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University of Baghdad
College of Science
Department of Geology

Qualitative, Quantitative and Radiological Assessment of Marl Layer in the Euphrates Formation for Portland Cement Industry in Kufa Cement Quarry at Al-Najaf Governorate

A thesis
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(Geochemistry)

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1434 **2013**

بسم الله الرحمن الرحيم

وَقُلِ اعْمَلُوا فَسَيَرَى اللَّهُ عَمَلَكُمْ وَرَسُولُهُ
وَالْمُؤْمِنُونَ وَسَتُرَدُّونَ إِلَى عَالِمِ الْغَيْبِ
وَالشَّهَادَةِ فَيُنَبِّئُكُمْ بِمَا كُنْتُمْ تَعْمَلُونَ ۝

صَدَقَ اللهُ العَظِيم

التوبة (١٠٥)

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We certify that this thesis entitled "**qualitative, quantitative and radiological assessment of marl layer in the Euphrates Formation for Portland cement industry in Kufa Cement Quarry at Al-Najaf Governorate**" has been prepared under our supervision in the Department of Geology, College of Science, University of Baghdad in partial fulfillment of the requirements for the degree of master of Science in Geology (Geochemistry).

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Dedication

To

Memory of my Father

My Mother

My Wife

My friends

My children

Who Taught Me Letter in the Present Life

I Dedicate This Effort Let It Be Light In

Present Life and
The Hereafter

Muhanned

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Muhanned

Abstract

This Research involves qualitative, quantitative and radiological studies to assess the marl layer in the Euphrates Formation (Lower Miocene) as a raw material for Portland cement industry. The study area is located within the quarry of the Kufa Cement Plant in the Bahr Al- Najaf, which locates 26 km to the southwest of Al-Najaf city. Samples are collected from the marl layer and adjacent exposures.

The mineralogical study using XRD shows that the mineral composition of the marl layer consists of non-clay and clay minerals. The non- clay minerals are calcite a dominant mineral, followed by quartz, and a little amount of dolomite. Clay minerals are represented by montmorillonite, a prevailing mineral, and then followed by palygorskite and kaolinite. The geochemical study shows that the percentages of oxides in the marl layer are: CaO (37.81), SiO_2 (17.88), Al_2O_3 (4.24), Fe_2O_3 (2.79), MgO (1.79), SO_3 (0.35), K_2O (0.73), Na_2O (0.06), P_2O_5 (0.14), TiO_2 (0.27) in addition to Cl^- (0.02) and the traces in ppm are Sr (273) and Mn (279). Most of the oxides are within the standard quality guideline of the raw mix coming into the kiln, except for the concentration of calcium oxide (CaO) which is low, and a slight increase in the amount of silica (SiO_2). For the purpose of obtaining a mixture of standard specifications for clinker industry, the decrease and increase in the amount of raw materials must be treated. For this reason, calculations relating to the design of the raw mix that go into the kiln have been made. These calculations showed that the marl should be mixed with 22% limestone of high calcium oxide (CaO) available in the areas adjacent to the quarry. During preparing the raw mix based on the appropriate oxide ratios for feeding the kiln, it is necessary to calculate the parameters affecting the clinker production, the results of these parameters are: Lime Saturation Factor, Silica Factor, Alumina Factor, hydraulic Factor, Silica Saturation Factor and the ratio of Lime to Silica Ration. These results indicate that these parameters are within the limit of standard specifications, and capable of producing a high-quality cement.

Clinker is produced by burning two samples of the raw mix at 1450°C for 220 minutes. Then, the produced clinker is tested by XRD which confirmed that clinker contains the essential compounds (C_3S, C_2S, C_3A and C_4AF). The formation of these compounds in the clinker is an evidence of the success of the manufacturing method of the Portland cement. The reserve is estimated using several methods (Triangles and polygons, graphical,

geographic coordinates, geographic information systems (GIS) and the Boldyrev method), showed the reserve is a proved reserve of approximately 53 million tons which can be increased in future. This reserve is enough to operate a cement plant with a capacity of 1.5 million tons / year for a period exceeding 26 years.

Radiological study of the quarry using a scintillation counter is made to record the radiation levels and ensure the worker safety in the quarry. The results are within the normal background radiation. Radioactivity measurement is conducted on marl samples for assessing the marl layer in terms of ^{226}Ra, ^{232}Th and ^{40}K for. Results obtained (14.91, 5.16 and 223.98 Bq/kg, respectively) indicate that the radiation doesn't exceed the globally permissible limits. The radiation level is also examined in clinker and cement samples prepared from raw materials, to assess its impact on the consumer. The results of the radiological measurements in clinker are ^{226}Ra=31.18, ^{232}Th = 7.6 and ^{40}K= 91.5 Bq/kg, while in cement are ^{226}Ra=35.55, ^{232}Th=7.42 and ^{40}K=110.18 Bq / kg.

Advantages that encourage investing the marl layer as cement raw material is the low hardness which help its extraction by hydraulic excavators, without need for the use of explosives. The lack of overburden in 72% of the total area of the quarry with very low of the stripping ratio (up to 0.033), its exposure on the surface, and the proximity to area of transport routes facilitates the movement of workers and equipment.

List of contents
Chapter One: Introduction

Chapter Tow: Qualitative assessment of marl layer

Chapter Three: Quantitative and economic assessment

Chapter Four: Radiological assessment

Chapter Five: Conclusions and Recommendations

List of Figures

List of Tables

Chapter One

Introduction

1. Introduction

1.1 Preface

Portland cement will remain the key material to modern infrastructure industry and the criterion for advancement of urbanization in countries. It is the basic and the predominate material for building and civil engineering construction. Cement industry is one of the most important industries in the world and is considered strategical and economical industry. Furthermore, for period of time the national development was measured by production and consumption of cement. The cement is mostly found everywhere in everyday life and it is hard to imagine a modern society without it (Tourki, 2010).

Cement, in the general sense of the word, can be described as a material with adhesive and cohesive properties (Gambhir, 2004) which make it capable of binding mineral fragment into a compact whole. The cements of interest in the making of concrete have the property of setting and hardening under water by virtue of a chemical reaction with it and are, therefore, called hydraulic cement (Neville, 2012). Cement is a binding material, which gains the strength after hardening, and can be used for the building and construction purposes (Eijk, 2001 and Hewlett, 2004). It acts as a bonding agent, holding particles of aggregate together to form concrete (Schumacher, 1999). It is a hydraulic compound; it reacts with water, produces insoluble compounds and thus forms a solid product (Eijk, 2001 and Hewlett, 2004). The term ‘hydraulic’ means that the product is water-resistant when hardened (Brandt, 2009).

Cement product obtained by finely pulverizing clinker is produced by calcining to incipient fusion and intimate and properly proportioned mixture of argillaceous and calcareous materials by wet or dry process. Naturally occurring calcareous deposits such as limestone, marl or chalk provided the source for calcium carbonate ($CaCO_3$). Silica (SiO_2), iron oxide (Fe_2O_3) and alumina (Al_2O_3) are found in various sediments, such as sand, shale, clay and iron ore (Newman, 2003). These components are seldom found in the needed proportion in only raw materials (Duda, 1985). Marls are an excellent raw material for cement manufacture, because they contain the lime and the clay component in already homogenized condition, but this deposits of such raw materials are not common (Duda, 1985). In other words, marl is a mixture of calcareous and argillaceous materials, is also used as raw materials for the manufacture of Portland Cement are found in nearly an countries and cement plants operate all over the world (Peray, 1979; Gutcho, 1980 and Neville, 2012). They are present in such proportion that the lime standard is around 100 and desired moduli can be obtained by the addition of only small quantities of corrective materials (Kohlhaas, 1983 and Newman, 2003). Therefore, the good selection of high pure raw material is considered the first and essential stage for cement industry (Al-Ali, 2004) which is the subject of geological exploration (Kohlhaas, 1983). There is no two cement plant will have exactly the same raw mix design formula because the vast range of raw materials and their different composition (Ibrahim, 1986 and Alsop, 2007).

The accuracy in achieving the basic requirements for specification of raw materials in the cement industry leads the production of clinker with metal and chemical compound identical to the standard specifications. Partial fusion occurs, and nodules of clinker are produced (Taylor, 1997).

1.2 Kiln reaction zones

The raw materials must be grinded and homogenous before burning in kiln to produce clinker. The homogeneity of the chemical composition of the feed added has an important relationship to fuel consumption, kiln operation, clinker formation and cement performance (Aldieb and Ibrahim, 2010). When the kiln feed (raw mix) enters the high temperature zones in the rotary kiln, a series of chemical reactions occur. The lime, alumina, ferric oxide, silica, and other metal oxides are reacted to form four main compounds (phases) of cement (chemically known as calcium aluminosilicate) which are: Belite C_2S ($2CaO.SiO_2$), Alite C_3S ($3CaO.SiO_2$), Aluminate C_3A ($3CaO.Al_2O_3$) and Ferrite C_4AF ($4CaO.Al_2O_3.Fe_2O_3$) (Soroka, 1979; Taylor, 1997 and Brandt, 2009). The formation temperatures of these compounds differ, which therefore defines the axial zones in which each compound is formed. Several chemical reactions zone to these substances by temperature in the kiln, which illustrates in Figure 1-1, are as following:

1. Dehydration zone (up to ~ 450˚C)
   Evaporation and removal of the free water and moisture in the raw mix are occurred.
2. Calcination zone (450˚C – 900˚C)
   $CaCO_3$ and $MgCO_3$ are decomposed and released carbon dioxide (Boateng, 2008 and Bhatty et al., 2011). Clay minerals are dehydrated, the process is known as dehydroxlation (Grim, 1968).
3. Solid-state reaction zone (900˚C - 1300˚C)

CaO and reactive silica combine to form small crystals of C_2S (Boateng, 2008) and form C_3A and C_4AF (Bhatty et al., 2011).

4. Clinkering zone (1300˚C – 1450˚C)

   The zone begins as soon as the intermediate calcium aluminate and ferrite phases melt (Taylor, 1997). The C_3S forms by reaction between C_2S crystals and CaO (Boateng, 2008) and then forms a large, glassy red hot ball called clinker. Figure 1-2 illustrates the interaction of oxides resulting from the decomposition of raw materials by heat in the rotary kiln.

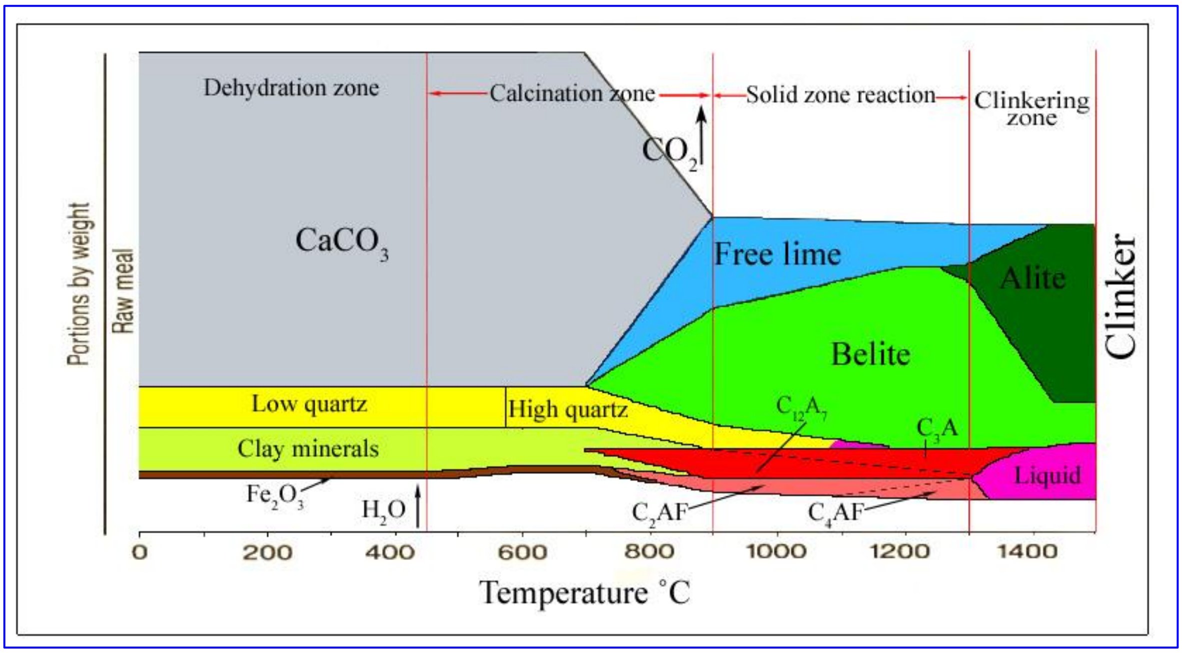


Figure 1-1: Sequence of reactions taking place during the formation of Portland cement clinker (Bhatty, 2011).

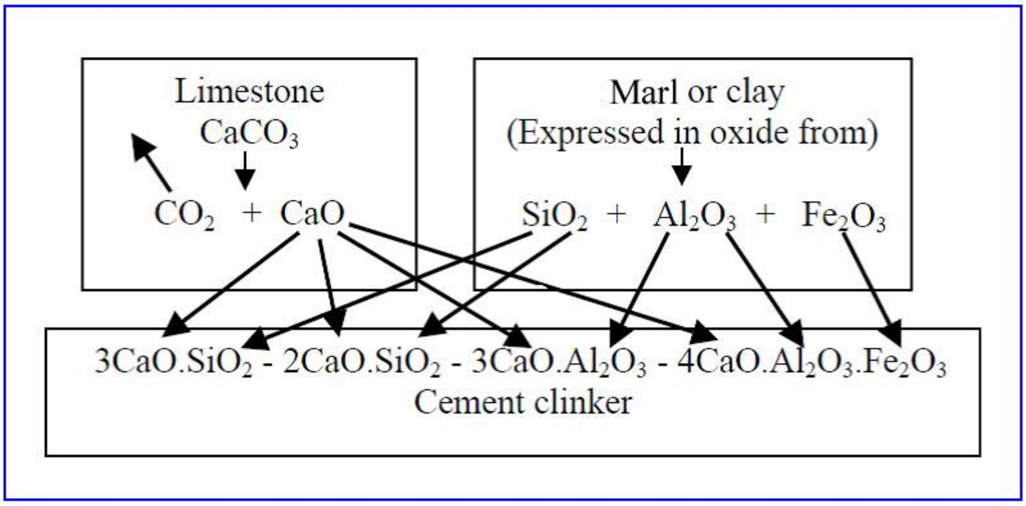


Figure 1-2: The combine the main oxides to form clinker (Jefferson, 1983)

1.3 Observation and research problem

At the limestone quarry of Kufa Cement Plant in Al- Najaf Governorate in the middle of Iraq, the rock bed exploited to produce the raw material (lime) for Kufa cement plant consist of 2.5 – 3.5 m of hard limestone. After extracting the limestone layer, a thick layer of marl appears below the limestone extending throughout the quarry covering 2 x 6 km^2. This layer (marl), part of the Euphrates Formation, is the study target. It will be evaluated qualitatively, quantitatively and radiologically to investigate its suitability as raw material for the cement industry. In the Najaf Governorate, the suitable clays with good specification for producing the Portland cement are scarce, due to the high content of sulfates. The workers in Kufa Cement Plants bring the clay which is a source of silica and alumina from quarries that are open in the arable areas of neighboring governorates (Babylon and Diwania). This clay is actually not easy available, and the long distance between quarry and plant leads to increase the total cost of the final product. Many plants are planned to construct a new exploitation cement plant in the Najaf Governorate, but it faced troubles in the scarcity of suitable clays. It is, therefore, quite necessary to find new reserves of clay as raw material to continue this exploitation. Marl layer appears at first glance to be suitable to use as raw material for producing the Portland cement or may be as corrective material.

Hence, and according to the concepts of scientific research, it is very necessary to invest this layer of marl as raw material for the manufacture of Portland cement. Moreover, this layer is characterized by the attributes of encouraging mining; it is directly exposed on the surface without overburden, easy for crushing and grinding because it is not hard. The hardness of marls is lower than that of limestone; the higher the content of a clay substance, the lower their hardness (Duda, 1985).

1.4 Location of the studied areas

The study area is a part of the limestone quarry of the Kufa Cement Plant. It is situated to the west of Al-Najaf city with a distance of about 26 km. The limestone layer at quarry belongs to the Euphrates Formation in the Khreba valley (Al-Ali, 2004; Faraj, 2009 and AL-Khersan et al., 2011). It is accurately determined by the latitude and longitude coordinates E 427122.7-N 3524181.7 and E 426305.1-N 3521444.6.

Geologically, the study area is located within the Salman Subzone which belongs to the Stable Shelf Zone (Jassim and Goff, 2006). The detailed location of the study area is illustrated in Figure 1-3.

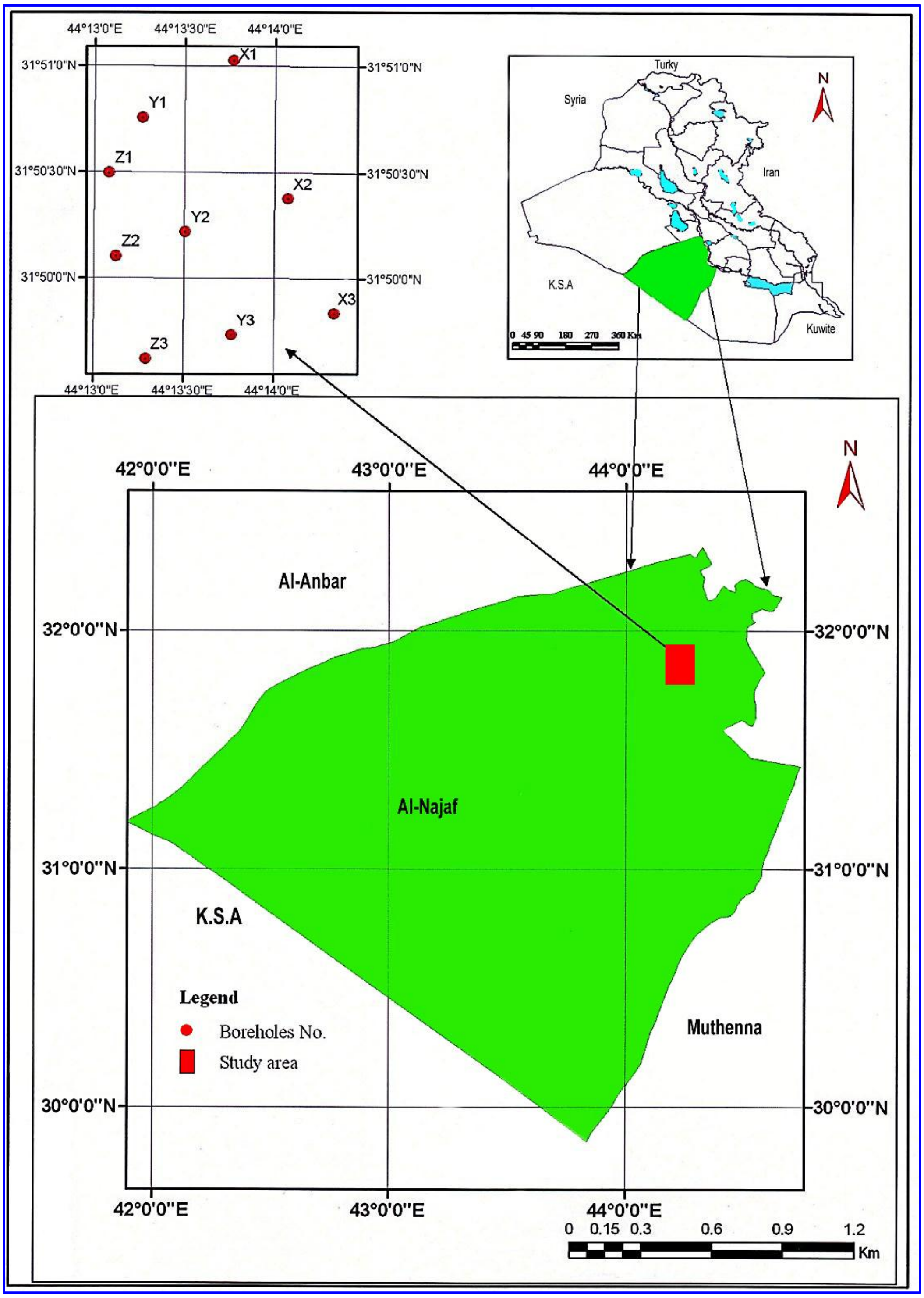


Figure 1-3: Location map of the study area.

The satellite image (Figure 1-4) displays the actual study area with nine boreholes that are drilled during the present study to obtain the required data.

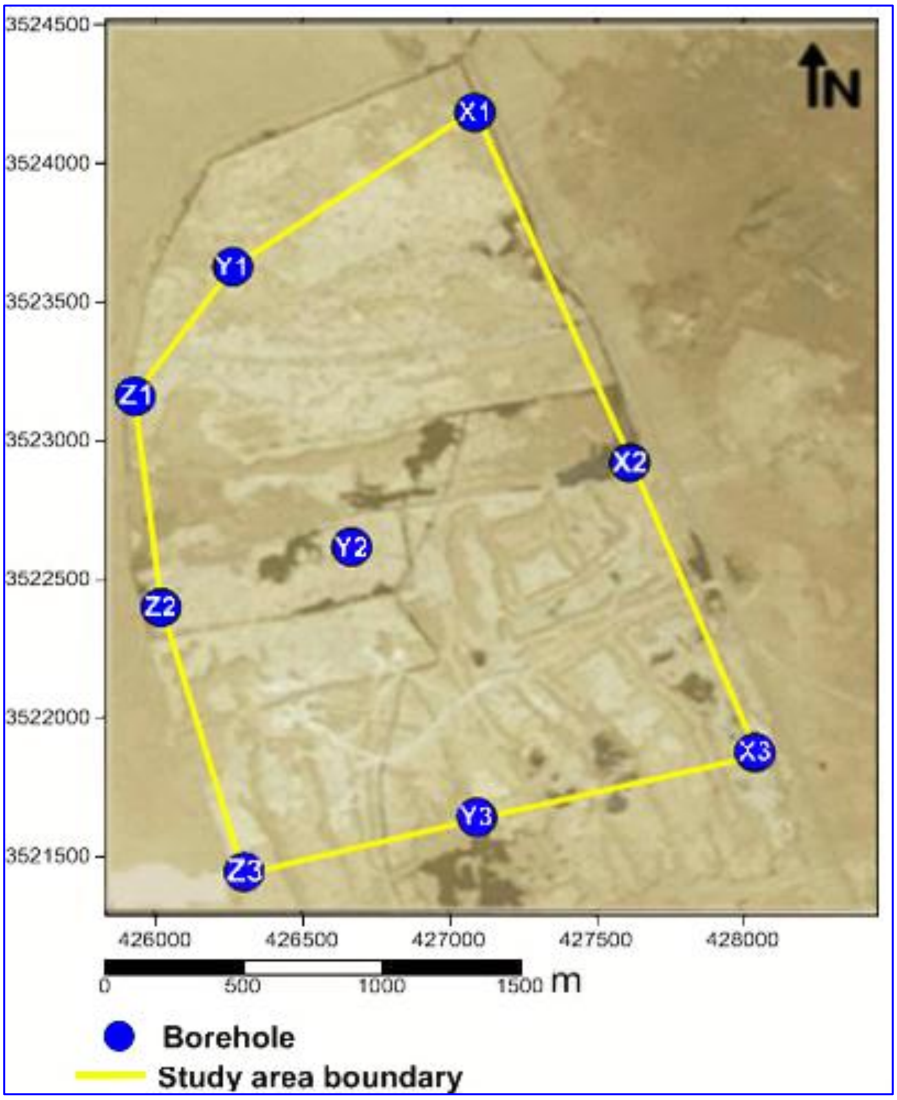


Figure 1-4: Satellite image for study area.

1.5 Previous studies

There are many previous studies about Euphrates Formation and suitability of its rocks for cement industry. Cytrocky and Karim (1969); Youkhanna (1971) and Ajina (1973) showed that the Euphrates Formation is deposited in shallow marine environment. Prazak (1974) indicated that the Euphrates Formation is heterogeneous in Karbala-Al-Najaf region. Buday (1980) studied the surface and subsurface sections of the Euphrates Formation, and showed that this Formation is deposited under shallow marine, reef and lagoonal condition and divided it into three members. Al-Mubarak and Amin (1983) achieved regional geological survey of the eastern part of the Western Desert and the western part of the Southern Desert. They studied the Euphrates Formation in the Southern Desert, and also divided it into three members. Barwary and Lateef (1984) carried out a general regional geological survey for Bahr Al-Najaf area. Barwary and Naseira (1995) submitted a detailed report about the geology and stratigraphy Al-Najaf region. Ahamed (2004) studied the stratigraphy and sedimentology of the Miocene succession in Karbala and Al-Najaf area. Al-Kaaby (2006) through field trip in Bahr Al-Najaf, studied the Euphrates Formation outcrops. He postulated that the uncovered rocks were belonging to Euphrates Formation and described it briefly to investigate the limestone for the cement industry in Al-Najaf area. High percent of quartz is appeared in limestone which considered unfavorable for cement industry.

Many studies conducted in Iraq not only on the Euphrates Formation. Salih (1984) investigated the gypsum and clay suitability for Portland cement industry in Sinjar area – Nainava Governorate, north of Iraq. Al-Qaraghuli (1993) studied the suitability of Shaqlawa marl in Erbil Governorate in north of Iraq for the cement industry. She found that marl is suitable as a raw material except the low lime percent with high magnesia content. Modification requires by adding highly pure limestone with low content of magnesia, to decrease the magnesia content in the marl. Jabboori et al., (2001) wrote a report about limestone amounts used in cement factories from different quarries in Iraq. Al-Ali (2001) studied the raw material and ordinary Portland cement produced in the old and new cement plants of Kufa. Jabboori (2005) studied the mining geology and environmental impacts of raw material quarrying for the cement industry in Badush area, Nainava Governorate, north of Iraq. Tochmachy (2005) carried out a geotechnical and mining evaluation of limestone utilized in Kirkuk cement factory and its environmental effects. Al-Samarrai (2010) studied marl deposits in three locations in Sulaimaniya Governorate NE of Iraq and testing the suitability to Portland cement industry. He found that marl was suitable as a raw material with need a little corrective materials in sometimes. Al-Dabbas et al., (2013) studied the mineralogy, geochemistry and reserve estimation of the Euphrates limestone for Portland cement Industry at Al- Najaf area which is suitable for cement in quality and quantity.

1.6 The objectives

To find a new indigenous source of alternative raw materials suitable for cement industry, a qualitative and quantitative assessment are required and recommended. The closer to the investigation area of the cement plant gives an economic significance for this subject. This study is an attempt to determine a new marl quarry serve the current and future demand of cement plant and provide the raw materials. This study is focused on finding new potential sources of raw materials (marl) and in the same location to be an alternative source of clay and limestone. The objectives of this study are:

1. Qualitative assessment of the marl layer to know the suitability of its chemical composition and parameters for Portland cement industry.
2. Quantitative and economic assessment to calculation the tonnage reserve of marl layer.
3. Radiological assessment to detect the radiation level in the quarry (raw materials) and in the products (cement) as well.

1.7 Geology of the studied area

At the end of Middle Eocene, the Stable Shelf, with exception of the north-south trending strip in the Rutbah Uplift, was covered by shallow neritic shoal type basin (Jassim and Goff, 2006), where the sediments of Dammam Formation were laid down (Buday and Jassim, 1987). The increase in uplifting and folding followed during the Oligocene associated with an almost general regression of the sea, a part from some restricted basins in the northwestern to the southeastern parts of Iraq (Buday, 1980). The Oligocene basin was located in the Mesopotamian Zone. The Salman Zone and the Euphrates and Zubair subzones of the Mesopotamian Zone were uplifted in Oligocene time (Jassim and Goff, 2006). As a result, there is no deposit in the study area in a period of Oligocene to Late Miocene. Then it was followed by new transgression in the Miocene. During the Late Miocene, the basin in the area was very shallow and relatively littoral at the beginning clastic and calcareous like Euphrates Formation. In the Middle Miocene, the development of the basin was similar as it had been during the Lower Miocene subcycle. At the beginning, calcareous in shallow water limestone was deposited (Nfayil Formation) (Buday, 1980). In the Upper Miocene-Pliocene the renew uplift on the whole Stable Shelf area was occurred. The paleogeographic development is directly influenced by this movement, and is marked by the deposition of terrigenous clastic syn and postorogenic molasses in the still subsiding and mobile foredeep (Injana Formation). The Quaternary era is characterized then by the development of the river systems (Buday, 1987).

1.7.1 Lithostratigraphy

The study area is located within the Salman Subzone which belongs to the Stable Shelf Zone characterized by shallow basement rocks (Jassim and Goff, 2006). The exposed formations in Bahr Al-Najaf area in upward sequence are: Dammam, Euphrates, Nfayil, Injana, Zahra and Dibdibba, in addition to the Quaternary deposits. The geological map shows the formations exposed in Al- Najaf Governorate (Figure 1-5).

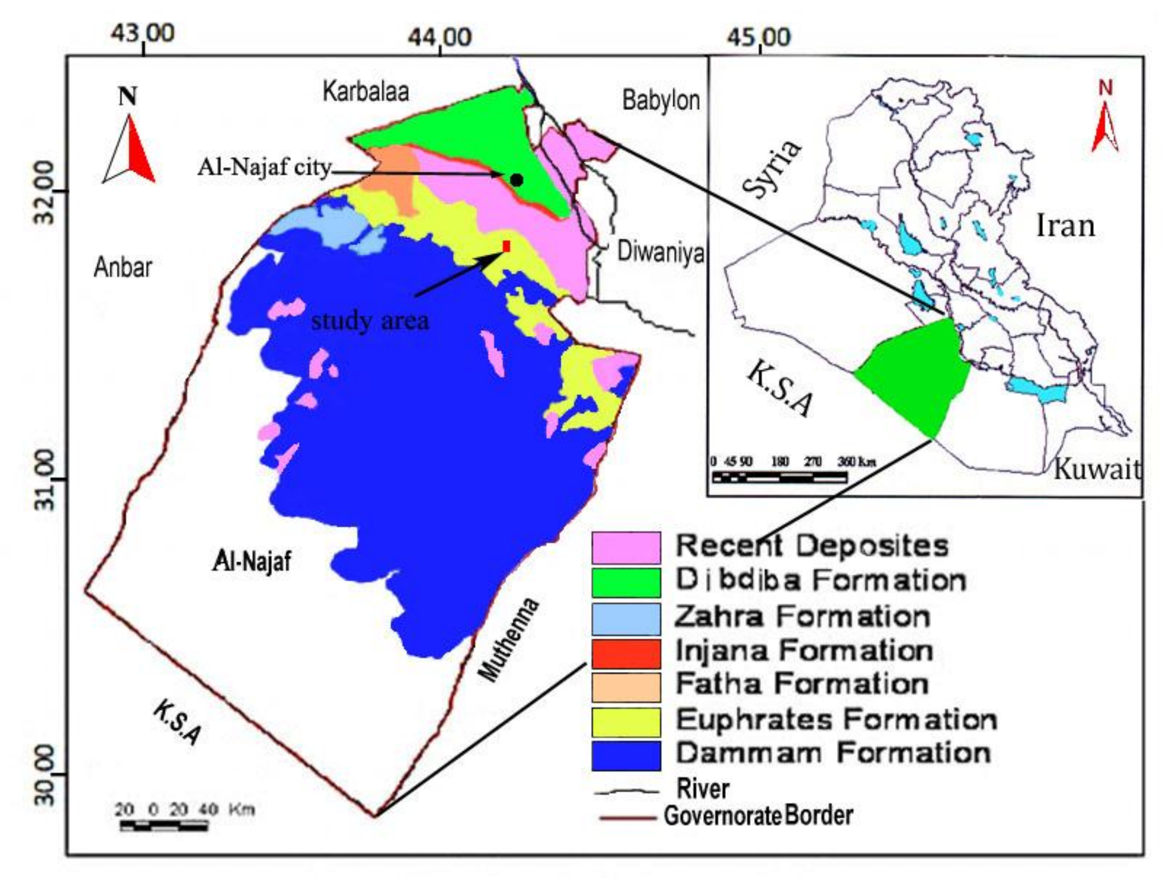


Figure 1-5: The geological map of study area (after Sissakian, 2000).

1.7.1.1 Dammam Formation (Middle Eocene)

The formation extends along large distances in the Western and Southern of Iraqi Deserts. It comprises limestone (chalky, organodetrial or dolomitic), dolomite, marl, and shale; it was divided into five informal members (Tamar-Agha et al., 1997). The Dammam Formation was deposited within carbonate inner shelf lagoons and shoals environmental and deposited under neritic to littoral condition (Jassim and Goff, 2006) with distinctive Nummulite species as index fossils (Al-Sayyab et al., 1982). It appears largely in the west and southwest of the study area in AL-Ghazal valley Al-Dabbas et al., (2013).

1.7.1.2 Euphrates Formation (Lower Miocene)

This Formation is widely distributed along the Euphrates River. It can be detected from Al-Qaim to Samawa-Busaiya areas. The formation is composed of dolomitic, fossiliferous and oolitic limestone with green marls at the top (Al-Hashimi and Amer, 1985). Facies identified by Al-Juboury et al., (2007) include fossiliferous packstone dominated by benthic foraminifera together with gastropods, algae and non-skeletal components such as oolites and pellets. The typical section of this formation locates in Wadi Fuhaimi-Khan Al-Baghdadi and reaches 8m thickness which unconformably and extensively oversteps the Dammam Formation (Aqrawi et al., 2010). Buday (1980) divided this formation into three units from bottom to top Unit (A) Cavernous and conglomeratic limestone; Unit (B) Shelly limestone; and Unit (C) marly and chalky limestone. Al-Mubarak and Amin (1983) and Al-Jumaily (1985), divided the Euphrates Formation into five unites in well Anah-2. The thickness reaches 15m and it has unconformable contact with the underlying Dammam Formation by a layer of pebbles and cobbles of carbonates (Tamar-Agha, 1984). Depending on the existed fossil types in this formation, the depositional environment was considered as a shallow marine (Al-Sayyab et al., 1982 and Jassim and Goff, 2006) in tropical and semi-tropical climate (Abawi and Hani, 2005). It was deposited during the Early Miocene transgression that followed the continental erosional period during the most Late Oligocene and Early Miocene (Fouad et al., 1986). The formation is considered to be of Lower to Middle Miocene age depends on the distribution of identified fossils assemblage (Al-Gherairy, 1985) which proved the presence of *miogypsina globulina* and *miogypsina intermidia* (Cytroky and Karim, 1971). It is clear that there are large facial changes in Euphrates Formation along its extension in the Iraqi Western Desert. It is led to totally different lithological constituents of the formation, in different areas it is due to the tectonic effect of Abu-Jir Fault and the position within the depositional basin (Sissakian and Salman, 2007). The upper contact, of the formation is conformable the covering formation, is mostly the Nfayil Formation (Al-Mehaidi et al., 1975). The thickness and distribution of the Euphrates Formation in Iraq illustrates in Figure 1-6.

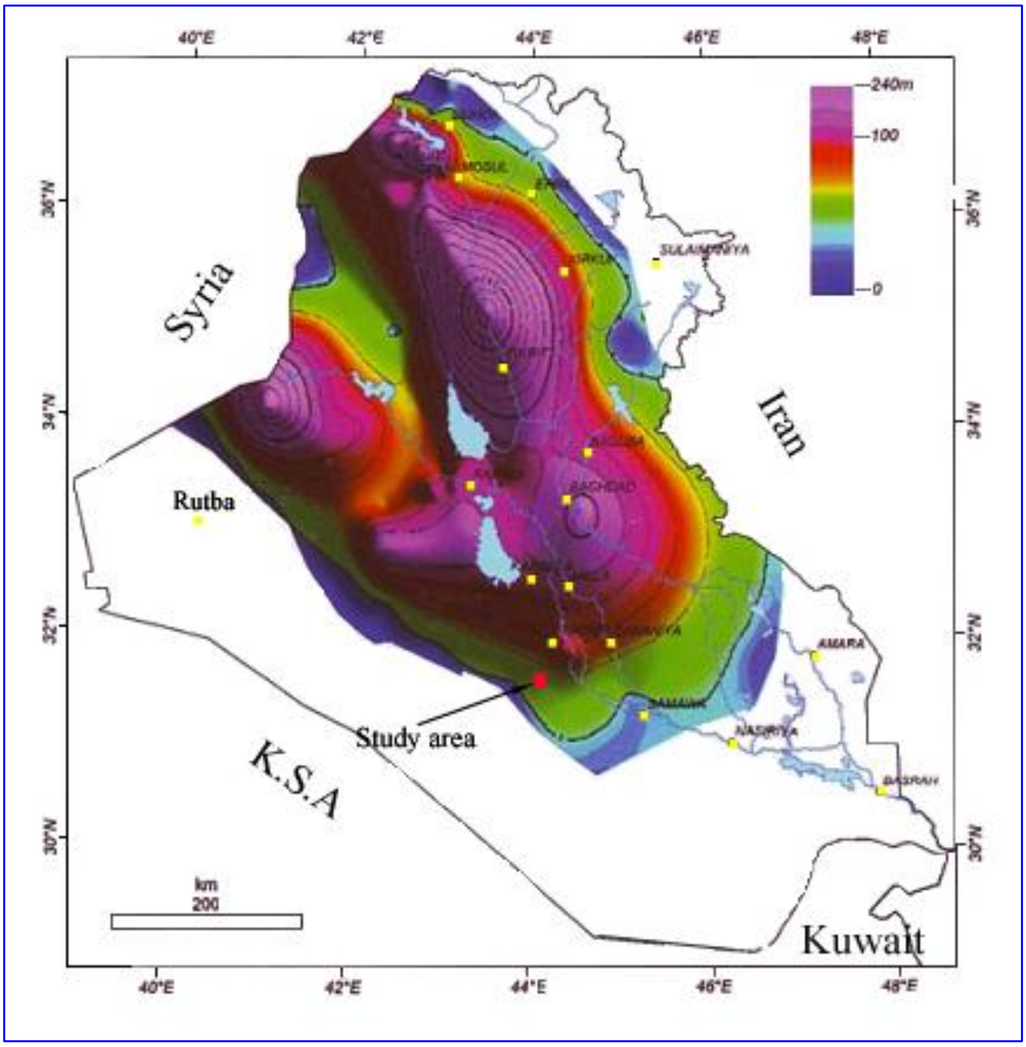


Figure 1-6**:** Isopach map of the Euphrates Formation within the stratigraphic column of Iraq (after Jassim and Goff, 2006).

1.7.1.3 Nfayil Formation (Middle Miocene)

The Nfayil Formation is recently added to the stratigraphic column of Iraq; previously the involved sequence was included with in Euphrates, Fatha and partly Injana Formations and announced by Sissakian et al., (1997). The gypsum of the Fatha Formation is changed to limestone and marl toward the south. This indicates the basin is becoming deeper (Al-Ankaz, 2012). The environment of deposition is the shallow marine water of high salinity (Sissakian, 1999). The age of this formation is considered for the third up to the middle Miocene. This formation is composed of siltstone, green marlstone and sandstone; their colors are grey and brown (Sissakian et al., 1997). The upper contact of the Nfayil Formation with the Injana Formation is conformable and gradational (Ahamed, 2004).

1.7.1.4 Injana Formation (Upper Miocene)

This formation is exposed along Tar Al-Najaf and in the south part of it and in the north of study area. It is composed in general of sequences of claystone, siltstone, sandstone and silt layers of chalky limestone. The depositional environment of it is a changeable environment; it's a lagoon at the beginning, then it changes to riverine and maritime fluviolacustrine system (Buday and Jassim 1987). The Injana thickness ranges from27m to 9m (Dawood, 2000). The upper contact is conformable of the Dibdibba Formation (Karim et al., 2002).

1.7.1.5 Zahra Formation (Upper Miocene-Pliocene)

The age of Zahra Formation is Late Upper Miocene-Pliocene. It lies unconformably over the Injana Formation in Tar-Al-Najaf area. The Zahra Formation lies in karst depressions. The thickness of Zahra Formation in the studied area is about 18 to 23 meters and the rocks of this formation consist of an alternation of sandstone and limestone (Al Mubarak and Amin, 1983).

1.7.1.6 Dibdibba Formation (Pliocene-Pleistocene)

The exposures of the Dibdibba Formation appear in the Karbala-Najaf Plateau (Hassan and Al-Khateeb, 2005) in Tar Al-Najaf. It comprises of clay, sand and gravel contained pebbles of igneous rocks (including pink granite and white quartz). The Dibdibba Formation represents fluvial sedimentation in extensive sheets probably as large old alluvial fans. It is often covered by sand sheets or by the alluvial fan sands of Wadi Al-Batin (Jassim and Goff, 2006).

1.7.1.7 Quaternary deposits

The Quaternary deposits are referred to the Quaternary period; these deposits cover most parts of the study area and include:

1. Aeolian sediments

It is distributed in many places in study area. It is a result of physical processes lead to deposition of aeolian or wind-borne sediments. The deposit becomes progressively finer in the downwind direction belong to Pleistocene-Holocene (Karanth, 2008).

2. Gypcrete soil

Gypcrete deposits are weakly consolidated earthy mixtures of secondary gypsum, sand and clay. It covers most the study area surrounding. It is formed as a result of raising deep water which is containing high $CaSO_4$ throughout the cracks (Al-Naqash, 1977). It is indicated arid climate. Thickness of it varies between 0.5 to 2 meters (Al Mubarak and Amin, 1983).

3. Slope sediments

Slop sediment spreads between Al-Najaf and Abo-Skhiare cities with thickness reaches to 1.5m. They are composed of a delicate mixture of a produced substances exposure to form Dibdibba as they gathered at feet of these little dip of clay, silt and sand with some small rocks (Al-Atia, 2006).

The lithological column of study area illustrates in Figure (1-7).

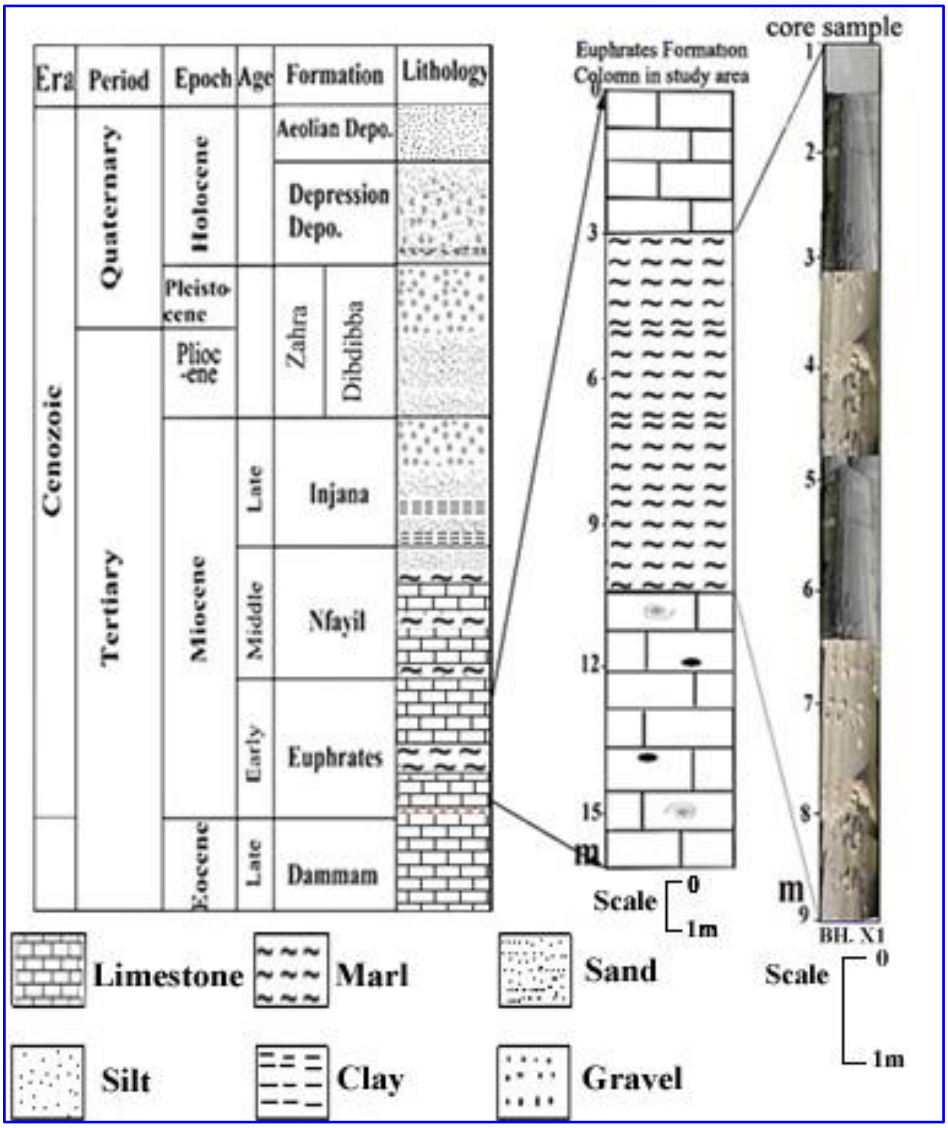


Figure 1-7: Stratigraphic sequence modified for Bahr Al-Najaf area.

1.7.2 Geomorphology and Topography of the study area

Generally the study area is a sub flat and the average rate of the height is between 30-35m above sea level. Bahr Al-Najaf basin locates in the north of study area and to the west of Al-Najaf city with a distance of about 26Km. The study area location, which represents the study site, bordered by cliffs on all sides with heights ranging 3-5m resulting from extraction operations of limestone layer for the cement industry. It interspersed with some hilly areas that have not been extracted or resulted from the collection of overburden ripping upon remnant layers of unextracted limestone. The low topography helps the work in quarry because easily reach to area and easily open roads that facilitate the raw materials transfer to the plant crusher. These will be helped to ease traffic and transport workers and equipment and its implications on the speed of the performance and the final cost.

1.8 Materials and methods

This section includes the field, laboratory and office works.

1.8.1 Field work

The field work comprises reconnaissance trips to determine the effective location of borehole and sampling sites. The study area is selected and determined accurately. Field work is carried out on marl layer exposed in the limestone cement quarry. Consequently, nine sites were chosen depending on accessibility, the overburden and the approximate and equal distance between them. Nine boreholes are drilled in order to get the required data (the entire thickness of marl layer, core samples for mineralogical, chemical and radiological analyses, and reserve estimation). The outcrops are also used for collecting data. Three boreholes (X1, Y2 and Y3) are drilled by Nordmeyer drill machine with diameter 102 mm by the Iraq Geological Survey to depth 11-15 m in 11/9/2012. Another six boreholes (X2, X3, Y1, Z1, Z2 and Z3) are drilled by heavy duty excavator (Komatsu PC600) to depth 8-9 m in 17/12/2012. The drilling methods are illustrated in Figure 1-8.

A total 66 samples of sedimentary rocks were collected from the marl layer and exposure of limestone of the Euphrates Formation in adjacent area. The samples are collected from each borehole from core or from wells (Figure 1-9) at deferent depths depending on the lithology changes. Total number of samples from borehole is sixty two in addition to four samples from adjacent area. Samples were taken from cores in boreholes X1, Y2 and Y3 (Figure 1-10) and other samples were taken from trench of other boreholes.

Figure 1-8: Methods of drilling the borehole in the study area. Trench method (left); rotary drilling (right).

Figure 1-9: Sampling of marl from drilled well.

Table1-1: Location of borehole in study area by UTM (Universal Transverse Mercator).

BH No.	**UTM-Coordination**		**Elevation (m)**	**Marl layer thickness (m)**
	Easting	**Northing**		
X1	427122.7	3524181.7	32	9.00
X2	427637.6	3522915.6	33	8.70
X3	428062.3	3521863.2	34	8.50
Y1	426282.1	3523630.0	36	8.75
Y2	426683.1	3522616.9	37	8.50
Y3	427104.4	3521636.9	38	8.40
Z1	425947.6	3523163.2	38	8.75
Z2	426026.8	3522402.3	40	7.75
Z3	426305.1	3521444.6	41	7.80

Figure 1-10: Core samples of boreholes.

Radiological survey was carried out by Scintillometer counter SSP-2-NF France made to detect the radiation level and draw an isorad map of the study area. The radiation measurements are taken in situ of about 20-25m round the well location. Four to five readings per site are recorded and then used for calculating the average (Figure, 1-11).

Figure 1-11: Scintillometer counter measurement.

1.8.2 Lab work

A total of 66 samples collected from the marl layer and the exposed limestone of the Euphrates Formation in the study area are subjected to various lab techniques. The mineralogical, chemical and physical analyses were made in several laboratories. The CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, LOI and SO_3 were analyzed in laboratories Southern Cement Company plants for every well depending on the changes in the lithology and a representative sample is taken as average for every well. The alkalis (K_2O, Na_2O) were analyzed in the chemistry department of the Science College / Baghdad University. The P_2O_5, TiO_2, SrO, Cl^- MnO was analyzed for every well in addition to physical tests for selected samples in the (GEOSURV) laboratories

1.8.2.1 Mineral identification

X-ray diffraction (XRD) for clay and non-clay fractions is used for analyzed 15 samples. All them were analyzed by D2 Phaser Bruker X-ray diffractometer with the following conditions: Target Cu tube, Power: 40 kV, current 20 mA, Speed 1cm/min, Filter Ni. German made in X-ray laboratory in the Earth Science Department in the Science College / Baghdad University.

A. Clay minerals

The identification of clay minerals is made by using oriented clay mineral mounts and <2µ particle size fraction for X-ray (Gibbs, 1965). The <2µ size fraction was used for all experiments performed in this study and was prepared by following procedure:

Isolation of clay-sized fractions started with drying and gentle grinding of the marl by agate mill. 20 grams of powder was taken and dissolved in 500 ml of distilled water in a glass beaker to dispose salt (Tucker, 1988). Then it is shaken and left to settle by gravity. If the water becomes unclouded within one hour it is spilled. This process of washing is repeated 4 or 5 times until the sample remains suspended.

Weak acid which prepared by adding 13 ml of acetic acid to 987 ml of distilled water with concentration 1.3% was added in order to not effect on clay minerals and to remove all carbonates with stirrer until the completion of the bubbles. The beaker was placed on sandy bath at 60ºC until the recession end, and then left to the next day. After confirming the ends of the interaction, excess liquid will be poured. The sample was filtered by filter paper to dispose the acid with continued adding distilled water until the solution becomes neutral, and then dried sample at 60ºC. The sample on filter paper was emptied in volumetric cylinder, added water up to 250 ml, and shake well by stirrer then left for an hour. For separation clay material from the coarser constituents of samples, 20 ml of suspension was taken by pipette from upper quadrant of cylinder and placed in small beaker which then put in oven at 50ºC to concentrate the suspension for one hour (Tucker, 1988).

Part of the sample is taken by a dropper and placed on three glass slides at a minimum and the amount of three drops to form oriented specimens by gravity settling on glass slide and leave to dry in room temperature. The clay mineral separation was done in the geochemistry laboratory, College of Science, University of Baghdad. Then the specimens were analyzed to identify the clay minerals by scanning angle 2θ ranging 5°– 20° as follows:

a. Normal sample

The oriented clay-fraction specimens were scanned without any treatments.

b. Heated sample

The clay-fraction specimens were heated to 550°C in a furnace for two hours. Then samples cooled in desiccator to avoid the moisture. This treatment is commonly used to help in identification of some clay minerals (Tucker, 1988).

c. Glycol ethylene

The clay-fraction specimens were put in a desiccator and were treated with the ethylene glycol (vapor) for 24 hours less than 60°C (Drever, 1973) in an oven by pouring ethylene glycol to about 1 cm depth in the base of the desiccator. Then the samples will be scanned. Ethylene glycol is extensively used as an auxiliary treatment to expand swelling clays. The mineral expands and the amount of expansion can provide essential supplementary information aiding in clay mineral identification.

B. Non-clay minerals

The XRD identification of non-clay minerals is done by using one gram of powder sample. The preparing of sample is by grinding 10g from the sample in agate mill, and then one gram is taken for analysis. The procedure is done by putting the powder and compact strongly in the cavity of a metal in the XRD instrument. Soften its upper part by pressing it by a slab of glass and thus owns part of orientation, especially in the upper surface and who is responsible for X-ray diffraction in the angle 2θ ranging 10-40 as the most basal reflections primary and secondary minerals generally fall within this range.

C. Semi-quantitative analyses of XRD results.

Semi-quantitative analyses are carried out for the XRD results by measuring the area under the peak according to the procedure often used (Al-Janabi et al., 1993).

1.8.2.2 Geochemistry

Forty one samples are prepared and then analyzed for CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, Na_2O, K_2O, SO_3, SrO, P_2O_5, TiO_2 and MnO in addition to loss on ignition (LOI) Cl^-. The raw material quality depends mainly on CaO, SiO_2, Al_2O_3 and Fe_2O_3 components done by comparing the results with the standard specification of the raw material of cement industry according to Kohlhaas (1983). Many analytical methods are used such as follows:

A. Flame spectrophotometry

The alkalis analyses K_2O and Na_2O are analyzed by flame spectrophotometric method based on Vogel (1989). 1gm of each sample powder were digested using Aqua Regia which a mixture of HCl and HNO_3 (3:1 by volume) in glass beaker 500 ml. The digested samples were filtered for ridding from insoluble materials and then the liquid must be saved in a tightly sealed glass container after completing the amount to 100 ml. by adding distilled water.

B. Chloride is determined by titration against $AgNO_3$.

C. XRF

X- Ray fluorescence is a common technique for geological studies (Beckhoff et al., 2006), which have been used for analysis of major elements in rocks and minerals (Hagan, 1982). The XRF-type panalatical-cubix in the Southern Cement Company was used to determine CaO, MgO, SiO_2, Fe_2O_3 and Al_2O_3. For preparing the sample, 30 gm. was grounded by agate mill to prevent contamination and reduce the particle size to less than 63µm. 10 gm. of sample is taken and carefully mixed with 1 gm. of wax. They are put in stainless steel cylindrical cast with 25mm dimension of inner diameter, 35mm outer diameter and 10mm thickness. The cast is filled by the sample and pressed to 150 N/cm^2 to form pellet which became ready for analyzing.

D. Calcination

Loss on ignition (LOI) is calculated by burning the sample powder in the furnace in a temperature of 1050 °C for 2.5h (Cox et al., 1977). LOI is the difference in weight before and after burning.

E. IR

Insoluble residue is represented quartz and clay minerals. It is calculated depending on (Ireland, 1971) by added dilute HCl acid concentration of 10% to10 gm. of the marl sample powder for dissolving the carbonate to the end of reaction. For removing the acid, the dissolved sample must be filtration, dried and weighed to determine the weight of IR.

F. Atomic Absorption

The trace elements Sr, Ti, p and Mn are analyzed by Atomic Absorption. To prepare the sample for this analysis, the marl sample must be digestion 1gm of sample powder by Aqua Regia. The digestion sample filtered for ridding from insoluble materials and then the liquid must be saved in a tightly sealed glass container after completing the amount to 100 ml. by adding distilled water. The Atomic Absorption that used for this purpose is Type/ PYE UNICON, SP 2900 in Iraq Geological Survey laboratories.

1.8.2.3 Radiation measurements

Gamma ray in the study area is measured using Scintillometer counter. Radioactive elements ^{226}Ra, ^{232}Th and ^{40}K concentrations are measured in samples of marl layer. Isorad map of the marl layer is drawn. Radiation level in the produced cement is also determined.

For radioactivity test, the samples are crushed into homogenized powder of particle size 1 mm using a grinder machine. The powder of samples was dried at 105°C for a period of 24 h in furnace to remove moisture (Benke and Kearfott, 1999). Then it was sieved through a 100 mesh (Walley El-Dine et al., 2001). One kg of each sample is put into standard Marinelli beaker and the activity of ^{226}Ra, ^{232}Th and ^{40}k is determined using the technique of gamma spectrometry. This technique depends on the high-purity germanium detector with an efficiency of 40% and resolution of 2 keV at 1332 keV of a standard source of radioactive isotope ^{60}Co. The measurements are done directly without any chemical treatment and the background and sample counting was carried out for a time of 3600 second. Nine samples are used for radiation measurement. Each sample represents one borehole. In addition to two samples of cement and two samples of clinker are measured too. The measurements of gamma ray for samples were done in the laboratories of the Radiation Research Department of Radiation Protection Center in the Ministry of Environment.

The Scintillometer counter was used at scale f-150 to give an idea to determined out all the concentrations of radionuclides ^{238}U, ^{232}Th and ^{40}K without determining concentrations each nuclide of them where were measured concentrations radioactivity in surface (total count).

1.8.2.4 Physical test

Physical tests include bulk density, porosity and compressive strength. Six selected core samples are subjected to these tests using procedures of Iraq

Geological Survey. The device that used for compressive strength is Toni pact 1000 (Figure 1-12).

Figure 1-12: The compressive strength device Toni pact 1000.

1.8.2.5 Clinker manufacturing in the laboratory

The clinker is manufactured by using raw materials consisting of 78% marl and 22% limestone. To produce 1 kg of clinker 1.65 kg of raw materials must be used. The sample was crushed and ground in mill to a high fineness, passing the sample completely through the sieve No.200 mesh 75 microns (Chatterjee, 2009) in order to reach a uniform size of the grains. The sample is put in aluminum pots and then placed in electrical furnace type Nabertherm type, German made (Figure 1-13).

The sample was passed into several heating stages in analogy with the rotary kiln through controlling the furnace temperature regulator and this have been applied by the following steps; up to 150°C the moisture content is driven away. The temperature was increased after that to 900°C and kept for about 90 minutes in order to insure the complete transfer of calcium carbonate to calcium oxide that remains in the mixture while the carbon dioxide is scattered with the united water steam present in the clay mineral. Then the temperature was increased up to 1450°C gradually with time intervals 10 deg. /min and kept for about 30 minutes (Ono, 1981). The sample was quenched rapidly by dropping the temperature to 900°C then cooled to room temperature. After the cooling, the sample was put in polythene bags for preventing hydration process in the produced clinker. The manufacturing clinker has been done in the laboratories of Building Research Center, Ministry of Construction and Housing.

Figure 1-13: Oven that burning raw materials for manufacturing clinker in 1450˚C.

1.8.3 Office Work

This stage includes collecting data and reference and then presenting and interpreting results obtained from the field laboratory works. Computerize software programs (GIS, surfer11, Photoshop and Coraldraw X3) are used to produce maps and diagrams. GIS, surfer11 are used for calculating the reserve area and volume tonnage of the raw material and then to estimate the reserve. Many processes are calculated:

1.8.3.1 Cement parameters

Lime Saturation Factor (LSF), Silica ratio (SR), Alumina ratio (AR) and Hydraulic modulus (HM) are named the cement parameters. The cement parameters of the raw materials are used as indicator for the suitability of the raw material to the kiln feed. These parameters are calculated from specific equations mentioned in chapter two

1.8.3.2 Reserve estimation

The reserve of raw material is calculated according to many methods such as following:

a. Block method included triangle and polygon method.
b. Graphical method.
c. Coordinates method.
d. Geographic Information Systems (GIS) method.
e. Boldyrev method**.**

Chapter Two

Qualitative Assessment

2. Qualitative assessment of marl layer

2.1 Preface

This chapter focuses on the raw material description in terms of the chemical and the physical characteristics of the marl layer in comparison with the standard specifications of cement raw materials. A comprehensive understanding of the chemical and physical aspects of raw material transformation into clinker is an important foundation for increasing production, reducing costs and improving quality of the cement plant. Generally, the main composition of Portland cement clinker (70% limestone + 30% clay) depends on the chemical composition of the raw materials (Dabous et al., 1989). For the evaluation of marl as raw materials for the cement industry, it is necessary to determine CaO, MgO, SiO_2, Fe_2O_3, Al_2O_3, SO_3, Na_2O, K_2O, and Cl^-. The mineralogical content at the marl layer also should be identified. The manufacturing and production of the Portland cement include many fundamental stages such as checking the chemistry of the raw materials and the kiln feed parameters such as lime saturation factor (LSF), silica ratio (SR) and alumina ratio (AR). The main goal of choosing a good quality of raw material is to produce a clinker of high specifications. Clinker of Portland cement contains four major compounds (phases) (C_2S, C_3S, C_3A, and C_4AF). The silicates C_3S and C_2S are the most important compounds responsible for the strength of hydrated cement paste. The presence of C_3A in cement is undesirable. C_4AF is also present in cement in small quantities with no significant effect on the cement behavior (Neville, 2010).

2.2 Raw materials and cement clinker

The initial production step in Portland cement manufacturing is raw materials acquisition. More than thirty different raw materials classified under four distinct categories are used in the manufacture of Portland cement. These categories are calcareous (limestone), siliceous (sand), argillaceous (clay, shale), and ferriferous (iron ore). Because of the chemical compatibility, today as in the past, alternative materials such as industrial wastes, by-products, and other marginal materials can be easily and economically utilized as raw material in cement manufacture. Therefore, the best selection of high purity raw material is considered the first and the essential stage in the cement industry (Al-Ali, 2004). The raw materials for cement manufacture which are the subject of geological exploration are mainly limestone and clays (Kohlhaas, 1983). In rare places in the world, marl can also be used as resource for oxides of cement manufacture (Duda, 1985 and Schneider et al., 2011). So the geologist may contribute in new ways to increase the profits of his firm (Schenck, 1966) through using a mixture of raw materials contains an essential oxides with true percentages (Jefferson, 1978). This may require a proportional correction of constituents to produce a cement clinker of the desired composition (Kohlhaas, 1983). The location of a cement works is usually determined by the availability of adequate supplies of the raw material within a reasonable distance of each other (Bye, 1999). The principal raw materials used in cement manufacturing are almost always supplied from adjacent quarries in order to avoid the high costs of transporting large tonnages of low cost raw materials (Ertek, 2008). Raw mix preparation, clinker formation and cement grinding are fundamental stages in the process of cement manufacturing (Johansen et al., 2002 and Mejeoumov, 2007).

The raw mix preparation process starting from the stage of quarrying to feeding into the kiln is a fairly complex one (Chatterjee, 2011). The Usual steps in quarry operations include stripping, drilling, blasting, excavating, handling, loading, hauling, crushing, screening, stockpiling and storing. Correction ingredients and homogenization also required between the necessary stages. Grinding to proper particle-size is important to ensure optimal fuel efficiency in the kiln and strength in cement (Figure 2-1).

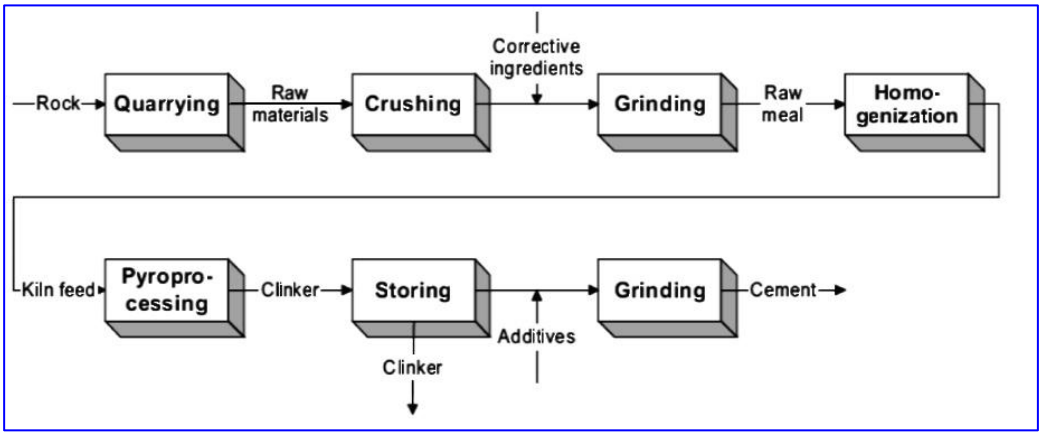


Figure 2-1: Block schematic of cement process (after Tokheim, 1999).

The raw material proportion should be calculated during preparing the raw mix by mixing adequate quantities of raw materials, so that the producing cement will have the desired chemical composition (Liu and Li, 2005).

These ingredients need to be ground into very fine particles to 75 µ (200 mesh) size (Chatterjee, 2009) to be more reactive and blended together. The resulted raw mix is then fed into a huge cylindrical kiln lined with firebrick and inclined 3-4% to the horizontal level and rotated l-4 rpm (Taylor, 1997). The Rotary kiln will fuse the raw mix at extreme temperature (1450°C) and become partially molten allowed to react as solid–solid and solid–liquid forming the final composition of the clinker. Raw material fed to a kiln system needs to be as chemically homogeneous as practicable. The main function of the rotary kiln in the minerals and materials industry is to convert raw materials into useful product materials (clinker) (Boateng, 2008). Clinker is gray lava-like material about the size of golf balls in the form of glassy balls (Chatterjee, 2009). The fineness and homogeneity of raw materials lead to a large reactive surface area that help in reaction in the kiln, therefore solid reaction velocities will be higher than coarser material.

Before igniting, the raw materials in the kiln should be designed to get quality clinker with the required clinker compositional parameters (Lime Saturation Factor (LSF), Silica Ratio (SR), Alumina Ratio (AR) and Silica Saturation Factor (SSF)) in addition to major oxides (CaO, SiO_2, Al_2O_3, and Fe_2O_3). When the kiln feed enters the high temperature zone in the rotary kiln, a series of chemical reactions occur in which the quicklime, alumina, ferric oxide, silica, and other metal oxides react to form main compounds of cement (C_3S), (C_2S), (C_3A), and (C_4AF) (Boateng, 2008). The percentages of the oxides of the chemical composition of the clinker are listed in Table 2-1.

Table 2-1: Chemical composition of Portland cement clinker (Duda, 1985 and Dabous et al., 1989).

Chemical name	**Abbreviated name**	**Chemical formula**	**Abbreviated notation**	**Mass contents (%)**
Calcium oxide	Lime	CaO	C	58 – 66
Silicon dioxide	Silica	SiO_2	S	18 – 26
Aluminum oxide	Alumina	Al_2O_3	A	4 – 12
Ferric oxides	Iron	Fe_2O_3	F	1 – 6
Magnesium oxide	Magnesia	MgO	M	1 – 5
Sulphur trioxide	Sulphuric anhydrite	SO_3	$\overline{S}$	0.5 – 3
Alkaline oxides	Alkalis	K_2O and Na_2O	K + N	1

Naturally occurring calcareous deposits such as limestone, marl or chalk provide the source for calcium carbonate. Silica, iron oxide and alumina are found in various ores and minerals, such as sand, shale, clay, marl, and iron ore (Table 2-2) but a single raw material with the desired chemical composition is seldom found. Theoretically, any material that can contribute oxides (CaO, SiO_2, Fe_2O_3, and, Al_2O_3) may constitute the raw mixture (Mejeoumov, 2007).

The overall chemical composition and structure of the individual raw ingredients can vary considerably. The reason for this is that at the very high temperatures of the kiln, many chemical components in the raw ingredients are burned off and replaced with oxygen from the air. Chemical composition of Portland cements compounds depending on Brandt (2009) are illustrated in Table 2-3.

The ingredients listed in Table 2-2 include both naturally occurring materials such as limestone and clay, and industrial byproduct materials such as slag and fly ash. Materials that contain more than minor (or in some cases trace) amounts of alkaline and alkali earth metals such as Mg, Na, K, Sr and various heavy metals cannot be used, as these will not burn off in the kiln and will negatively affect the cement. Another consideration is the reactivity, which is a function of both the chemical structure and the fineness. Clays are ideal due to its fine particles already and thus need little processing prior to use, and are the most common source of silica and alumina.

Table 2-2: Raw materials for Portland cement manufacture (Kosmatka et al., 2000).

Calcium (C)	**Silicon(S)**	**Aluminum(A)**	**Iron(F)**
Limestone	Clay	Clay	Clay
Marl	Marl	Marl	Iron ore
Calcite	Sand	Aluminum ore refuse	Mill scale
Aragonite	Shale	Shale	Shale
Shale	Fly ash	Fly ash	Blast furnace dust
Sea Shells	Rice hull ash	——	——
Cement dust	kiln Slag	——	——

Calcium is most often obtained from quarried rock, particularly limestone (calcium carbonate) which must be crushed and ground before entering the kiln. The most readily abundant sources of silica are quartz. Pure quartz is very unreactive even at the maximum kiln temperature, and therefore cannot be used. When it is ready to enter the kiln, the dry raw mix has 85% of the particles less than 90 μm in size (Taylor, 1997).

2.3 Kiln feed parameters

A set of parameters (modules) is currently used in cement manufacturing to characterize the quality of the raw materials and to ensure the quality of the produced cement. These parameters have considerable effect on the burnability of raw mix (Kebede, 2010). They are in fact proportioning formulas into which the percentage of the various oxides, as determined by chemical analyses should be substituted (Kohlhaas, 1983). The determination of cement quality is based on a set of criteria. These criteria need to be computed after design the raw mix of kiln feed. The results of these criteria are calculated by the present study in the last subject (raw mix design) of this chapter. These criteria are:

2.3.1 Lime Saturation Factor (LSF)

LSF is a measurement of the degree of conversion of silica, alumina, and iron oxide to their most highly basic calcium compounds (Bhatty et al., 2011). The ranges of LSF for the ore mixture in clinker of Portland cement from 66% to 1.02% (Pollitt, 1964 and Taylor, 1997). The LSF is the most critical control ratio, which is determined by the ratio of lime (C) to silica (S), alumina (A) and iron oxide (F) such as follows:

$$\text{Lime Saturation Factor (LSF)} = \frac{100\,(C)}{2.8\,(S) + 1.18(A) + 0.65(F)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2-1)}$$

It governs the relative proportions of C_3S and C_2S. Clinker with a higher LSF will have a higher proportion of C_3S to C_2S than will a clinker with a low LSF (Kebede, 2010). According to (Duda, 1985), it ranges from 90% to 95%, but according to (Chatterjee, 2009) is 90-97%. (Newman, 2003) thought that the correct ratio LSF ranging between (95-98) %. In Iraq, LSF is from 90% to 100% according to the Iraqi Quality Standard number 5 (I.Q.S, 1984). Specification of raw materials and type and economic value of the product determines the percentage of LSF which is used in the production of cement. Values above 1.0 indicate that free lime is likely to be present in the clinker.

This is because all the free lime at LSF 1.0 should have combined with C_2S to form C_3S. LSF 1.02 would mean 100% C_3S in cement and 0.66 would mean 100% C_2S (Kebede, 2010). A high LSF requires high heat consumption for clinker burning inside the kiln. Thus gives more strength to the cement but that means more fuel consumption which leads to high cost of product and damages to the kiln walls. When the raw materials are correctly mixed and under proper burning conditions, no free CaO should be left in the clinker.

If LSF is below 92, extra free lime (CaO) will be form in the cement. When used concrete with high free lime cement in gypsum soil, the CaO dissolved in water and with presence of Al_2O_3 it will be reactive with gypsum to form Ettringite with 26 molecule of H_2O which cause slow destruction of concrete (Al-Mufty, 1997) according to the equation.

$$3CaO + 3CaSO_4.2H_2O + Al_2O_3 + 26H_2O \rightarrow Ca_6\ (Al\ (OH)_6\ )\ 2(SO_4)\ 3.26H_2O.$$

2.3.2 Silica Saturation Factor (SSF)

The value of SSF is inversely proportional to the liquid phase at burning zone temperatures. The combining efficiency of silica with lime left after forming C_3A and C_4AF. Which is maintained between 0.85 and 0.95 can give very satisfactory cement (Kebede, 2010). The formula to calculate SSF is:

$$Silica\ Saturation\ Factor\ (SSF) = \frac{C-(1.65\ A+0.35\ F+0.7\ \bar{S})}{2.8\ S} \text{……..……..} \quad (2\text{-}2)$$

Where: C: CaO

A: Al_2O_3

F: Fe_2O_3

$\bar{S}$: SO_3

S: SiO_2

2.3.3 Hydraulic modulus (HM)

Hydraulic modulus is represented the optimum lime content which ranges 1.7- 2.3 but the good quality is 2 (Ghosh, 2002). Increasing HM more heat is required for clinker burning; the strengths, especially the initial set up and also the heat of hydration rises; and simultaneously the resistance to chemical attack decrease (Rao et al., 2011). Hm is calculating by formula 2-3:

$$Hydraulic\ modulus\ (HM) = \frac{C\ \%}{(S + A + F)\%} \quad (2\text{-}3)$$

Where: C: CaO

A: Al_2O_3

F: Fe_2O_3

S: SiO_2

Generally cements with HM lesser than 1.7 showed mostly insufficient strength; cements with HM greater than 2.3 had poor stability of volume (Aldieb and Ibrahim, 2010).

2.3.4 Silica ratio (SR)

The SR is called 'silica modulus' in some literatures. It's measurement of the ratio of silica (S) to that of the sum of aluminum (A) and iron (F) oxides (Peray, 1986 and Bhatty et al., 2011).

$$Silica\ Ratio\ (SR) = \frac{S\ \%}{(A+F)\%} \quad (2\text{-}4)$$

It has one of the greatest effects on burnability; in the presence of 2% or more MgO, a ratio of 1.63 gives the maximum liquid phase at the minimum temperature (Bhatty et al., 2011). The range of silica ratio for the cement clinker is between 1.8 and 3.2 (Knofel et al., 1984), but the optimal value is between 2.2 and 2.6 (Gouda, 1979; Kohlhaas, 1983 and Duda, 1985). A higher SR decreases the liquid phase content, the clinker harder to burn (Peray, 1986) meaning higher temperatures or more time to combine C_2S with free lime chemically to produce C_3S (Young and Miller 2011), and produce dusty clinker (Hills et al., 2002 and Young and Miller, 2011). It impairs the burnability of the clinker and exhibits poor coating properties (Peray, 1979). The high SR was deteriorates the kiln lining (Ghosh, 1991). A lower SR higher melt phase and coating can become thick may be led to ring formation and low early strength (3-7) days in the cement (Peray, 1979). This factor is inversely proportional to the liquid phase at burning zone temperatures (Miller, 2011).

2.3.5 Alumina ratio (AR)

The alumina ratio is also called "alumina modulus". It's measurement of the ratio of aluminum oxide (A) to iron (F) oxide.

$$\text{Alumina Ratio (AR)} = \frac{A\,\%}{F\,\%} \quad \text{(2-5)}$$

In industrial cements, the optimum values of this ratio should range between 1.3 and 2.8, but the range between 1.4 and 1.6 is desirable optimum level (Peray, 1986). This modulus expresses the composition of the liquid phase in the clinker. If the iron oxide content is higher, the modulus is lower, and the viscosity of the melt decreases (Alsop, 2007). This ratio can influence the rate of development of clinker liquid in the burning zone; in the presence of 2% or more MgO, a ratio of 1.63 gives the maximum liquid phase at the minimum temperature (Miller, 2011). This determines the potential relative proportions of C_3A and C_4AF phase in the clinker. An increase in clinker AR (sometimes written as A/F) means there will be proportionally more C_3A and less C_4AF in the clinker (Kohlhaas, 1983 and Kebede, 2010). This leads to produce with high early strength but makes the reaction between the silica and calcium in the burning zone more difficult (Peray, 1979).

2.3.6 Calcium to Silica

This ratio is between calcium and silica (CS) (Almeida, 2010).

$$CS = \frac{Ca}{Si} \quad \text{(2-6)}$$

Generally in cement industry, the ratio of Calcium to Silica (Ca / Si) should be not less than 2 (Kebede, 2010).

2.4 Clinker phases

The main purpose of the kiln feed (raw mix) parameters and compounds of raw material is to conclude the principal chemical compounds C_3S, C_2S, C_3A and C_4AF in clinker phases (Taylor,1997; Bye, 1999 and Neville, 2012) that showed in Table 2-4.

Several other phases, such as alkali sulfates and calcium oxide, are present as a minor amount. Chemists normally denote these major phases in cement as: Alite (C_3S), Belite (C_2S), Aluminate (C_3A) and Ferrite (C_4AF).

Table 2-3: Mineralogical composition percent of Portland cements, (after Newman, 2003 and Brandt, 2009).

Cement Notation	Mineral name	Typical level (Mass %)	Typical range (Mass %)	Chemical composition
C_3S	Alite	57	38 – 60	$3CaO.SiO_2$
C_2S	Belite	16	15 – 38	$2CaO.SiO_2$
C_3A	Aluminate	9	7 – 15	$3CaO.Al_2O_3$
C_4AF	Ferrite	10	6 – 18	$4CaO.Al_2O_3.Fe_2O_3$

Theoretically the relationship between composition and clinker phases was essentially solved by Bogue calculations (Bogue, 1955; Ghosh, 2002 and Neville, 2010) such as follows:

$$C_3S = 4.0710\,CaO - 7.6024\,SiO_2 - 1.4297\,Fe_2O_3 - 6.7187\,Al_2O_3 \ldots (2\text{-}7)$$
$$C_2S = 8.6024\,SiO_2 + 1.0785\,Fe_2O_3 + 5.0683\,Al_2O_3 - 3.0710\,CaO \ldots (2\text{-}8)$$
$$C_3A = 2.6504\,Al_2O_3 - 1.6920\,Fe_2O_3 \ldots\ldots (2\text{-}9)$$
$$C_4AF = 3.0432\,Fe_2O_3 \ldots\ldots (2\text{-}10)$$

The major clinker phases are:

2.4.1 Alite (C_3S)

C_3S is the most important constituent of all normal Portland cement clinkers, which is a solid solution forming around 38-60 % of the clinker (Brandt, 2009). It is responsible for the setting characteristics and development of the early strength of cement from 1 to 28 days (Mejeoumov, 2007). In general, the early strength is higher for Portland cement with increased percentages of C_3S (Tennis and Kosmatka, 2011). This compound requires a greatest amount of CaO and high sintering temperatures for its formation (Soner, 2009). C_3S does not form below 1250°C in the non-mineralized system (Johansen and Bhatty, 2011). This compound always incorporates foreign oxides e.g., approximately 2% MgO, also Al_2O_3, Fe_2O_3, TiO_2 and others (Kohlhaas, 1983).

2.4.2 Belite (C_2S)

This phase has a content of 15–38 % (Brandt, 2009) of the clinker. It is hardened slowly and is contributed largely to the beyond one week (Tennis and Kosmatka, 2011). It reacts slowly with water, thus contributing little to the strength during the first 28 days, but substantially to the further increase in strength that occurs at later ages (Taylor, 1997).

2.4.3 Aluminate (C_3A)

The content of C_3A in clinker is approximately 7–15 % (Brandt, 2009). It liberates a large amount of heat during the first days of hardening. It also contributes slightly for early strength development. C_3A hydrates very rapidly and will influence early bonding characteristics. Abnormal hydration of (C_3A) and poor control of this hydration by sulfate can lead to such problems as flash set, false set, slump loss, and cement-admixture incompatibility (Previte, 1977). The amount of gypsum added to clinker is curial, and depend on C_3A content for controlling the hydration (Neville, 2010). Cement with low percentages of this compound is especially resistant to soil and water containing sulfates. This compound always incorporates foreign ions especially alkalis (Na_2O and K_2O) (Kohlhaas, 1983).

2.4.4 Ferrite (C_4AF)

The average composition and constitutes is about 6–18 % of a typical clinker (Brandt, 2009). It reduces the clinkering temperature and acts as a flux in burning the clinker. It hydrates rather rapidly but contributes very little to strength development. Most color effects are due to C_4AF series and its hydrates. This compound always incorporates foreign oxides e.g., SiO_2 and MgO (Kohlhaas, 1983).

The compounds tricalcium aluminate and tricalcium silicate develop the greatest heat, then follows tetracalcium aluminoferrite, with dicalcium silicate developing the least heat of all.

2.5 Marl description

Several definitions of marl were placed. Marl is a general term for limey mud or an intimate mixture of clay and limestone. Pettijohn (1975) defined marl is loose earthy deposits mostly formed under marine and is usually gray, soft friable, less fissile than the shales, and like mudstone, have a blocky subconchoidal fracture. Feyznia (2003) defined marl as sedimentary rocks that contain destructive particles (silt and clay) and in the chemical fraction involve carbonate calcium with one or some chemical minerals. In another ward marl is a calcareous mudrock (Tucker, 2011) consisting of carbonate and (35-65) % clay (Pettijohn, 1975 and Flugel, 2004) formed under marine or freshwater conditions (Scholle, 2003). The Scheme of the transitional lithotypes limestone to marl presents in Figure 2-2 (http://en.wikipedia.org).

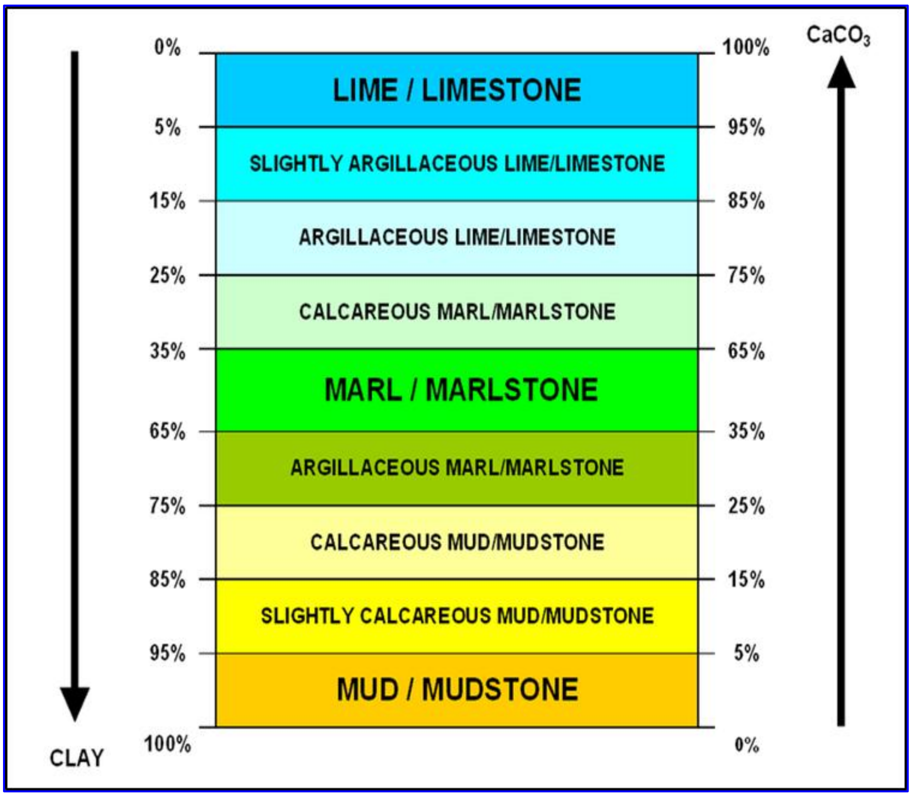


Figure 2-2: Scheme of the transitional lithotypes limestone to marl.

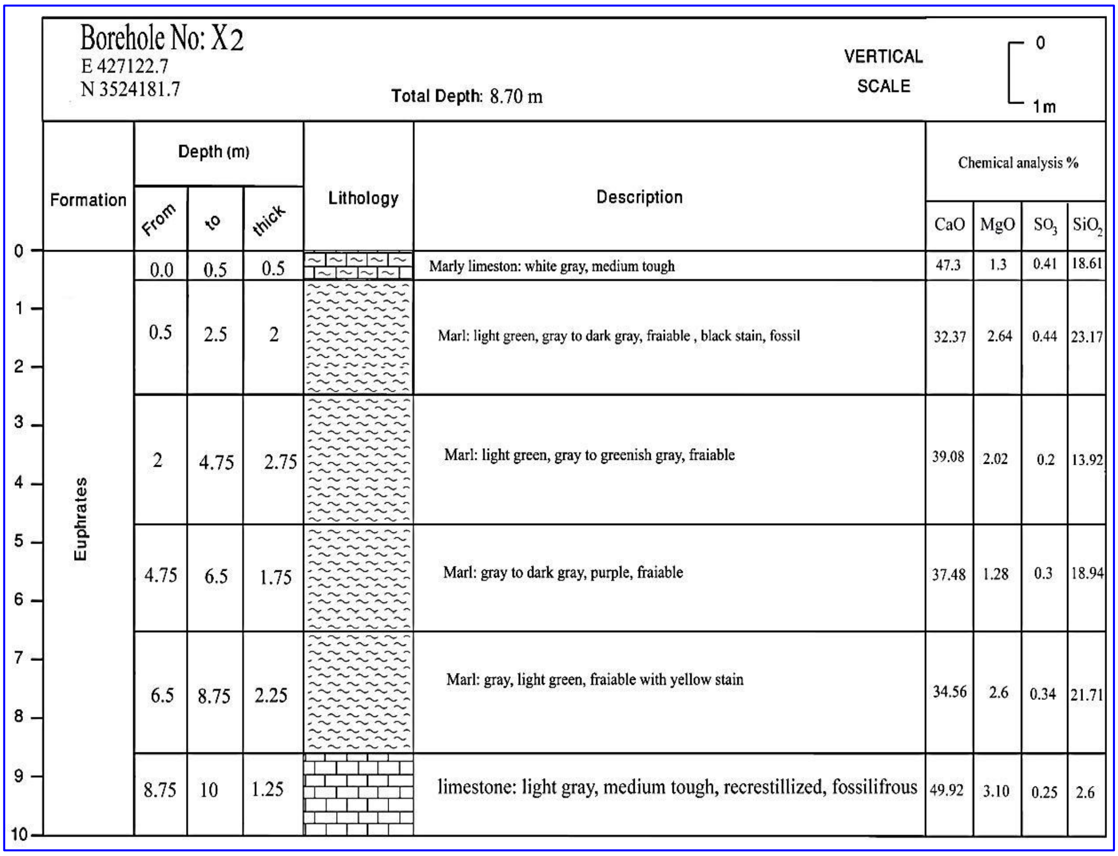
The hardness of marls is lower than that of limestone; the higher the content of a clay substance, the lower their hardness (Duda, 1985). That means easy to crushing and grinding when used as raw materials for manufacturing Portland cement.

The marl layer in the Euphrates Formation was identified by Bellen et al., (1959) and Buday, (1980). The thickness of marl layer in Al-Najaf area is 2 m. (Barwary and Naseira, 1995 and Ahamed 2004).

Many slides for limeston layer below the marl layer are studied in order to identify the fossils species; the *miogypsina globulina*, which consider as the index fossil for Euphrates Formation are identified. (Personal communication in 4/11/2012 with Mrs. Lamees in Science College/ Baghdad University and in 12/11/2012 with Dr. Buthaina in Iraqi Geological Survey).

The marl of Euphrates Formation deposited in brackish quite marine environment because of presence of fossil fauna of *Ostracods*, *Foraminifera* and *Plysipoda* which high percent of its bivalves was still dovetail.

The marl layer is consisted from five horizons that illustrated in Figure 2-3. It is altered from white gray in the upper to dark gray in the lower (Figure 2-4).



Borehole No: X2
E 427122.7
N 3524181.7
Total Depth: 8.70 m

Formation	Depth (m)			Lithology	Description	Chemical analysis %			
	From	to	thick			CaO	MgO	SO_3	SiO_2
Euphrates	0.0	0.5	0.5		Marly limeston: white gray, medium tough	47.3	1.3	0.41	18.61
	0.5	2.5	2		Marl: light green, gray to dark gray, fraiable , black stain, fossil	32.37	2.64	0.44	23.17
	2	4.75	2.75		Marl: light green, gray to greenish gray, fraiable	39.08	2.02	0.2	13.92
	4.75	6.5	1.75		Marl: gray to dark gray, purple, fraiable	37.48	1.28	0.3	18.94
	6.5	8.75	2.25		Marl: gray, light green, fraiable with yellow stain	34.56	2.6	0.34	21.71
	8.75	10	1.25		limestone: light gray, medium tough, recrestillized, fossilifrous	49.92	3.10	0.25	2.6

Figure 2-3: Lithology of marl in study area.

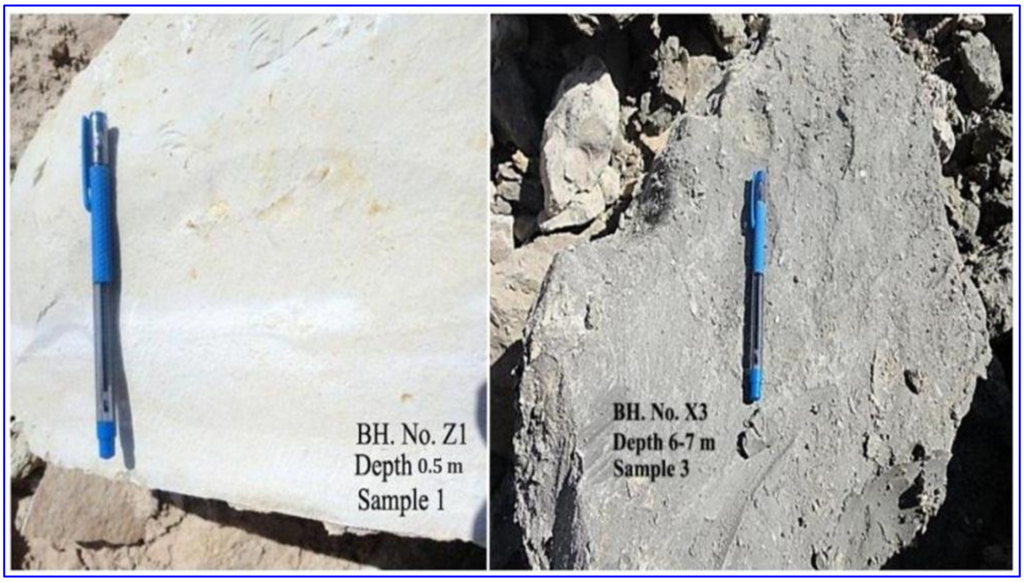


Figure 2-4: Marl of Euphrates Formation.

2.6 Kiln feed specifications

The basic chemistry of the clinker manufacturing process is depending on kiln feed raw mix. The kiln feed properties are effected on the qualitative of product, energy (electric and fuel) consumption and corrosion of equipment. There are many percentages standards for several researchers of the cement materials as raw mix for kiln feed that produced typical clinker, expressed as oxides, and are listed in Table 2-4.

All these specifications are the major demands to produce the clinker, in accordance with the quality standards, and congruent with the most universal properties. The cement plants are designed depending on the presence, type, and chemical composition of raw materials formula. There is no two cement plants in the world have exactly same design (Ibrahim, 1986).

Table 2-4: Oxides boundaries of typical raw mix material.

Oxide	**Range in raw mix for kiln feed**				
	Chatterjee, 1979	**Kohlhaas, 1983**	**Duda, 1985**	**Alsop, 2007**	**Miller, 2011**
CaO	63 - 67	60 - 69	57 - 67	65 - 68	62 - 68
SiO_2	21 - 24	18 - 24	16 - 26	20 - 23	19 - 23
Al_2O_3	4 – 7	4 - 8	4 - 8	4 - 6	3.5 - 6.5
Fe_2O_3	2 – 4	1 - 8	2 - 5	2 - 4	2 - 4
MgO	5 - 6 max	5 max	4 max	1 - 5	5 max
SO_3	1.5 max	3 max	1.5 max	0.1 - 2	1.5 max
R_2O (Na_2O+K_2O)	1.2 max	2 max	2 max	0.1 - 1.5	1.6 max

2.7 Qualitative assessment of marl layer

The quantitative assessment of marl layer is included mineralogical and geochemical studies:

2.7.1 Mineralogy

The mineralogical information can be very useful in predicting the severity of wear that will occur in the crushing and grinding machinery in addition to kiln refractory lining (Kohlhaas, 1983). The knowledge of mineral composition is of interest both in the choice of preparatory processing machinery and in obtaining information on burning behavior of the material in the kiln. For that, eight samples were chosen for analyzing by using X-Ray Diffraction (XRD) for mineral identification depends on the variation in the marl layer column**.** The clay minerals and non-clay minerals were identified by using XRD techniques.

2.7.1.1 Non clay minerals

XRD results show that the non-clay minerals are calcite, dolomite and quartz.

2.7.1.1.1 Calcite $CaCO_3$

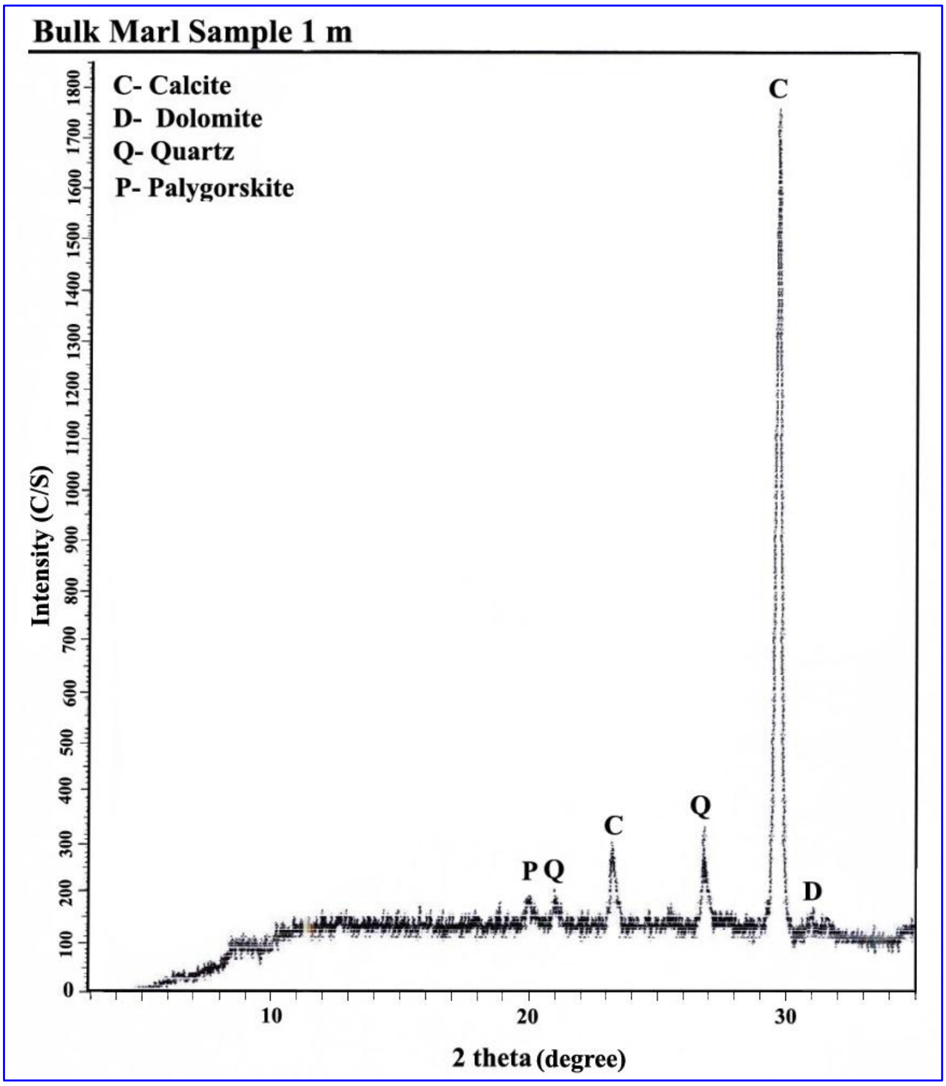
Calcite is the main mineral in marl samples. It is identified by the (104) reflection: d space =3.03Å (major peak), 2Ө = 29.40 ° as well as another less intense reflections in d space= 3.86 Å, 2 Ө = 23.04° (Hutchison, 1974). Peaks of calcite are quite clear in the XR-D patterns of all samples in Figures 2-5 and 2-6. Most CaO required for cement raw materials comes from calcite. Calcite decomposes at 800–900 °C.

$$CaCO_3 \xrightarrow{\qquad} CaO + CO_2 \uparrow$$

2.7.1.1.2 Quartz SiO_2

This mineral comes in a second rank in abundance after calcite in all samples of marl in Euphrates Formation. The main basic reflection of quarts mineral is (101), major peak of quartz: d=3.34 Å, 2 Ө = 26.63° and 100: d=4.26 Å, 2Ө = 20.8° and (110): d= 2.45 Å, 2Ө = 36.54° (Cosgrove and Sulaiman, 1973) in another samples. Peaks of quartz are quite clear in XRD patterns of all samples as in Figure 2-5 and 2-6.

Quartz is pure silica; therefore it will contribute to the raw material of cement industry as SiO_2. Large amount of quartz will cause heavy mechanical wear. It acts to erode and consume the grinding and crushing machines and kiln refractory lining by abrasive action because of its high hardness reach 7 depending on Moh's scale of hardness. It will become reactive only at high temperature (Kohlhaas, 1983). In particular, silica containing large-grain quartz is very difficult to grind and more difficult to chemically react that can result in hard burning and high fuel consumption. If quartz silica is employed it should, preferably, have a natural grain size of less than 50 µ (Alsop, 2007), but depending on Mishulovich (1996) less than 63 µ.



Where: C/S count / second

Figure 2-5: X-ray diffractogram of bulk sample No. (M5), depth (4-5m).

Tow samples of marl from 3 and 7 m depth, each one was waited 100 gm., were dissolved in distilled water. Every sample was sieved on sieve 50 µ and then the remaining on sieve was dissolved by HCl consetrated20% to remove the carbonate. The reminder after filtration by filter paper was quartz and the percent of them was 0.23% and 0.55% respectively. The particles of quartz boundary as below depend on Alsop (2007):

> 200 µ	Not more than 0.5 %
90 – 200 µ	Not more than 1.0 %
> 45 µ	Not more than 2.0 %

The percentage of quartz particle size was appropriate cement industry and was in the safe side of limit.

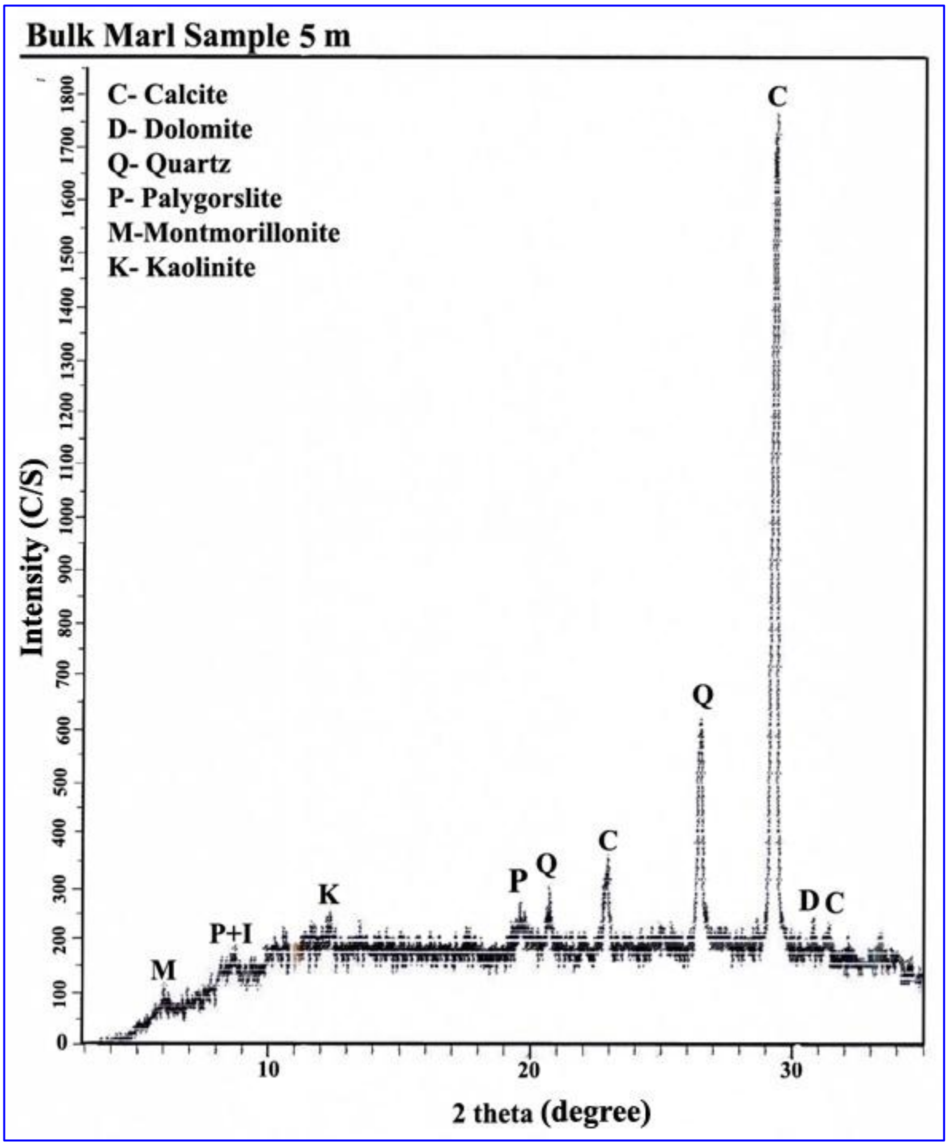


Figure 2-6: X-ray diffractogram of bulk sample No. (M1), depth (0-0.5m).

2.7.1.1.3 Dolomite CaMg $(CO_3)_2$

It is very difficult to distinguish this mineral by XR-D technique because it is present in quite small amounts (not exceeding 5 %). The X-ray scanning showed dolomite with characteristic peaks of 2.89 Å at 2Θ = 30.92° for reflection (Figure 2-5 and 2-6). The small quantity of dolomite will provide the cement raw material with little amount of MgO and CaO. Dolomite decomposes at 600–700°C.

$$CaMg(CO_3)_2 \xrightarrow{\qquad} CaCO_3 + MgO + CO_2 \uparrow$$

Bulk samples were investigated for identifying minerals using XR-D tachnique. Calcite appears the prodominante mineral with mean percent 58.12% followes by quartz with 6.36% and in the lastes is dolomite with percent 1.75%. The semi quantitative method was used for this porpose. the percentages of non-clay minerals are allustrated in Table 2-5.

Table 2-5 : Percent of non-clay minerals in marl layer.

Sample No.	**Depth (m)**	**Calcite**	**Dolomite**	**Quartz**	**Clay minerals**
		%			
M1	0.5-2	63.21	0	6.70	30.09
M2	2.5-3.5	60.01	0	7.75	32.15
M3	4-5	56.60	2.60	2.65	38.15
M4	6-7	60.1	3.54	6.44	29.96
M5	7-8	47.45	4.35	11.73	36.47
M6	8-9	61.3	0	2.91	35.79
Mean		58.12	1.75	6.36	33.77

2.7.1.2 Clay minerals

Clay minerals are formed by the stacking of layers composed of alternating tetrahedral (SiO_4) and octahedral ($AlO_4(OH)_2$) sheets. There are interlayer spaces which are known for their ability to scavenge a wide range of trace element from aqueous environment. Clay minerals cannot be considered pure minerals as they contain some impurities such as quartz, feldspars or other clay types in minor amounts. Some examples are Al^{3+} substituting for Si^{4+} in the tetrahedral layers, and Fe^{2+} and Mg^{2+} substituting for Al^{3+} in the octahedral layer. These substitutions usually produce a negative layer charge which then needs to be balanced by cations (e.g. Na^+ and K^+) which reside in the interlayer space. Clays are used in cement industry as a source of silica, ferric oxide and alumina. Clay minerals are separated from all marl samples collected from the Euphrates Formation. The types of clay minerals effect on raw materials of cement depend on their chemical composition because of increasing the impurities. The clays are source of SiO_2, Al_2O_3 and Fe_2O_3. Between temperature of 100˚- 400˚C, the clay minerals give their adsorptive bound water. At higher temperature, between 400˚-750˚C when burns in rotary kiln clay minerals decompose and form ($Al_2O_3.SiO_2$). Then this component will be dehydration between 600˚ - 900˚C and form Al_2O_3+ SiO_2.

Samples are investigated by XRD and appeared containing palygorskite, montmorillonite, Kaolinite and illite.

2.7.1.2.1 Palygorskite $2MgO.3SiO_2.4H_2O$ to $Al_2O_3.5SiO_26H_2O$

Palygorskite is considered from inosilicates and is similar to amphiboles mineral in crystal structure (Grim, 1968) have 2:1 layer silicate structures. It is structural formula of: ($2Mgo.3SiO_2.4H_2O$) To ($Al_2O_3.5SiO_2.6H_2O$) (Carroll, 1970). Most major deposits of these mineral were originally formed in shallow marine and lakes as chemical sediments, or by the reconstitution of smectite. This mineral requires alkaline conditions and high silicon and magnesium activities for stability (Singer, 1989). In chemical composition there is significant substitution of Mg^{2+} by Al^{3+} and Fe^{3+} occur in the octahedral position and Ca^{2+} , Na^+ and K^+ occur as interlayer cations (Grim, 1968). The X-Ray results showed palygorskite with characteristic peaks at d space 10.5 ($2\Theta = 8.49°$) and 6.4Å ($2\Theta = 13.91°$) for (110, 200), respectively. Glycolation had minor effect, where the 110 reflection became 10.7 Å. At 550ºC the 10.5Å peaks were noticeably shifted to about 10.0Å and the peak suffered significant reduction in intensity due to further dehydration and possible folding of the structure (Soong, 1992 in Kadhum, 2009) (Figures 2-7, 2-8 and 2-9). Interlayer water is driven off by 250-450°C, followed by dehydroxylation between 450-610°C, and irreversible structural breakdown at 860°C.

2.7.1.2.2 Montmorillonite (Mg, Ca). $Al_2O_3.5SiO_2.nH_2O$

This mineral, a member of smectite group of clay minerals, is a 2:1 layer lattice silicate with swelling properties, has a characteristic of inter water quantity in crystal structure (Carroll, 1970). The basic structural unit is a layer consisting of two inward-pointing tetrahedral sheets, with central alumina octahedral sheet with weak bound (Grim, 1968). There is varying degree of substitution of octahedral Mg^{2+} for Al^{3+}, charge balance being achieved by presence of interlayer cations such as Ca^{2+} or Na^+ (Brown et al., 1987). The mainly (100) reflections are ranged between (12Å-15Å) (Brindley and Brown 1980). This d-space is an indicator for Ca, Mg-montmorillonite type (Nelson, 2003). When saturated with ethylene glycol, it will swell to about 17Å, when it is heated to 550 ºC, the 001 reflection will collapse to about (10 Å). This collapse is often reflected to the exchange cations present and to the smectite itself (Poppe et al., 2002). This mineral is identified by the reflection of the main face (100) major peak: d space= 13.60Å, $2\Theta = (6.49)$

(Figures 2-7, 2-8 and 2-9). Depending on McConnell (1950), Interlayer water is driven off by 300°C, followed by dehydroxylation between 500-750°C, and irreversible structural breakdown ~900°C.

2.7.1.2.3 Kaolinite $Al_2O_3.2SiO_2.2H_2O$

Kaolinite has a 1: 1 layer silicate structure. The low cationic exchange capacity of kaolinite is justified by the low isomorphic structural substitution (usually Al^{3+} for Fe^{2+} or Fe^{3+}) (Wypych and Satyanarayana, 2004). The identification of this mineral was based on its basal reflection of the main face (001): d space= 7.17Å, 2Ɵ = (12.32°), and d space= 4,84Å, 2Ɵ = (18.28), without treatment and when glycolated. This reflection disappears when heated to 550°C (Figures 2-7, 2-8 and 2-9). Interlayer water is driven off by 30-200°C, followed by dehydroxylation at 550°C, and irreversible structural breakdown ~600°C (Bhatty, 2011 and Fernandez et al, 2011).

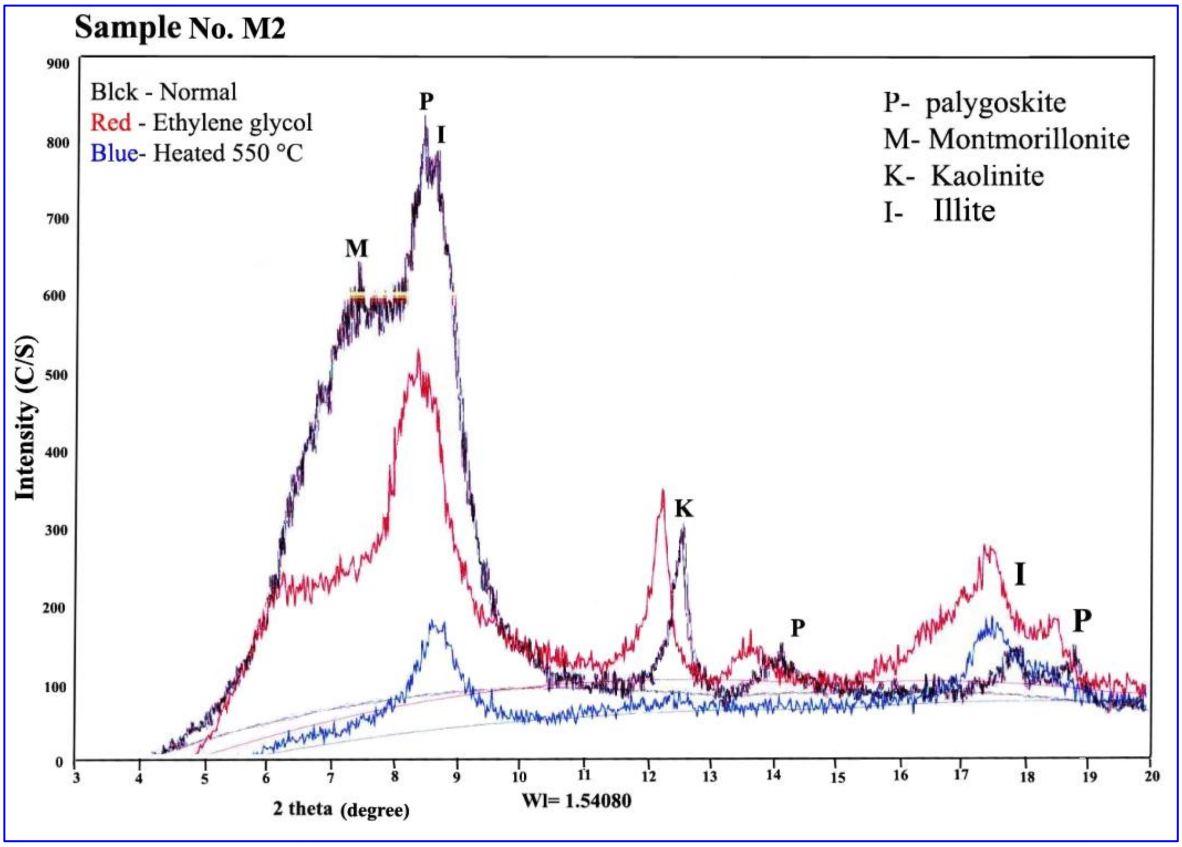


Figure 2-7: X-ray diffractogram of bulk sample No. (M2), depth (0.5-2.5m).

2.7.1.2.4 Illite $KAl_2 (OH)_2[Al\ Si_3 (O,OH)_{10}]$

Illite has 2: 1 layer silicate structures. The negative charge generated by isomorphous substitution is compensated by a layer of potassium ions (Wypych and Satyanarayana, 2004). In addition to other ions like mg^{2+} and

Fe^{3+} in octahedral layer, Al^{3+} in tetrahedral layer and Ca^{2+} and Na^{+} in interlayer (Weaver and Pollard, 1975).

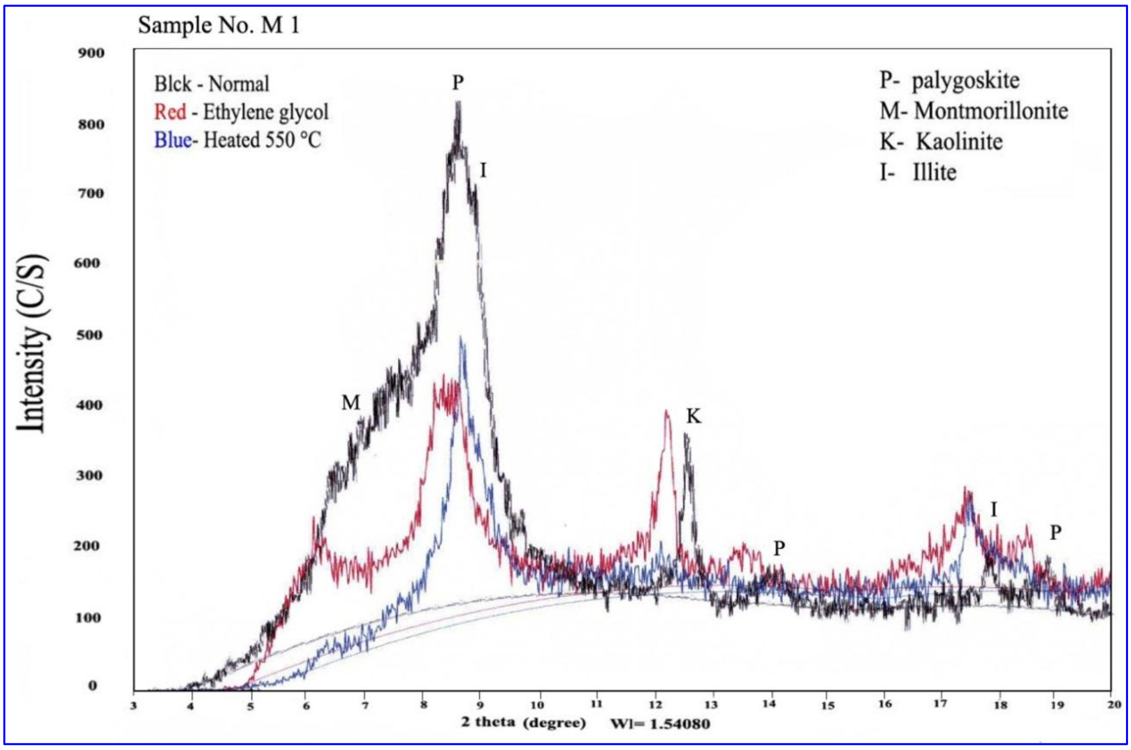


Figure 2-8: X-ray diffractogram of bulk sample No. (M1), depth (0.0-0.5m).

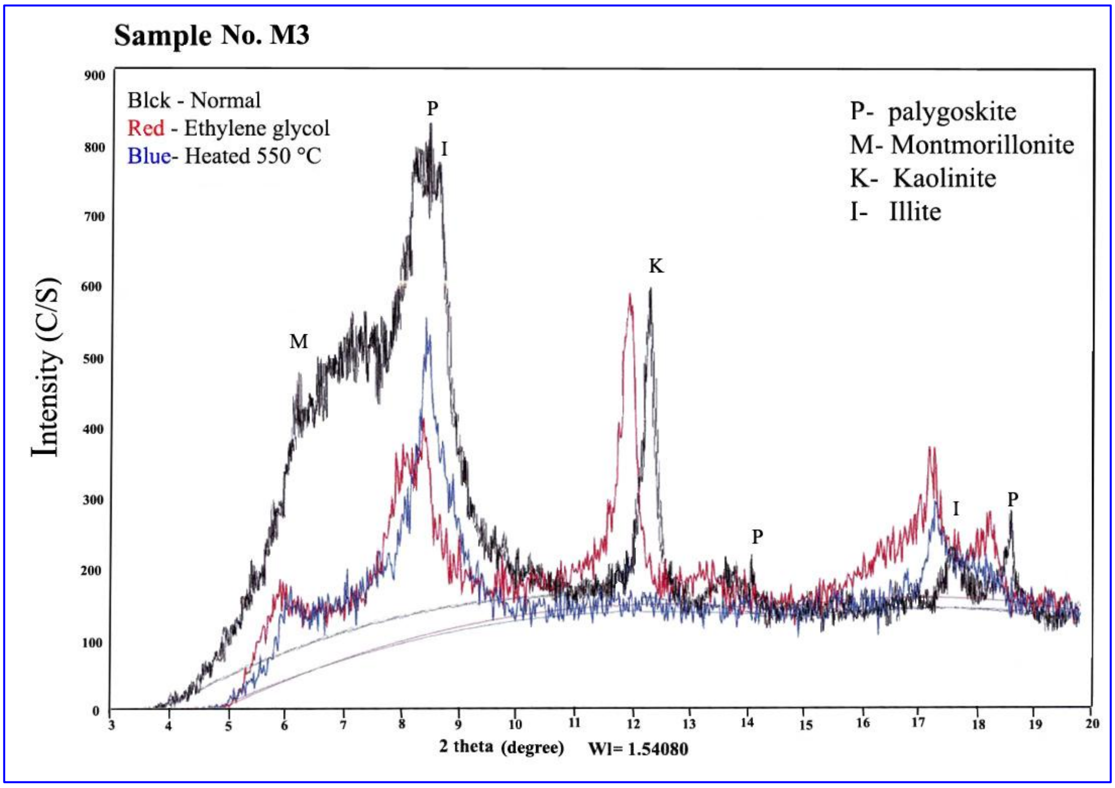


Figure 2-9: X-ray diffractogram of bulk sample No. (M3), depth (3.5-4.0m).

This mineral is recognized on the basal reflection of the main face (001): d space= 9.94Å, 2ϴ= (8.88°). Peaks of Illite are quite clear in study samples. They are identified by reflection of the main face (004): d space= 4.99Å and 2ϴ= (17.5°). Two peaks of this mineral appear with Kaolinite mineral Figures 2-7, 2-8 and 2-9. Dehydration, dehydroxylation, structural breakdown and recrystallization of illite are in the rising the temperature. Interlayer water is driven off by 350-400°C, followed by dehydroxylation between 450-700°C, and irreversible structural breakdown ~900°C (Carroll et al., 2005).

After separated and analyzed the clays of marl layer, montmorillonite appears the predominant minerals of clay minerals in marl layer with mean percent 13.16% follows by palygorskite, illite and kaolinite with percentages 10.46, 6.46 and 3.74% respectively. The percent and type of clay minerals are illustrated in Table 2-6.

Table 2-6: Percent of clay minerals in marl layer.

Sample No.	**Depth (m)**	**Montmor-illonite**	**Palygorskite**	**Illite**	**Kaolinite**	**Non-clay minerals**
		%				
M1	0.5-2	11.64	9.97	4.99	3.49	69.91
M2	2.5-3.5	14.61	10.67	5.26	1.61	67.85
M3	3.5-4	14.80	11.35	7.07	4.93	61.85
M4	4-5	9.41	8.01	5.69	6.85	70.04
M5	6-7	15.46	10.59	8.4	2.02	63.53
M6	7-8	12.66	11.93	7.27	3.93	64.21
M8	8-9	13.54	10.68	6.53	3.35	-
Mean		13.16	10.46	6.46	3.74	66.23

2.7.2 Geochemistry of the marl layer

A geochemical study is carried out on the marl layer in the Euphrates Formation to determine its possible use in Portland cement industry and to estimate the raw materials reserve. The marl layer consists of five horizons illustrated in Figure 2-3. They alter from white gray at the top to dark gray at the bottom (Figure 2-4). Thirty seven core samples were collected from boreholes and analyzed using wet chemistry, XRF and XRD to investigate the chemical characterization of marl layer in the study area. They were analyzed for major oxides (CaO, SiO_2, Fe_2O_3, and Al_2O_3) in addition minor oxides (MgO, K_2O, Na_2O, P_2O_5, TiO_2, Mn, Sr and SO_3) as well as Cl^- and LOI. The chemical analyses of major oxides in every well presented in Table 2-7 depend on the lithology variation. The average of all oxides in every well is presented in Table 2-8.

Table 2-7: Chemical analysis of marl (major oxides).

Well No.	Sam. No.	CaO %	MgO %	SO_3 %	SiO_2 %	Fe_2O_3 %	Al_2O_3 %	LOI %	Total %
X1	1	36.32	2.64	0.41	18.61	2.37	4.5	32.68	97.53
	2	40.98	1.95	0.21	14.05	2.03	2.91	35.85	97.98
	3	35.7	2.2	0.25	19.79	2.66	4.83	31.75	97.18
	4	37.13	2.16	0.14	19.15	3.14	6.08	30.1	97.9
X2	1	47.03	1.3	0.17	7.58	2.08	1.59	39.26	99.01
	2	32.37	2.64	0.44	23.17	2.59	5.68	30.29	97.18
	3	39.08	2.02	0.2	13.92	2.62	3.38	35.8	97.02
	4	37.48	1.28	0.3	18.94	2.73	4.59	32.1	97.42
	5	34.65	2.6	0.34	21.71	3.47	5.93	28.67	97.37
X3	1	36.85	1.82	0.46	17.58	2.48	3.97	34.96	98.12
	2	35	1.93	0.57	19.89	2.71	4.57	33.31	97.98
	3	35.83	2.06	0.37	19.88	2.89	5.51	31.5	98.04
	4	35.46	2.11	0.31	20.21	3.04	4.56	31.81	97.5
Y1	1	39.15	1.55	0.42	16.85	2.8	3.67	34.68	99.12
	2	38.73	1.56	0.47	18.26	2.59	4.57	32.08	98.26
	3	35.15	1.75	0.66	21.35	3.44	6.1	29.54	97.99
	4	36.57	1.55	0.4	19.19	3.11	4.64	32.57	98.03
Y2	1	42.83	1.74	0.52	12.08	1.57	2.07	38.23	99.04
	2	39.37	1.87	0.6	17.23	2.51	3.49	33.41	98.48
	3	36.03	2.05	0.54	20.72	2.82	5.48	30.14	97.78

Well No.	Sam. No.	CaO %	MgO %	SO_3 %	SiO_2 %	Fe_2O_3 %	Al_2O_3 %	LOI %	Total %
	4	36.81	1.81	0.46	18.56	2.63	4.39	33.65	98.31
Y3	1	41.45	2.65	0.51	14.5	2.17	3.27	34.17	98.72
	2	42.52	1.96	0.19	13.42	1.83	2.76	36.34	99.02
	3	37.29	2.2	0.34	18.08	2.31	4.36	32.85	97.43
	4	37.82	2.61	0.27	16.95	2.66	4.28	33	97.59
Z1	1	40.3	2.01	0.11	16.3	1.69	3.71	34.44	98.56
	2	34.11	2.7	0.22	19.81	3.35	5.82	31.19	97.2
	3	37.52	1.7	0.22	19.59	1.91	5.31	31.57	97.82
	4	37.14	1.77	0.14	18.88	2.52	4.41	32.97	97.83
Z2	1	42.64	2.44	0.5	11.74	1.78	2.22	36.92	98.24
	2	38.61	1.57	0.55	16.04	1.9	3.06	36.33	98.06
	3	36.63	1.69	0.4	20.68	2.56	4.5	31.1	97.56
	4	36.64	1.7	0.35	20.98	2.36	4.24	30.94	97.21
Z3	1	41.14	1.12	0.23	12.64	1.68	2.78	37.85	97.44
	2	36.74	2.26	0.1	18.39	2.87	5.15	33.43	98.94
	3	35.53	1.58	0.18	20.81	2.04	5.52	31.78	97.44
	4	36.87	1.99	0.25	19.93	2.65	4.55	32.44	98.68

The results of chemical analyzes (Table 2-7) showed that no significant change in the concentrations of elements horizontally and vertically throughout the study area. Each well was divided into four parts according to change in lithology. Samples were taken from each depth appearing that the chemical composition changes very little horizontally according to the depths. This demonstrates that the study area is approximately homogeneous, as the lithological and chemical changes are horizontally very little.

2.7.2.1 Calcium oxide (CaO) and loss on ignition (LOI)

The CaO is derived from calcite which is the main component of the $CaCO_3$ in marl and in low percent from dolomite. Clay minerals may also contain a little amount of Ca^{2+} as exchangeable cations (Weaver and Pollard, 1975). The proper lime content is limited due to the lower early strength produced when lime content is too low, and unsoundness when it is too high (Duda, 1985 and Neville, 2010). High lime content is associated with early strength whereas; slightly lower content of lime favors ultimate strength which develops gradually over a long period of time (Duda, 1985). In order to increase the strength, it is necessary to raise the lime content, or grind finer, or both. But higher temperatures are required to burn the high lime mixtures (Neville, 2010). If appreciable lime is left uncombined, it may cause expansion and cracking of the mortar or concrete (Duda, 1985 and Neville, 2010). The greater the values the higher the temperature at which the lime is burnt (Lea, 1977).

Table 2-8: Average percent of oxides and elements for each well.

	X1	X2	X3	Y1	Y2	Y3	Z1	Z2	Z3	AVE.
CaO	36.53	37.52	35.67	37.34	38.44	40.02	37.43	39.63	37.67	37.81
MgO	2.23	1.97	1.98	1.63	1.91	2.35	2.08	1.85	1.7	1.97
SO_3	0.25	0.29	0.42	0.43	0.66	0.32	0.18	0.45	0.18	0.35
SiO_2	19.28	18.36	19.72	19.37	17.16	15.38	18.18	16.71	16.73	17.88
Fe_2O_3	2.55	2.71	2.81	3.04	2.67	2.84	2.75	2.85	2.86	2.79
Al_2O_3	4.58	4.33	4.59	4.99	3.08	3.67	4.87	3.51	4.55	4.24
LOI	32.34	32.82	32.26	31.02	33.26	34.09	32.48	33.82	34.08	32.91
Na_2O	0.073	0.081	0.052	0.048	0.072	0.055	0.054	0.062	0.058	0.06
K_2O	0.71	0.68	0.82	0.78	0.7	0.69	0.76	0.62	0.82	0.73
TiO_2	0.28	0.26	0.31	0.31	0.25	0.26	0.29	0.26	0.24	0.27
P_2O_5	0.14	0.15	0.12	0.15	0.13	0.14	0.15	0.14	0.14	0.14
Mn (ppm)	282	284	285	278	264	268	294	266	288	279
Sr (ppm)	272	278	274	257	268	266	274	297	276	273
Cl^-	>0.02	>0.02	>0.02	>0.02	>0.02	>0.02	>0.02	>0.02	>0.02	>0.02
Total	97.76	98	97.45	97.82	97.18	98.67	97.97	98.82	97.77	97.94

	X1	X2	X3	Y1	Y2	Y3	Z1	Z2	Z3	AVE.
SR	2.70	2.61	2.66	2.41	2.98	2.36	2.39	2.63	2.26	2.54
AR	1.80	1.60	1.63	1.64	1.15	1.29	1.77	1.23	1.59	1.52

SR: Silica ratio, AR: Alumina ratio

The concentration of CaO in the studied marl ranges from 32.37 to 47.03 % with an average of 37.81 % as in Tables 2-7 and 2-8. These percentages are less than the required percentages as in Table 2-4. Corrective materials must be added to increase the percentage $CaCO_3$ to the appropriate levels to the cement industry. This concentration distribution is shown in Figure 2-10.

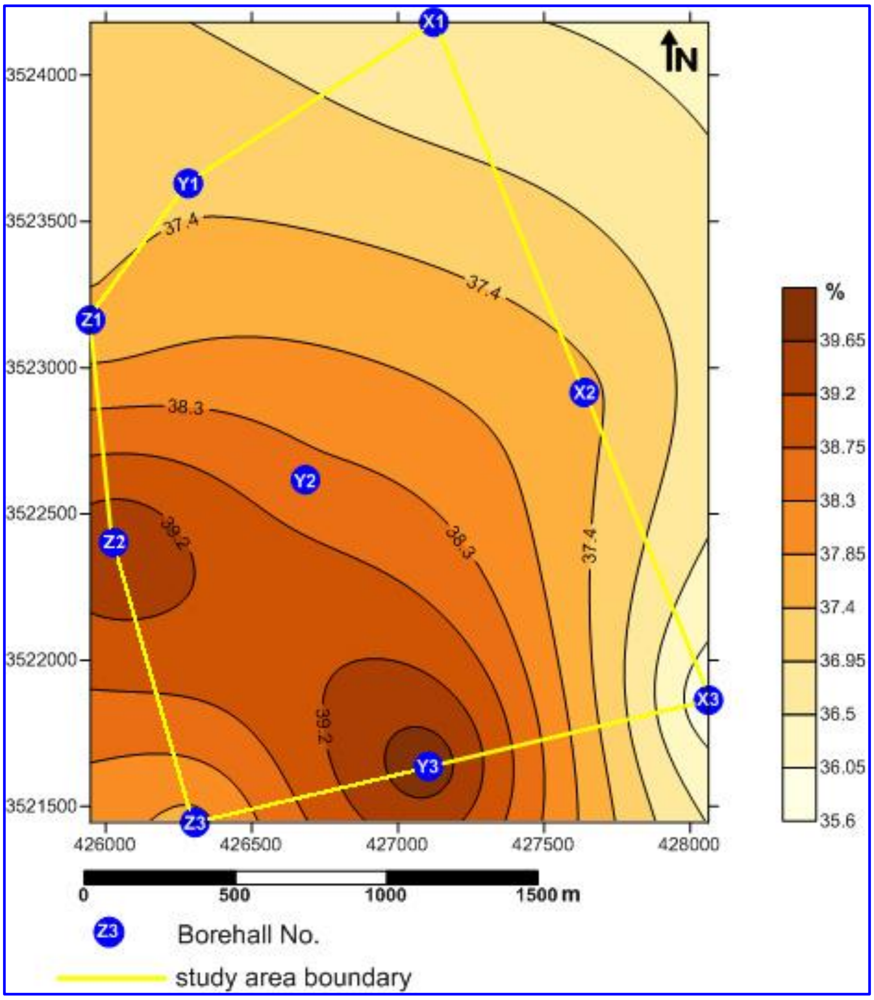


Figure 2-10: CaO iso-concentration map of study area.

Loss on ignition (LOI): Generally, the determination LOI includes other volatile components, such as CO_2 and SO_3 in addition to the combined water (White, 2013). It is produced mainly by decomposition of carbonate minerals (calcite and dolomite) as CO_2 and by dehydroxlation clay minerals (Grim, 1968). It is the ranges between 28.67 to 39.26 % with an average of 33.17% shown in Tables 2-7 and 2-8.

2.7.2.2 Silica (SiO_2)

Silica (SiO_2) is the most abundant oxide of minerals in clay. It is present in cement in a state of combination, and is derived from the clay minerals in marl used as a raw material (Lea, 1977). The sources of silica in marl layer are clay minerals and quartz. The true melting-point of quartz is not known accurately, but is probably below 1470˚C. At high temperature, silica behaves as acid oxide and is capable of combining with bases to form silicates and of expelling other acids from their compounds.

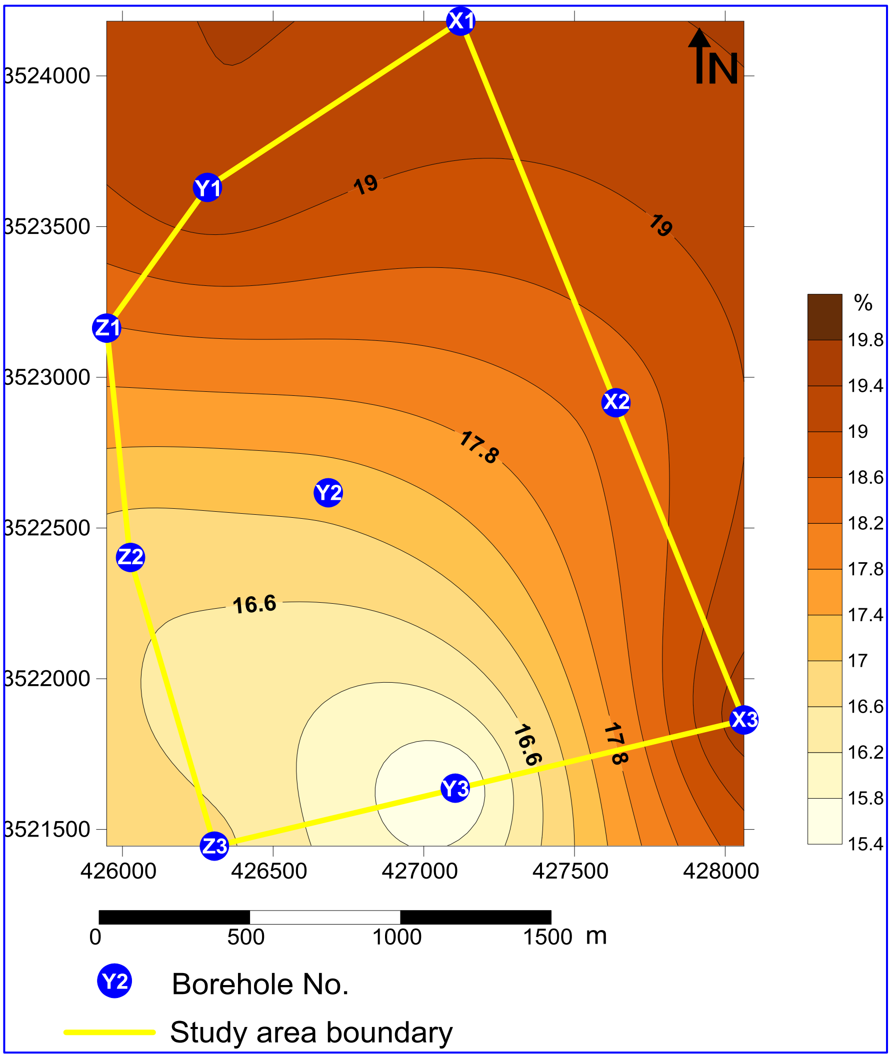


Figure 2-11: SiO_2 iso-concentration map of study area.

The study samples contain a suite of clay minerals which basically consist of SiO_2 and Al_2O_3. In this study, silica came from clay minerals and quartz as insoluble residue (I.R). The insoluble residue includes all minerals and materials that the insoluble in hydrochloric acid (HCl) (10%), generally it consists of clay minerals and quartz. SiO_2 ranges from 7.85% to 24.17% with an average of 17.88 % as shown in Tables 2-7 and 2-8. The distribution of SiO_2 is showed in Figure 2-11. The average percentages of SiO_2 are suitable for cement industry as raw material in comparison with results of Table 2-4.

2.7.2.3 Magnesium Oxide (MgO)

Magnesium oxide or magnesia (MgO) is only present in small quantities in Portland cement ranging typically (1-5) %. Too high MgO content leads to soundness (expansion) cement and consequently strength loss of the concrete, but this can avoid by sufficiently quick quench of the clinker (Peray, 1986 and Hewlett, 2004). The quench will effect on the degree of crystallization and amorphous material present known as glass (Neville, 2010) and this form is inert. The magnesia does not combine with the major oxides. Some of it is taken up in solid solution in the clinker material, and the remainder crystallizes as periclase (MgO). This component is combined up to 2% by weight with the main clinker phases (Soroka, 1979). Periclase reacts with water to form $Mg(OH)_2$, and this is the slowest reaction among all other hardening reactions. Since $Mg(OH)_2$ occupies a larger volume than the MgO and is formed on the same spot where the periclase particle is located. It can expansive and split apart the binding of the hardened cement paste, resulting in expansion cracks commonly known as magnesia expansion (Lea, 1977; Duda, 1985; Ghosh, 2002 and Neville, 2012). Liu and Li, 2005 confirm that the addition of MgO at about 2–5 % can improve the burnability of raw meal and promote the clinkering process.

The concentration of MgO ranges between 1.12 - 2.70 % with an average of 1.97 % as in Tables 2-7 and 2-8. In marl layer, it is derived from magnesium carbonate present in dolomite $CaMg(CO_3)_2$ which is considered as the base resource for this oxide. In sedimentary rocks, Mg is substituted for Ca. Another source is as small extent, from the clay (Lea, 1977) (mainly Palygorskite) because Mg ions occupy octahedral sites by substituted for Si. MgO concentrations are mostly less than 2.0%. These percentages of MgO are very suitable for cement industry in comparison with results of Tables 2-4. From XR-D identification, the Mg-bearing minerals are clay minerals (montmorillonite, palygorskite, illite) and dolomite.

2.7.2.4 Alumina (Al_2O_3)

Alumina occurs combined with silica in all clays and forming clay minerals structure. It can also be octahedral coordinated and form solid solutions with elements such as Ca, Mg, and Fe. All clay mineral that determined by XR-D (montmorillonite, palygorskite, illite and Kaolinite) are the sources of alumina in marl layer. Alumina in a combined state is an important constituent of raw materials, in which it behaves as an acid. This oxide (Al_2O_3) ranges from 1.59 % to 6.10 % with an average of 4.24% (Tables 2-7 and 2-8). It's suitable as a raw mix for kiln feed for cement industry in comparison with the result in Table 2-4.

2.7.2.5 Ferric oxide (Fe_2O_3)

The oxides of iron only occur in a relatively small extent in Portland cements, being derived from the clay in marl layer. It resembles alumina in character and acts as an acid radical in cements, being combined with the bases (mainly CaO) present. The source of ferric oxide is clay minerals because Fe^{3+} enters in the octahedral layer of the Palygorskite, montmorillonite and chlorite (Weaver and Pollard, 1975) it substitutes for Al^{3+}. Some of ferrous (Fe^{2+}) could replace Mg^{2+} in dolomite (Rankama and Sahama, 1950 in Al-Dabbas, 2013)

All studied samples of marl have low concentration of Fe_2O_3; it ranges from 1.57 % to 3.27 % with an average of 2.79 (Tables 2-7 and 2-8). The average percent value is suitable as a raw mix for kiln feed for cement industry in comparison with the result in Table 2-4.

2.7.2.6 Alkalis ($Na_2O + K_2O$)

The alkalis ($Na_2O + K_2O$) are amongst the most widely distributed elements in nature and are found as small quantities in the raw materials as clay and marl that used for cement manufacture (Duda 1985). They occur together in raw feed, and by virtue of similarities in their behavior in cement manufacture. Theoretically, any material composed of silica and aluminum can be alkali-activated, (Li et al, 2010). Also, the salts are considered a resource for sodium (Duda 1985). The base source for alkalis is the clay minerals because the network forming cations are Si^{4+} and Al^{3+}, and the divalent Ca^{2+} and Mg^{2+} act as network modifiers along with any alkalis present (Li et al, 2010). The K is occurrence in clay minerals like illite which is considered K-rich clay minerals. In contrast with K, there is no major Na-rich clay mineral of major geological importance and most sedimentary Na resides in detrital feldspar. In addition to Na^+ and K^+ are present in clay minerals held by adsorption to the surface of them forming interlayer cation because of the negative charge of clay minerals surface. The alkali content (K_2O+Na_2O) of Portland cement typically range from 0.3 to 1.5%, their total amount, expressed as alkali (Na_2O) equivalent (Na_2O + 0.658K_2O) (Mehta, 2001). Alkali equivalent in ASTM C150-85 is below 0. 6. Excessive alkalis are deleterious effect on kiln operation (build-ups) (Alsop, 2007). They are evaporated in burning zone and condense when cooled at kiln inlet and preca1ciner. They are posed considerable operating problems (Peray, 1986) by increase viscosity of the melt and decrease the formation of C_3S (Taylor, 1997). Due to kiln process reasons, it's desirable to have an alkali to sulfate molar of about (1). Too little sulfate may lead to alkali clogging effect, while excess sulfate may lead to low melting eutectic based on alkali-and calcium sulfate, which also increases the clogging risk and problem in kiln operation (Peray, 1986 and Hewlett, 2004). The alkali sulfates and chlorides may be continuously removed and end up in the cement kiln dust which collected from by-pass dust collector are typically high in alkali contents (Bhatty, 1995). By-pass is a loss of productivity due out part of the raw material to the outside of the production process. They affect cement quality causing alkali silica reactions and form a swelling gel (Ertek et al, 2008). The gel has a disruptive effect on the concrete, and can lead to serious problems in aged structure (Hewlett, 2004) which can affect the rate of the gain of strength of cement (Neville, 2012). Na_2O ranges from 0.03% to 0.2% with an average of 0.06 %; whereas, K_2O ranges from 0.02% to 0.35% with an average of 0.73% (Tables 2-7 and 2-8). Alkalis equivalent of marl is 0.54. These percentages of K_2O + Na_2O are suitable for cement industry in comparison with results of Table 2-4 in addition to alkalis equivalent is within the acceptable limit.

The presence of Al, Fe and Mg ions, and alkalis in the raw mix has a mineralizing effect on the formation of calcium silicates. They facilitate the formation of the calcium silicate at considerably lower temperatures than would otherwise be possible (Mehta, 2001).They are an assistant material on flux which favorable influence on speed reaction between lime and silica that leads to easier burning by acts a flux at sintering temperatures (peray, 1986). The flux is responsible for the transport of the reactants forming C_3S in the clinker (Emanuelson, 2003) because Ca_2S and f-CaO gradually dissolute in the liquid state. It leads to a decrease in the amount of fuel and energy that mainly spent in mineral dehydration, decomposition and melting in mineral clusters (Qiu et al., 2010). It achieves economic benefit as a result of reducing the cost of cement. Insufficient Al and Fe lead to difficult burning of the clinker, while excessive amounts lead to low strength due to dilution of the silicates by C_3A and C_4AF.

2.7.2.7 Sulfur (SO_3)

The sulfate content in raw materials as (SO_3), generally, ranges from 0.1% to 3% (Soroka, 1979 and Duda, 1985). In ordinary Portland cement the source of most of the sulfate (expressed as SO_3) is gypsum ($CaSO_4.2H_2O$), calcium sulfate in one of its several possible forms, added to the clinker. The main purpose of this additive is to retard the quick setting tendency of the ground Portland cement clinker due to the very high reactivity of C_3A present (Mehta, 2001) thereby ensure sufficient workability time (Glasser, 2011).

According to Iraqi Quality Standard number 5 (I.Q.S, 1984), it ranges from 2.5% to 2.8%. Generally, the sulfur (S) source in cement is a raw material; the added gypsum to the cement clinker and the used water in clinker mix, as well as the used fuel (the black oil) (Duda, 1985 and Schafer, 1987). In raw materials, the sulfur is derived from clayey sediments, marls; also contain both sulfides and sulfates (Bahatti, 2011) in addition to the gypsum. When sufficient sulfate is not present in the kiln system, the alkalis are preferentially taken up by C_3A and C_2S, which may then be modified to compositions of the type NC_8A_3 and $KC_{23}S_{12}$, respectively. Sometimes large amounts of sulfate in the form of gypsum are purposefully added to the raw mix either for lowering the burning temperature or for modification of the C_3A phase to C_4A_3S, which is an important constituent of certain types of expansive as well as rapid-hardening cements (Mehta, 2001). Sulfates have a very strong affinity for alkalis so they act to bind in clinker as Na_2SO_4 and K_2SO_4 which are more thermodynamically stable than $CaSO_4$ (Nielsen et al, 2011). The SO_3 is a part of loss on ignition which was analyzed separately. The access SO_3 in raw materials leads to kiln build-pups (Alsop, 2007). Concentration of SO_3 in study wells in raw materials is less than 1.0%. SO_3 concentration ranges from 0.10 % to 0.66 % with an average of 0.35% shown in Tables 2-7 and 2-8, therefore, these percentages of SO_3 are suitable for cement industry compared within the range of standard results of Table 2-4.

2.7.2.8 Chlorine (Cl^-)

The source of chloride may be the precipitation of halite through of digenetic process or evaporation of sea water or from ground water, which increases the percentage of the chloride in the marl (Schafer, 1987). The predominant chloride in clay is sodium chloride (Akstinat and Rott, 1988). The Chloride reacts with the alkalis in the rotary kiln, forming alkali chlorides which are highly volatile and cause build-ups and blockages, and leave the rotary kiln with gases as bypass. The chloride content of cement raw mix fluctuates generally between 0.01% and 0.1%, and sometimes it rarely reaches over 0.3%. However, traces of chlorides to a maximum of 0.1% are admitted by (Duda 1985). The chloride **(**Cl^-) in the marl layer is below 0.02% (Table 2-8).

2.7.2.9 Phosphorous (P_2O_5)

Phosphorus (P) as phosphates is present in detrital clays (Bucchi, 1980). P_2O_5 concentration is not considered to be critical unless increases above 2% (Schafer, 1987). P_2O_5 ranges in study area from 0.12 % to 0.15 % with an average of 0.14 % (Table 2-8).

2.7.2.10 Titania (TiO_2)

The titanium oxide in cement raw materials is a minor. The acceptable percent of Ti below 4% (Ghosh, 2002).The percent in the marl layer ranging from 0.24 % to 0.31% with average 0.27 % (Table 2-8).

2.7.2.11 Manganese (Mn)

The source of Mn is found in the cement raw materials. The economic reasons it is not to increase the percentage above 3% (Lea, 1977). Mn ranges from 264 to 294 ppm with an average of 278.78 ppm in marl as shown in Tables 2-8.

2.7.2.12 Strontium (Sr)

The strontium oxide in cement raw materials is a minor. Its limiting rate is ranging between 0 and 4 % (Ghosh, 2002). The concentration is ranging from 257 ppm to 297 ppm with average 273.56 ppm as shows in Table 2-8.

2.7.2.13 Insoluble residue (IR)

Eight samples are analyzed to determine insoluble residue (IR) represented quartz and clay minerals. After dissolved the samples in HCl, the IR results are illustrated in Table 2-9.

Generally, the chemical composition of marl layer indicate suitability of marl for cement industry alternative to clay in addition to high percent of limestone except CaO and SiO_2. The percentage of CaO is lower but SiO_2 is higher than the specifications in Table 2-7 and 2-8.

Table 2-9: The IR results of marl layer.

Sample No.	**BH No.**	**Depth (m)**	**Carbonate %**	**IR %**
M1	X2	1.5-2	63.21	36.79
M2	X3	2.5-3.5	60.1	39.9
M3	Y1	4-5	59.2	40.8
M4	Y2	6-7	63.6	36.4
M5	Z3	7-7.5	51.8	48.2
M6	X1	8-9	61.3	38.7
Average			59.86	40.13

These ratios must be corrected by adding specific amounts of limestone from adjacent areas. Chemical analyses of limestone show it is suitable for the cement manufacture, as in Table 2-10. Raw mix of kiln feed should be designed from these materials (marl and limestone).

Table 2-10: Chemical composition of limestone in adjacent area.

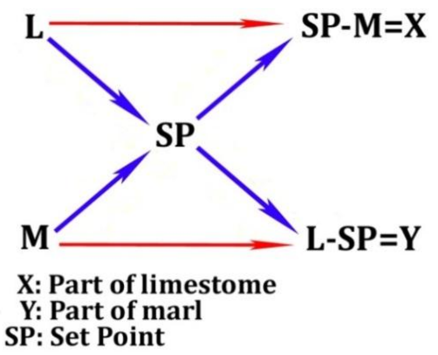
Sample No.	**CaO %**	**MgO %**	**SO_3 %**	**SiO_2 %**	**Fe_2O_3 %**	**Al_2O_3 %**	**LOI %**	**Total %**
1	53.60	1.61	0.74	2.24	0.12	0.14	41.47	99.92
2	52.88	1.88	0.7	2.72	0.18	0.32	40.75	99.43
3	54.27	0.28	0.29	2.6	0.44	0.54	41.39	99.81
4	54.12	0.64	0.64	1.5	0.56	0.23	41.43	99.12
Ave.	53.72	1.10	0.59	2.27	0.33	0.31	41.26	99.57
Ave. Free LOI	92.11	1.89	1.01	3.89	0.57	0.53	-	100

2.8 Raw Mix Design

Raw mix designing must be made very carefully. The purpose of optimum raw material preparation for the cement manufacturing process is to supply the downstream burning process with a raw meal whose quality and homogeneity assures the economical production of high-quality cements and to make appropriate improvements. Such clinker must have very restricted compositional targets (Miller, 2011). Before igniting the materials in the kiln for clinker production, the proportioning of raw mix should be designed to get quality clinker with the required compositional parameters such as: LSF, SSF, SR and AR. The design of raw mix is based on the clinker compositional parameters and the value of major oxides from complete chemical analysis of the raw materials (limestone, marl). Fluctuations in the chemical composition of excavated raw materials are unavoidable at the start of the manufacturing process. However, if undetected or left uncorrected, stable kiln operation becomes difficult. Effective raw-mix preparation for cement manufacturing requires a tight control on the chemistry of the raw meal entering the kiln (Bond et al., 2000).

The raw mix proportions are calculated based on the values of major oxides of marl layer which its CaO average below the percent of raw mix of kiln feed, so it's must complement by additive amount of CaO that obtained from limestone in the adjacent area. The raw mix has been calculated by using the Alligation Alternate Method (AAM) (Kohlhaas, 1983 and Duda, 1985) depending on the percent of CaO. The percent of marl to limestone that used in the raw mix of kiln feed by using the percent of oxides with free LOI in.

The AAM is the simplest course of calculation for solving blending problems; this method allows the determination of the proportion of two raw material components (Duda, 1985). From the chemical analysis of marl layer only the required lime content is fixed as a set point (SP) because its value below the percentage required, therefore additional quantities from lime must be added to improve ratio to the required specification limits by additive limestone from another place. The raw mix designe can be corrected by the following equations:



Where L: limestone
M: Marl
Set point: CaO required for kiln feed.

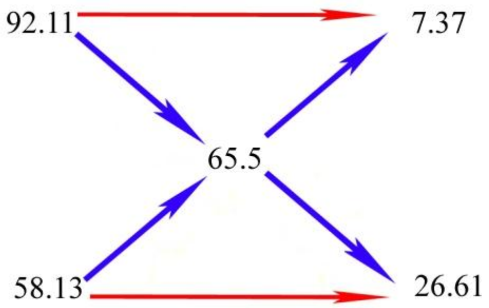
To get raw mix with CaO content as SP, X part of limestone and Y part of marl will be mixed for optimal raw materials kiln feed mix. These components represent CaO with free LOI. Thus the proportion of the component in the raw mix, i. e. limestone: marl = X: Y. that mean

$$X\,\% = \frac{X}{X+Y} \times 100 \ldots\ldots \tag{2-11}$$

$$Y\,\% = \frac{Y}{X+Y} \times 100 \ldots\ldots \tag{2-12}$$

Where
X%: percentage of limestone
Y%: percentage of marl

Generally the set point is 65.5%. The percent of CaO (free of LOI) from limestone is 92.11% and the percent of CaO (free of LOI) from marl is 58.13% (Table 2-11). The results of raw mix design can be obtained by application the AAM as follows:



Now, the part of limestone is 7.37, whereas the part of marl is 26.61. The final proportions (%) of limestone and marl are computed as follows:

$$X\% = \frac{7.37}{7.37 + 26.61} = 21.69\%$$

$$Y\% = \frac{26.61}{7.37 + 26.61} = 78.31\%$$

The percentages of all oxides in the raw mix as free LOI are illustrated in Table 2-11.

Table 2-11: Results of the raw material (%) calculation.

Raw material oxides	Raw material free LOI		Percent of raw material by AAM.		Design of raw mix using AAM.		Total %
	Marl %	Limestone %	Marl %	Limestone %	Marl %	Limestone %	
CaO	58.13	92.11	78.31	21.69	45.52	19.98	65.5
MgO	3.03	1.89			2.37	0.41	2.78
SO_3	0.54	1.01			0.42	0.22	0.64
SiO_2	27.49	3.89			21.53	0.84	22.37
Fe_2O_3	4.29	0.57			3.36	0.12	3.48
Al_2O_3	6.52	0.53			5.11	0.11	5.22
Total	100	100			78.13	21.69	100

The kiln feed parameters (raw mix) are computed for the corrected raw mix design and illustrated in Table 2-12.

Table 2-12: Result of computed kiln feed parameters.

SR	AR	HM	SSF	LSF	CS
2.57	1.50	2.11	0.88	92.16	4.29

SR: Silica ratio, AR: Alumina ratio, HM: hydraulic modulus, SSF: silica saturation factor, LSF: lime saturation factor, CS: calcium silica ratio.

The clinker phases percent obtained from the above raw mix using Bogue Calculations Method are close to the limits of the clinker specification as in the Table 2-3.

C_3S (Ailite) = 56.94 %
C_2S (Belite) = 21.45 %
C_3A (Aluminate) = 11.84 %
C_4AF (Ferrite)= 10.60 %

2.9 Clinker manufacturing

Two samples of designed raw mix (78% of marl and 22% of limestone) are burned at 1450˚C in furnace to manufacture clinker in laboratory. The clinker models are shown in the Figure (2-12). Every sample was weighed (1.650 Kg). The clinker samples weight after burning are 1050 and 1080g respectively. The diminution in weight is 600 and 570gr. resulted due to volatiles materials (CO_2, SO_3, alkalis, Cl^- and combined water).

Figure 2-12: Clinker manufactured in laboratory.

Then, the samples of clinker are analyzed by XR-D Shimadzo type XR-D 6000 German made. They are analyzed in the Directorate of Materials Research, department of chemistry and physics research materials laboratories of the ministry of science and technology. The scanning 2theta is from 10 to 70 degree for showing all the beaks of clinker phases. They are illustrated in Figures 2-13 and 2-14.

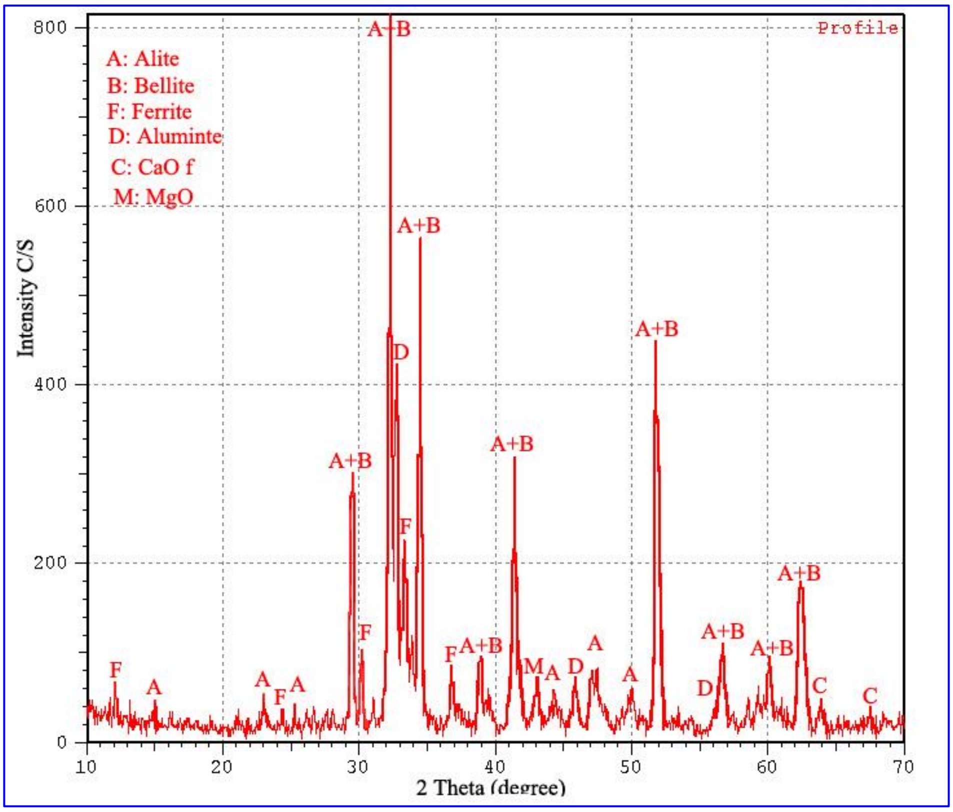


Table 2-13: X-ray diffractogram of clinker sample No. 1.

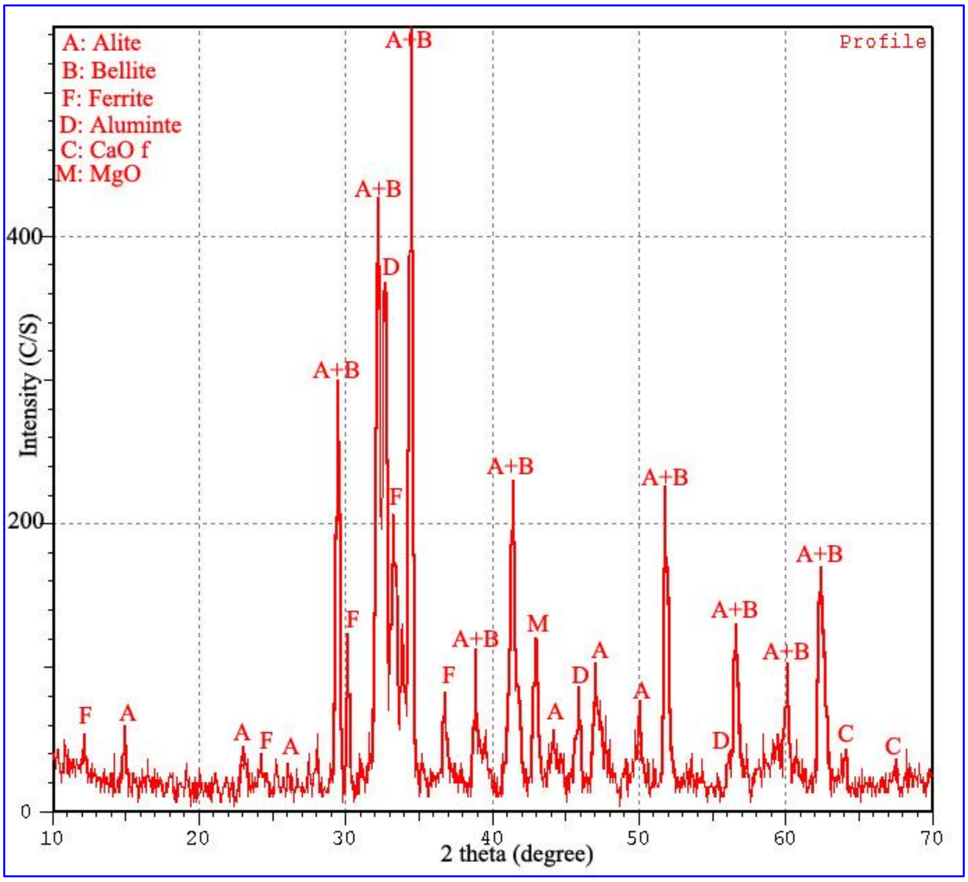


Table 2-14: X-ray diffractogram of clinker sample No.2.

The clinker phases that appeared are Alite, Belite, Ferrite and Aluminite in addition to free Cao and Periclase in low percent. That mean the burning of designed raw mix is achieved positive results in the industrial production of clinker in the laboratory.

2.10 Discussion

The marl layer of the Euphrates Formation is mineralogically composed of calcite (58.12%), dolomite (1.75%), quartz (6.36%), montmorillonite (13.16%), palygorskite (10.64%), illite (6.46%) and kaolinite (3.74%). The percentages of the Al_2O_3 and Fe_2O_3 are within the acceptable guide line of the standard. MgO, alkalis (Na_2O and K_2O) and SO_3 are quite suitable for Portland cement industry. SiO_2 appears at the maximum limit while the CaO is lower than the standard. The chemical quality of the Euphrates marl is compared with the international standards. Duda (1985) is a famous reference used to determine the acceptable limit of oxides in raw materials and is adopted in this study as. The results revealed that the marl as raw materials needs to be corrected. Accordingly, limestone is used for correction. The limestone in adjacent area has a good quality for correcting this deviation in the limits of kiln feed. A quantity of limestone is computed using the

Alligation Alternate Method (AAM) and appears to be 22% approximately. Consequently, the proportion of marl is 78%. The marl of the Euphrates Formation have MgO (1.97), SO_3 (0.35), SiO_2 (17.88), Fe_2O_3 (2.79), Al_2O_3 (4.24), LOI (32.91), Na_2O (0.062), K_2O (0.731) and Cl^- (0.02) values appear to fit the standard with the exception of CaO (37.81) which is lower than the standard. Therefore the value of CaO is corrected by adding the limestone. Kiln feed (raw mix) composition has a large effect on kiln operations (Young and Miller, 2011). The chemical composition of marl is naturally homogenized. The homogeneity of feed chemical composition has an important relationship to fuel consumption, kiln operation, clinker formation and cement performance. Parameters of raw mix (LSF, SR, AR, HM, SSF and CS) are checked carefully for clinker phases (C_3S, C_2S, C_3A and C_4AF) and appeared suitable. The exact temperature of melt the raw mix depends on its chemical composition. The economic use of raw materials is by reducing the melting degree and forming liquid phase which leads to reduce the amount of fuel used in the burning process. The good quality of Al_2O_3, Fe_2O_3 and MgO in the marl layer will improve the burnability of raw mix and will form liquid phases at lower temperatures than the proper clinker liquid. The liquid will promote the clinkering process that will be reflected on reducing the fuel consumption used in the kiln. The composition required of the clinker will reduce the sintering temperature, and help to form the protective layer (coating) protecting the refractory lining. Presence of silica is within acceptable limits. The percentage of Na_2O, K_2O and Cl^- in the marl layer is in lower acceptable limit will reduce the production loss and increase the clinker production rate, as well as reduce the operational problems. This positively reflects on reducing the production costs.

Chapter Three

Quantitative and Economic Assessment

3. Quantitative and economic assessment

3.1 Preface

Cement raw materials in cement plant must be available in sufficiently large quantities to justify the large capital investments (Ertek, 2008). So the new reserves of industrial rocks appropriate for cement must be found. Reserve, in general, is defined as that portion of an identified resource from which usable mineral, material, and energy commodity can be economically legally extracted at the time of determination (Kleppe and McKelvey, 1976). The reliable reserve estimation is of critical importance particularly as a basis for quarry planning. Estimation of the reserve is essentially one of the most important platforms upon which a successful mining operation, planned and designed. The first step in the evaluation and design of an open-pit mine is the determination of reserves.

This chapter deals with quantitative and economic assessment which means reserve estimation. For this reason, nine wells were drilled in the study area and compared with three wells (BH.1, BH.2 and BH.3). these wells drilled by the Danish Geotechnical Institute in 1976 during the period of opening the quarry of the Kufa Cement Plant. Area of deposits, thickness of the economic layer, horizontal and vertical sampling, chemical characterization (grade), bulk density, porosity and thickness, volume and weight of overburden are basically controlling the reserve (Wellmer et al., 2008), consequently, all these factors are calculated. Famous systems (American, British, Russian and Joint Ore Reserve Committee (JORC)) in reserve estimation are applied and discussed. Categories of reserve estimation based on the degree of assurance and economic consideration are also classified.

3.2 Classification of reserve estimation

The reserve is that identified deposits (raw materials) that can be known by drilling or other specific measurement and can be economically extracted and tonnage estimated. Globally, there are four systems of reserve (Taylor, 1994 and Diehl and David, 1982), these are:

3.2.1 American System

This system was introduced by US geological survey (USGS) in 1944. Under this classification, there are three categories of reserves based on degree of assurance of reserve. Al-Atia (2001) was explained these categories.

3.2.1.1 Measured reserve

This category needs sampling from all directions (outcrop, trenches, wells and tunnels). They are resources for which tonnage is computed from dimensions revealed in outcrops, trenches, workings, and drill holes, and for which the grade is computed from the results of detailed sampling. The site of inspection, sampling, and measurement are closely spaced, and the geological character is so well defined, that size, shape, and mineral content are well established (Kennedy, 1990). They are materials whose quality and quantity have been determined within a margin of error of less than 20% by quantitative data, including appropriate analyses, from closely spaced and geologically well-known sample site.

3.2.1.2 Indicated reserve

They are resources for which tonnage and grade are computed from information similar to that used for measured resources, but the site of inspection, sampling, and measurement are farther apart or are otherwise less adequately spaced. The degree of assurance, although lower than the resources in the measured category, is high enough to assume continuity between points of observation. Demonstrated is a collective term for the sum of the measured and indicated resource.

3.2.1.3 Inferred reserve

It is the material used in identifying but unexplored deposits whose quality and quantity have been estimated from geological projections. They are resources for which quantitative estimates are based largely on broad knowledge of the geological character of the deposits and for which there are few, if any, samples or measurements. The estimates are based on an assumed continuity or repetition for which there is geological evidence. This evidence may include comparison with deposits of similar type. Estimates of inferred resources should be stated separately and not combined in a single total with measured or indicated resources.

3.2.2 British System

This system was introduced by the British Institution of Mining and Metallurgy in 1902. The equivalent categories in a different classification are listed in Table 3-1. These categories were explained by Al-Atia (2001).

3.2.2.1 Proved reserve

The estimation is based on the sufficient data that does not vary much from the actual tonnage and grade when mined. Degree of geological assurance is high probability reaching up to 80%. This category is equivalent to the first category (Measured) in the American system (Table 3-1).

Table 3-1: Relationship of the reserve classification systems with each other.

<table>
<tr><td>British System</td><td>Possible</td><td colspan="4">Probable</td><td colspan="2">Proved</td></tr>
<tr><td>American System</td><td>Inferred</td><td colspan="4">Indicated</td><td colspan="2">Measured</td></tr>
<tr><td>Russian System</td><td colspan="2">C2</td><td colspan="2">C1</td><td colspan="2">B</td><td>A</td></tr>
<tr><td>JORC Code</td><td colspan="3">Probable</td><td colspan="4">Proven</td></tr>
</table>

3.2.2.2 Probable reserve

This estimation carries a lesser degree of assurance and based on limited data on sampling and core logging. Degree of geological assurance is a probability that reaches 50%. This category is equivalent to the second category (Indicated) in the American system (Table 3-1).

3.2.2.3 Possible reserve

The reserve estimation when done from exploration of sampling data in areas where no data of sampling is available termed possible. Degree of geological assurance is a low probability reaches 15%. This category is equivalent to the third category (Inferred) in the American system (Table 3-1).

3.2.3 Russian System

This system was introduced by Soviet academy of sciences in 1933. This system is divided into four main categories (A, B, C1 and C2). These categories are seen as commercial, whose extraction is economically viable. The (A, B and C1) reserves are industrial and C2 geological (Kreiter, 1968). The Russian system is relatively simple. The categories are explained as follows:

3.2.3.1 Class A reserve

The reserves in place are known in detail. The boundaries of the deposit have been outlined by trenching, drilling, or underground workings. This category is equivalent to the first category (Measured and proved) in the American and British System (Table 3-1) respectively. Reserves in this class are designed for production planning and mine production. The permissible error rate is allowed between 15-20% (Kreiter, 1968).

3.2.3.2 Class B reserve

The reserves in place have been explored but are only known in fair detail. This category is equivalent to the second category (Proved-Probable and Measured- Indicated) in the American and British Systems (Table 3-1) respectively (Henley, 2004). Reserves B are used for estimating mining investment and for planning the development of deposit. The permissible error rate is allowed between 20-30% (Kreiter, 1968).

3.2.3.3 Class C1 reserve

Sparse grids of trenches, drill holes or underground workings are required to estimate the reserves in place. This category is equivalent to the third category (Probable and Indicated) in the American and British Systems respectively (Table 3-1). Reserves in C1 class are used for the long term developments plans of industry and for projecting detailed exploration. The permissible error rate is allowed between 30-60% (Kreiter, 1968).

3.2.3.4 Class C2 reserve

These reserves are based on an extremely loose exploration grid, with poor data. This category of Russian classification represents the estimates obtained from a small exploratory data by a large-scale interval of sampling. This category is equivalent to the third category (Possible and Inferred) in the American and British System classifications respectively (Henley, 2004) (Table 3-1). Reserves in class C2 are used for planning further prospecting. The permissible error rate is allowed between 60-90% (Kreiter, 1968).

3.2.4 JORC Code

This code is an abbreviation of the Joint Ore Reserves Committee which sets in 1971 by the Joint Ore Reserves Committee of the Australian institute of mining and metallurgy, Australian Institute of Geoscience and minerals council of Australian. The task of resource classification under the JORC

Code is the duty of the Competent Person, and therefore is ultimately a subjective duty, but in spite this, the resource classification should ideally be based upon as many objective factors as possible. The JORC Code provides a system for classification of tonnage and grade estimates according to geological confidence and technical/economic considerations (JORC, 2012). This code divided the reserve into two categories:

3.2.4.1 Proven reserve

It's fully explored reserves ready for extraction. It is a part of definite reserves and it has proven economic viability. They can serve as the basis for bankable feasibility study, production schedule and realistic economic analysis of the project.

3.2.4.2 Probable reserve

Probable reserve is explored reserves ready for extraction. It is a part of indicated reserves and in some cases of definite reserves, whose economic viability has been proven. They also can serve as the basis for bankable feasibility study, production schedule and realistic economic analysis of the project. Table 3-1 presents the relationship between the classification systems for these reserves.

3.3 Quantitative and economic assessment

The quarry of the Kufa cement plant consists of three parts (overburden, limestone and marl). The upper parts of the quarry (overburden and limestone) were extracted (Figure 3-1) through the daily mining work in the quarry.

In the quarry, the marl layer is exposed on the surface in all the places where limestone had been extracted. It has horizontal continuous extension underlying the limestone layer. It has been detected in bore holes BH.1, BH.2 and BH.3 at distance 6.128, 4.506 and 4.522 km respectively from X1borehole with average thickness 6.5 m (Figure 3-2). These bore holes have been drilled to 15m depth by the Danish Geotechnical Institute (1976).

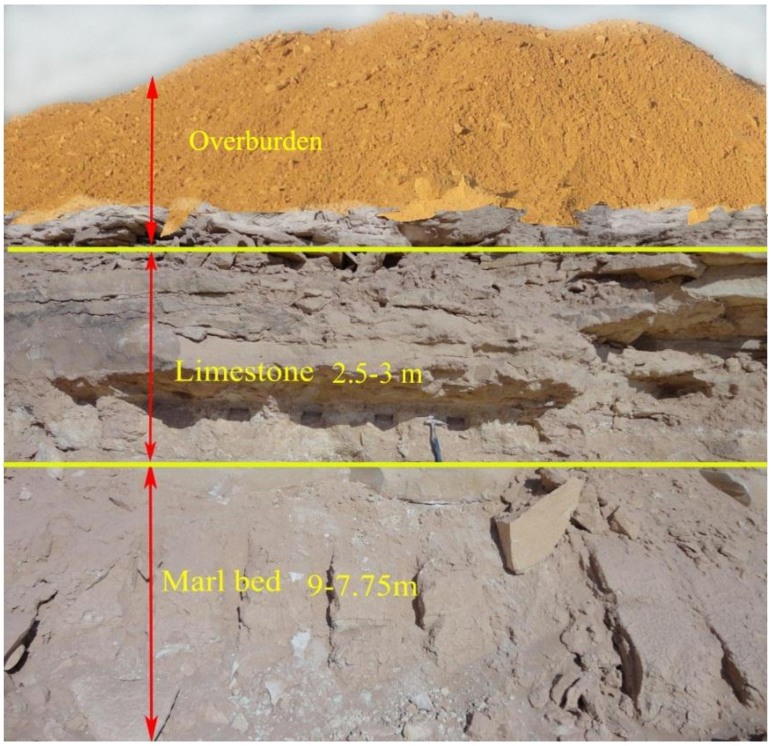


Figure 3-1: Sequence of quarry.

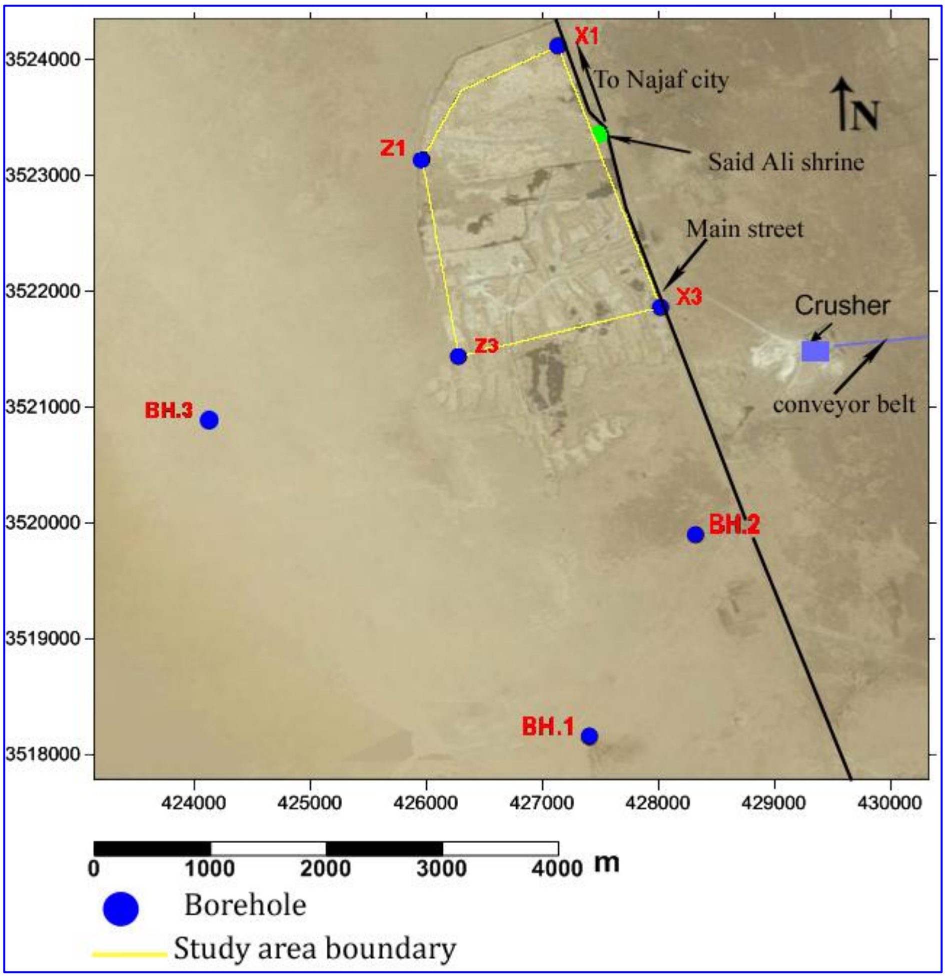


Figure 3-2: Land sat image of the study area shows the study area and 3 bore holes outside the study area confirm a presence of the marl layer beneath the limestone layer.

The reserve estimation process is a process of volumetric and weight calculations of the qualified raw materials in the study area. The volume estimation can be computed by determining the dimension of marl layer, calculating of the thickness and the bulk density of that area (Al-Atia, 2001).

To calculate the reserve potential of a deposit, the equation of Moon et al., (2006) is applied as follows:

$$T = A \times Th \times B.D \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3-1)}$$

Where T: Tonnage (in tons)
A: Area of influence on a plan or section in (m^2).
Th: Thickness of the deposit within the area of influence in (m).
B.D: bulk density (Kg/m^3).

The quantitative assessment of the study area includes two major parts as follows:

1. Quantitative assessment of overburden.
2. Quantitative assessment of marl layer.

3.3.1 Quantitative assessment of overburden

The raw material deposit is seldom found not covered by a layer of overburden. In any case, the overburden has to be removed separately from the deposit material. This layer contains polluting and unsuitable materials for the cement industry. This is based on chemical results of the major oxides CaO, MgO, SiO_2 and SO_3. It consists of Quaternary deposits composed of clays, rock fragments and gypsum sand. This layer is not appropriate for cement industry due to high content of SO_3. The overburden is computed and appears to occupy an area of approximately 625600 m^2 (Table 3-2) from the total area of 3639350 m^2. Overburden exists in ten sites (Figure 3-3) with different thickness covering about 17.5% of the total studied area.

The remaining area is exposed without overburden. The thickness of overburden changes from place to place ranging between 1.4-1.9 m and the density is 1.55 gm/cm^3. The surface area, thickness and volume of overburden are computed and listed in Table 3-2. The total surface area of overburden was computed using the Google Earth Professional Software Program as 625600 m^2.

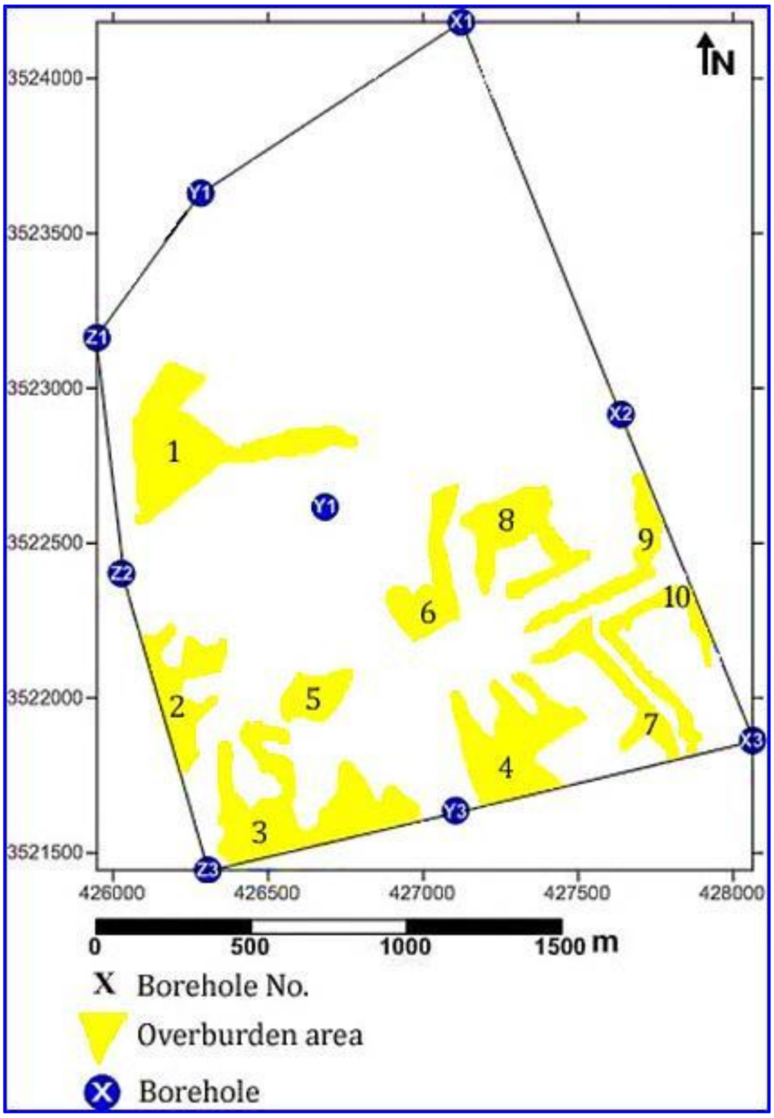


Figure 3-3: Location map of overburden areas

Then, the equation below was used to calculate the volume of overburden in the study area.

$$V.of(O.B)(m^3) = total\ A. \times Ave.Th.of\ O.B \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3\text{-}2)$$

Where V: Volume

A: Area

O.B: Overburden

Ave.: Average

Th.: Thickness

Total volume of overburden= 1021575 m^3

Total weight = Total volume × Density

= 1021575× 1.55 = 1583441 ton

Table 3-2: Surface area, thickness and volume of overburden in the study area.

Shape No.	Surface area (m^2)	Thickness (m)	Volume (m^3)
1	121500	1.7	206550
2	58507	1.6	93611.2
3	129627	1.9	246291.3
4	91848	1.5	137772
5	30249	1.5	45373.5
6	33930	1.5	50895
7	22116	1.4	30962.4
8	61146	1.6	97833.6
9	49366	1.5	74049
10	27312	1.4	38236.8
Total	625601		1021574.8
Average thickness		1.65	

3.3.2 Quantitative assessment of marl layer

The quantitative assessment means reserve estimation which typically made by tonnage for the significant grade. The actual estimation process, however, involves estimation of three parameters: grade, volume and bulk density (Lipton, 2011). The calculation of reserve estimation of marl layer in the study area is depended on data collected from nine wells. The factors controlling the possibility of the reserve utilizing for industrial purposes include:

a. Thickness of marl layer
b. Thickness of overburden
c. Stripping ratio
d. Bulk density

3.3.2.1 Thickness of the marl layer

The thickness of marl layer (industrial layer) was accurately determined by the information obtained from the drilled bore hole. The thickness of the marl layer ranges from 7.75 m in the borehole Z2 to 9m in the borehole X1 with an average of 8 m (Table 3-3) and can be shown by the isopach map (Figure 3-4). It tends to increase towards the northwest with very low inclination toward the north. The middle and southwestern parts are clearly characterized by low thickness. The marl layer continues to boreholes BH.1, BH.2 and BH.3 in the south and southeast of the study area with thickness of 6.5-7m covered by limestone and overburden. The marl layer has a similar chemical specification throughout the study area.

Table 3-3: Location and average thickness of the marl layer.

Borehole No.	**UTM-Coordination**		**Marl layer Thickness (m)**	**Elevation (m)**
	Easting	**Northing**		
X1	427122.7	3524181.7	9.00	32
X2	427637.6	3522915.6	8.70	33
X3	428062.3	3521863.2	8.50	34
Y1	426282.1	3523630.0	8.75	36
Y2	426683.1	3522616.9	8.50	37
Y3	427104.4	3521636.9	8.40	38
Z1	425947.6	3523163.2	8.75	38
Z2	426026.8	3522402.3	7.75	40
Z3	426305.1	3521444.6	7.80	41
BH. 1	427516.5	3518093.6	6.50	42
BH. 2	428405.9	3519899.8	6.50	38
BH. 3	424122.2	3520823.4	7.0	45

3.3.2.2 Thickness of overburden

The overburden is distributed in ten sites with different thickness (Figure 3-3). The thickness of the overburden ranges from 1.4 -1.9m with average 1.56m. The overburden covers about 17% of the study area.

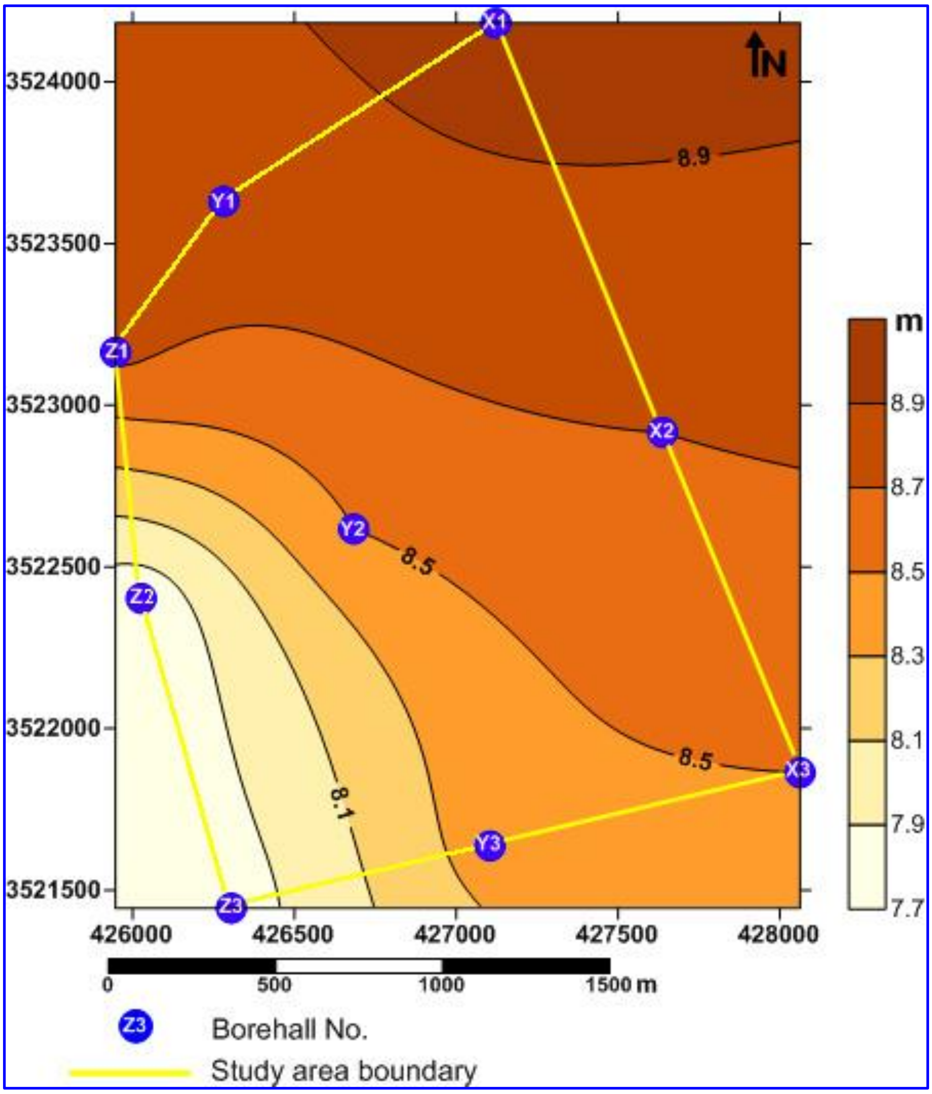


Figure 3-4: Isopach map of the marl layer in the study area.

3.3.2.3 Physical tests

Physical tests include dry bulk density, uniaxial compressive strength and apparent porosity. The dry bulk density is measured by g /cm³ or ton /m³**,** uniaxial compressive strength is measured by mega N/m². The uniaxial compressive strength with apparent porosity is used to estimate the reserve tonnage. It is the most important rock parameters required and determined for rock mechanical studies in mining projects. Six samples were systematically selected for determining porosity, bulk density and uniaxial compressive strength as a mainly part of the physical tests (Table 3-4).

Density is defined as mass per unit volume (g/cm³); it is an important rock characteristic used to transform measured volumes into tonnages. The density that takes voids into account is termed a bulk density, but when excluding any natural water content called dry bulk density (Edwards, 2001).

It is an important parameter and should be measured in samples. Porosity is a measure of the volume of voids in a material or mass (Price, 2009).

The compressive strength is the capacity of a material or structure to withstand loads tending to reduce size. It can be measured by plotting applied force against deformation in a testing machine. Some material fracture at their compressive strength limit; others deform irreversibly, so a given amount of deformation may be considered as the limit for compressive load. Compressive strength is a key value for design of structures (Callister, 2010).

The density of the marl layer in the wells of the study area ranges from 1.659 to 2.069 g/cm³ with an average of 1.735 g/cm³, whereas porosity ranging varies from 19.462 to 37.025%. The compressive strength ranges from 8.756 (first 0.5m) to 1.968 MegaN/m² with an average of 3.59 MegaN/m² (Table 3-4).

Table 3-4: Results of physical tests of selected samples.

BH. No.	**Sample No.**	**Interval depth (m)**		**Length of core (m)**	**Well depth (m)**	**Porosity (%)**	**B.D (g/cm³)**	**C.S (MegaN/m²)**
		from	**to**					
X1	1	0.00	0.50	0.05	9.00	19.462	2.069	8.756
X3	2	4.00	6.00	0.05	8.50	37.025	1.659	2.037
Y2	3	6.00	8.00	0.05	8.75	34.092	1.644	1.968
Y3	4	2.00	4.00	0.05	8.50	36.132	1.659	2.018
Z1	5	0.5	2.0	0.05	8.75	21.016	2.01	4.776
Z3	6	8.00	9.00	0.05	7.80	35.092	1.644	1.984
Av.						30.47	1.735	3.59

B.D: Bulk density (g/cm³). C.S: Compressive strength (MegaN/ m²).

According to the physical tests, Chatterjee (1979) divided degree of rock hardness into two levels shown in Table 3-5. Depending on the results of physical tests (Table 3-4), the marl layer in the study area is divided into two horizons based on the hardness of Hoek et al. (1998) as follows:

a. Weak or medium tough rocks: the horizon extends from exposed surface in 0.5m which is recognized with bulk density 2.069 g/cm³**.** Porosity varies between 19.462% and the value of uniaxial compressive strength is less than 8.8 mega N/ m². This horizon has a grade of R2. This horizon occupies about half of the surface area of the study area, while the remaining area has been extracted during the work in the quarry.

Table 3-5: Classification of rock hardness.

Level*	**Grade****	**Degree*** (mega N/ m^2)**	**Hardness type***	**Hardness*** description**	**Excavation* characteristic**
The first	R0	0.25– 1	Very Friable	Extremely weak	Easy ripping
	R1	>1 –5	Friable	Very weak	
	R2	>5 – 25	Medium tough	Weak	Hard ripping
	R3	>25 – 50		Medium strong	Very hard ripping
	R4	>50 – 100	Tough	Strong	Blasting
	R5	>100 – 250		Very Strong	
The second	R6	>250	Very tough	Extremely Strong	

*According to Chatterjee (1979); ** According to Brown (1981); ***According to Hoek et al. (1998)

b. Very weak or friable rocks: The horizon below 0.5m is recognized with an average of bulk density ranges from 1.644 to 2.01 g/cm^3 with average 1.7156 g/cm^3. Porosity varies between 21.06 to 37.052% and the uniaxial compressive strength value ranges from 4.776 to 1.984 mega N/ m^2, with an average of 2.002mega N/m^2. This horizon is classified as of grade R1 (Table 3-5).

The costs of mining, crushing and milling are greatly affected by rock hardness. These items affect both the number and size of the equipment needed, and the energy usage and the cost of the consumables needed (Lewis, 2001). The values of the porosity, density and uniaxial compressive strength are illustrated in Table 3-4.

Porosity has a major influence on bulk density. Porosity and bulk density are inversely related due to the fact that an increase in the voids in the sample causes reduction of the weight. Thus it reduces the compression strength of the sample and vice versa. The relationship between density and compressibility is positive, because the high-density evidence of the lack of pores and increase material within the unit volume leading to increase the resistance of sample to compression.

3.4 Reserve estimation methods

Reserve estimation reveals the economic effectiveness of the exploration and provides the data needed to assess the quality of the exploration geologist's work (Kreiter, 1968). One of the most frequent calculations geologists have to do is weightings (Wellmer et al, 2008). The main points to consider in selecting a method are that it must be appropriate to the geology of the deposit and to the available data (the spacing of drill holes and the quality of the data), and that it should also take some account, if possible, of the probable mining method (Edwards, 2001).

The reserve estimation of the cement raw material (marl) in the study area is calculated according to various methods such as these of Kreiter (1968), Dorokhin et al. (1969), Al-Atia (2001) and Wellmer, et al. (2008). Two types of the reserve estimation are used for calculating the marl reserve in this study. The first depends on interpolation point within the boundary of the study area. This type includes block, graphical, geographic information systems and coordinate methods. The error factor must not exceed 5% among all methods (Al-Bassam, 1993) in probable reserve. Another type depends on extrapolation point that represents the extent of the impact of the concentrations of the chemical compounds for every well. This type has low accurately than the first type and can be used for determining the possible reserve. It is used the Boldyrev method. The methods for estimating the reserve of marl as cement raw material are described below:

3.4.1 Blocks method

This method is expressed by dividing the total study area into geometrical blocks according to differences in composition or position as triangle, polygons or squares (Wellmer et al, 2008). The area of every triangle or polygon will be calculated and the whole area is the sum of all blocks. Then the volume and tonnage can be determined depending on the bulk density and the depth of industrial layer (marl). Three sub block methods are known; these are:

1. Triangles method
2. Polygons method
3. Squares method

Because of unsymmetrical dimensions of the boreholes, the square method was difficult to use in this study, therefore, it was ignored.

A. Triangles method

The study area is a quadrate shape with dimension 1.8x2.5 km. to estimate the reserve of the marl layer; the study area was divided into nine triangles. Each triangle links a three adjacent borehole (Figure 3-4).

Because of the triangle sides are unequal, and its angle degree unequal 60°, the correction factor is used to correct the marl layer thickness in each triangle depending on Al-Atia (2001) and Wellmer et al., (2008) as follows:

$$\text{Correction factor (C.F.)} = \frac{angle\ of\ the\ triangle\ peak}{60} \quad \text{................ (4-3)}$$

The reserve was calculated by the equation:

$$R = A \times ACT \times B.D \quad \text{.. (4-4)}$$

Where:

R: The reserve (ton), A: The triangle area (m^3), ACT: Average of corrected thickness (m) and B.D: Average of bulk density (g/cm^3)

The average of corrected thickness of each triangle in the study area was calculated by the following equation:

$$\text{ACT} = \frac{(t_1 \times Cf_1) + (t_2 \times Cf_2) + (t_3 \times Cf_3)}{3} \quad \text{................................ (4-5)}$$

Where:

ACT: Average of corrected thickness of triangle (m).

t_1, t_2 and t_3: Thickness of the marl layer in wells (X3, Y2 and Y3) respectively.

Cf_1, Cf_2 and Cf_3: Correction factors for each triangle.

3: Number of wells.

The area of the triangle is in unit of m^3, according on the equation below (Figure 3-5):

$$A = \frac{1}{2} B \times H \quad \text{.. (4-5)}$$

Where:

A: The area of triangle, *B*: Base and *H*: Height of triangle

The total Area (m^2) = $\sum$ triangles area.

= 3 639 350 m^2

Results of reserve calculations depended on the triangle method is listed in (Table 3-6).

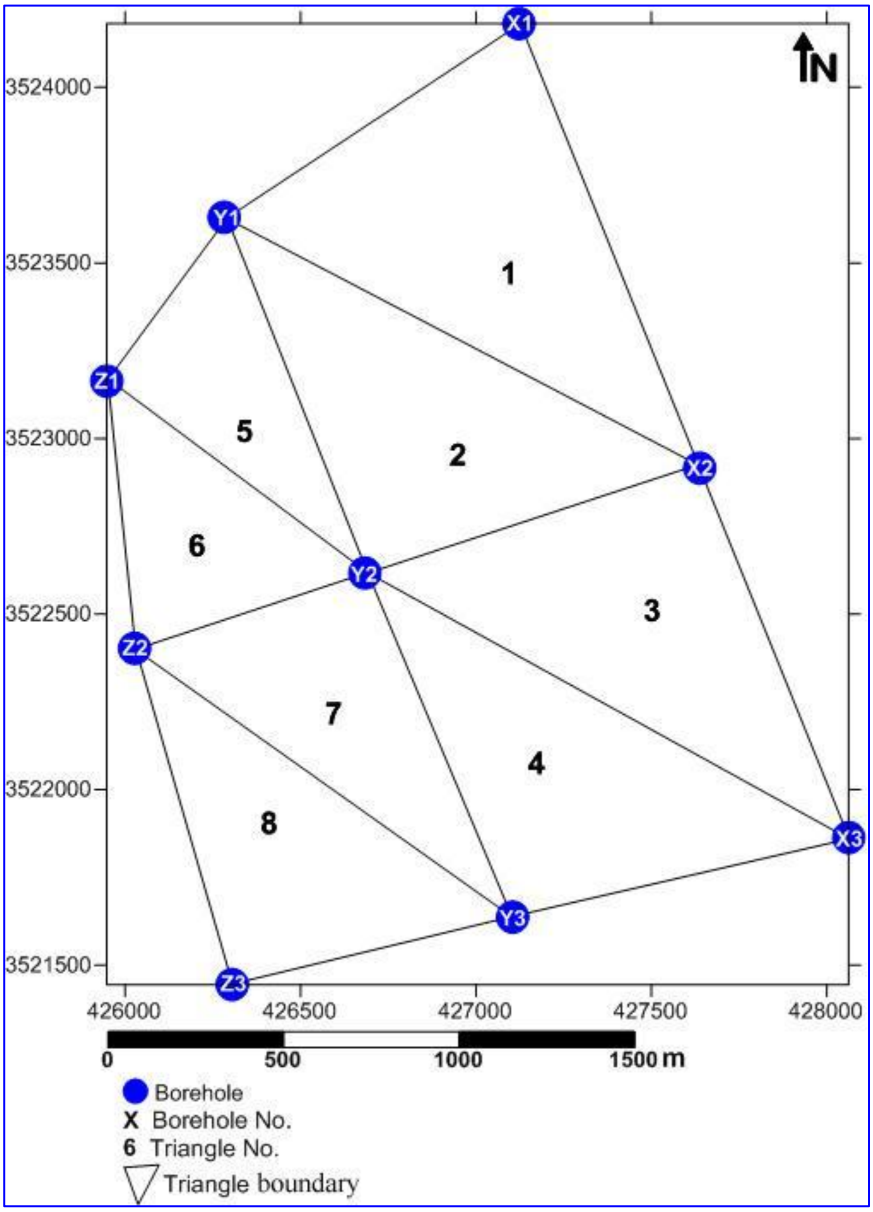


Figure 3-5: Plan map of the study area illustrates the triangular blocks link the boreholes.

The average of bulk density in the study area = 1.735 (g/cm³) (Table 3-4).

The total reserve (R.) = ∑ reserve in each the triangle

The total reserve (tonnage) by this method = 53 642 838 tons

The Table 3-6 is illustrated the results of reserve calculation depending on triangle method.

Table 3-6: Results of the reserve estimation by the triangle method.

Tr. No.	Wells No.	Th. of layer (m)	angle (degree)	C.F (m)	C.T (Th×C.F) (m)	Av. C.T. (m)	long of the rib (m)	Area (m^2)	Av. B.D. (gm/cm^3)	Reserve (ton) (C.T×A× B.D)
1	X1	9	79	1.32	11.85	8.85	1016	690572	1.735	10601892
	X2	8.7	40	0.67	5.80		1385			
	Y1	8.75	61	1.02	8.90		1553			
2	X2	8.7	45	0.73	6.38	8.56	1011	551466	1.735	8187500
	Y1	8.75	40	0.67	5.83		1095			
	Y2	8.5	95	1.58	13.46		1553			
3	X2	8.7	95	1.58	13.78	8.61	1011	564620	1.735	8430137
	X3	8.5	40	0.67	5.67		1121			
	Y2	8.5	45	0.75	6.38		1572			
4	X3	8.5	42	0.70	5.95	8.45	993	526755	1.735	7718054
	Y2	8.5	39	0.65	5.53		1074			
	Y3	8.4	99	1.65	13.86		1572			
5	Y1	8.75	57	0.95	8.31	8.70	592	272319	1.735	4112488
	Y2	8.5	33	0.55	4.68		920			
	Z1	8.75	90	1.50	13.13		1095			
6	Z1	8.75	55	0.92	8.02	8.25	770	260075	1.735	3723275
	Z2	7.75	78	1.30	10.08		691			
	Y2	8.5	47	0.78	6.66		920			
7	Y2	8.5	95	1.58	13.46	8.26	1076	370193	1.735	5303846
	Y3	8.4	31	0.52	4.34		691			
	Z2	7.75	54	0.90	6.98		1331			
8	Y3	8.4	49	0.82	6.86	7.95	808	403350	1.735	5565646
	Z2	7.75	37	0.62	4.78		1001			
	Z3	7.8	94	1.57	12.22		1331			
							Total	3639350	1.735	53642838

Tr. No.: triangle number, Th.: Thickness, C.F: Correction Factor, C.T: Correction Thickness, B.D: Bulk density (g/cm^3), A: Area (m^2)

B. Polygon method

This method is applied by dividing the study area into many polygonal (4 polygonal) (Figure 3-6). Because of the polygon sides are unequal, and its angle degree unequal 90°, the correction factor is used to correct the marl layer thickness.

$$\text{Correction factor (C.F.)} = \frac{angle\ of\ the\ polygone\ peak}{90} \text{...... (4-6)}$$

Average thickness of polygon must be corrected depend equation below:

$$ACT\ (m) = \frac{(t_1 \times Cf_1) + (t_2 \times Cf_2) + (t_3 \times Cf_3) + (t_4 \times Cf_4)}{4} \text{................. (4-7)}$$

Where:

4 is number of polygon, *ACT*: Average of corrected thickness of wells in each polygon, t_1, t_2, t_3, and t_4: Thickness of the industrial layer (marl) in four wells (X1, X2, Y1 and Y2).
Cf_1, Cf_2, Cf_3 and Cf_4**:** Correction factors for each polygon.

The reserve tonnage of each polygon was calculated by the following equation:

$$R = A \times ACT \times\ B.D \text{ .... (4-8)}$$

Where:

R: Reserve (ton), ACT: Average of corrected thickness (m), *A*: polygonal area (m^2), B.D: Average of bulk density (g/cm^3).

The total area $= \sum polygonal\ area$
= 3 625 642 m^2

Average of Bulk density in the study area = 1.735 (g/cm^3) (Table 3-4).

The total reserve tonnage (R.) = $\sum polygon\ reserve$
= 53 428 158 ton

Table 3-7 illustrates the calculation of reserve depending on polygons method.

In terms of reserve estimation, the difference between triangle and polygon methods is 214 680 tons. This ascribes to the differences of a considerable thickness in each. The error factor between the two methods is safe (0. 4%) depending on Al-Bassam (1993). The triangle method is more accuracy than squares method due to uses more data for small area; this provides accurate thickness and reserve closest to reality.

Table 3-7: Results of the reserve estimation by the polygons method.

P. No.	Wells No.	Th. (m)	Angle (degree)	C.F. (degree)	C.T. (T×C.F) (m)	ACT (m)	Long of the rib (m)	Area (m^2)	BD gm/cm^3	R. (ton) ACT×A× BD
1	X1	9	79	0.88	7.90	8.73	1016	1204185	1.735	18233155
	X2	8.7	85	0.94	8.22		1385			
	Y1	8.75	101	1.12	9.82		1010			
	Y2	8.5	95	1.06	8.97		1095			
2	X2	8.7	95	1.06	9.18	8.53	1011	1100071	1.735	16271543
	Y3	8.4	99	1.10	9.24		1121			
	X3	8.5	81	0.90	7.65		993			
	Y2	8.5	85	0.94	8.03		1074			
3	Y1	8.75	57	0.63	5.54	8.47	592	532707	1.735	7832348
	Y2	8.5	85	0.94	8.03		1095			
	Z1	8.75	140	1.56	13.61		770			
	Z2	7.75	78	0.87	6.72		691			
4	Y2	8.5	95	1.06	8.97	8.11	1076	788679	1.735	11091112
	Y3	8.4	80	0.89	7.47		691			
	Z2	7.75	91	1.01	7.84		1001			
	Z3	7.8	94	1.04	8.15		808			
								3625642	1.735	53428158

P. No.: Polygonal number, Th.: Thickness, C.F.: Correction Factor, C.T.: Correction Thickness, ACT: Average of Corrected Thickness, B.D.: average of Bulk Density (g/cm^3).

3.4.2 Graphical method

Uniform extensions are calculated by using irregular transparent graphic paper. It demonstrates the limits of space required calculated; then calculating the number of full boxes within sprawl and multiplying the scale of the map of by extensions of the industrial layer (marl). This is a practical easy and logic to match accuracy with the scale of the map (Al-Atia, 2001). The calculated area by this method is 3 542 886 m^2 and the volume is 29 981 673 m^3. The tonnage of the reserve is 52 018 202 tons.

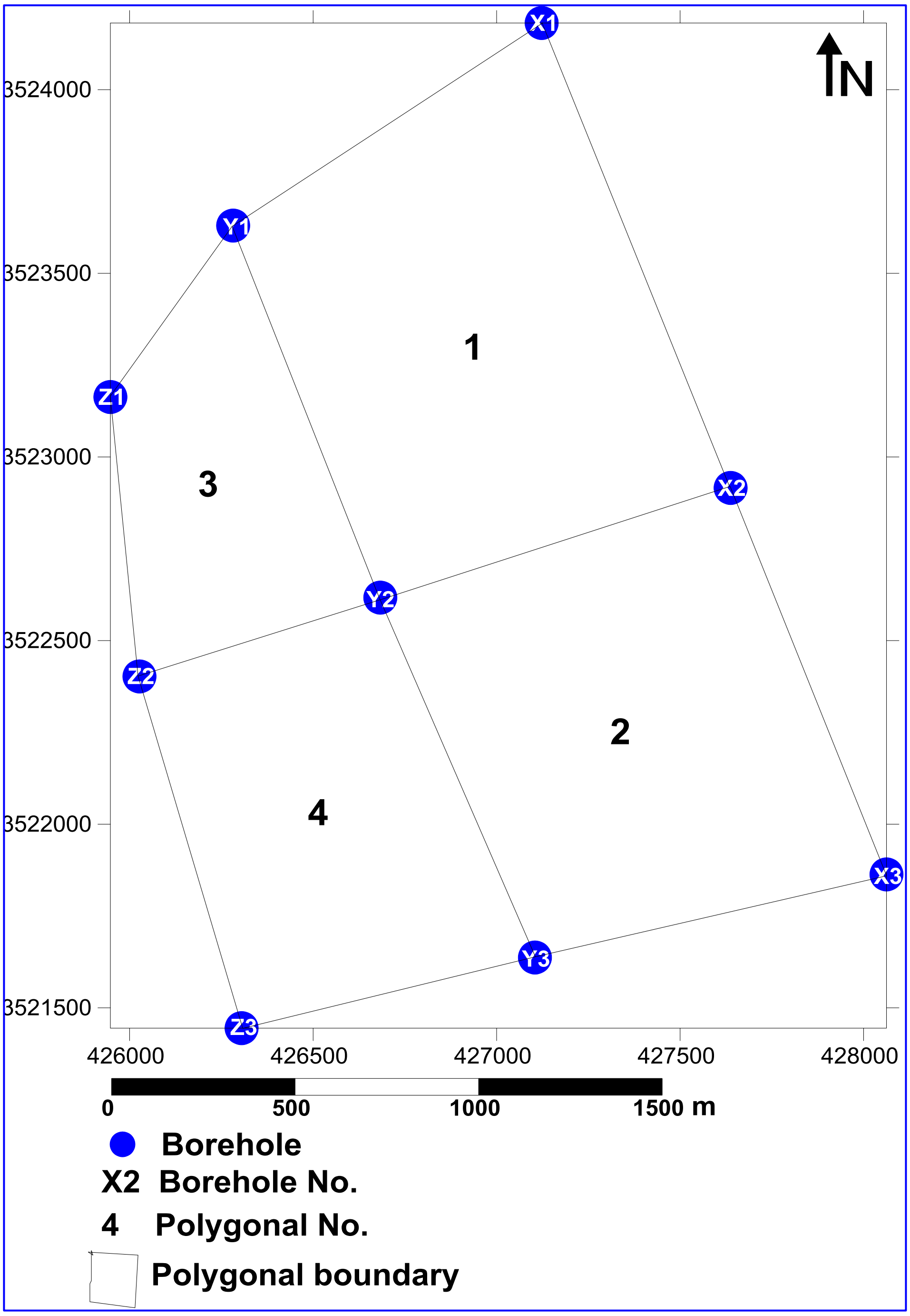


Figure 3-6: Plan map of the study area illustrates the polygon blocks link the borehole.

3.4.3 Geographic Information Systems (GIS)

Geographically referenced data consists of any type of measurement or observation whether analog or digital, which have a known distribution across the surface of the ground, and hence can be presented as a map or section. Data of this sort are fundamental to all phases of mineral exploration.

Any map is an example of a geographical information system– commonly known by its acronym GIS. However, today GIS is more specifically understood to refer to Geo referenced data that are stored digitally on, and manipulated by a computer. There are a number of commercially available GIS software programs, and although they are not generally specifically designed for mineral exploration. They are powerful programs that can handle a wide range of GIS applications (Marjoribanks, 2010). The help of geographic information systems (GIS) is applied in an attempt to estimate the marl reserve (Figure 3-7).

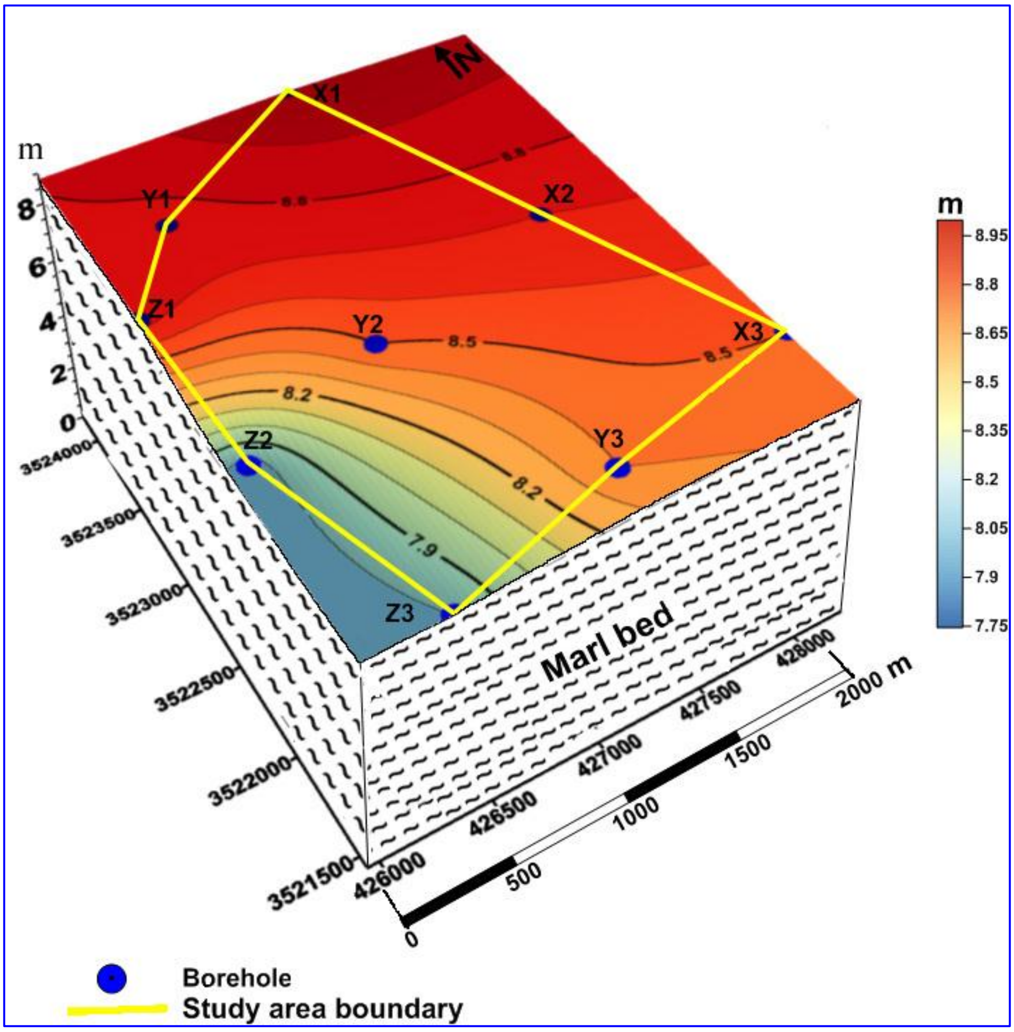


Figure 3-7: 3D-diagram of the marl layer (GIS method) shows the distribution of thickness in the study area.

When the data was inputted into the computer and used GIS program software the results appeared as in the below. They were computerizing calculated by this program.

$Area = 3\ 557\ 000\ m^2$

$Avarege\ Thickness =\ 8.48\ m$

$Volume =\ 30\ 768\ 000\ m^3$

$Bulk\ Density = 1.735\ gm/cm^3$

$Reserve\ Tonnage = 53\ 936\ 304\ \ ton$

The simple difference in total volume value between GIS and triangle method was attributed to the average of thickness. The software program depends on hinge points for calculating the average of thickness. In this method, distribution of major oxides in the area is not clear. This is a difficulty in planning to work in the quarry and control the quality of Raw Materials.

3.4.4 Coordinates method

After determining the coordinates (X, Y) of several points on boundaries of the study area. The area can be calculated according to Al-Atia (2001) using the equation below:

$$A = X1Y2 + X2Y3 + X3Y4 + \cdots + XnY1 \ldots\ldots\ldots\ldots\ldots (4\text{-}9)$$

$$B = X2Y1 + X3Y2 + X4Y3 + \cdots + X1Yn \ldots\ldots\ldots\ldots\ldots (4\text{-}10)$$

$$Area = \frac{|A-B|}{2} \ldots\ldots\ldots\ldots\ldots (4\text{-}11)$$

Where:
X1: X- coordinates value of first point
Y2: Y- coordinates value of the second point
A, B: summation factor

The area was calculated by this method to be 3 803907 m^2 and the tonnage of the reserve was 55 841 461 tons.

This method is generally less accurate than other methods because of the limited coordinates of points on the boundaries of the study area. To increase the accuracy, the coordinate points along the boundaries of the study area should be increased. The thickness is imprecise because it will depend generally average.

3.4.5 Stripping Ratio (S.R.)

Stripping ratio is almost universally used and represents the amount of uneconomical material that must be removed to uncover one unit of ore (Hartman, 1992). This ratio is a unitless arithmetic value represents the percentage between volumes of the overburden (O.B) to the volume of the industrial layer (I.B) (Al-Atia, 2001). Depending on Jefferson (1983) when the overburden is fragile, disassembled and easily removed, this ratio can be up to1: 4.

$$S.R. = \frac{V.\ of\ (O.B)\ (m^3)}{V.\ of\ (I.B)\ (m^3)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4-12)}$$

$$S.R. = \frac{1021574.8\ (m^3)}{30918062\ (m^3)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4-13)}$$

$S.R$= 0.033

The volume of overburden presented in Table 3-2 and volume of industrial layer (marl layer) presented in Table 3-7 as summation the volume of each triangle which a result of multiplying the area by the average depth.

3.4.6 Comparison among the methods of reserve estimation

Five methods had been used for the reserve estimating of the marl layer that has given varying results (Table 3-8). The lowest reserve was 52 018 202 ton computed by the graphical method; whereas the highest reserve was 55 841 461 ton computed by coordinate method.

Table 3-8: Reserve tonnage computed by different methods

Method		**Area (m^2)**	**Volume (m^3)**	**Reserve (ton)**
Graphical		3 542 886	29 981 672	52 018 202
Block	**Triangle**	3 639 350	30 918 062	53 642 838
	Polygonal	3 625 642	30 794 327	53 428 158
GIS		3 577 000	30 936 304	53 936 304
Coordinate		3 803 907	321 852 80	55 841 461

The variation in computing reserve of these methods is due to the reasons below:

Graphical method does not give confidence intervals for the parameters like density and thickness. The scale of the area cannot be set accurately on graph paper, as well as the difficulty in calculating the area of irregular shapes.

The coordinate method depends on increase coordinates of points on the path of the external borders of the study area. But in fact, there is no further coordinate's measurement in the study area.

The triangles and GIS methods were relatively more accurate. The difference percent between them is (0.54 %) which calculated by the equation below:

$$\text{Difference percent} = \frac{V.in\ triangle\ method - V.in\ GIS\ method}{V.in\ GIS\ method} * 100$$

$$\text{Difference percent} = \frac{53\ 642\ 838 - \ 53\ 936\ 304}{53\ 936\ 304} * 100$$

= 0.54 %

This difference (0.54 %) of the tonnage is non-significant and very low.

3.4.7 Economic evolution of marl reserve

To evaluate the reserve of industrial layer (marl), Kreiter (1968) put statistical quantitative method from 10-point scale by using five parameters Table 3-9. These parameters include size, grade, productivity, mining condition and economic conditions of the locality. Each was also roughly divided into three categories. A definite number of points are assigned in Table 3-9.

Table 3-9: Statistical quantitative evaluation method for deposit (after Kreiter 1968).

Parameters	**Valuation points**		
	2 point	**1 point**	**0 point**
Scale of deposit	Large	Medium*	Small
Grade	High	Medium*	Low
Productivity	High*	Medium	Low
Mining condition	Very favorable*	Usual	Unfavorable
Economic condition	Very favorable*	Usual	Unfavorable

*marl layer of study area valuation

To evaluate the marl layer according to Kreiter (1968), the properties of it must compare with the parameters in Table 3-9. The scale of deposit is medium (1 point) on the work context of the Iraq Geological Survey Al-Bassam (1993). The grade is considered as medium (1 point) because the marl layer needs to be corrected for CaO, but other components are fit for Portland cement industry.

Production of marl is high (2 points) as a result of easily extraction by using excavator because of its friable properties. The morphology of the study area which considered as flat to semi flat area are encourage for mining work with condition very favorable (2 point) in addition to accessibility for the work site and road transport accessible and easy construction. The marl is exposure on the surface and accessible with low stripping ratio in addition to quarry without explosive. This leads to facilitate the mining and economic conditions be very favorable (2 point).

However, the marl reserve recorded eight points in statistical quantitative method (Table 3-9). According to this principle, all deposits fall into the five categories (Table 3-10) depending on Al-Atia, 2001.

Table 3-10: Category of reserve evaluation.

Evaluation of deposit	**Points**
Very valuable deposit	9-10
Deposits of greater economic importance	7-8
Ordinary workable deposit	5-6
Doubt workable deposit	3-4
Unworkable deposit	< 3

The marl layer as reserve in the study area was lying in the deposit of the greater economic importance category (Table 3-10) because it has 8 points in the statistical quantitative method in Table 3-9.

3.4.8 Boldyrev method

This method uses the range influence of average chemical composition of borehole location. The reserves of metalliferous and non-metallic deposits have estimated by this method depending upon Kreiter (1968). It's calculated the proximate reserve. This method depends on the polygons shape for calculating the surface area and then estimated the reserve marl. By connecting adjoining boreholes with each other, a net of triangles is created. The equidistance lines, perpendicular bisectors, the half sides of these triangles and bound the polygonal area of influence centered on each borehole (Wellmer et al, 2008) (Figure 3-8).

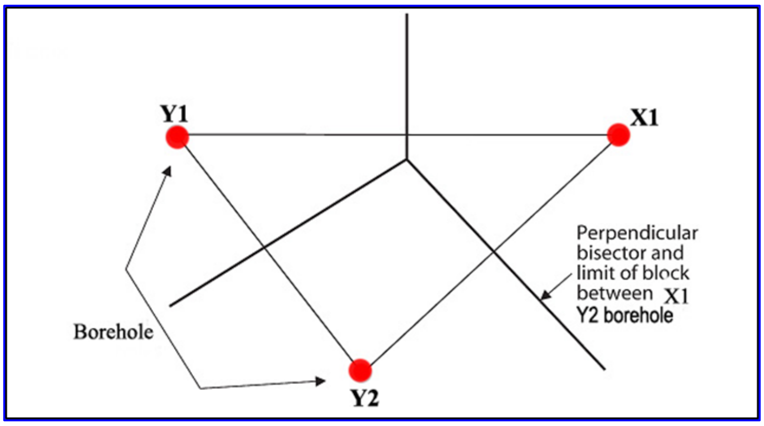


Figure 3-8: Construction of equidistance lines.

When connecting perpendicular lines of equidistance boreholes in study area, the polygon grid will form (Figure 3-9).

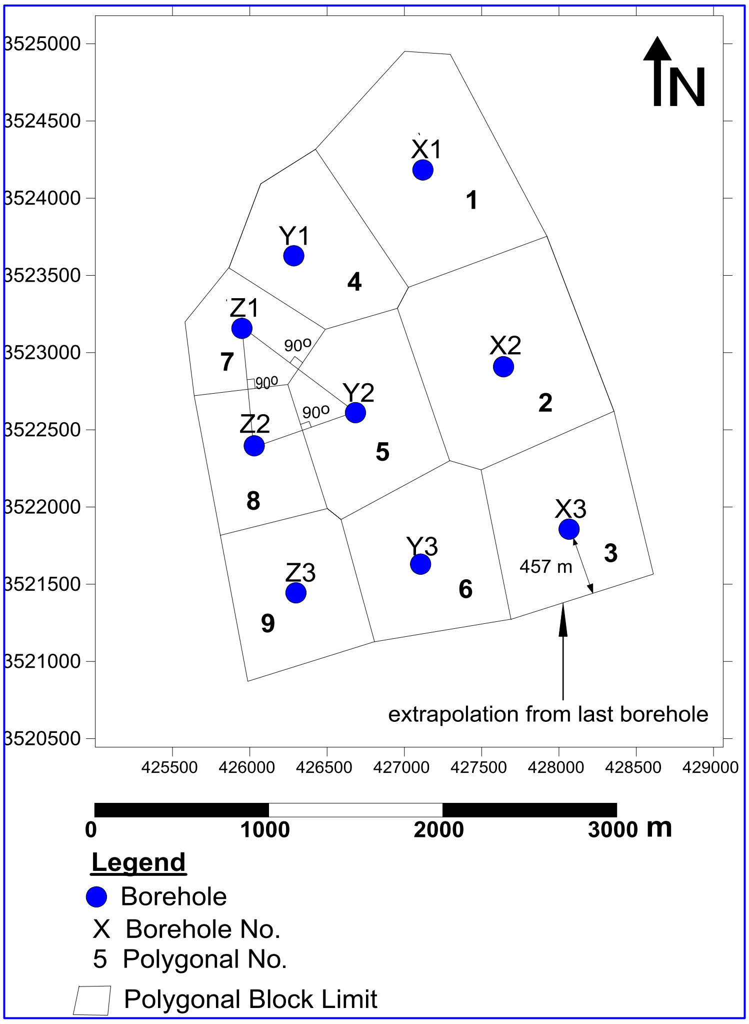


Figure 3-9: Plan map of polygonal shape for reserve estimating of extrapolation boreholes for Boldyrev method.

The volume and tonnage of each polygon are calculated depended on the thickness and density of the borehole that located in the middle the polygon. The volume and grad depend on thickness, density and chemical properties of the central borehole of the polygon that constructed around the borehole. The tonnage was estimated first and then the marl quality was determined by chemical analyses to know the location of appropriate site of reserve.

Boldyrev method definitely has weaknesses (Giroux, 1990) because the outer limit is not identified. The reserve tonnage by this method was computed in Table 3-11 depending on the polygon that illustrated in Figure 3-9. The area of each polygon is calculated by Surfer version-11 software program. The tonnage is computed using by this method is 118 606 704 tons. This reserve is represented the probable and possible reserve which corresponds to C1 and C2 respectively. So the proximity reserve is represented the sum of probable and possible reserve or C1+C2.

Table 3-11: Calculations of reserve tonnage of marl by Boldyrev method in the study area.

BH. No.	**Polygon No.**	**Area (m^2)**	**Thickness (m)**	**Volume (m^3)**	**Density (gm/cm^3)**	**Tonnage (ton)**
X1	1	1295823	9.00	11662407	1.735	20234276
X2	2	1338874	8.70	11648202.3	1.735	20209631
X3	3	988287	8.50	8400435.471	1.735	14574756
Y1	4	773494	8.75	6768069.828	1.735	11742601
Y2	5	895104	8.50	7608384.116	1.735	13200546
Y3	6	892255	8.40	7494944.375	1.735	13003728
Z1	7	487907	8.75	4269182.315	1.735	7407031
Z2	8	584696	7.75	4531394	1.735	7861969
Z3	9	766435	7.80	5978193	1.735	10372165
Total	------	8022874	------	68361212	------	118606704

3.5 Specific quality evaluation of quarry planning

For opening a new quarry to employ in the production, the distribution and variation of the chemical components in it must be determined. The first step, in conjunction with the planning of the work in the quarries, is to determine the average chemical composition at the site. Then followed by the second step is calculating the raw mix composition. The technique methods of operation, planning and exploitation direction must be determined by the workers in the quarry that depended on the data of major element distribution. In quarry, the raw materials are daily extracted in small amounts for production purposes. When there is a deviation in raw materials quality, it must modify the chemical composition. Triangle method gives accurate perception of the major oxides distribution of in the quarry within relatively small areas. It can be easily corrected. The concentration of major oxides in each triangle was calculated by equation (Moon et al, 2006) as below:

$$Avaregegrade = \frac{G1T1+G2T2+G3T3}{\sum T} \quad \text{……...………..………………….. (4-14)}$$

Where: G = Grade or concentration of oxides, T = Length of the core sample

For example, when the equation applied to find out the concentrations of CaO in the triangle 1, which the wells (X1, X2 and Y1) are in its peak the result is 37.12%.

$$Avarege\ grade = \frac{(36.53*9)+(37.52*8.7)+(37.34*8.75)}{\sum 26.45} \text{……...…… (4-15)}$$

$$= 37.12\%$$

Other oxides concentration results can be calculated in the same way in every triangle shown in Table 3-12.

Table 3-12: The concentration of oxides in the triangle blocks.

Tr. No.	**BH No.**	**Th. (m)**	**Reserve (ton)**	**CaO**	**MgO**	**SO_3**	**SiO_2**	**Fe_2O_3**	**Al_2O_3**
				%					
1	X1	9	9854990	37.12	1.946	0.323	19.01	2.76	4.63
	X2	8.7							
	Y1	8.75							
2	X2	8.7	7465801	37.76	1.836	0.458	18.31	2.81	4.14
	Y1	8.75							
	Y2	8.5							
3	X2	8.7	8560543	37.21	1.953	0.455	18.41	2.73	4.00
	X3	8.5							
	Y2	8.5							
4	X3	8.5	7775425	38.04	2.099	0.343	17.83	2.79	4.20
	Y2	8.5							
	Y3	8.4							
5	Y1	8.75	3870101	37.73	1.873	0.421	18.25	2.82	4.33
	Y2	8.5							
	Z1	8.75							
6	Z1	8.75	38790263	38.46	1.870	0.521	16.86	2.79	3.36
	Z2	7.75							
	Y2	8.5							
7	Y2	8.5	5747039	39.35	2.041	0.478	16.41	2.78	3.42
	Y3	8.4							
	Z2	7.75							
8	Y3	8.4	5434792	39.13	1.977	0.316	16.25	2.85	3.90
	Z2	7.75							
	Z3	7.8							

3.6 Discussion

The quantity of the proved reserve of marl as industrial layer is approximately 53 million tons of qualified raw materials for cement industry which is considered as a medium reserve depending on the work context of the Iraqi Geological Survey (Al-Bassam 1993). This quantity can be increased in the future by expanding the required geological studies. In addition to the quarry of Kufa Cement Plant is continuing to invest the upper layer of limestone which covered overlain the marl layer and the area is expanding 125000 m^3 annually.

The marl quantity estimated by this study appears to be enough for establishing a new cement plant in Al-Najaf Governorate. This new raw material will be an alternative to clay as a source of silica, alumina and ferrite and high percent of limestone as a source of lime. This is based on the annual capacity of designed new plants.

The reserve in the study area is considered as a proved reserve according to the British System and C1 in Russian System.

When designing a new plant with production capacity of 1.5 million tons annually, the raw materials that consumed in product must be calculated depending conversion factor. This factor is kiln feed to clinker ratio which used to calculate the amount of raw materials. This factor is ranging 1.65-1.75 (Alsop, 2007).

For converting the product to raw material must multiply the product in average of conversion factor which is equal to 1.7.

$$1.5 \times 1.7 = 2.55 \, million \, tons \, / year$$

The reserve of marl represents 78% of the raw materials of kiln feed, so the amount of marl that consumed every year is:

$$2.55 \times 0.78 = 1.989 \, million \, tons \, / year$$

The adequacy of marl reserve to product in years is:

$$53 \div 1.989 \approx 27 \ year$$

The calculated reserve can be increased by studying the surrounding areas.

Two methods types for calculating reserve are used in this study. The first type depends on interpolation point which is divided to:

1. Block method which contains triangle and polygon.
2. Graphical method.
3. GIS method.
4. Coordinate method.

The second type, Boldyrev method, depends on extrapolation point and measuring the extent of the impact of the concentrations of the chemical compounds for every well.

The reserve estimated by triangles method is preferable and accurate chemical components in each triangle. This leads to the clarity of extracting, modifying paths and helping to control and resolve quality problem. The polygonal method is different from the previous method because the distribution of chemical components is more accurate in the triangles method than the polygon method.

The Boldyrev method calculates the possible reserve. The polygon s measures the extent of major oxides which is inaccurate because there is no enough information. Every well occupies the center of polygon.

Furthermore, several reasons lead to prefer the triangle and express it better than other methods. These reasons are:

1- The study area has uniform shape and homogeneous dimensions (semi-flat).
2- The study area is plain except some scattered of piled rock resulting from removal of overburden.
3- This method gives the estimator a chance of using all the areas in the reserve calculation completely.

The graphical, the coordinate and Boldyrev methods are generally less accurate than other methods. The GIS method has high-accuracy to calculate the area and volume of the marl layer in the study area but major oxides distribution is not clear.

There are four systems used to classify the marl reserve in study area:

1. American system
2. The Britain system
3. Russian system
4. JORC system

The reserve of marl layer in the study area is classified as Probable reserve according to the Britain system and the Russian system is classified as C1. This classification is preferable and generally used in the literature of the Iraq Geological Survey.

The overburden covers a little of the study area with a very low value of the stripping ratio indicating an excellent condition for opening a quarry. This means an economic benefit.

The degree of layer hardness is friable from the depth 0.5 m to the end of layer but the upper part from surface to depth 0.5 m is low tough indicating that the industrial layer can be excavated by hydraulic excavators without using explosive materials. This is of great economic importance; avoiding the large cost of using explosives for rock breakage and drilling equipment to drill borehole for the blast. Since blasting is required for quarrying marl, and the crushing process can also be omitted this kind of raw material considerably lowers the cement production cost. Marl is easy for crushing, grinding and milling, which are the parameters that consume energy. Specific electrical energy consumed in the raw milling process is represented by about 24% and in blending 6% of the total energy consumed in the cement plant (Alsop, 2007). Since the marl has low hardness and a highly naturally homogeneous material, this leads to a reduction in electrical energy consumption and reduces the wear of equipment productivity and increase production raw mills, which is reflected in the reduction of the cost of the final product (cement).

Chapter Four

Radiological Assessment

4. Radiological assessment

4.1 Preface

Portland cement as it is used as a building material can cause significant gamma dose indoors, due to their natural radionuclide content depending on the naturally occurring radioactivity of its raw materials. Natural radioactive materials under certain conditions can reach hazardous radiological levels. So, it becomes necessary to study the natural radioactivity levels in cement and its raw materials to assess the dose for the population in order to know the health risks and to have a baseline for future changes in the environmental radioactivity due to human activities. Humans are exposed to ambient ionizing radiation from ^{40}K, ^{238}U series and ^{232}Th series and their decay products which widely spread in the earth's environment (Damla et al., 2011). Workers exposed to cement or its raw materials for a long time especially in mines and at manufacturing sites as well as individual typically spend 80% of their time indoors (Sonkawade, 2008). Knowledge of the natural radioactivity levels in building materials is an important issue in the assessment of overall human exposure to natural radiation associated with ^{226}Ra and ^{232}Th (and their decay progeny) and the primordial radionuclide ^{40}K (Mollah et al., 1986; Paredes et al., 1987 and Flores et al., 2008).

This chapter deals with radioactivity in marl, clinker and cement to assess the radiation hazard.

4.2 Radioactivity elements specification

The half-life of the uranium decay chain is illustrated in the Figure 4-1. The three nuclides ^{226}Ra, ^{232}Th and ^{40}K have very long half-lives and as a result control the decay rate of the active daughters which have much shorter half-lives. Their presence in soils and rocks (finally in building materials) can simply be considered as permanent. Hence, it is of a great benefit for the entire society to examine the radioactivity of the raw materials used in its manufacture evaluation of the specific activity. The measurement of the natural radioactivity in the cement and its raw material is very important to determine the environmental hazards. It is very essential to set the standard radiation levels and national guide line according to the international recommendation. Generally all of the building materials contain natural radionuclides representing ^{238}U decay series, ^{232}Th series and ^{40}K. In the ^{238}U series, the decay chain segment starting from Radium ^{226}Ra which has a half-life of 1600 years is radiologically the most important in addition to its decay products which produce 98.5% of the radiological effects of uranium series (Hassan et al., 2010). Therefore, reference is often made to ^{226}Ra instead of ^{238}U (Turhan and Gurbuz, 2007).

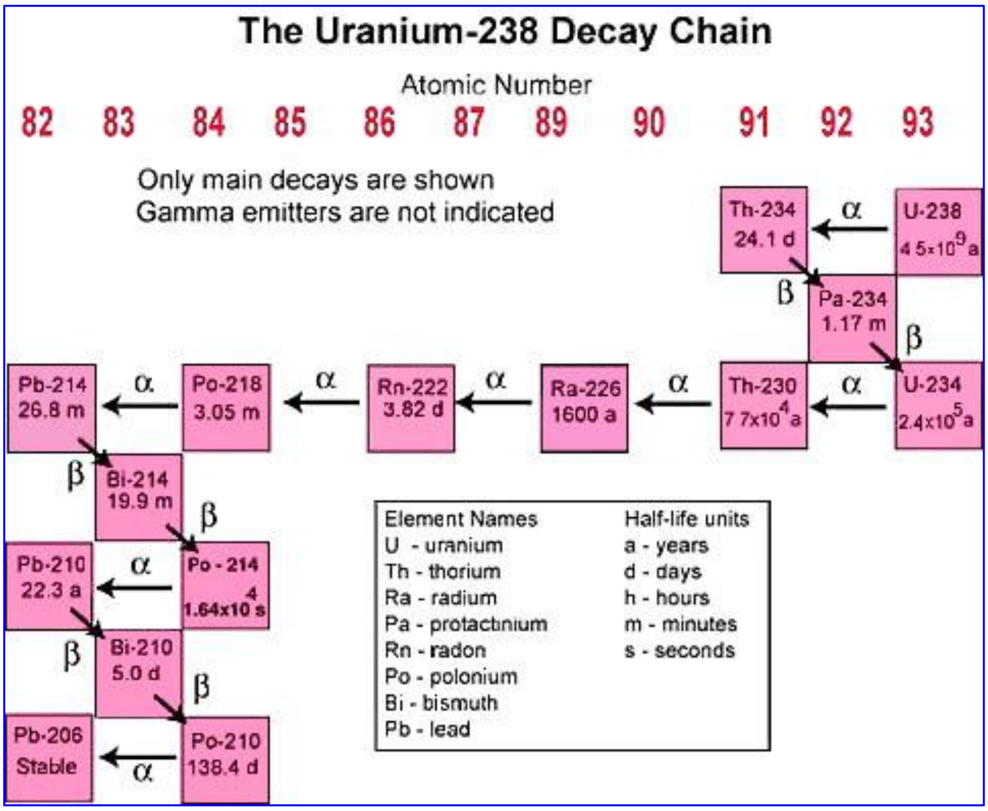


Figure 4-1: half-life of the uranium decay chain (after Siegel and Bryan, 2003)

The worldwide average concentration of Radium, Thorium and Potassium in the earth crust are about 40, 40 and 400 Bq/kg respectively (Mehra, 2005). The terrestrial background radiation is related to the type of rocks. The higher concentrations of them are associated with phosphate and granite rocks (Abbady, 2005). Recent studies have also demonstrated a high content of these elements in calc-silicate rocks (Santos et al., 2010). The world ranges for building materials of 50, 50 and 500 Bq kg^{-1} for ^{226}Ra, ^{232}Th and ^{40}K, respectively (UNSCEAR, 1993).

The specific activities are averaged from gamma-ray photo peak at several energies. The gamma-ray lines at 295.2 and 351.9 keV from ^{214}Pb and at 609.3 and 1764.5 keV from ^{214}Bi were used to determine the specific activity of ^{226}Ra. The gamma-ray lines of 338.4 and 911.2 keV from ^{228}Ac, the 727.3 keV from ^{212}Bi and 583.2 and 2614.5 keV from ^{208}Tl were used to determine the specific activity of ^{232}Th. The specific activity of ^{40}K was measured directly by its own gamma-ray line at 1460.8 keV (Ali, 2012).

4.3 Radioactivity analyses

Radiological analyses had been carried out for representative samples of the marl layer as a raw material in the manufacture of Portland cement to determine the radioactive elements ^{226}R, ^{232}Th and ^{40}K. Standard mixture of raw mix was prepared as kiln feed and then burned in furnace for 1450 ˚C to manufacture clinker. The clinker samples are crushed with 0.3% of gypsum to produce cement. Then, clinker and cement samples are radiologically analyzed.

4.3.1 Radioactivity of marl layer

Nine samples were collected from nine well's locations, mostly from the study area. They were analyzed in the laboratory of Radiation Protection Center / Ministry of Environment.

Table 4-1: Activity concentration of ^{226}Ra, ^{232}Th and ^{40}K in raw materials.

Sample No.	**Well No.**	**Activity concentration (Bq kg^{-1})**		
		^{226}Ra	**^{232}Th**	**^{40}K**
1	X1	15.4	4.5	235.4
2	X2	12.4	6.2	222.05
3	X3	13.4	5.1	185.8
4	Y1	11.9	4.4	244.1
5	Y2	16.9	5.7	255.4
6	Y3	12.7	4.9	174.4
7	Z1	10.6	5.2	242.2
8	Z2	12.8	5.06	211.1
9	Z3	28.1	5.4	245.4
minimum		10.6	4.4	174.4
maximum		28.1	6.2	255.4
Mean		14.91	5.16	223.98

Table 4-1 summarizes the measured concentrations of the naturally occurring radioactive elements ^{226}Ra, ^{232}Th and ^{40}K in samples of marl layer and the Figures 4-2 and 4-3 displayed the of gamma-ray spectrum for boreholes X3 and Y3.

Al-Bassam et al. (2006) clarified the origin of U in the Euphrates Formation (Early Miocene) from source rocks, lying several kilometers underneath. The late Early Miocene tectonic unrest triggered fracturing and faulting that allowed for uranium–rich groundwater, trapped in the Paleozoic aquifers, to ascend to surface in the shallow parts of the late Early Miocene Sea, together with bitumen and H_2S seepages. Uranium was precipitated below sediment–water interface within the Euphrates Formation sediment.

4.3.2 Radioactivity of clinker and cement

Tow samples of clinker were analyzed in the Radiation Protection Center and then milled with 3% of gypsum to produce Portland cement which analyzed in the same center. The clinker was produced from 78 % marl and 22 % of limestone depending on their chemical composition as in Table (2-8). Radioactive elements ^{226}Ra, ^{232}Th and ^{40}K had been measured by gamma spectrometry to determine their concentration in the clinker and cement samples. Table 4-2 summarizes the measured activity concentrations.

Table 4-2: Activity concentration of ^{226}Ra, ^{232}Th and ^{40}K in clinker and Portland cement (in Bq kg^{-1}).

Sample No.	**Material**	**Activity concentration (Bq kg$^{-1)}$**		
		^{226}Ra	**^{232}Th**	**^{40}K**
1	Clinker	31.8	7.0	83.7
2	Clinker	31.8	6.3	99.3
Mean		31.8	6.75	91.5
3	Cement	35.3	8.09	107.3
4	Cement	35.8	7.6	114.3
Mean		35.55	7.42	110.8

Figures 4-4 and 4-5 show the diagram of gamma-ray spectrum for clinker and cement.

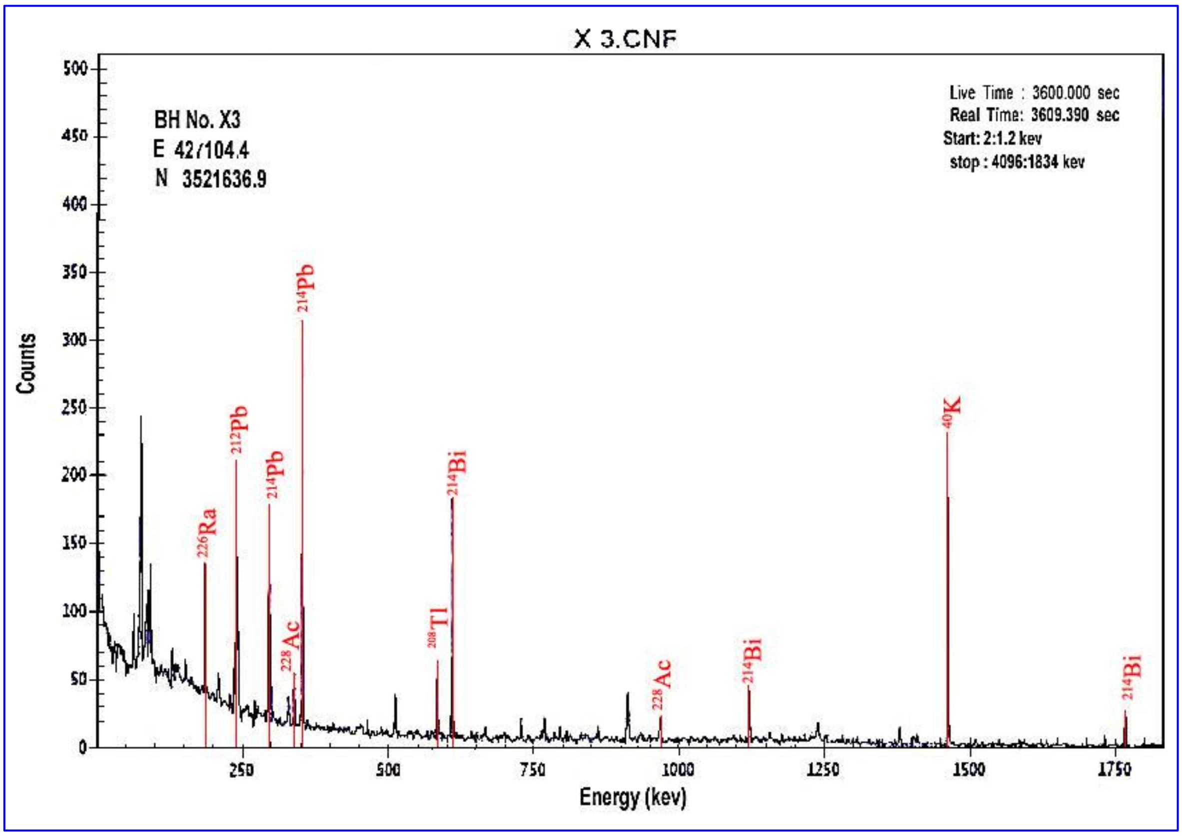


Figure 4-2: Gamma-ray spectrum of marl in BH X3.

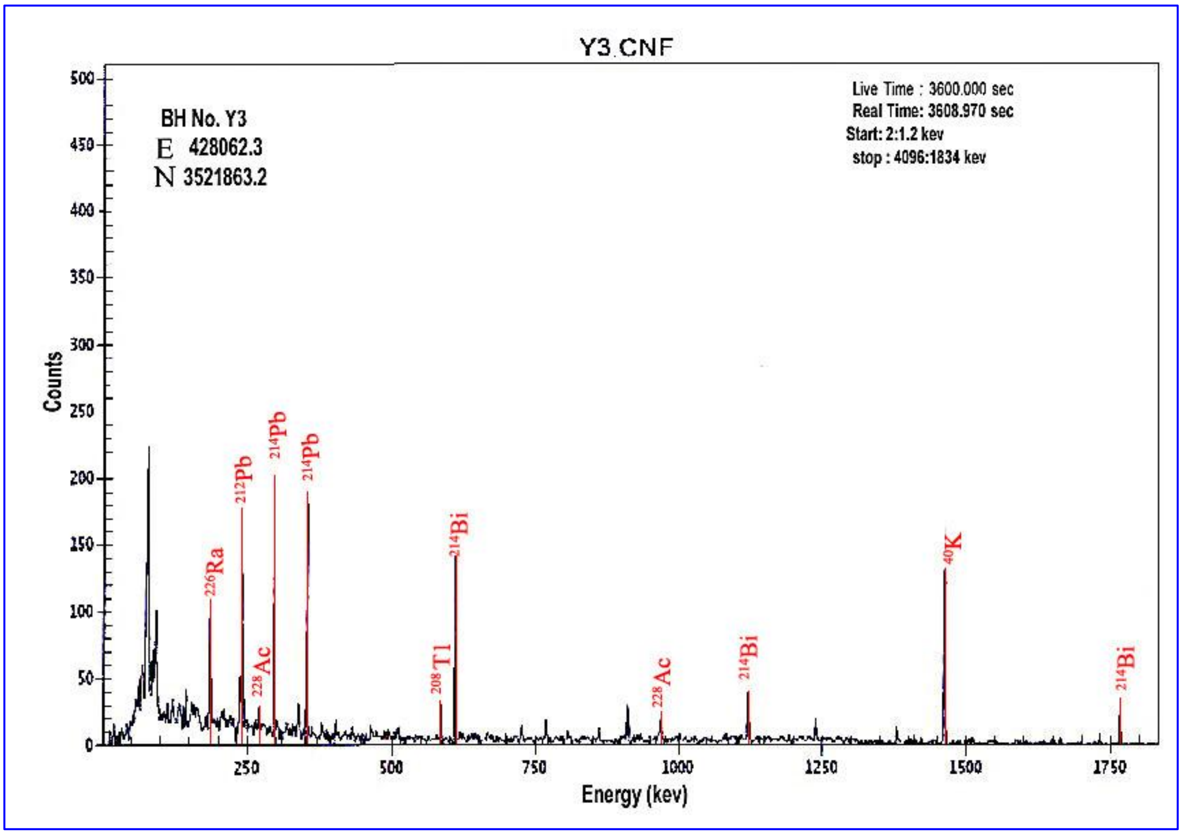


Figure 4-3: Gamma-ray spectrum of marl in BH Y3.

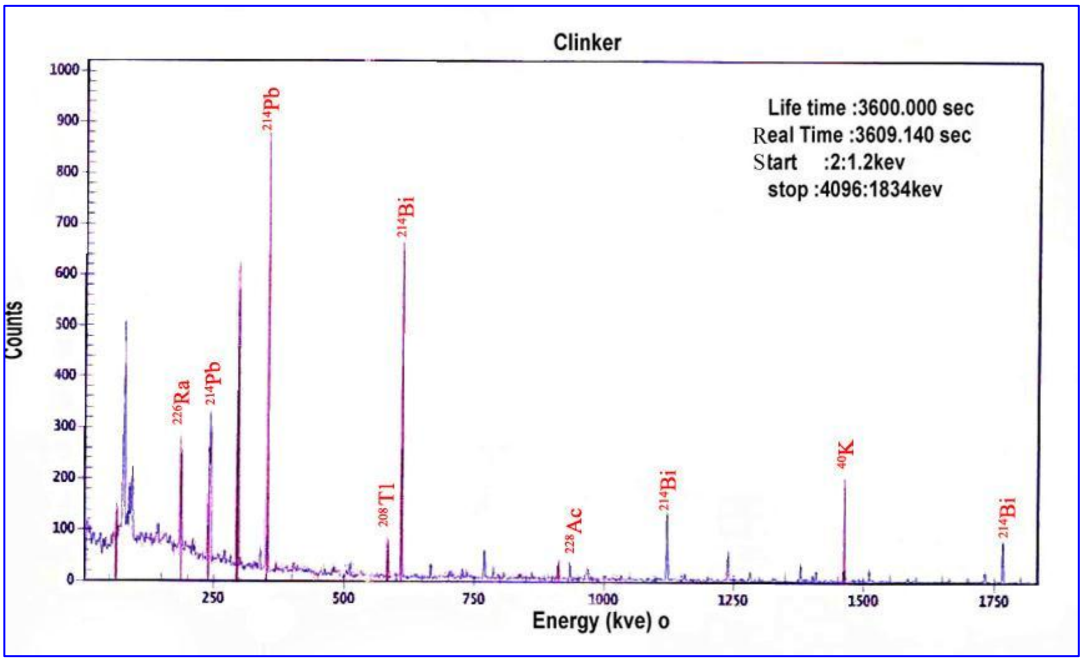


Figure 4-4: Gamma-ray spectrum of clinker sample.

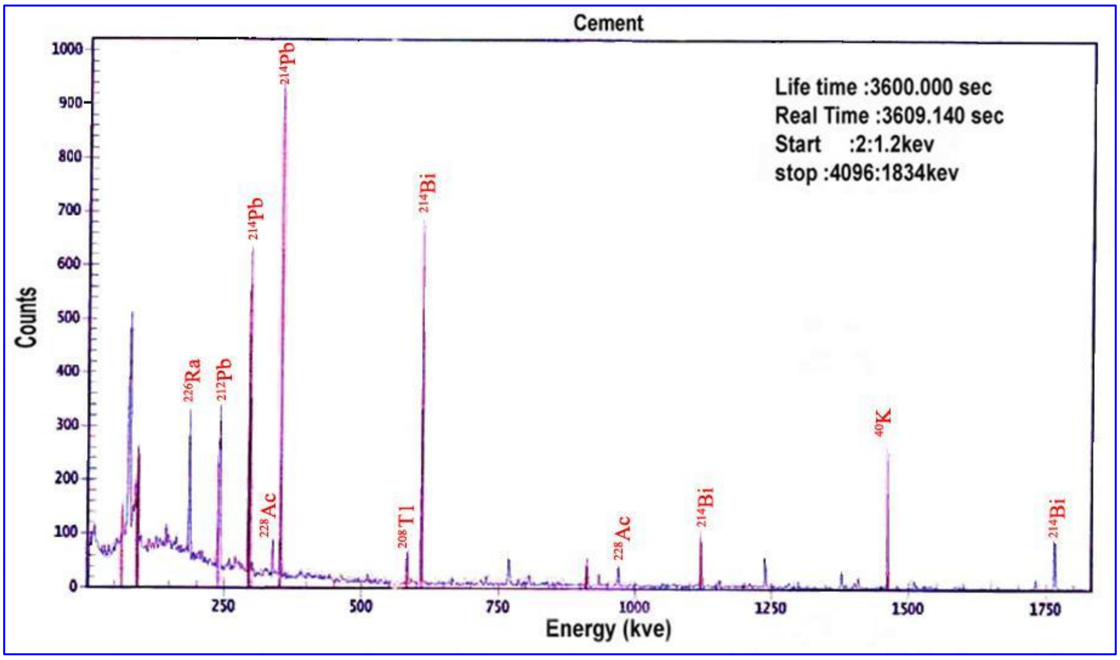


Figure 4-5: Gamma-ray spectrum of Portland cement sample.

4.3.3 Radium-226

Radium is the heaviest in alkaline earth elements. It is well known that strontium and radium are chemically similar to Ca and radium exists in the environment typically as a divalent cation. Ra, which behaves similarly to Ca, may form aqueous complexes with sulfate ions or carbonate ions (Zhang et al., 2002). Zhang et al. (2001) suggests that Ra can form both inner- and outer-surface complexes on the clay surface. In addition Ra has higher affinity for Mn hydrated oxides (Moore and Reid, 1973). The elements ^{214}Pb and ^{214}Bi are represented ^{226}Ra (Papastefanou et al., 2005). Activity concentration of ^{226}Ra of marl layer is ranging between 10.6 Bq kg^{-1} and 28.1 Bq kg^{-1} with mean 14.91 Bq kg^{-1}. In clinker is 31.8 Bq kg^{-1} and in cement is ranging between 35.3 Bq kg^{-1} and 35.8 Bq kg^{-1} with mean 35.55 Bq kg^{-1}. The distribution of ^{226} Ra in the study area is shown in Figure 4-6.

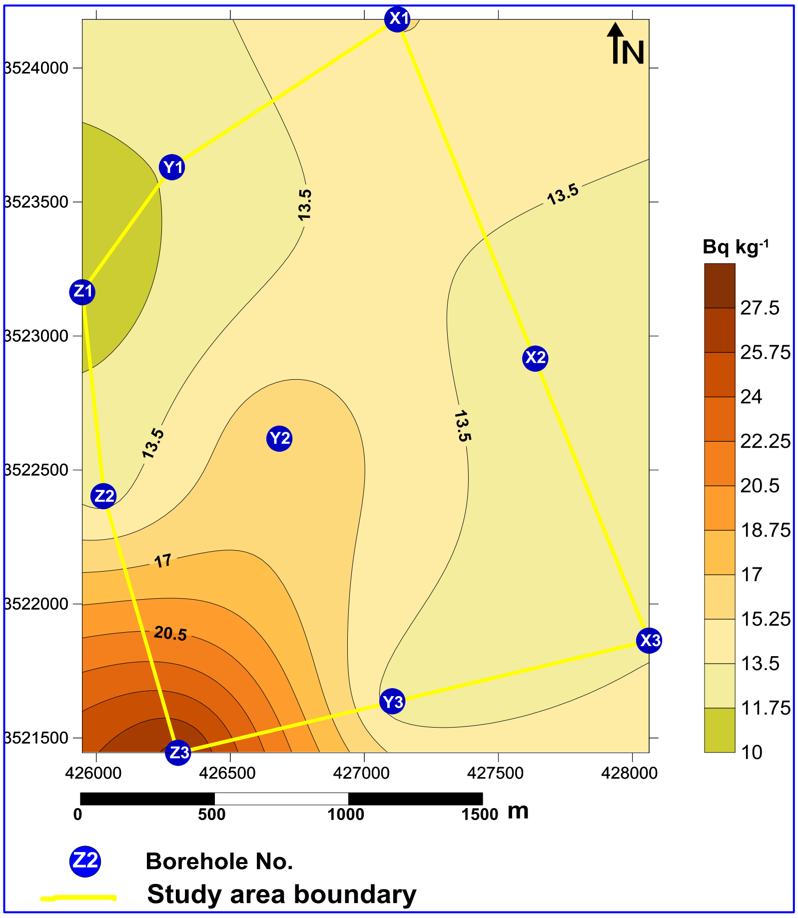


Figure 4-6: Pattern distribution of ^{226}Ra in marl layer of study area.

4.3.4 Thorium-232

Naturally occurring thorium is mainly the single isotope ^{232}Th (Herranz et al., 2008) which has a half-life of 1.4 x 10^{10} year. Hydroxides of thorium are the dominant species in soil and aquatic systems, although carbonate complexes also form (Zhang et al., 2002). The elements ^{208}Ti and ^{228}Ac are represented ^{232}Th (Papastefanou et al., 2005). Activity concentration of ^{232}Th of marl layer in is ranging from 4.4 Bq kg^{-1} to 6.2 Bq kg^{-1} with mean 5.16 Bq kg^{-1}. In clinker is ranging from 6.3 Bq kg^{-1} to 7.0 Bq kg^{-1} with mean 6.75 Bq kg^{-1} and in cement is ranging from 7.6 Bq kg^{-1} to 8.09Bq kg^{-1} with mean 7.42 Bq kg^{-1}. Any Th released by weathering has a transient existence in solution as it is strongly sorbed by clay minerals. Limestone is normally very low in

Th, since Th^{4+} cannot form a stable carbonate similarly and almost completely absent from evaporite deposits. Long-term exposure to Th increases the chances of developing lung diseases and lung, pancreas and bone cancer (Siegel and Bryan, 2003).

4.3.5 Potassium-40

^{40}K is a radioactive isotope of potassium which has a very long half-life of 1.248×10^{9} years. Activity concentration of ^{40}K in marl layer is in minimum 174.4 Bq kg^{-1} and in maximum 255.4 Bq kg^{-1} with mean 223.98 Bq kg^{-1}. In clinker is in minimum 83.7 Bq kg^{-1} and in maximum 99.3 Bq kg^{-1} with mean 91.5 Bq kg^{-1} and in cement is in minimum 107.3 Bq kg^{-1} and in maximum 114.3 Bq kg^{-1} with mean 110.8 Bq kg^{-1}. The percent of ^{40}K from total potassium percent was 0.72% because each 310 Bq kg^{-1} equal to 1% of potassium depending on Al-Kubaysi (2004). The results obtained from marl layer, clinker and cement in this study are compared with data from other countries. The activity concentration means of ^{226}Ra and ^{232}Th is lower than most of them but the activity concentration means of ^{40}K is higher than most of them as shown in Tables 4-3 and 4-4.

Table 4-3: Comparison specific gamma activities (Bq kg $^{-1}$) of the marl layer Euphrates Formation as raw materials with other countries.

Country	**Specific activity (Bq kg ¯1)**			**Reference**
	^{40}K	**^{226}Ra**	**^{232}Th**	
Iraq/ marl	223.98	14.91	5.16	Present study
Pakistan	13.80	14.32	2.05	Ali et al. (2012)
China	113.20	24.20	20.20	Xinwei and Xiaolan, (2008)
Greece	-	16.00	1.60	Papaefthymiou and Gouseti (2008)
India	64.60	73.09	-	Kumar et al. (2003)
Italy	13.50	13.10	6.00	Righi and Bruzzi (2006)
Syria	22.00	29.00	2.00	Othman and Mahrouka(1994)
Algeria	36	16	13	Amrani and Tahtat (2001)
Turkey	55.00	20.20	5.00	Turhan (2010)
Egypt	19.30	20.40	4.40	Sharaf et al. (1999)
Bangladesh	928.00	60.20	60.80	Alam et al.(1999)
Hong Kong	30.00	3.00	5.00	Tso et al. (1994)
Malaysia	222.00	40.70	25.90	Chong and Ahmed (1982)

The obtained results indicate that the distribution of natural radionuclides in the marl, clinker and cement samples are semi uniform (Tables 4-1 and 4-2).

Table 4-4: Comparison the specific gamma activities (Bq kg ¯1) in cement produced from marl raw material with other countries.

Country	**Specific activity (Bq kg ¯1)**			**Reference**
	^{40}K	**^{226}Ra**	**^{232}Th**	
Iraq/ cement produced by marl	110.8	35.55	7.42	Present study
Iraq/ Kufa cement	73.00	67.00	23.00	Ali (2012)
Iraq/Najaf cement	149.4	223.7	15.2	
Pakistan	245	25	37	Faheem et al. (2008)
China	163	68	52	Xinwei (2005)
Greece	284	63	24	Papaefthymiou and Gouseti (2008)
India	36	46	24	Kumar et al. (2003)
Italy	218	38	22	Righi and Bruzzi (2006)
Kuwait	240	13	9	Bou-Rabee and Bem (1996)
Algeria	422	41	27	Amrani and Tahtat (2001)
Turkey	267	26	41	Turhan (2010)
Egypt	220	48	22	Medhat (2009)
Bangladesh	1133	61	80	Roy et al. (2005)

The overall values of ^{226}Ra, ^{232}Th, and ^{40K} are also much lower than the activity concentration of 50, 50, and 500 Bq kg¯1 for ^{226}Ra, ^{232}Th, and ^{40}K, respectively, in typical masonry (UNSCEAR 1993). The concentration of ^{40}K and ^{232}Th in marl layer depends upon the relative amounts of the clay minerals (Ali et al, 2012). Depending on the mineralogical and chemical results there are K-bearing clay minerals in the marl. Illite contains high percent of K in the crystal lattice in addition to palygorskite as a result of substitution.

4.4 Assessment of radiation hazard

The knowledge of radioactivity in these materials is important to estimate the radiological hazards on human health. Conversion factors to transform specific activities A_K, A_{Ra} and A_{Th} of K, Ra and Th, respectively, in the absorbed dose rate at 1m above the ground (in nGy h^{-1} by Bq kg^{-1}) are calculated by many equations. There are many hazard indices commonly used to measure the exposures to gamma rays in building materials.

4.4.1 Radium equivalent activity

Radium equivalent activity (Ra_{eq}) is used to assess the hazards associated with materials that contain ^{226}Ra,^{232}Th and ^{40}K in Bq kg^{-1} (UNSCEAR, 2000) because their distribution in raw materials is not uniform (Slunga, 1988). The radium equivalent activity is a weighted sum of activities of the ^{226}Ra, ^{232}Th and ^{40}K radionuclides based on the assumption that 370 Bqkg^{-1} of ^{226}Ra, 259 Bq kg^{-1} of ^{232}Th and 4810 Bq kg^{-1} of ^{40}K produce the same gamma ray dose rate (Krisiuk et al., 1971). Radium equivalent activity can be calculated from the following formula suggested by Beretka and Mathew (1985). The published maximal admissible Ra_{eq} is 370 Bq kg^{-1} to keep the external dose below 1.5 mSv y^{-1} (UNSCEAR, 2000).

$$\mathrm{Ra}_{\mathrm{eq}} = 1.43A_{Th} + A_{\mathrm{Ra}} + 0.077A_{\mathrm{k}} \quad \text{.....................................} \quad (4\text{-}1)$$

Where: A_{Th}, A_{Ra} and A_{K} are the activity concentration of ^{232}Th, ^{226}Ra and ^{40}K in Bqkg^{-1} respectively.

The Ra_{eq} in the marl layer is 37.97 Bq kg^{-1}, in clinker is 47.86 Bq kg^{-1} and in Portland cement is 53.92 Bq kg^{-1}. It appears acceptable value and no hazard because it is lower than the standards.

4.4.2 Gamma index

In order to assess whether the safety requirements for building materials are being fulfilled, a gamma index proposed by the European Commission (EC, 1999) was used the following formula (Stojanovska et al., 2010):

$$I\gamma = \frac{A_{Ra}}{300} + \frac{A_{Th}}{200} + \frac{A_{k}}{3000} \quad \text{..} \quad (4\text{-}2)$$

The (EC, 1999) recommends that gamma dose rate due to building materials should be in the range of 0.3 – 1 mSv y^{-1}. The value of Iɣ of marl layer is 0.0755 mSv y^{-1}, in clinker is 0.1397 mSv y^{-1} and in Portland cement is 0.1556 mSv y^{-1} which below the EC index. Consequently, it appears acceptable value and no hazard.

4.4.3 External hazard index

The external hazard index (H_{ex}) resulting from the exposure to gamma rays of naturally occurring radioactive materials has been evaluated as an estimate of radiation risk. In order to evaluate this index, a model proposed by Beretka and Mathew (1985) was used in the current study:

$$\mathrm{H_{ex}} = \frac{A_{\mathrm{Ra}}}{370} + \frac{A_{Th}}{259} + \frac{A_{\mathrm{k}}}{4810} \leq 1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4-3)}$$

Where: A_{Ra}, A_{Th} and A_{K} are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K respectively. This index value must be less than unity in order to keep the radiation hazard in significant (Krieger, 1981). The total air absorbed dose rate (nGyh^{-1}) due to the mean activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K (Bq kg^{-1}) can be calculated using the formula of UNSCEAR (1988). The value of H_{ex} in the marl layer is 0.1068 nGyh^{-1}, in clinker is 0.131 nGy h^{-1} and in Portland cement is 0.1478 nGy h^{-1}. The results appear acceptable value within the limits of standards and no hazard.

4.4.4 Outdoor absorbed dose

The total air absorbed dose rate (nGy h^{-1}) due to the mean activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K (Bq kg^{-1}) can be calculated using the formula of UNSCEAR, 2000.

$$D\_out = 0.462\, A\mathrm{Ra} + 0.604\, ATh + 0.042\, Ak \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4-4)}$$

Beck et al. (1972) derived this equation for calculating the absorbed dose rate in air at a height of 1.0 m above the ground from measured radionuclides concentrations in environmental materials. The UNSCEAR (2000) recommends that the average absorbed dose rates due to building materials less than 51 nGy h^{-1}. The value of the marl layer in the study area is 19.41nGyh^{-1}, in clinker is 22.61 nGy h^{-1} and in Portland cement is 25.65 nGy h^{-1}. The results appear acceptable value within the limits of standards and no hazard.

4.4.5 Internal hazard index

In addition to the external hazard, Radon (^{222}Rn), a radioactive noble gas with a half-life of about 3.8 days and daughter product of ^{226}Ra, accounts for half of the radiation dose to the general population (Porstendörfer, 1994) and is currently considered as a major source of lung cancer (Al-Zoughool and Krewski, 2009). The internal exposure to Radon and its daughter products are quantified by the internal hazard index (H_{in}) which has been calculated by the following relationship (Beretka and Mathew, 1985):

$$H_{in} = \frac{A_{Ra}}{185} + \frac{A_{Th}}{259} + \frac{A_k}{4810} \leq 1 \ldots\ldots (4\text{-}5)$$

Where: A_{Ra}, A_{Th} and A_K are the mean activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K, respectively, in (Bqkg^{-1}). H_{in} should be less than unity for a radiological safe material (Turhan et al., 2008). The H_{in} value in marl layer is 0.1471 nGyh^{-1}, clinker is 0.21698 nGy h^{-1} and cement is 0.24384 nGy h^{-1}. The results appear acceptable value within the limits of standards and no hazard.

4.4.6 Indoor absorbed dose

The activity indices presented above are used for assessing whether the safety requirements are being fulfilled for materials which might be of concern. Any actual decision for restriction of use of materials should be based on a separate dose assessment into a scenario for the materials to be used (EC, 1999). The conversion factor used for calculation of the absorbed gamma dose rate D (nGyh^{-1}) (EC, 1999). A background dose rate of 50 nGyh^{-1} was corresponding to an average outdoor value in Europe was used.

$$Din = 0.92\, A_{Ra} + 1.1\, A_{Th} + 0.08\, A_k \ldots\ldots (4\text{-}6)$$

The value of Indoor absorbed dose of marl layer is 37.3116 nGyh^{-1}, in clinker is 44.001 nGy h^{-1} and in Portland cement is 49.732 nGy h^{-1} which are below the EC index. The results appear acceptable values within the limits of standards and no hazard.

4.4.7 Alpha index

The excess alpha radiation due to radon inhalation originating from building materials is assessed through the alpha index (Iα), which was calculated by using the following formula that proposed by Righi and Bruzzi (2006):

$$I\alpha = \frac{A_{\mathrm{Ra}}}{200} < 1 \ldots\ldots (4\text{-}7)$$

The recommended exemption level and recommended upper level of ^{226}Ra activity concentrations are 100 and 200 Bq kg^{-1}, respectively, in building materials as suggested in many countries of the world (Nordic, 2000). When the ^{226}Ra activity concentration of a building material exceeds the value of 200 Bqkg^{-1}, it is possible that radon exhalation from this material could cause indoor radon concentrations exceeding 200 Bq m^{-3}. On the other hand, when the ^{226}Ra activity concentration is <100 Bq kg^{-1}, then radon exhalation from the building materials could not cause indoor radon concentrations exceeding 200 Bq m^{-3} (Nordic, 2000). These considerations are reflected in the alpha index. The recommended upper limit concentration of ^{226}Ra is 200 Bq kg^{-1}, for which $I\alpha=1$. As can be observed from Table 4-1, the average activity concentration values of ^{226}Ra in the marl layer samples analyzed in the current study are less than the recommended exemption level of 100 Bq kg^{-1} and $I\alpha<0.08$, in clinker is 0.159 and in Portland cement is 0.1778 which are lower than the acceptable level. The safe use of materials in building construction requires Iα to be less than 1 (EC, 1990).

4.5 Radioactivity measurement of marl surface

The surface scan of radiation is conducted to measure the radioactivity of peripheral gamma-ray emitted from the marl layer under the measuring point on the surface to a depth of 30-50 cm (Eisenbud and Gesell, 1997). The sensitivity for gamma-ray is increased at greater depths if fractures and joints are present. The unit count per second is used or measurements. The values of count per second are adopted in the current measurements of radioactivity to the total count for gamma-ray by using the Scintillometer with scale f-150. The extent and rate of surface radioactivity (total count) and the location of borehole are illustrated in Table 4-5.

It was giving an idea to know out total concentration of radionuclides ^{238}U, ^{232}Th and ^{40}K without determining concentration of each nuclide where were concentrations measured. The measurement of radiation in every borehole site is an average of four to five reading by Scintillometer.

Field measurements by Scintillometer in the current study show the rates of normal background radiation (prevailing) in the study area to be between 91.92-141.22 C/S. In addition four outcrops of limestone are measured too from adjacent areas and the results appear less than that of the marl layer. The distribution of count gamma- ray portable spectrometer values of study area are shown in Figure 4-7. The higher values of measurement in study area are Axis extending from Y3 to Y1 boreholes and the lower in the sides of study area especially in boreholes X2 and Y2.

Table 4-5: Results of gamma ray in the study area.

BH No.	UTM-Coordination		Gamma ray (c/s)
	Easting	Northing	
X1	427122.7	3524181.7	111.91
X2	427637.6	3522915.6	93.26
X3	428062.3	3521863.2	133.22
Y1	426282.1	3523630.0	119.9
Y2	426683.1	3522616.9	133.22
Y3	427104.4	3521636.9	141.22
Z1	425947.6	3523163.2	96.92
Z2	426026.8	3522402.3	91.92
Z3	426305.1	3521444.6	130.56
Limestone Outcrop near Z2			87.93
Limestone Outcrop near Z3			87.93
Limestone Outcrop near Y1			79.93
Limestone Outcrop near Z1			87.93

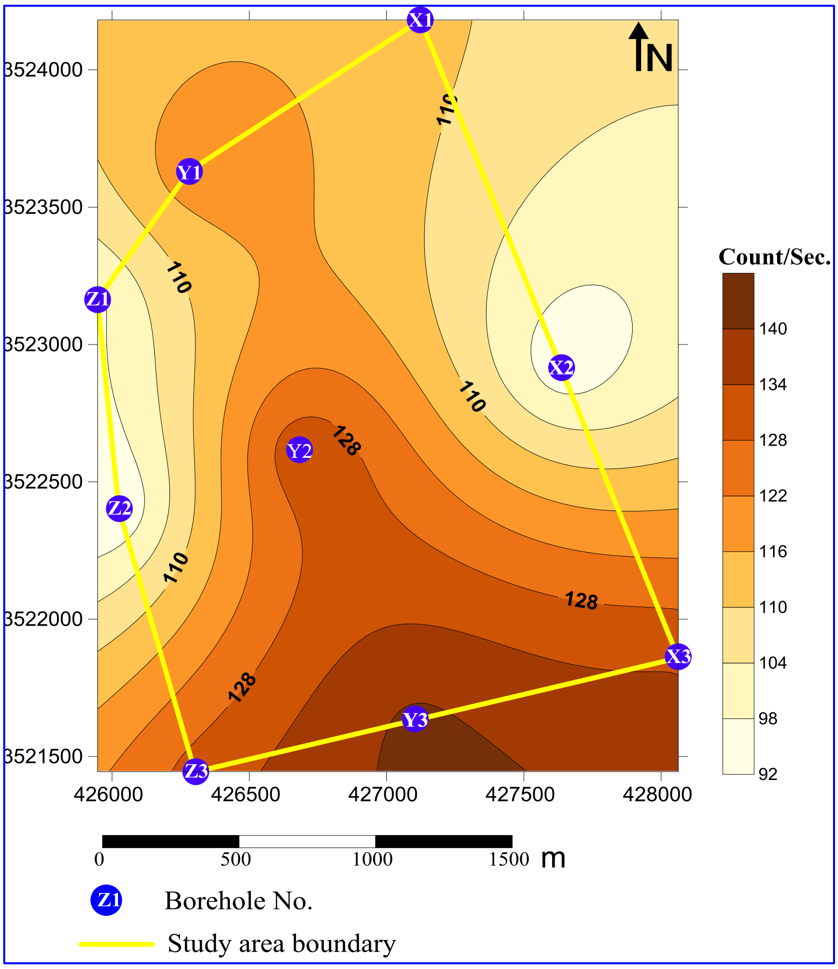


Figure 4-7: Distribution c/s values of gamma- ray spectrometer in study area.

4.6 Discussion

The natural radioactive series notably ^{40}K, ^{226}Ra and ^{232}Th are measured for marl samples and the products of clinker and cement. The results indicate that the main contribution to the background Gamma-radiation in samples of marl which consists of clay minerals and carbonate are within the universal limits. The occurrence of radioactive element is concentrated in clay minerals because of the capability of clays to adsorption the radioactive elements (Grim, 1962). The results of the marl and cement analyses show that they are safe within the limits of the European Commission specifications (1999) for building materials. Therefore, the use of cement produced from marl in construction of dwellings is considered to be safe for inhabitants. The hazard indices of marl layer, clinker and cement are within the limits of (UNSCEAR, 2000). That means the marl layer is suitable for industry and cement is suitable for construction. The activity concentration of ^{226}Ra, ^{232}Th and ^{40}K for all measured samples of raw materials clinker and cement are comparable with the corresponding values of other countries. The obtained results show that the averages of radiation hazard parameters are lower than the acceptable level. Therefore, the use of the marl as raw materials is considered to be safe for human habitation. The clinker and cement parameters are quite safe to be used for residential construction. The high concentration of radiation in construction material is very harmful for all domestic uses including digestion and inhalation. Cancer is a major effect of low radiation doses expected from exposure to radioactive contamination especially cancers of the lungs, female breast, bone, thyroid and skin (Siegel and Bryan, 2003). The ^{40}K of raw material is higher than the product as a result of the volatilization alkalis during the burning of raw materials.

Chapter Five

Conclusions and Recommendations

5. Conclusions and Recommendations

5.1 Conclusions

The following conclusions are drawn from the present study:

1. This study indicates the existence of marl layer with 8.5 m thick within the Euphrates Formation consisting of two horizons. Upper horizon is marly limestone (0.5m) thickness; lower horizon is marl of about 8 m.

2. Calcite is a dominant non-clay mineral with mean percentage of 58.12%. Other minerals such as quartz (6.36%), dolomite (1.75%) occurred in minor amounts. Suite of clay minerals like montmorillonite (13.16%), Palygorskite (10.46), illite (6.46%) and kaolinite (3.74%) also present in the marl layer. These minerals are suitable for cement industry.

3. The cement would be a good quality product at a lower cost due to the components CaO, SiO_2, Fe_2O_3 and Al_2O_3 being naturally present in a very finely crystalline stat and naturally well blended. They lead to a large reactive surface area helped in the reaction in the kiln and reduce the duration time for mixing processes in the preparation of the raw materials. That leads to reduced production costs and extend the life of production equipment.

4. All analyzed oxides show that the marl layer contains a qualified raw material appropriate for the cement industry and alternative raw material can be used instead of clay and limestone. The appropriate raw mix of kiln feed must be corrected by adding 22% limestone from adjacent areas. The kiln feed parameters of marl layer are within the typical limits.

5. The use of marl in the cement industry will help to improve conditions of burnability in the rotary kiln because of good content of Al_2O_3 and Fe_2O_3. These oxides will work to increase the liquid phase in the kiln, which facilitates the process of ion exchange between the components of the raw materials mixture and the formation of compound C_3S in lower temperature. This will lead to reducing fuel consumption and forming coat that help to protect the refractory lining and kiln shell and increase the time period for the use of bricks. As a result, this will reflect positively on the cost of the clinker and reduce the cement price.

6. Low alkali and sulfate concentrations will lead to the production of low-alkali cement which is a favorite in the cement manufacture and reduce detrimental contaminants in the kiln. In addition to, they reduce of build-up, blockages and operating problems resulting from their presence.

7. Depending on Bogue calculations, the percentage of C_3S is relatively high within the standard specification which means good quality cement.

8. A new resource of raw materials (marl) suitable for cement industry with 53 million tons is determined. A probable reserve is estimated using many methods. The triangle method is preferred due to its accuracy.

9. The low stripping ratio of the overburden with weak hardness has a significant economic benefits making the reserve mineabilty very easy and then eventually reducing the final cost of cement.

10. The distribution of Gamma ray and ^{232}Th, ^{226}Ra and ^{40}K concentrations and the radiation hazard are assessed and appear safe and within the acceptable limits.

11. Many economic advantages are expected when using the marl layer in the study area in the cement industry. It easily reached, exposed at the surface, flat occurring in areas with good transport roads. All of these are encouraging reasons to exploitation as a raw material in the cement industry.

5.2 Recommendations

1. The marl layer needs to be corrected by mixing with limestone of high $CaCO_3$ from adjacent area in order to do an optimum kiln feed raw mix.

2. New exploitation for cement plant in Al-Najaf Governorate will be benefit from this marl layer as a raw materials alternative for clay quarry.

3. Marl is perfect for dry process rather than for wet process because the ability of the clay minerals for swelling causes many operational problems

in the raw mill such as blocking and closing the slits of the diaphragm which cause increase moisture in the raw mixture.

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المستخلص

يتضمن البحث دراسة نوعية وكمية واشعاعية لتقييم طبقة المارل في تكوين الفرات (المايوسين الاسفل) كمادة اولية لصناعة السمنت البورتلاندي. تقع منطقة الدراسة ضمن مقلع معمل سمنت الكوفة في بحر النجف، وتبعد مسافة 26 كم الى الجنوب الغربي من مدينة النجف الاشرف.

اظهرت الدراسة المعدنية باستخدام تقنية الاشعة السينية الحائدة ان التركيب المعدني لطبقة المارل يتألف من معادن غير طينية ومعادن طينية. تمثلت المعادن غير الطينية بمعدن الكالسايت، وهو السائد، يليه بنسبة اقل معدن الكوارتز، ونسبة ضئيلة من معدن الدولومايت. أما المعادن الطينية فالسائد فيها هو معدن المونتمورلونايت ثم الباليغورسكايت والالايت والكاؤولين.

اظهرت الدراسة الجيوكيميائية بان معدلات النسب المئوية للأكاسيد في هذه الطبقة هي: CaO (37.81%)، SiO_2 (17.88%)، Al_2O_3 (4.24%)، Fe_2O_3 (2.79%)، MgO (1.79%)، SO_3 (0.35%)، K_2O (0.73%)، Na_2O (0.06%)، P_2O_5 (0.14%)، TiO_2 (0.27%)، Sr (273 ppm)، Mn (279 ppm) بالاضافة الى Cl^- (<0.02%).

تبين أن اغلب الاكاسيد ضمن حدود الجودة المطلوبة في المواصفات القياسية لخليط المواد الاولية الداخلة الى الفرن، فيما عدا تركيز أوكسيد الكالسيوم (CaO) فقد كان منخفضا، مع زيادة طفيفة في كمية السليكا (SiO_2). لغرض الحصول على خلطة ذات مواصفات قياسية لصناعة الكلنكر، يجب معالجة الزيادة والنقصان في كميات المواد الاولية. لهذا السبب، تم أجراء الحسابات المتعلقة بتصميم خلطة المواد الاولية الداخلة للفرن. بينت هذه الحسابات ان المارل يحتاج الى ان يخلط مع 22% من صخور جيرية ذات محتوى عالي من أوكسيد الكالسيوم (CaO) وهي متوفرة في المناطق المجاورة للمقلع.

عند تهيئة خلطة للمواد الاولية وفق نسب الاكاسيد الملائمة لتغذية الفرن، فان من الضروري حساب المعاملات المؤثرة في إنتاج الكلنكر. تم حساب هذه المعاملات وهي معامل الاشباع الكلسي (92.16) ومعامل السيليكا (2.57) ومعامل الالومينا (1.5) و المعامل الهيدروليكي (2.11) ومعامل الاشباع السيليكي (0.88) ونسبة الجير الى السليكا (4.29). تدل هذه النتائج الى ان هذه المعاملات هي ضمن المواصفات القياسية، وكفيلة بإنتاج سمنت عالي النوعية.

تم انتاج الكلنكر بواسطة حرق عينتين من خلطة المواد الأولية بحرارة 1450°م وبمدة 220 دقيقة. بعد ذلك تم فحص الكلنكر بالأشعة السينية التي اكدت وجود المركبات الاساسية (, C_2S, C_3A, C_3S و C_4AF). إن تكون هذه المركبات دليل على نجاح طريقة تصنيع السمنت البورتلاندي.

تم تقدير الاحتياطي بعدة طرق (المثلثات والمضلعات والطريقة البيانية وطريقة الاحداثيات الجغرافية وطريقة نظم المعلومات الجغرافية و طريقة بولدريف)، بينت انه احتياطي مؤكد قدره 53 مليون طن تقريبا قابل للزيادة مستقبلا. هذا الاحتياطي يكفي لتشغيل معمل سمنت بطاقة 1.5 مليون طن/ سنة لمدة تتجاوز 26 سنة.

أجريت دراسة اشعاعية للمقلع باستعمال العداد الومضي لتسجيل مستويات الاشعاع وضمان سلامة العاملين في المقلع. كانت النتائج ضمن الخلفية الاشعاعية الطبيعية. أجريت قياسات اشعاعية لعينات مارل لتقييم طبقة المارل بدلالة ^{226}Ra و ^{232}Th و ^{40}K للعينات. دلت النتائج ألمستحصلة ^{226}Ra (14.91)، ^{232}Th (5.16) ، ^{40}K (223.98) بكريل/ كغم بان الاشعاع لم يتجاوز الحدود المسموح بها عالميا.

وكذلك تم فحص مستوى الاشعاع في عينات الكلنكر والسمنت المحضر من المواد الاولية ، لتقييم تأثيره على المستهلك. كانت نتائج الفحص الاشعاعي للكلنكر ^{226}Ra (31.18 ، ^{232}Th (7.6) ، ^{40}K (91.5 بكريل/ كغم وللسمنت ^{226}Ra (35.55 ، ^{232}Th (7.42) ، ^{40}K (110.18) بكريل/كغم وهي ضمن حدود المواصفات العالمية.

من المزايا التي تشجع على استغلال طبقة المارل هو صلابته الواطئة جدا مما يتيح قلعها بوساطة الحفارات الهيدروليكية، ولا توجد حاجة لاستخدام المتفجرات، وانعدام الطبقة الغطائية في 72% من المساحة الكلية للمقلع مع معامل كشف واطئ جدا لا يصل الى 0.033، وأنكشافها على السطح، وقربها من طرق المواصلات الذي يسهل حركة العاملين والمعدات.

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة بغداد
كلية العلوم
قسم علم الارض

تقييم كمي ونوعي واشعاعي لطبقة ألمارل في تكوين الفرات لصناعة السمنت البورتلاندي في مقلع سمنت الكوفة في محافظة النجف

اطروحة مقدمة الى
مجلس كلية العلوم/ جامعة بغداد
وهي جزء من متطلبات نيل درجة الماجستير
في علم الارض (الجيوكيمياء)

من قبل
مهند راسم عباس العويدي

بكلوريوس علوم جيولوجي (١٩٩٠) جامعة بغداد

بإشراف
أ .م . د صالح محمد عوض و أ. م. د كمال كريم علي

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