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STUDY OF POLLUTION LOAD IN ENVIRONMENT DURING CO-PROCESSING OF SOLID WASTE (CARBON BLACK) IN CEMENT ROTARY KILN

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ABSTRACT

Fuels made from waste have been used by power plants and various industrial plants (including cement plants) using high-temperature processes. The fuels applied can be solid or liquid, made from municipal waste, industrial waste, or their mixtures. Replacement of some conventional fuels with alternative fuels (AF) brings both economic and ecological benefits. Use of alternative fuels for meeting energy requirement is a sustainable initiative which not only help save fossil fuel and mitigate GHG emissions, but also facilitate the intimidating task of waste disposal in an environmentally sound manner. An industry that is especially suitable for the application of such fuels, from the technological and environmental points of view, is the cement industry. Ambuja Cements Ltd., Unit: Rabriyawas has started using carbon black (derived from pyrolysis of waste tyre) in cement rotary kiln as a partial replacement of fossil fuel. In the present work pollution load alteration in environment during co-processing of carbon black with conventional fuel was studied. The resulting pollutants were monitored at stack and ambient level. The pollutant load was studied in terms of particulate matter (PM), sulphur dioxide (SO_2) and oxides of nitrogen (NOx) from process stack and in ambient level particulate matter (PM_{10} and $PM_{2.5}$), SO_2, nitrogen dioxide (NO_2) and carbon monoxide (CO). The pollutant load at ambient level was measured at four locations in different directions (north-west, south-east, north-east and south-west) with respect to stationary source (stack). The results are promising and the waste (carbon black) studied as co-processing material is sufficiently efficient in providing energy without any significant alternation in the pollutant load emissions at stack and ambient level. Interestingly, the NOx level reduced marginally with the use of carbon black. Over all no major changes were observed in baseline emission concentrations of pollutants in the environment.

KEY WORDS : Alternative fuels, Fossil fuel, Carbon black, Energy recovery, Thermal energy, Stack, Ambient air quality, Green house gases, Cement rotary kiln.

INTRODUCTION

The environment is a hotly debated topic in today's society. With modern and changing technologies industries are able to combat pollution to some extent. Yet in order to decrease the environmental impact of the industries and provide a viable and convenient end-of-life option for waste and industrial by-products, the use of alternative fuels to obtain thermal energy in cement manufacturing is growing rapidly in these days.

Cement manufacturing consists of raw meal grinding, blending, precalcining, clinker burning and cement grinding. In short, limestone and other minerals containing calcium, silicon, aluminum and iron oxides are crushed and milled into raw meal. This raw meal is blended and is then heated in the pre-heating system to initiate the dissociation of carbonate to calcium oxide and carbon dioxide. The fuels fed into the preheating system to keep the temperature sufficiently high. The meal then proceeds to the kiln for heating and reaction between calcium oxide and other elements to form calcium silicates and aluminates at a temperature up to 1450 ^{0}C. The reaction product leaves the kiln as a nodular material called clinker. The clinker will be

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inter-ground with gypsum, and/or ashes to a fine product called cement.

Cement kilns have traditionally been fired by primary fuels like coal/lignite/pet coke but various hazardous, non hazardous, mixed wastes as alternative fuels offer the joint benefits of overall CO_2 reduction by avoiding incineration without utilizing its energy content and lower production costs. The fact that the energy costs have a considerable influence on large part of the production costs (about one third of the cost) leads many manufactures to reduce consumption of conventional sources of energy in favor of alternative fuels.

Alternative fuels contribute towards lowering the emission of green house gases by replacing the use of fossil fuels with materials that would otherwise have to be incinerated with corresponding emissions and final residue. Incineration of any waste in dedicated to incinerator results in non-utilization of energy from this valuable waste rather it requires additional energy for incineration and increments the green house gas emissions.

Alternative fuels may contain high percentages of chlorides, sulphur, heavy metals, moisture etc. Thermal substitution levels must be carefully determined in case of raw materials with high chlorine and/or sulphur content. High input of these volatiles may lead to operational issues causing pre-heater blockages necessitating a gas bypass system. High moisture content in alternative fuels such as refused derived fuel (RDF) may lead to reduction in kiln capacity if the exhaust fan has a limited margin. The specific heat rate of the kiln may also get adversely affected. Careful preprocessing is needed and the substitution rate needs to be adjusted based on the existing fuel characteristics (European Commission, 2010).

Co-processing (substitution of primary fuel and raw material by waste to desired extent) helps in safe and environmentally sound disposal of a variety of waste materials (e.g. used tyres, biomass, industrial plastic wastes, carbon black, trade rejects (pesticides, FMCG wastes), paint sludge, ETP/ CETP sludge, municipal solid waste or refused derived fuels (RDF), various hazardous waste etc.), which otherwise are hard and troublesome to be removed from the nature. Keeping in view the above aspects regarding alternative fuels the present study was carried out with carbon black as alternative fuel, co-processed with conventional fuel in cement kiln to know the alterations in the pollutants loads, if any, at stationary source and ambient level.

REVIEWS

Co-processing is defined as an incineration carried out in rotary kilns for clinker production with the use of energetic inside and/or mineral fraction exploitation as raw material without generation of new waste.

Carrasco *et al.,* (2002), reported a 37% increase in the rate of emission of CO when using a combination between tyres and coal, a 24% increase in SO_2 and a 11% decrease for NO*x*.

Positive impact of co-processing demonstrated by Wendell *et al.,* (2013) are (a) Reduction and greater control of emission levels of pollutants; (b) replacement of conventional fuel up to 30%; (c) reduction in energy consumption; (d) increased investment in the environmental area; (e) competitiveness gain; and (f) improving the company image in the community.

A study done by Gautam *et al*. (2009) on Energy recovery from solid waste in cement rotary kiln and its environmental impacts at Vikram Cement, Khor and exhaustive monitoring of emission like particulate matter, heavy metals, hydrochloric acid, oxides of sulphur, oxides of nitrogen, Dioxins, Furans, total organic carbons, volatile organic compounds etc. were analyzed for the impact on environment. Ambient air quality has been monitored for the parameters like suspended particulate matter, sulfur dioxide, oxides of nitrogen and carbon monoxide during the use of refused derived fuel, agro waste and tyre chips.

MATERIALS AND METHODS

The present study, co-processing of carbon black as a co-fuel for the part replacement of traditional fossil fuels, i.e. coal/ lignite/pet coke in cement manufacturing process was done in rotary kiln at the feed rate of 5.1 MT/Hour. This study was carried out in three phases, viz; pre, during and post co-processing. The co-processing and monitoring schedule was;

Phase-I: pre phase, day one (day first of study), pollutants measurement only with traditional fuels (coal/lignite/pet coke)

Phase-II: during co-processing phase, three days (two to fourth days of study) pollutants measurement with alternative fuel (15-20%

depending on operational limit of alternate fuel charging unit) and traditional fuels.

Phase-III: post phase, day one (day fifth of study), pollutants measurement only with traditional fuels.

Source emission monitoring from kiln stack (stack monitoring-emission from stationary source)

Particulate matter and sulphur dioxide were monitored by using Vayubodhan Stack Sampler, VSS1 along with gases attachment (series of midget impingers). NOx was monitored by using collection flask as per procedure led down in IS 11255 (part 7): 2005, by means of spectrophotometer (colorimetrically).

Particulate Matter: Particulate matter, one of the common pollutants is discharged in to air by industrial processes. Particulates are known to be potentially harmful both for plants and animals. The particulate matter was determined following IS: 11255 (Part 1)-1985, for measurement of emission from stationary sources. The average exit gas velocity in stack was determined from the gas density using 'S' type pitot tube. To obtain a representative particulate sample, the sampling was carried out isokinetically.

Sulfur dioxide: All fuels in common use contain variable amounts of sulphur and most of which is discharged to the atmosphere as sulphur dioxide during combustion. Sulphur dioxide was determined following IS: 11255 (Part-2)-1985, for measurement of emission from stationary sources. The gas sample isokinetically was extracted from the sampling point in the stack by passing the gas through series of midget impingers. The acid mist, including sulphur trioxide, was separated from the sulphur dioxide and the sulphur dioxide fraction was measured by the barium thorin titration method.

Oxides of nitrogen: Nitrogen oxides (NOx), the term is used to describe the total NO, NO_2 and other oxides of nitrogen are considered important due to their role in the formation of ozone (a secondary air pollutant) through a complex series of petrochemical reactions involving volatile organic compounds. NOx, are emitted as part of most fuel combustion process, with nitric oxide (NO) being a primary constituent. To determine the NOx method IS: 11255 (Part 7): 2005, was followed. A grab sample was collected in a dilute sulphuric acid-hydrogen peroxide absorbing solution. The nitrogen oxides, except nitrous oxide, were measured colorimetrically using the phenoldisulphonic acid (PDS) procedure. The optical density of the solution was measured by means of a spectrophotometer at the wavelength of 410 nm.

Source monitoring at ambient level (Ambient air quality monitoring)

Ambient air quality was monitored for the parameters suspended particulate matter (PM_{10} & $PM_{2.5}$, sulfur dioxide, nitrogen dioxide and carbon monoxide during the study at about 500-800 meters away from source (stack), at four locations in north-west (AAQM-1), south-east (AAQM-2), north-east (AAQM-3) and south-west (AAQM-4) directions.

Particulate matter (size less than 10µm or PM_{10}): Sampling was done for eight hours by using respirable dust sampler (RDS), (Make: Envirotech, 460BL). To estimate the PM_{10} IS -5182 (Part 23)-2006, methods of measurement of air pollution, part 23, Respirable suspended particulate matter (PM_{10}), cyclonic flow technique was followed. Air is drawn through a size-selective inlet and through a 20.3 cm x 25.4 cm filter at a flow rate, which is typically 1132 L/min. Particles with aerodynamic diameter less than the cut-point of the inlet are collected by the filter. The mass of these particles is determined by the difference in filter weights prior to and after sampling. The concentration of PM_{10} in the designated size range is calculated by dividing the weight gain of the filter by the volume of air sampled.

Particulate Matter (size less than 2.5µm or $PM_{2.5}$): Sampling was done for eight hours by using fine particulate sampler (FPS), (Make: Envirotech, APM550). Air samples were drawn at a constant volumetric flow rate (16.7 LPM, i.e. 1 m^3/hr) maintained by a mass flow/volumetric flow controller coupled to a microprocessor into specially designed inertial particle-size separator (i.e. cyclones or impactors). The suspended particulate matter in the $PM_{2.5}$ size range is separated for collection on a 47mm polytetrafluoroethylene (PTFE) filter. Each filter is weighed before and after sample collection to determine the net gain due to the particulate matter. The mass concentration in the ambient air is computed as the total mass of collected particles in the $PM_{2.5}$ size ranges divided by the actual volume of air sampled, and is expressed in µg/m^3.

Sulphur dioxide: To measure sulphur dioxide in ambient air Modified West & Gaeke Method (IS: 5182 (Part 2), 2001), methods for measurement of Air Pollution: Sulphur dioxide) was followed. The air sampling was carried out by using RDS (Make: Envirotech, 460BL and APM611TE) for eight hours at flow rate of 0.5 liter per minute (LPM). Sulphur dioxide from air is absorbed in a solution of potassium tetrachloromercurate (TCM). A dichlorosulphitomercurate complex, which resists oxidation by the oxygen in the air, is formed. Once formed, this complex is stable to strong oxidants such as ozone and oxides of nitrogen and therefore, the absorber solution may be stored for some time prior to analysis. The complex is made to react with para-rosaniline and formaldehyde to form the intensely coloured pararosaniline methylsulphonic acid. The absorbance of the solution is measured by means of a spectrophotometer at the wavelength of 560 nm.

Nitrogen dioxide: To measure nitrogen dioxide in ambient air Modified Jacob & Hochheiser Method (IS: 5182 (Part 6), 2006), methods for measurement of Air Pollution: Oxides of nitrogen) was followed. Ambient nitrogen dioxide (NO_2) is collected by bubbling air through a solution of sodium hydroxide and sodium arsenite by using RDS (Make: Envirotech, 460BL and APM 611TE) for eight hours at flow rate of 0.5 LPM. The concentration of nitrite ion (NO_2) produced during sampling was determined colorimetrically by reacting the nitrite ion with phosphoric acid, sulfanilamide, and N-(1-naphthyl)-ethylenediamine dihydrochloride (NEDA) and measuring the absorbance of the highly coloured azo-dye at 540 nm on spectrophotometer.

Carbon Monoxide: Carbon monoxide is a temporary atmospheric pollutant from incomplete combustion of various fuels. Pollution Protection Systems Mumbai Pvt. Ltd. gaZguard Tx CO (Carbon Monoxide) is small lightweight personal portable Indicator with audio/visual alarm designed to detect CO in ppm range was used to measure CO in ambient air. A small electrochemical sensor with three electrodes is used for detection of gas. Exposure to CO will produce an electrical current directly proportional to gas concentration.

Experimental results

The average monitoring results while co-processing of carbon black for source emission is given in figure-1 and ambient air quality is given Fig. 2.

Stack emission monitoring : The emission from stack were monitored, after all the three phases of the study it was observed that the pollutant load individually as well as cumulatively did not vary much during pre and post co-processing phase. PM values ranged from 12.84 – 17.59 mg/Nm^3 during the study period with an average value of 15.59 mg/Nm^3 against the permissible CPCB limit of 50 mg/Nm^3 (Fig. 1).

Similarly, in case of SO_2 no significant variation in the load could be observed at all three phases studied. Its value ranged from 27.79 – 42.06 mg/Nm^3 (Average value 34.10 mg/Nm^3) which is very less against permissible CPCB limit of 100 mg/Nm^3. However, an interesting observation was noted in

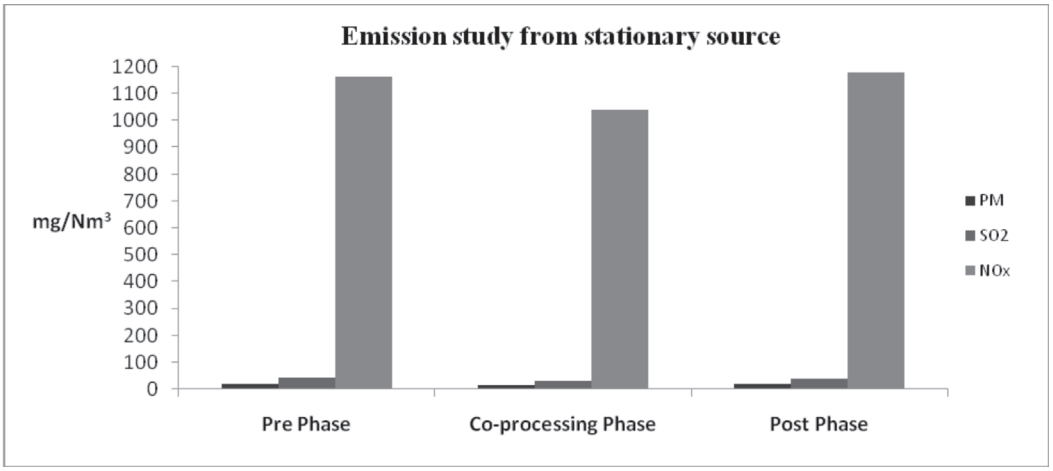

Fig. 1. Emission study from stationary source (stack monitoring of different pollutants during the three phases)

the case of NOx emissions during co-processing phase, a considerable reduction in NOx level was recorded. Net reduction in NOx emission is approx. 11.18% during co-processing of carbon black. Emission of NO_X reduced to 1038.68 mg/Nm^3 when compared with utilization of conventional fuel where its average value was found 1169.39 mg/Nm^3. However value is slightly higher side against the permissible CPCB limit of 1000 mg/Nm^3 (for rotary kiln using mixed stream of Inline calciner, separate line calciner (SLC). Over all there is no major deviation observed on base line emission values of different pollutants. The observations of the present study are supported by Gautam *et al*., 2009, that the emissions to be more depend on other associated activities and operational conditions of the kiln rather than the type of fuel used.

Ambient air quality monitoring: The ambient air quality monitoring as well during the present study for different pollutants in four different directions are present in Fig. 2.

Average values of PM10 were 76.78, 91.42, 88.79 and 92.56 µg/m^3 during pre, during co-processing and post phase at locations AAQM-1, AAQM-2, AAQM-3 and AAQM-4 respectively, against the standards 100 µg/m^3 (National Ambient Air Quality Standards, CPCB, 2009).

Average values of $PM_{2.5}$ were 38.49, 50.61, 46.72 and 49.21 µg/m^3 during pre, during co-processing and post phase at locations AAQM-1, AAQM-2, AAQM-3 and AAQM-4 respectively, against the standards 60 µg/m^3 (National Ambient Air Quality Standards, CPCB, 2009).

Average values of SO_2 were 9.59, 11.32, 11.69 and 11.80 µg/m^3 during pre, during co-processing and post phase at locations AAQM-1, AAQM-2, AAQM-3 and AAQM-4 respectively, against the standards 80 µg/m^3 (National Ambient Air Quality Standards, CPCB, 2009).

Average values of NO_2 were 14.67, 18.69, 18.08 and 20.08 µg/m^3 during pre, during co-processing and post phase at locations AAQM-1, AAQM-2, AAQM-3 and AAQM-4 respectively, against the standards 80 µg/m^3 (National Ambient Air Quality Standards, CPCB, 2009).

Average values of CO were 190.67, 254.22, 260.57 and 203.38 µg/m^3 during pre, during co-processing and post phase at locations AAQM-1, AAQM-2, AAQM-3 and AAQM-4 respectively, against the standards 2000 µ/m^3 (National Ambient Air Quality Standards, CPCB,2009).

Keeping in view the upwind as well as downwind profiles during the study period the ambient pollutants load were recorded. It was observed that the pollutants load was slightly more in south-east and north-east direction at AAQM-2 and AAQM-3. At AAQM-1 (north-west direction in township), the load was minimum, since it is located farthest (approx. 800m) from all the other sites studied and the township location covered by dense green belt. (Fig. 2)

As this juncture of the study it seems that carbon

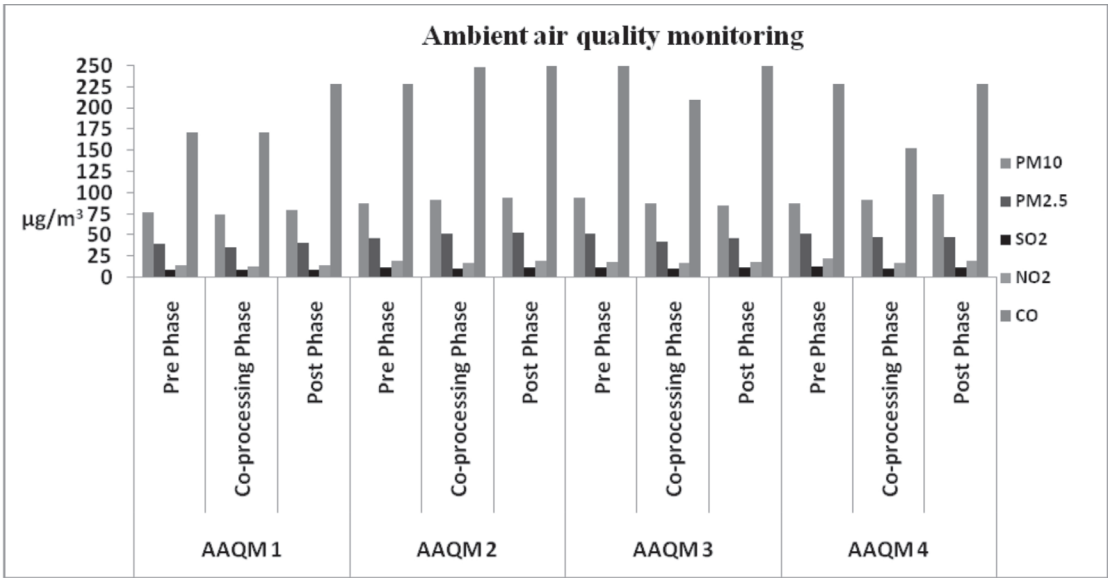

Fig. 2. Ambient air quality monitoring at up-wind and down-wind profile (north-west (AAQM-1), south-east (AAQM-2), north-east (AAQM-3) and south-west (AAQM-4) directions).

black is a promising alternative fuel that can be co-processed with conventional fuel with no alternation in baseline pollutant load (both stack and ambient levels). Carbon black (waste of other industry), has a huge potential to save conventional fuel and further the cost on disposal of waste can be eliminated. It not only saves the fuel cost but also reduces the waste disposal problems.

Use of carbon black as alternate fuels has also contributed to some extent, in the net reduction in emission of oxides of nitrogen and thus, negative impacts of NOx could be minimized in environment.

Utilization of carbon black in cement kiln is win-a-win options for both waste generator and co-processor by recovering their energy potential as well as their disposal by environment friendly manner.

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