AIR POLLUTION CONTROL TECHNIQUES FOR THE CEMENT MANUFACTURING INDUSTRY: A CASE STUDY FOR ZIMBABWE

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ABSTRACT

Technological advancement has resulted in cement making companies being able to produce higher volumes compared to the past. However the higher production levels have also been largely labelled as the leading cause of pollution. The main sources of air pollution in the industry include excavation activities, dumps, tips, conveyer belts, crushing mills and kiln emissions. Harnessing appropriate technology for use in the cement industry could go a long way towards minimising on-site wastes and pollution. This review examines various options in practice for reducing pollution at cement manufacturing companies, which help ensure legislative compliance. By adoption of appropriate technology and computer modelling, industry will not only reduce production waste but also comply with legislation to do with environmental protection. The paper examines certain methods of pollution control used for air and looks at how computer modelling can be adopted for the classification, quantification and control of particulate matter; and how efficient energy use can contribute to better air quality. An analysis of gas stack emissions was done for a cement manufacturing company in Zimbabwe where compliance was investigated. Emissions samples were randomly selected at various points within the company and concentration of various emission constituents were analysed.

1 INTRODUCTION

The cement industry contributes significantly to the imbalances of the environment; in particular air quality. The key environmental emissions are nitrogen oxides (NOx), sulphur dioxide (SO_2) and grey dust (Albeanu et al) [1]. Industrial plant smokestacks from cement and construction companies are some of the biggest contributors to poor air quality, especially in urban developments. As of 2007, the cement industry alone was reported to produce 5% of total greenhouse gasses in the atmosphere (Air Quality Resources) [2]. The principal aim in pollution control in the cement industry is to minimise the increase in ambient particulate levels by reducing the mass load emitted from the stacks, from fugitive emissions, and from other sources (clentechindia.com) [3]. This paper looks at emission and control of gaseous and particulate matter.

2 CEMENT PRODUCTION TECHNOLOGY

Cement is produced from raw materials such as limestone, chalk, shale, clay, and sand.

These raw materials are quarried, crushed, finely ground, and blended to the correct chemical composition (US EPA) [4]. Figure 1 shows part of a cement making factory in Zimbabwe.

Figure 1: Cement Production Plant (Cement Company, Zimbabwe)

After the mining, grinding and homogenization of raw materials, the process of calcination is followed by burning the resulting calcium oxide together with silica, alumina and ferrous oxide at high temperatures to form clinker; the clinker is then ground or milled together with other constituents (as gypsum, slag etc.) to produce cement. (Karstensen et al) [5] The main stages in cement production can thus be discussed under the following sub-headings:

2.1 Quarrying (Raw material acquisition)

Most of the raw materials used are extracted from the earth through mining and quarrying and can be divided into the following groups: lime, silica, alumina, and iron (Albeanu et al) [1]. Limestone (calcium carbonate – $CaCO_3$) is the predominant raw material therefore most plants are situated near a limestone quarry or receive this material from a source via inexpensive transportation. The plant must minimize the transportation cost since one third of the limestone is converted to carbon dioxide (CO_2) during the pyro-processing and is subsequently lost. Quarry operations consist of drilling, blasting, excavating, handling, loading, hauling, crushing, screening, stockpiling, and storing.

2.2 Raw Materials Preparation (Raw Milling And Fuels Preparation)

Raw milling involves mixing the extracted raw materials to obtain the correct chemical configuration, and grinding them to achieve the proper particle-size to ensure optimal fuel efficiency in the cement kiln and strength in the final concrete product (Karstensen et al) [5]. Three types of processes may be used: the dry process, the wet process, or the semidry process. If the dry process is used, the raw materials are dried using impact dryers, drum dryers, paddle-equipped rapid dryers, or air separators, before grinding, or in the grinding process itself. In the wet process, water is added during grinding. In the semidry process the materials are formed into pellets with the addition of water in a pelletizing device.

2.3 Clinker Burning

In pyro-processing, the raw mix is heated to produce cement clinkers. Clinkers are hard, grey, spherical nodules with diameters ranging from 0.32 - 5.0cm created from the chemical reactions (sintering) between the raw materials. The pyro-processing system involves three steps: drying or preheating, calcining (a heating process in which calcium oxide is formed), and burning (sintering). The pyro-processing takes place in the burning/kiln department. The raw mix is supplied to the system as a slurry (wet process), a powder (dry process), or as moist pellets (semidry process). All systems use a rotary kiln and contain the burning stage and all or part of the calcining stage. For the wet and dry processes, all pyro-processing operations take place in the rotary kiln, while drying and preheating and some of the calcination is performed outside the kiln on moving grates supplied with hot kiln gases.

2.4 Cement Grinding

This stage is also known as finish milling. Here the clinker is ground with other materials (which impart special characteristics to the finished product) into a fine powder. Gypsum and/or natural anhydrite are added to regulate the setting time of the cement. Other chemicals, such as those which regulate fluidity or air entrainment, may also be added. Material that has not been completely ground is sent through the system again.

2.5 Cement Packaging And Dispatch

The finished product is transferred using bucket elevators and conveyors to storage silos. Most of the cement is transported to customers in bulk by railway, trucks, and in bags (normally 50kg bags). Cement is mostly used in mortar and concrete in the construction industry.

3 ENVIRONMENTAL IMPACTS OF CEMENT MANUFACTURE

Cement manufacturing is a “high volume process” and correspondingly requires adequate quantities of resources, that is, raw materials, thermal fuels and electrical power. The main environmental (air quality) impacts of the manufacture of cement in general are related to the categories discussed below.

3.1 Gaseous atmospheric emissions of CO_2, NOx, SO_2, Volatile Organic Compounds (VOCs) and others

Carbon dioxide is released during the production of clinker, a component of cement, in which calcium carbonate ($CaCO_3$) is heated in a rotary kiln to induce a series of complex chemical reactions (Conneely et al) [6]. Specifically, CO_2 is released as a by-product during calcination, which occurs in the upper, cooler end of the kiln, or a precalciner, at temperatures of 600-900°C, and results in the conversion of carbonates to oxides. The simplified stoichiometric relationship is as follows:

$$CaCO_3 + heat \rightarrow CaO + CO_2$$

Additional air pollutants emitted include such materials as sulphur oxides and nitrogen oxides generated from the kiln and drying processes. Sulphur dioxide is generated from the sulphur compounds in the ores and the combusted fuel and varies in amount produced from plant to plant. The efficiency of particulate control devices is inconclusive as the result of variables such as feed sulphur content, temperature, moisture, and feed chemical composition, in addition to alkali and sulphur content of the raw materials and fuel. The combustion of fuel in rotary cement kilns generates nitrogen oxides from the nitrogen in the fuel and incoming combustion air. The amount emitted depends on several factors including fuel type, nitrogen content, and combustion temperature. Both sulphur dioxide and some of the nitrogen oxide react with the alkaline cement and are removed from the gas stream. Volatile organic carbon compounds (VOCs) are a class of chemicals that are emitted directly to the air as a result of evaporation or another type of volatilization. Sources include stored gasoline, stored solvents and other industrial chemicals, and certain industrial processes. Incomplete combustion of fuels of many types is also an important source of VOC discharge to the ambient air. The principal harmful effects of VOCs are toxicity, possible contribution to smog via photochemical reactions in the atmosphere, and possible contribution to the "greenhouse effect" and consequent global warming (Woodard) [7]. Examples are Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) which comprise a family of 210 chemically related organic compounds containing from one to eight chlorine atoms. PCDDs and PCDFs are commonly and colloquially referred to as PCDD/Fs.

3.2 Dust

Dust emissions originate mainly from the raw mills, the kiln system, the clinker cooler, and the cement mills. A general feature of these process steps is that hot exhaust gas or exhaust air is passing through pulverised material resulting in an intimately dispersed mixture of gas and particulates. The nature of the particulates generated is linked to the source material itself, that is, raw materials (partly calcined), clinker or cement (Karstensen) [8]. Dust emissions have been linked to respiratory problems such as Tuberculosis.

Figure 2: Emissions From A Cement Plant

3.3 Bad Odour

Foul smell is sometimes a direct result of the gases emitted during cement manufacturing. Moreover, since cement manufacture has life threatening impacts to plants and animals, the manufacturing process then directly and indirectly gives rise to offensive smells as the dead plants and animals decay.

3.4 Environmental Legislation In Zimbabwe

The current constitution of Zimbabwe under section 4 of the Environmental Management Act (EMA), (Chapter 20:27), 2002, affords every citizen of Zimbabwe the following environmental rights:

1. The right to live in a clean environment that is not harmful to their health;
2. Access to environmental information;
3. The right to protect the environment for the benefit of present and future generations;
4. The right to participate in the implementation of legislation and policies that prevent pollution, environmental degradation and sustainable management and use of natural resources, while promoting justifiable economic and social development. (Parliament of Zimbabwe) [9]

3.5 Pollution Indicators For World-Class Cement Manufacturers

The data in Table 1 represents PCDD/F stack emissions for the same furnace type but different pollution control technologies for Lafarge Cement Company.

Table 1: PCDD/F Emission Statistics for Lafarge (Karstensen *et al.*) [5]

Plant	Filter type	Clinker production (tons per year)	Stack emissions (ng/Nm^3)	Standard regulation
1	ESP	305 000	0.001	< 0.1
2	ESP	70 000	0.021	< 0.1
3	ESP	350 000	0.002	< 0.1
4	ESP	130 000	0.004	< 0.1
5	BAG HOUSE	450 000	0.1714	< 0.1
6	BAG HOUSE	500 000	0.231	< 0.1
7	BAG HOUSE	250 000	0.0921	< 0.1
8	WET SCRUBBER	390 000	0.007	< 0.1
9	WET SCRUBBER	370 000	0.002	< 0.1

4 AVAILABLE AIR POLLUTION CONTROL TECHNOLOGIES AND EQUIPMENT

Controlling particulate emissions from sources other than the kiln usually entails capturing the dust using a hood or other partial enclosure and transporting it through a series of ducts to the collectors. The type of dust collector used is based on factors such as particle size, dust loading, flow rate, moisture content, and gas temperature. The best disposal method for collected dust is to send it through the kiln creating the clinker. However, if the alkali content of the raw materials is too high, the dust must be discarded, or must be pre-treated before introduction into the kiln. The highest allowable alkali content is 0.6% (as sodium oxide).

4.1 Flexible Pulse Jet Filters

Raw gas enters the filter compartments via inlet ducts equipped with guide vanes that distribute the gas uniformly across the filter bags. This arrangement creates a downward gravimetric gas flow along the filter bags, precipitating the dust into the hopper below. In contrast to filters where raw gas enters through dampers located in the hoppers, the design of the flexible pulse jet filter gas distribution system prevents the creation of high can velocities (or vertical, upward gas flow). High gas velocities prevent fine particulate from settling into the hoppers during on-line cleaning cycles. The raw gas is filtered by the fabric from the outside, and the clean gas exits at the top of the bag. The fan is located on the clean gas outlet side of the filter (Alstom) [10].

4.2 Electrostatic Precipitators

Electrostatic precipitators use electrostatic forces to separate the dust from the exhaust gas. By means of discharge electrodes, the dust particles are negatively charged and can be separated on corresponding collecting electrodes. The particles are then discharged from the collecting electrodes to dust hoppers by electrode rapping (Karstensen et al) [5].

4.3 Wet Scrubbers

In a wet scrubber, the polluted gas stream is brought into contact with the scrubbing liquid, by spraying it with the liquid, by forcing it through a pool of liquid, or by some other contact method, so as to remove the pollutants. Scrubbers can be designed to collect particulate matter and/or gaseous pollutants. Wet scrubbers remove dust particles by capturing them in liquid droplets. Wet scrubbers remove pollutant gases by dissolving or absorbing them into the liquid (Wikipedia) [11].

4.4 Ordinary Bag House Method

This is a filtration method and is one of the oldest and most efficient methods of particulate control. The most commonly-used filtration device is known as a bag-house and consists of fabric bags through which the air stream is directed as shown in Figure 3. Particles become trapped in the fibre mesh on the fabric bags, as well as the filter cake which is subsequently formed (Wikipedia) [11].

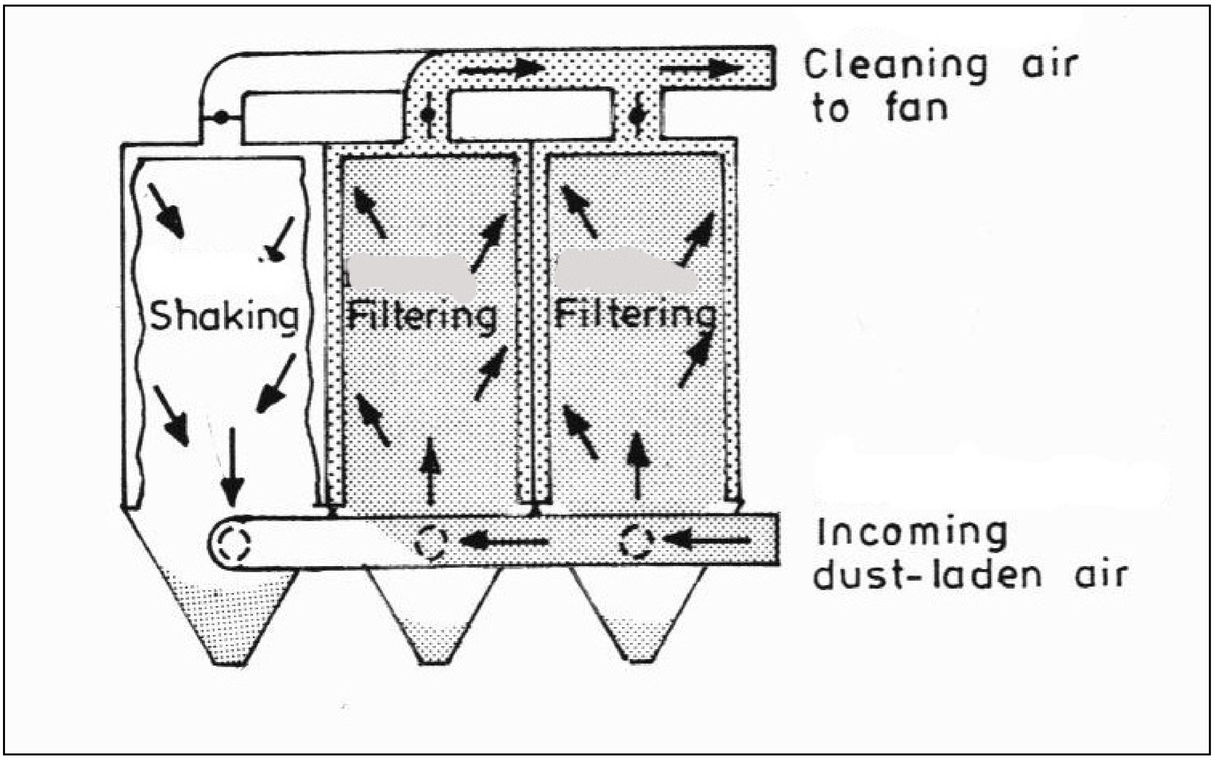

Figure 3: Bag-House Schematic

5 COMPUTER MODELLING FOR QUANTIFICATION OF CARBON DIOXIDE (CO_2) EMISSIONS

Database systems can be taken advantage of, together with Visual Basic applications to quantify or estimate and display CO_2 emissions based on composition of the $CaCO_3$ and amounts of lost cement kiln dust. Estimating emissions generally involves two emission factors: an emission factor for clinker production and an emission factor for Cement Kiln Dust (CKD) production (Conneely) [6].

5.1 Clinker Emission Factor

The clinker emission factor is the product of the fraction of lime in the clinker multiplied by the ratio of the mass of CO_2 released per unit of lime. This factor can be estimated as illustrated below:

$$EF_{clinker} = \text{fraction CaO} \bullet 0.785 \text{ (Conneely) [6]}$$

The multiplication factor (0.785) is the molecular weight ratio of CO_2 to CaO in the raw material mineral calcite ($CaCO_3$), from which most or all of the CaO in clinker is derived. The result gives the amount of carbon dioxide (in tonnes) emitted per tonne of clinker. Databases and Visual Basic can be used to process and store data and to provide a graphical user interface for monitoring the emissions as production runs. Any deviations above company and legal limits can be easily observed and corrected.

5.2 Cement Kiln Dust (CKD)

CO_2 is also emitted during the calcination of cement kiln dust (CKD) in the kiln. CKD is a by-product of the kiln process and a portion of the CKD is placed back in the kiln and incorporated into the clinker. The remaining portion is lost – placed in a landfill or used for other purposes. The lost CKD represents additional CO_2 emissions not accounted for in the clinker emissions estimate. The recommended method to estimate the additional CO_2 emissions from the lost CKD is to multiply an emission factor by the amount of lost CKD. The CO_2 from the lost CKD is generally equivalent to about 2-6% of the total CO_2 emitted from clinker production (Conneely) [6].

6 METHODOLOGY

Emission measurement was done for sulphur oxides, nitrogen oxides, carbon monoxide, carbon dioxide and gas exit temperature for X Cement Company in Zimbabwe Plant. Thermocouples and Opacimeters are the main apparatus that were used to measure/quantify the emissions. Thermocouples were used to measure exit gas temperature whilst opacimeters were used to quantify particulates.

6.1 Opacimeter Working Principle

Two types of Opacimeters were used – online and an offline. The basic working principle of an opacimeter is that exhaust gas from the chimney is directed into the opacimeter chamber. Opacity is an optical property that refers to the ability to stop light from being transmitted. The basic principle of the opacimeter is that light is emitted from a light source and a sensor some distance away registers the intensity of the light. If a sample with opacity more than 0% is placed in between the light source and the sensor the measured light intensity will decrease. Through calibration the measured intensity can be correlated to the opacity of the sample. When there is a perfect transparent matter, e.g. air, in between the opacity is 0% and in the opposite case, where no light is transmitted, the opacity is 100% (Bodin) [12].

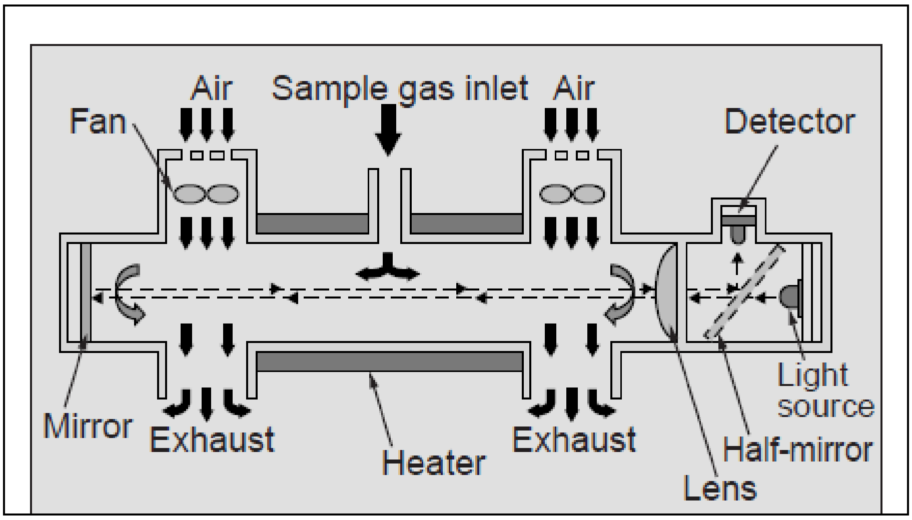

Figure 4: Opacimeter Schematic (Kihara) [13]

6.2 Thermocouple Working Principle

A thermocouple is a device made by two different wires joined at one end, called the junction end, or measuring end. The two wires are called thermo-elements or legs of the thermocouple. The other end of the thermocouple is called the tail end or reference end.

This arrangement is shown in Figure 5 below. Because of the temperature difference between junction end and tail end a voltage difference can be measured between the two thermo-elements at the tail end. Thus, the thermocouple is a temperature-voltage transducer (Scervini) [14].

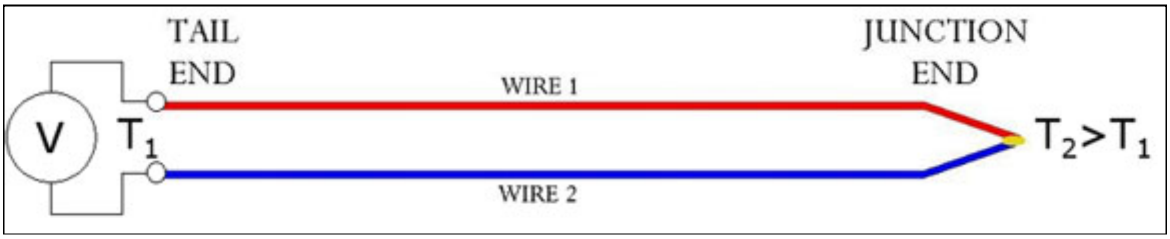

Figure 5: Thermocouple Schematic

6.3 Gas Conditioning Towers

Exhaust gases leaving the kiln is at very high temperature which destabilises the ecosystem by killing creatures which cannot survive such high temperature. Conditioning towers in the cement industry are used for cooling the exhaust gases from the kiln before it is fed into the precipitators. The exhaust hot gases are fed from the top of gas cooling tower and are cooled by injected water; the gases are drawn through the tower by a fan. Conditioning towers in the cement industry treat exhaust gases with temperatures between 300 and 400°C, cooling them down to 150° C.

7 RESULTS

From the measurements that were done, sulphur oxides and carbon monoxide were notably out of control relative to the other emissions and results for these are presented below.

7.1 CO Emissions

Table 2 shows the levels of carbon monoxide emissions in parts per million for randomly selected points for the tower exit.

Table 1: CO Emissions

Point	CO emission (ppm)
1	0.09
2	0.10
3	0.08
4	0.07
5	0.04
6	0.10

7.2 Sulphur Oxides Emissions

Figures 6 and 7 are plots of percentage SO_3 (vertical axis) against positions (horizontal axis).

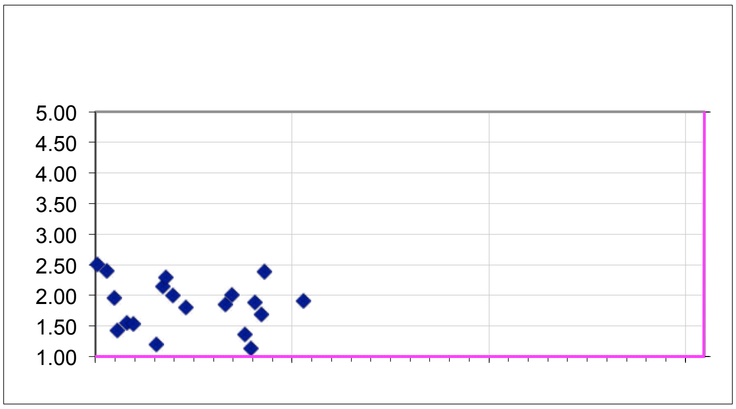

Figure 6: SO_3 (%) For Stage 4 East

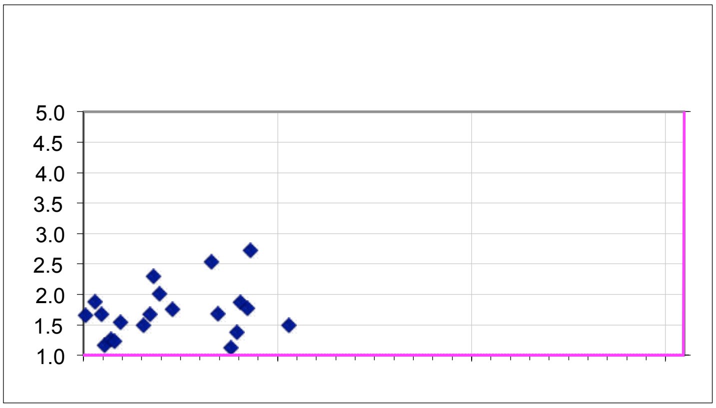

Figure 7: SO_3(%) For Stage 4 West

After the sampled points have been analysed and are found to be above the required concentration level, the source of emisions is investigated and an appropriate technical solution is recommend. The random sampling can be scheduled and the process becomes continous throughout the life span of the plant.

7.3 Gas Conditioning Towers

The vertical axes of the plots in Figures 8 and 9 represent temperature while the horizontal axes represent positions.

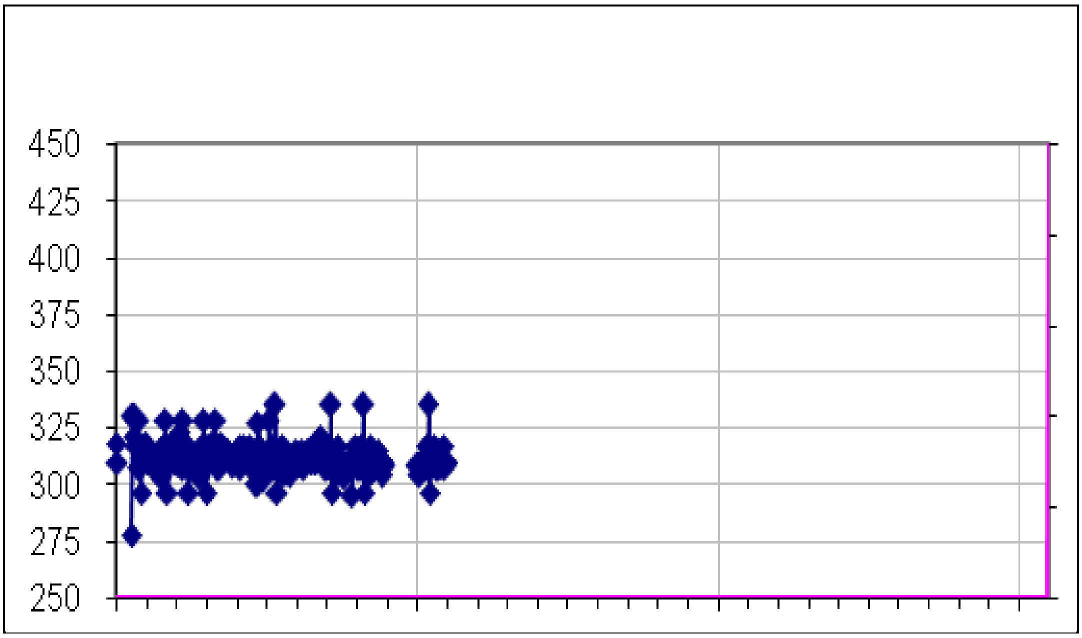

Figure 8: GCT Inlet Temperature

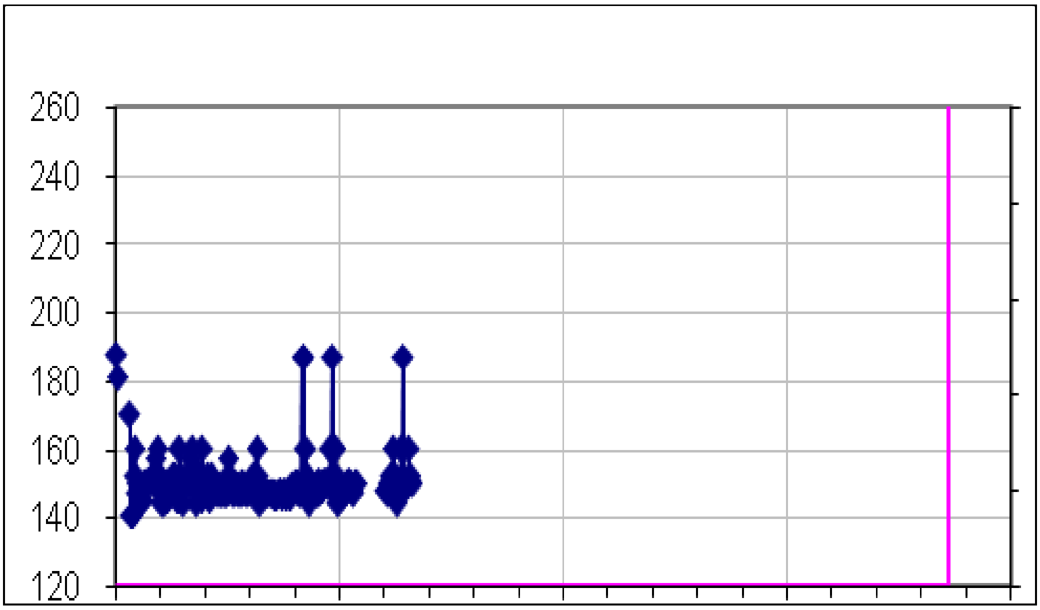

Figure 9: GCT Outlet Temperature (°C)

Figure 8 shows the temperature of flue gases before entering the gas cooling tower and Figure 9 shows the temperature at the outlet of the cooling tower. An analysis of figure 11 shows that some points have temperaturs well above the rexcommended range of 140 to 150 degree celcius. Hence there is need to investigate such outlet high temperatures possibly using the fishbone diagrams or other problem solving techniques.

7.4 Stage By Stage Pollution Control Techniques For Cement Industry

The various techniques that can be used to control pollution in the cement manufacturing process can be easily identified by considering the major process stages as outlined below.

7.4.1 Raw Materials Acquisition And Handling

During raw material acquisition the primary air pollutant emitted is particulate matter. Particulate matter is emitted from the quarrying, handling, loading, unloading, and transport of raw materials. The following methods are used to control particulate emissions generated from the quarry and handling of raw materials:

1. Fabric filters (pulse-jet or reverse-air/shaker)
2. Equipment enclosures
3. Water sprays – to suppress dust
4. Mechanical collectors
5. Chemical dust suppressants
6. Paving (where possible)

Dust that is collected by these means is restored to the process. This therefore means that the Reduce, Reuse, Recycle and Recover (4Rs) techniques can be employed to minimise and manage waste during raw materials acquisition.

7.4.2 Clinkerisation (Pyro-Processing)

The main pyro-processing system emissions are nitrogen, carbon dioxide, water, oxygen, nitrogen oxides, sulphur oxides, carbon monoxide, and hydrocarbons. Cement kiln dust (CKD) is also produced. The cement kiln itself has been designated as best available control technology (BACT) for the control of SO_2. The highly alkaline conditions of the kiln system enable it to capture up to 95% of the possible SO_2 emissions. However, if sulphide (pyrites) is present in the kiln feed, this absorption rate can decline to as low as 50%. Therefore, sulphur emissions can be decreased through careful selection of raw materials. Options are available to move from coal fuel to oil or gas fuel as these will result in considerably lower sulphur oxides and carbon monoxide emissions. Possible areas of exploitation for the control of NOx are as follows:

1. stable kiln operation (reduces long term NOx emissions)
2. staged combustion for precalciner kilns;
3. recirculation of the flue gas (oxygen deficient air in the rotary kiln); and
4. Alternative/low-nitrogen fuels.

7.4.3 Cement Loading And Despatch

In the shipping department particulate matter is emitted from the silos and the handling and loading operations. Active and passive fabric filters can be used to collect this dust. To ensure dust-free loading onto the transport vessel, a flexible loading spout consisting of concentric tubes is used. The outermost tube seals the delivery spout to the transport vehicle. The product is then delivered through the inner tube and displaced air drawn up the outer tube to a filter. At distribution terminals, fabric filters are again used and the collected dust is returned to the product.

8 RECOMMENDATIONS

1. Rapid flue gas quenching or other measures to minimize post-furnace particulate residence time in the critical temperature zone;
2. Use of formation inhibitors;
3. End-of-pipe flue gas cleaning techniques for removal or catalytic decomposition of emissions.
4. Measuring equipment and instruments such as opacimeters should be upgraded to enhance accuracy of measurements.

9 FURTHER OPPORTUNITIES FOR IMPROVEMENT (X CEMENT ZIMBABWE)

Carbon monoxide emission (up to 0.1ppm) is due to incomplete combustion during clinkerisation. There is need to look at alternative fuel composition and raw materials residence time in the kiln. The levels of SOx emissions for X Cement Zimbabwe (below 5%) are an indication of a good furnace/kiln design. However there is still need to completely eliminate SOx emissions into the natural atmosphere. Catalytic reduction of SOx emissions at end of pipe can also be taken advantage of to further reduce such emissions.

10 CONCLUSION

The world has become increasingly aware of the need to preserve and conserve resources. Control of pollution is not only a legislative requirement, but has also become a tool for competitiveness. Those companies that choose to implement sound pollution prevention methods are likely to enjoy better business than those that do not, mainly because the former will generally be regarded as socially responsible. Therefore the technological advancement that is being witnessed everyday is an opportunity for industry to minimise waste, and become greener, and more lucrative. There is great potential for cement industries to minimise emissions, particularly those in Africa.

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