CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

1. General

Cement is considered as first hydraulic water bound material in this age. It is used in concrete and mortar industry, projects and residential building ,and roads. Cement industry is of strategic industry that relies on the simple availability of raw materials.

Cement, in the general sense of the word, can be described as a material with adhesive and cohesive properties which make it capable of bonding mineral fragments into a compact whole, for constructional purposes the meaning of cement is restricted to the bonding materials used with stones, sand, bricks, building, blocks, etc (Neville 1981).

1.1 Historical note:

The use of cementing materials is very old, the ancient Egyptians used calcined impure gypsum, the Greeks and Romans used calcined lime stone and later learned to add to lime and water, sand and crushed stone, this was the first concrete in history.

The middle age brought a general decline in the quality of cement, and it is only in the 18th century that an advance in the knowledge of cements can be reported. Then followed a development of hydraulic cement, (Neville 1981).

Hydraulic cement is considered the most versatile binders yet known to man (cement and concrete association 1987), they enable him to make massive constructions such as dams and foundation, slender highly stressed such as bridges and high rise buildings and paved areas such as roads and airfield runways. Hydraulic cements react exothermally with water to form hard, strong masses having extremely low solubility.

The world demand for these cements is measured in hundreds of millions of tons per year, which means that they have to be produced from naturally occurring raw materials rather than from pure chemicals. Because of this, commercials hydraulic cements contain a range of active compounds rather than one compound alone, (Shirley et al. 1985).

Each year sees the use of vast qualities of concrete composed only of cement, natural aggregate and water, mixed and placed on site with relatively simple and inexpensive equipment's

1.2. Types of cements:-

The cement currently can be grouped into four main categories:-

- Portland cement.
- Blended Portland cement.
- Portland cement with additives.
- High alumina cement.

The first two categories are the most widely used, the last two being required mainly for special purposes. High alumina cements differ completely from Portland cements both in compositions and methods of manufacture. The techniques for their use too, differ significantly in some respects from those appropriate to Portland cement, (Shirley et al. 1985).

1.3. Portland cement:-

Portland cement is the most common type of cement in general use around the world, used as basic ingredient of concrete and mortar.

There are different standards for classification of Portland cement. The two major standards are the ASTM C 150 used primarily in the USA and European EN197. ASTM C150 defines Portland cement as "hydraulic cement" (cement that can not only hardens by reacting with water but also form a water -resistant product).

1.3.1 Back ground:-

Portland cement was developed from natural cements made in Britain in the early part of nineteenth century, its name is derived from its similarity to Portland stone, a type of building stone quarried on the isle of Portland in Dorset England, (‘Portland cement’ 2014).

Joseph Aspdin , a British brick layer from Leeds, is considered to be one of the originator, of Portland cement after Louis vacant in 1817. A process for the manufacture of Portland cement was patented in 1824 (‘Portland cement’ 2014). This cement was an artificial cement similar in properties to the material known as "Roman Cement ", which had being patented in 1796 by James Parker. Aspdin's process was similar to a process patented in 1822 an used since 1811 by James Frost who called his cement "British Cement", the name "Portland cement "is also recorded in directory published in 1823 being associated with a William Lock Wood, Dave Stewart, and possible others (‘Portland cement’ 2014).. James Frost is reported to have erected a manufactory for making of artificial cement in 1826 (‘Portland cement’ 2014).

In 1843, Aspdin's son William improved their cement. William Aspdin made what could called meso - Portland cement (a mix of Portland cement and hydraulic lime), (‘Portland cement’ 2014). John Grant, in 1859 set out requirements for cement to be used, and this became specification of Portland cement. The association of German cement manufactures issued a standard on Portland cement in 1878 (‘Portland cement’ 2014).

There are several methods of preparing and blending the raw materials for feeding into the kiln. These generally are the wet process and the dry process. The choice of each method is influenced by economic and technical considerations. The wet process is suited to friable raw materials such as chalk and clay, which readily break down in water to form slurries. For hard raw materials such as limestone and shale the dry process may be preferred where each component is ground to a fine powder before being blended and transported to the kiln in an air stream.

1.3.2 Uses:-

The most common use for Portland cement is in the production of concrete. Concrete is a composite material consisting of aggregate (gravel and sand), cement, and water. As a construction material, concrete can be casted in almost any shape desired, and once hardened, can become a structural (load bearing) element. Users may be involved in the fas panels, beams, road furniture, or may make cast-in situ concrete such as building superstructures, roads and dams.

Portland cement is also used in mortars (with sand and water only) for plasters and screeds and grouts. When water mixed with Portland cement, the product sets in few hours and hardens over a period of weeks. This process can vary widely depending upon the mix used and the conditions of curing of the product.

The low cost and widespread availability of the naturally occurring materials make Portland concrete one of the most versatile construction material available in the world.

1.3.3 Raw materials of Portland cement:-

Portland cement was first produced in 1824 by Joseph Aspdin. Since then many refinement changes in the scale and type of plant, and improvement in methods of control and testing have been made.

The basic materials for the manufacture of Portland cement are usually forms of limestone and clay. Chalk commonly provides the calcareous materials, while clay provide argillaceous materials, which is mainly alumina and silica. The calcareous and argillaceous materials most commonly used are those which occur naturally.

1.3.3.1 Calcareous materials:-

The most important calcareous material is limestone which occurs in a variety of forms, chalk, other sedimentary limestone, coral, and secondary limestone and carbonate.

Other calcareous materials include shell deposits which may be dredged from the sea, lake or river beds and also marls which calcareous muds whose composition is sometimes suitable for cement making without admixture of other materials.

1.3.3.2 Argillaceous materials:-

Natural weathering processes tend to remove soluble components of rocks leaving the insoluble oxides of silicon, iron and aluminum as a result; many weathered rocks can provide argillaceous materials for cement manufacture.

The most common materials are clays, marls and mudstones. Clays and mud can be converted to slurries by vigorous stirring in water. Usual impurities are free silica, sulphur and alkalis. The behavior of raw materials throughout the manufacturing process is much influenced by the minerals present in clay and chalks.

1.3.3.3 Other materials:-

Many cement works are based on one calcareous and on argillaceous materials. At least as many use three or more components materials in order to obtain the required control of composition. Usual “correcting” materials are iron oxide in various forms, and sand or sand stone to gives sufficient silica.

An additional calcareous material of high calcium carbonate content is frequently used to raise calcium carbonate of the raw materials mixture.

Certain industrial waste products containing one or more of the four basic oxides may also be regarded as raw materials (Blast-furnace slag, pulverized fuel ash and precipitated calcium carbonate). The use of these wastes for the manufacture of Portland cement is small compared with that of naturally occurring materials.

However, the sites of cement works are normally chosen at places where both these types of materials (calcareous and argillaceous materials) occur adjacent to one another.

1.4 Portland cement compounds:-

Portland cement consists of four compounds:

Tri calcium silicate C_3S, dicalcicm silicate C_2S, tri calcium aluminates C_3A and tetra calcium alumina ferrite, C_4AF. According to B.S these main compounds are given in table 1. These compounds are formed by series of reactions at temperatures rising to region 1300 -1500^{o}C between lime on one hand and silica, alumina and iron oxide on the other. Optimum cement quality is obtained when the required proportions of the four oxides are consistent throughout the cement, (Pollitt, cited in Bogue 1955).

The basic cement making process consists therefore in quarrying calcareous and argillaceous materials in the required proportion, reducing these materials to finely divided states, blending them to a uniform composition and heating them, first: to drive off any water and carbon dioxide, secondly: to the point of incipient fusion when the cement compounds are formed, finally, the resulting clinker as it is termed is cooled and grinded with gypsum to fine powder which is Portland cement, (Pollitt 1964).

Gypsum is added during the grinding clinker to control the setting properties of the cement and can thus be considered a raw material.

Table 1: Compounds in Portland cement:-

Name	**Empirical formula**	**Oxide formula**	**Short formula**
Tricalcium silicate	Ca_3SiO_5	$3CaO.SiO_2$	C_3S
dicalcicm silicate	Ca_2SiO_4	$2CaO.SiO_2$	C_3S
Tricalcium aluminates	$Ca_3A1_2O_6$	$3CaO.A1_2O_3$	C_3A
Tetracalcium aluminoferrite	$2Ca_2A1FeO_5$	$4CaO.A1_2O_3.Fe_2O_3$	C_4AF

1.5 Types of Portland cement:-

Various classes of Portland cement have been developed:

I. Ordinary Portland cement:-

This cement is suitable for most types of work and is thus the most widely used of hydraulic cement, (Shirley et al. cited in B.S.12.1978).

II. Rapid hardening Portland cement :-

It is similar in composition to ordinary Portland cement but more finely grinded. The finer grinding, however, increase the rate of hydration at early ages, and this leads to the increased rate of early hardening.

III. Ultra – rapid – hardening Portland cement:-

It has a chemical composition similar to that of ordinary and rapid hardening Portland cement, but is much finer than either of these. This fineness imparts an exceptional rate of early strength development.

IV. Sulphate – resisting Portland cement:-

B.S. 4027 limits the permissible Tricalcium aluminates ($Ca_3A1_2O_6$) content of this cement. It is the hydration product of this compound which is susceptible to attack by the sulphates present in some soil. Sulphate – resisting Portland cement tends to be darker in colour than ordinary Portland cement , but has otherwise broadly similar properties to ordinary Portland cement.

V. Low-heat Portland cement:-

This cement contains less tricalcium silicate and more dicalcicm silicate than ordinary Portland cement, it thus hydrate more slowly and evolves heat less than the latter. Low-heat Portland cement is at present made to special order only.

VI. White Portland cement:-

This cement is used primarily in work where a white concrete is required for visual effect. It complies with (B.S. 12) and is thus suitable for all application where ordinary Portland cement can be used. It is made from raw materials such clay and high – grade chalk, which are specially selected as being substantially free from colour – forming impurities such as iron oxide. Adding suitable pigments to white cement concrete produces a range of attractive colours.

VII. Portland – blast furnace cement:-

This cement is made by incorporating a controlled proportion of ground granulated blast furnace slag during manufacture. To comply with (B.S. 146.1958), the proportion of slag must not exceed 65% by mass of the combination.

The slag particles hydrate slower than those of cement, so that this cement evolves less heat and hardens more slowly than ordinary Portland cement.

VIII. Portland-pulverize fuel ash cement:-

It is a by –product of electricity generation. Ash complying with (B.S. 3892) is incorporated into this type of cement in a controlled proportion during manufacture. The properties of the product broadly resemble those of Portland – blast furnace cement.

IX. Low-heat Portland –blast furnace cement:-

In this cement a reduced rates of hydration and heat evolution are achieved by modifying the mineral composition and adding selected slag. This cement is normally made to special order only, (Shirley et al. 1985).

1.6 Physical and chemical Properties of raw material:-

The raw materials used for cement manufacture must be uniform in composition and texture and must have suitable chemical and physical properties.

The temperature at which the raw materials will satisfactory combine is function of the maximum size of particles present in them: the larger the particles the higher the temperature required. It is common to burn ordinary Portland clinker at temperature up to 1450^{o}C (produced materials for the kiln with no particles greater than 90 µ in size).

Much depends on the relative proportions of the silica, alumina, and iron oxide and of the form of silica. The fineness required for combination of the four principal oxides depends on their relative proportion in the mix and on the form of silica. Adequate combination also requires reasonable homogeneity of the composition of the mix. From ideal arrangement of particles of raw materials uniform clinker composition should follow.

The demand for homogeneity therefore rests on, first, the need to avoid uncombined lime and silica, and, second ,the possibility of achieving combination with a minimum on burning.

The principal impurities occurring in raw materials and having significant effects on the properties of cement are, magnesia, fluorine compound, phosphates, lead oxide and zinc oxide, sulphides and alkalis.

Magnesia is considered harmful because in normal processing with relatively slow cooling of the clinker it can emerge in the cement as percales, which is capable of expansion on hydration long after the cement has hardened and can thus disrupt the mortar or concrete. In British standard, the maximum permitted magnesia content is 4% -in ASTM is 5%.

Fluorine compounds have been found variably successful as fluxing agent. On the other hand, the presence of more than 0.1% in the raw materials has been proved in Britain to produce disastrous reduction in cement strength below that obtainable if the fluorine is absent. There for, unless there is especial need for it is fluxing action it is regarded as undesirable and removed from the raw materials.

Phosphates affect adversely both kiln operation and the setting and hardening of the cement produced; 0.20- 0.25%in the cement has an optimum beneficial effect on strength but more than that 0.5% is deleterious.

Lead and zinc oxides have fluxing action, thus, 1% zinc oxide reduce from 7.5 to 2.7% the uncombined lime. Both oxides have deleterious effect on cement properties.

Sulphides are important for three principal reasons: First; they may oxidize to sulphates, producing calcium sulphate in the clinker, which being less soluble than gypsum, Secondly, they may oxidize to produce alkali sulphates with the consequences discussed above. Thirdly, they may help to promote reducing conditions in the kiln with adverse effects on cement strength under certain conditions.

Alkalis affect plant operation and the properties of the finished cement. In wet processes corrosion of the kiln shell dust precipitator housing are promoted by alkali chloride in association with sulphur gases. In semi-dry processes alkali sulphates accumulate in inconvenient deposits which can be removed at regular intervals. In dry processes also an inconvenient deposit of alkali sulphate may again form. Alkali sulphates are recognized accelerators of the cement hardening processes. The U.S Federal specification limit is 0.6% of total alkali expressed as Na_2O, more alkali being required to promote expansion with high opaline silica content, (Pollitt 1964).

1.7 Processes and manufacture of Portland cement:-

The processes involved in Portland cement manufacture can be divided into the three stages of raw material preparation, heat treatment and clinker cooling and grinding, at all stages control is essential.

a) Raw Material Preparation:-

The objective of raw material preparation is to produce for heat treatment a properly blended materials and good mixed and sufficient fineness to ensure that proper combination can take place in the kiln.

The required uniformity of composition and fineness are obtained by methods which vary according to the nature of the raw material. Blending often begins during quarrying. The first step in quarrying is removal of overlying material known as over burden, which may be thrown away or sometimes used as correcting materials.

The next step with the hardest rocks, such as limestone, slates and certain shale's, is to loosen them by blasting, detonation permits the desired degree of fragmentation to be softer rocks such as chalk, marl, schist, clay and shale can be dug from the face by excavator.

Transport of the materials from the quarry face is by variety of methods, dug materials are usually handled by excavators into dump trucks or railway wagons or on to converter belts, dredged materials are transported wet by pipeline. The destination of the transported materials is the crushing and grinding plant, all the materials are crushed by crushers and their performance are described by

(Pollitt, cited in Taggart 1950), The crushed rock is then ground, often in ball and tube mills, which are used for both wet and dry processes.

A novel mill lift drop the coarse material, causing it to grind itself, this in dry process, soft materials are usually associated with wet processes and are broken down by vigorous stirring with water in wash mills.

The products of the mills are classified in order: (a) to reject unwanted coarse in the case of open - circuit grinding material or (b) to obtain the desired freedom from coarse particles in closed - circuit (feedback) grinding.

Classification in wet process milling has been effected by variety of means. Recent development of importance are the hydrocyclone (Pollitt, cited in symposium on recent development in mineral dressing 1953). The hydrocyclone is basically similar to the familiar dust collecting cyclone, but has water instead of gas as carrier fluid and a slurry pump instead of fan.

Classification in dry process grinding contains elutriation, in which the air velocity is sufficient to carry ground material, assisted by centrifuged action which tend to throw coarse particles out of the air stream.

By careful control of the feeding of the raw materials to the crushing and grinding processes, first approximation to the required chemical composition is obtained. A notable example of the control that can be achieved is provided by works in the USA (Pollitt, cited in Nalle 1960) with very variable raw materials. Chemical analyses showing the variation in content magnesia and siliceous rock , are fed to digital computer which, by linear programming techniques optimizes the quarrying programming in such away as to minimize the need for (a) expensive additional materials such as iron ore , and (b) switching the quarry of plant too frequently. The optimized program also ensures that the maximum least satisfactory limestone is used and produces the theoretically correct composition in the mix. The crushed and imported materials are laid down in thin layers on long stockpile.

Samples are taken automatically and analysis of these are fed back to the computer to correct the quarrying programmers. Mixing in the wet process is affected by stirring the slurry in large cylindrical tank by mechanical or compressed air action. In dry process the dry powdered mix is often blended in silo by vigorous circulation induced by fluidization, (Pollitt, cited in Maneck, 1954).In most cases the procedure described results in slurry or powder which can be fed to the kiln.

Soft material rich in impurities is removed from coarse hard rock by washing and screening. The most complex is flotation process, (Pollitt, cited in Craddock 1952). In the types of flotation process the materials must be sufficiently finely ground to break down aggregation of the desired and undesired material and to permit flotation. Flotation produces slurries of high water content and is therefore usually followed by sedimentation, as in a thickener, to reduce the amount of water to be boiled off and thus improve heat economy.

The demand for economy in fuel has led to the development of other means of reducing the water content of slurry from its normal level of 35-45 % by weight.

Dry powder, as normally fed to dry process kiln, is sometime nodules.The powder is fed into a rotating dish whose axis is inclined from the horizontal so as to retain the feed. Cylindrical and conical drum nodulizers are also used. A fine water spray causes the powder to form nodules. The water is commonly 10-15% depends of the nature of the materials, and behavior during heat treatment.

b) Heat treatment:-

Reactions and temperatures in rotary kilns are discussed by (Pollitt, cited in Lea 1956 and Lyon 1962). The basic steps in the heat treatment are boiling off any slurry water at up to 100^{o}K, combustion of any organic matter and decarbonation of the calcium carbonate at up to100^{o}K, heating the decarbonated feed to 1300-1500^{o}C according to its composition and fineness, maintaining this temperature sufficiently long for the cement compound to form, and finally cooling the resulting clinker. These operations may proceed in one kiln, as in the case of shaft kilns, in a kiln and cooler, as in the majority of wet and dry processes, and, more recently, in preheater, kiln and cooler. In shaft kilns, the raw material is mixed with the fuel, usually coke, briquetted or nodulized, and introduced at the top the vertical cylindrical kiln. An upward flow of combustion air from the bottom is maintained by blowers. Combustion occurs in the lower half, the descending feed thus being heated by the rising products of combustion until it passes through the combustion zone. After this it is cooled by the air for combustion.

By far the majority of the worlds cement works operate the rotary kiln. Rotary kiln are up to 575ft (175m) in length and up to 19ft (6m) in diameter, (Pollitt, cited in Comte 1959). The heat requirement for the wet process is of the order of 1500- 2000 kcal/kg. Similar figures obtained for the traditional dry processes and they reflect how much heat is wasted in the kiln gasses.

The prepared raw material feed is introduced at the upper" back" end, from which it is transported by the slope and rotation of the kiln to the lower, hotter, end. Here, a flame is maintained by injecting fuel through a pipe. The flame creates in its immediate vicinity the burning zone, where the cement compounds are formed. From the burning zone, the combustion gases pass up the kiln losing heat to the incoming feed, until they pass from the kiln, to dust collector system. The feed passes successfully through the cyclones and finally inters the kiln at about 750^{o}C. The final gas temperature is about 300-350^{o}C.

Extremely efficient heat and mass transfer is obtained in this process, and special measures have had to be taken in certain installation to reduce the incidence of alkali sulphate deposits in the plant, (Pollitt, cited in Mussgnug 1962). The flame in rotary kiln is maintained by injecting fuel and air through burner pipe. The two principal fuels are pulverized coal and oil, natural gas is also used. Coal is ground in mills, air –mills are common, since air is necessary to transport the ground coal and hot air can dry damp coal. Oil for firing kilns often requires heating to reduce Its viscosity to level suitable for pumping and for atomization i.e. production of droplets by oil pressure or by air steam jets. Gas is supplied by pipeline and after necessary reduction in pressure is fed straight to the kiln.

The characteristics of flames are influenced by the fineness of ground coal or oil droplets, by the proportion, temperature and velocity of the primary air. The nature of the fuel is also important. Coal produces high emissivity and therefore greater radiant heat transfer than does oil. It is for this reason that the kiln exit gas temperature rises appreciably when rotary kiln is changed from coal to oil firing. The change also commonly increases the heat requirement in kcal /kg about 10 % on the other hand, coal ash, particularly when it varies, creates problems in controlling clinker composition, (Pollitt, cited in Hillman 1962).
Choice of fuel is normally based on economics, and in the USA its known for works to vary the fuel according to the supply and price position, Oil may contain light fractions capable of volatilization in the pipes to and from the burner and, thus causing difficulty in metering. Gas may vary in composition and supply pressure. On balance, however, better control can be obtained with oil than with coal.

This control is effected by simultaneous adjustment of fuel and air input in relation on to the raw material feed rate. This is normally done manually, but automatic control is increasingly used. The use of an electric arc to burn clinker has been tried in Switzerland.

Before leaving the kiln, mention should be made of refractories, ring formation and dust.

It is common to use different grads refractory to meet the differing requirements in the drying, decarbonating, burning and cooling zones at the kiln. The brick in the burring zone, by reacting with the clinker, aquire coating which help them to resist the severe condition. The lifetime of refectories is much affected also by operating conditions.

Ring formation occurs in three zones. Slurry or mud rings occur at the back end of wet process kilns, usually at a point where the feed is plastic. Concentration of sulphates have been observed, and clinker dust may be caught, thus promoting stiffening and accumulation of the feed.

Clinker rings occur where the feed is about to enter the burning zone. Refractory manufactures suggest that correct choice brick can avoid clinker rings. Ash ring occur also to the front end of the kiln.

Dust is an important problem, not only as regards atmospheric pollution and public relation but also as it affects the economy of the process. Every pound of dust lost from chimney has been quarried, ground, blended and dried, and represents wasted money. Naturally, therefore, every efforts is made to minimize the loss. Settling chambers and cyclones have been used to deal with relatively coarse dust, modern works are equipped with electrostatic precipitators or bag-filter system. Dust in rotary kiln is produced by the passage of gases at velocities of the order of 20ft/sec over the bed of feed. With a very friable feed, kiln output may be limited by the fact that increased feed, full and air rates lead to increased dust loss and decreased clinker production, (Pollitt 1964).

c) Clinker cooling and grinding:-

There are three main types of clinker cooler: integral, rotary and grate. In each, secondary combustion air at atmospheric temperature is drawn through the clinker by the fan at the back end of the kiln, thus heating the air and cooling the clinker. T hey are sometimes equipped with their own fans and may use more air than is required for the kiln. The reason for clinker cooling is that cooling rate affects the properties of cement. C_3S is unstable below 1250^oC. It has also been demonstrated that slow cooling produces y- C_2S, which dusts and gives less strength than β - C_2S, and permits the flux to crystallize out, leading to setting time difficulties due to crystalline MgO. Rapid cooling, on the other hand, preserves the β form of C_2S and tends to freeze flux as glass, so minimizing the effect of C_3A and MgO, any crystal of which are small. Finally, cooled clinker is easier to convey and grind.

Cooled Clinker is ground with gypsum in a mill which consists essentially of horizontal steel cylinder with end closed except for orifices for feeding and discharging.

Rotation of the mill inclines the bed of balls and causes them to pound and abrade the clinker and gypsum, which are normally fed in at one end and discharge at the other.

1.8 Control:-

Production of cement of consistent quality involves close control throughout the process. Selective quarrying based on raw material analyses is followed by feeding of controlled proportions to the crushing, grinding and washing plant. Regular sampling at this stage and in the storage tanks ensures the correct fineness and composition in the mixers or blending silos. The feed is metered in to the rotary kiln at constant rate. The burner who controls the kiln has at his disposal indicators showing the temperature and the oxygen and carbon monoxide contents of the gas leaving the kiln. In some cases optical pyrometers measure and record the burring zone temperature and thermocouples may be inserted into the kiln at points of lower temperature. With this information, the burner controls the fuel and air supplies and, when required, the rates of raw material feed and rotation of the kiln.

Preheater are usually equipped with additional instruments for recording gas flow and temperature. Automatic combustion control is common, and in the USA the best method of kiln control is begin sought by applying data logging and processing techniques to the recorded information.

Cement grinding mills are equipped with ammeters or K W h- meters and various forms of feed control, of which the weigh feeder is increasingly used. Acoustic control has been applied; the noise made by the mill is electronically filtered and used to control the feed rate.

Finally, the cement is regularly sampled an analyzed for tests of setting time, soundness, fineness and strength according to the appropriate standards (Pollitt 1964).

1.9 Minor constituent of Portland cement:-

Portland cement is hydroscopic materials tending to absorb moisture during storage under damp or moist conditions. Therefore, great care must be taken in order to ensure that it is stored in dry and draught- free conditions.

The minor constituent of Portland cement as given by chemical analysis is an"insoluble residue ".This represents that fraction of cement which is insoluble in hydrochloric acid. Almost all the clay compounds present in the raw mixtures of Portland cement are insoluble in acids. It is only after reaction with lime that this property is radically altered in such a way that, after burning to clinker, all the minerals present become soluble residue in acids. For this reason, the amount of “insoluble residue” in a given cement can serve as an indication of the completeness of the clinkering reactions which have occurred in the kiln.

The component of cement denoted as MgO (magnesium oxide), (magnesia), is a compound closely resembling CaO. It is present in small quantities in almost all Portland cement because it is often found in nature as magnesium carbonate in association with calcium carbonate. Limestone with a high magnesia content are known as "dolomitic limestone" and are unsuitable for the manufacture of Portland cement. This is because magnesia, as distinct from lime, does not combine with acidic oxides present in cement and remains as "free magnesia" in the finished product. However, since, as in case of lime, slaking of magnesia is accompanied by an increase in it is volume, there is the danger of delayed expansion setting in if the free magnesia is present to large extent in cement. Expansion due to magnesia is much more dangerous than that due to lime , because the rate of its development is extremely slow (its first signs may became apparent after many years) with the result that the danger of such delayed expansion cannot be recognized with any degree of certainty in short term tests. For this reason, most standard specification for Portland cement impose maximum limit of 5 % for the magnesia content. It may also be of interest to note that the greenish, grey colour of cement is due to its magnesia content. Magnesia - free cement are brownish in colour.

A constituent of Portland cement, one which is important in spite of its small proportion is SO_3(sulfuric anhydride) and derived from the method of gypsum analysis. Gypsum, $CaSO_4$, consists CaO and SO_3.

Gypsum is added to Portland cement for the purpose of regulating its setting time. If the addition of gypsum exceeds a certain limiting value, it may cause what is known as expansion of cement due to suphates. Thus the addition of gypsum and its action on cement have double interest, and the subject deserves a thorough examination. Small amounts of gypsum, of the order used for regulating the setting time of cement, react with in the first 24 hours of the cement hardening process. If the gypsum addition is too high, there is a danger of gypsum expansion during subsequent hardening in the presence of additional moisture. Therefore, the gypsum content of Portland cement is limited in all standard specification. The maximum permissible SO_3 content as specified in BS 12.1958 is 2.5 and 3 % respectively, according to the Tricalcium aluminates content. (Wolf Gang Czerng 1962).

Cement making is essentially a chemical process industry. Close control of the chemistry of the product is essential if cement with consistent properties is to be produced. This control applies not only to the principal oxides which are present but also to impurities, which can have a marked influence on both the manufacturing process and cement properties.

1.10 ALKALIS IN PORTLAND CEMENT

The alkalis present in Portland cement are shown in the chemical analysis as Na_2O and K_2O. These two compounds are invariably associated with cement raw materials and, if present in quantities of the chemical composition of Portland cement are quite harmless. However, larger amounts of alkalis can cause, difficulties on the mechanical properties of cement (Wolf Gang Czerng 1962).

1.10.1 Effects of alkali addition on the mechanical properties:-

The effects of alkalis on various properties of cement paste, mortar, and concrete, including early hydration and setting, strength development and ultimate strength, drying shrinkage, susceptibility to cracking, microstructure of cement hydrates, and durability, have been a subject of concern since many decades (Smaoui et al. 2005).

This present study addresses the effects of alkalis, especially, Na_2O and K_3O on the mechanical properties like strength development, drying shrinkage, and expansion, in Sudanese cement.

1.10.2 Effect of alkalis on cracking and drying shrinkage:-

Smaoui, cited in Burrow 1998, suggesting that the high – alkali cement are more susceptible to drying shrinkage.

Smaoui, cited in Blaine et al. 1971 they have performed shrinkage test on cement pastes made with also different cements, and they found that cement pastes containing more alkalis were undergoing more shrinkage, but they did not observe any correlation between the alkali content and the amount of drying shrinkage for their companion concrete specimens. Based on the work by (Carlson 1939) (Burros 1998) attributes this behavior to the development of micro cracking within the concrete subjected to drying, which decreases the bulk shrinkage.

So, it has been well demonstrated that higher cement alkali content tend to increase the susceptibility to shrinkage under drying conditions in the case of cement pastes and mortars. This effect is not so clear in the case of concrete.

1.10.3 Effect of alkalis on strength development and ultimate strength:-

A number of experimental studies showed that the higher the alkali content in the cement, the lower the ultimate strength of the corresponding tests specimens.

Osbaeck 1984 concluded that a higher alkali content in cement accelerates the strength development in short term but decreases the ultimate strength. Jawed and Skalny 1978 also concluded that high alkali content in cement generally results in a higher strength at early age, but to lower strength after 28 days. (Gouda 1986) observed similar trend for concrete specimens made with both low alkali (0.58% Na_2O) and very high – alkali (1.76% Na_2O) cement. Avery low – alkali cement can result in abnormally low strength development at early ages. On the other hand, (Odler and Wonnemann 1983) observed that the alkalis incorporated into the cement clinker did not affect the compressive strength, whereas an external addition of alkali sulfate considerably reduces the strength at any age up to 28 days (Mullick 2007) observed that the higher the alkali increase, the lower the compressive strength of cement pastes. However, intermediate alkali additions, increase the modulus of rupture whereas smaller and larger additions decreased it (Shayan and Ivanuse, 1989) studied the changes in the mechanical properties(compressive strength and modulus or rupture) and mierostructural characteristic of cement pastes and mortars of various alkali contents. The others found that the higher the alkali content to the level (1, 2, 3% Na2O Eq), the lower the compressive strength and modulus of rupture at any age. (i.e,.7, 28, and 90 days). Unfortunately, most studies one the effects of alkies on the mechanical properties of hydraulic systems were performed on cement paste and mortar specimens. In addition, in most studies, the mechanical properties involved were usually limited to compressive strength. Last studies of concrete that increasing alkali content from 0.6 % to 1.25 % of Na2Oe shows more reticular and porous microtexture which could explain the reduction in strength (Smaoui et al. 2005).

1.10.4 Effect of alkalis on expansion potential:-

Shayan and Ivanuse 1989 reported an increase in the expansion of mortar bars using sodium hydroxide doping. The expansion was reported to be approximately 0.04 % at 12 weeks at 3.8% Na_2O. This study did not provide data about the cement composition or the sulfate content.

Luxan et al. 1994; reported that incorporation of alkali carbonate and sulfate salts (Na_2CO_3 1 and 2% by weight, K_2SO_4 1.2 and 3% by weight) reduced the expansion of Portland cement mortars, mainly when C_3A content is low (<5%). It was concluded that there is an optimum concentration for the alkali salt for each cement. Again, this study did not provide any details about the hydration products, or any details Na_2O levels.

Vivian 1950 showed no significant expansion to occur when the alkali content of the cement was increased to 4.08% using NaOH in the mixing water. The study was done on mortar prisms (1 in x 1 in x 10 in). The expansion did not exceed. 007% at 196 days. The study did not show any details about cement composition (Smaoui et al. 2005).

As can be seen from this review, the finding in the literature about the exact effect of the alkali on the progress of hydration and the expansion behavior is complicated and needs further investigation.

1.10.5 Effect of alkali-aggregate reaction:-

Alkali – aggregate reaction (AAR) is a mechanism of deterioration of concrete resulting from an interaction between alkaline pore fluids in the concrete principally originating from the Portland cement and certain types of aggregates. The most common type of the reaction is the alkali silica reaction (ASR) which occurs with siliceous aggregates forming a calcium alkali-silica gel. This gel imbibes water producing a volume expansion which disrupts the concrete. Other alkali – aggregate reactions are the alkali - carbonate reaction when the attack is on certain argillaceous dolomitic limestone's and alkali – silicate reaction in which layered silicate minerals are attacked (El-Tilib 1992).

The present investigation deals only with alkali – silica reaction (ASR) as the other reaction are rare and are generally less important than ASR in terms of the deterioration of the concrete and are less well researched and understood.

Deterioration of concrete structures due to alkali- aggregate reaction was first recognized in the USA in 1940, in Denmark during the early 1960s, in the UK in 1971, in Japan in the early 1980s and in adjacent Kenya in 1988. Although the occurrence of such reaction is limited when considering the large the number of concrete structures built the reaction can cause serious problems of serviceability when it does occur.

The mechanisms that control this reaction are not well understood, and the measures to prevent or control the reaction have been based largely on empirical consideration. No known cure exists since the essential ingredients of the reaction were irretrievably mated in the concrete during mixing and hardening processes. Now alkali silica reaction has received wide spread publicity and it has been described in the media as a concrete cancer.

(i) Concrete:-

Concrete is a mixture of coarse and fine aggregates, Portland cement and water with or without incorporation of one or more other materials which are called admixtures (El-Tilib, cited in Dolar-Mantuani 1983).The concrete must have sufficient strength to resist forces that result from applied loads and from the weight of the concrete itself. The durability is influenced by the quality of the materials used, the mechanics of mixing, placing, curing and finishing, as well as ambient conditions during construction and throughout the life of concrete structure.

(ii) Deterioration of concrete:-

The two most common causes of deterioration in structural concrete according to the (El-Tilib, cited in Hobbs 1998) are:

a) Chloride penetrations into the concrete leading to corrosion of steel resulting in spoiling of concrete cover.

b) Inadequate cover to the reinforcing steel.

(iii) Aggregates:-

The term “Aggregates” is used to describe the gravels, crushed rocks and sands which are mixed with cement and water to make concrete. Most concrete is made from natural aggregates which are usually specified to comply with the requirements of for example, BS 822.

The properties of aggregates have an effect on the quality and performance of concrete. According to Cement and Concrete Association (1987) these properties depend less on the type of rock than the factors such as the shape and size of the particles. Quality requirements such as durability are very important.

Aggregates should be hard and do not contain materials which are likely to decompose or change volume when exposed to the weather. Examples of undesirable materials are lignite, coal, pyrites, lumps of clay and potentially alkali reactive substances. Potentially alkali reactive materials may react with the alkalis in Portland cement and cause excessive expansion of mortar or concrete.

The deleteriously alkali-reactive aggregates have been investigated thoroughly than any other group of materials used for concrete aggregates. The special attention paid to this group is justified because such expansive aggregates may cause server distress in concrete but in many instances preventive measures can be taken if expansively reactive aggregates can be recognized before they are used. (ASTM C 33-97).

(iv) Properties of aggregate:-

The aggregate limit the strength of concrete. Weak aggregate cannot produce strong concrete. The properties of aggregate greatly affect the durability and structural performance of concrete. Aggregate was originally viewed as an inert material dispersed throughout the cement paste largely for economic reasons. In fact aggregate is not truly inert and its physical, thermal, and sometimes chemical properties influence the performance of concrete.

Aggregate is cheaper than cement it confers considerable technical advantages on concrete, which has a higher volume stability and better durability than the cement paste alone. Aggregate formed from naturally occurring materials and also was manufactured from industrial products; these artificial aggregates are generally either heavier or lighter than ordinary aggregates.

Aggregate can be divided into several groups of rocks having common characteristics. The classification of natural aggregates according to rock types is most convenient (BS 812: part1:1975). ASTM standard C294-69 (reapproved 1975) gives a description of common or important minerals found in aggregates. Mineralogical classification helps of recognizing properties of aggregate.

1.10.6 Types of alkali - aggregate reaction:-

In most concrete, some aggregates react with the alkali hydroxide in concrete, causing expansion and cracking over a period of many years. This alkali, aggregate reaction has two forms, alkali- silica reaction (ASR) and, alkali-carbonate reaction (ACR).

Alkali- silica reaction (ASR) is of concern because aggregates containing reactive silica materials are more common. In ASR, aggregates containing certain forms of silica will react with alkali hydroxide in concrete to from a gel that swells as it adsorbs water from the surrounding cement paste or the environment. These gels can swell and induce enough expansive pressure to damage concrete.

1.10.6.1 Alkali-carbonate reaction:-

ACR is observed with certain dolomitic rocks. Dedolomitization, the breaking down of dolomite is normally associated with expansion. This reaction and subsequent crystallization of brucite may cause considerable expansion. The deterioration caused by ACR is similar to that caused by ASR, however, ACR is relatively rare because aggregates susceptible to this phenomenon are less common and are usually unsuitable for use in concrete for other reasons (American’s Cement Manufacture 2015).

1.10.6.2 Alkali-silica reaction:-

Alkali–silica reaction occurs when there is an interaction between the alkali hydroxides associated with Portland cement and siliceous minerals in some aggregates (building research establishment digest 1988). The pore solution in mortars and concretes contains entirely sodium, potassium and hydroxides ions with very low concentration of other ions such as calcium, sulphate and chloride (concrete society working party 1987). ASR is therefore essentially an attack by sodium or potassium hydroxide solution on silica producing an alkali – silica gel. The rate of this attack will depend on the relative concentration of these hydroxides in the pore solution. The concentration of sodium, potassium and hydroxyl ions is dependent on the quantity of sodium and potassium compounds in the anhydrous Portland cement. It is only in pore solutions of high hydroxyl ion concentration that significant attack on reactive silica occurs (El-Tilib, cited in Hobbs 1988).

The gel of calcium silicate hydrate (C-S-H) rapidly takes up calcium produced by the cement hydration reactions such gels are capable of absorbing water into their structure and expanding. It is this expansive force which creates tensile stresses within the concrete and can ultimately cause cracking (Concrete society Working party (El-Tilib, cited in Hobbs 1998).

(i). Alkali-silica reaction mechanism:-

Alkali–silica reaction is a reaction takes place between the reactive silica contained in aggregates and the alkalis in the cement paste.

For the reaction to take place in concrete three conditions must exist: high pH, moisture, and reactive silica. Various types of silica present in aggregates react with the hydroxyl ions present in the pore solution in concrete. The silica, now in solution reacts with the sodium (Na^+) and potassium (K^+) alkalis to form a volumetrically unstable alkali-silica gel. Once formed, the gel starts imbibing water and swelling to a greater volume than that of the reacted materials. Water absorbed by the gel can be water not used in the hydration reaction of the cement, free water from the rain, snowmelt, tides, rivers, or water condensed from air moisture (ACI 221, 1998). In general, the reaction can be viewed as a two step process (Farny 1996):-

Step 1:

Silica + Alkali → Alkali-silica gel (sodium silicate)

$SiO_2 + 2NaOH + H_2O \longrightarrow Na_2SiO_3.\ 2H_2O$ (2KOH can replace 2NaOH).

Step 2:

Gel reaction product + Water → Expansion

Since the gel is restrained by the surrounding mortar an osmotic pressure is generated by the swelling. Once that pressure is larger than the tensile strength of the concrete, cracks occur leading to additional water migration or absorption and additional gel swelling (ACI 221, 1998).

(ii). Conditions necessary for the reaction to occur:-

Alkali-silica reaction will occur only when three components are met simultaneously: reactive silica, sodium and potassium alkalis and water. (El-Tilib, cited in Dolar-Mantuni 1983) and (El-Tilib, cited in Hobbs 1988).

(a)Reactive silica:-

The difference between reactive and un-reactive aggregate, according to (Smith and Raba 1986) depends on several factors such as crystallographic form, strain and amorphous content and crystal imperfection. An un-reactive silica such as unstrained quartz has a very ordered crystalline structure of silicon and oxygen atoms which is resistant to attack by alkalis, whereas reactive forms of silica such as opal are amorphous, irregularly spaced groups of silicon and oxygen. These amorphous form of silica are easily attacked by alkalis; according to the draft B.S 1989 and ASTM 1990.

Opaline silica being the most disordered form of the silica and most reactive and these forms of silica can give rise to deleterious expansions at lower equivalent alkali contents than the less disordered forms (El-Tilib, cited in Hobbs 1998).

(b) Sodium and potassium alkalis:-

The sodium and potassium alkalis found in cement originate from the raw materials used for the manufactures of Portland cement. These alkalis are released during normal hydration. The pore fluid present in Portland cement concrete is a mixture of calcium, sodium and potassium hydroxides. Most of the calcium hydroxide produced during hydration is present as a crystalline hydroxide but most of the sodium and potassium are present in the pore solution and are primarily responsible for high alkalinity (El-Tilib, cited in Hobbs, 1988).

Because in general, Portland cement is usually the first to be accused of contributing alkali to the concrete mix, the reaction is normally assumed to be a reaction between disordered silica and the sodium and potassium alkalis released by a high alkali Portland cement. Cement plants produce a variety of cement types using basically two processes: The wet process is being phased out because of its high energy requirement and is being replaced by the dry process. However, the energy-efficient process and stricter air pollution laws generate a kiln dust that is high in alkalis. The kiln dust is a disposal problem that can be minimized by recycling. The end result is higher alkali cement. The total alkali content of Portland cement is, according to ASTM C150, the sum of sodium oxide and potassium oxide expressed as equivalent sodium oxide ($Na_2O + 0.658K_2O$).

(c)Water:-

Water from an external source is normally responsible for the formation of alkali-silica gel and its subsequent swelling to cause expansion and damage to the concrete.

(iii)Reaction product of silica aggregates:-

The alkali-silica reaction produces alkali-silica gel (plate 1). The composition of the gel in a reactive particle is variable and depends mainly on the amounts of alkalis and the reactive silica available.

Thoulow and Knudsen in 1975 investigated the gel composition in the transition zone between the aggregate particle and the cement paste and showed that alkali-silica gel is formed in the particle and that it takes up calcium when migrates into the cement paste which is rich in calcium hydroxide, but calcium may move through a reaction rim into the reactive particle (Poole, 1976). So the gel analyzed in concrete are usually found to contain calcium, sodium, and potassium silicates and to be of a variable composition (El-Tilib, cited in Hobbs, 1998).

(iv). ASR mitigation measures:-

Mitigating or preventing deleterious expansions caused by the alkali-silica reaction can be achieved by:-

(a). Limiting moisture:-

The alkali-silica reaction will not take place in a concrete structure if the internal relative humidity of the concrete is lower than 80%. As a result, keeping the concrete dry will prevent the reaction from occurring. However, a low water cement ratio results in higher cement content, higher alkali content, and a reduced pore space which could lead to higher expansions lowering the permeability of concrete using mineral admixtures is a more viable approach to reducing the deleterious effects of ASR (ACI 221, 1998). Applying a protective coating to concrete is a good solution provided that the coating is correctly installed. Because of the high cost of concrete coatings, this method has been used on a limited basis.

(b). Selecting non-reactive aggregates:-

Using a non-reactive aggregate and avoiding reactive aggregates will prevent ASR damage. (ACI 221.1998)

(c). Minimizing alkalis:-

The maximum limit of 0.6% Na_2O equivalent in cement was the result of a study initiated in 1940 (Hill 1996). In 1945 Blanks and Meissner determint that 0.5% in cement is much safer limit. Several other research studies performed between 1941 and 1963, namely by Tremper in 1941 and 1944, Kammer and Carlson in 1941, Woolf in 1952, Bryant Mather in1952, and Oleson in1963, all concluded that cement with alkali contents lower than 0.60% have shown every little to no ASR damaging effects (Hill 1996).

The most commonly used mitigation method is to control the alkali content in the concrete for the purpose of reducing the hydroxyl ion concentration and eventually the pH of the concrete. Cement is the major source of alkali in the concrete, chemical admixtures, aggregates, and external sources such as deicing salts and seawater.

Controlling the alkali content of the cement has been proven to decrease the expansions caused by ASR. A proposed limit of 0.60% has been recommended for the alkali content of cement to be used in concrete to reduce ASR expansions (ACI 221 1998).

(d). Mineral admixtures:-

Effective mineral admixtures (ACI 221 1998) include fly ash, silica fume, ground granulated slag, and calcined clay. Mineral admixtures reduce ASR expansions by one or more of the following mechanisms:

- Reducing the alkali content of the concrete mix
- Reducing the pH of the pore solution
- Consuming the calcium hydroxide, which might result in lower swelling.
- Reducing concrete permeability.

(e). Chemical admixtures:-

Lithium salts have been used to prevent excessive ASR expansions. Several salts have been tried, some of which have been shown to be effective. The best results were obtained using lithium nitrate ($LiNO_3$) because: 1) it is non-toxic. 2) Mineral amounts were found significantly reduce the ASR expansions (ACI 221 1998).

ASR can be controlled using certain supplementary cementitious materials, in proper proportion, silica fume, fly ash, and ground granulated blast furnace slag. Several natural pozzolans such as calcined clay have also been reported effective in mitigation the ASR effects.

Effective mitigation methods need to be available for use with aggregates that are prone to ASR. In order to reduce the cost of construction it is important that reactive aggregate sources be used as effectively as possible.

In Sudan, no example concerning deterioration of concrete due to ASR has been reported and no investigations of cracked or otherwise deteriorated concrete to establish whether it is a case of alkali-aggregate reaction have been conducted until 1992.

Nour-Allah El-Tilib, 1992 carried out a survey on Sudanese aggregates for their alkali-silica reactivity and reported that alkali-silica reaction has been found in some aggregates. (Nour-Allah El-Tilib 1992) collected types of rock samples (granitic, volcanic, sedimentary and recent deposits) from many areas in Sudan River Nile, Red Sea, Blue Nile and Northern State. His recommendations in all of studies were very useful; they were considered and used in Merowe Dam which is the biggest in Sudan.

Remedial treatment for damage due to ASR may be very costly, and the reaction can cause serious problems of serviceability when it does occur. So it is important to minimize the risk by all means necessary to avoid ASR from the very beginning that is from the initial choice of the aggregate (the easiest way) and the cement.

Nour-Allah study is essentially an empirical investigation and evaluation of Sudanese aggregates using various conventional, rapid and accelerated standard methods (petro graphic, chemical and expansion tests) for detecting the alkali aggregate susceptibility and determining how far an aggregate may be harmfully reactive with alkali in mortars on concretes. In the present study the ASR and the conditions under which it can occur are discussed and also future recommendations will be provided.

ASR can be controlled using certain supplementary cementitious materials. In proper proportion, silica fume, fly ash, and ground granulated blast furnace a slag have significantly reduced expansive due alkali, silica reactivity. In addition, lithium compounds have been used to reduce ASR. ASR distress in concrete is not that common because of the measures taken to control it. It is also important to note that not all ASR gel reactions destructive swelling.

Note:

The availability of Portland cements will be affected for years to come by energy and pollution requirements. In fact, the increased attention to pollution abatement and energy conservation has already greatly influenced the cement industry, especially in the production of low- alkali cements. Using high-alkali raw materials in the manufacture of low-alkali cement requires bypass systems to avoid concentrating alkali in the clinkers, which consumes more energy. It is estimated that 4% of energy used by the cement industry could be saved by relaxing alkali specification. Limiting use of low-alkali cement to cases in which alkali –reactive aggregates are used could lead to significant improvement in energy efficiency (U.S Department of Transportation 2015).

This research was initiated in order to address the role of alkali content on cement paste, mortar and concrete durability. In order to address this objective in a thorough and systematic way, three ordinary Portland cements of different alkali levels and variable raw materials have been used in the investigation. These cements are Sudanese Portland cements, obtained from Atbara, Al Salam and Berber factories.

The following chapters will present experimental techniques, methodology, results, discussion and conclusions.

CHAPTER TWO

MATERIAL and METHODS

CHAPTER TWO

EXPERIMENTAL WORK

2.1 Introduction:

In the present work, the effect of increased alkalinity on strength, soundness, setting time and expansive alkali reactivity, a numbers of tests were performed using the three cements (Berber, Atbara and Al salam) of different alkali contents, another series of test were performed using Berber cement but with the addition of alkali as sodium hydroxide solution to the same cement.

2.2 Test samples:-

Three cement samples have been collected from Berber, Atbara and Al salam cement factories, in the river Nile state, to be evaluated for their alkali levels in order to check the effect of cement alkalis on the mechanical properties of cement and on the alkali reactivity of concrete aggregates using the existing strength and mortar-bar expansion tests

Since the significance of the alkali reaction depends on the reactivity of the aggregate, one rock aggregate sample (rhyolite) from the Seleit area north east of Khartoum, known of being potentially reactive, has been used in the investigation

The raw materials which are used to controls the major four compounds in cement industry of Atbara and Al Salam cements includes limestone and clay, while Berber cement raw materials consist of limestone, schist, clay and iron ore which gives the flexibility in raw mix control for Berber cement rather than others.

2.3 Experimental procedures:-

2.3.1 Chemical Test: Flame photometry determination of sodium and potassium oxides

This test method covers the determination of sodium oxide (Na_2O) and potassium oxide (K_2O) by flame photometry.

This test method is suitable for hydraulic cements that are completely decomposed by hydrochloric acid and should not be used for determination of total alkalis in hydraulic cements that contain large amounts of acid-insoluble materials for example, pozzolana cement.

Materials

- Three Samples Berber, Atbara and Al salam cements. (2g)
- HCl conc. (5ml).
- Distilled water.
- NaCl and KCl.

Apparatus:-

- Instrument: - flame photometer PFP7 (plate2).

Method

2.0000g of each samples was weighed in a 100 ml beaker and stirred with distilled water, 5ml of HCl added all at once, the beaker is filled half with distilled water and left for 15 minutes on a hot plate at 90-100^{o}C. The solution is then filtered through a filter paper into a 250ml volumetric flask. The beaker and filter paper are washed with hot distilled water and filled to the mark with distilled water after cooling to room temperature.

Then solution of 100ppm was prepared from 1000ppm stock solution and series of standard solutions which includes 2, 4, 6, 8 and 10ppm was prepared from 100ppm solution.

Standard and samples were determined and calculated from recorded averages for Na_2O and K_2O in the unknown samples, (Tables 2,3,4,5,6 and 7 and Figures 1,2,3,4,5, and 6).

2. 3.2 Determination of cement strength:-

In order to assess the effect of cement alkalies on the cement strength property Berber cement product was chosen. The strengths were measured at 2, 7 and 28 days. Four series of tests were performed. In one series the tests were carried out without alkali addition. In the other three series, the alkali content was increased using sodium hydroxide pellets by 2%, 4% and 6%.The procedure used for determination of the compressive and flexural strength followed to a large extent that described in the European standard EN 197-1(1994 E).

Materials

- Berber cement (740g).
- Sand (2220g).
- Distilled water (359ml).
- Sodium hydroxide (15g, 30g, 45g).

Apparatus

- Flexure strength instrument
- Compressive strength instrument.

Method

Prismatic test specimens 40mm x 40mm x160mm in size are cast from a batch of plastic mortar containing one part by mass of cement and three parts by mass of standard sand with a water/cement ratio of 0.50.

The mortar is prepared by mechanical mixing and is compacted in a mold using a standard jolting apparatus. The specimens in the mold (plate3) are stored in a moist atmosphere for 24 h at a temperature of 20±1 ^{o} C, relative humidity of 95% ± 1and then the demoulded specimens were stored under distilled water in standard environment of temperature of 20±1 ^{o} C, & relative humidity of 50% ± 1 in until strength testing.

At the required age, the specimens are taken from their wet storage, broken in flexure (plate4) into two halves and each half tested for strength in compression (plate 5), (Table 9 and Figures 7, 8 and 9).

2.3.3 Determination of setting time:-

The setting time is determined by observing the penetration of a needle into cement paste of standard consistence until it reaches a specified value.

Material:-

- Berber cement (500g)
- Distilled water (125ml)
- Sodium hydroxide (10g, 20g, 30g).

Apparatus:-

- Digital sensitive balance
- Measuring cylinder

- Cement mortar mixer
- Vicat apparatus.

Method:-

500g of cement was weighed accurately, required percentage of sodium hydroxide has been added to the cement (0%, 2%, 4% and 6%), 125ml of distilled water added in the mixer. Cement was added carefully within 10 seconds to the water in order to avoid loss of water or cement. Zero time for addition is registered The mixer was started at low speed for 90 seconds, stopped for 15 seconds to scrap the mixer paddle, and then again started for 90 seconds with high speed. then cement paste was removed from mixers jug and transferred into vicat apparatus (plate 6), The paste &the mould were stored in a moist atmosphere with a temperature of 20 ± 1^{o} C, and relative humidity of 95% ± 1(EN 196-4 specifications restricted the minimum value of the setting time should be 60 minutes and the maximum final setting time should be 390 minutes).

Initial setting time needle has been fitted to vicat apparatus and zero reading adjusted using base plate and after then every 5 minutes penetration of needle is observed till the height of needle from the base plate has reached 4~6 mm, initial setting time was registered, final setting time needle fitted, test continued till the impression of the needle for cement paste gone, final setting time registered, (Table 10 and Figures 10 and 11).

2.3.4 Determination of soundness:-

The cement paste once it has set, does not undergo a large change in volume, the expansion occur due to reactions of free lime, magnesia and calcium sulfate, and cement exhibiting this type of expansion are classified as unsound. Le

Chatelier’s accelerated test is prescribed by BS EN 196-3:1995 for detecting unsoundness due to free lime only.

Material:-

- Berber cement (500g)
- Distilled water (125ml)
- Sodium hydroxide (10g, 20g, 30g).

Apparatus:-

- Le chatelier apparatus

Method:-

A cement paste from the above setting time test was taken,& transferred into Le chatelier apparatus (plate 7) and compacted well to remove any air gap, Le chatelier apparatus had been covered from top side and bottom side with glass sheet (4mm thickness), kept for 24 hours at same standard environment. After 24 hours distance between Le chatelier apparatus legs has been measured, paste and apparatus has been immersed into hot distilled water (100^oC) for three hours and half. Cooled down to room temperature & gap between both legs again measured, difference has been registered, (Table 11 and figure 12).

2.3.5 Determination of mortar-bar expansion:-

The expansive forces generated by alkali-silica reaction in concrete are caused by the formation and subsequent swelling of alkali-silica gel within and around the boundaries of reacting aggregate particles. The mortar-bar expansion tests were used in this study to cover the determination of the susceptibility of Sudanese cements to expansive reactions involving the alkalis (sodium and potassium) by measurement of length changes of mortar-bar containing cement aggregate combinations during storage conditions given by the ASTM C 227 (1997) method.

Material:-

- Berber (300g), Atbara (300g), and Al salam (300g) cements
- Distilled water
- Non-reactive aggregate (675g).

Apparatus

- Mortar-bar

Method

In this test mortar-bars 25x25x280mm in size (plate8) are prepared with an aggregate/cement ratio of 2.25 by weight. The specimens remained in the molds for 24 hours, then they were removed for initial length measurement. The specimens were stored above water at 38^{o} C in a closed container with blotting paper on the inside walls to act as a wick to maintain a high humidity throughout the container. The specimens were removed periodically for length measurement. The average expansion at 3 months is taken as a measure of the potential alkali-reactivity, (Tables 12 and 13 and Figures 13 and 14).

CHAPTER THREE

RESULTS, DISCISION, CONCLUSION & RECOMENDATION

CHAPTER THREE

RESULTS, DISCISION, CONCLUSION & RECOMENDATION

3.1 Results of chemical test:-

The chemical test results are given in tables (2-7) and are summarized in table (8).

Table 2: Potassium in Berber cement

Conc/ppm	Emission
0	0
2	10
4	20
6	29
8	40
10	50
Sample	12

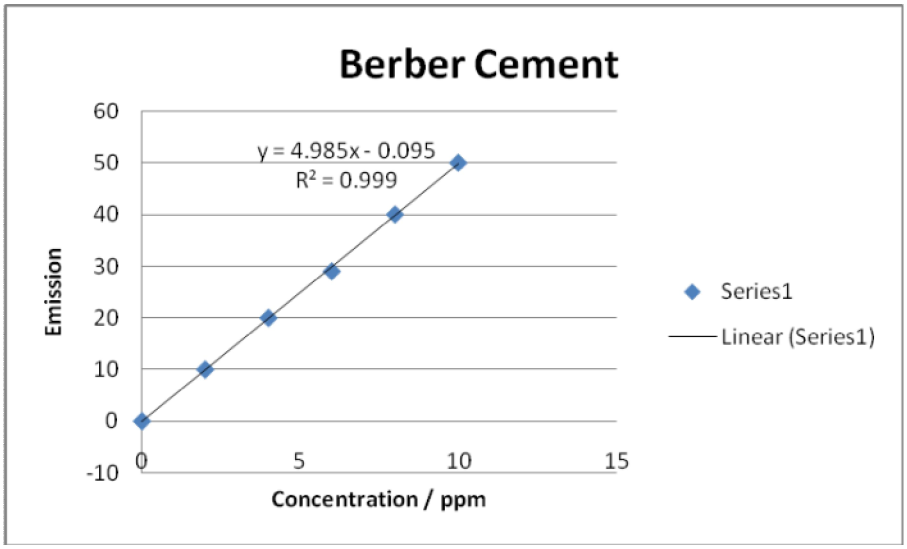
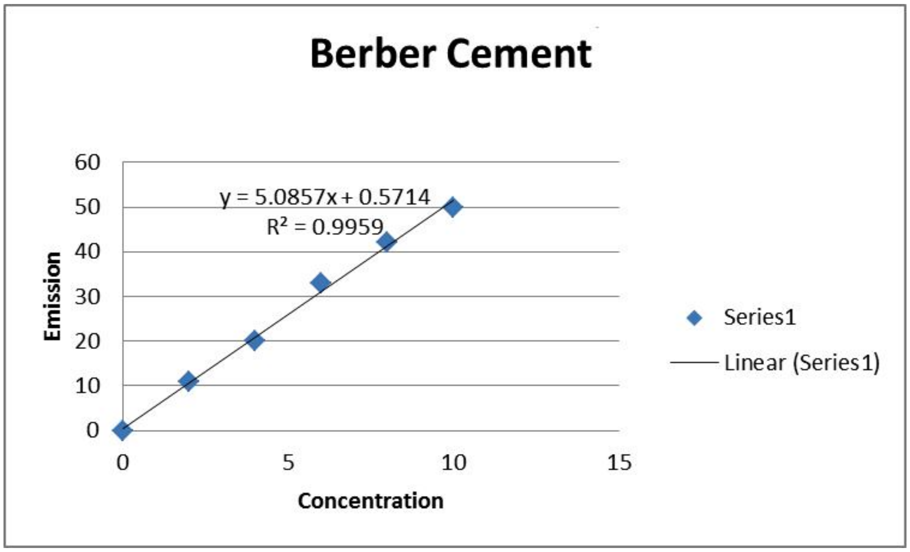


Figure 1: Potassium in Berber cement

Table 3: Sodium in Berber cement

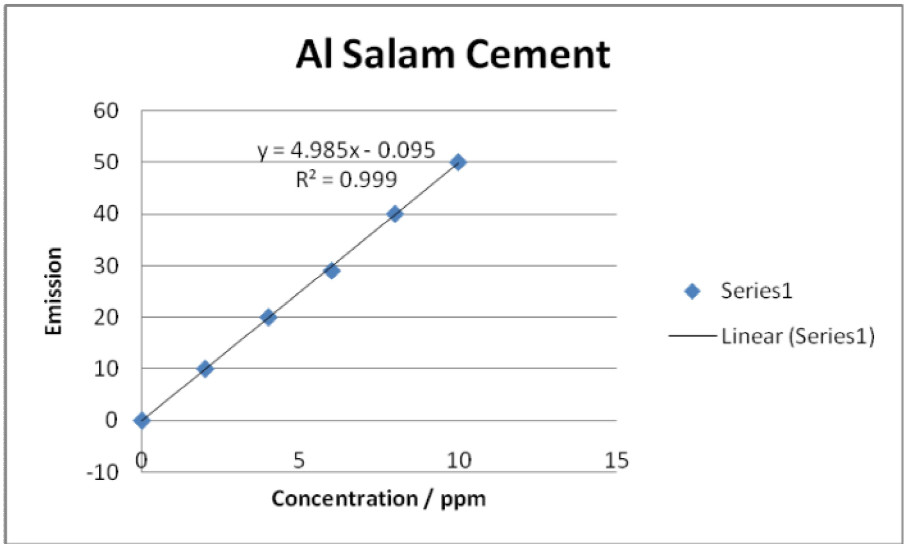
Conc/ppm	Emission
0	0
2	11
4	20
6	33
8	42
10	50
Sample	17



Figuer 2: Sodium in Berber cement

Table 4: Potassium in Al salam cement

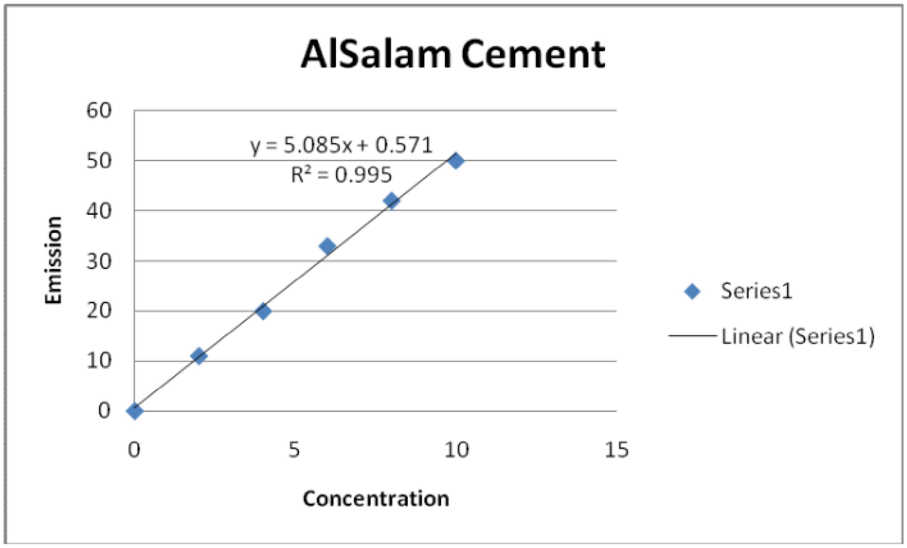
Conc/ppm	Emission
0	0
2	10
4	20
6	29
8	40
10	50
Sample	13



Figuer 3: Potassium in Al salam cement

Table 5: Sodium in Al salam cement

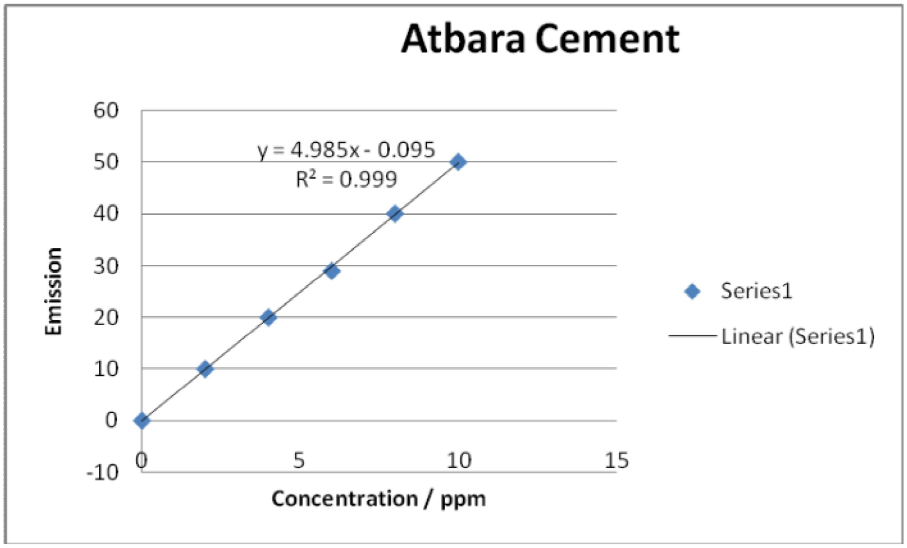
Conc/ppm	Emission
0	0
2	11
4	20
6	33
8	42
10	50
Sample	22



Figuer 4: Sodium Al salam cement

Table 6: Potassium in Atbara cement

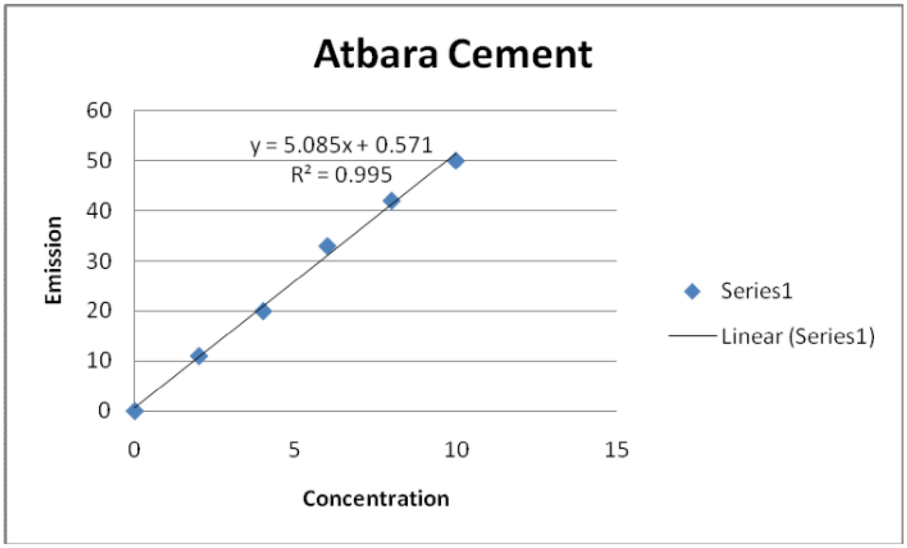
Conc/ppm	Emission
0	0
2	10
4	20
6	29
8	40
10	50
Sample	14



Figuer 5: Potassium in Atbara cement

Table 7: Sodium in Atbara cement

Conc/ppm	Emission
0	0
2	11
4	20
6	33
8	42
10	50
Sample	27



Figuer 6: Sodiumin Atbara cement

Concentration of Potassium oxide

Considering that all the potassium which exist in the cement as potassium oxide

* Formula weight of potassium oxide =94

K_2O= 2*39 + 16 =94

Potassium percentage in potassium oxide = 78*100%/94 = 82.979 %

The equation from the chart *

Y = 4.985X – 0.095

X = Y +0.095/4.985

X= ppm is the concentration obtained against emission of sample

Potassium in Berber cement

Sample E mission = 12

Sample weight= 0.2008g

From the equation

X = Y +0.095/4.985

Potassium concentration = 12 + 0.095 / 4.985 = 2.426 ppm = 2.426 mg/l

= 2.426 / 1000 = 0.002426 g/l

In 250ml = 0.002426 / 4 = 0.00065675 g/250ml

*Potassium oxide weight in 250ml =

0.00065675*100/82.979 =0.00073091 g/250ml

*Percentage of Potassium oxide in cement =

0.00073091*100% /0.2008 =0.3640%

Potassium in Al Salam cement

Sample Emission =13

Sample Weight= 0.2003 g

From equation

X = Y +0.095/4.985

Potassium Concentration= 13 + 0.095 / 4.985 = 2.627ppm = 2.627 mg/l

= 2.627 /1000 = 0.002627 g/l

In 250ml = 0.002627 /4 = 0.0006575 g/250 cm^3

Potassium oxide weight in 250 cm^3 =

0.00065675*100/82.979 =0.0007915 g/250cm^3

*Percentage of potassium oxide in cement=

0.0007915*100% /0.2003 =0.3951%

Potassium in Atbara cement

Sample Emission=14

Sample weight = 0.2002 g

From the equation

X = Y +0.095/4.985

Potassium concentration = 14 + 0.095 / 4.985 = 2.827 ppm = 2.827 mg/l

= 2.827 /1000 = 0.002827g/l

In 250ml = 0.002827 /4 = 0.00070675 g/250 cm^3

Potassium oxide weight in 250 cm^3=

0.00070675*100/82.979 =0.00085172g/250 cm^3

*Percentage of potassium oxide in cement=

0.00085172*100% /0.2002 =0.4254%.

Concentration of Sodium oxide

Considering that all the Sodium which exist in the cement in form of Sodium Oxide.

Formula weight of Na_2O= 2*23 + 16 =62

Percentage of Sodium in Sodium Oxide = 46*100%/62 =74.194 %

Equation from the chart

Y = 5.085X + 0.571

X = Y -0.571/5.085

X= ppm as concentration of Sodium oxide by Emission is

Y=

Sodium in Berber Cement

Sample Emission =17

Sample weight = 0.2008g

from the equation

X = Y -0.571/5.085

Sodium Concentration= 17 – 0.571 / 5.08 = 3.231 ppm = 3.231mg/dm^3

3.231/1000 = 0.003231 g/ dm^3

Sodium Concentration in 250cm^3 = 0.003231 / 4 = 0.00080775 g/250 cm^3

Sodium Oxide weight in 250ml= 0.00080775*100/74.194 =0.0010887g/250 cm^3

Percentage of sodium Oxide in cement = 0.0010887*100% /0.2008
=0.5422%

Sodium in Al salam Cement

Sample Emission = 22

Sample Weight = 0.2003g

From the equation

X = Y -0.571/5.085

Sodium Concentration= 22 – 0.571 / 5.085 =4.214 ppm = 4.214mg/ dm^3 4.214 /1000 = 0.004214 g/ dm^3

Sodium concentration in 250 cm^3= 0.004214 /4 = 0.0010535 g/250 cm^3

Sodium oxide weight in 250 cm^3 = 0.0010535*100/74.194 =0.001419926g/250 dm^3

Percentage of Oxide Sodium in cement = 0.001419926*100% /0.2003 =0.7089%

Sodium in Atbara cement

Sample E mission=27

Sample weight =0.2002g

From the equation

X = Y -0.571/5.085

Sodium Concentration =27 – 0.571 / 5.085=5.197 ppm = 5.197mg/ dm^3
5.197 /1000 = 0.005197 g/ dm^3
Sodium concentration in 250 dm^3 = 0.005197 /4 = 0.00129925 g/250 dm^3

Weight of Sodium Oxide in 250ml= 0.00129925*100/74.194
=0.00141993g/250 dm^3

Percentage of Sodium Oxide in cement = 0.00141993*100% /0.2002 =0.7093%

The results of content of three cement sample were concluded in table (8).

Table 8: Alkali Content of Berber, Al salam and Atbara Portland Cement used

Cement	K_2O%	Na_2O%	Alkalis as Na_2O equivalent
Berber	0.3640	0.5422	0.77
Salam	0.3951	0.7089	0.97
Atbara	0.4254	0.7093	0.99

3.2 Results of physical tests:

3.2.1 Result of strength determination tests:-

Results of the compressive and flexural strength measurements for Berber cement without and with alkali additions, are listed in table 9, and are summarized below.

(The minimum compressive strength should be 10 MPa in 2 days, 30 MPa in 7 days and 42 MPa for 28 days.)

Table 9: Compressive and flexural strength properties of Berber cement in the presence and absence of alkali additions:

Test duration(day)	Alkali addition%	Average compressive strength (MPa)	Flexural strength (M Pa)
2	0	19.8	4.1
	2	16.8	4.35
	4	8.4	2.6
	6	5.0	3.05
7	0	32	5.8
	2	25.7	4.8
	4	13.6	4.3
	6	7.6	4.2
28	0	45.9	7.75
	2	37.3	7.75
	4	22.3	4.6
	6	11.5	2.8

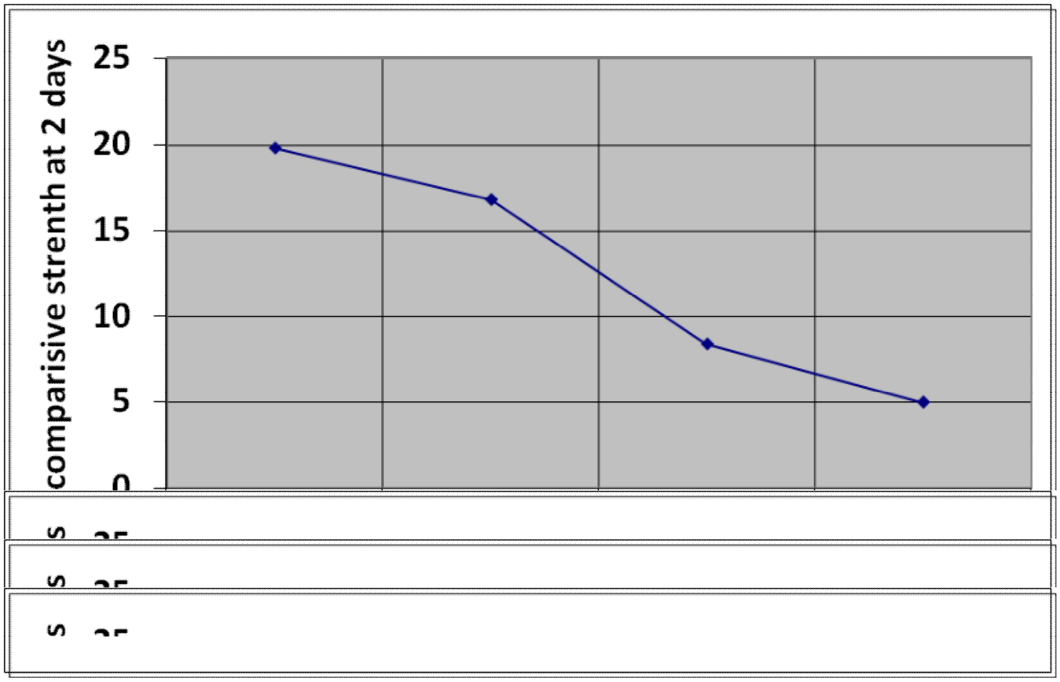


Figure 7: Relation between compressive strength at 2 days and alkali addition

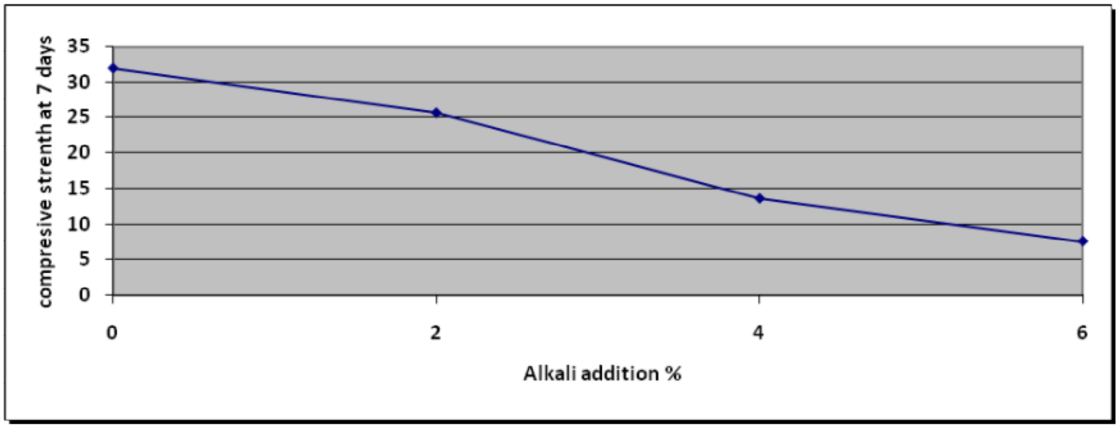


Figure 8: Relation between compressive strength at 7 days and alkali addition

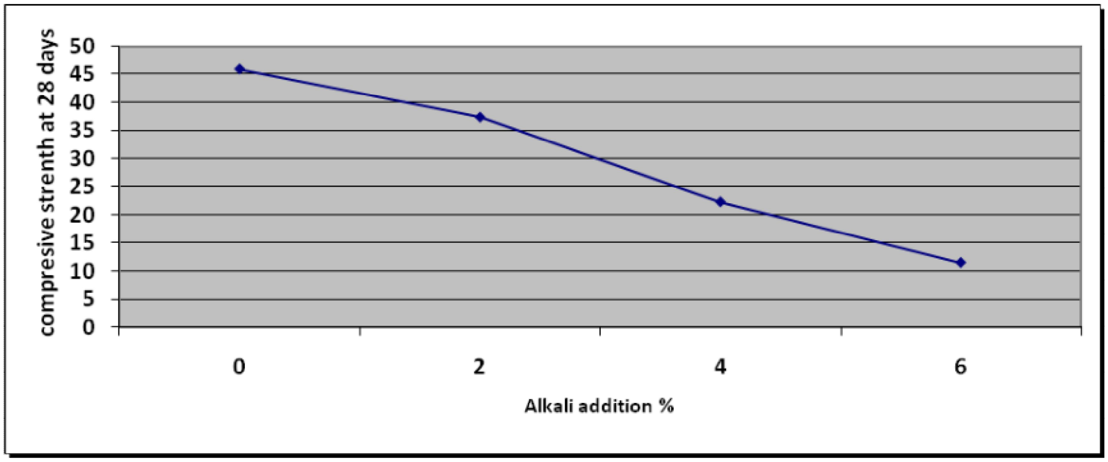


Figure 9: Relation between compressive strength at 28 days and alkali addition

3.2.2 Results of setting time test:-

Table 10: Setting time of Sudanese cement:

Alkali content	Initial setting time	Final setting time
0%	185 min	275 min
2%	175 min	235 min
4%	45 min	75 min
6%	10 min	20 min

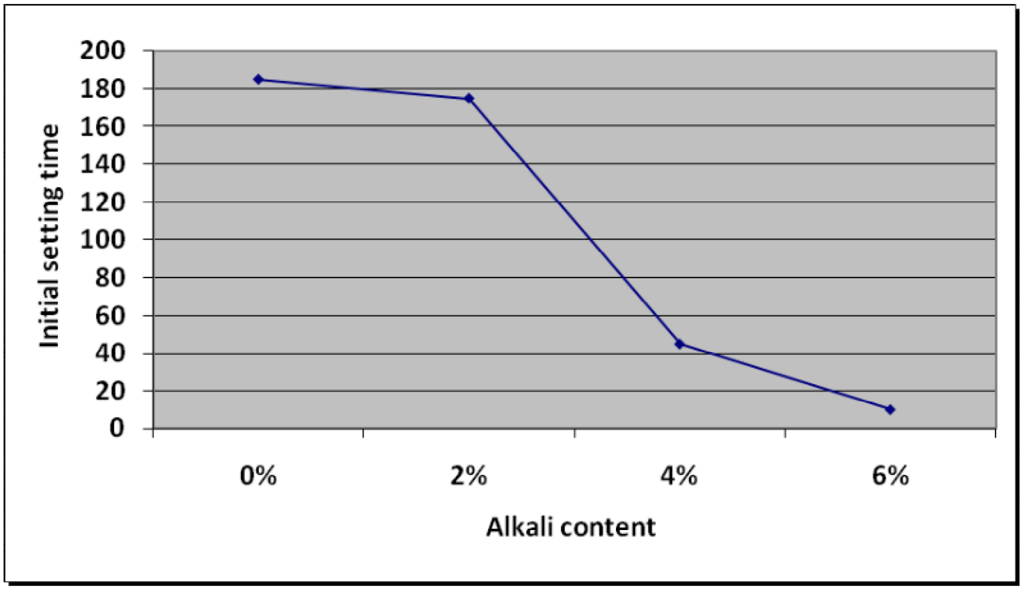


Figure 10: Relation between initial setting time and alkali content of Sudanese cement

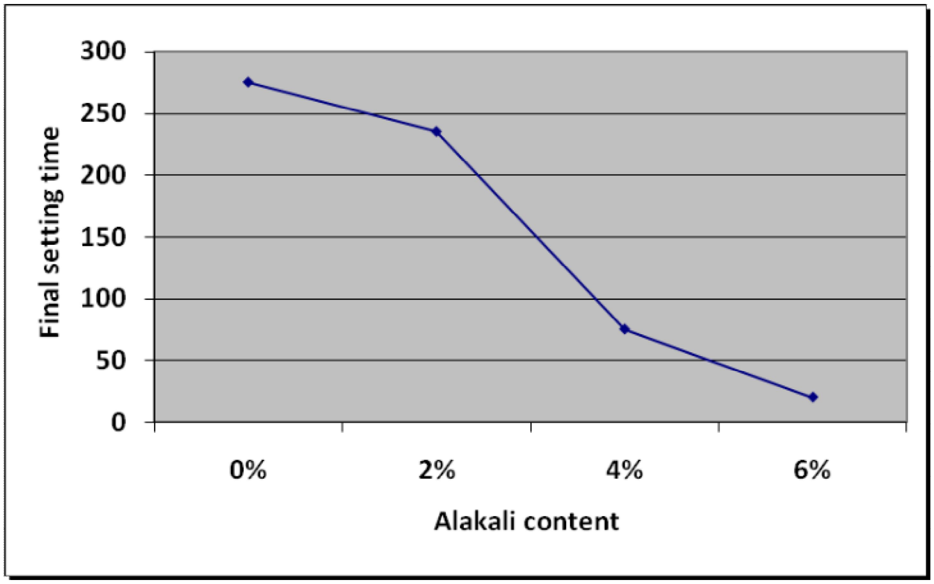


Figure 11: Relation between final setting time and alkali content of Sudanese cement

3.2.3 Result of soundness test:

Table 11: Soundness of Sudanese cement:

Alkali content	Initial	Final	Value of soundness
0%	7.5	9.5	2
2%	9.7	11.5	1.8
4%	9.8	10.7	0.9
6%	7.4	8.2	0.8

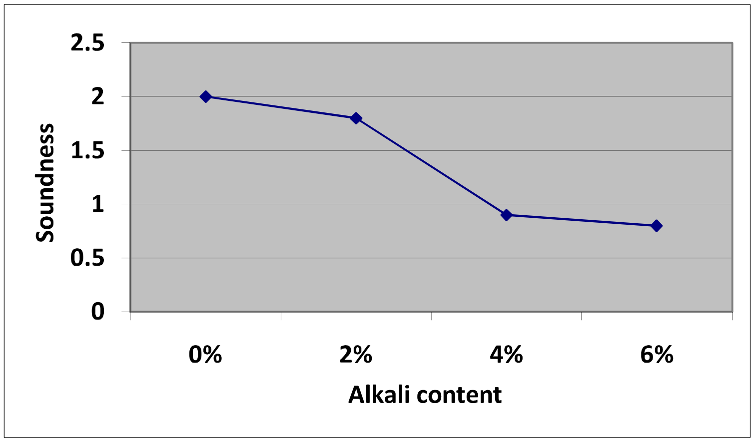


Figure 12: Relation between soundness and alkali content of Sudanese cement

3.2.4 Result of mortar-bar expansion test:

Results of the expansion measurements in the ASTM test for each cement-aggregate combination, with and without alkali addition, are listed in tables 12 and 13, plotted in Figs.8 and 9.

Table 12: Percentage expansion of an aggregate material subjected to the ATSM C227 mortar bar expansion test run over 3 months period using Berber, Atbara and Al Salam cements without alkali addition.

Cement	Berber	AL Salam	Atbara
Time (days)			
0	0	0	0
15	0.02	0.021	0.022
30	0.027	0.029	0.031
60	0.038	0.038	0.039
90	0.040	0.043	0.044

Figure 13: Expansion of an aggregate subjected to the ASTM C227 mortar bar expansion test run over a -3 months period using Berber, Atbara and Al Salam cements without alkali additions.

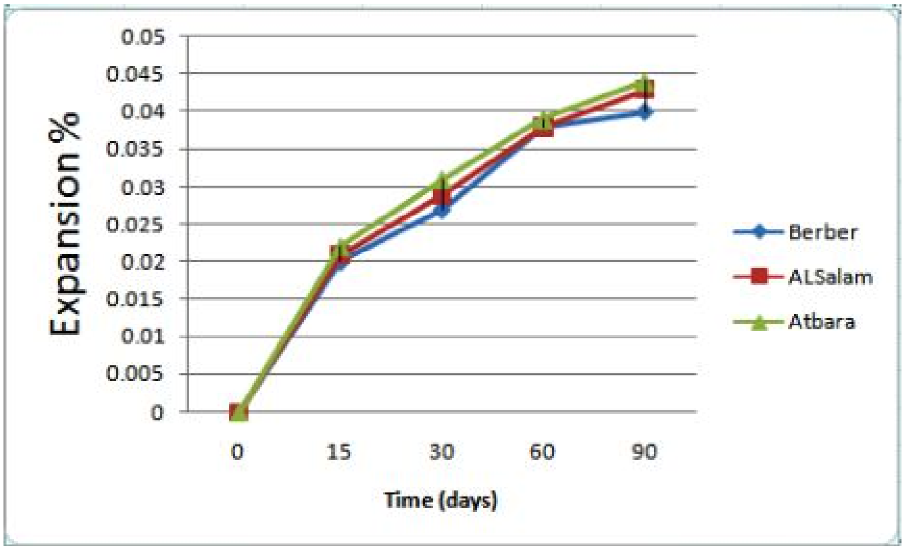
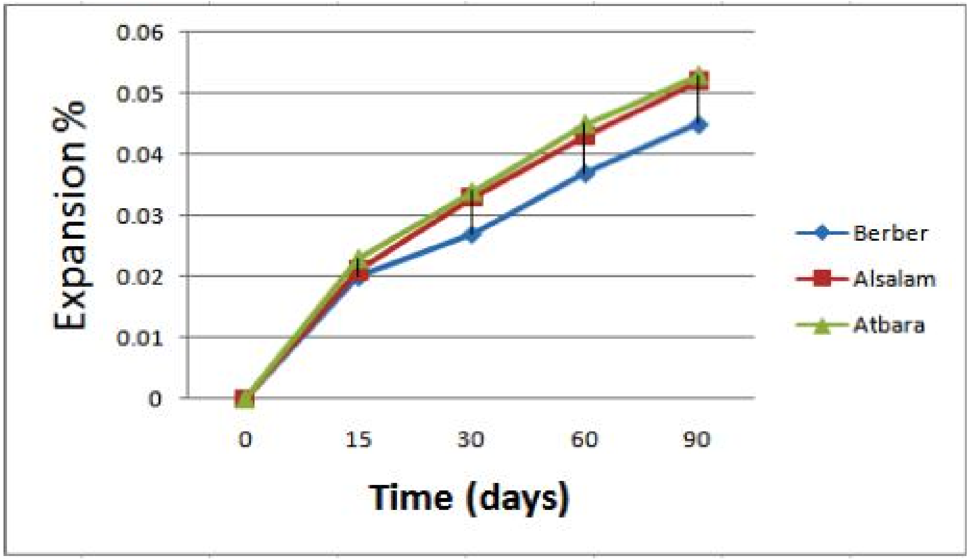


Table 13: Percentage expansion of an aggregate material subjected to the ASTM C227 mortar bar expansion test run over 3 months period using Berber, Atbara and Al Salam cements with 5% alkali addition.

Cement	Atbara	Alsalam	Berber
Time (days)			
0	0	0	0
15	0.023	0.021	0.02
30	0.034	0.033	0.027
60	0.045	0.043	0.037
90	0.053	0.052	0.045

Figure 14: Expansion of an aggregate material subjected to the ASTM mortar bar expansion test run over 3 months period using Berber, Atbara and Al Salam cements with 5% alkali addition.



3.3 DISCUSSION:

The results of chemical test shows that Berber cement alkalis percentage (0.77 %) is relatively of a lower alkali level than Al Salam cement percentage (0.97%) which, in turn, is of a lower alkali than Atbara cement percentage (0.99%). The three cement, however, are of alkali contents greater than the ASTM C 150 specifications of (0.6%) if the cement is to be used with potentially reactive aggregate for concrete. The alkali content of Portland cement is expressed, according to ASTM C150, as sodium oxide equivalent to $Na_2O+0.658K_2O$.

Results of strength test show that with more alkali addition there was more reduction, in both, the compressive strength and flexural strength. Furthermore, the reduction in strength was more pronounced at the 28th day strength, particularly, the compressive strength. The obtained test results are in agreement with the findings of Smaoui et al. (2005), Osbaeck (1984) and Alexander and Davis (1960). From the results obtained it can be deduced that a high alkali cement produces, specially in the long term, lower compressive and flexural strength than a low alkali cement. Results of setting time and soundness shows that with more alkali addition there was more reduction, in both testes, and the microstructure of the cement will be changed and become weaker. Results of the expansion measurements in the ASTM test for each cement-aggregate combination, without and with alkali addition, shows that before the addition of alkali the tested cement gave expansions, with the three cements (Berber, Atbara and Al Salam.), less than ASTM test failure criterion of 0.05% in three months. However, with Atbara cement of alkali content equals to 0.99% the observed expansion was found to be greater than that shown by Al Salam cement with alkali content of 0.97%. Berber cement with alkali level of 0.78% recorded the lowest expansive reactivity.

When the alkali level of the three cements was increased by 5%, Atbara and Al Salam cements showed expansion greater than the ASTM test failure criterion of 0.05% in three months, and again Atbara cement gave expansion greater than that shown by Al Salam cement, as for Berber cement, it recorded expansive reactivity less than Atbara and Al Salam cements and less than the ASTM test failure criterion of 0.05%.

3.4 CONCLUSION:

1. The alkalis content generally affected the mechanical properties of cement.
2. Optimum alkali content was about (0.6 %).
3. Any addition of alkali content more than (0.6%) can reduce the strength, soundness, setting time and increased expansion in cement paste.
4. Addition of alkali made the structure of cement more weaker.
5. The high alkali concrete shows more reticular and porous microtexture which could explain the reduction in strength.

3.5 RECOMMENDATION:

1. Owing to their high alkali oxide content, we recommend that Atbara and Alsalam factories vary their sources of raw materials to obtain the principal oxides for the manufacture of cement with less quantity of alkali oxides as does Berber factory by adding schist mineral to the main minerals of clay and limestone.

2. Also pozzlana can reduce the distress of alkalinity in final products.

APPENDIX

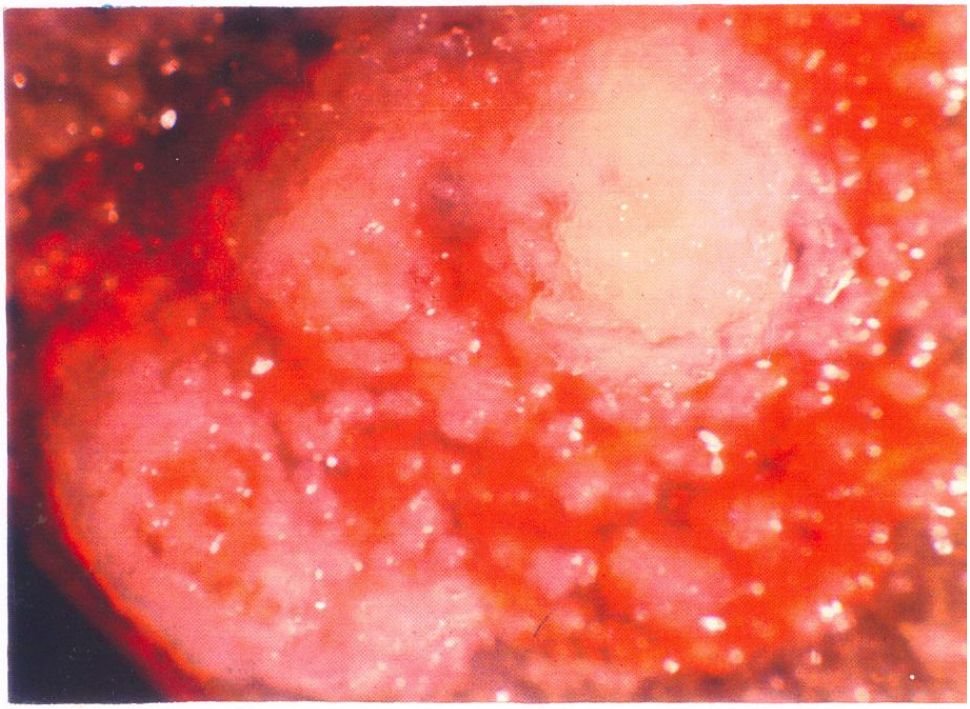


Plate 1: Alkali-silica gel

Plate 2: Flame – photometer PFP7

Plate 3: Molds

Plate 4: Instrument of compressive strength

Plate 5: Instrument of flexure strength

Plate 6: Vicat apparatus

Plate 7: Le chatelier apparatus

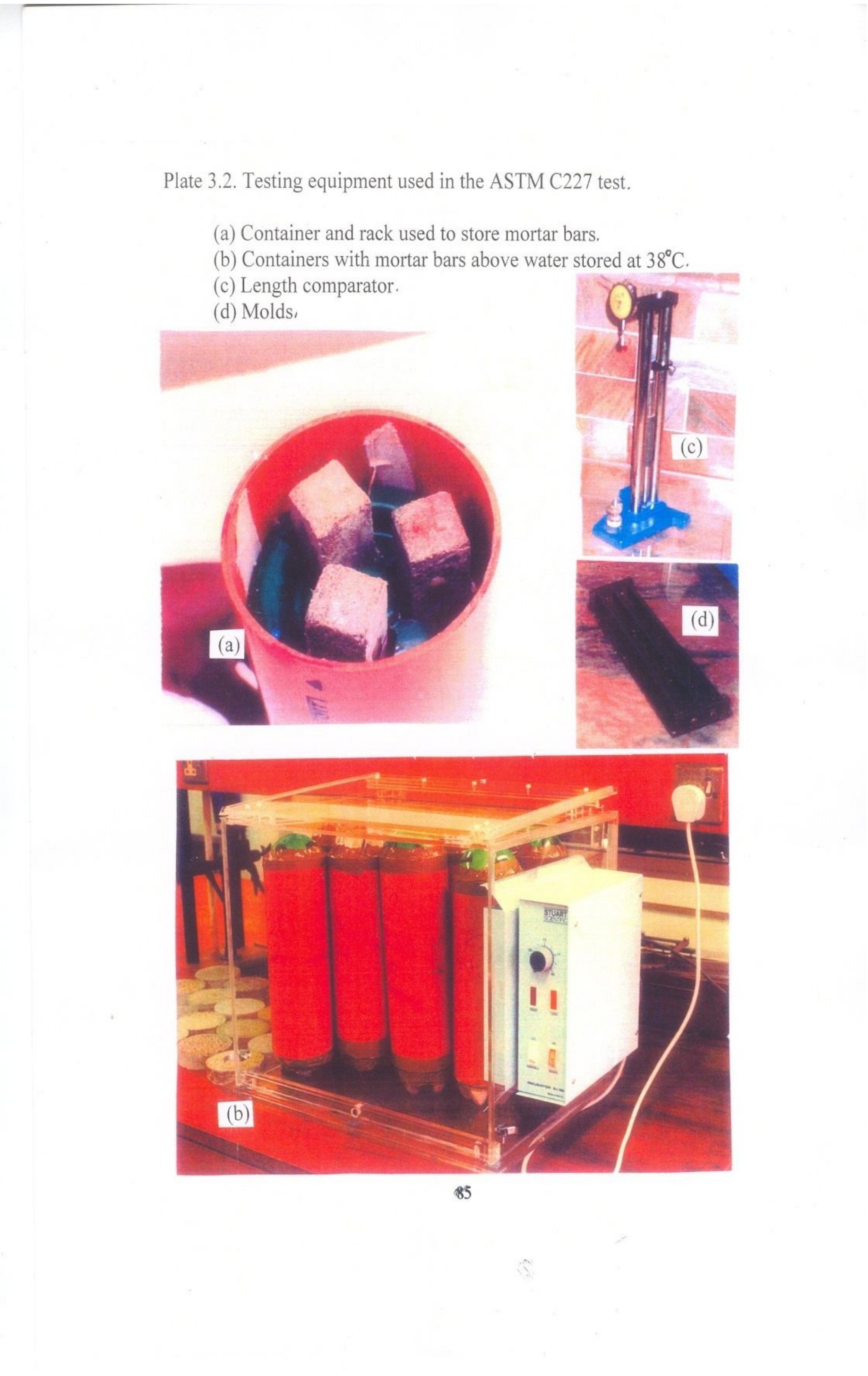


Plate 3.2. Testing equipment used in the ASTM C227 test.

(a) Container and rack used to store mortar bars.
(b) Containers with mortar bars above water stored at 38°C.
(c) Length comparator.
(d) Molds.

85

Plate 8: Testing equipments used in ASTM C227 test,

(Mortar-bar)

REFERENCES:

1. ACI 221. 1R 1998, *State of the Art. Report on Alkali-Aggregate Reactivity,* American concrete Institute, Farmington Hills, MI.
2. Alexander, KM, & Davis, CES 1960, *Effect of alkali on the strength of Portland cement paste*, Cement and Concrete, Aust. J. Appl. Sci. 11 (1960) 146-156.
3. American's Cement Manufacture 2015, Alkali-Aggregate Reaction. Available from: http://www.cement.org. [January 2015].
4. ASTM, 1997, *Specification for Portland cement*, Annul book of ASTM standards. ASTM, vol. 04. 01: cement: lime: gypsum, section 4, c 150-97, 156-162.
5. ASTM, 1990, *Standard practice for petrographic examination of aggregate for concrete*, Annual book of ASTM standards, ASTM. vol. 04.02: Concrete and mineral aggregate, section 4, C-295-90 221-232ASTM, 1997, *Standard Specification for Concrete Aggregates*, Annul book of ASTM standards. ASTM C33.
6. Blaine, RL, Arni, HT, Evans, DH, Defore, MR, Clifton, JR, & Methey, RG, 1971, *Compilation of data from laboratory studies*, Builing Science Series, 36, part 6 42, 1971, 115 pp. National Bureau of Standards, Washington, DC.
7. Bogue, R H, 1955, *The chemistry of Portland and cement*, Reinhold, New York.
8. BS, 1989, *Testing aggregate. Method for sampling*, BSI 812.Part 102. BSI, London.
9. BS, 1978, *Specification for ordinary and rapid hardening Portland cement,* BSI 12. BSI, London.
10. Building research establishment, 1988, *Alkali-aggregate reactions in concrete,* Digest 330, 8. Building Research Station, Garston.

11. Burrows, RW, 1998, *The visible and invisible creaking of concrete*, ACI Monograph No. 11, Farmington Hills, MI: The American Concrete Institute, Campbell Allen, D.
12. Carlson, RW 1939, *Remarks on the durability of concrete*, ACIJ. 35(1939) 359-364. Journal Proceedings.
13. Cement and concrete association, 1987, *Introduction to concrete,* Wexham Springs, Slough UK.
14. Comte, JMA 1959, *"Rock Products"*. Vol. 62 (5), pp. 128-131. 6 Ekonomlcheskaya Gazeta, Moscow.
15. Craddock, QL 1952, *Cement Chemists, and Works Managers, Handbook,* P.78. Concrete Publication, London.
16. Early hydration of ordinary Portland cement, 2005, *Advances in cement Research,* No 17, PP. 1-8.
17. Dolar-mantuani, L 1983, *Handbook of concrete aggregates- A petrographic and technological evaluation,* Noyes publications, NewJersey, USA.
18. *Effects of alkali addition on the mechanical properties and durability of concrete*, 2005, Cement and concrete research, No. 35, 2005, PP.203-212.
19. El-Tilib, NM 1992, *Alkali-aggregate reactivity of the major rocks in Sudan,* 20-30, Building and road research institute, Khartoum, Sudan.
20. Gouda, GR 1986, *Microstructure and properties of high-alkali clinker*, 8th International congress on the chemistry of cement Rio de Janeiro, Theme 1, vol. 2, pp 234-239, Alba Grafica e Editora Ltda, Rio de Janeiro, Brazil.
21. Heilmann, T 1962, *"Chemistry of cement"*. Proceeding of the Fourth Inter-national Symposium, Washington 1960, P. 87. National Bureau of Standards Monograph 43. U.S. Department of Commerce. Washington, USA.

22. Hobbs, DW 1988, *Alkali-silica reaction in concrete*, Thomas Telford Ltd, London.
23. Jawed, I, & Skalny, J 1978, *Alkalis in cement: a review: II. Effects of alkalis on hydration and performance of Portland cement,* Cement and concrete research. Vol. 8. Pp. Martin Marietta Laboratories Baltimore, Maryland.
24. Lea, FM 1956, *The Chemistry of Cement and Concrete*, 2nd Ed., ed. By F. M. Lea, p. 112. Arnold, London.
25. Lyons, JW, Min, H S, Tarisot, PE, & Paul, J F 1962, *I. & E.C. process Design and Development* 1 (1), 29.
26. Luxan, MP, Frias, M, & Dorrego, F 1994, *Potential Expansion of Cement Mortars in the Presence of K2SO4 and Pozzolan,* Cement and Concrete Research, Vol. 24, No. 4 (1994), pp. 728-734. Madrid, Spain.
27. Manecke, G 1954, Z, Elektrochem, 58, 369.
28. Mullick, AK 2007, *Performance of concrete with binary and ternary cement blends*, The Indian concrete Journal, pp. 15-22.
29. Mussgnug, G 1962 *contribution to alkali question in floating gas heat exchanger furnace cement-lime plaster 5*, 1962, p. 197-204.
30. Nalle, PB, & Weeks, LW 1960, Min. Engng 12 (9), 1001.
31. Neville, AM 1981, *Properties of concrete*, 3rd addition, The English language Book society and Pitman Publishing, London.
32. Odler, I & Wonnemann, R 1983, *Effect of alkali hydration on Portland cement hydration: I. Alkali oxides incorporated into the crystal lattice of the clinker minerals,* Cement and concrete research. Vol. 13, pp. 477-482.
33. Osbaeck, B 1984, *Influence of alkalis on strength development of blended cement,* In proceeding of the 35th international conference on the chemistry and chemically related properties of cement, pp. 375-383. Norway: University of Oslo.

34. Pollitt, HWW 1964, *Raw material and processes for Portland cement manufactures,* In H.F.W Taylor (ed.). The chemistry of cement. Vol.1 Academic Press.

35. ‘Portland cement’ 2014, Wikipedia, wiki. Available from: https://en.wikipedia.org/wiki/Portland_cement. [January 2014].

36. Saikia, Mimi Das, Bhargab Mohan Das, Madam Mohan Das 2010, *Elements of Civil Engineering*, New Delhi: PHI Learning Private Limited. 2010. 30. Print. New Delhi.

37. Shayan & Ivanuse 1989, *Influence of NaOH on mechanical properties of cement paste and mortar with and without reactive aggregate,* Proceeding of 8th International Conference on Alkali-aggregate reaction. Society of material sciences. Pp 715-720. Kyoto, Japan.

38. Shirley, DE 1985, *Introduction to concrete,* Bsc, Micheme, Minste cement and concrete association.

39. Smaoui, N, Berube, MA, Fournier, B, Bissonnette, B & Durand, B 2005, *Effects of alkali addition on the mechanical properties and durability of concrete,* Cement and Concrete Research, 35, 203-212. Elsevier.

40. Smith, R L & Raba, CF, Jr 1986, *Recent developments in the use of fly ash to reduce alkali-aggregate reaction,* Alkalis in concrete. ASTM STP 930. 58-68. American Society for Testing and Materials, Philadelphia.

41. Symposium on Recent Development in Mineral Dressing 1953, Institution of Mining and Metallurgy, London.

42. Taggart, AF 1950, *Handbook of Mineral Dressing*, Wiley. New York.

43. Thoulow, N & Knudsen T 1975, *Alkalis in concrete,* In Proceedings from the Symposium on Alkali-Aggregate Reaction—Preventative Measures; Reykjavik, Copenhagen.

44. Vivian, HE 1950, *Studies in cement-aggregate reaction,* XV: The reaction product of alkalis and opal. CSIRO, Melbourne, Australia. Bulletin 259, 60. Melbourne.

45. Wolfgang, C 1962, *Cement chemistry and physics for civil engineers*, Chemical Publishing Co. New York.

46. U.S Department of Transportation Federal Highway Administration 2015, *Portland cement*. Available from: http://www.fhwa.dot.gov/infrastructure/materialsgrp/cement.html. [20June 2015].

47. http://civilblog.org/wp-content/uploads/2014/06/Vicat-Apparatus.jpg

48. http://pimg.tradeindia.com/00712456/b/1/Le-Chatelier-Mould.jpg [June 2015].