

Thermo-economic and Environmental Assessment of Cement Production Plant

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Abstract

In this paper, the thermodynamic, economic and enviromental analyses of a cement plant are made using the first and second law of thermodynamics based on actual operational data. The thermo and economic calculations provide information about the cost formation and the interactions among the cement plant components. The enviromental analysis quantifies the emission and provides alternative ways of operating environmentally friendly cement production plant

Keywords: : Cement, Economic, Environment, Exergy and Thermodynamic.

1. Introduction

The cement industry is an energy intensive industry and has high enviromental implications. It is difficult to envisage a life without the industry as it is the bedrock of most construction works. The demand for cement product continues to rise as the population increases and hence the need to mitigate the down sides of the production process. It has been reported that the amount of cement used in construction more than double that of all the other building materials such as aluminium, wood, steel and plastic.

The energy economy of the cement production process is of particular interest. Huang et al., (2016) studied the energy efficiency improvement for the Taiwan's cement industry. The study concluded that 25% savings for electricity and 9% savings for fuel is achievable in a given period of time. The cost of energy in most cement production units accounts for more than 25% of the total cost of production (Khurana et al, 2002). It was recently reported that the cement industry is one of the top energy consuming industry in developing countries. (Liu et al., 2017).

Many of the aspects of cement production are potentially environmentally damaging (Oyinloye, 2015), although these risks can be minimized. Emissions to air are the main environmental challenge faced by cement industry. The production of cement being one of the most energy intensive production process known, also emits a lot of $CO₂$ due to the decomposition of CaCO₃. Cement production accounts for about 8% of total $CO₂$ emissions from all human activities and in a country like China, it accounts for about 15% of total CO₂ emission (Zhang et al., 2016).

The increased cost of energy, increased stringent environmental regulations and global competition in product pricing and quality has increased research interest in energy and enviromental implications of cement production process. This paper presents the economy implication of the energy consumed in a cement production plant in

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pollutants resulting from the production process. Section 4 gives the method of analysis while the results and discussion are given in section 5. Section 6 concludes the paper.

2. The system

Portland cement consists of pulverized clinker and gypsum. Basic chemical components of Portland cement are calcium (Ca), silicon (Si), aluminium (Al) and iron (Fe). Clinker consist of tricalciumsilicate $(3CaO.SiO₂)$, dicalciumsilicate (2CaO.SiO₂), tricalcium aluminate (3CaO.Al₂O₃). The major mineral constituent of Portland cement is given in Table 1.

The cement manufacturing process involves four distinct stages. These are Quarrying, Raw material preparation,

Clinkering or Pyroprocessing and Milling. Most of the raw materials used are extracted from the earth through mining and quarrying. Quarry operations consist of drilling, blasting, excavating, handling, loading, hauling, crushing, screening, stockpiling and storing. The raw material for cement manufacture is a rock mixture which is about 80% limestone (which is rich in $CaCO₃$) and 20% clay or shale (source of silica, alumina and Fe₂O₃).

The steps involved in the raw material preparation depend on the process used. There are two main cement manufacturing process; the Dry process and Wet process. In the dry process, the quarried clay and limestone are crushed separately. Samples of both rocks are then sent to the laboratory for mineral analysis. If necessary, minerals are then added to either clay or limestone to ensure that the correct amounts of aluminum, irons etc. are present. The clay and limestone are then fed together into a mill where the rock is ground until more than 85% of the material is less than 90mm in diameter. In the wet process however, the clay is mixed to form a paste in a mill (a tank in which the clay is pulverized in the presence of water). Crushed lime is then added and the whole mixture is further grinded. The slurry is then tested to ensure that it contains the correct balance of minerals and any extra ingredient blended in as necessary.

In the Clinkering or Pyroprocessing stage, the finely ground material is dried, heated (to enable sintering reaction to take place) and then cooled down again. While it is being heated various chemical reactions take place to form the major mineral constituents of Portland cement. The powder from the dry process doesn't contain much moisture so it can be dried in a pre-heater tower and then fed into the kiln. The slurry from the wet process contains too much moisture to be successfully dried in a preheater tower. Instead, the slurry is fed directly into the kiln where it is formed into dry balls by the heat and rotation of the kiln. The wet process kilns therefore are generally longer than dry process kilns. The kilns used in both processes are inclined on a shallow angle and lined with heat resistant bricks. The reaction processes occurring within the kiln can be broken into a number of simple zones. In zone 1, Calcination, formation of $3Cao.A₁₂O₃$ above 900° C and melting of fluxing compound $A₁Q₃$ and Fe₂O₃ take place. In zone 2, is the exothermic reactions and the formation of secondary silicate phases between 1100-1300°C. Sintering take place in zone 3 and in zone 4 Cooling and crystallization of the various mineral phases formed in the kiln. The fused material is called clinker. Immediately following the kiln is a large cooler designed to drop the temperature of the clinker from 1000 to 150° C. This is achieved by forcing air through a bed of clinker via perforated plates in the base of the cooler. At this point in the process, the materials have been formed into all the required minerals to make cement.

In the milling stage, the clinker is mixed with gypsum $(CaSO₄.2H₂O)$ which is added as a set retarder. The cement flow from the inlet to the outlet of the mill (a rotating chamber) being first ground with 60mm then 30mm diameter steel balls. The first grinding breaks up the material and second grinds it to fine powder. The particle size is measured by laser diffraction analysis.

3. Pollutants from Cement Production Process

 Emission to air by cement industries can pollute the ambient air. The air pollutants of importance include: particulate dust and green-house gases (GHG) viz: oxides of nitrogen (NO_x) , carbon dioxide, oxides of sulphur (S_{α}) and carbon monoxide. Emissions to air also include Dioxins, Furans, Metallic Compounds, Gaseous Inorganic Fluorine Compound (HF), Polycyclic Aromatic Hydrocarbons (PAH), Benzene, Toluene, ethyl benzene and xylene (Hua 2016).

Cement industries contribute between $5-8\%$ of the total $CO₂$ emission. (Ali et al. 2011). During the clinker burning process carbon dioxide is emitted. CO_2 emission is both raw material-related and energy-related. CO_2 is produced from fuel combustion for power and process heat generation (Shen et al. 2014). $CO₂$ is also produced during calcination of limestone. Carbon dioxide $(CO₂)$ causes global warming and climate change (Xu et al. 2014). Increase in the amount of carbon dioxide cause average global temperature to increase, unless dramatic action is taken, global temperature will continue to increase and the consequence may be devastating (Akeredolu, 1989). About 40% of the $CO₂$ emission comes from the burning of fossil fuels, 5% from the fossil fuel required for electricity, 50% from the conversion of limestone $(CaCO₃)$ to calcium oxide and 5% from the transport of

raw materials. This is illustrated in Figure 1.

Figure 1: $CO₂$ Emission in Cement Production

The emissions of carbon monoxide (CO) during clinker burning process are caused by the small quantities of organic constituents input via the natural raw materials. These are converted during kiln feed preheating and become oxidized to form CO and CO₂. Carbon monoxide reacts with other pollutants to produce ground-level ozone, which can harm human health, damage buildings and crops. Excessive exposure to carbon monoxide may affect the blood, brain, heart and unborn child in human.

 NO_x has nitrogen dioxide (NO₂) in significant quantity. NO₂ is produced under high temperature from the reaction of nitrogen (N_2) and oxygen (O_2) during kiln firing. Nitrogen dioxide (NO_2) is harmful to vegetation, can fade and discolour fabrics, reduce visibility and react with surfaces and furnishings. Vegetation exposure to high level of nitrogen dioxide can be identified by damage to foliage, decreased growth or reduced crop yield. Elevated levels of $NO₂$ cause damage to the mechanism that protect the human respiratory tract and can increase a person susceptibility to and the severity of respiratory infections and asthma. Long-term exposure to high levels of $NO₂$ can cause chronic lung diseases.

Sulphur is input into the clinker burning process via raw materials and fuels. $SO₂$ is produced from oxidation of volatile sulphur present in the kind of limestone used as raw material. The sulphur input with the fuel is completely converted to $SO₂$ during combustion in the rotary kiln. Sulphur dioxide react with water and other chemicals in the air to form sulphuric acid in the atmosphere when present in sufficient quantity and under favorable reaction conditions, acid rain is produced. The acid rain reacts chemically with any object they contact. In soil, acid rain dissolves and washes away nutrients needed by plants. It can also dissolve toxic substances such as aluminum and mercury.

Emission of metal compounds from Portland cement kilns can be grouped into three general classes: volatile metals including mercury (Hg) and thallium, Semi-volatile metals including antimony (Sb), Cadmium (Cd), lead (Pb), selenium (Se), Zinc (Zn), potassium (K) and sodium (Na), non-volatile metals including barium (Ba), chromium (Cr).

Although the partitioning of these metal groups is affected by kiln operating conditions, the non-volatile metals tend to concentrate in the clinker while the volatile and semi-volatile metals tend to be discharged through the primary exhaust stack and bypass stack respectively.

Once mercury has reach surface of water or soils, microorganism can convert it to methyl mercury, a substance that can be absorbed quickly by most organisms and is known to cause nerve damage. Some of the effects that mercury has on animals are kidney damage, stomach disruption and DNA alteration.

Zinc is a threat to cattle and also to plant spaces. Plants often have a zinc uptake that their system cannot handle due to the accumulation of zinc in soils. Zinc negatively influences the activity of microorganism and earthworms in the soil.

Kiln bricks used to be made of hexavalent chrome which is carcinogenic and causes dermatitis in some people. By the process of coal combustion, chrome finds its way to the air and in soils through waste disposal. The chromium in the air also eventually ends up in the soil or water. Chromium compounds in the soil attach

well to particles making it almost impossible for them to transfer to round water. Chromium VI is highly toxic not only to humans but other organisms as well. It has the capacity to alter genetic configuration which have the potential of causing mutation.

4. Method of Analysis

4.1 Exergy analysis

The system operating data are collected from a cement production plant in Nigeria. The system was simulated using HYSYS and the exergy analysis was conducted.

The physical exergy of a given stream is given by

$$
Ex_{phy} = m\{(h - h_0) - T_0(s - s_0)\}\tag{1}
$$

where m is the molar flow, h is the specific enthalpy, s is the specific entropy. The chemical exergy is calculated as

$$
Ex_{ch} = (\mu^o \cdot \mu_o^o) + RT_o \ln\left(\frac{c}{c_o}\right) \tag{2}
$$

The work equivalent of a heat source is calculated as

$$
Ex_{heat} = \left(1 - \frac{T_o}{T}\right)Q\tag{3}
$$

The total exergy of a stream is then calculated as

$$
Ex_{total} = Ex_{phy} + Ex_{ch} + Ex_{heat}
$$
 (4)

The exergy efficiency of each sub system and the overall system is calculated as

$$
\dot{\eta} = \frac{\text{Total output exergy}}{\text{Total input exergy}} \times 100\tag{5}
$$

The irreversibility is calculated as

$$
reversibility = \sum E_{xin} \sum E_{xout} \tag{6}
$$

Where, E_{xin} is input exergy and E_{xout} is output exergy.

The method of analysis has been previously discussed in Osuolale and Osuolale (2016). The exergy efficiency of the system was found to be 38.44% and with the inclusion of chemical exergy, the exergy efficiency was 46.85%.

4.2 Economic Analysis

Having carried out the exergy analysis of the process, economic analysis which gives the complete diagnosis of the system in terms of monetary costs follows thereafter.

Monetary values of each component in the inlet and outlet streams of each unit are determined, this is found in \$/kg. The values are then multiplied with the corresponding flow rates of each component in the inlet and outlet streams to give the total costs of the raw materials in the inlet stream(s) and the cost of the product(s) in the outlet stream(s). The overall monetary cost for the system is also obtained. The profitability or the loss of each unit as well as the overall system is then calculated.

4.3 Environmental analysis

An emission factor is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant. These factors are usually expressed as the weight of pollutant divided by a unit weight, volume, distance, or duration of the activity emitting the pollutant (e.g. kilograms of particulate emitted per megagram of coal burned). Such factors facilitate the estimation of emissions from various sources of air pollution.

In most cases, these factors are simply averages of all available data of acceptable quality and are generally assumed to be representative of long-term averages for all facilities in the source category (i.e. a population average). The equation for the estimation of emission is:

$$
E = A \times EF \tag{7}
$$

Where $E =$ Emissions

 $EF =$ Emission factor

A = Activity rate in unit of weight, volume, distance or duration.

Amount of pollutants emitted per year is estimated from amount of each pollutant as calculated by HYSYS using equation 8. Amount of pollutants per year is also estimated using emission factor technique. Emission factor is a representative value that attempts to relate the quantity of pollutant released to atmosphere with an activity

associated with the release of that pollutant. It is expressed as weight of substance emitted per tonne of clinker produced.

Emission factor is used to estimate amount of pollutants using equation 9.

$$
E_{kpy,i} = [Ap \times OpHrs] \tag{8}
$$

$$
E_{kpy,i} = [A \times OpHrs] \times EF_i \tag{9}
$$

Where:

 $E_{kpy,i}$ = emission rate of pollutant i, lb/yr

AP = amount of pollutants as calculated by HYSYS

A =activity rate, ton/hr (ton of clinker produced per hour)

OpHrs = operating hours, hr/yr

 EF_i =Uncontrolled emission factor of pollutant i, lb/ton

5. Results and Discussion

5.1 Economic analysis.

The economic analysis which analyzes the system in terms of monetary and exergy costs is used to evaluate the performance of the units and the overall system in terms of profits and losses.

The monetary values of each component as obtained are presented in the Table 2.

Table 2: Components' monetary values

Components	Values $(\frac{5}{kg})$
Oxygen	0.3
Sulphur	230
Hydrogen	5
Carbon	28.24
H ₂ O	$3.96*10^{-4}$
SO ₂	70 (allowance price)
CO ₂	20
SO ₃	68.14 (mitigation cost)
CaCO ₃	6.997
SiO ₂	6280
Na ₂ O	19
K_2O	19
Al_2O_3	8.549
Fe ₂ O ₃	5.952
MgO	33.11
CaO	49
$Ca3Al2O6$	572
Ca ₂ SiO ₄	1280
Ca ₃ SiO ₅	1280
CaSO ₄ (Gypsum)	0.419
$Ca4Al2Fe2O10$	7.2

The results for the monetary costs of the inlet and outlet streams of each unit as well as the overall system are shown in Table 3. Some unit like the mill has the cost of the inlet stream to be equal to the cost of the outlet stream. This is because the unit as a whole has no chemical reaction taking place. There was only a change in size of the inlet product and the outlet product. Some unit like the combustion reactor show a marked increase in the outlet monetary value compared to the inlet monetary value. The economic analysis of each unit reveals the unit with premium profit. The overall economic analysis shows a profit margin of about \$57 million

Exergy and economic cost.

The result for the economic cost and exergy of each stream in one of the unit is given is Table 4. It can be seen that the exergy of the stream has a direct relationship with the cost of the stream. This is also reflected in the overall balance of the plant. Improving the exergy of the stream is a sure way of improving the economic cost of the stream too.

Table 4: Comparison of exergy and economic cost.

5.2 Emission estimation result

The pollutants focused on here are sulphur dioxide $(SO₂)$ and carbon dioxide $(CO₂)$. The quantity of each pollutant produced according to HYSYS calculation is given in Table 5 and quantity of each pollutant produced as estimated using emission factor technique is given in Table 6.

Quantity Table 6. Quantity of each pollutant produced as calculated using emission factor technique

It can be seen that there the emission from HYSYS has about 18.76% increment compared to that from the emission factor technique. This is possibly due to the fact that the emission factor is an approximate number to reflect the emission based on the amount of clinker produced. The HYSYS calculation however is based on the true emission from the simulation. It might be advised to be more reliable.

The mass fraction of hydrogen (H), Carbon (C), Sulphur (S) in the fuel (gas) used for combustion was reduced from their original values of H =0.128, C =0.863, S =0.009 to H =0.304, C =0.690, S=0.006 and H =0.400. The quantity of each pollutant produced as estimated from HYSYS calculation is given in Table 7. There is a reduction of 32.68% in SO₂ emission and 14.88% reduction in CO₂ emission. The mass fraction of Sulphur and Carbon in the fuel has significant importance on the quantity of the pollutant from the cement production process. Alternative fuel might be used and concerted effort to see to the reduction of these components in the fuel is highly encouraged.

Table 7. Quantity of each pollutant produced when mass fraction of $H = 0.304$, $C = 0.690$, $S = 0.006$ in the fuel.

With the use of electrostatic precipitator in the kiln as control equipment, the quantity of each pollutant as calculated using emission factor technique is given in Table 8. There is 35.36% reduction in SO₂ emission and 4.76% reduction in $CO₂$ emission. The two pollutants considered here have adverse effect on the environment. Every means of mitigating them should be seriously considered and stringent policies should be put in place to see to their reduction especially for developing nations.

Table 8. Quantity of pollutant produced with the use of electrostatic precipitator

6. Conclusion
There is a direct relationship between the economic cost and exergy of stream in the cement production plant. Improving therefore the exergetic efficiency of the plant will improve the energy efficiency of the plant as well as the economic benefit of the plant. The release of significant quantity of carbon dioxide makes the cement production a concern for global warming. The mass fraction of carbon, hydrogen, and sulphur in the fuel used for combustion during cement production have effect on the quantity of carbon dioxide and sulphur dioxide produced during the cement production process. The use of electrostatic precipitator as a control equipment for release of carbon dioxide and sulphur dioxide will reduce the quantity of carbon dioxide and sulphur dioxide released.

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