed et al. 1992). Satellite photographs reveal an extensive network of lineaments and some of these are likely to be traces of buried basement faults. Such lineaments are the common features in other major shield areas of the world (Wise 1968, Withington 1973).

Most of the Late Cretaceous basement faults and rift structures are likely to be associated with detachment of the Indian plateform Gondwanaland, whereas the Tertiary faults may have resulted from bending of the crustal plate due to collison and rebound relief tension or compression release. Seismic studies and fault plane solutions indicate that some of these faults are extensional features, while others are strike slip faults (Seeber et al. 1979). The Punjab Seismic zone is comprised of buried active faults. Along the fold belt region, the western margin of the foredeep is seismically active and contains a number of active faults (Kazmi 1979a, 1979c).

SEDIMENTARY COVER

The Indus plateform and foredeeps are covered by unconsolidated Quaternary deposits with a maximum thickness of up to about 500 m. They constitute a vast groundwater reservoir. They are underlain by Siwalik molasse in northern and western part of the plateform and in then foredeep region. The Quaternary deposits are underlain by post-Eocene, largely fluviatile deposits (Nari and Murree Formations). In southern part of the plateform, east of Indus, the Quaternary deposits are underlain by Paleogene marine and deltaic sedimentary rocks. This shallow Cenozoic sequence is likely to contain substantial secondary groundwater aquifers in non-marine facies and vast deposits of coal have been already proved in Lower Paleogene sequence of Sindh.

The Precambrian and Paleozoic sequence is restricted to Punjab part of the plateform and the Sulaiman foredeep. Structurally the sedimentary cover of Indus plateform and foredeep is comprised of several large, gently dipping anticlinal flexures and fault blocks. Oil and gas reserves have been found in some of these structures. In the Punjab part of the plateform gas reserves have been found in Mesozoic sandstones at Nandapur and Panjpir.

North and west of Indus plateform and the foredeeps, the sedimentary cover has been deformed intensely by collison of the Indo-Pakistan plate with Eurasia. It forms a broad and extensive fold-and-thrust belt characterised by fold festoons with arcuate or sinuous fold axes and intervening sharp structural flexures the "syntaxis". The northern and western margins of this zone are characterised by sutures and obducted masses of ophiolite, whereas the southern and eastern part of the zone, on the other hand, is comprised of contorted fold and thrust belts (Fig. 2.1).

2) Northwest Himalayan Fold-and-Thrust Belt

The Northwest Himalayan fold-and-thrust belt occupies a 250 km wide and about 560 km long, irregularly shaped mountainous region stretching from the Afghan border near Parachinar, upto the Kashmir Basin. The Hazara-Kashmir and Nanga Parbat Syntaxes form its eastern margin. It covers all the terrain between the Main Mantle Thrust (MMT) in the north and the Salt Range Thrust in the south. This region is comprised of the mountain ranges of Nanga Parbat. Hazara, southern Kohistan, Swat, Margalla, Kalachitta, Kohat, Sufaid Koh, Salt Range and its western extension.

A major thrust fault, the Panjal-Khairabad Fault divides the NW Himalayan sequence into a deformed southern zone.

The Himalayan crystalline belt is comprised of the exposed northern margin of Indo-Pakistan crustal plate and it is characterised by intensely deformed, tightly folded and imbricated Precambrian to Early Mesozoic metamorphic and igneous rocks. Southward these crystalline rocks have been thrust over the Kurram-Cherat-Margalla thrust belt which is comprised of several thrust sheets of largely unmetamorphosed Precambrian to Paleogene rocks. Further to the south, the latter sequence has been emplaced over the Kohat-Potwar fold belt which terminates southward in the Salt Range and Trans-Indus Ranges. The Kohat-Potwar region is characterised by Paleogene and Precambrian evaporites which effectively decouple the sediments from the basement and control the tectonics of this belt through formation of decollement zones and thrusts having upto 100 km south-ward translation (Lilie et al. 1987).

The eastern margin of the NW Himalayan fold-and-thrust belt in Pakistan comprises the north-south trending Hazara-Kashmir Syntaxis and further to the northeast, the Nanga Parbat-Haramosh Massif. These syntaxes separate the above fold belt from the Central Himalayan fold-and-thrust belt of India.

3). Kohistan Magmatic Arc

Kohistan is an intraoceanic island arc bounded by the Indus Sture zone

(MMT) to the south and the Shyok Suture zone (Main Karakoram Thrust or KMT) to the north. This E-W oriented arc is wedged between the northern promontory of the Indo-Pakistan crustal plate and the Karakoram block. The northern and western part of the arc, along MKT, is covered by a sequency of Late Cretaceous to Paleocene volcanic and sedimentary rocks. This sequence is comprised of several formations. The central part of the arc terrain in mainly composed of Kohistan Batholith gabbro and diorite, followed by more extensive intrusions of gabbro, diorite and granodiorite, which are intruded by much younger dykes and sills of leucogranite.

The southern part of Kohistan is comprised of a thick sequence of mafic and ultramafic rocks. These rocks may be divided into three teconometamorphic complexes separated by major thrust zones.

4). Karakoram Block

This 70 to 120 km wide and 1,400 km long structural zone comprises the Karakoram crustal plate which is one of the fragments of the Cimmerian colpege derived from Gondwanaland and accreted to Eurasia. In the north, the South Pamir Fault (Desio 1979) separates it from the Southern Pamir Block. To the east it is terminated by the Karakoram Fault and to the west by the Sarobi Fault.

KARAKORAM BATHOLITH

The most ubiquitous feature in the Karakoram is the Axial Batholith (Ivanac et al. 1956, Desio 1979), which forms the central part of this belt and hosts the tallest mountain peaks of the region, including K2. Along the northern margin of the Karakoram Batolith, near Baroghil Pass, there are small outcrops of pre-Ordovician granites. The granitic rocks and the surrounding sedimentary sequence have been metamorphosed to varying extent during at least three main thermotectonic events and a later retrograde phase. The Karakoram Batholith divides the region into a northern and southern sedimentary belt. The western part of the region, the Tirich Mir zone, is separated from the main body of the Karakoram belt by the Tirich Fault.

TIRICH MIR ZONE

This zone is largely comprised of the highly deformed and imbricated metasediments of the Arkari Formation (Jurassic) which mainly consists of dark grey phylites with subordinate quartzites and marbles. Southward it is intruded by numerous stocks and sills of leucogranites and the metamorphic grade increases to the amphibolite facies.

SOUTHERN SEDIMENTARY BELT

The Southern belt forms an arcuate, north-verging belt of highly deformed and imbricated metasediments, thrust southward over the Kohistan-Ladakh sequence along the Shyok Suture zone or MKT. In the western part of the belt, between Chitral twon and Mastuj, Late Paleozoic to Tertiary rocks are exposed. The Darkot Group is the oldest sedimentary unit with Carboniferous to Permian fossils. It consists of slates, schists and quartzites intercalated with crystalline limetone (Ivanac et al. 1956).

NORTHERN SEDIMENTARY BELT

The Northern sedimentary belt extends westward from Shaksgam, through Upper Hunza and Chapursan Valleys, up to Baroghil Pass. It then bends southward and follows the Yarkhun Valley. In the Upper Hunza region, it consists of three tectonostratigraphic units separated by two major faults. An E-W trending reverse fault, the Upper Hunza Fault, has placed the southerly Gujhal Unit over the centrally located Sost Unit. The sedimentary sequences in these tectonostratigraphic units range from Permian to Cretaceous in age and are largely comprised of interbedded limestones, shales and sandstones (Zanchi 1993, Gaetani et al. 1995).

STRUCTURE

Structurally the Karakoram block is characterised by broad, asymmetrical to tight, isoclinal folds which are commonly imbricated. Small isoclinal, recumbent folds, chevron folds, drag folds and crenulations are common. The Karakoram block has undergone multiple deformation since the Cambrian. Parts of Karakoram (Baltoro, Masherbrum, Mango Gausar) have undergone at least four more deformations since the Kohistan-Karakoram collision. According to Searle (1991), the early two deformations, crustal thickening and regional metamorphism, the third one occurred during Oligocene as indicated by intrusion of under formed Early Oligocene granites in sheared thrust sheets, and the last one took palce during Mio-Pliocene (biotite-muscovite dates 15-5 Ma) and was associated with rapid uplift.

LOCAL GEOLOGICAL SETTING

The Gandghar Range is located in the Hazara Division, some 40 km north west of Islamabad. It forms a partial barrier between the plio-pleistocene Haripur and Peshawar basin (Fig. 2.2). The Gandghar Range is bounded in the east by the Khanpur Hills and in the south-east by the Margala Hills. The Gandghar Range strata are transitional between the high grade metamorphic and plutonic rocks to the north and unmetamorphosed foreland basin strata to the south. It is structurally continuous with the northern block of the Attock-Cherat Range (Yeats & Hussain, 1987) and records the transition between the Himalayan rocks and foreland basin strata.

The Gandghar Range, Attock-Cherat Range, Margala Hills and Kalachitta are collectively termed the Hill Ranges separated from each other by alluvial plain. These Ranges are composed of sedimentary and meta-sedimentary formations where some of the non-metallic mineral occurrences have been reported. These minerals occurrences may be favourable for the presence of economic rocks and minerals such as limestone, slate, shales, clay and sand. Rocks of the Hill Ranges are brought to the surface along major ramps branching from a single detachment surface (Yeats & Lawrence, 1984).

The Gandghar Range was probably uplifted along the Panjal Fault (Fig. 2.2) which was first reported by Wadia (1957). This fault form the Hazara-Kashmir syntaxis.

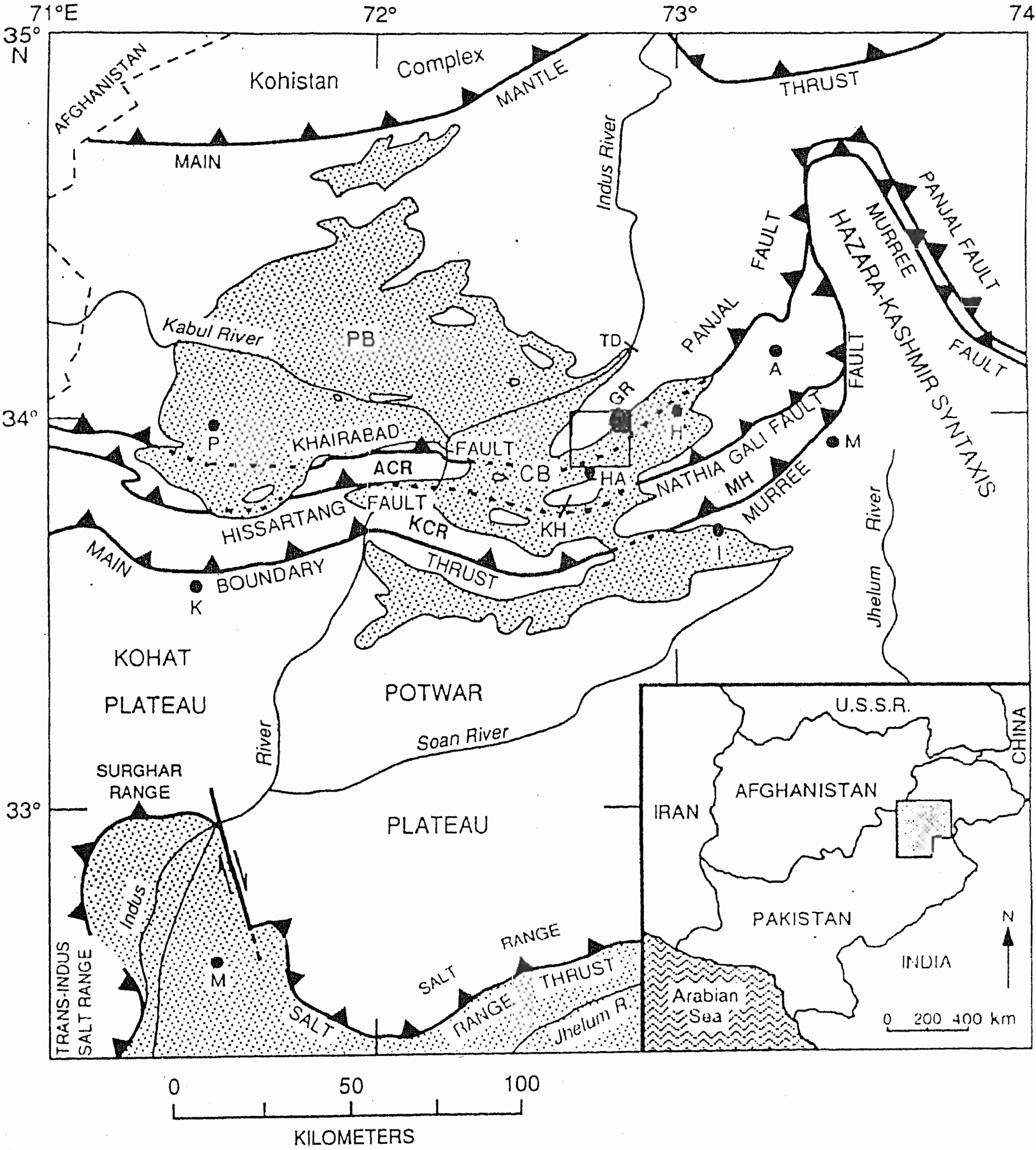

Fig. 2.2. Tectonic map of northern Pakistan, showing major structural boundaries. P = Peshawar, PB = Peshawar basin; TD = Tarbela Dam; A = Abbottabad; M = Murree; I = Islamabad; MH = Margala Hills; H = Haripur, GR = Gandghar Range, HA = Hassan Abdal: KH = Kherimar Hills; CB = Cambellpur basin; ACR = Attock Cherate Range; KCR = Kala Chitta Range; K = Kohat; M = Mianwali. (After Hylland et al., 1988).

The panjal was originally recognised by Wadia (1957) in the area constituting the Hazara-Kashmir syntaxes. The Gandghar range displays different stratigraphic succession in south and north of the range. According to Riaz (1990) and Riaz et al. (1991) the northern Gandghar range include four stratigraphic succession (Fig. 2.3). These are;

Rock unit	**Age**
Intrusive rocks	Permian (?)
Tanawal formation	Early to middle Cambrian (?)
Shekhai Formation	Late precambrian (?)
Shahkot formation	Precambrian
Manki formation	Precambrian

The basal sequence (Manki formation) is mainly comprised of slates and phyllites which are successively overlain by two carbonate lithologies (Shahkot and Shekhai Formation) and an alternating sequence of quartizite and phyllite (Tanawal Formation). The entire succession is profusely intruded by basic igneous dikes of unknown age. The range is divisible into a western and an eastern block, separated by the Baghdarra fault (Riaz et al (1990).

Manki Formation

The Manki formation forms a major bulk of the strata comprising the hanging-wall of the Baghdarra fault (Fig. 2.3). The formation is mainly composed of argillites, slates, phyllites, sandy phyllites and minor limestone. The argillites are gray, greenish gray and brownish on weathered surfaces. The slates are dark grey to black and fine grained, **(Photo 1).**

Shahkot Formation

The small patches of limestone occurring all along the contact of the Manki and Tanawal formation are remnants of the basal limestone of the Shahkot formation (Fig. 2.3). The maximum thickness of the limestone of Shahkot formation, exposed in the northern Gandghar range is 3 meters. The entire formation is very well exposed in the southern Gandghar (Hylland, 1990) and also in the Attock-Cherat Range (Hussain, 1984; Yeats and Hussain, 1987).

The Shahkot formation consists of limestone, argillite and shale. The limestone is fine to medium grained, medium-bedded, yellowish-gray on fresh surfaces and brownish-gray on weathered surface. It contains patches of white Chert and is extremely hard.

Shekhai Formation

The name Shekhai formation was actually assigned by Tahirkheli (1970) to a small out crop of dolomitic limestone, quartzite and shale in Shekhai village located at the northern slop of Attock-Cherat range. Similar type of lithology in Gandghar range was named as early Mohat Nawan limestone. Calkins et al. (1975) has latter on assigned a similar unit in the northern Gandghar range as the Kingriali formation of triassic age. Based on its similar stratigraphic position and identical lithological characters as those of the Shekhai formation of the Attock-Cherat Range, **Photo 2**). Riaz (1990) and Riaz et al. (1991) has distinguished as the "Shekhai Formation".

The Shekhai formation is only exposed in the southeastern part of the northern Gandghar range. It forms the foot-wall strata of the Baghdarra fault (Figs. 2.3 & 2.4). The formation attains its maximum thickness south of the Ali Masjid stream, whereas, in the north its outcrop gets narrower because of slicing by the Baghdarra fault, which runs close to the eastern front of the range, (Riaz, 1990).

The Shekhai formation is composed of limestone and marble with subordinate argillite, shale and quartzite, **Photo 3)**. The limestone, which is the main part of this study, is fine- grained, thin-to medium bedded, with occasionally thicker beds or massive units. It is usually yellowish-gray to light and dark-gray but brownish-gray and light-brown or pink beds are also seen. A few beds show parallel alignment of iron streaks defining a mineral lineation. The weathered surfaces are typically light-gray or light-brown and are relatively smooth. The limestone is locally metamorphosed to white or creamy marble in the close vicinity of basic igneous intrusions.

Argillite and shale occur as intercalations. They are mostly green, greenish gray, thinly laminated, occasionally calcareous and weather to greenish-brown powdery stuff. The base of the Shekhai formation is not exposed in the northern Gandghar Range. However, in the southern Gandghar Range the Shekhai formation has a conformable lower contact with the Utch Khattak formation. The upper contact of the Shekhai formation is faulted against the Manki Formation.

The formation is about few hundred meters thick and is devoid of fossils. Based on its relative stratigraphic position in the Attock-Cherat range (Yeats and Hussain, 1987) and in the southern Gandghar Range (Hylland, 1990), it is tentatively assinged a late Precambrian age by Riaz (1990).

Tanawal Formation

The Tanawal Formation is exposed on the southeastern and northwestern side of the northern Gandghar Range (Figs. 2.3 & 2.4). In the Gandghar Range the Tanawal Formation consists of three members: the basal conglomerate member, the middle quartzite-phyllite member and the upper Quartzite member.

The basal conglomerate represents an unconformity between the underlying Shahkot Formation and the overlying Tanawal Formation. The conglomerate member is exposed only in the western part of the northern Gandghar Range (Figs. 2.3 & 2.4).

The middle member is only exposed in the eastern part of the northern Gandghar Range (Figs. 2.3 & 2.4). This member consists of an alternating sequence of quartzites and phyllites. The upper quartzite member is exposed in the northwestern part of the northern Gandghar Range (Figs. 2.3 & 2.4). It is dominantly composed of quartzite with shaley or phyllitic partings.

Tanawal Formation has been assigned different ages by early workers. The most reliable age of the formation comes from the radiometric dating of the Mansehra Granite which includes the Tanawal Formation in northern Hazara, Riaz (1990).

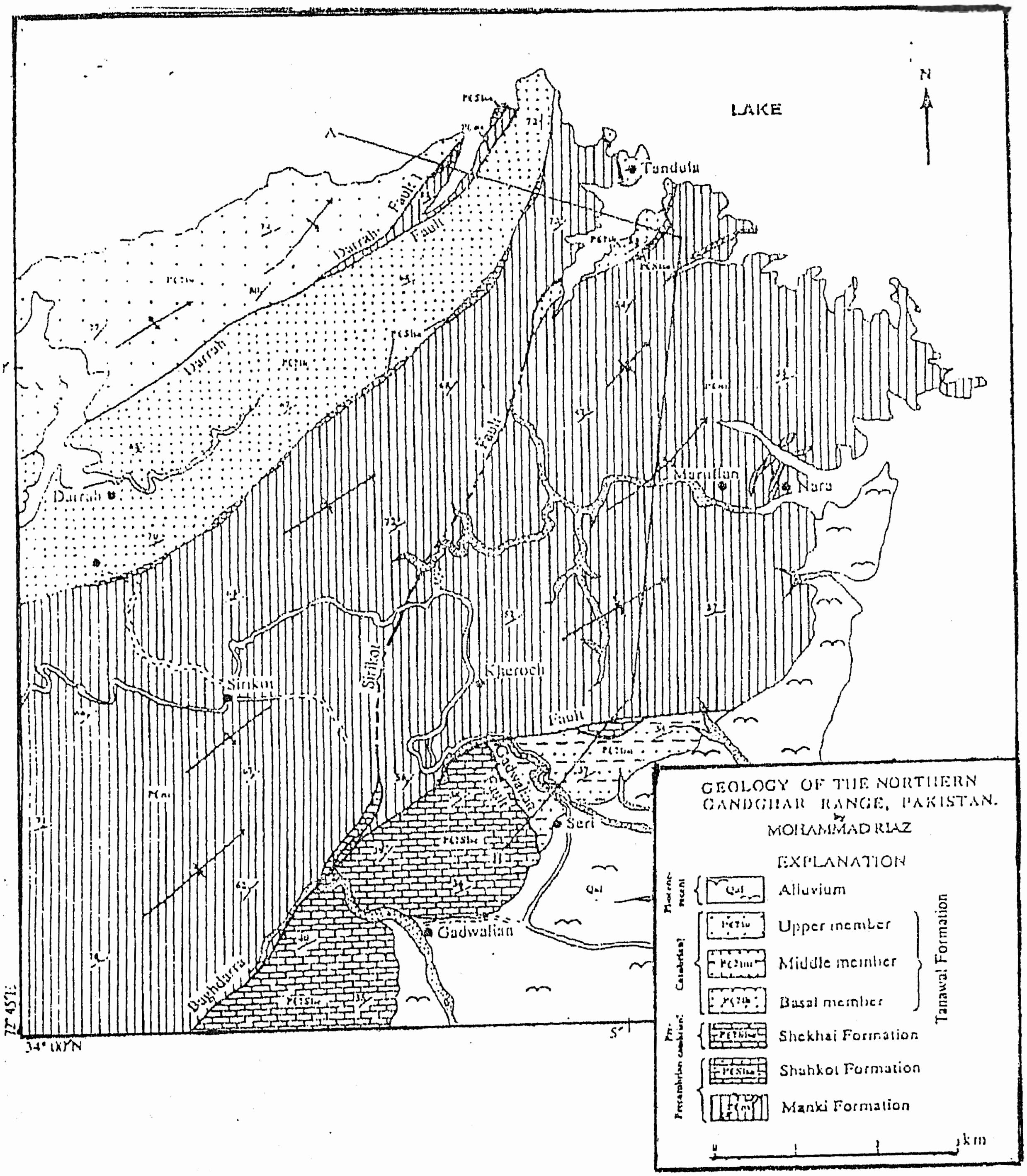

Fig. 2.3. Geological map of northern Gandghar Range. Line AB is the location of the Fig. Thickness of the Shahkot limestone is much exaggerated. (After Hylland, 1991).

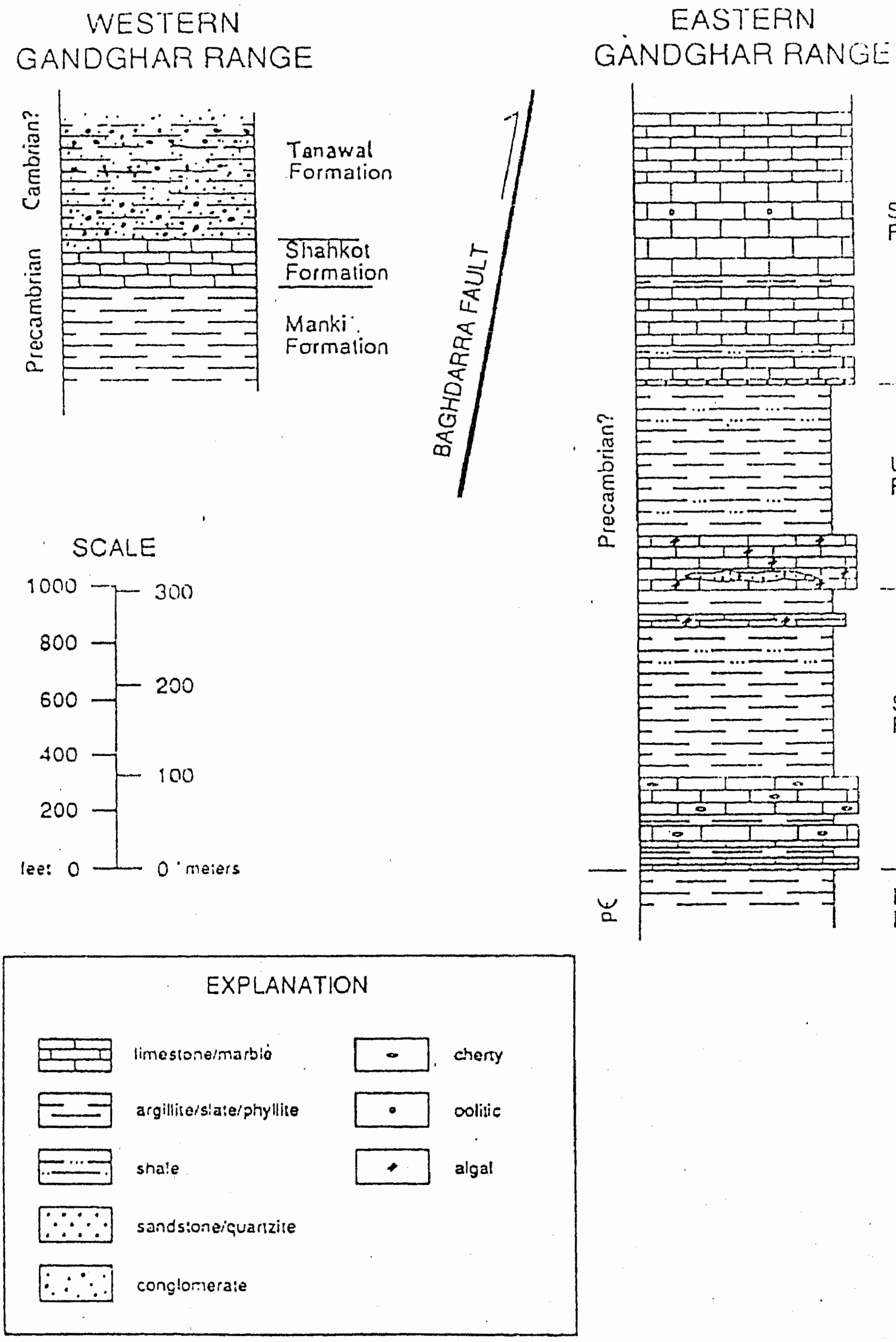

Fig. 2.4. Stratigraphic column of the eastern (from Hylland et al., 1988) and western Gandghar Range.

Intrusive Rocks

The entire Gandghar Range is intruded by basic igneous rocks which occur as dikes and sills. The same kind of dikes have also been reported from the Attock-Cherat Range, (Hussain, 1984; Karim and Sufyan, 1989), from the western Hazara Ranges (Shams and Ahmed, 1968; Ahmed 1985) and from the Peshawar basin (Riaz, 1990). These intrusive bodies are generally less than 5 meters thick. They are diabasic in nature and are structurally deformed alongwith the country rocks.

Utch Khattak Formation

The rocks of Utch Khattak formation are generally exposed in the southeastern Gandghar Range in the foot wall of the Baghdara fault, (Fig. 2.5). The Utch Khattak has conformable contact with the underlying Shahkot Formation and overlying Shekhai Formation.

The Utch Khattak formation is composed of limestone, argillite, and shale (Figs. 2.5, 2.6 & 2.7). Limestone occurs at the base of the formation and is quite distinctive. It is composed of fine-to-medium-grained, thin-bedded, blush-gray to darkgray limestone generally has clayey material, **(Photo 4)**. Occasionally calcite veins crosscut both the carbonate and clay material. In place, stromatolites are well developed. The limestone varies in thickness from approximately 10 m to 70 m and is overlain by dark greenish-gray, thinly-laminated argillite with subordinate interbeds of light-gray to light-brown thin bedded shale.

An intraformational conglomerate within the Utch Khattak formation contain clasts of Manki formation and Shahkot formation, indicating that the Utch Khattak formation is younger than both, Riaz (1990). This conglomerate is exposed in both the Gandghar range, at the mouth of the Canyon near Amgah and the Attock-Cherat Range, just west of the Indus river (see Tahirkheli, 1970 and Riaz, 1990).

The Gandghar ranges are characterized by numbers of fault such as Gadwalian fault, Baghdara fault and Darrah fault (Fig. 2.3).

The Gadwalian fault

According to Riaz (1990) the Gadwalian fault is a small fault, named after the Gadwalian village, which is located about 14 km west of Haripur (Fig. 2.3). This fault was earlier mapped as a normal contact between the Shekhai and Tanawal Formations (Calkins et al. 1975). It birngs the Shekhai limestone (foot-wall) against the Tanawal formation (hanging-wall). The fault is not visible as a line or zone and is mainly covered by scree (Riaz, 1990).

The Baghdarra fault

The Baghdarra fault is named after the Baghdarra village by Riaz (1990) which is located approximately 3 km southwest of the Pirthan, the highest peak in the southern Gandghar Range (Fig. 2.3). The Baghdarra fault juxtaposes the Precambrian Manki formation and the Proterozoic Shekhai and Tanawal Formations (Fig. 2.3). The Manki formation is exposed in the hanging-wall of the Baghdarra fault and the foot-wall is composed of Shekhai and Tanawal formations.

The Sirikot fault

The Sirikot fault is named after the Sirikot village by Riaz (1990) which is located approximately 19 km west-northwest of Haripur, (Fig. 2.3). The major portion of the fault runs through the Manki formation, but the northern part of the fault brings the Manki formation against the basal conglomerate member of the Tanawal formation (Riaz, 1990).

The Darrah fault

This fault is located in the extreme northwest of the Gandghar range. It is named after the Darrah village by Riaz (1990) which is located about 4 km northwest of the Sirikot village, (Fig. 2.3).

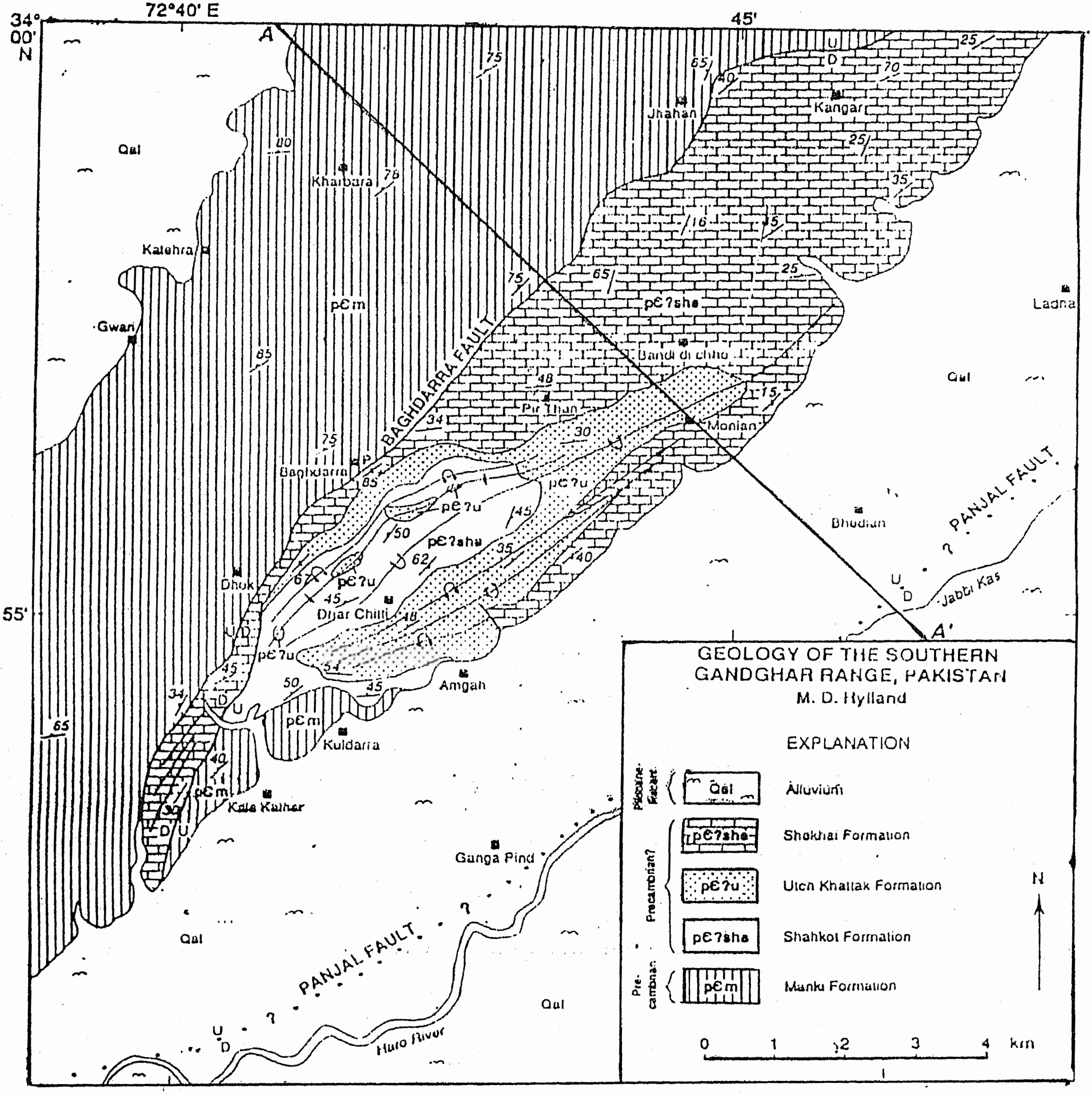

Fig. 2.5. Simplified geologic map of the southern Gandghar Range. Base from Survey of Pakistan topographic sheets 43 (C/9 and 43 C/13. A-A is line of cross section shown in Figure 5.P = oriented phyllite sample locality discussed in text. (After Hylland et al., 1988).

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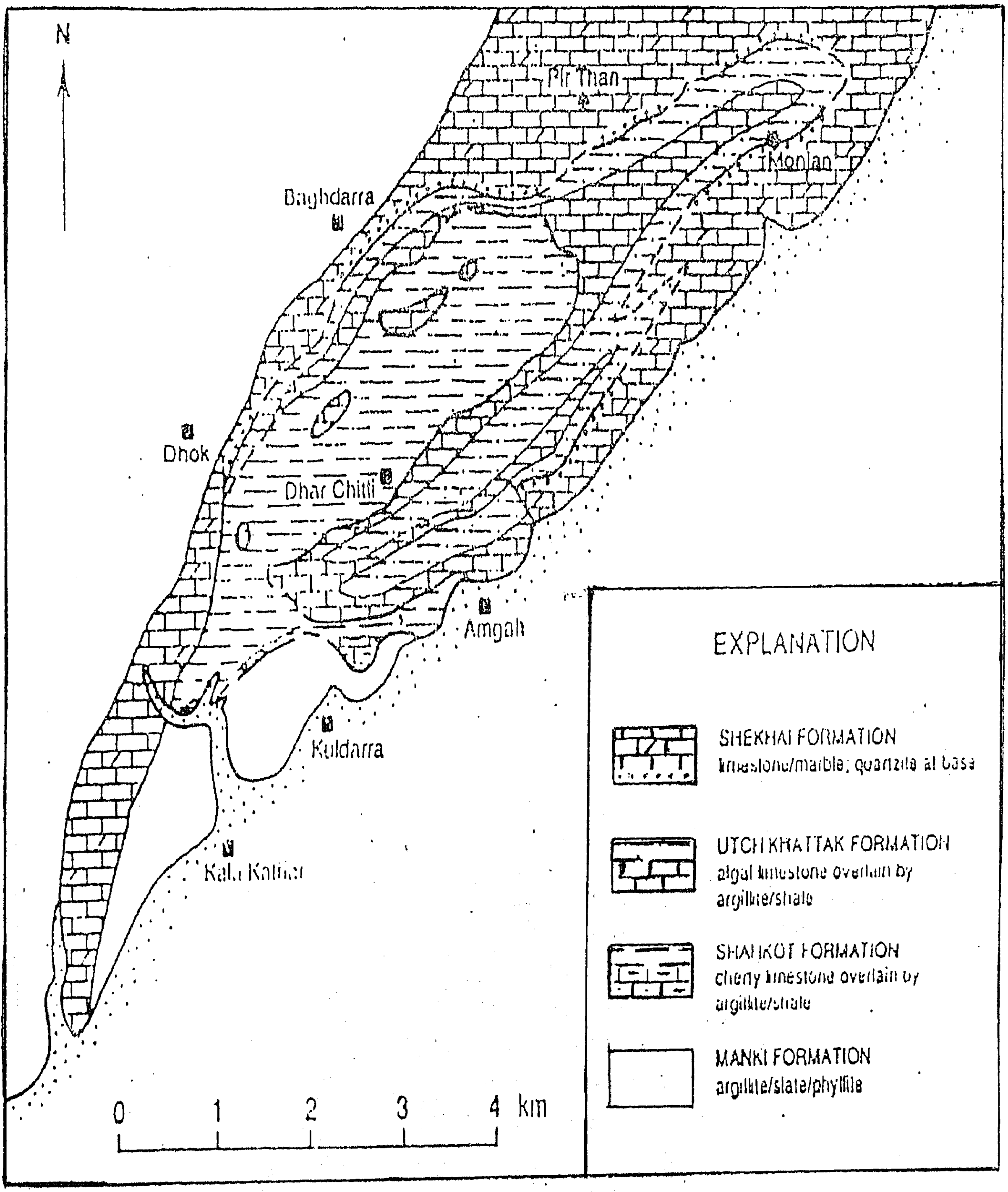


Fig. 2.6. Lithologic map of the southern Gandghar Range in the vicinity of Dhar Chitti, showing basal Shekhai quarzite and distribution of limestone versus argillite and shale in Shahkot and Utch Khattak Formations. Formation contacts (heavy lines) dashed where approximately located. (After Hylland et al., 1988).

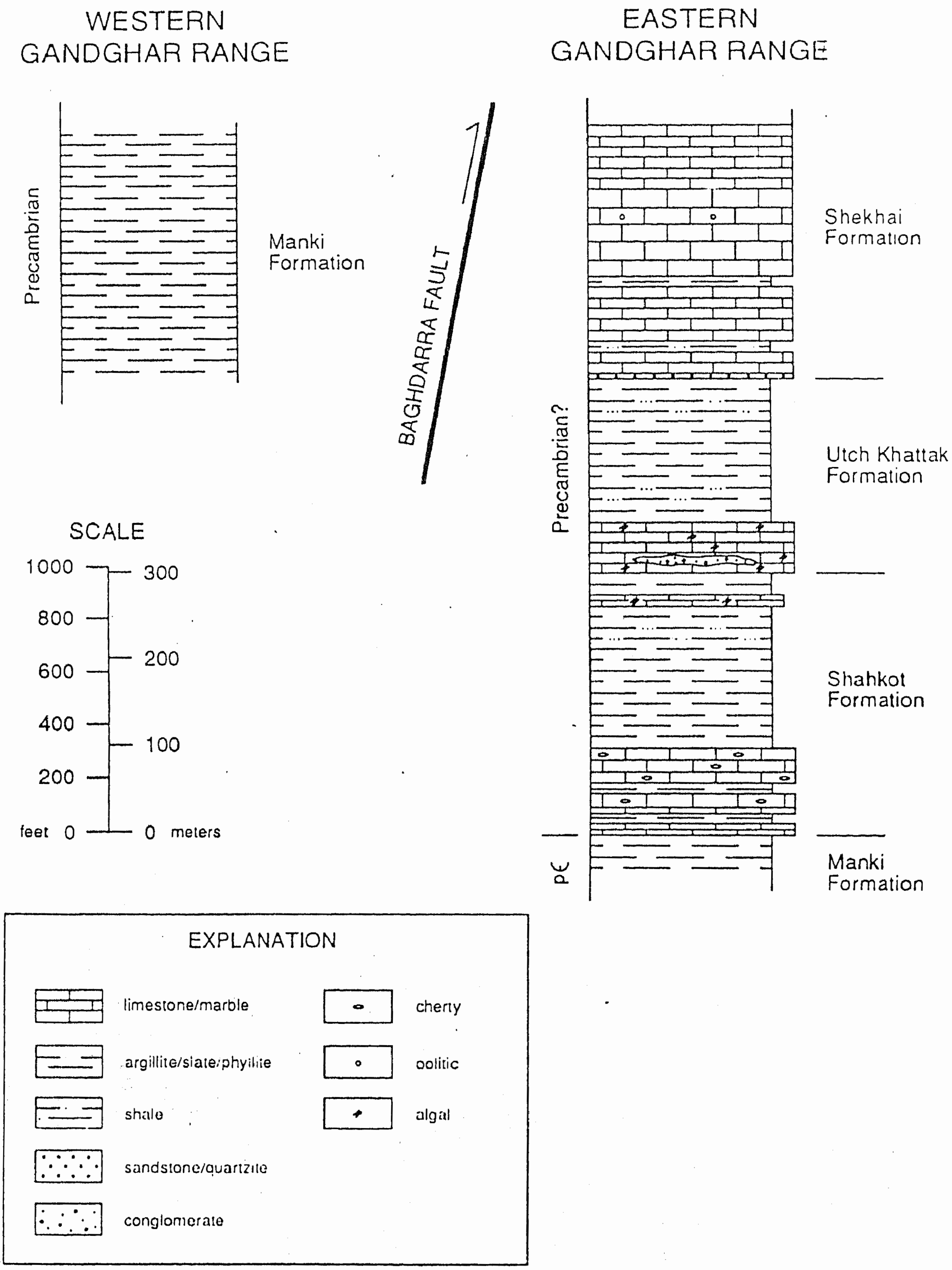
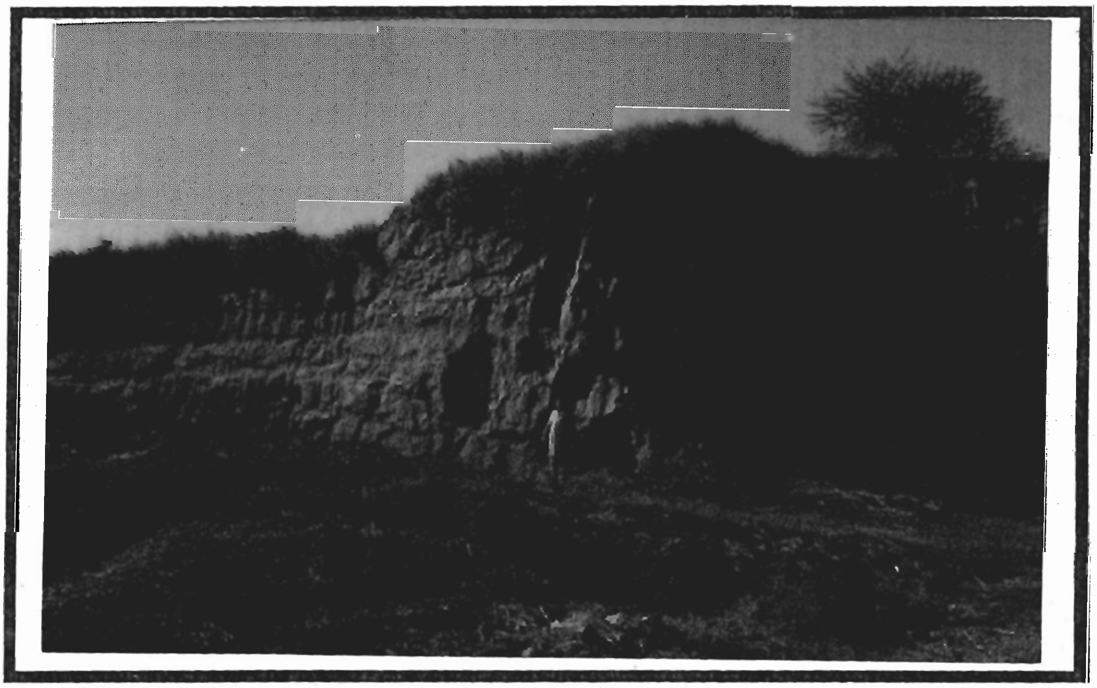


Fig. 2.7. Composite stratigraphic column showing rock units comprising two structural blocks juxtaposed along the Baghdarra fault in the southern Gandghar Range. (After Hylland et al., 1988).

(Photo 1). A view of the phyllite deposits in Manki formation.

(Photo 2). A view of the outcrop of limestone exposed in at Shekhai formation.

(Photo 3). Delomatic limestone, quartzite and shale at Shekhai formation.



(Photo 4). The clay deposits in the Haripur plain.

CHAPTER III

CEMENT MANUFACTURING

The history, types of cements, raw material for cement manufacturing, proportioning of raw material and their manufacturing process have been taken from the chemistry of cement and concrete by Lee (1976), cement raw materials in Gilgit agency by Shah et al., (1982) and Encyclopedia of chemical technology V.4, by Kirk and Ottomer (1964) and are discussed briefly in this chapter.

HISTORY

Cement may be defined as adhesive substances capable of compacting fragments or masses of solid matter together. The name comes from Latin word "coementum" the name of Limestone whose chips were used in morter more than 2000 years ago in Italy. A cement was used by Egyptians in constructing the pyramids. Greeks and Romans used volcanic tuff mixed with lime for cement purposes and a number of these structure are still standing in an excellent state of preservation. During the middle ages "Cement" or "Sement" generally denoted mortar. Today it means any binding material mostly used for a hydraulic binding material capable of uniting into a cohesive mass that are not in themselves adhesive. There are many kinds of cement but the most important one is Portland cement. The name Portland was given by Joseph Aspdin (1824), because the cement, when mixed with water and sand, hardened into a block that resembled a natural limestone quarried on the Isle of Portland in England.

Now the portland cement is generally prepared by burning powdered limestone mixed clay or shale to a temperature of 1500^{0}C (2,800 F). The resulting glossy clinker composed of silicates and aluminates, is ground so fine that it passes through a screen with 40,000 openings per square inch. A small amount of about 3-6 percent gypsum is added to the finished product to slow down the rate of hardening. Portland cement is distinguished from other kinds of commercial cement by the different phases of which it is composed, and fulfilling the particular standard specifications. Under these requirements white cement and oil well cement may be portland but high alumina and natural cement can not be so classified. Some cements are mixture of portland with other materials as masonary, slag, and pozzolon cements.

Portland cement (as distinguished by sintering in the Kiln) was first made in the United States by David Saylor in 1871 in vertical Kilns in Copley, pennsylyania. The first rotary kiln was introduced in 1899 and within a decade the vertical Kiln for portland cement in the United States became obsolate. The efficiency of the vertical Kiln has been greatly improved, and in many countries this type of Kiln is used extensively.

Upto the turn of century, low-temperature natural cements were produced in a larger amount than high temperature portland but after that time they became relatively unimportant and their production became very limited. The portland cement of today differs from that of many years back and undoubtedly future requirements will necessitate a different cement.

PORTLAND CEMENT

Portland cement is a powdered material which, with water forms a paste that hardens slowly, bonding inter mixed crushed rock or gravel and sand into rock, hard concrete. It is made by sintering a mixture of raw materials one of which is composed mainly of calcium carbonate (as limestone) and the other of aluminum silicates (as clay or shale). During the sintering process, chemical reactions take place producing nodules, called clinkers, which are composed principally of calcium silicate and aluminali. When the clinkers is pulverized with a small amount of gypsum, the resulting powder is the portland cement of commercial use.

Roughly the limestone component is about 70 to 75 percent by weight of the total raw materials of cements, the other being clay (25%) and Gypsum (4%). About 123 tons of limestone, 0.31 tons of clay and 0.41 tons of gypsum, are required for producing one ton of cement (Ghani 1962), therefore, for selecting a site for establishing a cement factory, attention should be paid on the availability of Lime Stone.

For manufacturing portland cement, the proportion of limestone in a mixture will vary in accordance with the composition of clay or shale. A suitable mixture of limestone and clay, roughly contain the following proportions of ingredient. $CaCO_3$ (75%), SIO_2 + AL_2O_3 + Fe_2O_3 (20%); Mgo and alkalies (5%). The low early strength in cement is produced when the lime is too low and unsoundness when it is too high. In order to increase the early strength it is necessary to raise the lime content or grind finer or mixture. A high lime cement rapidly hardens but a slightly lower lime mixture gives a cement which continues to become stronger over a long period of time.

The following main processes are involved in the manufacture of cement:

i. Grinding and mixing of suitable raw material in correct proportion.

ii. Burning of "raw mix" at specified temperature.
iii. Grinding the burnt product "Clinker" with gypsum as to give a finished product of cement.

TYPES OF CEMENTS

Many types of cements are manufactured for their use in different types of building material. These are briefly mentioned as follows:

Rapid hardening portland cement: It is normally ground finer and slightly altered in composition. Its setting time is similar to ordinary cement but it develops its strength more rapidly.

Quick-setting Portland cement: It differs only from a normal Portland cement in that its setting time is less. Its rate of hardening may be similar to that of ordinary or rapid-hardening Portland cement.

Water-proofed portland It is an ordinary portland cement to which a small proportion of calcium stearate or a non saponifiable oil is usually added during grinding.

Hydrophobic cement: It is a material obtained by grinding portland cement clinker with a water repellent film-forming substance such as a fatty acid in order to reduce the rate of deterioration under unfavourable storage or transport condition.

Low-heat portland cement: It is a material in which the chemical composition has been to adjusted as to reduce the heat of hydration. Its strength is, however, lower than that of ordinary Portland cement.

Sulphate-resistant portland cement: It is a material with a composition so adjusted as to give it an increased resistance to sulphate-bearing water.

Kuhl cement: It is a portland cement of low silica and high alumina and iron oxide content that has been made in a number of European countries and Japan. In strength it corresponds to rapid-hardening portland cement.

Iron ore cement or erz cement: It is a type of Portland cement at one time manufactured near Hamburg in Germany with iron or replacing the normal clay.

It originally had a high iron oxide (about 8 percent) and low alumina (about 2 percent) content and was light to chocolate brown in colour and with a higher specific gravity, about 3.3. Later the AI_2O_3: Fe_2O_3 ratio was some what increased and now its, place has been taken by Ferrari cement.

Ferrari cement: It is a portland cement with, originally, a ratio of alumina to iron oxide of 0.64, but now often approaching unity, and having improved resistance to chemical attack. It falls in the class of sulphate resistant portland cements.

Expanding or non-shrinking cement: It is a cement which expand slightly on hardening or have no shrinkage on subsequent air-drying. They are manufactured in the USA and USSR and were formally made also in France.

Air-entraining cement: It is a portland, or portland blast furnace, cement to which a small amount of an air-entraining agent has been added during grinding. Air-entraining agents may also be used as additions to a concrete mix instead of being interground with the cement.

According to Clausen (1960), and Bogue (1947) some of the major kinds of hydraulic cement are recognized on the basis of composition, characteristics or uses.

White portland cement: It is one in which the iron oxide is so reduced in concentration and the manufacture is so controlled that the product is practically white. This requires the selection of limestone and clay of exceptional purity. Unusual precautions against iron contamination are necessary throughout the operations in the plant. White cement is of special importance in architectural concrete where a pure white is required or where brilliant colors are sought by the addition of pigments or colored aggregates.

Colored cements: These are usually made by intergrinding 5-10% of pigment with white cement. The pigments must be unaffected by the constituents of the cement and durable in the exposures to which they will be subjected. Iron oxides are used to give red, yellow, brown, and black colors, manganese dioxide for brown and black, cobalt blue for blue, chromium oxide for green, and carbon black for black.

Oil well cement: It is designed for use under high temperature and pressure by modification in the composition or heat treatment.

Masonary cement: It is used in mortar for bonding brick and masonary, and not to any particular composition. Many kinds of commenting materials have been used in masonary cements including, as reported in 1934, hydraulic limes, hydrated limes, natural limes, blast furnace slag cement, and cement whose compositions, could not be positively determined as well as Portland cements with and without admixtures (Rogers et al., 1934). At the present time, masonary cements consist mostly of a finely interground mixture of portland cement and limestone, give high plasticity and water retention with an air-enteraining agent, and regulated in setting time by gypsum.

Natural cement: It is a product made by burning below sintering temperature an argillaccous limestone or a mixture of limestone with clay or shale.

This cement represents a type of hydraulic lime. Natural cement is made in both vertical and rotary kilns at temperatures of 850-1000^{0}C with the use of variously sized rock. This type of cement finds use in masonary projects that do not require the special qualities of the portlands.

Bauxitland cement: It is prepared when waste bauxite is substituted for clay or shale, the product is high in alumina and iron but low in silica, which give high early strength and used for refractory purpose.

Sord cement (magnesium oxychloride cement): It is prepared when magnesia is mixed with a solution of magnesium chloride (about 20%). A product is obtained which is useful only in absence of water.

Silikat cement of Sweden: It is produced by grinding a siliceous mixture with portland clinker.

Portland blast furnace slag cement: It is produced by grinding certain amounts of suitable blast furnace slag with portland cement clinker. The light weight froth or sandlike product that result is called granulated slag.

Granulated slag alone has no appreciable cementing action but in the presence of certain activators, such as Ca $(OH)_2$ and $CaSO_4$. Slag cements have lower early strengths than portlands but at a year may equal the latter.

The heat evolved on setting is relatively low, which has given slag cements some preference in mass concrete construction. They have superior resistance to corrosion in sea and sulfate waters and have found favour in such exposures.

Pozzolanas and Pozzolanic cements: A pozzolana may be defined as a material which is capable of reacting with lime in the presence of water at ordinary temperature to produce cementitious compound. Italian pozzolana/trass and Santeria earth are examples of naturally occurring pozzolanas are prepared by burning at suitable temperatures certain clays, shales, and diatomaceous earths containing a proportion of clay. Diatomaceous silica and some natural amorphous silica deposits may also form pozzolanas either with or without a heat treatment.

Pulverised fuel ash (fly-ash) is also used as a pozzolana. Pozzolanic cements are produced by grinding together portland cement clinker and a pozzolana, or by mixing together a hydrated lime and a pozzolana.

High-alumina cement: Aluminous, or high-alumina, cement is manufactured by heating until molten, or more rearely by sintering, a mixture of limestone and bauxite. The product is cooled and finely ground. High-alumina cement is characterized by a very rapid rate of development of strength and approaches closely to its final strength in twenty four hours after gauging. Its setting time is similar to that of portland cement. Its color is black.

PROPERTIES OF CEMENT

The classical method for studying the nature and behaviour of the phases that are produced by any given thermal treatment of any system is by the discipline of heterogeneous phase equilibrium. Previous studies on the system $CaO.AI_2O_3SiO_2$ were made in the first quarter of this century at the Geophysical Laboratory of the Carnegic Institution in Washington (Rankin & Wright 1915). Those studies were followed by the solution of many other systems of two, three, four and five components at the National Bureau of Standards in Washington, the Building Research Station in England, and similar laboratories in many other countries. As a result of these investigations, a clear picture is now available of the phases, their compositions, properties and fields of stability for the principal systems involved in portland cement. The several phases have been prepared and studied, their characteristics ascertained when mixed with water, and the physics and chemistry of their function as bonding agents were established, (Bogue, 1955).

The principal reactions in the formation of portland cement are those by which calcium oxide combines with the acidic components to form tricalcium silicat di-calcium, silicat tri-calcium aluminate and tetra-calcium aluminate. Lime and silica react readily to form C_3S. The reaction, $2\ CaO.SiO_2 + CaO - 3\ CaO.SiO_2$ is the essential reaction in the production of portland cement. That is because C_3S is the principal active hydraulic compound of the cement. The C_2S is slowly hydraulic when in the beta form, but early strength is dependent almost entirely on C_3S. The alumina combines with the lime to form C_3A, and with lime and ferric oxide to form C_4AF. The C_3A is rapidly hydrated in water with the evolution of considerable heat, but the product has little cementing value. The C_4AF has no cementing value. Magnesia remains in portland cement as MgO or periclase, which is limited in the specifications because it may give rise to excessive expansions. A small amount of lime also remains uncombined in the clinker as free CaO. During burning in the kiln, about 20-30% of liquid is formed, from which the constituent compounds will crystallize if cooled slowly. But if the liquid is cooled rapidly, a considerable amount of it will be supercooled and freeze to a glassy phase which imparts a different set of properties to the clinker and the cement. The C_3A in this phase is less reactive, and MgO dissolved in it is nonexpansive. Hence rapid cooling of clinker is often demanded for the control of C_3A and MgO activity. Recent data from the portland cement Association Laboratory indicate that there is no appreciable amount of true glass in commercially cooled clinkers. These results show that the interstitial phases are essentially completely crystalline to x-rays, although in a very fine state of subdivision.

Most of the clinker compounds take up small amounts of other components to form solid solutions. Best known of these phases is the C_3S solid solution called "alite", which has been assigned the formula $54CaO.16SiO_2.Al_2O_3.MgO$. This may be understood as eighteen molecules of C_3S in which one SiO_2 has been replaced by Al_2O_3, and another by MgO, (Nurse, 1960). The clinker phases are best observed by examining polished sections selectively etched with special reagents (Insley, 1936). The C_3S or "alite" appears as clear crystalline grains, the β-C_2S as rounded and twinned grains, the C_3A and glass as dark interstitial material, and the C_4AF as light interstitial material.

Some of the optical and thermal properties of the clinker compounds are given below.

Tricalcium silicate (C_3S) occurs as small, equidimensional colorless grains having refractive indexes α 1.718 and τ 1.724, and a very weak birefringence. The grains appear uniaxial or biaxial with a small axial angle; the optical character is negative. The C_3S is not stable with liquid of its own composition. It was formerly believed that C_3S dissociates at 1900^{0}C into C_2S and CO, but recent work at the Building Research Station in England indicates that this compound does not decompose at 1900^{0}C but, rather, melts incongruently at 2070^{0}C, forming CO and liquid. On cooling below 1000-1300^{0}C, C_3S decomposes slowly but, if cooling is not prolonged, it comes down to ordinary temperature in a practically unchanged state and remains relatively stable.

Dicalcium silicate exists in several forms, the interrelationship of which is not yet completely resolved (Nurse, 1960). The α form melts at 213^{0}C and inverts to the α' form at 1425^{0}C, which in turn inverts to the ß form at 670^{0}C. The ß form may invert to the τ form at any temperature below 525^{0}C, but may be stabilized to resist that inversion. The ß-C_2S forms rounded grains usually showing polysynthetic twinning and having refractive indexes α 1.717 and τ 1.735, with medium briefringence. The optic axial angle is large, and the optical character is positive. The τ-C_2S is prismatic in habit, refractive indexes α 1.642, ß 1.645, τ 1.654, briefringence medium, optic angle about 52^0, and optical character is negative.

Tricalcium aluminate forms isometric crystals having a refractive index of 1.710. It dissociates below its melting point forming CaO and liquid at 1535^{0}C. The iron phase approaches C_4AF in composition but takes up other components in solid solution. It melts congruently at 1415^{0}C. The compound is biaxial negative with a medium optic axial angle, and refractive indexes of α 1.96, ß 2.10, and τ 2.04. Other phases that may be present in clinker include isometric periclase (MgO), refractive index 1.737; isometric CaO, refractive index 1.83; and glass which varies with the composition.

The bonding properties of a cement-water paste are all associated with the reactions of the cement phases during hydration. Our understanding of cement hydration has been immeasurably enhanced by studies in many laboratories in recent years. According to Brunauer (1962), it has been found that the principal constituent of cement paste is a tobermorite gel which is produced by the hydration of the calcium silicates according to the following reactions:

$$2\ (3\ CaO.SiO_2) + 6H_2O - 3\ CaO.2SiO_2.3\ H_2O + 3\ Ca(OH)_2$$

$$2\ (2\ CaO.SiO_2) + 4H_2O - 3\ CaO.2SiO_2.3\ H_2O + Ca(OH)_2$$

A unique property of this gel is its specific surface which has been reported to be on the order of 300 m^2/g. Electron micrographs show predominantly long fibers, often rolled up in sheets. The dimention in the *c* direction is colloidal and verges on the molecular but that in the *b* direction is on the order of 1 μ or more. X-ray diffraction patterns indicate that the gel is very poorly crystalized, having a density of 2.70 g/cm^3, and an interlayer distance of 10.3 A. The mean diameter of the gel pores has been reported as 20-40 A (Powers & Brownyard, 1947).

The adhesion of the tobermorite particles to each other and to the embedded aggregates is responsible for the strength of concrete. More definitely, the surface area and porosity are responsible for the important engineering properties of strength, shrinkage, permeability, and resistance to the stresses of freezing and thawing. The tobermorite sheets are two or three molecular layers thick and admit the entry of water between them or adsorbed on their surface. The entry of water molecules causes an expansion of the layers resulting in swelling of the structure. The removal of the water causes contraction of the layers and shrinkage of the structure, with possible cracking.

The hydration of the C_3A proceeds in different ways depending on the temperature. Above 21^0C, isotropic crystals are formed having the composition $3CaO.AI_2O_3.6H_2O$ and a refractive index of 1.604. Below 21^0C, hexagonal crystals are formed of di- and tetracalcium aluminate hydrates, $2CaO.AI_2O_3.5\text{-}9H_2O$ and $4CaO.AI_2O_3.12\text{-}14H_2O$. The latter compound has been reported to be biaxial negative with refractive indexes α 1.522, ß 1.538, and τ 1.542. The tetracalcium aluminoferrite phase hydrates slowly to form the calcium aluminate hydrates as above, and an amorphous calcium ferrite phase.

The rate of development of strength in a cement paste is determined chiefly by the C_3S content and the fineness of the cement (Lea & Desch, 1956). The ß-C_2S gives low strength at early ages but within a year it attains a strength comparable to that of C_3S. The strength of C_3A by itself is low, but the introduction of 15% of C_3A to C_3S has been found to raise the strength of concrete upto three days. At later stages, the strength is sharply reduced by large amounts of C_3A. The iron compound develops no appreciable strength at any stage. The introduction of gypsum has little effect on the strength of the silicates but markedly improves that of the aluminate when added in the optimum amount.

During the process of setting and hardening, considerable heat is liberated by the reactions of hydration. This heat is usually of no special concern for it is rapidly dissipated, but in some cases it is of great importance. In massive concrete structures, such as large dams, the heat so liberated could raise the temperature to such values that, on cooling, thermal contraction would produce serious damage. In cold weather, the heat liberated during hydration may be of value in preventing freezing of the grout and in accelerating the setting and hardening of the concrete. The rate of heat liberation is determined principally by the composition of the cement. Thus, at three to seven days, the heat liberated from one cement may be more than double that liberated from another cement. The C_3A evolves heat more rapidly than the other cement compounds; the amount is 50% greater at two days than that of C_3S. The heat evolved from the C_2S and C_4AF is relatively small.

If a portland cement clinker is ground without the addition of a retarder, its interaction with water is usually rapid, the temperature rises sharply, and a flash set occurs. This is due to the rapid hydration of C_3A, accompanied by crystallization of the calcium aluminate hydrates that congal the paste. Gypsum, added as a retarder of set, reacts rapidly with the dissolved aluminate in the presence of calcium hydroxide to form calcium sulfoaluminate, $3CaO.AI_2O_3.3CaSO_4.31H_2O$. The latter compound is much less soluble than the calcium aluminate hydrates and so is preferentially precipitated. The calcium sulfoaluminate hydrate does not cause the paste to congal and so the set is retarded. An excess of gypsum is deterimental to the concrete and hence the amount permitted in cement is limited by all specifications. The optimum gypsum requirement can be determined, and is found to be influenced not only by the C_3A content but also by the fineness of the cement and its alkali content (Lerch, 1946). Tests on strength, expansion in water, contraction in air, and other properties all indicate that the best results are obtained when the optimum amount of gypsum is present.

The durability of concretes in sulfate waters has been found to be determined largely by the content of crystalline C_3A, which reacts rapidly with soluble sulfates to form calcium sulfoaluminate hydrate. This is the same compound that is formed by the gupsum in the retardation of set. The significant difference is that, in retarding set, the reaction takes place before set occurs and so does not affect the volume of the paste after set. But, when a hardened concrete is attacked by sulfate ions, the crystals form in the pores of the structure with a volume increase of about 227%, which may bring about a disintegration of the structure.

RAW MATERIAL FOR CEMENT MANUFACTURING

Cement raw materials may be divided in to four groups: namely; calcareous, supplying lime; siliceous, supplying silica; argillaceous, supplying alumina; and ferrieous, supplying iron. Gypsum in very small amount is required to control the setting time of cement. Thirty different rock materials can be used in the manufacture of Portland cement. The calcareous materials include cement rock, limestone, marl, alkali waste, oystershell, coquina shell, chalk and marble. The argillaceous materials include clay, shale, slag, fly ash, copper slag, aluminum ore refuse, staurlite, diaspora clay, and Kaolin. The siliceous materials include sand, trap rock, quartzite, calcium silicate, and fuller;s earth. The ferriferous material includes iron or, iron calcine, iron dust, iron pyrite, iron smiters, iron oxide, and blast furnace flue dust. The cement rock is an ideal low-magnesium bearing argillaceous lime stone with such a composition that it may be used for cement manufacturing without addition of other earth materials or with addition of only a relatively small amount of such materials.

Limestones are composed essentially of calcium carbonate with varying percentages of magnesium carbonate and admixed impurities of clay and sand. For the manufacture of Portland cement, the limestone should have above 50 percent lime (CaO) if the percentage is less than 50, the rock should be given other names with the appropriate qualifying adjectives (Twinhofel, 1950).

Limestones may be white, grey, dark grey, yellowish blue and some times black in colour.

A general classification is given in the chart below.

Rock	Clay	Content % Calcite	Dolomite
Clayey limestone	10-30	35-90	0-4.5
Slightly clayey dolomitic limestone	5-10	90-45	5-47.5
Slightly clayey limestone	5-10	95-85	0-5
Limestone	0-5	100-90	0-5
Slightly dolomitic limestone	0-5	95-80	5-20
Dolomitic limestone	0-5	80-65	15-35
Highly dolomitic limestone	0-5	65-47.5	30-50

Limestone is wide spread in nature. Calcium carbonate of all geological formations qualifies for the production of portland cement. The purest grades of limestone are calcspar (calcite) and aragonite. Calcite crystallizes hexagonally, and aragonite is rhombic. The specific gravity of calcite is 2.7 and of aragonite 2.95. A macroscopic-granular variety of calcite is marble. It would not be profitable to use marble for cement manufacturing.

The most common forms of calcium carbonate, most similar to marble, are limestone and chalk, limestone is of a predominantly fine grained crystalline structure.

The hardness of limestone depends on its geological age; usually, the older the geological formation, the harder the limestone. The hardness of limestone is between 1.8 and 3.0m of the Mohs'scale of hardness; its specific gravity is 2.6 to 2.8. Only the purest varieties of limestone are white. Limestone usually contains admixtures of clay substance of iron compounds, which influence its color. Limestone used in different industries such as manufacture of portland cement.

Limestone are used in the manufacture of Portland cement, lime burning, metallurgical and chemical purposes (metallic calcium and its allays). Calcium by deride, alkali manufacturing sugar refining, paper manufacturing, glass manufacturing, bleaching powder, leather dressing, varnish manufacturing, calcium carbide, abrasives, carbondi-oxide, water treatment, silica brick manufacturing, grease manufacturing, mineral treatment process, agricultural uses, rock or mineral wool. According to Khan (1958), in an exceptional case, the calcareous sandstone of st. Marathon's Island, bearing 30-40% $CaCO_3$ was recommended by P.S. Pedersen, for cement manufacturing after mixing it with better quality limestone.

Clay: The other important raw material for cement manufacture is clay. Clay is formed by the weathering of alkali and alkaline earth containing aluminum silicates and of their chemical conversion products, mainly feldspar and mica. The main component of clays is formed by hydrous aluminum silicates. Clays are divided into the following mineral groups:

1. **Kaolin group:**

- Kaolinite	$AL_2O_3.2SiO_2.2H_2O$
- Dickite	$AL_2O_3.2SiO_2.2H_2O$
- Nacrite	$AL_2O_3.2SiO_2.2H_2O$
- Halloysite	$AL_2O_3.2SiO_2.2H_2O$

Minerals of the kaolin group differ in content of SiO_2 as well as by the crystallographic structure and optical properties. The designation kaolinite refers to the pure kaolin mineral. Texturally, clays are fine grained; clay particle are usually under 2 microns in diameter.

2. **Montmorillonite group:**

- Montmorillonite	$AL_2O_3.4SiO_2.H_2O+nH_2O$
- Beidellite	$AL_2O_3.3SiO_2.nH_2O$
- Nontronite	$(AL,Fe)_2O3.3SiO_2.nH_2O$
- Saponite	$2\ MgO.3SiO_2.nH_2O$

The chemical composition of clay may vary from those close to the pure clay, to that containing a considerable amount of chemical admixtures as iron hydroxide, iron sulfide, sand, calcium carbonate, etc. Iron hydroxide is the principal coloring agent in clays; also organic matter may give the clay different colours. Clays with no impurities are white. The major source of alkalies in cement is found in the argillaceous component of the raw mix.

3. Group of alkali bearing clays

K_2O-MgO-Al_2O_3-SiO_2-H_2O

Clay and Sand: Clay and sand are not objectionable impurities as they supply alumina,silica and iron oxide,necessary for the formation of the desired silicater in the cement. Dolomite can not be used for the manufacture of Portland cement, because of its high magnesium content. The most important factor controlling the suitability of limestone for the manufacture of Portland cement is its magnesium oxide content. The per misspell limit of which is 5 percent in the finished cement or less than 3 percent in limestone because during calcination the magnesium oxide content will increase due to elimination of carbon dioxide (Clausen & Bates, 1960). The excess of magnesia may be dangerious to the soundness of concrete, specially at later stages. If the contents of silica and alumina are high, pure high-calcium, limestone must be added to lower the impurities. Alkalis (soda and potash) generally amount upto 1.5 percent.

Marl: Limestone with admixtures of silica, clay substance, and iron oxide are called marls. Marlesave earthy friable accumulations of calcareous materials secreted by plants and animals in lakes and marshes overlong periods of time to skeletal remains of plants mixed with shells of animals may form some thick beds of marl suitable for cement manufacture, but such deposits are not common.

Marls form the transition element to the clays. Because of the wide distribution of marls, they are frequently used as raw material for cement production. Geologically, marls sedimentary rocks generated by simultaneous sedimentation of calcium carbonate and clay substance, the hardness of marls is lower than limestone, the higher the content of clay substances the lower their hardness sometimes marls contain also bituminous constituents. The color of marls depends on the clay substance and ranges from yellow to grayish black. Marls are an excellent raw material for cement manufacture, because they contain the lime and the clay component in an already homogenized condition. Calcareous marl of the chemical composition equal to that, portland cement raw mix, used for manufacture of so-called natural cement; however, deposits of such raw materials are not common. As to the quantitative proportions of the lime and clay components in cement raw materials, the following classification is established.

Chalk: Chalk is a sedimentary rock which was formed during the cretaceous period in geological time; geologically it is relatively young. In contrast to limestone, chalk is characterized by a soft earthy texture; this property qualifies chalk as a raw material especially for the wet process of cement manufacture. Since blasting is not required for quarrying of chalk, and the crushing process can also be omitted, this kind of raw material considerably lowers the cement production costs. In some deposits the calcium carbonate content of chalk amounts to 98-99% with small admixtures of SiO_2, $AL2O_3$, and $MgCO_3$. In cement raw materials the lime component is generally represented upto an amount of 76-80%. Therefore, the chemical and physical properties of this component are of decisive influence, when it comes to selecting a methods of cement manufacturing as well as the type of production machinery.

Clay and Shale: Clay stone and similar rocks are earthy, easily disintegrated mass of colloidal clay or silt size material. Shale is a similar material but it does not disintegrate as easily as clay stones. Where alumina and silica are not present in the limestone in sufficient amounts (which is true for rocks other than cement rock), it is necessary to add clay or shale. Both clays and shales have wide variations in mineralogical and chemical content from essentially hydrated aluminum silicate to more than 50 percent free silica along with alumina and iron oxide. So adjustment of silica, magnesia and iron oxide contents becomes necessary. A typical shale or clay will contain silica 58.7%, alumina 15.3%, iron oxide 7.4%, calcium oxide 3.7% and alkalis 0.5%.

Lateriate and bauxite:

Residual deposits formed under special climatic condition in tropical regions.

Lateriate consists essentially of hydrated iron oxides, bauxite of hydrated aluminium oxides, the most common impurity in both being silica; aluminous laterites and ferruginous bauxites are quite common.

Ocassionally bauxite and lateriate are eroded and redeposited, although it is unlikely that they can be transported overgreat distances. They may become mixed with other sedimentary material, to form such rocks as bauxites and lateriates.

Lateriate is sometimes used in the manufacture of cement for increasing iron - aluminium percentage to any desired extent. It's special use, however, is in the preparation of cement with low heat of hydration. Lateriate occurrences are widely distributed in Pakistan (Gauhar, 1966).

Sand or sand stone; is added if the raw material is deficient in silica (Clausen, 1960). According to the British standard specifications, presence of free silica as quartz, flint or chert is not desired, but only in form of silicates in clay and limestone Siddiqui (1973). The manufacture of type II cement (moderate low heat and moderate sulfate resisting) and type IV cement (low heat of hydration) requires a raw materials high in iron. If such a materials is not available, iron ore, pyrite cinders (product of calcination of pyrite) and will scales may be added. Literate is some times used in cement manufacturing for increasing Fe-AL percentage to a desired extend. However, its special use is in the preparation of cement with low heat of hydration. Raw gypsum is used in the manufacture of Portland cement from 3 percent to a maximum of about 6 percent that is added to clinker to retard the setting time and as strengthening agent.

PROPORTIONING OF RAW MATERIAL FOR CEMENT MANUFACTURING

The two basic types of cement constituents are the argillaceous (clayey) and calcarious (lime bearing) materials. Limestone, chalk, marl, shell comprise calcarious materials while slate, shale, clay comprise argillaceous materials.

The mineral constituents of cement and their average percentages are:

1.	Tricalcium silicate (C_3S)	50%
2.	Dicalcium silicate (C_2S)	25%
3.	Tricalcium Aluminate (C_3A)	10%
4.	Tricalcium Aluminaferrite (C_3AF)	10%
5.	Other compounds	5%

According to (Lee, 1976) the limits of composition of Portland cements are approximately:

	Percent
CaO	60-67
SiO_2	17-25
Ai_2O_3	3-8
Fe_2O_3	0.5-6.0
MgO	0.1-5.5
$Na_2O + K_2O$	0.5-1.3
SO_3	1-3.

Cement of many years ago some times had lime contents below 60 percent, but modern cements almost always show values in excess of that figure.

The change in composition over the years may be illustrated by a comparison of the composition and Bogue compound contents of some cements manufactured between 1900 and 1910 and the corresponding values for modern cement.

The average composition of sixteen cements of the 1900-1910 period is CaO 62.2, MgO 1.84, Ai_2O_3 7.27, Fe_2O_3 3.48, SiO_2 21.6, SO_3 1.27. The corresponding average compound contents are C_4AF 10 percent, C_3A 13 percent, C_3S 32 percent, C_2S 39 percent, making no allowance for free lime for which nodata are available.

The average values for modern ordinary Portland cements are about 45 percent C_3S and 25 percent C_2S. The sum of the contents of C_3A and C_4AF has decreased slightly in the modern cements.

The silica in a Portland cement form with lime the essential cementing compounds C_3S and C_2S; any change in the silica content which increases the proportion of C_3S will affect the early strengths favourably, but at along ages the strength depends only on the sum of the two present. An increase in silica content at the expense of the content of alumina and ferric oxide will make the cement harder to clinker and its setting time easier to control. An increase of silica, at the expense of the lime content, reduces the rate of development of strength.

Alite (C3S) is the prevalent clinker mineral, determining its property of strength. Six modification of C3S are known, of which only 2 high temperature modifications appear in cement clinker; these modifications are stabilized by insertion of unrelated atoms.

Belite is mairly the B-modification of C2S. At sintering temperature of the clinker if this temperature is above 2590^{0}F, a-C2S is generated; if this temperature is below 2590^{0}F, a-C2S is formed. This modification changes during clinker cooling at about 1240^{0}F into the metastable B-C2S. Belite hardens considerably slower than alite, after a longer period of time it attains the same strength.

The increase of alumina with no change, or with a reduction, in the ferric oxide content, hastens the setting of a cement and a point is eventually reached at which it becomes impossible to control the setting time adequately.

Magnesia in most British Portland cements is averaging around 1 percent, but in many foreign cements it may rise to 3-4 percent. Specifications in all countries place a maximum limit, usually 4 or 5 percent, on the permissible content of MgO because higher contents lead to long-term un-soundness. Thus Bates (Bates, 1927) obtained cements which were sound and had satisfactory strengths with MgO contents of upto 6.5 percent and similar instances were quoted in a paper (Gonnerman, et al. 1953). Summarizing later U.S.A. investigations. It has also been claimed that still higher contents can be tolerated in cements of high iron oxide content. (Budnikov, and Vorobev, 1958). Nicoletti, (1956) or to which pozzolanas have been added J.Rosa, (1965) and Majumdar and Rehsi, (1969).

There are other various minor constituents in amounts varying from a trace to one or two percent. Alkalis are always present in amounts varying from below 0.2 percent $Na_2O + K_2O$ upto about 1.3%. Titanium oxide is commonly present to the extent of 0.1-0.4%. TiO_2 and may rise to 1% Manganese oxide is present to extent of 1%, Mn_2O_3 or above in Portland cements made from a blast furnace. Slag as raw material, but the content is usually less than 0.1% in cements made from the normal raw materials. Also blast furnace slag sometimes contains a high amount of MgO. When selecting such slages as a replacement of clay as the argillaceous component of the raw mix, care should be taken, to keep the MgO - content of the clinker within permissible limits. Sulphur trioxide in cement clinkers, before the gypsum is added during grinding varies from about 0.1 to 0.5%. Phosphorus pentoxide is found in amounts upto 2% in cement made from phosphatic limestones, but for most cements its content is small, 0.2% or less. In cases where raw materials with a higher phosphorus content are used (e.g. limestone with a high P_2O_5 - content, or industrial wastes from phosphorus production), an admissible limit of about 2.5% P_2O_5 in the clinker is quoted. However, it should be noticed that sometimes P_2O_5 - content as low as 0.5% can already cause a considerable decrease in strength, especially in the early strength of the cement. The fluoride content of conventional cement raw materials fluctuates within the limits of 0.03 and 0.08%. In contradistinction to the chlorides, the fluorides do not volatilize easily, and thus do not disturb operation, since they do not circulate in the kiln system. The former practice of adding up to approximately 1% of calcium fluoride to the raw mix, to facilitate clinker burning, is now in most cases abandoned, since the binding of lime can be achieved by a higher degree of homogenizing and finer grinding of the raw mix. Elements such as barium and strontium are usually only present in small amount, below 0.05% for BaO and 0.2% for SrO. The content of chromium oxide, though small, is of particular significance in relation to the incidence of cement dermatitis. Calman, (1960) and Pisters, (1966). In most Portland cements its content is below 0.01% Cr_2O_3 but it may rise to 0.02%. Analyses of minor components in a large number of U.S.A. cements have been reported (Miller and Manson. 1951).

The specifications for Portland cement in many countries contain some clauses relating to the composition. The limitation of cement composition is often placed on the lime content with the object of ensuring that the cement shall not contain an excess of lime over that which can combine with the acidic oxides and so be liable to show un-soundness. With the continued demand for cements of higher earlier strength it has been necessary for manufactures to raise the lime contents, and the specification limits have been progressively raised enable this to be done.

Sulphate resisting Portland cement, differs primarily from ordinary cement in having a low calculated content of tricalcium aluminate. Ferrai cement also falls into this class. This may be achieved either by using raw materials of low-alumina content or by adding iron oxide to produce a low ratio of Ai_2O_3: Fe_2O_3. About unity or less. Except for the farmer type of Erz cement it is not usual to drop this ratio below 0.64, corresponding to the compound 4CaO, AL_2O_3, Fe_2O_3.

Low-heat Portland cement was developed in the U.S.A. Soon after 1930 for use in mass concrete construction, such as dams.

A low-heat evolution is achieved by reducing the contents of 3CaO. SiO_2 and 3CaO. AL_2O_3 which are the + compounds evolving the most heat on hydration.

PROCESS OF CEMENT MANUFACTURING

The process of cement manufacture consists in the incorporation of the raw material to form a homogeneous mixture, the burning of the mix in a kiln to form a clinker, and the grinding of the clinker with the addition of a small proportion of gypsum to a fine powder.

There are two processes, for cement manufacture (i) wet process (ii) dry process.

It is according as to whether the raw materials are ground and mixed in a wet or dry condition are used in a variant of these processes, the semi-dry process, the raw materials are ground dry and then mixed with 10-14 percent water and formed in to nodules.

The wet process was originally used for very friable materials such as chalk and clay and later extended to the harder lime-stones and shales. For many years the wet process was preferred in Great Britain because of the more accurate control of the raw mix which was possible with it. With improved control, there has been a swing back towards the dry process, because in this process less fuel is required for burning than in the wet process.

Modern developments in the dry mixing of powdered materials have, moreover, now removed the disadvantage of the dry process.

Originally the dry process was preferred in the U.S.A where most of the raw material are hard rocks, but later the wet process was widely adopted because of its advantages in control of cement composition.

In the dry process the raw materials are crushed, dried in rotary driers, proportioned, and then ground in tube mills consisting of rotating steel cylinders containing a charge of steel balls or other grinding media. They are often divided into two, or three, or even four compartments containing balls of different size. The mills are contineous in operation, being fed at one end discharging the ground material at the other. Two mixtures, one high and one low in lime, are often prepared and blended in the required proportion in a silo with vigorous air circulation. The dry powder is fed to the kiln.

In manufacture by wet process the method differs some what with the nature of the raw materials, when chalks and marls are used, the raw materials are broken up and incorporated in wash mills. These usually consist of circular pits lined with bricks or concrete and containing gratings in the walls through which the raw materials can pass when reduced to sufficiently fine condition. The chalk and clay are fed in the required proportions to the wash mill together with sufficient water to form a liquid of creamy consistence.

A number of radial arms attached to a vertical spindle carry iron rakes which break up the lumps of solid matter as the arms revolve. The solid material is reduced to a fine state of division and passes as a slurry through the screens in the walls of the pit. Any flints present in the chalk remain at the botom of the wash mill and are removed periodically. In modern practice the raw materials are usually further reduced in size by treatment in another wash mill with finer screens, in contrifugal screening mills, or by passage through a tube mill. When the raw materials are harder limestones and shales the wash mill is inadequate to effect the reduction.

The raw materials are in such cases crushed and fed to large tube mills and water added to the mill in the amount required to form the slurry. When hard limestone and clay are the raw materials the clay is usually fed to the tube mill already dispersed in the water.

The finished slurry does not usually contain more than a few percent of materials remaining on a 170 mesh, and its water content varies from 35 to 45 percent with different raw materials. The slurry is pumped to slurry tanks or basins in which both rotating arms and agitation by compressed air are used to keep the mixture homogeneous. The proportion of lime in the mix is controlled by analysis and the charge fed to the wash mills or tube mills is adjusted periodically as required. Final adjustments of composition is often obtained by blending the slurry from two basins, one of which is kept slightly high and one slightly low in lime.

In some plants more elaborate blending systems are practiced, using a number of slurry basins, blending tanks, and final storage tanks.

The rotary kiln in which the cement is burnt at 1300^0 - 1500^0 is a long cylinder rotating on its axis and inclined so that the materials fed in at the upper end travel slowly to the lower end. Here the fuel, pulverised coal, oil or natural gas, is blown in by an air blast and ignited. In the upper part of the kilns chains are fixed to assist in the transfer of heat from the kiln gases to the raw materials. The slurry is dried in the upper part of the kiln and the water driven off as steam, and then, as it descends the kiln, the dried slurry undergoes a series of reactions, forming in the most strongly heated zone hard granular masses mostly from 1/8 inch to 3/4 inch diameter, known as clinker. At the lower end of the kiln the clinker passes into coolers. In most modern plants they form a composite part of the kiln.

In these cases they consist of a series of cylinders parallel with the body of the kiln and arranged around its periphery. The clinker after passing through the hottest zone in the kiln falls into them through openings in the walls of the kiln. In these cylinders, which revolve with the kiln, are hung loose chains which cause the particles of clinker to fall in a cascade, thus being brought into contact with the current of cold air which is drawn through grates serving both as a transporter and cooler are often favoured. These are enclosed in an air tight casing and a controlled amount of air is drawn through the bed of clinker. The heated air drawn from the coolers is used for the combustion of the coal so providing an economical exchange of heat. The comparatively cool clinker then falls on to conveyers and is transferred to storage hoppers or passed direct to the grinding mills. The grinding is usually done in modern plants in large three or four compartment tube mills which are usually water cooled in order to help to dissipate the heat generated. A small quantity of gypsum is added during grinding to control the setting, as described later, and the finely ground cement passes to silos from which it is drawn for packing. The packing is performed by automatic machines.

In modern cement plants elaborate instrumentation is installed to control the burning process, combined sometimes with automatic control of the kiln. The raw materials in some plants are sampled automatically and the raw mix composition requried is calculated by computer.

The tendency over the years has been to increase the length of the rotary kiln, particularly when working on wet process, in order to increase its thermal efficiency and often to add some form of pre-heater. Thus in dry process plants, it was formerly common practice to pass the exit gases through was to heat boilers but a cyclone preheater, in which the feed material is heated, is now preferred as a means of recovering heat from the hot gases, the temperature of which can be reduced to about 300^0. Wet process kilns go upto over 700 ft in length and 25 ft in diameter in order to obtain the most efficient heat interchange in the kiln and reduce the fuel gas temperature to 200^0 or even lower.

Numerous methods are used to improve fuel economy in wet process plants. Thus the water content of the slurry may be reduced by slurry filters consisting of large rotating discs or drums covered with filter cloth. The water content of the slurry, normally about 35-45 percent by weight, is reduced to 20-30 percent in the filter cake produced. The amount of water required in the slurry for it to be pumpable can in some cases be reduced a few percent by adding very small amount of agents such as sodium carbonate or silicate.

Various devices are also employed to improve the interchange of heat between raw feed and hot gases so as to use as much as possible of heat that would otherwise be lost up the chimney stack. These may take the form of spirals or guide vanes in the back-end of the kiln or of additional rotating cylinders through which the slurry passes before being fed to the kiln.

Another well known development is the Lepol Kiln in which a travelling chain grate enclosed by a casing is installed in advance of the kiln. The raw materials are prepared in the form of small nodules by the addition of a small percentage of water to the dry mix. These nodules are piled in a layer some 6 to 8 inches thick on the travelling grate which conveys them to the rotary kiln. The hot waste gases from the kiln are caused to pass into this chamber and are sucked through the raw mix, transferring their heat to it. The travelling grate can be used in combination with a short kiln having a high exit gas temperature, and it with reduce the gas temperature to as low as 120^{0}C.

A considerable economy in fuel consumption can thus be effected, combined with the advantages of a short kiln. In another method, nodules from the filter pressing of slurry are preheated on a horizontal rotating hearth through which the flue gases pass and which forms part of a chamber which is fed from above and discharges through a central orifice in the hearth. Various trials have also been made on fluidised beds formed by feeding the dry raw materials, fuel and preheated combustion air into the bottom of a reactor vessel (Pyzel, 1967).

Dust collection

The gases from rotary kilns carry with them a certain amount of dust which if allowed to escape can cause a nuisance. In wet process plants the dust at the kiln exit varies upto about 5 percent. Electrostatic precipitations, cyclone, separators, scrubbing towers and bag filters are used to trap the dust, which is usually returned to the kiln. The dust is relatively rich in the more volatile constituents of the charge, specially potash, and has sometimes been used as a source of this valuable salt (Wilson, 1919).

The choice of a refractory lining for rotary cement kilns presents certain difficulties. The lining has not only to withstand heavy wear due to abrasion by the raw materials and the clinker, but also to be resistant to chemical attack by the cement mix at the high temperature prevailing in the clinkering zone. Ordinary firebricks, containing a large proportion of silica, react with the more basic materials of cement, causing partial destruction of the lining in the hotter parts and building up of rings of sintered material which obstruct the passage down the kiln. They are used in the back part of the kiln where temperatures are relatively low, but as the burning zone is approached more refractory and resistant materials are required.

High alumina bricks containing 60 percent and upwards a alumina are widely used. Chrome magnesite and sometimes, dolomite bricks are also favoured. Portland cement clinker itself has also been used fragments of clinker being bonded with cement or a little refractory clay.

Another development (Meyer et al., 1952) in cement burning has been the suction grate in which the raw materials and fuel, mixed together, are fed on to a travelling chain grate on which they are burnt. A typical grate may be 40 feet long, 6 feet wide and travel at about 2 feet per minute. A layer of already burnt clinker is fed on to the grate, to protect it, followed by a layer of nodulised raw materials and coke fuel. The underside of the grate is enclosed by a suction box to draw air through it. The grate travels along. The burning process is rapid and the maximum clinkering temperature of 1300-1400^{0}C is only maintained for one or two minutes.

Stationary kilns of many different types were at one time used in cement manufacture, but with the exception of the automatic shaft kiln they have now fallen into disuse. The automatic shaft kiln is a continuous kiln of the vertical type some 30-50 feet high and 8-10 feet in diameter. It is fed at the top with the raw materials and fuel briquetted together. The raw mix is burnt to a clinker as it descends the kiln and an automatic discharge arrangement effects the removal of the clinker from the bottom of the kiln. The automatic shaft kiln has found a certain amount of favour in Europe on account of its low fuel consumption. A number of processes are also worked for the combined production of portland cement and other products. In one of these, operated in England, France and Germany and some eastern European countries, sulphuric acid and portland cement are made by burning in a rotary kiln a raw mix of calcium sulphate (hydrite or gypsum), clay and coke together with sand and Iron oxide as required to give correct mix proportions. Sulphur dioxide is produced from the calcium sulphate, the main reaction being:

(i) $CaSO_4 + 2C = CaS + 2\ CO_2$

(ii) $3\ CaSO_4 + CaS = 4\ CaO + 4\ SO_2$

The lime liberated reacts in the usual way with the alumina, silica and iron oxide constituents to form cement clinker. The presence of coke in the mix is necessary to obtain rapid decomposition of the calcium sulphate. The burning temperature is about 1400^0C, pulverised coal being used for firing. The gases leaving the kiln contain about 9 percent SO_2 which is converted to sulphuric acid by normal processes.

Pig iron and portland cement are produced together by the Bassett process used in a number of countries. The raw materials, lime stone, coke and iron are burnt in a rotary kiln having a section following the burning zone shaped to collect the motten iron in a pool from which it flows out through a tap hole at each revolution. The clinker passes on to the end of the kiln and the coolers. A reducing atmosphere is maintained in the kiln.

Alumina and portland cement can be made together by the seailles process. The raw materials are limestone and an alumina - containing material such as siliceous bauxite, and clay, slags, and coal ashes of high alumina content. The mix is proportioned so as to yield 5 CaO. $3AL_2O_3$ and 2 CaO. SiO_2 and burnt in the normal way in the rotary kiln. The product, which is self pulverising from the dicalcium silicate inversion, is extracted with water or sodium carbonate solution to dissolve the alumina. The solid residue, mainly dicalcium silicate and any iron compond, is mixed with additional limestone and reburnt to give cement clinker, while the alumina is recorded from the extract solution.

CHAPTER-IV

METHODOLOGY

CRUSHING OF ROCK SAMPLES

The samples were collected from the outcrops of the Gandghar Range in the study area and that of cement from the local market of Peshawar. Representative samples of limestone, phyllites and shale were crushed in Jaw crusher. For the geochemical examination selective crushed samples were pulverized in tungsten carbide ball mill to <200-mesh size. A portion of individual sample was collected after proper quartering and coning. During this whole process greater care was practiced to avoid contamination. The powdered samples of cement were stored in the airtight glass bottles after drying at 110^0C in an oven over night.

GEOCHEMICAL EXAMINATION

Preparation of stock solutions

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

Stock Solutions A, using acid digestion method

0.500 g of powdered rock sample was accurately weighed in a Tefelon beakers. It was than moist with few drops of deionized water and 10 ml of concentrated HCI (for limestone specimens) or 10 ml HF and 4 ml $HClO_4$ (for cement and argillaceous limestone specimens) was added. The sample was heated on the hot plate at low temperature 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 was 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 than about 2 ml of Hydrochloric acid 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.

Stock Solution B, using sodium hydroxide fusion method

NaOH solution was prepared by dissolving 30 g 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 g of limestone, phyllites, shales, clay, 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 dull 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 HCI. In most cases clear solution was obtained but if it was not clear then it was warmed 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 and alumina.

Determination of major and minor oxides

SiO_2 and AI_2O_3 were determined by the spectrophotometric method (using SP-400 PYE UNICAM UV/VIS spectrophotometer) whereas, Fe_2O_3, CaO, MgO, MnO, Na_2O and K_2O were determined by atomic absorption spectrophotometric method (using SP 191 PYE UNICAM atomic absorption spectrophotometer).

SiO_2

Reagents used during examination were;

1. Ammonium molybdate solution: 7.5 g of ammonium molybdate was dissolved

in 70 ml deionized water having 20 ml of 9N N_2SO_4. A solution of 100 ml volume was made and was kept in a polythene bottle.

2. Tartaric acid solution: 25 g of the tartaric acid was dissolved in 250 ml with deionized water.
3. Reducing solution: 0.7 g of sodium sulfite (Na_2SO_4), 0.15 g of 1-amino-2-naphthol-4-suphonic acid and 9 g of sodium metabisulfite ($Na_2S_2O_5$) was dissolved in 100 ml of deionized water. The solution was refrigerated and was prepared freshly as this solution deteriorates after 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 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 colour 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.

AI_2O_3

Reagents used during examination were;

1. 8-hydroxyquinoline solution: 1.25 g of the 8-hydroxyquinoline was dissolved in 250 ml of pure grade of chloroform and was stored in a refrigerator.
2. Complexing reagent: 1 g of hydroxylamine hydrochloride ($HONH_2HCI$), 3.6 g of sodium acetate trihydrate and 0.4 g of beryllium sulfate tetrahydrate were dissolved in 50 ml of deionized water. 0.04 g of 2,2 dipyridyl was also dissolved in 20 ml of 0.2 N HCI. Both the solutions were then mixed and diluted upto 100 ml with deionized water.

Procedure

5-10 ml of each stock solution B was taken into a series of 100 ml seperatory 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 shaked for about 8 minutes by an automated flask shaker. The organic layers obtained at the bottom of these solution in the seperatory 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 colour extracts obtained through this process were suitable for Spectrophotometric determination. The AI_2O_3 was determined at wavelength of 381 ηm relative to the reference rock standards.

Total Iron as Fe_2O_3

1. Stock solution of 1000 ppm was prepared from 1 g of pure iron metal which was dissolved in minimum amount of HCI and was made to the volume with deionized water in one liter volumetric flask.
2. Stock solution of 100 ppm was prepared by taking 10 ml from 1000 ppm stock solution 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.

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 aspirate as unknown. After verification of accuracy, the certified standard solution 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. Whenever the solution were out of range, those solutions were diluted accordingly.

MnO

1. Stock solution of 1000 ppm for Mn was made by using 4.058 g of $MnSO_4.4H_2O$ dissolved in 20 ml of 1N H_2SO_4. It was then transferred to 1000 ml volumetric flask and was made upto the mark with deionized water.
2. Stock solution of 100 ppm was made by taking 10 ml of 1000 ppm stock solution in 100 ml volumetric flask and was made upto 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 were then run to check the accuracy of the method. After verification, samples concentration was noted.

CaO and MgO

1. Stock solution of 1000 ppm for Ca and Mg was prepared dissolving 2.497 g of $CaCO_3$ and 3.057 g of $MgCO_3$ in 1N HCI and were 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 by taking 10 ml of 1000 ppm stock solution in 100 ml volumetric flask and was made upto the marked with deionized water.
3. Lanthanum solution (5%) was prepared from 58.64 g of La_2O_3 dissolved in 200 ml deionized water to which 150 ml of 60% $HCIO_4$ was added. It was heated until completely dissolved. The solution was than filtered through ordinary filter paper into 1000 ml volumetric flask and the volume was made upto 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 upto 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 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 upto the mark.

Procedure

Atomic absorption spectrophotometer was calibrated for Ca and Mg separately at wavelength of 422 ηm by using Ca and Mg cathode lamps, receptively. The instrument was then calibrated and standardized with the working standards of 4 and 8 ppm. All the working standards and the certified rock standards were checked and their actual concentration was verified. Then studies 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 more concentration solution were diluted to bring the concentration within the range.

Na_2O and K_2O

1. Stock solution of 1000 ppm for Na and K was prepared from 3.087 g of moisture free Na_2SO_4 and 2.228 g of moisture free K_2SO_4 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 by taking 10 ml of 1000 ppm standard solution 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 upto the mark with deionized water.
4. All the samples as well as certified rock standards were also diluted to 10 times.

Procedure

Atomic absorption spectrophotometer was calibrated for Na and K separately at wavelength of 589 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.

Determination of loss on ignition by using gravimetric method

Samples of known weight were taken in already weighed porcelain crucibles. The crucibles were kept in the furnace at 950^{0}C for 2 hours. They were cooled in the desecrator and weighed again. The difference in weight was noted and the amount of ignition loss (in percent) was calculated for each sample.

PREPARATION OF THIN SECTION

The petrographic study of the Gandghar Range limestone, thin sections of the rock specimens were prepared by using diamond cutter "Discoplan-TS" of approximately one square inch. The chip of rock specimen was mounted on a glass slide by using an adhesive and was grind on "Cut-Rock". Using corundum powder of mesh No. 400 and 1000 made further grinding of thin section. This thin section was covered by glass cover.

CHAPTER-V

GEOCHEMISTRY OF CEMENT RAW MATERIAL

Chemistry of Shekhai Limestone:

The major element chemistry of Shekhai Limestone is given in (Table 5.1). It is evident from this table that these limestone samples have SiO_2 in the range of < 0.38 to 21.7%, Al_2O_3 is upto 2.32%, Fe_2O_3 is less than 2.48%, MnO is negligible, MgO is ranging from 1.84 to 20.80%, and CaO is ranging from 35.2 to 52.4%. Among alkalis Na_2O is less than 0.52%, while K_2O is less than 2.2%. The loss on ignition (<01) is ranging from 30.41 to 46.51%.

The average composition of Shekhai limestone is SiO_2 = 8.33%, Al_2O_3 = 0.815%, Fe_2O_3 = 1.07%, CaO = 50.25%, MgO = 6.99%, K_2O = 0.776%, Na_2O = 0.176%.

SiO_2 in various forms is present as impurities in the limestone, for example as in cement stone and cherty limestone (Pettijohn, 1976; Boynton, 1980). The Shekhai limestone has variable amount of SiO_2. It generally has very low concentration of SiO_2 but at places the SiO_2 reaches upto the maximum of about 22% (Table 5.1, Fig. 5.1 a). Those having high SiO_2 are considered as argillaceous limestone.

Table 5.1. Chemical Composition of Shekhai Limestone

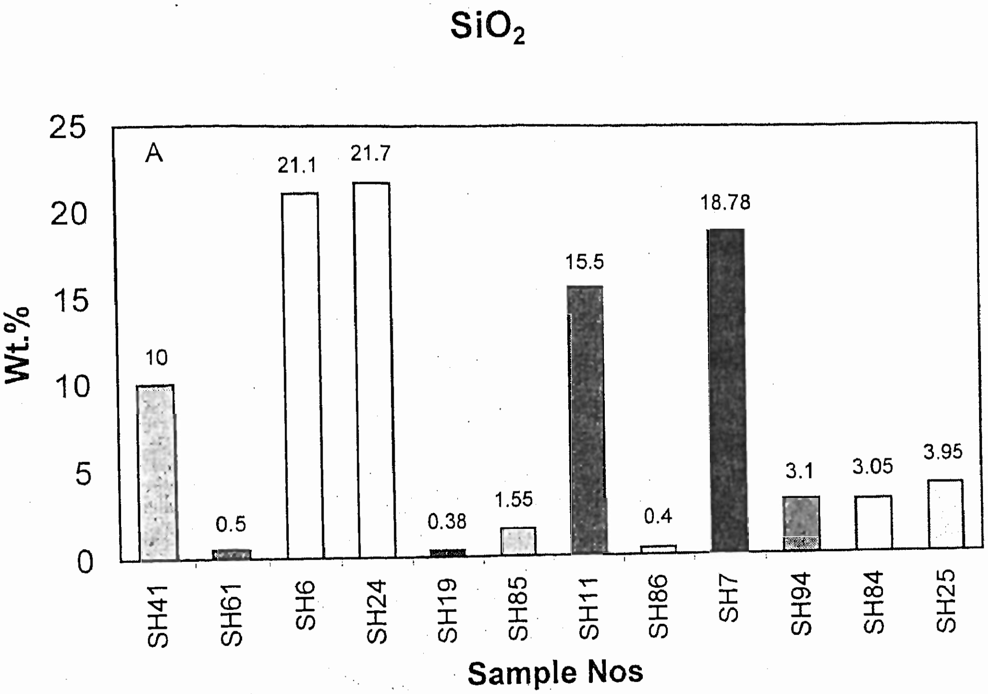
Sample No.	SH41	SH61	SH6	SH24	SH19	SH85	SH11	SH86	SH7	SH94	SH84	SH25	Average	Max.	Min.
SiO_2	10	0.5	21.1	21.7	0.38	1.55	15.5	0.4	18.78	3.1	3.05	3.95	8.334	21.7	0.38
Al_2O_3	1.23	0.31	2.1	2.32	0.05	0.25	1.31	0.31	1.1	0.21	0.3	0.24	0.811	2.32	0.05
Fe_2O_3	1.53	0.39	1.91	2.24	2.02	0.16	0.76	0.22	2.48	0.42	0.33	1.46	1.077	2.24	0.16
MgO	5.38	20.8	5.63	5.47	3.58	4.74	4.68	19.97	4.72	2.67	4.43	1.84	6.993	20.8	1.84
CaO	45.4	36.1	35.2	35.85	46.9	50.6	40.3	35.8	39.1	52.4	52.2	52.2	50.25	52.4	35.2
Na_2O	0.12	0.08	0.3	0.52	0.2	0.06	0.19	0.05	0.39	0.06	0.07	0.07	0.176	0.52	0.05
K_2O	0.74	0.14	1.31	1.56	1.3	0.13	0.69	0.16	2.2	0.29	0.43	0.36	0.776	1.56	0.13
LOI	35.21	38.78	32.33	29.54	46.51	42.57	35.28	41.01	30.41	41.89	40.25	40.81	-	-	-
Total	99.61	97.12	99.89	99.24	100.96	100.06	98.72	97.93	99.21	101.07	101.08	99.96	-	-	-

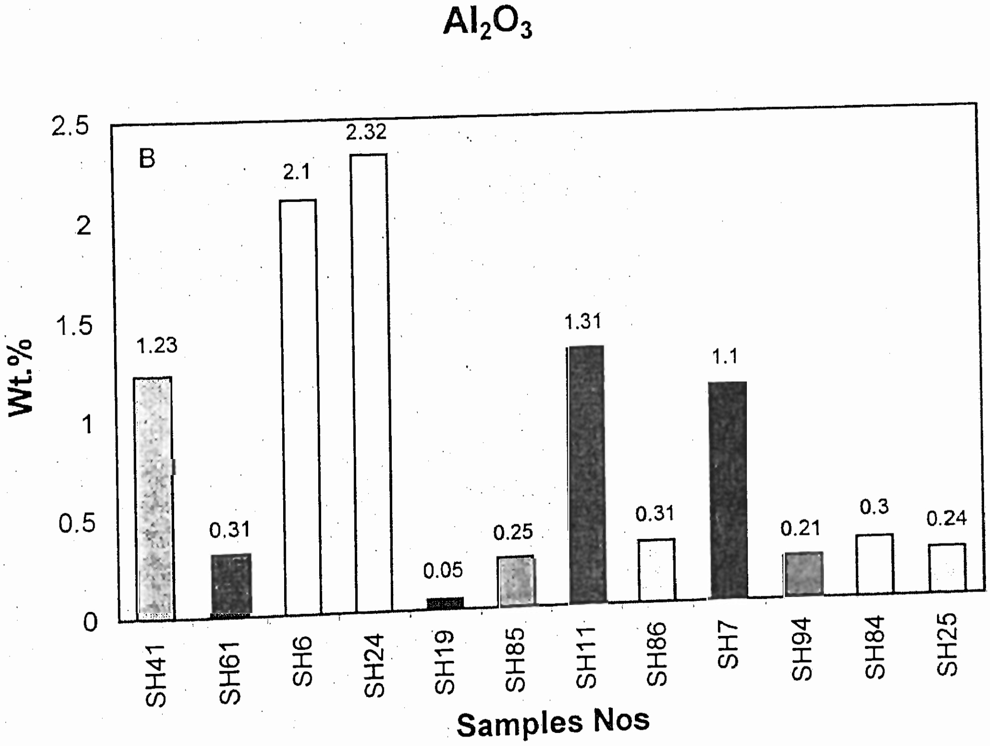
Alumina (Al_2O_3) is the second largest impurity in the limestone. Both the alumina and silica concentration in the limestone usually originate from the shally matters (Pettijohn, 1971). The Al_2O_3 content of studied samples are generally less than 1.3%. However, two samples are having little higher Al_2O_3 (Table 5.1, Fig. 5.1 b).

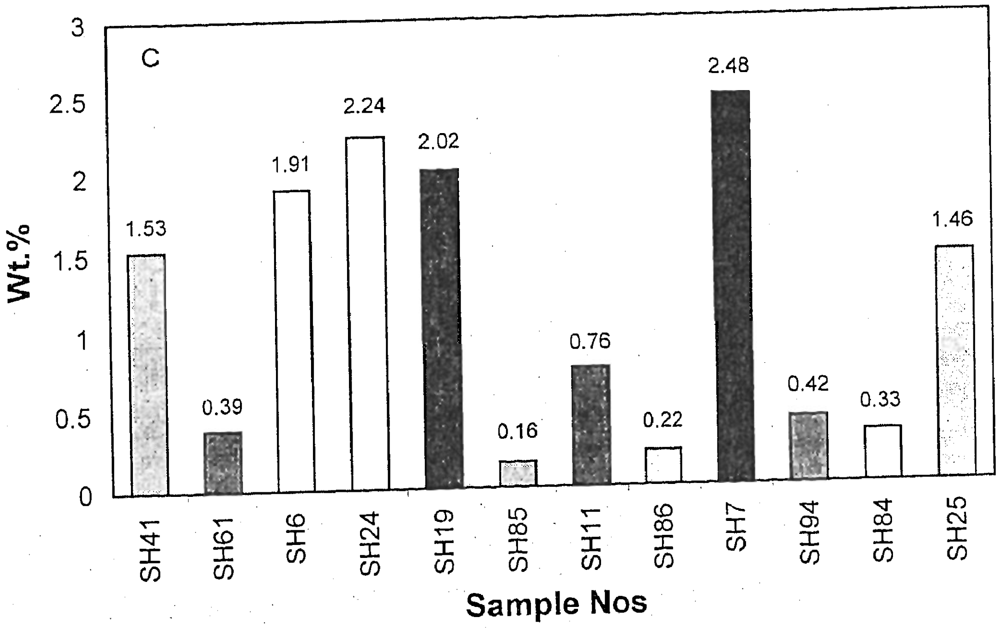
Iron in the form of oxides and sulfides occurs as another impurity in the limestone, which if present in higher amount can cause deterioration in the building construction. In limestone, iron can be homogeneously disseminated during chemical displacement of the calcium bearing iron carbonate or can hetrogeneously distributed through iron bearing strata. The Fe_2O_3 contents of the studied limestone are generally less than 1.5%. However, at places it has high concentration of iron (upto 2.50%) (Table 5.1, Fig. 5.1 c).

Manganese oxides (MnO) in limestone is generally found in traces (Boynton, 1980). There is no or negligible amount of MnO in almost all the samples (Table 5.1, Fig. 5.1 d). Magnesium oxide (MgO) in the limestone is a function of both the magnesium content of skeletal debries 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 dolomite can not be

Fig. 5.1. Variation of various Oxides in the Shakhai Limestone

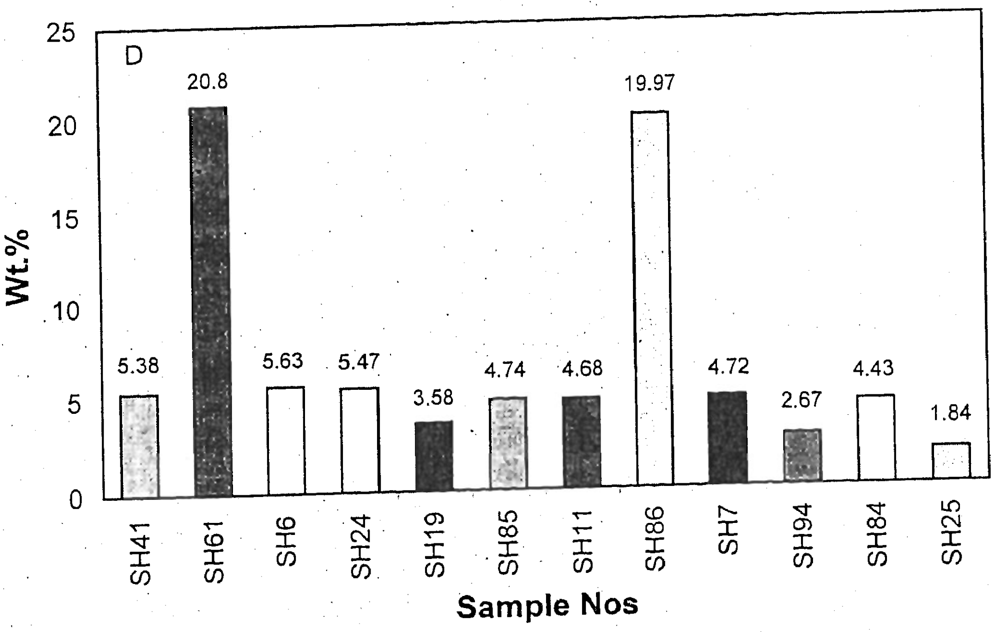






Fe_2O_3

C
Wt.%
3
2.5
2
1.5
1
0.5
0
1.53
0.39
1.91
2.24
2.02
0.16
0.76
0.22
2.48
0.42
0.33
1.46
SH41
SH61
SH6
SH24
SH19
SH85
SH11
SH86
SH7
SH94
SH84
SH25
Sample Nos



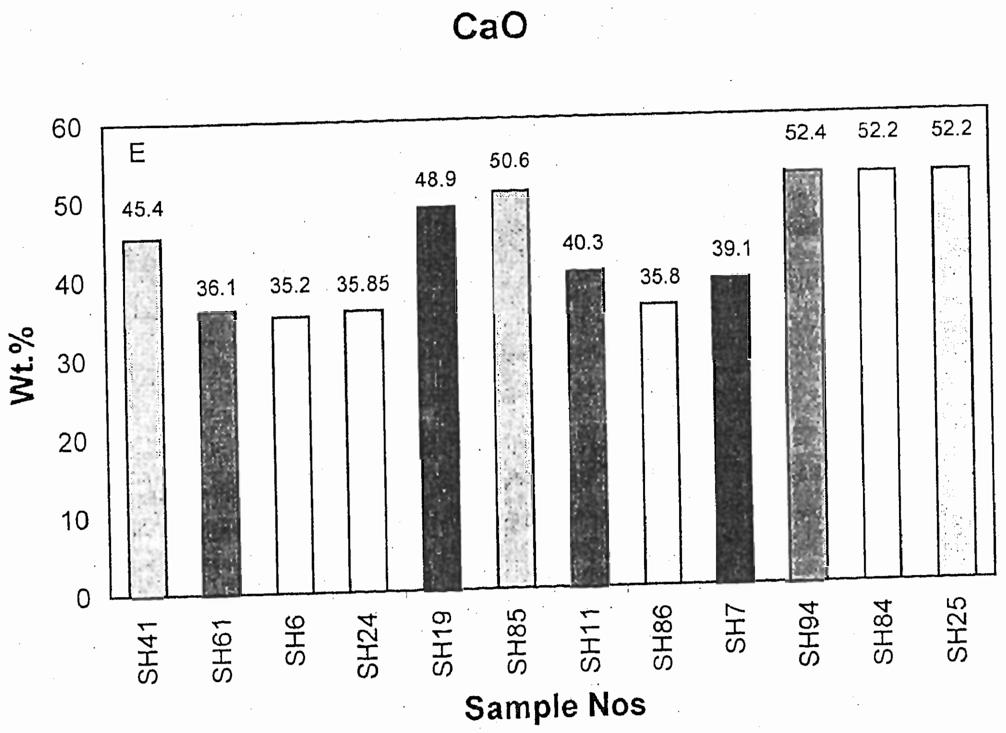
MgO

D
Wt.%
25
20
15
10
5
0
5.38
20.8
5.63
5.47
3.58
4.74
4.68
19.97
4.72
2.67
4.43
1.84
SH41
SH61
SH6
SH24
SH19
SH85
SH11
SH86
SH7
SH94
SH84
SH25
Sample Nos

used for the manufacture of Portland cement because of its high magnesium. The MgO content of the Shekhai limestone is generally less than 5% but at places it becomes dolomite in composition by having upto 21% MgO (Table 5.1, Fig. 5.1 e). 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 samples of the studied area generally have more than 40% of CaO which is the normal range of limestone. From samples, however, have less than 40% CaO (Table 5.1, Fig. 5.1 f) which is due to the siliceous nature of these limestones. This increase or decrease of CaO in the studied limestone is therefore, related to silica (SiO_2) concentration rather than magnesia (MgO).

Sodium oxide (Na_2O) and potassium oxide (K_2O) are considered as traces with respect to the pure stone chemistry (Boynton, 1980). Na_2O in the studied limestone is other in the range of normal limestone. K_2O is also within the range of normal limestone but at places the K_2O increases to more than 1% which could be due to the input of argillaceous material (Table 5.1, Fig. 5.1 g).

During the determination of loss on ignition (LOI), the bond between $CaCO_3$ molecule is borken to form lime (CaO) and CO_2. This CO_2 is the measure of ignition loss. It ranges from 29.54 to 46.51%.


CaO
E
Wt.%
0
10
20
30
40
50
60
45.4
36.1
35.2
35.85
48.9
50.6
40.3
35.8
39.1
52.4
52.2
52.2
SH41
SH61
SH6
SH24
SH19
SH85
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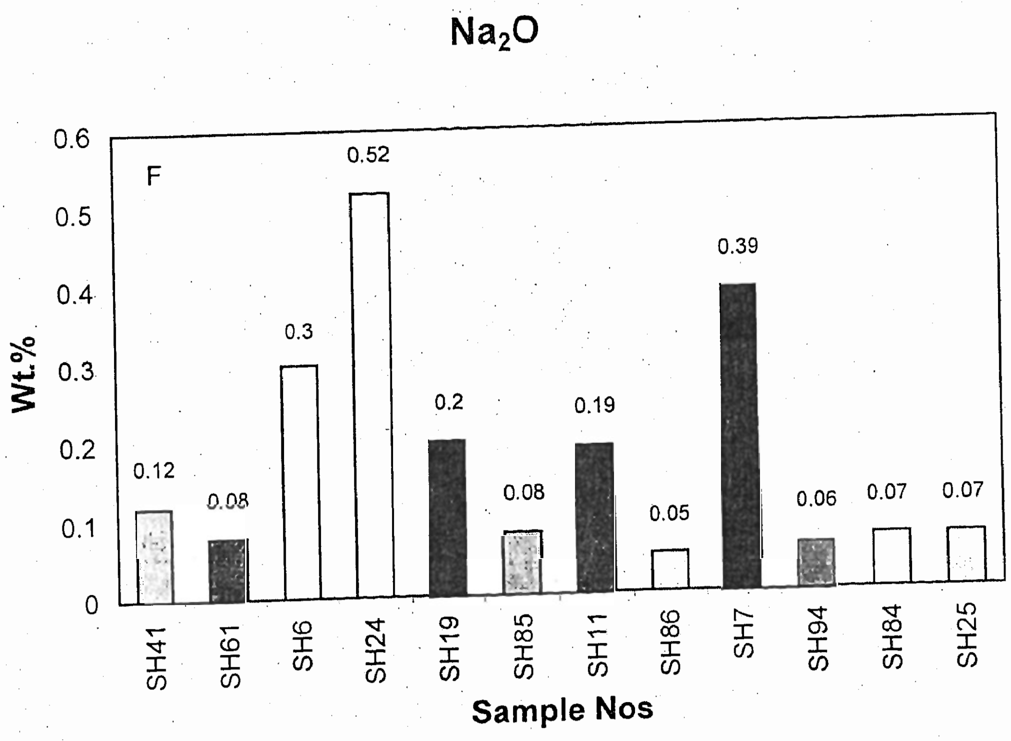
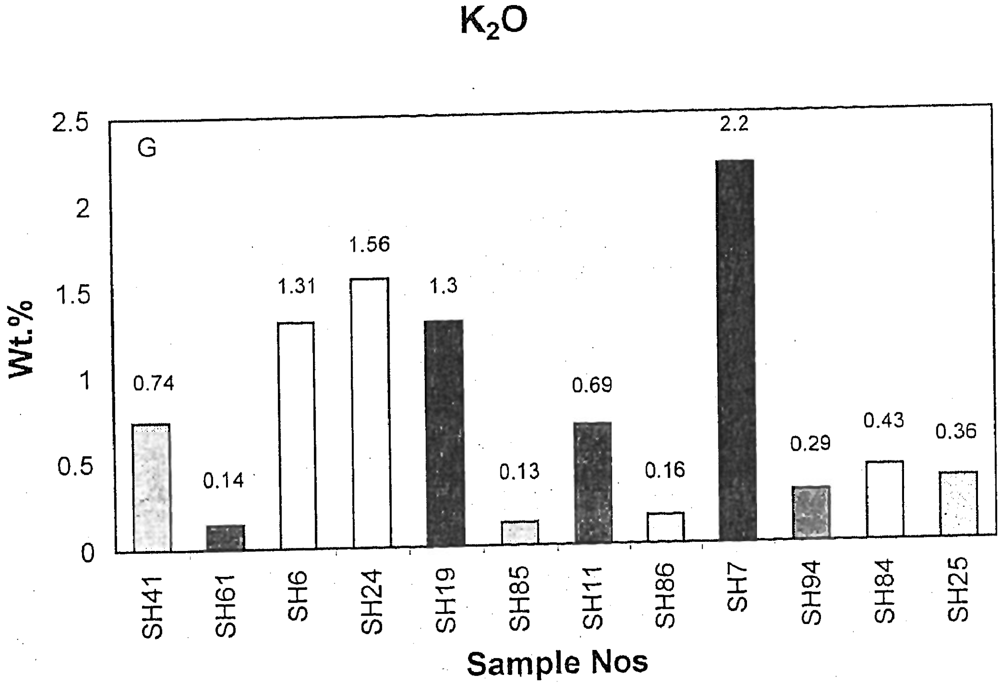
SH86
SH7
SH94
SH84
SH25
Sample Nos


Na2O
F
Wt.%
0
0.1
0.2
0.3
0.4
0.5
0.6
0.12
0.08
0.3
0.52
0.2
0.08
0.19
0.05
0.39
0.06
0.07
0.07
SH41
SH61
SH6
SH24
SH19
SH85
SH11
SH86
SH7
SH94
SH84
SH25
Sample Nos


K_2O
G
Wt.%
2.5
2
1.5
1
0.5
0
0.74
0.14
1.31
1.56
1.3
0.13
0.69
0.16
2.2
0.29
0.43
0.36
SH41
SH61
SH6
SH24
SH19
SH85
SH11
SH86
SH7
SH94
SH84
SH25
Sample Nos

5.2. Chemistry of Utch Khattak Limestone:

The major element chemistry of the Utch Khattak Limestone is given in (Table 5.2).

The SiO_2 content in the samples are generally high in the Utch Khattak limestone. It is in the range of < 4.4 to 23.7%, AI_2O_3 in the range of 0.56 to 2.32%, Fe_2O_3 is less than 2.44%. MnO is negligible. MgO is ranging from 1.61 to 3.91% and CaO from 38 to 50.3%. Among alkalis Na_2O is less than 0.66% while the K_2O is less than 1.56%. The loss on ignition is ranging from 28.71 to 40.124%.

By comparing the various major oxides of the Utch Khattak limestone in (Figure 5.2 a), it is clear that there is a greater variation in these constituents.

SiO_2 in sample numbers (90, 93, 98, 96) is high (upto 24%) (Fig. 5.2 b). AI_2O_3 is also high in these samples which suggest the detrital input in these limetones. Fe_2O_3 contents of studied limestone is generally less than 1.00%. However, three samples, (U.K. 93, 98, 90) have high Fe_2O_3 (Fig. 5.2 c). MnO is negligible in the Utch Khattak Limestone and is ranging from 0.00 to 0.09%.

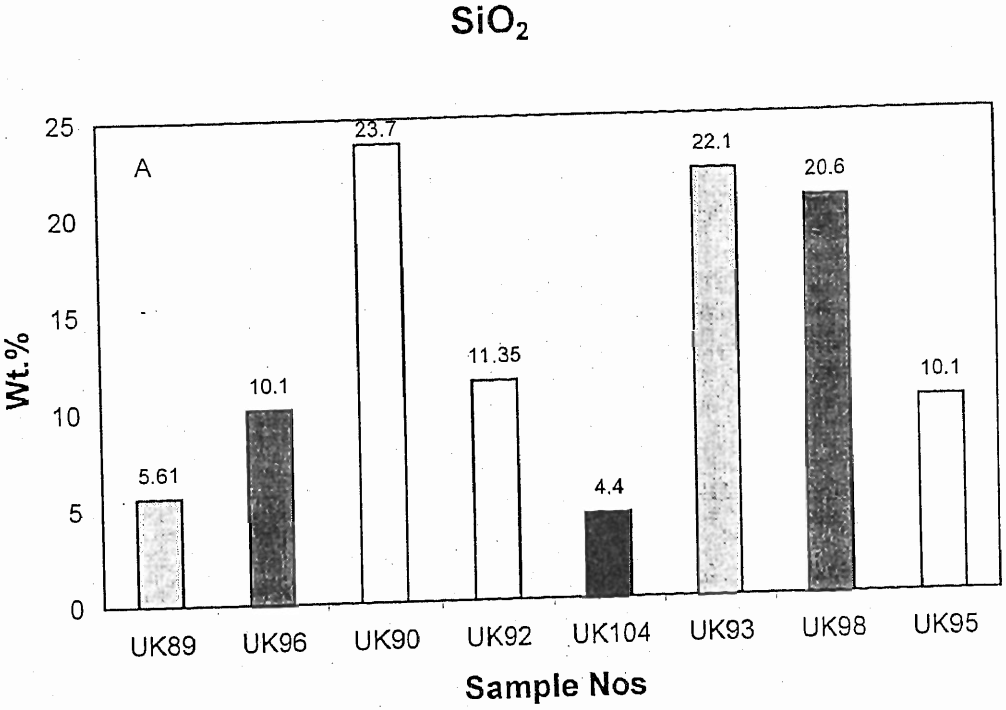
Table 5.2. Chemical Composition of Utch Khattak Limestone

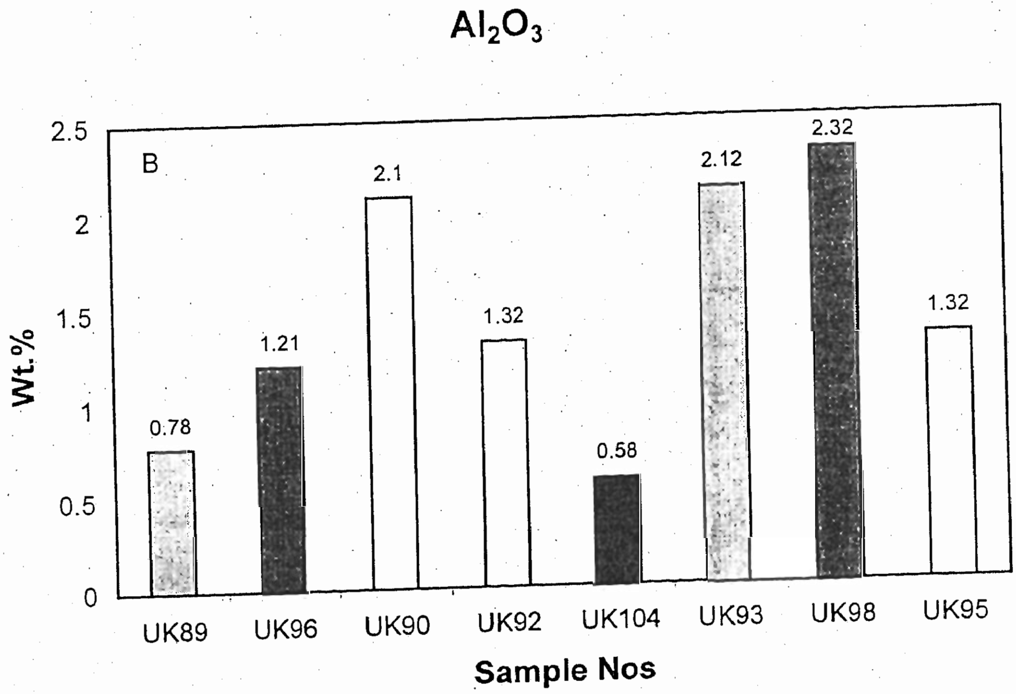
Sample No.	UK89	UK96	UK90	UK92	UK104	UK93	UK98	UK95	Average	Max.	Min.
SiO_2	5.61	10.1	23.7	11.35	4.4	22.1	20.6	10.1	13.493	23.7	4.4
Al_2O_3	0.78	1.21	2.1	1.32	0.56	2.12	2.312	1.32	1.466	2.32	0.56
Fe_2O_3	0.43	0.44	2.44	0.52	0.29	1.32	1.47	0.79	0.963	1.47	0.29
MgO	1.61	1.96	2.8	1.47	3.75	1.8	3.91	2.42	2.465	3.91	1.47
CaO	50.3	49.3	38.6	45.5	50.1	40.3	40.2	45.96	44.958	50.3	38
Na_2O	0.07	0.11	0.07	0.07	0.15	0.08	0.66	0.07	0.16	0.66	0.07
K_2O	0.21	0.17	0.49	0.19	0.14	1.56	0.58	0.6	0.493	1.56	0.14
LOI	40.24	38.14	30.73	38.19	40.18	28.71	31.66	38.82	-	-	-
Total	99.24	101.45	100.37	98.63	99.578	98.06	101.49	100.11	-	-	-

MgO content of studied limestone in Utch Khattak is relatively low as compared to that of Shekhai limestone. It is variable and reaches upto about 4% (Fig. 5.2 d). CaO in Utch Khattak limestone is also low as compared to that of Shekhai limestone of the area. CaO is also having greater variation (Fig. 5.2 e). Its concentration generally varies with increase and decrease of SiO_2.

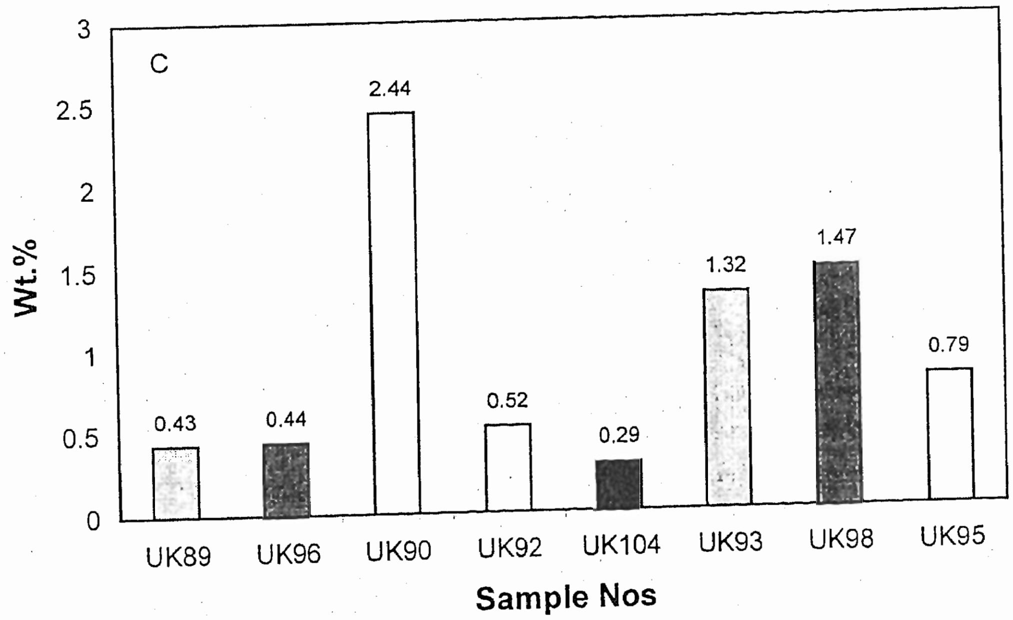
Sodium oxide (Na_2O) and potassium oxide (K_2O) are considered as trace with respect to the pure chemistry (Boynton, 1980). Both these oxides are very low (<1.70 %) in total and more or less constant, except in one; in almost all the samples (Fig. 5.2. f & g). The loss on ignition in the Utch Khattak limestone is low as compared to that of Shekhai limestone which suggest the relatively lower amount of $CaCO_3$ in these limestone.

Fig. 5.2. Variation of various Oxides in the Khattak Limestone

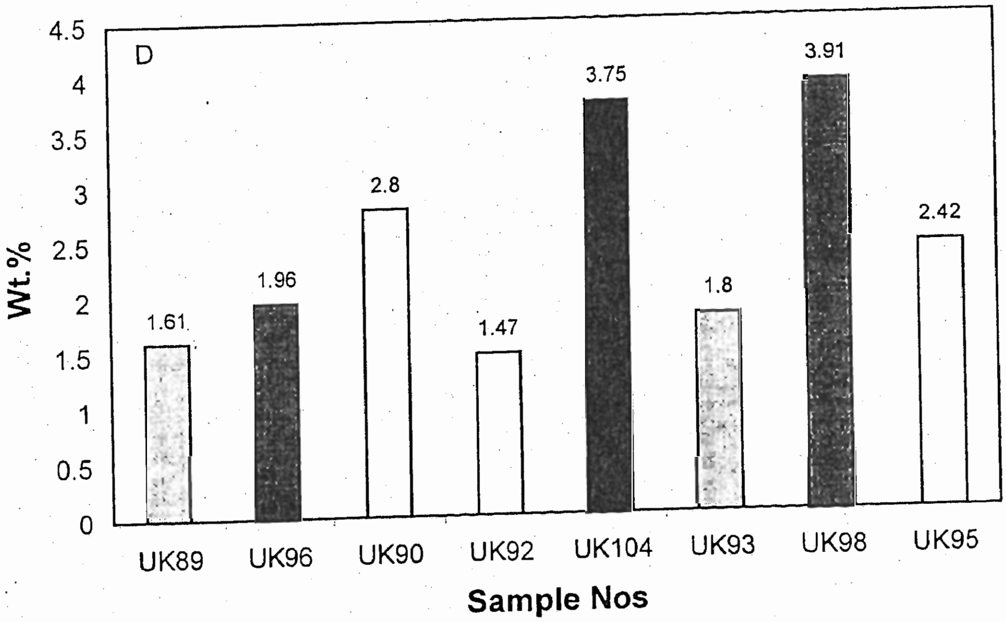




Fe_2O_3


C
Wt.%
0
0.5
1
1.5
2
2.5
3
0.43
0.44
2.44
0.52
0.29
1.32
1.47
0.79
UK89
UK96
UK90
UK92
UK104
UK93
UK98
UK95
Sample Nos

MgO


D
Wt.%
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
1.61
1.96
2.8
1.47
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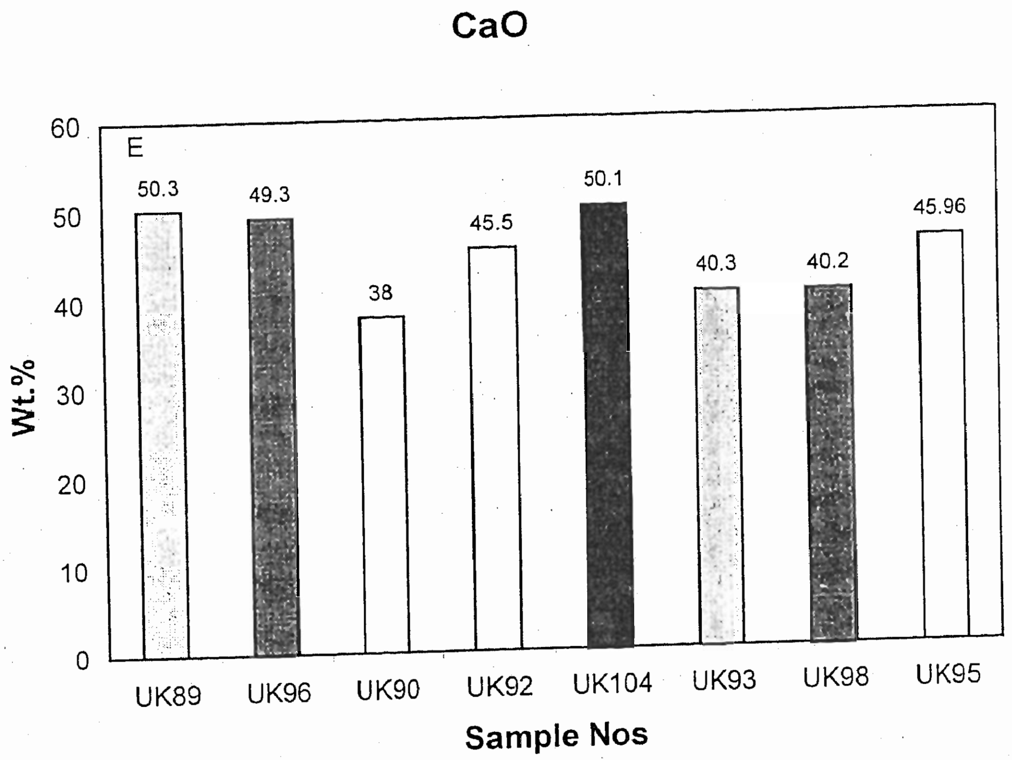
UK104
UK93
UK98
UK95
Sample Nos


CaO
E
60
50
40
30
20
10
0
Wt.%
50.3
49.3
38
45.5
50.1
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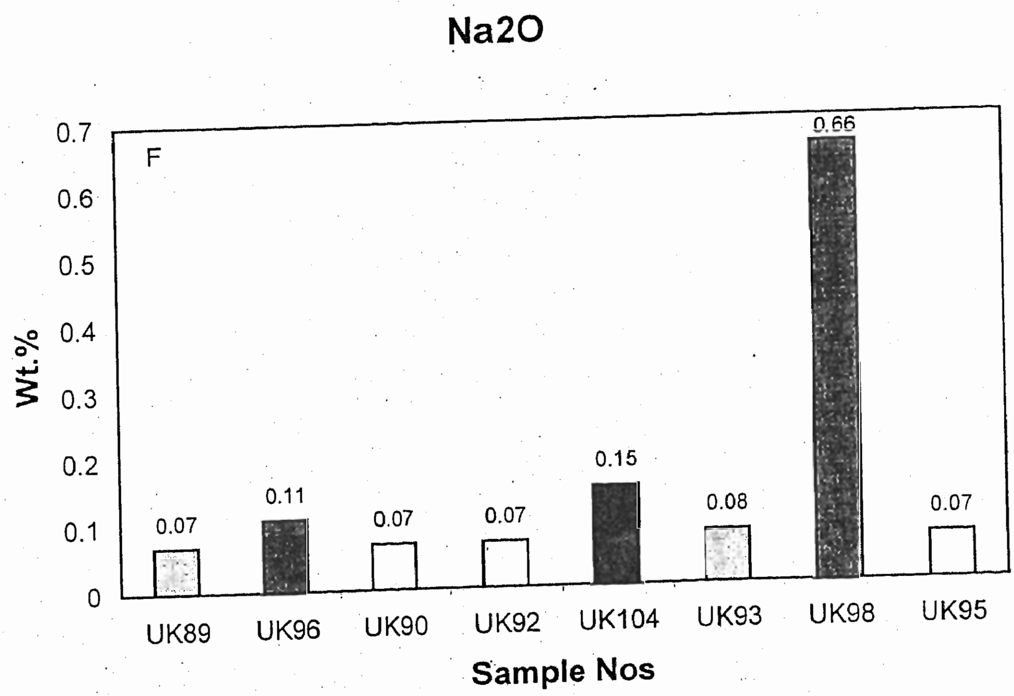
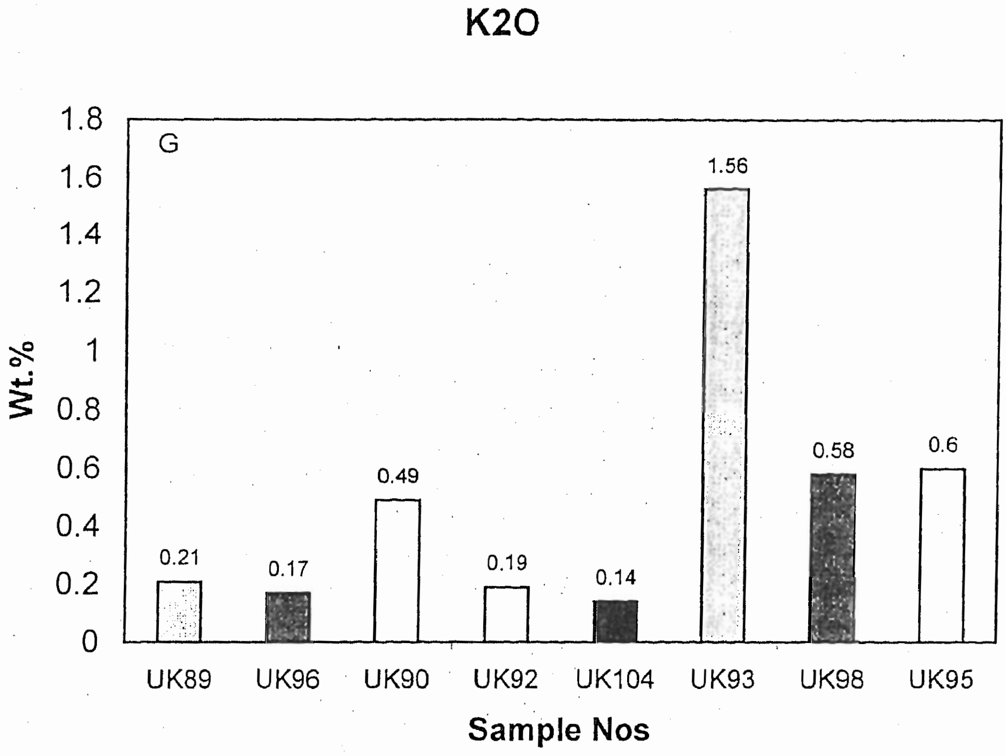
40.2
45.96
UK89
UK96
UK90
UK92
UK104
UK93
UK98
UK95
Sample Nos


Na2O
F
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Wt.%
0.07
0.11
0.07
0.07
0.15
0.08
0.66
0.07
UK89
UK96
UK90
UK92
UK104
UK93
UK98
UK95
Sample Nos


K2O
G
Wt.%
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0.21
0.17
0.49
0.19
0.14
1.56
0.58
0.6
UK89
UK96
UK90
UK92
UK104
UK93
UK98
UK95
Sample Nos

Chemistry of Greenish Gray Limestone:

The element chemistry of Greenish gray limestone is given in Table 5.3. The SiO_2 is ranging from 3.45 to 27.3%, AI_2O_3 from 0.53 to 2.15%, Fe_2O_3 from 0.4 to 1.7%. MnO is present in negligible amount. MgO is ranging from 2.56 to 6.91%, CaO from 32.96 to 49.9%. Na_2O is less than 0.67% and K_2O is less than 1.26%, loss on ignition is ranging from 28.9 to 41.94%. The chemistry of these limestone is similar to that of the Utch Khattak limestone.

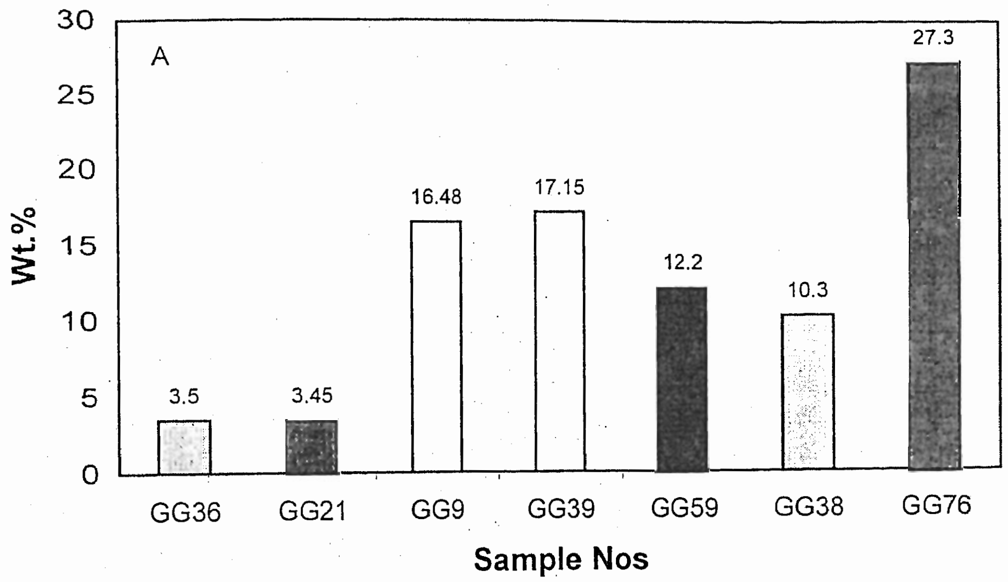
The SiO_2 content in most of the samples is high and can, therefore, be considered as silicious limestone. The SiO_2 is generally variable (Fig. 5.3 a). AI_2O_3 is also variable and is relatively higher than the normal limestone (Fig. 5.3 b). Iron oxide is generally within the range of normal limestone and occur in variable amount (Fig. 5.3 c). Magnesium oxide (MgO) is also present in variable amount and is reading upto about 7% (Fig. 5.3 d).

Calcium oxide (CaO) is the main constituent of limestone. The CaO of the studied limestone is generally within the range of siliceous limestone and is variable in composition (Fig. 5.3 e). The amount of CaO in the studied limestone varies with the increase and decrease of SiO_2. A greater variation in the Na_2O and K_2O contents has been observed in the studied limestone (Fig. 5.3 f & g).

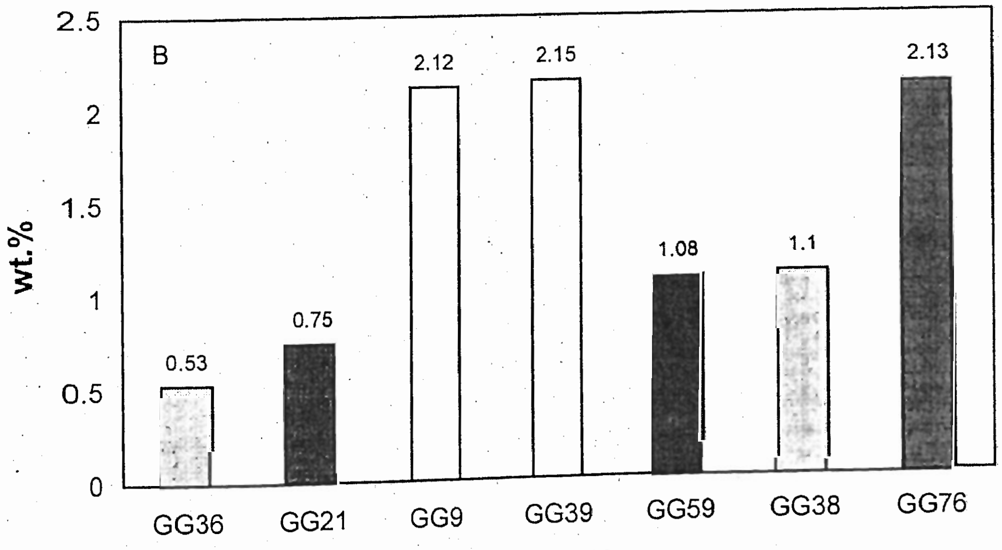
Table 5.3. Chemical Composition of Greenish Grey Limestone

Sample No.	GG36	GG21	GG9	GG39	GG59	GG38	GG76	Average	Max.	Min.
SiO_2	3.5	3.45	16.45	17.15	12.2	10.3	27.3	12.907	27.3	3.45
Al_2O_3	0.53	0.75	2.12	2.15	1.08	1.1	2.132	1.408	2.15	0.53
Fe_2O_3	0.4	0.28	0.76	1.7	0.53	0.61	0.61	0.699	0.76	0.28
MgO	6.91	2.56	4.43	5.69	4.64	3.58	5.55	4.767	6.92	2.56
CaO	49.9	49.6	45.2	40.3	45.52	45.3	32.96	44.103	49.9	32.9
Na_2O	0.24	0.06	0.67	0.27	0.05	0.51	0.38	0.311	0.67	0.05
K_2O	0.06	0.24	0.27	1.26	0.85	0.07	0.80	0.507	1.26	0.06
LOI	38.68	41.94	31.59	30.40	33.39	37.72	28.90	-	-	-
Total	100.24	98.88	101.51	98.97	98.27	99.24	98.60	-	-	-

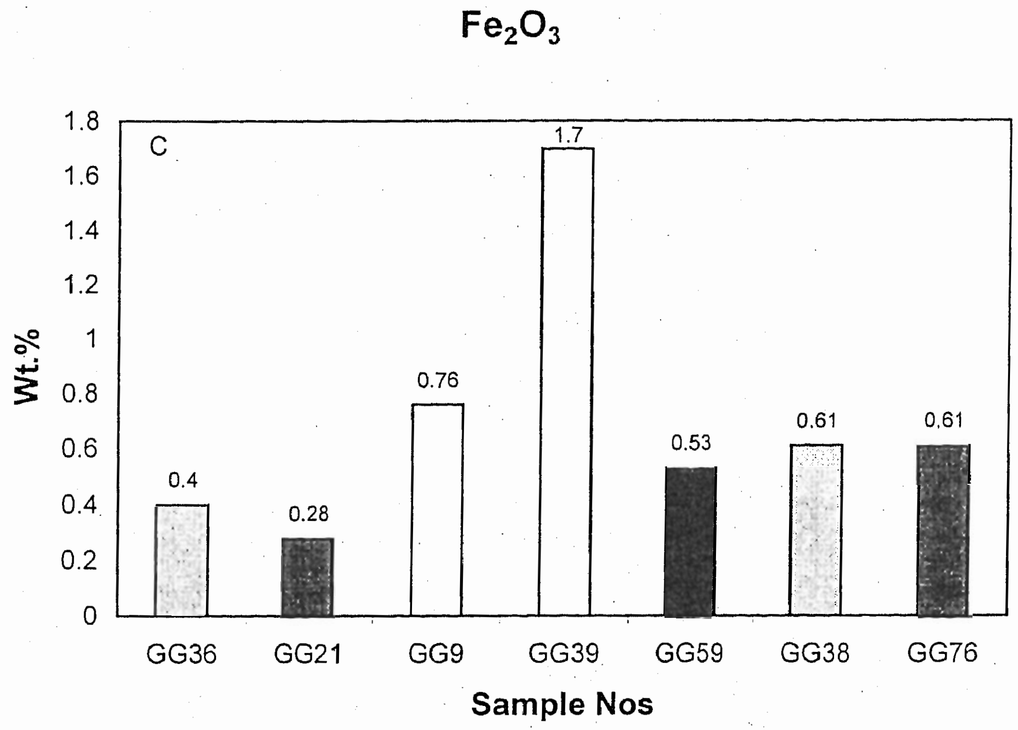
Fig. 5.3. Variation of various Oxides in the Greenish Gray Limestone

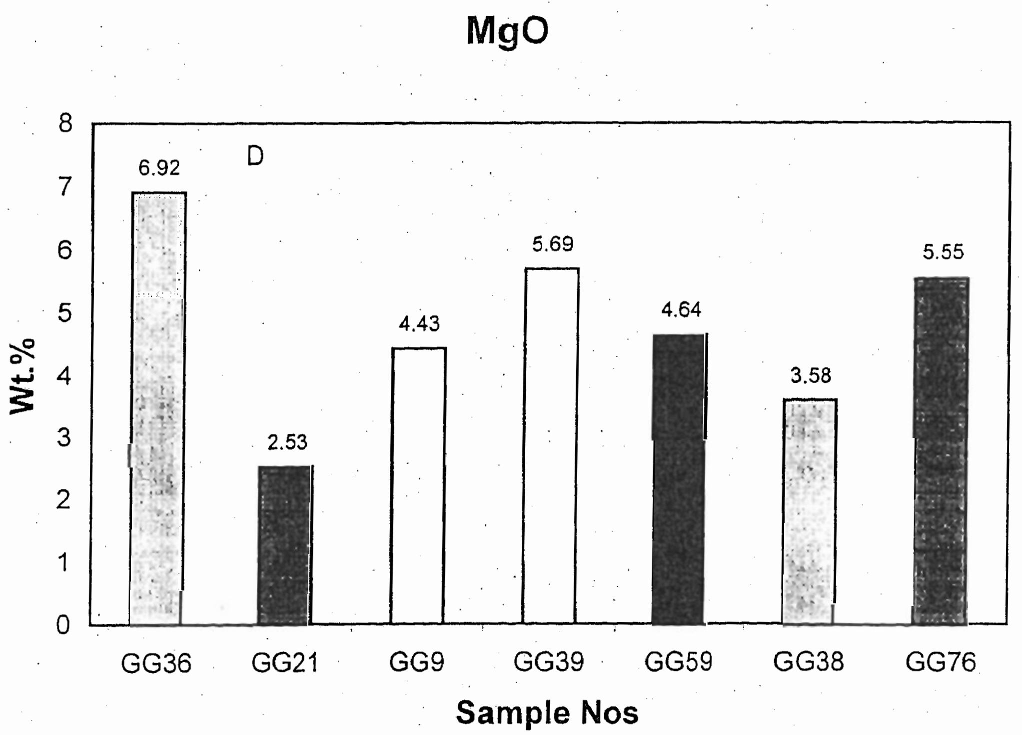


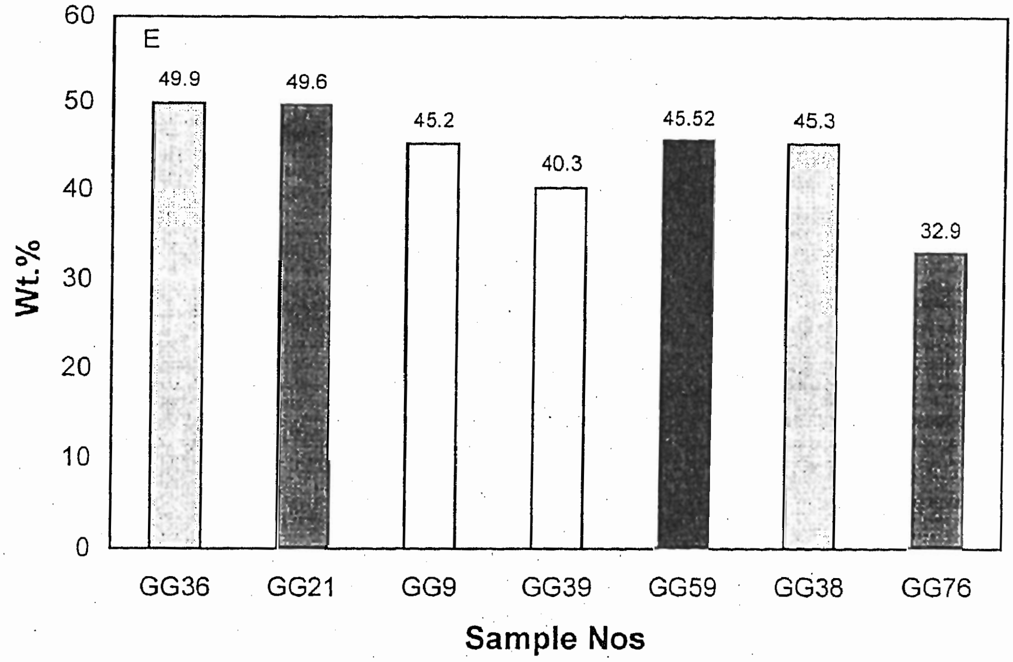
SiO_2



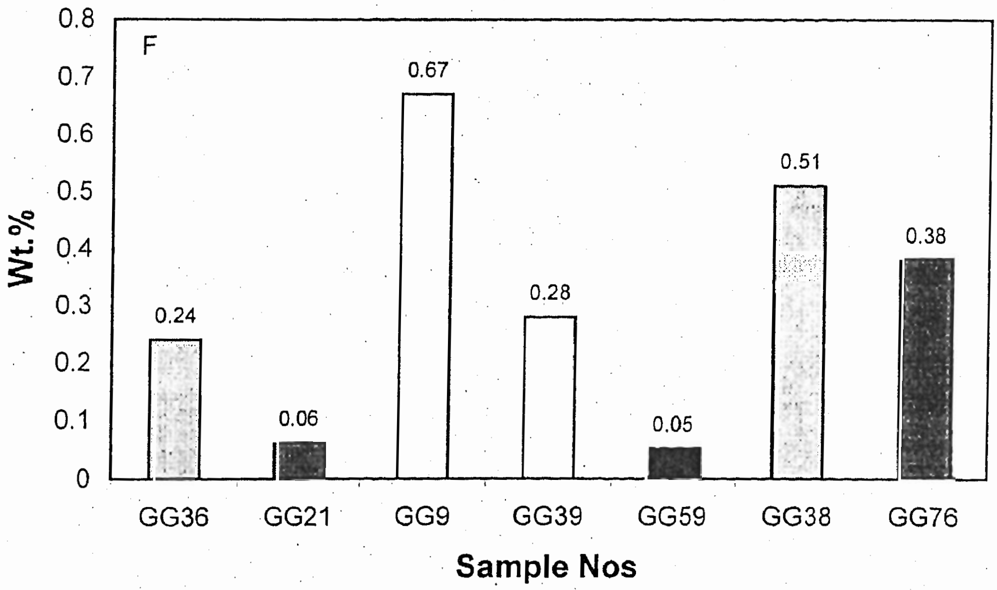
Al_2O_3


Fe$_2$O$_3$
C
Wt.%
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0.4
0.28
0.76
1.7
0.53
0.61
0.61
GG36
GG21
GG9
GG39
GG59
GG38
GG76
Sample Nos

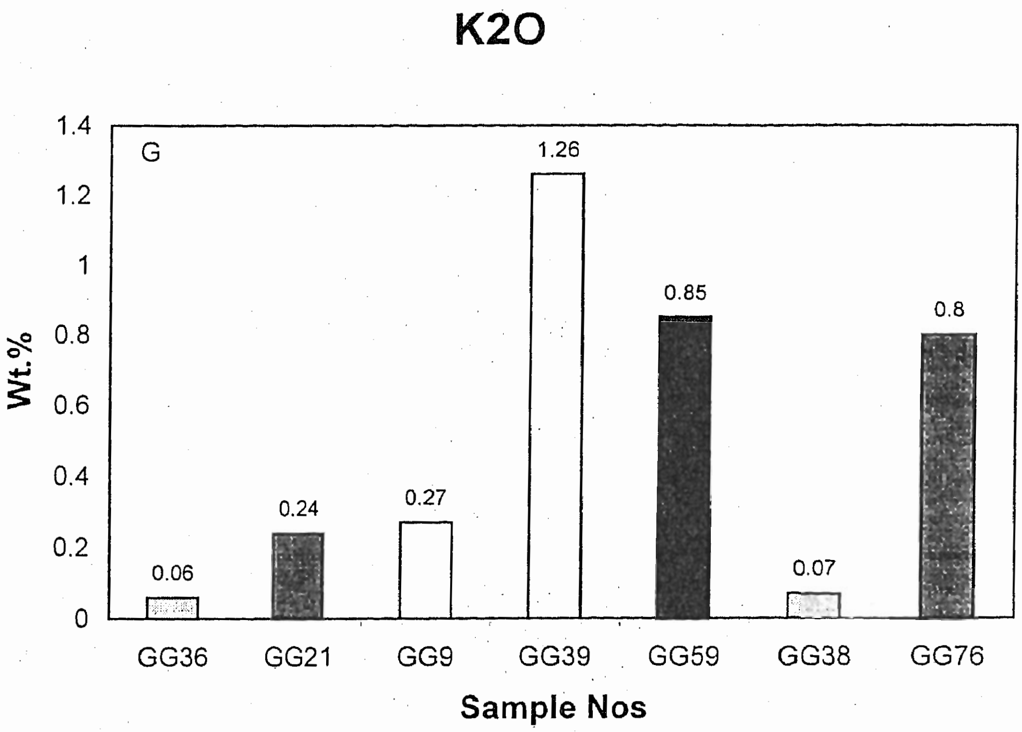

MgO
D
Wt.%
8
7
6
5
4
3
2
1
0
6.92
2.53
4.43
5.69
4.64
3.58
5.55
GG36
GG21
GG9
GG39
GG59
GG38
GG76
Sample Nos


CaO

E
Wt.%
60
50
40
30
20
10
0
49.9
49.6
45.2
40.3
45.52
45.3
32.9
GG36
GG21
GG9
GG39
GG59
GG38
GG76
Sample Nos


Na_2O

F
Wt.%
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.24
0.06
0.67
0.28
0.05
0.51
0.38
GG36
GG21
GG9
GG39
GG59
GG38
GG76
Sample Nos

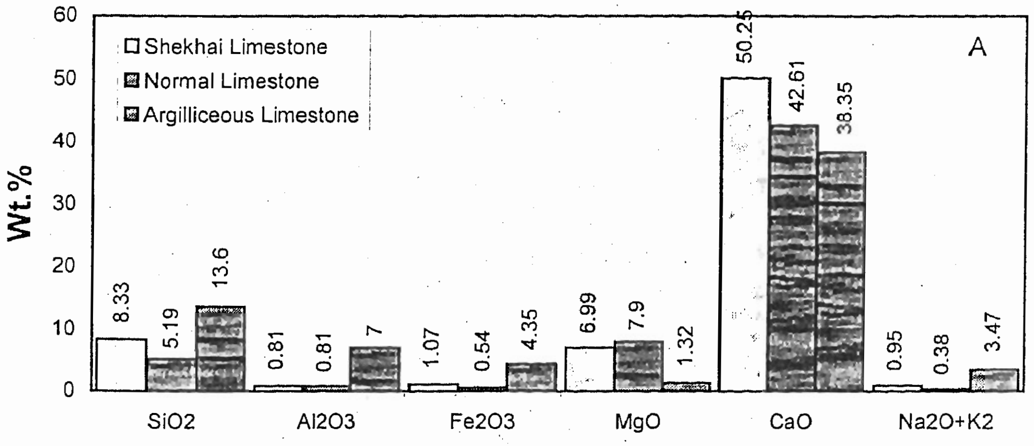

K2O
G
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Wt.%
0.06
0.24
0.27
1.26
0.85
0.07
0.8
GG36
GG21
GG9
GG39
GG59
GG38
GG76
Sample Nos

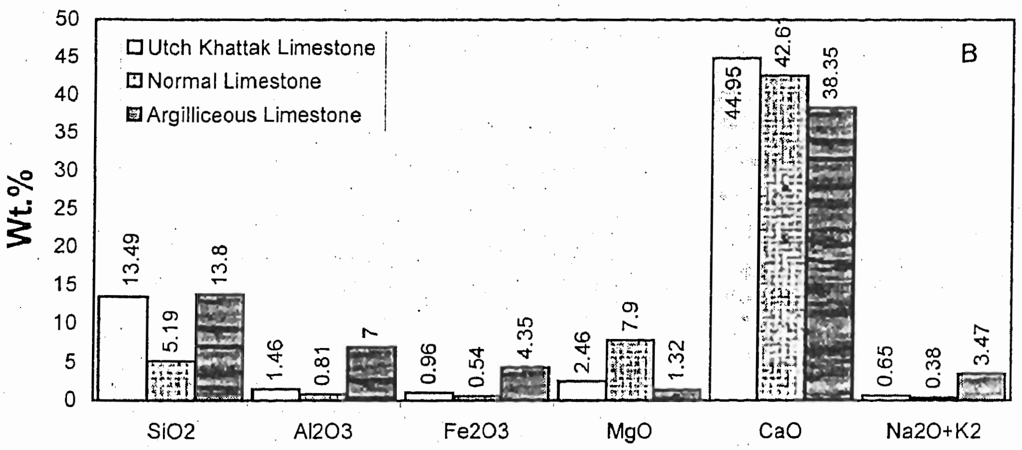
The average composition of the studied limestones are compared with that of the normal and argillaceous limestone (Table 5.3.1 and Fig.5.3abc).

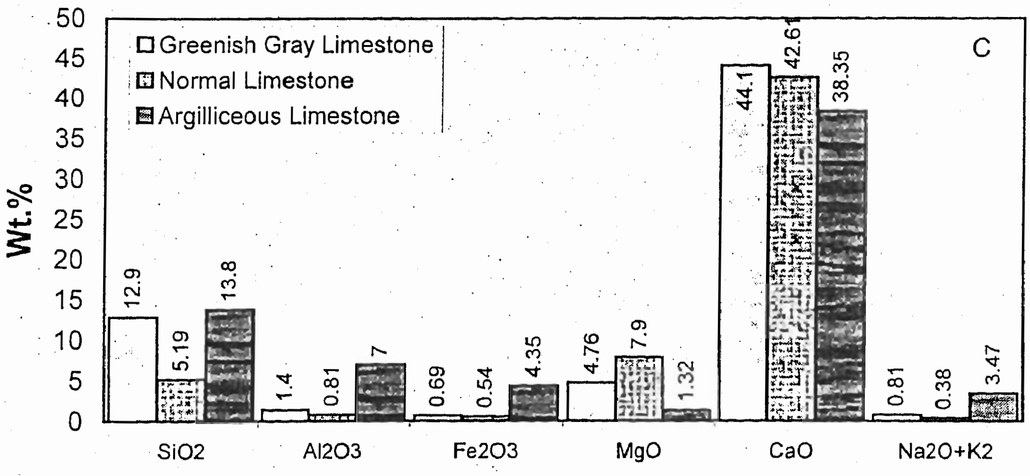
All the three varieties of the studied limestone have more silica (SiO_2) than normal limestone but less than that of the argilliceous limestone. Al_2O_3 and Fe_2O_3 are relatively high in the studied limestone as compared to that of normal limestone. These are, however, many folds less than that of the argilliceous limestone (Table 5.3.1 and Fig. 5.3abc). MgO in the studied limestone is less as compared to that of normal limestone and more as compared to that of argilliceous limestone, (Table 5.3.1 and Fig. 5.3abc). The CaO is, however, high in the studied limestone as compared to that of both normal and argilliceous limestones (Table 5.3.1 and Fig.5.3abc). Total alkalies in the studied limestones are relatively high as compared to that of normal limestone but many folds less than that of argilliceous limestone (Table 5.3.1 and Fig. 5.3abc).

Table 5.3.1. **The comparison of average composition of the studied Limestones with those of normal and argilaceous Limestones else where in the world.**

Samples	Shekhai Limestone (This Study)	Utch khattak Limstone (This Study)	Greenish Grey Limstone (This Study)	Normal Limestone (Clark, 1924)	Argilliceous Limestone (Stout and lambom, 1924)
SiO_2	8.33	13.49	12.90	5.19	13.80
Al_2O_3	0.81	1.46	1.40	0.81	7.00
Fe_2O_3	1.07	0.96	0.69	0.54	4.55
MgO	6.99	2.46	4.76	7.90	1.32
CaO	50.25	44.95	44.10	42.61	38.35
$Na_2O + K_2O$	0.95	0.65	0.81	0.38	3.47


A
☐ Shekhai Limestone
▨ Normal Limestone
▨ Argilliceous Limestone
Wt.%
60
50
40
30
20
10
0
8.33
5.19
13.6
0.81
0.81
7
1.07
0.54
4.35
6.99
7.9
1.32
50.25
42.61
38.35
0.95
0.38
3.47
SiO2
Al2O3
Fe2O3
MgO
CaO
Na2O+K2


B
☐ Utch Khattak Limestone
▨ Normal Limestone
▨ Argilliceous Limestone
Wt.%
50
45
40
35
30
25
20
15
10
5
0
13.49
5.19
13.8
1.46
0.81
7
0.96
0.54
4.35
2.46
7.9
1.32
44.95
42.6
38.35
0.65
0.38
3.47
SiO2
Al2O3
Fe2O3
MgO
CaO
Na2O+K2


C
☐ Greenish Gray Limestone
▨ Normal Limestone
▨ Argilliceous Limestone
Wt.%
50
45
40
35
30
25
20
15
10
5
0
12.9
5.19
13.8
1.4
0.81
7
0.69
0.54
4.35
4.76
7.9
1.32
44.1
42.61
38.35
0.81
0.38
3.47
SiO2
Al2O3
Fe2O3
MgO
CaO
Na2O+K2

Chemistry of Dolerite Dike:

The major element chemistry of dolerite dikes is given in Table 5.4. It is evident from this table that these dolerite samples have SiO_2 in the range of 47.6 to 50.6%, Al_2O_3 from 20.26 to 21.38%, Fe_2O_3 from 10.54 to 11.72%, CaO from 6.55 to 7.25%, MgO from 5.2 to 6.48%. Na_2O and K_2O are ranging from 1.07 to 2.11 and 0.22 to 0.64 respectively (Table 5.4). The studied dolerites dikes are chemically compared to those of similar dikes from Mansehra and Peshawar basin. The studied dolerites have SiO_2 similar to that of Mansehra but has less than that of Peshawar basin (Table 5.4.1 and Fig. 5.4a). Al_2O_3 higher than that of both Mansehra and Peshawar basin. Fe_2O_3 and MgO are more or less similar to that of both Mansehra and Peshawar basin (Table 5.4.1 and Fig. 5.4a). CaO and total alkalies in the studied dolerites are relatively less (Table 5.4.1 and Fig. 5.4a).

Table 5.4. Chemical Composition of Dolerite Dike.

Sample No.	GRD42	GRD63	GRD83	GRD8	Average	Max.	Min
SiO_2	47.6	50.6	50.5	49.5	49.55	50.6	47.6
Al_2O_3	21.38	20.48	20.26	20.91	20.758	21.38	20.26
Fe_2O_3	11.72	10.83	10.54	10.81	10.975	11.72	10.54
MgO	5.88	5.20	5.55	6.48	5.778	6.48	5.2
CaO	7.25	6.52	7.57	6.55	6.973	7.57	6.52
Na_2O	2.11	1.35	1.71	1.07	1.56	2.11	1.07
K_2O	0.22	0.44	0.47	0.64	0.43	0.64	0.22
LOI	3.48	3.05	2.45	2.50	2.87	3.48	2.45
Total	99.64	98.62	99.20	98.52	-	-	-

Table 5.4.1. The comparison of average composition of the studied Dolerite Dike with those of Manserha and Peshawar Basin Dolerite Dike.

Samples	Dolerite Dike (This Study)	Dolerite Dike Mansehra (Majid et al.,1991)	Dolerite Dike Peshawar Basin (Karim & Sofyan 1987)
SiO_2	49.55	48.45	51.62
Al_2O_3	20.75	13.04	13.51
Fe_2O_3	10.97	11.07	11.1
MgO	5.77	7.82	6.84
CaO	6.97	11.18	9.76
$Na_2O)_e$	2.00	3.73	2.73

Chemistry of Clay:

The major element chemistry of clay is presented in Table 5.5. SiO_2 is ranging from 48% to 52.5%, Al_2O_3 from 15.32% to 18.42%, Fe_2O_3 from 2.07% to 4.84% and CaO from 8.07% to 12.64%, MgO from 3.33% to 4.68%. Na_2O and K_2O are ranging from 0.48 to 1.52 of % and 1.44 to 2.14% respectively (Table 5.5). The average composition of the studied clays are compared with that of normal clay (Table 5.5.1 and Fig. 5.4b). SiO_2 and MgO are more or less similar to that of normal clay while other constituents are generally low in the studied clay except CaO which is multy fold higher in the studied clay as compared to that of normal clay (Table 5.5.1 and Fig. 5.4b).

Table 5.5. Chemical Composition of Clay.

Sample No.	GRC 74	GRC 65	GRC6 6	GRC7 3	GRC 78	GRC 79	GRC 70	GRC 69	Average	Max.	Min.
SiO_2	50.1	48.5	50.8	50.2	52.1	48.8	48.0	52.5	50.125	52.5	48
Al_2O_3	16.89	15.32	15.38	18.12	16.34	18.12	18.42	17.52	17.014	18.42	15.32
Fe_2O_3	3.34	4.84	3.81	4.43	4.62	2.07	4.34	4.26	3.964	4.84	2.07
MgO	4.25	4.06	3.77	3.35	4.58	3.33	4.68	4.53	4.069	4.68	3.33
CaO	9.00	12.64	8.20	8.60	9.16	8.07	9.86	8.13	9.208	12.64	8.07
Na_2O	0.87	1.04	1.33	1.16	1.52	0.48	1.09	1.11	1.08	1.52	0.48
K_2O	1.44	2.11	1.69	2.14	2.13	1.27	2.13	1.95	2	2.14	1.44
LOI	13.55	13.53	14.10	11.00	10.76	15.57	11.50	9.54	12.44	-	-
Total	99.50	102.13	99.14	99.07	101.31	97.73	100.09	99.62	-	-	-

Table 5.5.1. The comparison of average composition of the studied Clay with normal Clay else where in the world.

Samples	Clay (This Study)	Normal Clay (Eskola, 1932)
SiO_2	50.12	50.33
Al_2O_3	17.00	19.17
Fe_2O_3	3.96	6.50
MgO	4.06	3.77
CaO	9.20	1.43
$(Na_2O)_e$	3.08	5.81

Chemistry of Phyllite:

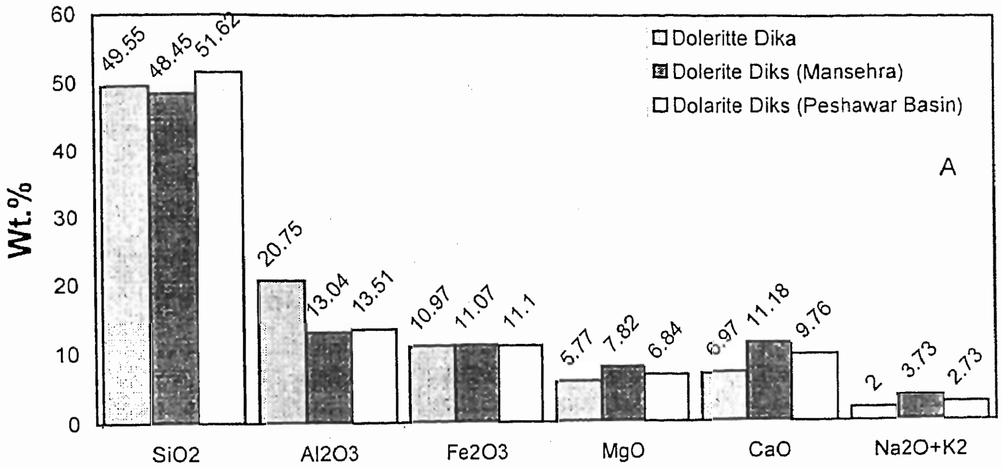
The major element chemistry of phyillite is given in Table 5.6. It is evident from this table that these phyillite samples have SiO_2 in range of 43.5% to 65.5%, Al_2O_3 from 16.12% to 23.65%, Fe_2O_3 from 0.25% to 5.32%, CaO from 0.78% to 5.75%, MgO from 0.93% to 3.64%. Na_2O and K_2O are ranging from 0.55 to 3.53% and 0.31 to 1.37 wt% respectively (Table 5.6). It is clear from the chemical composition of the studied phyillites (Table 5.6) that there is a greater variation in almost all the oxides. The studied phyllites are chemically compared with that of normal shale (Table 5.6.1 and Fig. 5.4c). The studied phyllites have high SiO_2, Al_2O_3 and MgO and low Fe_2O_3, CaO and total alkalies as compared to that of the normal shale (Table 5.6.1 and Fig. 5.4c).

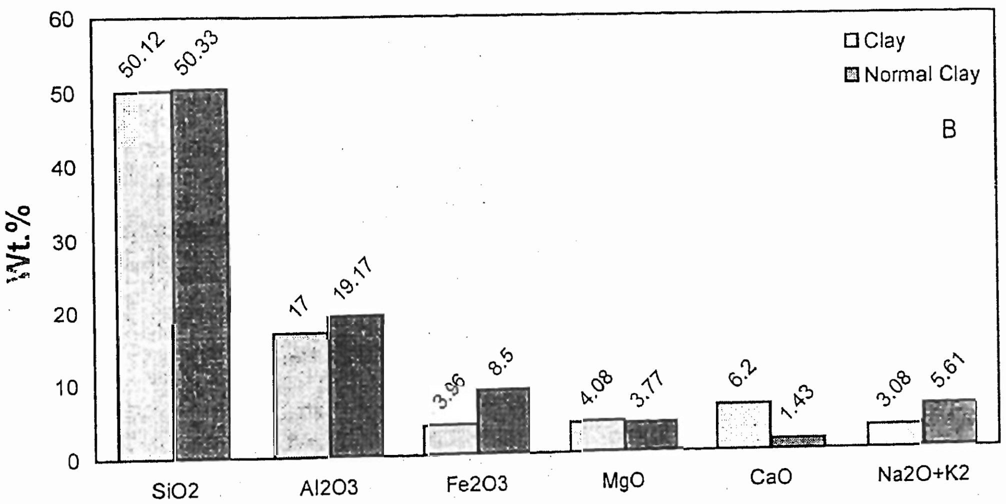
Table 5.6. Chemical Composition of Phyllite.

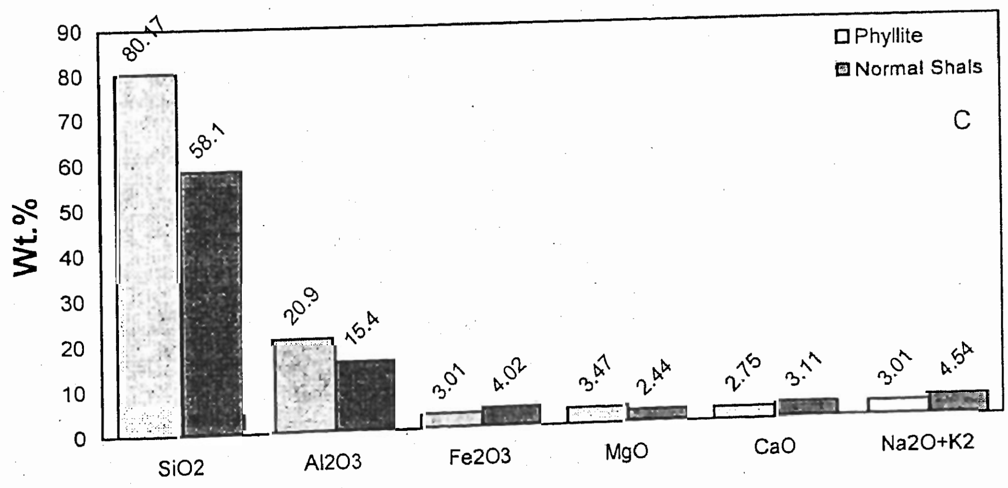
Sample No.	GRP 29	GRP 31	GRP 101	GRP 45	GRP 57	GRP 55	GRP 50	GRP 97	GRP 75	Average	Max	Min
SiO_2	64.50	63.70	55.00	63.60	63.80	64.20	65.50	57.80	43.50	60.178	65.5	43.5
Al_2O_3	16.12	17.64	18.86	22.72	23.12	23.52	20.12	23.65	22.38	20.903	23.65	16.12
Fe_2O_3	5.32	2.59	4.74	0.36	1.87	0.25	4.52	4.50	2.98	3.014	5.32	0.25
MgO	3.64	5.00	5.00	2.56	2.05	0.93	2.50	2.60	7.00	3.476	3.64	0.93
CaO	3.13	5.75	5.63	0.78	1.87	1.36	2.15	1.99	2.10	2.751	5.75	0.78
Na_2O	1.37	1.41	1.13	0.09	0.31	3.60	0.72	1.09	0.41	1.011	1.37	0.31
K_2O	3.53	1.89	3.04	0.67	0.89	0.55	2.30	2.00	3.13	2	3.53	0.55
LOI	3.18	3.26	5.08	2.53	3.51	3.20	2.63	5.11	6.85	-	-	-
Total	100.96	100.28	98.48	93.31	97.45	97.61	100.51	98.80	88.38	-	-	-

Table 5.6.1. The comparison of average composition of the studied Phyllite with normal Shale else where in the world.

Samples	Phyllite (This Study)	Shale (Clarke, 1924)
SiO_2	60.17	58.10
Al_2O_3	20.90	15.40
Fe_2O_3	3.01	4.02
MgO	3.47	2.44
CaO	2.75	3.11
$(Na_2O)_e$	3.01	4.54


Dolerítte Dika
Dolerite Diks (Mansehra)
Dolarite Diks (Peshawar Basin)
A
Wt.%
0
10
20
30
40
50
60
49.55
48.45
51.62
20.75
13.04
13.51
10.97
11.07
11.1
5.77
7.82
6.84
6.97
11.18
9.76
2
3.73
2.73
SiO2
Al2O3
Fe2O3
MgO
CaO
Na2O+K2


Clay
Normal Clay
B
Wt.%
0
10
20
30
40
50
60
50.12
50.33
17
19.17
3.96
8.5
4.08
3.77
6.2
1.43
3.08
5.61
SiO2
Al2O3
Fe2O3
MgO
CaO
Na2O+K2


Phyllite
Normal Shals
C
Wt.%
0
10
20
30
40
50
60
70
80
90
80.17
58.1
20.9
15.4
3.01
4.02
3.47
2.44
2.75
3.11
3.01
4.54
SiO2
Al2O3
Fe2O3
MgO
CaO
Na2O+K2

5.7. CHEMISTRY OF N.W.F.P. CEMENT

The chemistry of ordinary portland cement (OPC) largely depends upon the geochemistry of its raw materials that is, limestone, argillaceous rocks (i.e., clay, shale and phyillite), gypsum and silica sand (Lee 1976). Therefore, the lime content in any portland cement is very high. There is generally variation of lime content in cements which is dependent on the increase and decrease of SiO_2 (Lee, 1976). However, this problem can be solved by improving methods of manufacturing resulting soundness and rapid strength development.

The N.W.F.P. is rich in cement raw materials in different areas such as Haripur, Nizampur, Dera Ismail Khan, Kohat, Attock and Cherat. Therefore, three cement factories (i.e. Cherat cement company, Kohat cement company and Lucky cement company) are functioning in these areas. There are also other cement factories which are under these construction. These cement factories not only fulfill the cement demand in the area but also have wide net work of consumers in the country. Cement samples of these factories have been collected from different markets of Peshawar. These cements have been analysed for their chemical composition by using atomic absorption spectrophotometer. A brief chemistry of these cements is as follows:

Lucky Cement

It is clear from Table 5.7 that chemically the Lucky cement has SiO_2 = 19.10-21.70% AI_2O_3 = 4.21-5.89%, Fe_2O_3 = 2.73-2.79%, MnO = 0.05%, MgO = 1.92-2.38%, CaO = 65.66-66.45%, Na_2O = 0.52-0.56 % K_2O = 0.68-0.80%, loss on ignition = 0.77-1.22%, C_3A = 6.54-10.99 % and equivalent alkalies = 0.97-1.05%.

Kohat Cement

Kohat cement is having SiO_2 in the range of 16.60 to 19.50%, AI_2O_3 6.75 to 7.89%, Fe_2O_3 2.32-2./66%, MnO about 0.05% MgO 1.47-1.66%, CaO 64.92-65.75%, Na_2O 0.28-0.29%, K_2O 0.44-0.75%, loss on ignition 0.22-0.90% C_3A 13.81 to 16.41% and equivalent alkalies 0.58-0.78%.

Cherat Cement

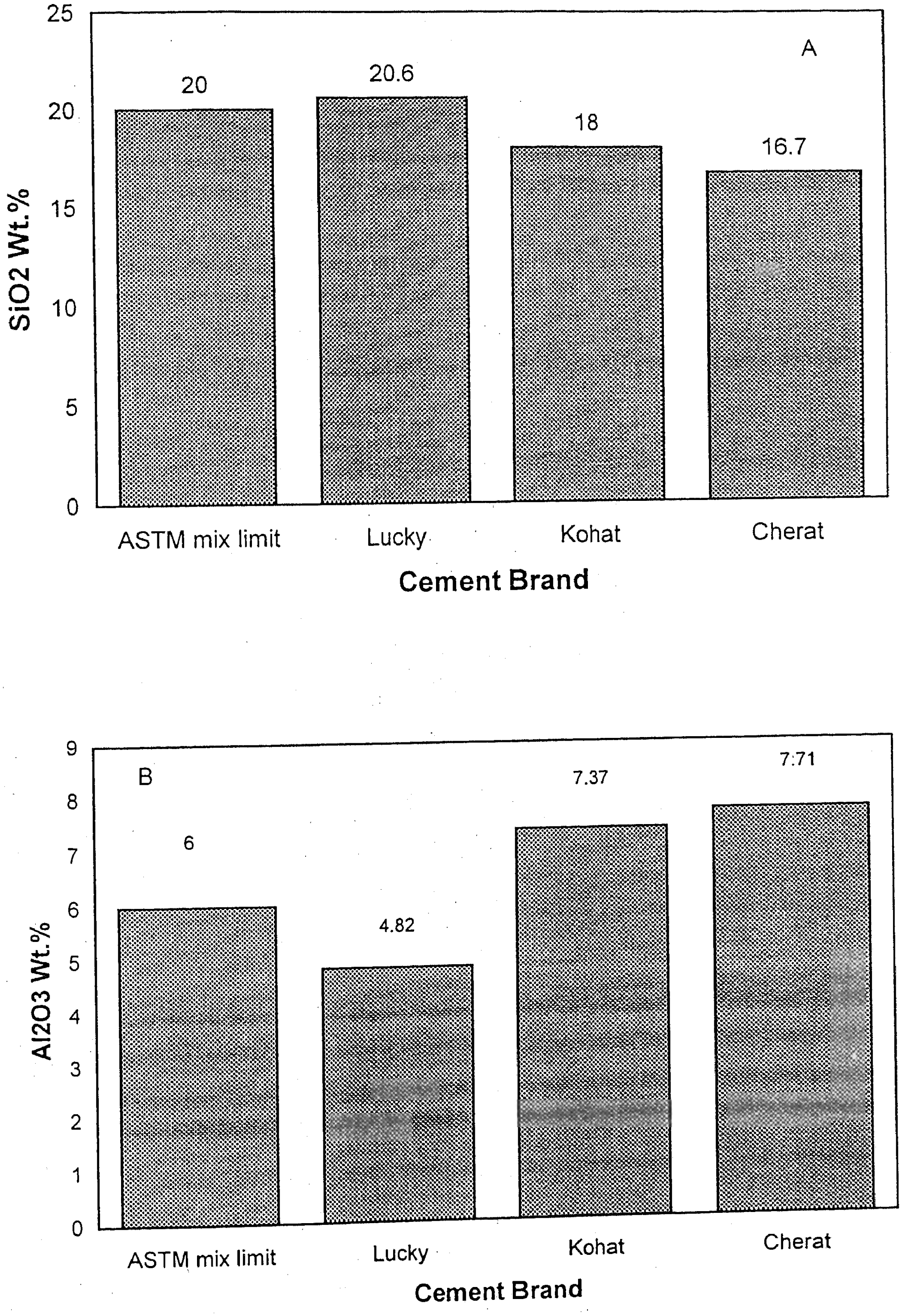
In Cherat cement, SiO_2 varies from 18.20-19.50%, AL_2O_3 from 7.58-7.81% Fe_2O_3 from 2.66 to 2.75 %, MnO about 0.05%, MgO from 0.99 to 1.77%, CaO from 64.53 to 65.84% K_2O from 0.66 to 0.71%, loss on ignition from 0.80 to 0.97% C_3A from 15.83 to 16.04% and equivalent alkalies from 0.87 to 0.94%.

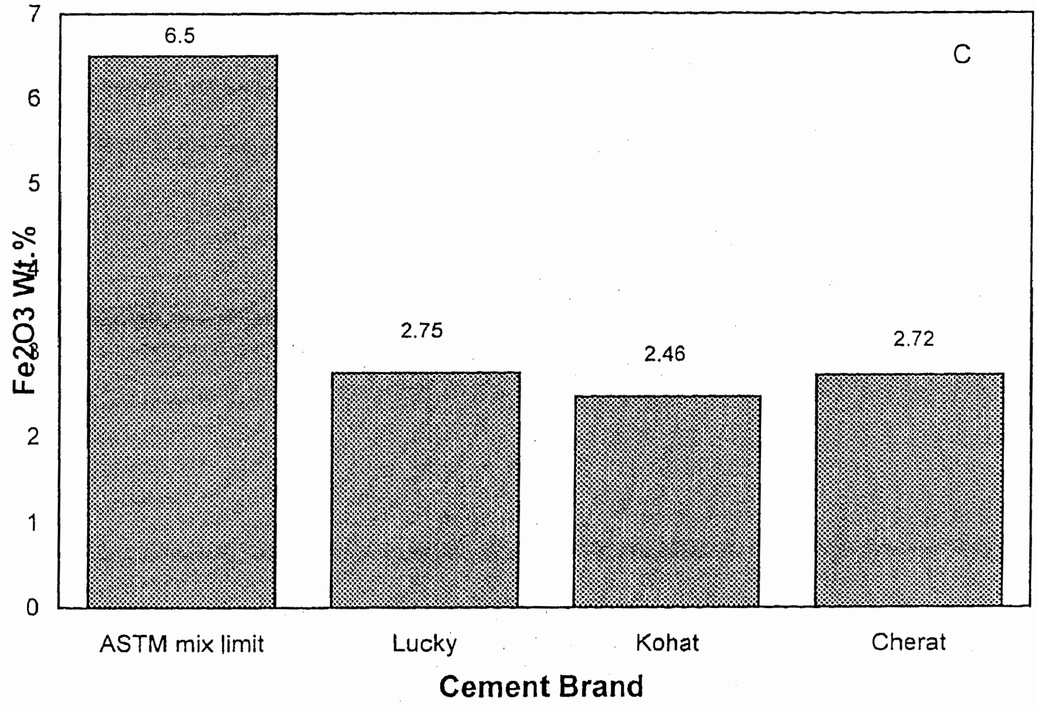
The averages of the major oxides of the portland cement of these three companies are diagrammatically compared with the maximum limits specified by ASTM C 150-94 in (Fig. 5.7 a-d).

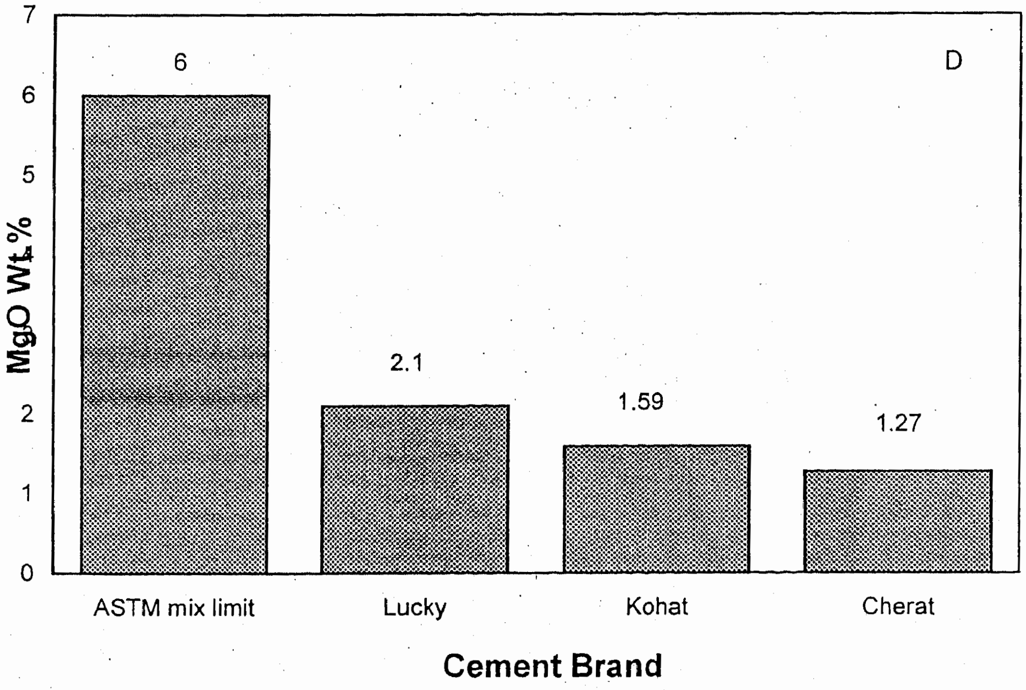
Table-5.7. Chemistry of N.W.F.P. Cement.

		Lucky Cement Co.				Kohat Cement Co.				Cherat Cement Co.			
	ASTM max. limit	I	II	III	Avr	I	II	III	Avr	I	II	III	Avr
SiO_2	20.0%	21.00	21.1	19.10	20.60	19.50	17.80	16.60	18.00	19.50	18.20	18.50	18.70
Al_2O_3	6.0%	4.36	4.2	5.89	4.82	6.75	7.48	7.89	7.37	7.73	7.81	7.58	7.71
Fe_2O_3	6.5%	2.79	2.70	2.73	2.75	2.41	2.32	2.66	2.46	2.75	2.75	2.66	2.72
MnO		0.05	0.00	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
MgO	6.0%	2.38	1.90	2.01	2.10	1.65	1.66	1.47	1.59	1.77	1.05	0.99	1.27
CaO		65.87	66.50	65.66	65.99	65.75	64.92	65.04	65.24	64.53	65.67	65.84	65.35
Na_2O		0.52	0.50	0.52	0.53	0.29	0.28	0.29	0.29	0.44	0.47	0.47	0.46
K_2O		0.80	0.70	0.68	0.73	0.75	0.69	0.44	0.63	0.66	0.71	0.71	0.69
Loss on ignition	3.0%	0.97	1.20	0.77	0.99	0.69	0.22	0.90	0.60	0.80	0.91	0.97	0.89
Total		98.74	99.50	97.41		97.84	95.42	95.34		98.24	97.62	97.77	
Tricalcium aluminate	15.0%	6.83	6.50	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	1.00	0.97	1.02	0.78	0.73	0.58	0.70	0.87	0.94	0.94	0.92

Fig. 5.7. Comparison of the Chemical Composition of Portland Cements of the Luchy, Kohat and Charat Cement factories with the standard set by ASTM C150-94 (1994)




7
6
5
4
3
2
1
0
Fe2O3 Wt.%
6.5
2.75
2.46
2.72
C
ASTM mix limit
Lucky
Kohat
Cherat
Cement Brand


7
6
5
4
3
2
1
0
MgO Wt.%
6
2.1
1.59
1.27
D
ASTM mix limit
Lucky
Kohat
Cherat
Cement Brand

Silica (SiO_2) in cement may comprises upto 25% of total constituents (Lea, 1976). The average SiO_2 contents in the studied cement are generally within the limits of ASTM. The Kohat cement, however, has relatively low SiO_2 (Fig. 5.7a).

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 portland cement is to reduce the clinking temperture and production of high early strength. The alumina content in the studied cement specimens of Kohat and Cherat brands are slightly higher where as in Lucky it is slightly lower as compare to that of the ASTM standards (Fig. 5.7b). The Fe_2O_3 concentration in all the three varieties are within the specified limits by ASTM (Fig. 5.7c).

The concentration of manganese oxide (MnO) is usually less than 0.1% for cement made from normal raw material. (Lea, 1976). The MnO content of all the three varieties of cement is almost negligible (Table 5.7).

Magnesia (MgO) usually act as flux, thus facilitating combustion and rendering of clinker. (Lea, 1976). But abnormality in its concentration led to long term unsoundness. The average MgO contents of Lucky Cement are relatively high but are within the maximum limits specified by ASTM (Fig. 5.7d).

Approximately 75% of portland cement raw material consists 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. The average CaO content in all the three varieties of cement are more or less similar, Table 5.7).

Sodium oxide (Na_2O) and potassium oxide (K_2O) are generally found as minor constituents in the portland cements, (Lea, 1976). They form water-soluble alkalies. The average Na_2O and K_2O contents of the Kohat cement are relatively low. (Table 5.7).

The tricalcium aluminate (C_3A) control's the setting time of the portland cement (Gilkey, 1962; Lea, 1976). Its concentration in the cement largely depends upon alumina and ferric oxide contents. The average tricalcium aluminate contents in the studied cements are within the specified limits (Fig. 5.7).

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 - silica reaction damaging the concrete structures. The equivalent alkalies in the studied cements are relatively higher to its permissible limits. Therefore, mortarobar test should be the best method to check any possibility of the alkalies reaction in cements.

CHAPTER VI

PROPORTIONING OF RAW MATERIAL FOR CEMENT MANUFACTURING

In cement manufacturing, the mixing of various raw material in different proportions is a very difficult job. Once the appropriate proportions are set then the portland cement of desired composition can be obtained. In this chapter, the emphasis has been given to the raw material available in the Gandghar range and their mixing proportions have been calculated to manufacture appropriate portland cement.

By considering various types of raw material (i.e., Shekhai, Utch Khattak and Greenish grey limestone, phyllite, lateriates and dolerites) about thirteen different mixture with different ratios are prepared. Assuming these ratios of mixing, the approximate clinker composition and other parameters have been calculated (Table 6.1-13).

Mixture No.1

Raw Material Available:

In this mixture the Shekhai limestone, Utch Khattak limestone, phyllite, Greenish grey limestone and dolerites are used as raw material. There average composition and resulted clinker's composition and other parameters are given in Table 6.1.

In this raw material the average composition of silica is 8.33 in Shekhai limestone, 13.49 in Utch Khattak limestone, 60.18 in phyllite, 12.91 in dolerites.

The average composition of aluminum oxide ($Al2O_3$) is 0.81 in Shekhai limestone, 1.47 in Utch Khattak Limestone, 20.90 in phyllite, 1.41 in greenish grey limestone, 20.76 in dolerite (Table 6.1).

The average composition of iron oxide is 1.08 in Shekhai limestone, 0.96 in Utch Khattak limestone, 3.01 in phyllite, 0.70 in greenish grey limestone, 10.98 indolerite (Table 6.1).

The average composition of CaO is 50.26 in Shekhai limestone, 44.96 in Utch Khattak liemstone, 2.75 in phyllite, 44.10 in greenish grey limestone, 6.97 in dolerite (Table 6.1).

Ratio of Usage:

By calculating the ratios of usage of the proposed raw material in Table 6.1, it is clear that 80% Shekhai limestone, 6% of Utch Khattak limestone, 2% phyllites and 12% dolerite will give the appropriate mixture in this case for portland cement. The Shekhai limestone has the highest percentage (80%) in this mixture. This limestone is relatively soft and can easily be pulverized. It is therefore, used in high proportion, this will save the power consumption and less efforts will be required to bring it to the desired mesh size.

Utch Khattak limestone is used less (6%) because it is relatively hard and, therefore, it will need much power consumption and more efforts for grinding. But here will be less expensive because of its huge reserves and availability in this area.

2% of phyllite is used here because it has high SiO_2 and low MgO, also having crystalline shape and is easily excavated and transported.

12% of dolerite rock is used here due to its high content of silica (SiO_2). When it is used in raw mixture, it will reduce the consumption of clay and phyllite. The total will, therefore, be 100%.

By considering the chemical composition of raw material and the ratio of usage, the SiO_2, Al_2O_3, Fe_2O_3 and CaO are calculated as 14.63%, 3.65%, 2.30% and 43.79% respectively (Table 6.1).

Raw Meal (RM) and Clinker Composition:

It is clear from Table 6.1 that the mixture of above mentioned raw material in proposed proportions will give rise to the final product as clinker. This clinker will have SiO_2 = 22.52%, Al_2O_3 = 5.61%, Fe_2O_3 = 3.54% and CaO = 67.44% (Table 6.1).

Raw Meal and Clinker Parameters:

The clinker parameters include; modulus of alumina (MA), modulus of silica (MS), lime saturation factor (LSF) and tricalcium aluminate (C_3A). These are calculated as follows:

$$\text{MA} = \frac{Al_2O_3}{Fe_2O_3} = \frac{3.65}{2.30} = 1.587$$

$$\text{Clinker} = \frac{Al_2O_3}{Fe_2O_3} = \frac{5.61}{3.54} = 1.587$$

MS = Modulus of silica

$$\text{MS} = \frac{SiO_2}{Fe_2O_3 + Al_2O_3} =$$

$$\frac{14.63}{2.30 + 3.65} = 2.458$$

RM = 2.46

$$\text{for Clinker} = \frac{SiO_2}{Fe_2O_3 + Al_2O_3} = \frac{22.52}{3.54 + 5.61} = 2.46$$

Lsf = Lime saturation factor

$$= \frac{CaO}{2.8\ SiO_2 + 1.18\ Al_2O_3 + 0.65\ Fe_2O_3}$$

$$= \frac{43.79}{2.8x14.63 + 1.18x3.65 + 0.65x2.30}$$

$$= 0.936$$

for Clinker = $\frac{67.44}{2.8x22.52 + 1.18x5.61 + 0.65x3.54}$ = 0.936

C_3A = Tricalcium aluminate

C_3A = 2.65 Al_2O_3 - 1.65 Fe_2O_3

= 2.65 x 3.65 - 1.65 x 2.30

= 5.87

for Clinker = 2.65 x 5.61 - 1.65 x 3.54 = 9.025

Table 6.1 **Chemical composition of raw material, their mixing ratios and the resulted chemical composition and other parameters of clinkers formed by mixture No.1.**

Chemical Composition of Raw Material Available

	S/L.S	U/K.L.S	Phyllite	G.G.L/S	Dolerite
SiO_2	8.33	13.49	60.18	12.91	49.55
Al_2O_3	0.81	1.47	20.90	1.41	20.76
Fe_2O_3	1.08	0.96	3.01	0.70	10.98
CaO	50.26	44.96	2.75	44.10	6.97

Usage of Raw Material

Ratio of Usage	S/L.S	U.K.L.S	Phyllite	G.G.L/S	Dolerite	Total
	80.00%	6.00%	2.00%	0.00%	12.00%	100.00%

Composition of Raw Mixture

SiO_2	14.63
Al_2O_3	3.65
Fe_2O_3	2.30
CaO	43.79

Raw meal & Clinker composition

Composition	RM	Clinker (RM x 1.54)
SiO_2	14.63	22.52
Al_2O_3	3.65	5.61
Fe_2O_3	2.30	3.54
CaO	43.79	67.44

Raw meal & Clinker parameters

Parameters	RM	Clinker
MA	1.587	1.587
MS	2.46	2.46
Lsf	0.936	0.936
C3A	5.875	9.025

Mixture No.2

Raw Material Available:

The raw material for mixture nO.2 include Shekhai limestone, Utch Khattak limestone, phyllite, greenishgrey limetone and laterite (Table 6.2).

The percentage of oxides is differents in each of this raw material. The average composition of SiO_2 in Shekhai limestone is 8.33% in Utch Khattak limestone is 13.49, in Phyllite is 60.18% in greenish-grey limestone is 12.91% and in Lateriate is 44%. The total of SiO_2 in this raw material is calculated as 14.34% (Table 6.2).

The average composition of Al_2O_3 in Shekhai limestone is 0.81% in Utch Khattak limestone is 1.47%, in Phyllites is 20.90% in greenish-grey limestone is 1.41 and in lateriate is 12.80%. The total of Al_2O_3 is calculated as 3.16% (Table 6.2).

The average composition of Fe_2O_3 in Shekhai limestone is 1.08% in Utch Khattak limestone is 0.96% in phyllite is 3.01% in greenish-grey limestone is 0.70% in lateriate is 40.50%. The total Fe_2O_3 is calculated as 2.42 (Table 6.2).

The average composition of CaO in Shekhai limestone is 44.96% in phyllite is 2.75% in greenish-grey limestone is 44.10% and in lateriate is 1.05%. The total CaO is calculated as 42.52% (Table 6.2).

Ratio of Usage:

The ratio of mixing of the raw material for mixture No.2 is calculated as: Shekhai limestone is 84%, phyllites is 10%, greenish-grey limestone is 3% and laterite is 3%. No Utch Khattak limestone has been used here as raw material.

The addition of laterite has several advantages in the raw mix preparation. Because it has high iron contents, high corrective efficiency and also has ability for better quality control.

Raw Meal and Clinker Composition:

After mixing of raw material in the given proportion (Table 6.2) the resultant clinker composition has been calculated and is presented in Table 6.2. The final product of clinker will have SiO_2 = 22.08%, Al_2O_3 = 4.86%, Fe_2O_3 = 3.73% and CaO = 65.48% (Table 6.2).

The other parameters such as MA, MS, LSF and C_3A are calculated as follows and are given in Table 6.2.

MA = Modulus of Alumina

$$MA = \frac{Al_2O_3}{Fe_2O_3} = \frac{3.16}{2.42}$$

$$= 1.303$$

for Clinker $= \frac{4.86}{3.73} = 1.303$

MS = Modulus of silica

$$= \frac{SiO_2}{Fe_2O_3 + Al_2O_3}$$

$$= \frac{14.34}{2.42 + 3.16} = 2.571$$

for Clinker $= \frac{22.08}{3.73+4.86} = 2.57$

L.Sf. $= \frac{CaO}{2.8SiO_2+1.18Al_2O_3+0.65\ Fe_2O_3}$

$$= \frac{42.52}{2.8x14.34 + 1.18x3.16 + 0.65x2.42}$$

$$= 0.921$$

for Clinker $= \frac{65.48}{2.8x22.08 + 1.18x4.86 + 0.56x3.73} = 0.921$

$C_3A = 2.65\ Al_2O_3 - 1.65\ Fe_2O_3$

$$= 2.65 \text{ x } 3.16 - 1.65 \text{ x } 2.42$$

$$= 4.266$$

for Clinker $= 2.65 \text{ x } 4.86 - 1.65 \text{ x } 3.73 = 6.724$

Table 6.2. Chemical composition of raw material, their mixing ratios and the resulted chemical composition and other parameters of clinkers formed by mixture No.2.

Chemical Composition of Raw Material Available

	S/L.S	U/K.L.S	Phyllite	G.G.L/S	Laterite
SiO_2	8.33	13.49	60.18	12.91	44.00
Al_2O_3	0.81	1.47	20.90	1.41	12.80
Fe_2O_3	1.08	0.96	3.01	0.70	40.50
CaO	50.26	44.96	2.75	44.10	1.05

Usage of Raw Material

Ratio of Usage	S/L.S	U.K.L.S	Phyllite	G.G.L/S	Laterite	Total
	84.00%	0.00%	10.00%	3.00%	3.00%	100.00%

Composition of Raw Mixture

SiO_2	14.34
Al_2O_3	3.16
Fe_2O_3	2.42
CaO	42.52

Raw meal & Clinker composition

Composition	RM	Clinker (RMx1.54)
SiO_2	14.34	22.08
Al_2O_3	3.16	4.86
Fe_2O_3	2.42	3.73
CaO	42.52	65.48

Raw meal & Clinker parameters

Parameters	RM	Clinker
MA	1.303	1.303
MS	2.571	2.571
Lsf	0.921	0.921
C3A	4.266	6.724

Mixture No.3

Raw Material Available:

The raw material for mixture No.3 include Shekhai limestone, dolerite dike, phyllite, greenish-grey limestone and laterite (Table 6.3).

The percentage of oxides is differents in each of this raw material. The average composition of SiO_2 in Shekhai limestone is 8.33%, in dolerite is 49.55%, in phyllite is 60.18%, in greenish-grey is 12.91% and in laterite is 12.80%. The total of SiO_2 in this raw material is calculated as 15.11% (Table 6.3).

The average composition of Al_2O_3 in Shekhai limestone is 0.81% in dolerite is 20.76%, in phyllite is 20.90%, in greenish-grey limestone is 1.41%, and in laterite is 12.80%. The total of Al_2O_3 is calculated as 3.54% (Table 6.3).

The average composition of Fe_2O_3 in Shekhai limestone is 1.08%, in doloerite is 10.98%, in phyllite is 3.01%, in greenish-grey limestone is 0.70%, in laterite is 40.50%. The total of Fe_2O_3 is calculated as 1.96% (Table 6.3).

The average composition of CaO in Shekhai limestone is 50.26%, in dolerite is 6.97%, in phyllite is 2.75%, in greenish-grey is 44.10%, in laterite is 1.05%. The total of CaO is calculated as 43.71% (Table 6.3).

Ratio of Usage:

The ratio of mixing of the raw material for mixture No.3 is calculated as; Shekhai limestone is 86%, dolerite dike is 3%, phyllite is 10%, no greenish-grey limestone has been used here as raw material and 10% laterite.

The addition of laterite has several advantages in raw mix preparation. Becuase it has high iron content, high corrective efficiency and also has ability for better quality control.

Raw Material and Clinker Composition:

After mixing of raw material in the given proportion (Table 6.3), the resultant clinker composition has been calculated and is presented in Table 6.3. The final product of clinker will have SiO_2 = 23.27%, Al_2O_3 = 5.45%, Fe_2O_3 = 3.02% and CaO = 67.32% (Table 6.3). The other parameters such as MA, MS, LSf, and C_3A are calculated as follows and are given in Table 6.3.

$$\text{MA} = \frac{Al_2O_3}{Fe_2O_3} = \frac{3.54}{1.96} = 1.804$$

$$\text{for Clinker} = \frac{5.45}{3.02} = 1.804$$

$$\text{MS} = \frac{SiO_2}{Fe_2O_3 + Al_2O_3}$$

$$= \frac{15.11}{1.96 + 3.54} = 2.747$$

for Clinker $= \frac{23.27}{3.02+5.45} = 2.747$

LSf $= \frac{CaO}{2.8SiO_2+1.18Al_2O_3+0.65Fe_2O_3}$

$$= \frac{43.71}{2.8x15.11 + 1.18x3.54 + 0.65x1.96}$$

$$= 0.901$$

the clinker is 0.901.

for Clinker $= \frac{67.32}{28x23.27 + 1.18x5.45 + 0.65x3.02}$

$$= 0.915$$

C_3A $= 2.65\ Al_2O_3 - 1.65\ Fe_2O_3$

$$= 2.65 \text{ x } 3/54 - 1.65 \text{ x } 1.96$$

$$= 6.057$$

for Clinker $= 265 \text{ x } 5.45 - 1.65 \text{ x } 3.02$

$$= 9.459$$

Table 6.3. **Chemical composition of raw material, their mixing ratios and the resulted chemical composition and other parameters of clinkers formed by mixture No.3.**

Chemical Composition of Raw Material Available

	S/L.S	Dolerite	Phyllite	G.G.L/S	Laterite
SiO_2	8.33	49.55	60.18	12.91	44.00
Al_2O_3	0.81	20.76	20.90	1.41	12.80
Fe_2O_3	1.08	10.98	3.01	0.70	40.50
CaO	50.26	6.97	2.75	44.10	1.05

Usage of Raw Material

Ratio of Usage	S/L.S	Dolerite	Phyllite	G.G.L/S	Laterite	Total
	86.00%	3.00%	10.00%	0.00%	1.00%	100.00%

Composition of Raw Mixture

SiO_2	15.11
Al_2O_3	3.54
Fe_2O_3	1.96
CaO	43.7

Raw meal & Clinker composition

Composition	RM	Clinker (RM x 1.54)
SiO_2	15.11	23.27
Al_2O_3	3.54	5.45
Fe_2O_3	1.96	3.02
CaO	43.71	67.32

Raw meal & Clinker parameters

Parameters	RM	Clinker
MA	1.804	1.804
MS	2.747	2.747
Lsf	0.901	0.915
C3A	6.057	9.459

Mixture No.4

Raw Material Available:

The raw material for mixture No.4 include Shekhai limestone, dolerite dike, phyllite, greenish-grey limestone and laterite (Table 6.4).

The percentage of oxides is differents in each of this raw material. The average composition of SiO_2 in Shekhai limestone is 8.33%, in dolerite dike is 49.55%, in phyllite is 60.18%, in greenish grey limestone is 12.91% and in laterite is 44%. The total of SiO_2 in this raw material is calculated as 14.11% (Table 6.4).

The average composition of Al_2O_3 in Shekhai limestone is 0.81%, in dolerite dike is 20.76%, in phyllite is 20.90%, in greenish-grey limestone is 1.41%, and in laterite is 12.80%. The total of Al_2O_3 is calculated as 3.57 (Table 6.4).

The average composition of Fe_2O_3 in Shekhai limestone is 1.08%, in dolerite is 10.98%, in phyllite is 3.01%, in greenish-grey limestone is 0.70%, and in laterite is 40.50%. The total of Fe_2O_3 is calculated as 2.09% (Table 6.4).

The average composition of CaO in Shekhai limestone is 50.26%, in dolerite dike is 6.97%, in phyllite is 2.75%, in greenish-grey is 44.10% and in laterite is 1.05%. The total of CaO is calculated as 41.51% (Table 6.4).

Ratio of Usage:

The ratio of mixing of the raw material for mixture nO.4 is calculated as; Shekhai limestone is 81%, dolerite is 10%, greenish-grey is 5%, phyllite is 4%, and no laterite has been used here as raw material (Table 6.4).

Raw Meal and Clinker Composition:

After mixing of raw material in the given proportion (Table 6.4), the resultant clinker composition has been calculated and is presented in Table 6.4. The final product of clinker will have SiO_2 = 21.13%, Al_2O_3 = 5.50%, Fe_2O_3 = 3.22% and CaO = 63.93% (Table 6.4).

The other parameters such as MA, MS, LSf and C_3A are calculated as follows and are given in Table 6.4.

$$\text{MA} = \frac{Al_2O_3}{Fe_2O_3} = \frac{3.57}{2.09} = 1.707$$

$$\text{for Clinker} = \frac{5.50}{3.22} = 1.708$$

$$\text{MS} = \frac{SiO_2}{Fe_2O_3 + Al_2O_3} = \frac{14.11}{2.09 + 3.57}$$

$$= 2.493$$

$$\text{for Clinker} = \frac{21.73}{3.22 + 5.50} = 2.491$$

L.Sf. $\frac{CaO}{2.8SiO_2+1.18Al_2O_3+0.65+Fe_2O_3}$

$= \frac{41.51}{2.8x14.11+1.18x3.57+0.65x2.09}$

= 0.907

for Clinker $= \frac{63.93}{2.8x21.73 + 1.18x5.50 + 0.65x3.22}$

= 0.920

C_3A = $2.65Al_2O_3$ - 1.65 Fe_2O_3

= 2.65 x 3.57 - 1.65 x 2.09

= 5.920

for Clinker = 2.65 x 5.50 - 1.65 x 3.22

= 9.262

Table 6.4 **Chemical composition of raw material, their mixing ratios and the resulted chemical composition and other parameters of clinkers formed by mixture No.4.**

Chemical Composition of Raw Material Available

	S/L.S	Dolerite	Phyllite	G.G.L/S	Laterite
SiO_2	8.33	49.55	60.18	12.91	44.00
Al_2O_3	0.81	20.76	20.90	1.41	12.80
Fe_2O_3	1.08	10.98	3.01	0.70	40.50
CaO	50.26	6.97	2.75	44.10	1.05

Usage of Raw Material

Ratio of Usage	S/L.S	Dolerite	Phyllite	G.G.L/S	Laterite	Total
	81.00%	10.00%	4.00%	5.00%	0.00%	100.00%

Composition of Raw Mixture

SiO_2	14.11
Al_2O_3	3.57
Fe_2O_3	2.09
CaO	41.51

Raw meal & Clinker composition

Composition	RM	Clinker (RM x 1.54)
SiO_2	14.11	21.73
Al_2O_3	3.57	5.50
Fe_2O_3	2.09	3.22
CaO	41.51	63.93

Raw meal & Clinker parameters

Parameters	RM	Clinker
MA	1.707	1.708
MS	2.493	2.491
Lsf	0.907	0.920
C3A	5.920	9.262

Mixture No.5

Raw Material Available:

The raw material for mixture No.5 include Shekhai limestone, dolerite dike, phyllite, greenish-grey limestone and laterite (Table 6.5).

The percentage of oxides is different in each of this raw material. The average composition of SiO_2 in Shekhai limestone is 8.33%, in dolerite dike is 49.55%, in phyllite is 60.18%, in greenish grey limestone is 12.91% and in laterite is 44%. The total of SiO_2 in this raw material is calculated as 14.93% (Table 6.5).

The average composition of Al_2O_3 in Shekhai limestone is 0.81%, in dolerite dike is 20.76% in phyllite is 20.90%, in greenish grey limestone is 1.41%, and in laterite is 12.80%. The total of Al_2O_3 is calculated as 4 (Table 6.5).

The average composition of Fe_2O_3 in Shekhai limestone is 1.08%, in dolerite is 10.98% in phyllite is 3.01%, in greenish grey is 0.70%, and in laterite is 40.50%. The total of Fe_2O_3 is calculated as 2.66% (Table 6.5).

The average composition of CaO in Shekhai limestone is 50.26%, in dolerite is 6.97%, in phyllite is 2.75%, in greenish-grey is 44.10%, and in dolerite is 1.05. The total of CaO is calculated as 43.33% (Table 6.5).

Ratio of Usage:

The ratio of mixing of the raw material for mixture No.5 is calculated as; Shekhai limestone is 84%, dolerite dike is 16%, no phyllite, greenish-grey limestone and laterite has been used here as raw materials.

Raw Meal and Clinker Composition:

After mixing of raw material in the given proportion (Table 6.5). The resultant clinker composition has been calculated and is presented in Table 6.5. The final product of clinker will have SiO_2 = 22.99%, Al_2O_3 = 6.10%, Fe_2O_3 = 4.10%, and CaO = 66.73% (Table 6.5). The other parameters such as MA, MS, LSf and C_3A are calculated as follows and are given in Table 6.5.

$$MA = \frac{Al_2O_3}{Fe_2O_3} = \frac{4}{2.66} = 1.504$$

$$\text{for Clinker} = \frac{6.16}{4.10} = 1.502$$

$$MS = \frac{SiO_2}{Fe_2O_3 + Al_2O_3}$$

$$= \frac{14.93}{2.66 + 4} = 2.240$$

$$\text{for Clinker} = \frac{22.99}{4.10+6.16} = 2.240$$

LSf. $= \dfrac{CaO}{2.8SiO_2+1.18Al_2O_3+0.65Fe_2O_3}$

L.Sf. $= \dfrac{43.33}{2.8x14.93 + 1.18x4 + 0.65x2.65}$

$= 0.884$

for Clinker $= \dfrac{66.73}{2.8x22.99 + 1.18x6.16 + 0.65x4.10}$

$= 0.898$

$= 2.65\ Al_2O_3 - 1.65\ Fe_2O_3$

$C_3A = 2.65\ Al_2O_3 - 1.65\ Fe_2O_3$

$= 2.65 \text{ x } 4 - 1.65 \text{x} 2.66$

$= 6.104$

for Clinker $= 2.65 \text{ x } 6.16 - 1.65 \text{ x } 4.10$

$= 9.559$

Table 6.5 **Chemical composition of raw material, their mixing ratios and the resulted chemical composition and other parameters of clinkers formed by mixture No.5.**

Chemical Composition of Raw Material Available

	S/L.S	Dolerite	Phyllite	G.G.L/S	Laterite
SiO_2	8.33	49.55	60.18	12.91	44.00
Al_2O_3	0.81	20.76	20.90	1.41	12.80
Fe_2O_3	1.08	10.98	3.01	0.70	40.50
CaO	50.26	6.97	2.75	44.10	1.05

Usage of Raw Material

Ratio of Usage	S/L.S	Dolerite	Phyllite	G.G.L/S	Laterite	Total
	84.00%	16.00%	0.00%	0.00%	0.00%	100.00%

Composition of Raw Mixture

SiO_2	14.93
Al_2O_3	4.00
Fe_2O_3	2.66
CaO	43.33

Raw meal & Clinker composition

Composition	RM	Clinker (RM x 1.54)
SiO_2	14.93	22.99
Al_2O_3	4.00	6.16
Fe_2O_3	2.66	4.10
CaO	43.33	66.73

Raw meal & Clinker parameters

Parameters	RM	Clinker
MA	1.504	1.502
MS	2.240	2.240
Lsf	0.884	0.898
C3A	6.104	9.559

Mixture No.6

Raw Material Available:

The raw material for mixture No.6 include Shekhai limestone, dolerite dike, phyllite, greenish grey limestone and laterite.

The percentage of oxides is differents in each of this raw material. The average composition of SiO_2 in Shekhai limestone is 8.33%, in dolerite is 49.55%, in phyllite is 60.18%, in greenish-grey limestone is 12.91% and in laterite is 44%. The total of SiO_2 in this raw material is calculated as 15.11% (Table 6.6).

The average composition of Al_2O_3 in Shekhai limestone is 0.81%, in dolerite is 20.76%, in phyllite is 20.90%, in greenish-grey is 44.10% and in laterite is 12.80%. The total of Al_2O_3 is calculated as 3.38% (Table 6.6).

The average composition of Fe_2O_3 in Shekhai limestone is 15.11%, in dolerite is 10.98%, in phyllite is 3.01%, in greenish-grey limestone is 0.70%, and in laterite is 40.50%. The total of Fe_2O_3 is calculated as 2.47% (Table 6.6.).

The average composition of CaO in Shekhai limestone is 50.26%, in dolerite is 6.97%, in phyllite is 2.75%, in greenish-grey limestone 44.10% and in laterite is 1.05%. The total of CaO is calculated as 43.55% (Table 6.6).

Ratio of Usage:

The ratio of mixing of raw material for mixture No.6 is calculated as; Shekhai limestone is 86%, no dolerite dike has been used here as raw material, in phyllite is 11%, no greenish-grey limestone has been used here as raw material, in lateriate is 3%.

The addition of laterite has several advantages in the raw mix preparation. Because it has high iron content, high corrective efficiency and also has ability for better quality control.

Raw Meal and Clinker Composition:

After mixing of raw material in the given proportion (Table 6.6). The resultant clinker composition has been calculated and is presented in Table 6.6. The final product of clinker will have SiO_2 = 23.26%, Al_2O_3 = 5.21%, Fe_2O_3 = 3.81%, and CaO = 67.07% (Table 6.6). The other parameters such as MA, MS, LSf and C_3A are calculated as follows and are given in Table 6.6.

$$\text{MA} = \frac{Al_2O_3}{Fe_2O_3} = \frac{3.38}{2.47} = 1.367$$

$$\text{for Clinker} = \frac{5.21}{3.81} = 1.367$$

$$\text{MS} \quad \frac{SiO_2}{Fe_2O_3 + Al_2O_3}$$

$$= \frac{15.11}{2.47 + 3.38} = 2.581$$

for Clinker $= \dfrac{23.26}{3.81 + 5.21} = 2.581$

LSf. $= \dfrac{CaO}{2.8SiO_2 + 1.18Al_2O_3 + 0.65\ Fe_2O_3}$

$$= \frac{43.55}{2.8x15.11 + 1.18x338 + 0.65x2.47}$$

$$= 0.895$$

for Clinker $= \dfrac{67.07}{2.8x23.26 + 1.18x5.21 + 0.65x3.81}$

$$= 0.895$$

C_3A $= 2.65\ Al_2O_3 - 1.65\ Fe_2O_3$

$$= 2.65 \text{ x } 3.38 - 1.65 \text{ x } 2.47$$

$$= 4.775$$

for Clinker $= 2.65 \text{ x } 5.21 - 1.65 \text{ x } 3.81$

$$= 7.354$$

Table 6.6 **Chemical composition of raw material, their mixing ratios and the resulted chemical composition and other parameters of clinkers formed by mixture No.6.**

Chemical Composition of Raw Material Available

	S/L.S	Dolerite	Phyllite	G.G.L/S	Laterite
SiO_2	8.33	49.55	60.18	12.91	44.00
Al_2O_3	0.81	20.76	20.90	1.41	12.80
Fe_2O_3	1.08	10.98	3.01	0.70	40.50
CaO	50.26	6.97	2.75	44.10	1.05

Usage of Raw Material

Ratio of Usage	S/L.S	Dolerite	Phyllite	G.G.L/S	Laterite	Total
	86.00%	0.00%	11.00%	0.00%	3.00%	100.00%

Composition of Raw Mixture

SiO_2	15.11
Al_2O_3	3.38
Fe_2O_3	2.47
CaO	43.55

Raw meal & Clinker composition

Composition	RM	Clinker (RM x 1.54)
SiO_2	15.11	23.26
Al_2O_3	3.38	5.21
Fe_2O_3	2.47	3.81
CaO	43.55	67.07

Raw meal & Clinker parameters

Parameters	RM	Clinker
MA	1.367	1.367
MS	2.581	2.581
Lsf	0.895	0.895
C3A	4.775	7.354

Mixture No.7

Raw Material Available:

The raw material for mixture No.7 include Shekhai limestone, Utch Khattak limestone, clay, greenish-grey limestone and dolerite dike (Table 6.7).

The percentage of oxides is differents in each of this raw material. The average composition of SiO_2 in Shekhai limestone is 8.33%, in Utch Khattak limestone is 13.49%, in clay is 50.13%, in greenish-grey limestone is 52.50%, in dolerite is 49.55%. The total of SiO_2 in this raw material is calculated as 14.43% (Table 6.7).

The average composition of Al_2O_3 in Shekhai limestone is 0.81%, in Utch Khattak limestone is 1.47%, in clay is 17.01%, in greenish-grey limestone is 18.42%, in dolerite is 20.76%. The total of Al_2O_3 is calculated as 3.57% (Table 6.7).

The average composition of Fe_2O_3 in Shekhai limestone is 1.08%, in Utch Khattak limestone is 0.96%, in clay is 3.96%, in greenish-grey limestone is 4.84%, in dolerite dike is 10.98%. The total of Fe_2O_3 is calculated as 2.32% (Table 6.7).

The average composition of calcium oxide (CaO) in Shekhai limestone is 50.26%, in Utch Khattak is 44.96%, in clay is 9.21%, in greenish-grey limestone is 8.20%, in dolerite dike is 6.97%. The total of CaO is 43.92% (Table 6.7).

Ratio of Usage:

The ratio of mixing of the raw material for mixture No.7 is calculated as Shekhai limestone is 80%, in Utch Khattak limestone is 6%, in clay is 2%, in dolerite is 12%, no greenish-grey limestone has been used here as raw material.

Raw Meal and Clinker Composition:

After mixing of raw material in the green proportion (Table 6.7). The resultant clinker composition has been calculated and is presented in Table 6.7. The final product of clinker will have $SiO_2 = 22.21\%$, $Al_2O_3 = 5.50\%$, $Fe_2O_3 = 3.57\%$, and $CaO = 67.64\%$ (Table 6.7). The other parameters such as MA, MS, LSf and C_3A are calculated as follows and are given in Table 6.7.

$$MA = \frac{Al_2O_3}{Fe_2O_3} = \frac{3.57}{2.32} = 1.541$$

$$\text{for Clinker} = \frac{5.50}{3.57} = 1.541$$

$$MS = \frac{SiO_2}{Fe_2O_3 + Al_2O_3}$$

$$= \frac{14.43}{2.32 + 3.57} = 2.451$$

for Clinker $= \frac{22.21}{3.57+5.50} = 2.448$

L.Sf $= \frac{CaO}{2.8SiO_2+1.18Al_2O_3+0.65\ Fe_2O_3}$

$$= \frac{43.92}{2.8x14.13 + 1.18x3.57 + 0.65x2.32}$$

$$= 0.938$$

for Clinker $= \frac{67.64}{2.8x22.21 + 1.18x5.50 + 0.65x3.57}$

$$= 0.952$$

C_3A $= 2.65\ Al_2O_3 - 1.65\ Fe_2O_3$

$$= 2.65 \ x\ 3.57 - 1.65 \ x\ 2.32$$

$$= 5.538$$

for Clinker $= 2.65 \ x\ 5.50 - 1.65 \ x\ 3.57$

$$= 8.684$$

Table 6.7 **Chemical composition of raw material, their mixing ratios and the resulted chemical composition and other parameters of clinkers formed by mixture No.7.**

Chemical Composition of Raw Material Available

	S/L.S	U/K.L.S	CLAY	G.G.L/S	Dolerite
SiO_2	8.33	13.49	50.13	52.50	49.55
Al_2O_3	0.81	1.47	17.01	18.42	20.76
Fe_2O_3	1.08	0.96	3.96	4.84	10.98
CaO	50.26	44.96	9.21	8.20	6.97

Usage of Raw Material

Ratio of Usage	S/L.S	U/K.L.S	CLAY	G.G.L/S	Dolerite	Total
	80.00%	6.00%	2.00%	0.00%	12.00%	100.00%

Composition of Raw Mixture

SiO_2	14.43
Al_2O_3	3.57
Fe_2O_3	2.32
CaO	43.92

Raw meal & Clinker composition

Composition	RM	Clinker (RM x 1.54)
SiO_2	14.43	22.21
Al_2O_3	3.57	5.50
Fe_2O_3	2.32	3.57
CaO	43.92	67.64

Raw meal & Clinker parameters

Parameters	RM	Clinker
MA	1.541	1.541
MS	2.451	2.448
Lsf	0.938	0.952
C3A	5.538	8.684

Mixture No.8

Raw Material Available:

The raw material for mixture No.8 include Shekhai limestone, Utch Khattak limestone, clay, greenish-grey limestone and laterite (Table 6.8).

The percentage of oxides is differents in each of this raw material. The average composition of SiO_2 in Shekhai limestone is 8.33%, in Utch Khattak limestone 1.47%, in clay is 50.13%, in greenish-grey limestone is 1.41%, in lateriate is 40.50%. The total of SiO_2 is calculated as 13.33% (Table 6.8).

The average composition of Al_2O_3 in Shekhai limestone is 0.81%, in Utch Khattak limestone is 1.47%, in clay is 17.01%, in greenish-grey limestone is 1.41%, in lateriate is 12.80%. The total of Al_2O_3 is calculated as 2.77% (Table 6.8).

The average composition of Fe_2O_3 in Shekhai limestone is 1.08%, in Utch Khattak limestone is 0.96%, in clay is 3.96%, in greenish-grey limestone is 0.70%, in laterite is 40.50%. The total of Fe_2O_3 is calculated as 2.52% (Table 6.8).

The average composition of CaO in Shekhai limestone is 50.26%, in Utch Khattak limestone is 44.96%, in clay is 9.21%, in greenish-grey limestone is 44.10%, in laterite is 1.05%. The total of CaO is calculated as 43.17% (Table 6.8).

Ratio of Usage:

The ratio of mixing of the raw material for mixture No.8 is caluclated as; Shekhai limestone 84%, no Utch Khattak limestone has been used here as raw material.

Raw Meal and Clinker Composition:

After mixing the raw material in the given proportion (Table 6.8). The resultant clinker composition has been calculated and is presented in Table 6.8. The final product of clinker will have SiO_2 = 20.53%, Al_2O_3 = 4.26%, Fe_2O_3 = 3.87%, and CaO = 66.48% (Table 6.8). The other parameters such as MA, MS, LSf and C_3A are calculated as follows and are given in Table 6.8.

$$MA = \frac{Al_2O_3}{Fe_2O_3} = \frac{2.77}{2.52} = 1.100$$

$$\text{for Clinker} = \frac{4.26}{3.87} = 1.10$$

$$MS = \frac{SiO_2}{Fe_2O_3 + Al_2O_3}$$

$$= \frac{13.33}{2.52 + 2.77}$$

$$= 2.524.$$

$$\text{for Clinker} = \frac{20.53}{3.87 + 4.26}$$

$$= 2.525$$

$$LSf = \frac{CaO}{2.8 x SiO_2 + 1.18 x Al_2O_3 + 0.65 Fe_2O_3}$$

$$= \frac{43.17}{2.8 x 13.33 + 1.18 x 2.77 + 0.65 x 2.52}$$

$$= 1.006$$

$$\text{for Clinker} = \frac{66.48}{2.8 x 20.53 + 1.18 x 4.26 + 0.65 x 3.87}$$

$$= 1.002$$

$$C_3A = 2.65 Al_2O_3 - 1.65\ Fe_2O_3$$

$$= 2.65\ x\ 2.77 - 1.65\ x\ 2.52$$

$$= 3.074$$

$$\text{for Clinker} = 2.65 x 4.26 - 1.65 x 3.87$$

$$= 4.903$$

Table 6.8 **Chemical composition of raw material, their mixing ratios and the resulted chemical composition and other parameters of clinkers formed by mixture No.8.**

Chemical Composition of Raw Material Available

	S/L.S	U/K.L.S	CLAY	G.G.L/S	Laterite
SiO_2	8.33	13.49	50.13	12.91	44.00
Al_2O_3	0.81	1.47	17.01	1.41	12.80
Fe_2O_3	1.08	0.96	3.96	0.70	40.50
CaO	50.26	44.96	9.21	44.10	1.05

Usage of Raw Material

Ratio of Usage	S/L.S	U/K.L.S	CLAY	G.G.L/S	Laterite	Total
	84.00%	0.00%	10.00%	3.00%	3.00%	100.00%

Composition of Raw Mixture

SiO_2	13.33
Al_2O_3	2.77
Fe_2O_3	2.52
CaO	43.17

Raw meal & Clinker composition

Composition	RM	Clinker (RM x 1.54)
SiO_2	13.33	20.53
Al_2O_3	2.77	4.26
Fe_2O_3	2.52	3.87
CaO	43.17	66.48

Raw meal & Clinker parameters

Parameters	RM	Clinker
MA	1.100	1.100
MS	2.524	2.525
Lsf	1.006	1.022
C3A	3.074	4.903

Mixture No.9

Raw Material Available:

The raw material for mixture No.9 include Shekhai limestone, Utch Khattak limestone, clay, greenish-grey limestone and laterite (Table 6.9).

The percentage of oxides is differents in each of this raw material. The average composition of SiO_2 in Shekhai limestone is 8.33%, in Utch Khattak limestone is 13.49%, in clay is 50.13%, in greenish-grey limestone is 12.91%, in laterite is 44% and the total of SiO_2 is calculated as 14.27% (Table 6.9).

The average composition of Al_2O_3 in Shekhai limestone is 0.81%, in Utch Khattak limestone is 13.49%, in clay is 50.13%, in greenish-grey limestone is 12.91%, in laterite is 44% and the total is calculated as 14.27% (Table 6.9).

The average composition of Fe_2O_3 in Shekhai limestone is 1.08%, in Utch Khattak limestone is 0.96%, in clay is 3.96%, in greenish-grey limestone is 0.70%, in laterite is 40.50%. The total of Fe_2O_3 is calculated as 2.57% (Table 6.9).

The average composition of CaO in Shekhai limestone is 50.26%, in Utch Khattak limestone is 44.96%, in clay is 9.21%, in greenish-grey limestone is 44.10%, in laterite is 1.05%. The total of CaO is calculated as 42.24% (Table 6.9).

Ratio of Usage:

The ratio of mixing of the raw material for mixture No.9 is calculated as; Shekhai limestone is 80%, in Utch Khattak limestone is 2%, in clay is 12%, in greenish-grey limestone is 3%, in laterite is 3%. The addition of laterite has several advantages in the raw mix preparation. Because it has high iron content, high corrective efficiency and also has ability for better quality control.

Raw Meal and Clinker Composition:

After mixing of raw material in the given proportion (Table 6.9). The resultant clinker composition has been calculated and is presented in Table 6.9. The final product of clinker will have SiO_2 = 2198%, Al_2O_3 = 4.78%, Fe_2O_3 = 3.96%, CaO = 65.05% (Table 6.9). The other parameters such as MA, MS, LSf and C_3A are calculated as follows and are given in Table 6.9.

$$MA = \frac{Al_2O_3}{Fe_2O_3} = \frac{3.10}{2.57}$$

$$= 1.207$$

$$\text{for Clinker} = \frac{4.78}{3.96} = 1.207$$

$$MS = \frac{SiO_2}{Fe_2O_3 + Al_2O_3}$$

$$= \frac{14.27}{2.57 + 3.10} = 2.515$$

for Clinker $= \dfrac{21.98}{3.96+4.78} = 2.514$

L.Sf $= \dfrac{CaO}{2.8xSiO_2+1.18xAl_2O_3+0.65xFe_2O_3}$

$= \dfrac{42.24}{2.8x14.27 + 1.18x3.10 + 0.65x2.57}$

$= 0.918$

for Clinker $= \dfrac{65.05}{2.8x21.98 + 1.18x4.78 + 0.65x3.96}$

$= 0.932$

C_3A $= 2.65\ Al_2O_3 - 1.65\ Fe_2O_3$

$= 2.65 \text{ x } 3.10 - 1.65x2.57$

$= 3.874$

for Clinker $= 2.65 \text{ x } 4.78 - 1.65 \text{ x } 3.96$

$= 6.133$

Table 6.9 **Chemical composition of raw material, their mixing ratios and the resulted chemical composition and other parameters of clinkers formed by mixture No.9.**

Chemical Composition of Raw Material Available

	S/L.S	U/K.L.S	CLAY	G.G.L/S	Laterite
SiO_2	8.33	13.49	50.13	12.91	44.00
Al_2O_3	0.81	1.47	17.01	1.41	12.80
Fe_2O_3	1.08	0.96	3.96	0.70	40.50
CaO	50.26	44.96	9.21	44.10	1.05

Usage of Raw Material

Ratio of Usage	S/L.S	U/K.L.S	CLAY	G.G.L/S	Laterite	Total
	80.00%	2.00%	12.00%	3.00%	3.00%	100.00%

Composition of Raw Mixture

SiO_2	14.27
Al_2O_3	3.10
Fe_2O_3	2.57
CaO	42.24

Raw meal & Clinker composition

Composition	RM	Clinker (RM x 1.54)
SiO_2	14.27	21.98
Al_2O_3	3.10	4.78
Fe_2O_3	2.57	3.96
CaO	42.24	65.05

Raw meal & Clinker parameters

Parameters	RM	Clinker
MA	1.207	1.207
MS	2.515	2.514
Lsf	0.918	0.932
C3A	3.874	6.133

Mixture No.10

Raw Material Available:

The raw material for mixture No.10 include; Shekhai limestone, Utch Khattak limestone, dolerite dike, clay, greenish-grey limestone and laterite (Table 6.10).

The average composition of SiO_2 in Shekhai limestone is 8.33%, in dolerite dike is 49.55%, in clay is 50.13%, in greenish-grey limestone is 12.91%, and laterite is 44%. The total of SiO_2 is calculated as 15.01% (Table 6.10).

The average composition of Al_2O_3 in Shekhai limestone is 0.81%, in dolerite is 20.76%, in clay is 17.01%, in greenish-grey limestone is 1.41%, and laterite is 12.80%. The total of Al_2O_3 is calculated as 3.48% (Table 6.10).

The average composition of Fe_2O_3 in Shekhai limestone is 1.08% in dolerite is 10.98%, in clay is 3.96%, in greenish-grey limestone is 0.70%, and in laterite is 40.50%. The total is calculated as 1.68% (Table 6.10).

The average composition of CaO in Shekhai limestone is 50.26%, in dolerite is 6.97%, in clay is 9.21%, in greenish-grey limestone is 44.10% and in laterite is 1.05%. The total is calculated as 43.64% (Table 6.10).

Ratio of Usage:

The ratio of mixing of the raw mateial for mixture No.10 is calculated as; Shekhai limestone is 84%, dolerite dike is 2%, in clay is 14%, no greenish-grey limestone and laterite has been used here as raw material.

Raw Meal and Clinker Composition:

After mixing of raw material in the given proportion (Table 6.10). The resultant clinker composition has been calculated and is presented in Table 6.10. The final product of clinker will have SiO_2 = 23.12%, Al_2O_3 = 5.36%, Fe_2O_3 = 2.59%, CaO = 67.21%. The other parameters such as MA, MS, LSf and C_3A are calculated as follows and are given in Table 6.10.

$$\text{MA} = \frac{Al_2O_3}{Fe_2O_3} = \frac{3.48}{1.68}$$

$$= 2.072$$

$$\text{for Clinker} = \frac{5.36}{2.59} = 2.072$$

$$\text{MS} = \frac{SiO_2}{Fe_2O_3 + Al_2O_3}$$

$$= \frac{15.01}{1.68+3.48} = 2.911$$

$$\text{for Clinker} = \frac{23.12}{2.59+5.36} = 2.908$$

$$L.Sf = \frac{CaO}{2.8xSiO_2+1.18xAl_2O_3+0.65xFe_2O_3}$$

$$= 0.910$$

for Clinker $= \frac{61.21}{2.8x23.12 + 1.18x5.36 + 0.65x2.59}$

$$= 0.923$$

$C_3A = 2.6xAl_2O_3 - 1.65xFe_2O_3$

$$= 2.65x3.48 - 1.65x1.68$$

$$= 6.376$$

for Clinker $= 2.6x5.36 - 1.65x2.59$

$$= 9.662$$

Table 6.10 Chemical composition of raw material, their mixing ratios and the resulted chemical composition and other parameters of clinkers formed by mixture No.10.

Chemical Composition of Raw Material Available

	S/L.S	Dolerite	CLAY	G.G.L/S	Laterite
SiO_2	8.33	49.55	50.13	12.91	44.00
Al_2O_3	0.81	20.76	17.01	1.41	12.80
Fe_2O_3	1.08	10.98	3.96	0.70	40.50
CaO	50.26	6.97	9.21	44.10	1.05

Usage of Raw Material

Ratio of Usage	S/L.S	Dolerite	CLAY	G.G.L/S	Laterite	Total
	84.00%	2.00%	14.00%	0.00%	0.00%	100.00%

Composition of Raw Mixture

SiO_2	15.01
Al_2O_3	3.48
Fe_2O_3	1.68
CaO	43.64

Raw meal & Clinker composition

Composition	RM	Clinker (RM x 1.54)
SiO_2	15.01	23.12
Al_2O_3	3.48	5.36
Fe_2O_3	1.68	2.59
CaO	43.64	67.21

Raw meal & Clinker parameters

Parameters	RM	Clinker
MA	2.072	2.072
MS	2.911	2.908
Lsf	0.910	0.924
C3A	6.376	9.662

Mixture No.11

Raw Material Available:

The raw material for mixture No.11 include; Shekhai limestone, dolerite dike, clay, greenish-grey limestone and laterite (Table 6.11).

The oxides percentage are differents in each of this raw material. The average composition of SiO_2 in Shekhai limestone is 8.33%, in dolerite dike is 49.55%, in clay is 50.13%, in greenish-grey limestone is 12.91%, in laterite is 44%. The total of SiO_2 is calculated as 13.71% (Table 6.11).

The average composition of Al_2O_3 in Shekhai limestone is 0.81%, in dolerite dike is 20.76%, in clay is 17.07%, in greenish-grey limestone is 1.14%, and in laterite is 12.80%. The total of Al_2O_3 is calculated as 3.41% (Table 6.11).

The average composition of Fe_2O_3 in Shekhai limestone is 1.08% in dolerite dike is 10.98%, in clay is 3.96%, in greenish-grey limestone is 0.70% and in laterite is 40.50%. The total of Fe_2O_3 is calculated as 2.13% (Table 6.11).

The average composition of CaO in Shekhai limestone is 50.26%, in dolerite is 6.97%, in clay is 9.21, in greenish-grey limestone is 44.10% and in laterite is 1.05. The total is calculated as 41.77% (Table 6.11).

Ratio of Usage:

The ratio of mixing of the raw material for mixture No.11 is calculated as; Shekhai limestone is 8%, dolerite is 10%, clay is 4%, greenish-grey limestone is 5% and no lateriate has been used here as raw material.

Raw Meal and Clinker Composition:

After mixing of raw material in the given proportion (Table 6.11). The resultant clinker composition has been calculated and is presented in Table 6.11. The final product of clinker will have SiO_2 = 21.11%, Al_2O_3 = 5.26%, Fe_2O_3 = 3.28%, CaO = 64.33% (Table 6.11). The other parameters such as MA, MS, LSf, C_3A are calculated as follows and are given in Table 6.11.

$$MA = \frac{Al_2O_3}{Fe_2O_3}$$

$$= \frac{3.41}{2.13} = 1.603$$

$$\text{for Clinker} = \frac{5.26}{3.28} = 1.603$$

$$MS = \frac{SiO_2}{Fe_2O_3 + Al_2O_3}$$

$$= \frac{13.71}{213 + 3.41} = 2.474$$

$$\text{for Clinker} = \frac{21.11}{3.28 + 5.26} = 2.471$$

$$L.Sf = \frac{CaO}{2.8xSiO_2+1.18xAl_2O_3+0.65xFe_2O_3}$$

$$= \frac{41.77}{2.8x13.71 + 1.18xAl_2O_3 + 0.65xFe_2O_3}$$

$$= 0.939$$

$$\text{for Clinker} = \frac{64.33}{2.8x2.11 + 1.18x5.26 + 0.65x3.78}$$

$$= 0.953$$

$$C_3A = 2.65\ Al_2O_3 - 1.65\ Fe_2O_3$$

$$= 2.65 \text{ x } 3.41 - 1.65 \text{ x } 2.13$$

$$= 5.443$$

$$\text{for Clinker} = 2.65x5.26 - 1.65x3.28$$

$$= 8.527$$

Table 6.11 **Chemical composition of raw material, their mixing ratios and the resulted chemical composition and other parameters of clinkers formed by mixture No.11.**

Chemical Composition of Raw Material Available

	S/L.S	Dolerite	CLAY	G.G.L/S	Laterite
SiO_2	8.33	49.55	50.13	12.91	44.00
Al_2O_3	0.81	20.76	17.01	1.41	12.80
Fe_2O_3	1.08	10.98	3.96	0.70	40.50
CaO	50.26	6.97	9.21	44.10	1.05

Usage of Raw Material

Ratio of Usage	S/L.S	Dolerite	CLAY	G.G.L/S	Laterite	Total
	81.00%	10.00%	4.00%	5.00%	0.00%	100.00%

Composition of Raw Mixture

SiO_2	13.71
Al_2O_3	3.41
Fe_2O_3	2.13
CaO	41.77

Raw meal & Clinker composition

Composition	RM	Clinker (RM x 1.54)
SiO_2	13.71	21.11
Al_2O_3	3.41	5.26
Fe_2O_3	2.13	3.28
CaO	41.77	64.33

Raw meal & Clinker parameters

Parameters	RM	Clinker
MA	1.603	1.603
MS	2.474	2.471
Lsf	0.939	0.953
C3A	5.443	8.527

Mixture No.12

Raw Material Available:

The raw material for mixture No12 include; Shekhai limestone, dolerite dike, greenish-grey limestone, and laterite (Table 6.12).

The percentage of oxides is differents in each of this raw material. The average composition of SiO_2 in Shekhai limestone is 8.33%, dolerite dike is 49.55%, in clay is 50.13%, in greenish grey limestone is 12.91% and lateriate is 44%. The total of SiO_2 is calculated as 14.93 (Table 6.12).

The average composition of Al_2O_3 in Shekhai limestone is 0.81%, in dolerite is 20.76%, in clay is 17.01%, in greenish-grey is 1.41%, and in lateriate is 12.80%. The total of Al_2O_3 is calculated as 4% (Table 6.12).

The average composition of Fe_2O_3 in Shekhai limestone is 1.08%, in dolerite is 10.98%, in clay is 3.96%, in lateriate is 0.70%. The total is calculated as 2.66% (Table 6.12).

The average composition of CaO in Shekhai limestone is 50.26%, in dolerite is 6.97%, in clay is 3.96%, in greenish-grey limestone is 44.10%, and in laterite is 1.05%. The total of CaO is calculated as 43.33% (Table 6.12).

Ratio of Usage:

The ratio of mixing of raw material for mixture No.12 is calculated as; Shekhai limestone is 84%, in doloerite is 16%, no clay, greenish-grey limestone and laterite has been used here as raw material.

Raw Meal and Clinker Composition:

After mixing of raw material in the given proportion (Table 6.12). The resultant clinker composition has been calculated and is presented in Table 6.12. The final product of clinker will have SiO_2 = 22.19%, Al_2O_3 = 6.16%, Fe_2O_3 = 4.10%, and CaO = 66.73% (Table 6.12). The other parameters such as MA, MS, LSf and C_3A are calculated as follows and are given in Table 6.12.

$$MA = \frac{Al_2O_3}{Fe_2O_3}$$

$$= \frac{4}{2.66}$$

$$= 1.504$$

$$\text{for Clinker} = \frac{6.16}{4.10} = 1.502$$

$$MS = \frac{SiO_2}{Fe_2O_3+Al_2O_3}$$

$$= \frac{14.93}{2.66+4}$$

$$= 2.240$$

for Clinker $= \frac{22.99}{4.10 + 6.16} = 2.240$

L.Sf $= \frac{CaO}{2.8xSiO_2+1.18xAl_2O_3+0.65xFe_2O_3}$

$= \frac{43.33}{2.8x14.93+1.18x4 + 0.65x2.66}$

$= 0.884$

for Clinker $= \frac{66.73}{2.8x22.99+1.18x6.16 + 0.65x4.10}$

$= 0.898$

C_3A $= 2.65\ Al_2O_3 - 1.65\ Fe_2O_3$

$= 2.65 \times 4 - 1.65 \times 2.66 = 6.104$

for Clinker $= 2.65x6.16 - 1.65x4.10$

$= 9.559$

Table 6.12 **Chemical composition of raw material, their mixing ratios and the resulted chemical composition and other parameters of clinkers formed by mixture No.12.**

Chemical Composition of Raw Material Available

	S/L.S	Dolerite	CLAY	G.G.L/S	Laterite
SiO_2	8.33	49.55	50.13	12.91	44.00
Al_2O_3	0.81	20.76	17.01	1.41	12.80
Fe_2O_3	1.08	10.98	3.96	0.70	40.50
CaO	50.26	6.97	3.96	44.10	1.05

Usage of Raw Material

Ratio of Usage	S/L.S	Dolerite	CLAY	G.G.L/S	Laterite	Total
	84.00%	16.00%	0.00%	0.00%	0.00%	100.00%

Composition of Raw Mixture

SiO_2	14.93
Al_2O_3	4.00
Fe_2O_3	2.66
CaO	43.33

Raw meal & Clinker composition

Composition	RM	Clinker (RM x 1.54)
SiO_2	14.93	22.99
Al_2O_3	4.00	6.16
Fe_2O_3	2.66	4.10
CaO	43.33	66.73

Raw meal & Clinker parameters

Parameters	RM	Clinker
MA	1.504	1.504
MS	2.240	2.240
Lsf	0.884	0.898
C3A	6.104	9.559

Mixture No.13

Raw Material Available:

The raw material for mixture No.13 include; Shekhai limestone, dolerite, clay, greenish-grey limestone and laterite (Table 6.13).

The average composition of SiO_2 in Shekhai limestone is 8.33%, in dolerite is 49.55%, in clay is 50.13%, in greenish-grey limestone is 12.91%, and in laterite is 44%. The total of SiO_2 is calculated as 14.84% (Table 6.13).

The average composition of Al_2O_3 in Shekhai limestone is 0.81% in dolerite is 20.76%, in clay is 17.01%, in greenish-grey limestone is 1.41%, and in laterite is 12.80%. The total of Al_2O_3 is calculated as 3.28% (Table 6.13).

The average composition of Fe_2O_3 in Shekhai limestone is 1.08%, in dolerite is 10.98%, in clay is 3.96%, in greenish-grey limestone is 0.70 and in laterite is 40.50%. The total of Fe_2O_3 is calculated as 2.64% (Table 6.13).

The average composition of CaO in Shekhai limestone is 50.26%, in dolerite is 6.97%, in clay is 3.96%, in greenish-grey limestone is 44.10% and in laterite is 1.05%. The total of CaO is calculated as 42.76% (Table 6.13).

Ratio of Usage:

The ratio of mixing of the raw material for mixture nO.13 is calculated as; Shekhai limestone is 84%, no dolerite has been used as raw material, in clay is 13%. no greenish-grey limestone 0%, in laterite is 3% (Table 6.13).

Raw Meal and Clinker Composition:

After mixing of raw material in the given proportion (Table 6.13). The resultant clinker composition has been calculated and is presented in Table 6.13. The final product of clinker will have, SiO_2 = 22.85%, Al_2O_3 = 5.05%, Fe_2O_3 = 4.06%, and CaO = 65.85%.

The other parameters such as MA, MS, LSf and C_3A are calculated as follows and are given in Table 6.13.

$$\text{MA} = \frac{Al_2O_3}{Fe_2O_3}$$

$$= \frac{3.28}{2.63} = 1.244$$

$$\text{for Clinker} = \frac{5.05}{4.06} = 1.244$$

$$\text{MS} = \frac{SiO_2}{Fe_2O_3 + Al_2O_3}$$

$$= \frac{14.84}{2.63+3.28}$$

$$= 2.510$$

for Clinker $= \dfrac{22.85}{4.06 + 5.05} = 2.508$

L.Sf $= \dfrac{CaO}{2.8SiO_2 + 1.18Al_2O_3 + 0.65Fe_2O_3}$

$= 0.893$

for Clinker $= \dfrac{65.85}{2.8x22.85 + 1.18x5.05 + 0.65x4.06}$

$= 0.907$

C_3A $= 2.65\ Al_2O_3 - 1.65\ Fe_2O_3$

$= 2.65 \text{ x } 3.28 - 1.65 \text{ x } 2.63$

$= 4.225$

for Clinker $= 2.65x5.05 + 1.65x4.06$

$= 6.683$

Table 6.13 **Chemical composition of raw material, their mixing ratios and the resulted chemical composition and other parameters of clinkers formed by mixture No.13.**

Chemical Composition of Raw Material Available

	S/L.S	Dolerite	CLAY	G.G.L/S	Laterite
SiO_2	8.33	49.55	50.13	12.91	44.00
Al_2O_3	0.81	20.76	17.01	1.41	12.80
Fe_2O_3	1.08	10.98	3.96	0.70	40.50
CaO	50.26	6.97	3.96	44.10	1.05

Usage of Raw Material

Ratio of Usage	S/L.S	Dolerite	CLAY	G.G.L/S	Laterite	Total
	84.00%	0.00%	13.00%	0.00%	3.00%	100.00%

Composition of Raw Mixture

SiO_2	14.84
Al_2O_3	3.28
Fe_2O_3	2.64
CaO	42.76

Raw meal & Clinker composition

Composition	RM	Clinker (RM x 1.54)
SiO_2	14.84	22.85
Al_2O_3	3.28	5.05
Fe_2O_3	2.63	4.06
CaO	42.76	65.85

Raw meal & Clinker parameters

Parameters	RM	Clinker
MA	1.244	1.244
MS	2.510	2.508
Lsf	0.893	0.907
C3A	4.225	6.683

CHAPTER VII

PETROGRAPHY

There are two main rock units in the study area:

1. Limestone
2. Phyllites

1. LIMESTONE

The limestone of Gandghar range, Haripur is mostly composed of micritic nature (very fine-grained calcite). The percentage of calcite in most of the localities ranges from 80-90%. These limestones are so fine grained that no structures can be observed, only micro-fractures can be seen. At certain places in most of the thin sections, calcite spars (coarse grained calcite) can be seen which show typical calcite twining. These calcite spars may be recrystallized calcite and is also present in calcite veins across some thin sections (Plate 1 a&b). The recrystallised calcite is also found as cavity-fillings of some fossil fragments.

Quartz mostly occurs as anhedral small clastic sand grains (continuing about 2-5% of the rock generally randomly scattered through the rock but where recrystallized calcite is present it is found associated with it. Chert and chalcedony are found as cavity fillings in fossils fragments besides calcite. In few thin sections very coarse grained quartz is seen along the recrystallized calcite veins.

Some carbonaceous matter is also present in the form of layers or bands. Iron leaching can be seen along the fractures. Few (traces) clay minerals are also present which may be illite.

At locality (sample-39), the limestone is very different from rest of the samples. Here the calcite is not micritic but it is pelletal shaped. These pellets are oval-shaped and all are alligned in one preferred orientation. These ovulitic calcite grains are embedded in micritic groundmass. At places dark areas can be seen which shows trace fossils. Quartz mostly occurs as anhedral small clastic sand grains (contituting about 5-7% of the rock) generally randomly scattered through the rock.

Phyllites

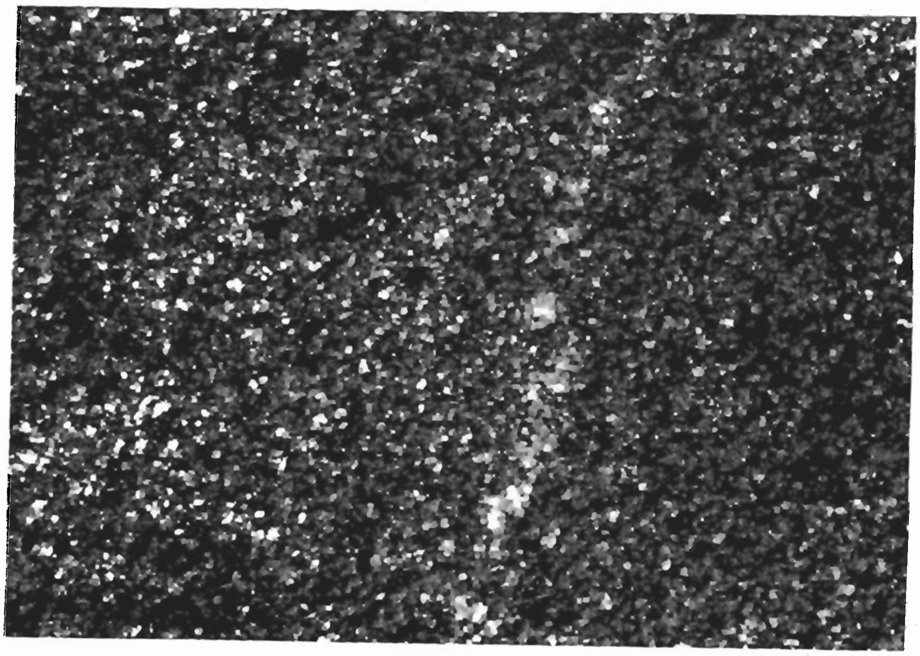
Highly foliated rock and these foliations are folded. The rock is mostly very fine-grained and no detailed features can be observed. In almost all the thin sections the grain fabric is alligned in one preferred orientation which may be due to stresses which acted upon the rock to cause low grade metamorphism (Plate 2). Almost all the thin sections show minor kind folds.

Quartz occurs in two main forms in these thin sections 1) as fine grained particles and 2) as coarse-grained particles. As fine grains it occurs as anhederal grains which are scattered randomly in the rock (Plate 3). The coarse grains of quartz occur as polycrystallin grains (Plate 4). These quartz grains are also folded along the kink folds in the rock (Plate 5).

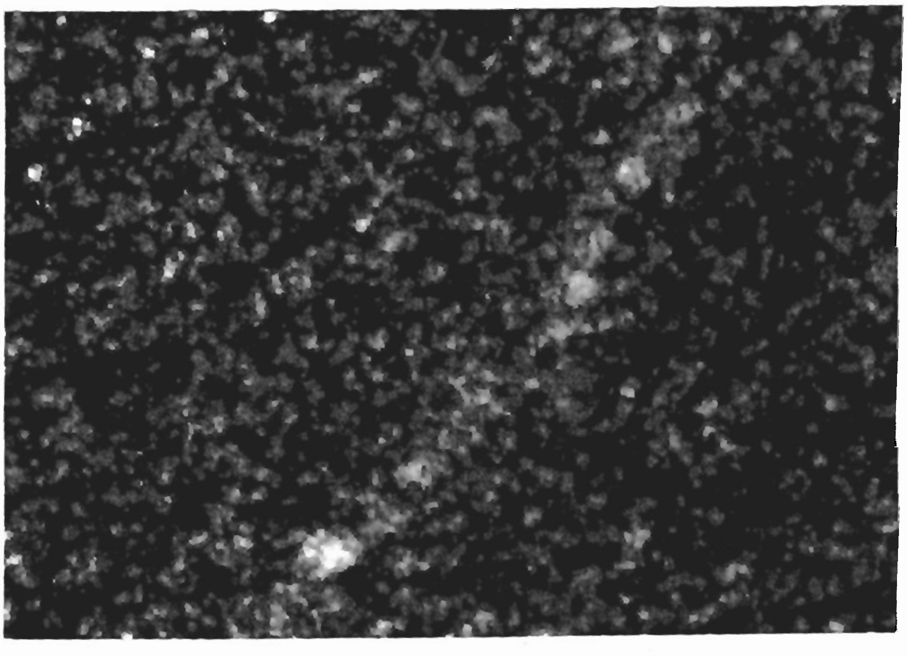
Muscovite occurs (2-5%) as long fibres which are also folded along the fabric of the rock. Mostly, the muscovite grains are found around the quartz grains and as the quartz grains are folded these muscovite grains are also folded along with them. Iron leacing is also seen present along mica.

Black ore which is reported most probably to be graphite occurs as small enhedral grains which is dessiminated throughout the rock randomly. The black ore seems to have no relationship with the foliation so it may be developed later to the foliations (Plate 6).

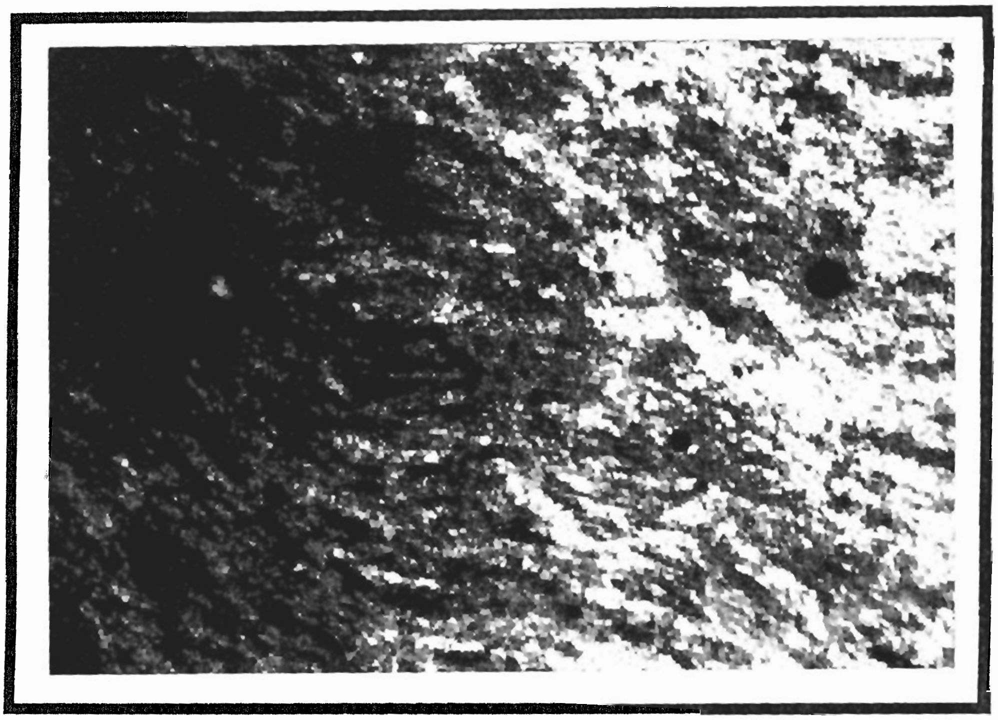
There are some resistant grains which are now eroded, enclosed in eye-shaped "pressure shadows" filled with introduced quartz, calcite or minor mica flakes (Plate 7 a&b).



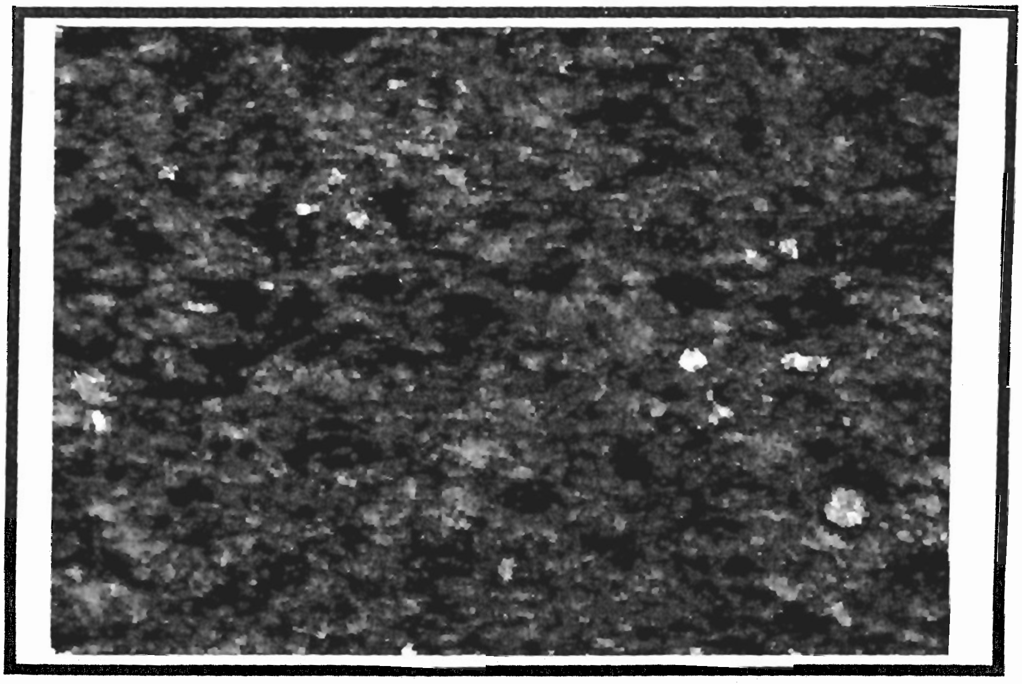
(Plate 1a). Recrystallised calcite vein in limestone cross nicols x 2.5.



(Plate 1b). Recrystallised calcite vein in limestone cross nicols x 4.

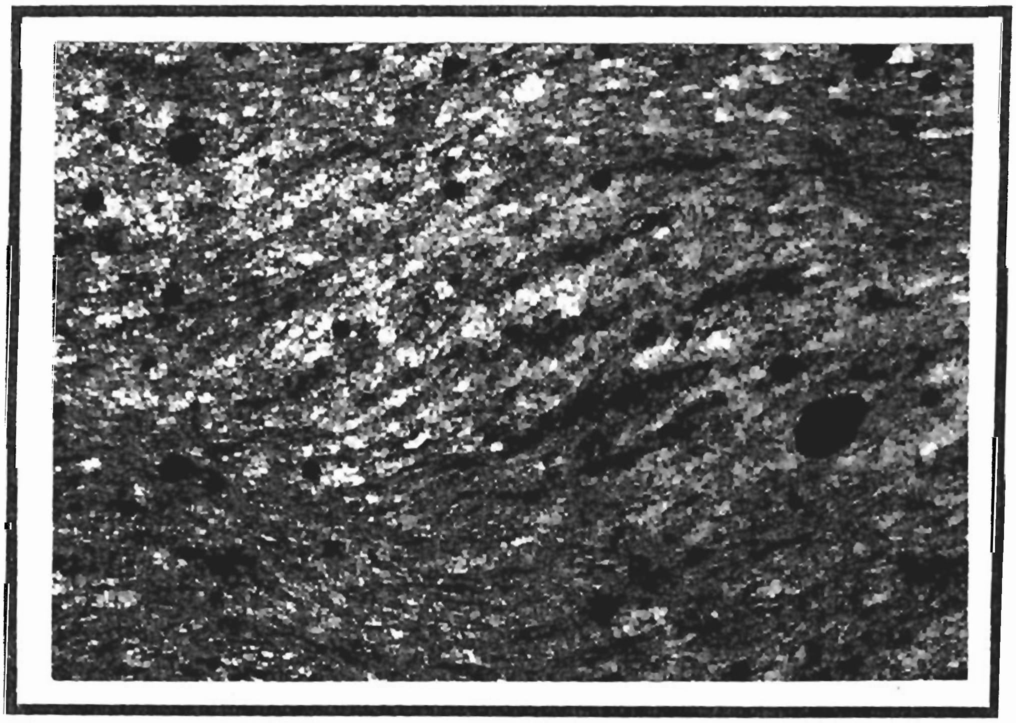


(Plate 2). Phyllite showing small (micro) Kink folds cross nicols x 2.5.

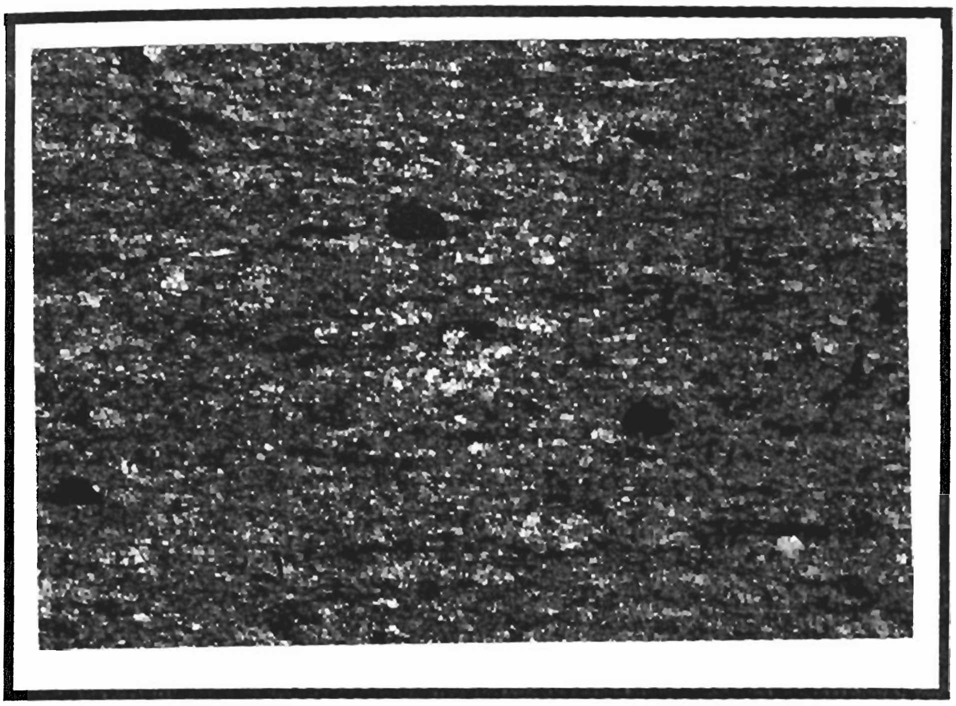


(Plate 3). Anhedral quarte grains (white in colour) scattered randomly cross nicols x 4.

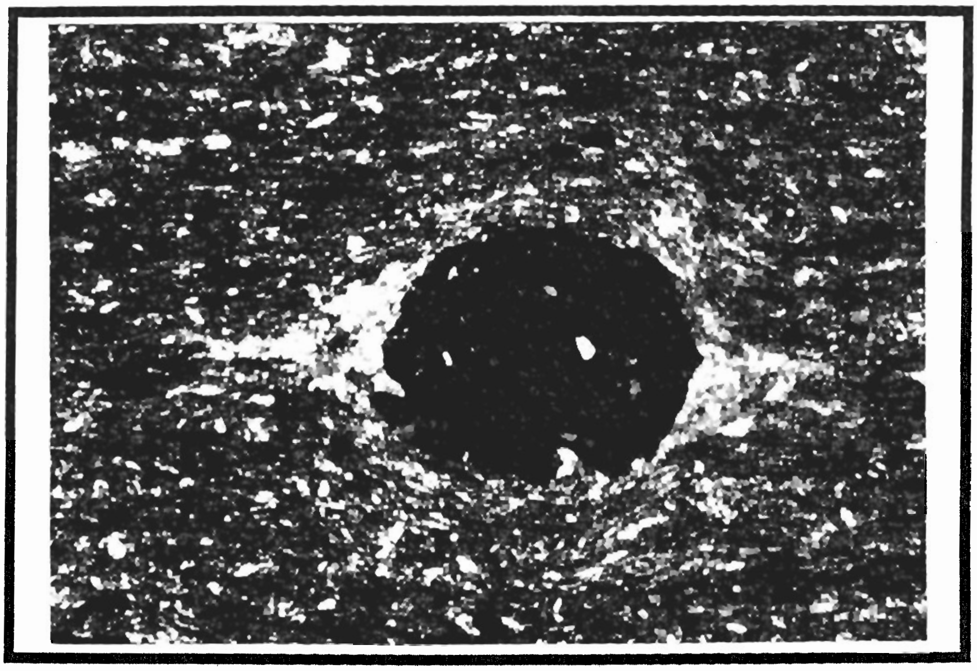
(Plate 4).Polycrystalline coarse grained quartz cross nicols x 4.



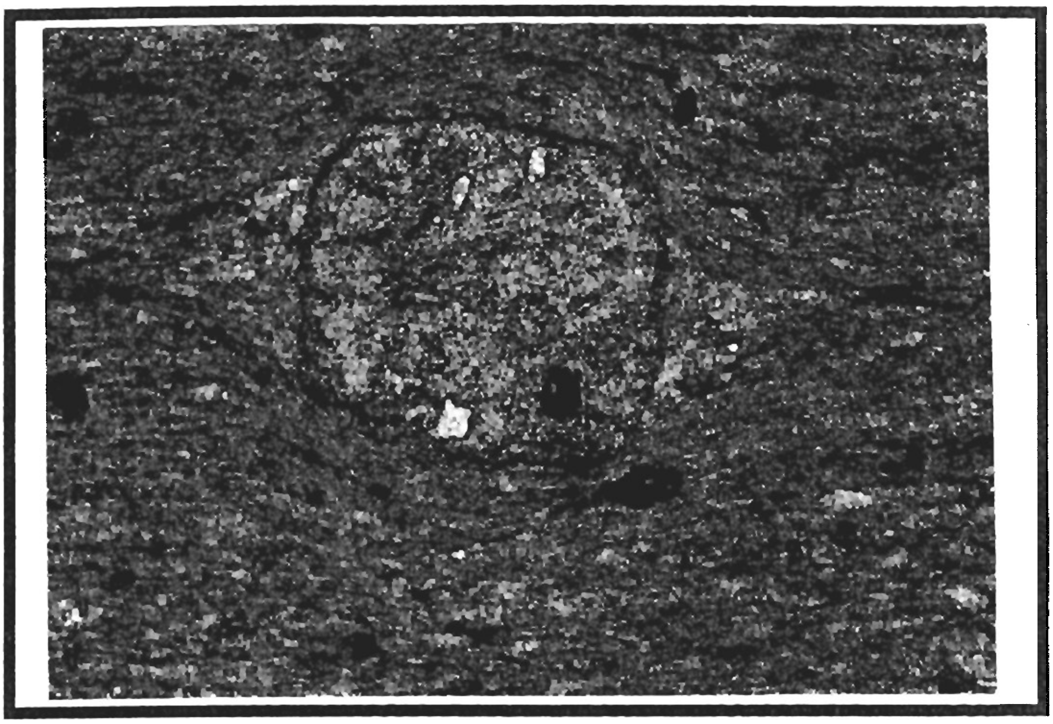
(Plate 5). Quartz grains folded along small kink folds plane x 4.



(Plate 6). Black arc in phyllite has no relationship with the foliation of the rock cross nicols x 4.



(Plate 7a). Eye-shaped pressure shadows filled with calcite.



(Plate 7b). Eye-shaped pressure shadows cross nicols x 4.

CONCLUSIONS

Chemical analysis and related studies suggest that the raw material available in the Gandghar Range allows a large flexibility in the raw mix preparation for cement manufacturing.

Maximum five components and minimum two components are required to prepare suitable raw mix for the manufacturing of Ordinary Portland cement.

- **Shekhai Limestone** sample no.61 and 86 have relatively high contents of MgO. Except these two samples, the Shekhai limestone is suitable for cement manufacturing, as for as the lime (CaO) component is concerned.

- **Utch Khattak limestone** sample no. 90, 93 and 98 have high contents of SiO_2. The MgO contents of this limetone is, however, low as compared to that of the Shekhai limestone.

- **Greenish Grey limestone** has relatively high silica contents in sample no. 9. 39 and 76. This limestone can only be used with the Shekhai limestone during raw material mixing for the manufacturing of cement.

- **Dolerite** contain high content of SiO_2, when it is used in the rawmix, it will reduce the consumption of clay/phyllite.

- **Clay is homogenous in composition** but during rainy season the excavation and transportation of clay will be difficult. Muddy clay will choke the crushing unit and other related equipments. Therefore, it is better to use the phyllites etc instead of clay.

- **Phyllite is generally homogenous in composition** and have several advantages over clay like its SiO_2 contents are higher than clay and, therefore, have more corrective property than clay. Its MgO contents are also low and is crystalline in shape. There will be no problem of its excavation and transportation during rainy season.

- Due to the presence of small amount of dolerite dikes in the area it will not be appropriate to use the raw mix which need dolerite for cement manufacturing. It is, therefore, recommended that the mixture No.2, 8 and 9 will be appropriate to prepare the portland cement from the raw material available in the Gandghar Range and in its vicinity.

RECOMMENDATIONS

- Core drilling is must for long term planning, it would enable to know and estimate the quantity and quality of reserves.

- Grindibility of the material should be checked, which will reduce the power consumption.

- Burnibility of the material at 1350 C^O and 1450 C^O should be determined at a burning index derived from free lime content of the sample after isothermal heating at the above mentioned temperatures.

- Chloride and SO_3 in the samples should also be determined.

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