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Review Article

Limestone as Solid Mineral to Develop National Economy

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Abstract: Limestone is a valuable raw material in the world production which signified the distribution or the availability of the raw material within the countries and the economic development also depends on the regular production. In Nigeria the cement industry has made a considerable improvement in production capacity and development. This has resulted to an increase in cement production in Nigeria with its attendant increase in carbon dioxide generation into the atmosphere. Nigeria will be producing over 25 million metric tonnes of cement annually and at the rate of one tonne of cement to one tonne of carbon dioxide, the country will likely be producing 25 million metric tonnes of carbon dioxide from cement production annually. The paper x-rayed this and showed the potential of the Nigeria cement industry in the contribution to global warming.

Keywords: Limestone, Cement, Minerals

1. Introduction

Limestone is one of the common types of rock found on the surface of the earth. About 10% of the land surface of our plant is made up of limestone or similar types of rock, while around 25% of the world' s population either live on or take their water from limestone. It is though that 50% of all our oil and gas reserves are trapped in lime stone buried beneath the surface [1].

Limestone is a sedimentary rock composed primarily of calcium carbonate with the occasional presence of magnesium. Most limestone is biochemical in origin meaning the calcium carbonate in the stone originated from shelled oceanic creatures. Limestone can also be chemical in origin as is the case with travertine. Chemical limestone forms when calcium and carbonate ions suspended in water chemically bond and precipitate from their aquatic sources. Because of its high calcium content, limestone is usually light in colour, although many variations exist. Commercially, the term limestone includes dolomite, dolomitic limestone, oolitic limestone, and travertine [6].

The rock limestone is almost made up one of two type of mineral-either calcite aragonite. Both of these are different crystal arrangements of the same chemical compound-calcium carbonate ($CaCO_3$) [8].

1.1. Limestone Is Special Types of Rock for Several Reasons

1) It is most commonly made by microscopic organisms living in the sea.
2) It can be dissolve in natural waters, allowing curves, shafts, natural bridges and sculptured rock outcrops to form (like those found in waitomo area)
3) It is the important ingredient in making agriculture lime and cement.

1.2. Sources of Limestone

Limestone originated from the biological deposition of shells and skeletons of plants and animals massive beds accumulated over millions of years [1].

In the cement industry limestone includes calcium carbonate and magnesium carbonate. Most industrial quality limestone is of biological origin. The ideal cement rock 77-78% is $CaCO_3$, 14% S_iO_2, 2.5%Al_2CO_3, 1.75%Fe_2O_3. [2].

Other Sources Are
Sedimentary deposits of marine origin (limestone)
Marble (metamorphosed (limestone)
Chalk
Marl
Coral
Aragonite
Oyster and clam shells
Travertine
Tuff.

1.3. Composition of Limestone

Limestone composed the following elements:
Calcium
Carbon
Oxygen

Limestone is originated from the biological deposition of shells and skeletons of plants and animals. Massive beds accumulated over millions of years.

1.4. Mining Method of Limestone

Limestone deposits are mainly extracted by bench mining in which holes are change with ammonium nitrate and fuel oil explosive and blasted.

The rock is excavated front end loaders ($10m^3$ capacity) and loaded into 70-90 tones trucks and then transported the primary crusher marl and chalk normally do not require blasting.

A trend is to used pit moveable primary crushers and belt conveyors to transport the rock to a fixed secondary crusher, thereby reducing the number of trucks and and haulage distance.

Underground mining of limestone is not typical, in the U.S one plant obtains it limestone from underground operation, using room and pillar mining method.

Clay and shale normally extracted using front end loaders and loaded into haul trucks.

When they occur as overburden the clays and shale not used are stored and often reused for reclamation in the mined out areas of the quarry. [9].

Figure 1. *Shows a typical trucker used in mining method in some counties.*

1.5. Minerals That Resemble Limestone

There are certain substances that resemble limestone but the differed in chemical composition. The following are some of them:

Marble: Buried limestone that has been caught in an active part of the earth' s crust can suffer huge increases in temperature and pressure. These can compress, melt, and then recrystallize the original limestone further a very beautiful and hard solid (rock).

Dolomite: Magnesium (Mg) is an element similar to Ca that also forms a carbonate. While limestone is mostly $CaCO_3$, if it has high level of magnesium then it is known as dolomite-as fount in the Dolomite Mountains of Italy.

Chalk: This variety of limestone is entirely made up of small coccohths's – shells from a form of algae. It is un-compacted and little cemented compared to other limestone it is found today almost as it was when laid down on the seabed

Waitomo Limestone: Limestone in the waitomo area were laid down on the bottom of a warm shallow sea around 25-40 million years ago. This period of time, and the limestone, is referred to as Oligocene.

Limestone around waitomo ranges from 40%-100% calcite (calcium carbonate). The rest of the limestone is made up of volcanic fallout and local basement rocks carried by river into the ancient sea.

About 80%-90% of the calcite is composed of skeletal fragments, while the rest is the calcite cement that was naturally precipitate from the sea. Sharks teeth and whale bones are also found and this means that, In general clearly limestone is a solid mineral. [9].

1.6. The Distribution of Limestone Around the World

In large parts of the United States there are extensive deposits of marine limestone of various ages from a few thousand to more than 350 million years old. Some deposits have chemical grades as high as 95% $CaCO_3$ [4].

However, some areas are completely without any suitable limestone deposits. Most of the cost of limestone to the customer is determined by how far away it comes from and how it is shipped. Shipping by barge on water is cheaper than by train which, in turn, is cheaper than shipping by truck. The following are some of the countries that have main deposition of limestone. Kentucky, Ukrainskaja in Ukraine, Berne, in Switzerland, Sarawak in Malaysia, Burgos in Spain, Naute-Garonne in France, Tamaulipas in Mexico Oberosterreich in Austria, Bahia in Brazil, Yorkshire Dales in UK [7].

1.7. The Distribution of Limestone in Nigeria

Nigeria has abundant Limestone. States with largest the deposits include; Cross-River, Ogun, Imo, Abia, Anambra, Ebonyi, Enugu, Benue, Ogun, Kogi, Nasarawa, Yobe, Adamawa, Borno, Edo and Kebbi States. It is used in Cement Industries, as lime fertilizer flux in glass ceramics, iron, and steel industries.

Table 1. Shows the distribution of limestone in Nigeria.

State	Areas where it is found
Cross River	Mfamosing, Oduk pani, uwet, Akpa,
Akwa Ibom	Obotime
Imo	Okigwe
Abia	Bende, Ohafia, Arochukwn
Anambra	Njikoka
Ebonyi	Abokaliki, Ikwo, ohaozara
Enugu	Nkanu, Agwu, Aninri
Benue	Ado, Apa, Gbako, Guma, Kastina, Makurdi, Oju, Ushango
Orgun	Shagamu, Ewekoro
Kogi	Ajaokuta, Osara
Nassarawa	Jakura, Adde, Itabe
Gombe	Funa-kaye, Nafada
Yobe	Garin Ari, Turmi, Kwayaya
Adamawa	Guyuk, Shalleng, Ngurore Numan
Borno	Yadi-Gilan (Dabnowa)
Edo	Akoko-Edo, Owan-East, Owan-West, Etsako East, Etsako central, Etsako west
Kebbi	Jago

1.8. Uses of Limestone

Limestone uses to manufacture many products such as:
Cement
Ceramics
Chemicals
Fertilizers
Industrial fillers

2. Economic Importance of Limestone to Nigeria

Mining is a major economic activity in many countries, in which Nigeria is included. The country is endowed with abundant mineral resources of international value, including gold, limestone, marble, gypsum, gemstones, iron ore, natural gas, topaz, coal, clay, lead, tar sand, construction stone and construction sand. While the exploitation of natural resources has traditionally been seen as a vital part of economic growth, it is now well recognized that concern for environmental and socio economic consequences must be included as a key component of development activities. In many developing nations like Nigeria, mining is an important contributor to the national economy. However, the negative environmental impacts of mining are increasingly being recognized as critical [10].

In response, many companies, especially international ones, are embracing Corporate Social Responsibility as a fundamental component of resource extraction operations, including mining [10].

The mining sector may strengthen the economy at the national scale; it may also present an entirely new set of problems at the scale of the local community. Exercising social responsibility in small, remote centres, however, often means that international and transnational corporations must interact with rural or indigenous people who have strong emotional and historical links to the land [3].

2.1. Relation to Socio-economy

According to International Journal of Development and Economic Sustainability Vol.3, No.5, pp.85-98, October 2015, majority of the respondents (34.57%) did not have income that is up to N90, 000 ($600) per annum from the jobs they engaged in. These jobs include farming, petty trading, unskilled labourer in the cement industry and some local government workers [civil servants]. While 24.69% made between N90, 000-N150, 000 ($600 –$1000) per annum, most of the civil servants and teachers (21.6 – 16.05%) used to make between N150, 000-N270, 000 ($1000 - $1800) per annum. Only a few people among the civil servants and teachers make (3.09%) above N270, 000 per annum. This statistics invariably shows that, the people are still living below standard economy values, more so, those that were earning above N 270, 000 ($1800) were business enterprise owners, whose business centres were located near the cement industry and some workers in the managerial positions (who are not indigenes of the villages, though, some are from the state) in the cement company. In most cases, these business owners were not permanent residents of the study area. It is therefore unrealistic to;

2.2. Relation to Health

According to Also International Journal of Development and Economic Sustainability Vol.3, No.5, pp.85-98, October 2015, during analysis of health data, the respondents claimed that dust emission from the cement works had adverse effects on their health; majority of them did not visit hospital. For instance, 162 of all the respondents did not visit hospitals occasionally; only about 13% of them visit the hospital regularly, while about 11% did not visit the hospital regularly. Figure 10 shows that the ailments commonly treated included headache/ fever (28.9%), malaria (19.8%), stomach problems (14.0%), eye problems (16.5%), cold/catarrh (9.9%), skin irritation (6.6%) and cough (4.1%). The frequency at which these ailments occur tends to suggest that the limestone quarrying and processing activities have no significant adverse effects on the health of surrounding communities.

2.3. Relation to Social Amenities

As a result of the effect of limestone mining and processing in Ewekoro, it has given rise to competition of social amenities in surrounding towns, such as Ifo, Papalanto, Arigbajo and Itori. This has increased the population of residents in these towns; hence it has stressed food, water and other suppliers to the limit. This increase in population has led to inflation, due to increase in demand for certain food item which had been unable to meet up with agricultural produce as a result of withdrawal of inhabitant from farming. There was high competition for available social amenities due to shortage of housing, school, electricity and medical facilities. The electricity supply in Ifo was being rationed due to high increase in number of residents, also the water supply from Papalanto was erratic in supply. The available schools were not enough, thereby increasing staff student ratio. Lastly, the following additional recommendation should be implemented to improve the existing relationship between the company and the host communities:

1. Regular assessment of environmental impacts and mitigation through technical initiatives with collaborative efforts of research institutes should be encouraged.
2. To improve access to qualitative education, the company should initiate the Provision of schools (primary and secondary) and finance all its expenses to assist the government's effort towards the development of the community.
3. Health is wealth as the common adage says' therefore, in order to sustain the wealth of the industry, another health centre should be provided with both medical personnel and facilities in place.
4. Royalties paid to government by the cement industry should be a benefit for all community members; hence the government should endeavour to provide basic amenities for the residents living around the cement factory.
5. The farming activities of the residents can be better encouraged by the provision of fertilizers to further help improves the soil quantity such as the supply of organic manure.
6. There is need to open a permanent office in the Local Government Secretariat for representative of the communities, Local Government nominated official and the company representative monthly meetings. This will enhance quick development rather than pumping money to the Local Government and nothing to show for it at the end of the day. [5]

2.4. Mining Implication of Limestone

Mining processes of limestone has many environmental implication the following are some of them

Increases in global warming due the generation of Carbone monoxide (CO_2)

Contamination of water due to irregular disposal of west products from the industries.

Pollution

Irritation

Erosion

Deforestation

Decreases the animal population

2.5. Products Made From Limestone

Many products are manufactured by limestone such as cement, chemicals, fertilizers, industrial fillers, ceramics, etc.

2.5.1. Cement

This is the general term given to the powdered materials which initially have plastic flow when mixed with water or other liquid, but has this properties of setting to a hard-solid structure several hours with varying degree of strength of bonding properties

A cement of far more quick setting and much greater strength was discovered by Joseph Aspidin, an English Brick layer in 1924. This cement is called *Portland cement* and nowadays, prepared artificially. Portland cement is one of the most important building materials at the present time. Joseph Aspidin (1924) found that a strong heated mixture of limestone and clay, when mixed with a small amount of water, set in few hours to a hard stone like substance. After setting, the stone like mass resembled famous Portland rock (stone) of England and hence it was named as Portland cement [12].

2.5.2. Portland Cement

This chemically defined as the finely ground mixture of calcium aluminate and silicates of varying compositions which hydrated when mixed with water to form a rigid solid structure with good compressive strength.

The essential raw materials used in the manufacture of Portland cement are limestone but the fundamental chemical compounds to produce cement clinker are:

Lime (CaO)

Silica (S_iO_2)

Alumina (Al_2O_3)

Iron oxide (Fe_2o_3)

2.5.3. Manufacture of Portland Cement

The chief raw materials for manufacture of Portland cement are limestone and clay and these are generally available in large amounts in the vicinity of cement factories. There are three methods of manufacturing Portland cement.

The Wet Process

Dry Process

Semi Dry Process

(i) Wet Process

This is the most common and almost universally employed process for the manufacture of cement. In the process, the raw materials are finely ground blend in the desired proportion and the mix is brought to the condition of free flowing slurry containing 40% water. This slurry is thoroughly homogenized and allowed to pass through the different sections of kiln (a region of different temperature) where at

Drying zone (at about 400°C) the slurry lost all its water

Calcining zone (at about 900-1000°C), the lime stone decomposes or follows

$$CaCO3_{(s)} \rightarrow CaO_{(s)} + CO_{2\,(g)}$$

Burning zone (at about 1400-1600), the lime clay combine to form calcium silicate and calcium aluminates, in a form of small balls or pellets with varying sizes called cement clinker. This is later pulverised (ground to powder) with 2-3 gypsum and packed in air tight bags. This first powdered product is called Portland cement

(ii) Dry Process

In this process, the raw materials are crushed into small pieces, dried and mixed in proper proportion in tube mill and homogenized with compressed air. This dry- raw meal is than introduced into the upper end of the rotary kiln while blast of burning coal is blown from the other end. The reaction taking place and the rest of the process is similar to that of the wet method, but only the different there is no water in this meth

(iii) Semi Dry Method

in this method, the raw materials are initially ground dry, but instead of introducing it to the rotary kiln as powder, it is mix with 10-14% water which are then fed (introduced) to a travelling great where they got dried and preheated before enter into a short rotary kiln where they are burnt to form ment clinker [14].

3. Sequence Operation of Portland Cement

The general sequence of operation for the manufacture of cement can be summarised as follows:

Selecting the raw materials

Crushing and grinding

Storage of the slurry

Burning the ground mixture to clinker in a rotary kiln.

This involves passing the slurry gradually into different temperature zones in the kiln such as:

Drying zone at 400°C

Pre-heating zone at 400-700°C, where calcium and magnesium carbonates decomposes.

Calcining (decarbonizing) zone at 700-100°C, where

$$CaCO_3 \rightarrow CaO + CO_2$$

Burning and clinkering Zone at 1350-1550°C, where lime and clay react with each other. [9].

3.1. Formation Aluminate Silicate

$$2CaO + S_iO_2 \rightarrow 2CaO.\ S_iO_2$$

Dicalcium silicate

$$3CaO + S_iO_2 \rightarrow 3CaO.\ S_iO_2$$

Tricalcium silicate

$$3CaO + Al_2O_3 \rightarrow 3CaO.\ Al_2O_3$$

Tricalcium aluminate

$$CaO + Al_2O_3 + Fe_2O \rightarrow 4CaO + Al_2O_3.\ Fe_2O_3$$

Tetracalcium aluminoferrite

These compounds (called constitutional compounds) combine together to form small hard, greyish pellets called cement clinkers, the composition in which depends on the ratio called the burn ability index which usually ranges from 0.45 to 0.85 that is 45-85%. All the reaction involved in these steps is exothermic.

Cooling of the hot clinker

Grinding the clinker with gypsum

Storage and packaging [9]

3.2. Character of Constitutional Compounds

1) Tetra calcium Aluminoferrite (C_3A): Undergoes hydration at a very fast rate and it is responsible for the initial set of first setting, with heat of hydration of about 879kj/Kg
2) Tricalcium silicate (C_3S): It developed very high strength quite early and the ultimate strength with highest rate of heat of about 502Kj/Kg
3) Tetra calcium aluminoferrite (C_4AF): It does not contribute to the strength of the cement because both its early strength is the ultimate strength poor and lower among the constitutional compounds. Its rate of hydration is slow and hence it is slow setting. It is of hydration is about 41Kj/Kg.
4) Dicalcium silicate (C_2S): This hydrates very slowly, with heat of hydration of about 251Kj/Kg.

3.2.1. Types of Portland Cement

The Five types of Portland cement are classified base on the amount of the clinker compounds that is C_2S, C_3S, C_4AF and MgO.

Regular Portland Cements: these are used concrete construction work and they harden full strength in about 28-30 days containing 40-60% C_3S, 10-30% CA_2S (Calcium dialuminate) and 7-13% C_3A.

Modified Portland Cement: These are sulphating cement which are used where moderate of hydration is required which does not exceed 292.88-334.72Kj/Kg after one weak and four weeks respectively. They are characterised by having higher C_2S/C_3S ratio.

High Early Strength (H. E. S) Portland cement: This cement contain higher% of C_3S and C_3A with finer grinding to increase hydration rate. Road constructed from HES cement can be putted into service much sooner than roads constructed for regular cements.

Low Heat Portland cement: These contain lower% of C_3S and C_3A thus decrease the heat evolution which does not exceed 25Kj/Kg to 292.88kj after 7 and 26 days respectively these types of cements are designed to massive structure work.

Sulphate Resisting Portland cement: These are generally for sea water contact, resist sulphates better than the earlier four types. The contain lower value% of C_3A and higher% of C_4AF [13].

3.2.2. Uses of Portland Cement

The main uses of cement is in the fabrication of concrete and mortars

MODREN USES

Building (floors, beams, columns, roofing, piles, bricks, mortar, panels, plaster)

Transport (roads, pathways, crossing, viaducts, tunnels, parking etc.)

Water (pipes, drains, canals, dams, tanks, pools, etc.)

Civil (piers, docks, retaining, walls, silos, warehousing, poles, pylons, fencing, etc.)

Agriculture (building, processing, housing, irrigation, etc)

Mortar holding weathered bricks

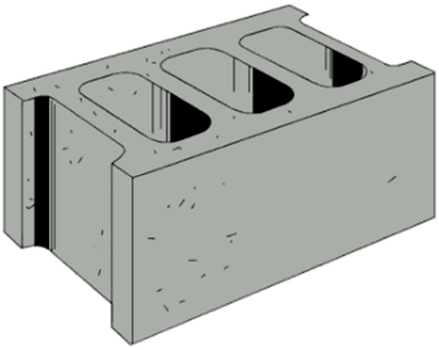

Figure 2. *Shows blocks of Portland cement.*

Figure 3. *Packages of Portland cement.*

4. Conclusion

It has been shown that the limestone is a valuable mineral and it is the key of the world economy. The constructions of the roads, school, houses, etc. are all depend on the cement which contains the limestone as an active ingredient. It also shown that the cement industries have capability of generating good cements. This paper is a wakeup call to what this is likely to lead to the development of economic future of a country.

5. Recommendation

Governments are expected to give more consideration of the research for the limestone deposition.

Mining of the limestone must be regularly improved through different modern methods so as to improve the cement production.

Cement industry and other industries depend mainly on the limestone production.

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